Synthesis and Reactivity of Phosphatetrahedranes

Dissertation

Zur Erlangung des Doktorgrades der Naturwissenschaften

Dr. rer. nat.

an der Fakultät Chemie und Pharmazie der Universität Regensburg

vorgelegt von:

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Regensburg, September 2025

Der experimentelle Teil der vorliegenden Arbeit wurde in der Zeit zwischen Januar 2022 und September 2025 unter Anleitung von Prof. Dr. Robert Wolf am Institut für Anorganische Chemie der Universität Regensburg angefertigt.

Die Arbeit wurde angeleitet von:		Prof. Dr. Robert Wolf
Promotionsgesuch eingereicht am:		17.09.2025
Tag der mündlichen Prüfung:		31.10.2025
Promotionsausschuss:	Vorsitz	Prof. Dr. Patrick Nürnberger
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Prologue

This doctoral thesis presents a study of the synthesis and reactivity of phosphatetrahedranes. Chapter 1 provides an overview of neutral tetrahedranes of groups 14 and 15, with a particular emphasis on the synthesis, stability, and reactivity of phosphatetrahedranes. Chapters 2-4 explore the reactivity of *tert*-butyldiphosphatetrahedrane towards $Ni(CO)_4$ (Chapter 2), reductants (Chapter 3), and oxidants (Chapter 4), thereby synthesizing a variety of organophosphorus compounds. Chapter 5 provides mechanistic insights into the catalytic diphosphatetrahedrane formation, obtained through DFT calculations and experimental studies. In Chapter 6, the evaluation of various Ni(0)-complexes for their ability to catalyse this transformation is described. Finally, Chapter 7 summarises the results described in this thesis and provides a short outlook.

Prolog

Diese Dissertation präsentiert eine Studie über die Synthese und Reaktivität von Phosphatetrahedranen. Kapitel 1 gibt einen Überblick über neutral Tetrahedrane der Gruppen 14 und 15, mit besonderem Schwerpunkt auf der Synthese, Stabilität und Reaktivität von Phosphatetrahedranen. Die Kapitel 2-4 untersuchen die Reaktivität von Di-*tert*-butyldiphosphatetrahedran gegenüber $Ni(CO)_4$ (Kapitel 2), Reduktionsmitteln (Kapitel 3) und Oxidationsmitteln (Kapitel 4), wobei eine Vielzahl von Organophosphorverbindungen synthetisiert wurde. Kapitel 5 liefert mechanistische Einblicke in die katalytische Bildung von Diphosphatetrahedranen, welche durch DFT-Berechnungen und experimentelle Studien gewonnen wurden. In Kapitel 6 wird die Fähigkeit verschiedener Ni(0)-Komplexe zur katalytischen Phosphaalkin-Dimerisierung analysiert. Schließlich fasst Kapitel 7 die in dieser Arbeit beschriebenen Ergebnisse zusammen und gibt einen kurzen Ausblick.

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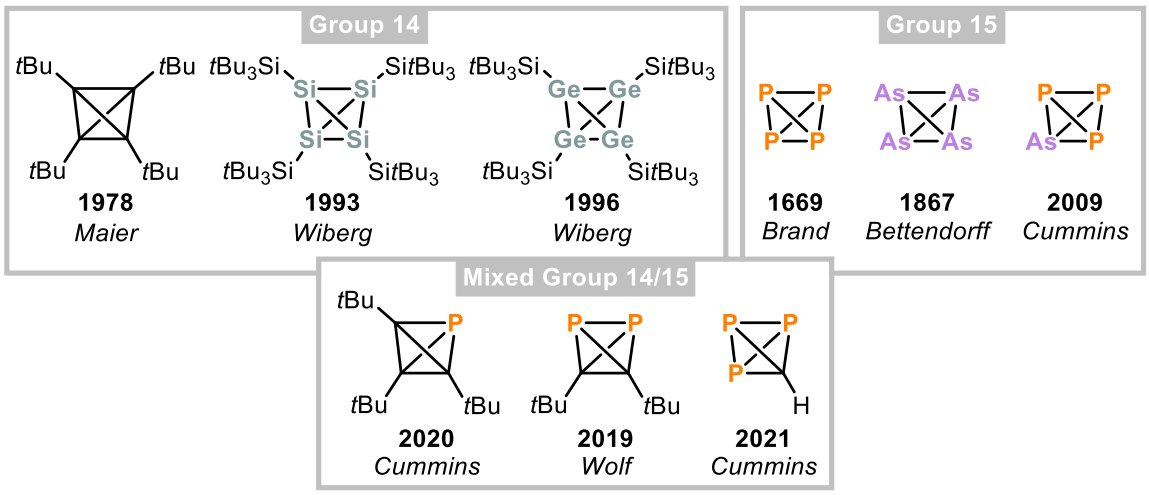
1 Phosphatetrahedranes[a]

Abstract: Tetrahedranes are highly strained molecules composed of four atoms arranged in a tetrahedral structure. They have attracted significant interest due to their rarity, high symmetry, and structural elegance. The first successful isolation of a carbon-based tetrahedrane represented a challenge for organic chemists. In contrast, white phosphorus (P_4), a tetrahedral allotrope of phosphorus, has been known since the 17th century. Although theoretical studies had long predicted the isolability of mixed phosphorus-carbon tetrahedranes, their experimental realisation remained elusive until recently. The successful syntheses of di-*tert*-butyldiphosphatetrahedrane, (tBuCP)$_2$, tri-*tert*-butylphosphatetrahedrane, (tBuC)$_3$P, and triphosphatetrahedrane (HC)P$_3$ have revitalised interest in this previously dormant research field. Reactivity studies have demonstrated that the unique bonding in these molecules enables access to novel organophosphorus compounds. This chapter provides an overview of group 14 and 15 tetrahedranes, followed by an analysis of the synthesis, stability, and reactivity of phosphatetrahedranes.



[a] This chapter was written by Maria K. Uttendorfer.

1.1 Tetrahedranes

1.1.1 Hydrocarbon Tetrahedranes

Symmetry has fascinated humanity since ancient times. A notable early example is Plato, who in his *Timaeus* describes five regular polyhedra (tetrahedron, cube, octahedron, icosahedron and dodecahedron) and associates them with the classical elements: fire, earth, air, water and ether, from which, according to his theory, the universe is composed.[1] When methine groups (CH) are placed at the vertices of these polyhedra, they form "Platonic hydrocarbons". Due to carbon's valence, the synthesis of the octahedrane and icosahedrane is not possible.[2] The synthesis of the remaining three Platonic hydrocarbons has posed a significant challenge for organic chemists. Notably, in 1964, Eaton and Cole successfully synthesised cubane (**1**, Figure 1)[3] and 18 years later, in 1982, Paquette and co-workers reported the preparation of dodecahedrane ($C_{20}H_{20}$, **2**).[4] The preparation of tetrahedrane (C_4H_4, **3**) has proven particularly difficult due to the strained C–C–C bond angles of 60°, which deviate significantly from the tetrahedral angle of 109.5°.[2] Theoretical studies suggest that tetrahedrane should be isolable.[5] This, however, remains an elusive goal.

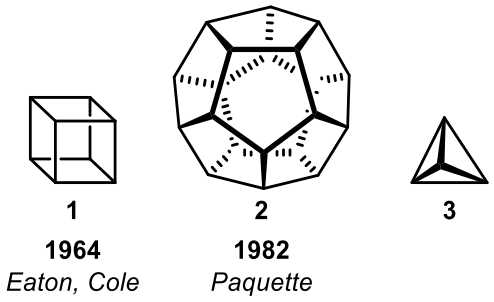
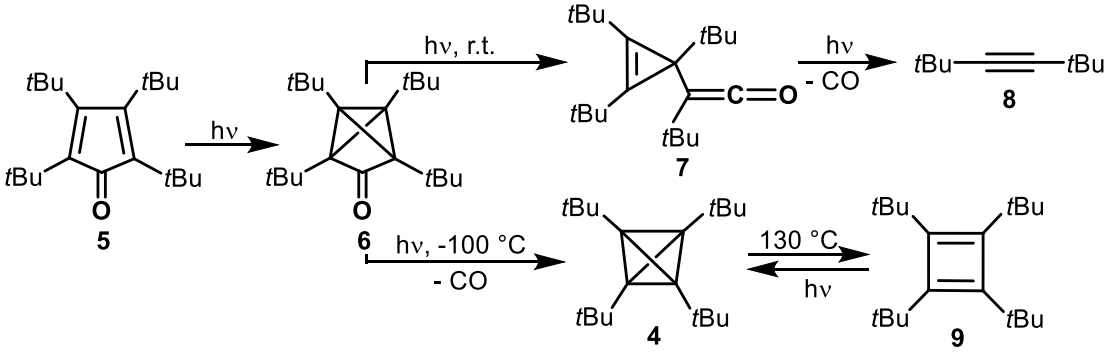


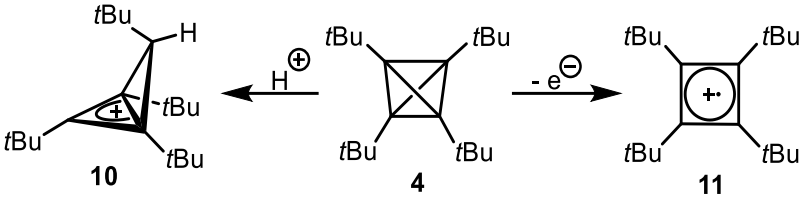
Figure 1. Platonic hydrocarbons.

In contrast, the synthesis of substituted tetrahedranes has been successful, with the first report being Maier and co-workers' synthesis of tetra-*tert*-butyltetrahedrane (**4**, Scheme 1) in 1978. Irradiation of tetra-*tert*-butylcyclopentadienone (**5**) with 254 nm light induces isomerisation, forming tricyclopentanone **6**. Prolonged irradiation at room temperature converts **6** to ketone **7**, which then forms di-*tert*-butylacetylene (**8**). However, at −100 °C, the reaction yields the desired tetra-*tert*-butyltetrahedrane (**4**). Upon heating, **4** isomerises to tetra-tert-butylcyclobutadiene (**9**), a transformation that can be reversed with irradiation ($\lambda_{max.}$>300 nm).[6]



Scheme 1. Synthesis of tetra-*tert*-butyltetrahedrane (**4**).

Surprisingly, **4** proved to be air stable despite the high bond strain in the molecule.[6] The high stability of **4** was attributed to the shielding provided by the four bulky *tert*-butyl groups, called the "corset-effect", which leads to large steric repulsion upon structural distortion and makes the tetrahedral core largely inaccessible to most reactants.[7] Experimental results support this explanation. However, protons are capable to pass through the sterically demanding substituents. Protonation of one of the tetrahedral carbon atoms results in C–C bond cleavage to form the homocyclopropenylium cation **10** (Scheme 2). Other reactivity observed for **4** begins with oxidation, forming a planar radical cation **11**, which then undergoes further conversions.[7,8]



Scheme 2. Reactivity of tetra-*tert*-butyltetrahedrane (**4**).

In the following years, a few more symmetrically and asymmetrically substituted tetrahedranes have been synthesised, all of which require sterically demanding substituents on the carbon atoms.[9–12]

1.1.2 Inorganic Tetrahedranes

In contrast to the few known examples of organic tetrahedranes, a broader definition, encompassing all molecules with a tetrahedral core, includes a variety of inorganic compounds. These inorganic tetrahedranes not only outnumber their organic counterparts but also surpass them in historical and industrial significance, with white phosphorus (P_4), the first isolated tetrahedral molecule, being the most prominent example.

Most known tetrahedranes are based on transition metals, spanning a range of charges, symmetries, and even incorporating different p-block elements.[13] In contrast, purely main group-based tetrahedranes are far less common. Among these, anionic species, particularly Zintl anions, have been most extensively studied and reviewed and will not be covered herein.[14] Cationic p-block tetrahedranes are exceedingly rare; the most prominent examples are $[EP_3]^+$ cations (E = S, Se, Te), formed by reaction of P_4 with ECl_3^+ and stabilised by weakly coordinating anions.[15] Recently, Krossing and co-workers have expanded this class to include to group 13 and 14 elements, by isolating clusters containing $[Al_4]^+$, $[SiAl_3]^+$, and $[GaAl_3]^+$ moieties.[16]

Neutral main group tetrahedranes have been reported for elements in groups 13, 14, and 15. The group 13 elements boron, aluminium, gallium, indium and thallium form tetrahedral compounds with a range of substituents.[17] These compounds are electron-deficient and form three-centre two-electron (3c2e) bonds. In contrast, neutral tetrahedranes derived from group 14 and 15 elements possess electro-precise two-centre two-electron (2c2e) bonds.

Heavier group 14 analogues of the organic hydrocarbon tetrahedranes have also been synthesised. In 1993, Wiberg and co-workers reported the preparation of tetrakis(tri-*tert*-butylsilyl)-*tetrahedro*-tetrasilane ([tBu$_3$Si)Si]$_4$ **12**, Figure 2),[18] followed by the analogous tetragermane compound ([tBu$_3$Si)Ge]$_4$ **13**) in 1996.[19] Both were synthesised via reactions of tBu$_3$SiNa with tetrabromo-l,2-bis(supersilyl)disilane or the analogous germanium compounds, eliminating NaBr and tBu$_3$SiBr.[18,19] Compound **13** can also be synthesised by reaction of tBu$_3$SiNa with GeCl$_2$(1,4-dioxane). Although octastannacubane [(2,6-Et$_2$-C$_6$H$_3$)$_8$Sn$_8$] was synthesised as early as in 1990,[20] *tetrahedro*-tetrastannanes and *tetrahedro*-tetraplumbanes have not been reported to date.

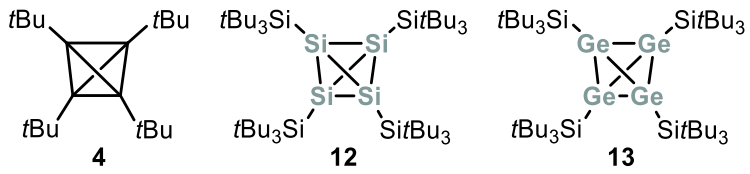


Figure 2. Selected group 14 tetrahedranes synthesised by the groups of Maier (**4**) and Wiberg (**12** and **13**).

While all the tetrahedranes mentioned above are products of synthetic advances from the 20th and 21st centuries, the most prominent group 15 tetrahedrane, white phosphorus (P$_4$, **14**, Figure 3a), was isolated much earlier, in 1669, by Henning Brand.[21] The molecular structure of this waxy, white material (at room temperature) was elucidated centuries later and found to consist of discrete tetrahedral P$_4$ units with P–P–P bond angles of 60°.[22,23] To date, white phosphorus remains an industrially significant tetrahedrane, produced on a multi-ton scale by reacting apatite, Ca$_5$(PO$_4$)$_3$(OH,F,Cl), with coke (C) and silica (SiO$_2$) in an electric arc furnace at 1400-1500 °C. This process forms P$_2$, which dimerises to P$_4$ upon cooling.[24,25] Academic research has extensively explored the reactivity of white phosphorus, revealing its transformation into a wide range of organic and inorganic phosphorus compounds.[26–30]

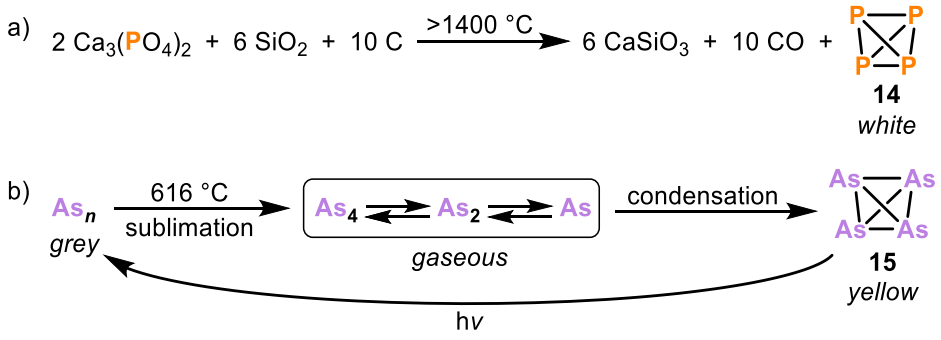


Figure 3. Synthesis of white phosphorus (a) and yellow arsenic (b).

Tetrahedral yellow arsenic (As$_4$, **15**, Figure 3b) is structurally similar to white phosphorus. First synthesised by Bettendorff in 1867, its molecular structure was not elucidated until the 20th century.[22,31] Sublimation of grey arsenic at 616 °C produces gaseous As$_4$ molecules, which can be condensed onto cold surfaces or in organic solvents, forming solid yellow arsenic. However, due to its extreme sensitivity to air and light, yellow arsenic polymerises back to grey arsenic. To

slow its decomposition, yellow arsenic is typically stored in solution, which has enabled the study of its rich reactivity. These investigations have led to the formation of a variety of main group and transition metal arsenic compounds.[32] The two heavier homologues, Sb_4 and Bi_4, have not yet been isolated as bulk compounds. Nevertheless, Sb_4 molecules have been detected in antimony thin films and in noble gas matrices[33] Laser fluorescence studies suggest the presence of tetrahedral Bi_4 in bismuth vapour.[34] In contrast, the lightest conceivable homologue, tetraazatetrahedrane (N_4), has not been detected. This can be rationalised by comparing the stability of P_4 and a hypothetical N_4 to the respective diatomic species: Due to the similar radii of the 2*s* and 2*p* valence orbitals, N_4 experiences stronger Pauli repulsion, which weakens the N–N σ-bonds and destabilises the tetrahedral structure. In contrast, the greater difference between the 3*s* and 3*p* orbital sizes in phosphorus reduces repulsion, enabling the formation of stable P_4 tetrahedra.[35]

Neutral heteroatomic tetrahedranes, uncharged compounds containing two different types of atoms in their tetrahedral core, of the composition As_nP_{4-n} (n = 1-3, **16**-**18**, Figure 4) were detected by Ozin in 1970 using gas-phase Raman spectroscopy of mixed phosphorus and arsenic vapours. Similarly, experiments with phosphorus and antimony vapours led to the formation of P_3Sb (**19**).[36]

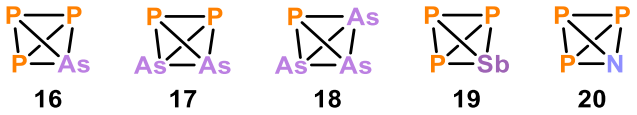
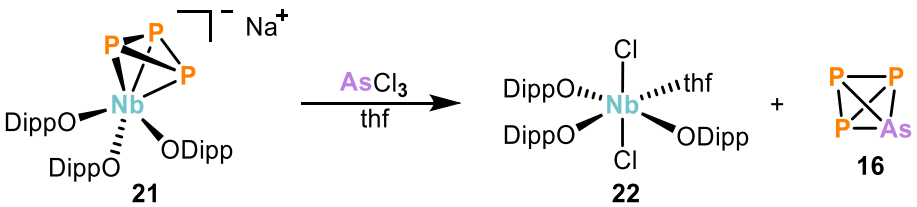


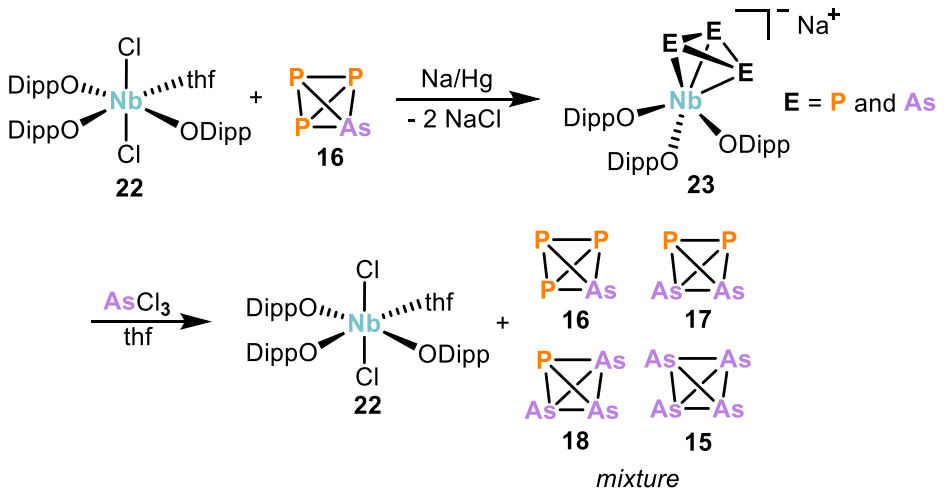
Figure 4. Heteroatomic tetrahedranes first detected by Ozin (**16**-**19**) and Kaiser (**20**).

The first successful isolation of a heteroatomic main-group tetrahedrane was reported by Cummins and co-workers in 2009. In this work, reaction of $[P_3Nb(ODipp)_3]^-$ (**21**, Scheme 3), a P_3^{3-} source, with $AsCl_3$ via salt metathesis yielded AsP_3 (**16**), which was obtained as a bright white solid upon crystallisation or sublimation. In a similar reaction, SbP_3 (**19**) was generated by treating **21** with $SbCl_3$. However, this compound could only be detected by ^{31}P NMR spectroscopy and was not isolated, likely due to its decomposition in solution, even at low temperatures (−30 °C, 60 min).[37]



Scheme 3. Synthesis of AsP_3 (**16**).

A mixture of all four anionic *cyclo*-E_3 compounds **23** (E = P, As; Scheme 4), analogous to **21**, is obtained from the reaction of AsP_3, $Cl_2Nb(ODipp)_3$ (**22**), and a Na/Hg amalgam. Treatment of **23** with $AsCl_3$ yields compounds **15**–**18**, which were identified by ^{31}P NMR spectroscopy and GC-MS. However, **17** and **18** have not yet been isolated in pure form.[38]



Scheme 4. Synthesis of As_nP_{4-n} (n = 1-4).

In 2022, Kaiser and co-workers reported the synthesis of P_3N (**20**, Figure 4) by irradiating phosphine-nitrogen ices with an electron beam of 5 keV energy at 5 K. **20** was subsequently detected using isomer-selective, soft photoionisation reflection time-of-flight mass spectrometry.[39]

Although no ^{31}P NMR spectrum of **20** has been reported to date, tetrahedral phosphorus-containing compounds generally exhibit ^{31}P NMR signals in the high-field region (Table 1). For instance, P_4 resonates at −520 ppm. Substitution of phosphorus atoms with arsenic in As_nP_{4-n} (n = 1-3) leads to a low field shift, attributed to the more negative paramagnetic shielding term of these tetrahedranes.[37,38,40]

Table 1. ^{31}P NMR shifts of phosphorus containing group tetrahedranes.[37,38,41–43]

	^{31}P NMR shifts
P_4 (**14**)	−520 ppm
AsP_3 (**16**)	−484 ppm
As_2P_2 (**17**)	−452 ppm
As_3P (**18**)	−432 ppm
SbP_3 (**19**)	−462 ppm
(tBuCP)$_2$ (**24**)	−468 ppm
(tBuC)$_3$P (**25**)	−488 ppm
HCP_3 (**26**)	−540 ppm

1.2 Phosphatetrahedranes

Phosphorus and carbon are linked by a 'diagonal relationship' in the periodic table, reflecting their similar electronegativity and the isolobal relationship between P and CH fragments.[44] This connection is evident in phosphorus's ability to form element-element bonds, as well as rings and networks that resemble analogous carbon-based structures.[25] These similarities also enable the substitution of carbon fragments with phosphorus in molecular structures, paving the way for the synthesis of a diverse range of organophosphorus compounds.[45] Although predicted by calculations, mixed P/C-containing tetrahedranes remained elusive until recently.[46] In late 2019, Wolf and co-workers reported the synthesis of di-*tert*-butyldiphosphatetrahedrane, (tBuCP)$_2$ (**24**, Figure 5),[41] followed by the report of tri-*tert*-butylphosphatetrahedrane, (tBuC)$_3$P (**25**), by Cummins and co-workers in March 2020.[42] Additionally, Cummins and co-workers synthesised the phosphorus-rich triphosphatetrahedrane HCP_3 (**26**), further advancing this previously dormant research field.[43] This section explores the synthesis, stability and reactivity of these distinctive compounds.

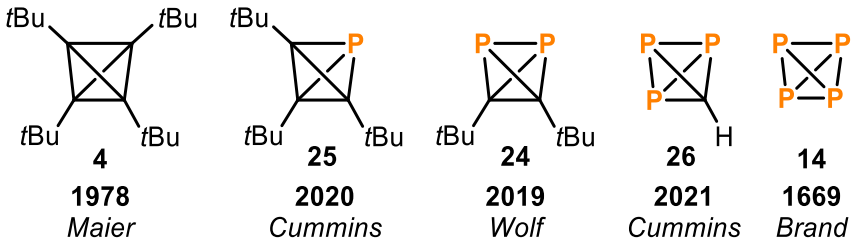
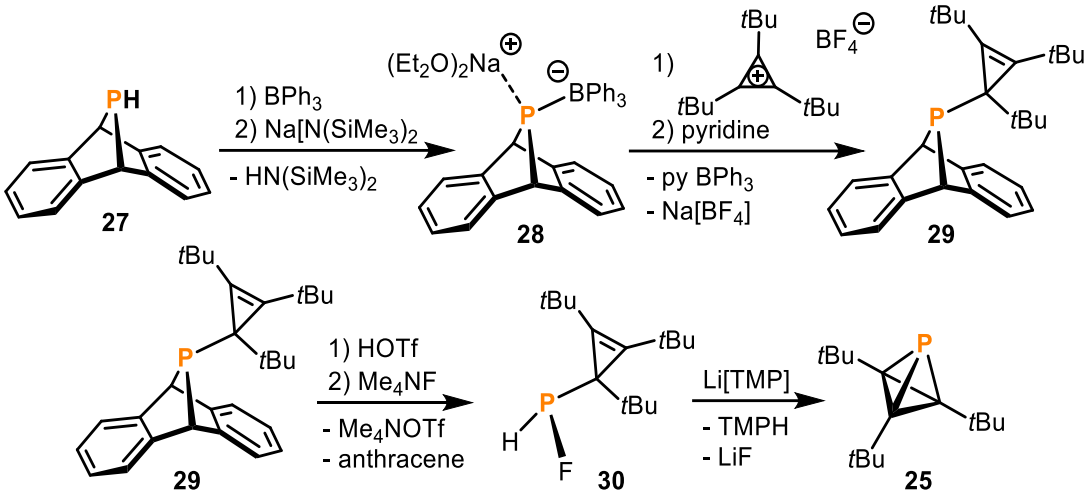


Figure 5. Carbon- and phosphorus based tetrahedranes.

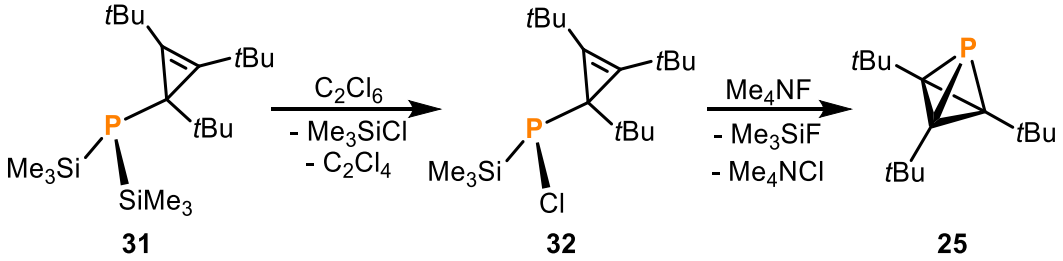
1.2.1 Synthesis

The initial multi-step synthesis of **25** commenced with deprotonation of the anthracene-based secondary phosphine **27** using sodium bis(trimethylsilyl)amide, in the presence of BPh_3 yielding **28** (Scheme 5).[42] While **27** does not react with the tri-*tert*-butylcyclopropenium ion, the activated Lewis acid adduct **28** does, resulting in the formation of cyclopropenylphosphine **29**. Irradiation of **29** (λ_{max} = 254 nm, 25 °C, 10 min) enabled the ^{31}P NMR spectroscopic detection of tri-*tert*-butylphosphatetrahedrane (**25**). However, the photoreaction lacked selectivity and had low conversions. Longer reaction times led to decomposition of **25**. This prompted the development of an alternative route, *i.e.* reaction of **29** with triflic acid followed by reaction with Me_4NF leading to anthracene elimination and formation of the fluorophosphane **30**. Elimination of HF from **29** by addition of a strong base yields **25** as a low-melting, colourless solid through intramolecular cycloaddition, though in low isolation yields (19%). **25** is remarkably stable at high temperatures (75 °C, 45 min) and can even be exposed to air for short periods (30 min).



Scheme 5. Initial synthesis of tri-*tert*-butylphosphatetrahedrane (**25**). TMP = tetramethylpiperidide; TMPH = tetramethylpiperidine.

To achieve a more efficient and higher-yielding synthesis of **25**, Cummins and co-workers developed a new route starting from the $(t\text{BuCP})_3P(SiMe_3)_2$ (**31**, Scheme 6), which is readily accessible on a large-scale.[47] Treatment with hexachloroethane produces chloro(trimethylsilyl)phosphine **32**, which, upon reaction with tetramethylammonium fluoride, eliminates Me_3SiF, yielding **25** in moderate isolated yield (33%).

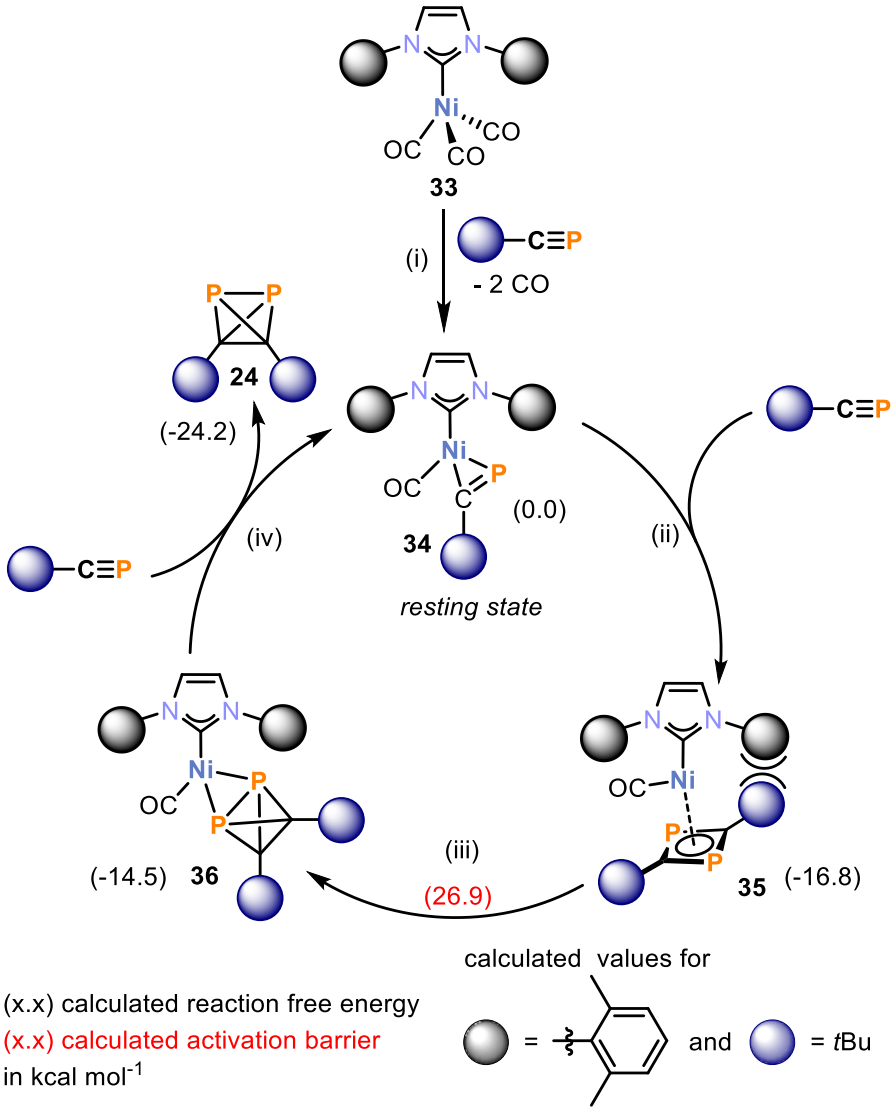


Scheme 6. Improved synthesis of tri-*tert*-butylphosphatetrahedrane (**25**).

Confirmation of the tetrahedral structure of **25** was provided by X-ray diffraction analysis, although the data quality was insufficient for a detailed discussion of bond metrics.

The synthesis of **24** was achieved through the nickel-catalysed dimerisation of *tert*-butylphosphaalkyne, allowing for its synthesis on a preparative scale.[41] Compound 24, with a melting point of −32 °C, can be isolated as a pyrophoric, yellow oil. To investigate the formation mechanism of **24**, ^{31}P NMR spectroscopic reaction monitoring and DFT calculations were used. These analyses revealed an initial substitution of two CO ligands on the Ni(0) precatalyst **33** by an η^2-coordinating phosphaalkyne, resulting in **34**, the resting state in the catalytic cycle (step i, Scheme 7). Reaction of a second equivalent of *t*BuCP with **34** then forms the 1,3-diphosphacyclobutadiene complex **35** (step ii, Scheme 7). Crucially, the intermediate **35** is destabilised by the steric repulsion between the bulky substituents on the N-heterocyclic carbene ligand (IMes or IPr) and the *t*Bu groups of the diphosphacyclobutadiene ligand. This destabilisation promotes the formation of a diphosphatetrahedrane unit, generating complex **36**

(step iii, Scheme 7). Substitution of **24** by phosphaalkyne regenerates the resting state **34** (step iv, Scheme 7). These findings indicate that sterically demanding NHC ligands and phosphaalkynes are essential for the diphosphatetrahedrane, as they destabilise the intermediates **35** and lower the activation barrier for the rate-determining step (step iii, Scheme 7). Notably, when 1-adamantylphosphaalkyne was subjected to the same reaction conditions, diadamantyldiphosphatetrahendrane was obtained in low yields (10%), although its isolation has not yet been achieved.



Scheme 7. Proposed catalytic cycle for the synthesis of **24** based on ^{31}P NMR spectroscopic observations and DFT calculations with calculated free reaction energies and activation barriers for NHC = IMes and *t*BuCP. Adapted from reference [48].

Initially, X-ray diffraction analysis faced challenges due to **24**'s sensitivity to light, air, and temperature, as well as its liquid aggregation state at room temperature.[41] However, structure determination was achieved by growing single crystals from a mixture of **24** with *n*-pentane within a capillary, which was then carefully cooled.[49] The resulting crystallographic data confirmed the similarities between the C–C bond lengths in **24** and (*t*BuC)$_4$, as well as between

the P–P bond lengths in **24** and P_4.[49,50] In light of these parallels, the electronic structures were compared. Earlier experimental studies had already suggested similarities between **24** and P_4.[41,51] DFT calculations (TPSS-D3BJ/def2-TZVP level of theory) supported these findings, revealing frontier orbitals that are comparable in both shape and energy (Figure 6). However, the frontier orbitals of **24** lack the degeneracy of the t_1 and e orbitals of P_4 due to its reduced symmetry.[49]

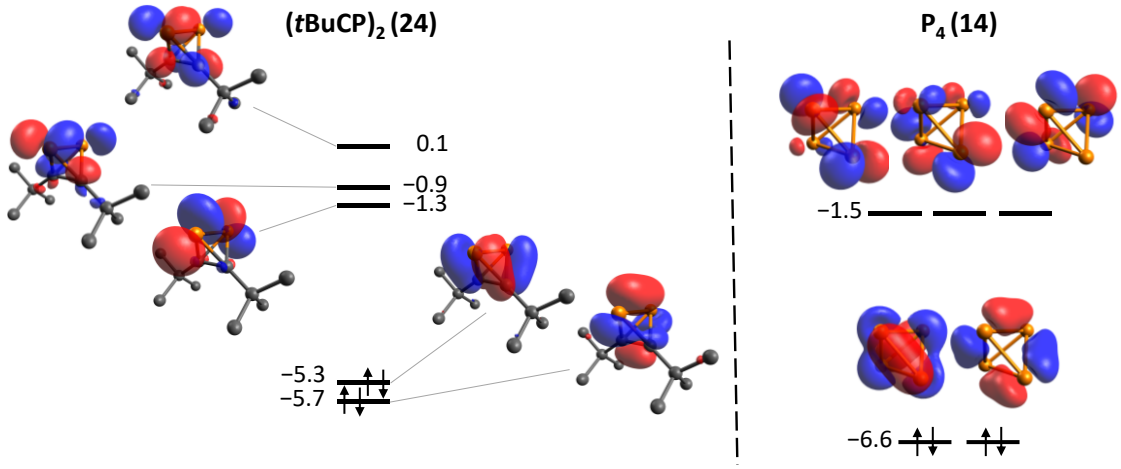
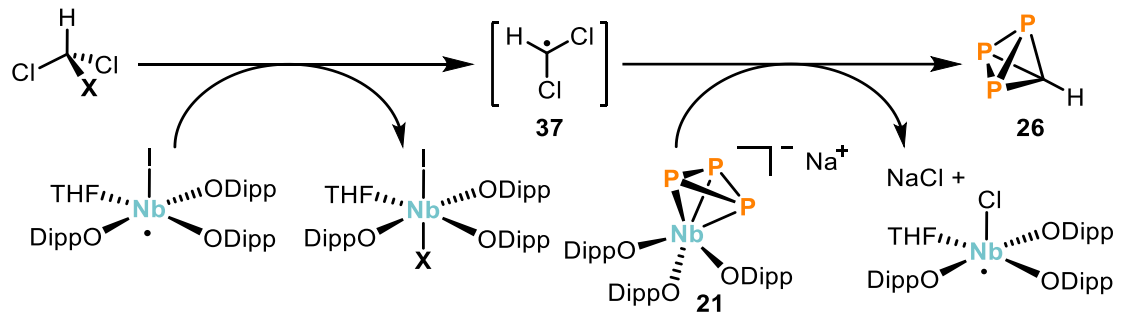


Figure 6. Frontier molecular orbitals of **24** (left) and P_4 (right). Calculated on the TPSS-D3BJ/def2-TZVP level of theory. Energies in eV. Adapted from reference [49].

Cummins and co-workers also reported the triphosphatetrahedrane HCP_3 (**26**, Scheme 8), which was the remaining unknown member in the phosphatetrahedrane series.[43] Compound **26** was synthesised by reaction of the dichloromethyl radical **37** (generated from $CHXCl_2$ (X = Cl or Br) and $[INb(ODipp)_3(THF)]$) with the anionic niobium complex $[Na(THF)_3][P_3Nb(ODipp)_3]$ (**21**, Scheme 8).



Scheme 8. Synthesis of **26** through the intermediary carbon-centred radical **37**. X = Cl, Br.

Compound **26** is only stable in dilute solutions and prone to polymerisation, which hampers reactivity studies.[43] However, the structural characterisation of **26** was enabled by coordination to an iron complex (*vide infra*, Scheme 14). The related $(Me_3SiC)P_3$ can be obtained by subjecting (bromodichloromethyl)trimethylsilane instead of $CHXCl_2$ to these reaction conditions. The identity of $(Me_3SiC)P_3$ was confirmed by multinuclear NMR spectroscopy and GC-MS, but its isolation was not reported so far.

The ^{31}P NMR resonances of the three isolated phosphatetrahedranes **24**, **25**, and **26** at −468 ppm, −488 ppm, and −540 ppm (see Table 1), respectively, indicate strongly shielded nuclei, similar to those observed for other tetrahedranes such as P_4 and P_nAs_{4-n} (n = 1-3, *vide supra*).[37,38,41–43,48]

1.2.2 Effects on Stability

Phosphatetrahedranes, like other 14 and 15 tetrahedranes, formally feature electron-precise 2-centre 2-electron (2c2e) bonds. A defining feature of these molecules are their unusual bond angles. As early as 1885, Bayer described strain in molecules as arising from deviations of bond angles from their ideal values (*e.g.* 109.5° for sp^3 hybridised carbon atoms).[25,52] Subsequent studies introduced the concept of bent bonds to describe the bonding in highly strained systems.[53] Indeed, determination of the electron by X-ray diffractions have revealed a displacement of the electron density away from the direct line of internuclear connection, supporting this model.[54]

To understand how ring strain affects the stability of phosphatetrahedranes, Cummins and co-workers investigated homodesmotic reaction energies for the series $(HC)_nP_{4-n}$ (n = 0-4).[43] For instance the all carbon tetrahedrane $(CH)_4$ (**3**), which contains six bent bonds, was found to possess a significant strain enthalpy of 135.8 kcal/mol. In contrast, white phosphorus (P_4) exhibits a much lower strain energy of only 13.7 kcal/mol, suggesting that it is relatively unstrained. This difference is attributed to the more diffuse frontier orbitals of heavier p-block elements like phosphorus as well as the high s-character of the phosphorus lone pairs, which reduces the s-character in the bonding σ-bonds, an effect known as σ-relaxation.[55] Consequently, the strain energy in phosphatetrahedranes decreases with the increasing phosphorus content: $(HC)_3P$ (95.5 kcal/mol), $(HCP)_2$ (63.3 kcal/mol), and $(HC)P_3$ (**26**, 37.3 kcal/mol).[43]

Many tetrahedranes exhibit remarkable stability despite being destabilised by significant ring strain. This counterintuitive stability is largely attributed to spherical aromaticity, a concept that extends classic aromaticity into three dimensions.[56] According to the Hirsch rule, originally proposed for fullerenes and later generalised, spherical aromaticity arises in systems with $2(n+1)^2$ delocalised electrons.[57,58] A well-established method to evaluate aromaticity is the calculation of nucleus-independent chemical shifts (NICS) at the centres of rings or polyhedra.[59] Strongly negative NICS values correspond to pronounced diamagnetic ring currents, indicating aromatic character, while positive values suggest antiaromaticity.[58,59] Indeed, significantly negative NICS values have been reported for carbon-based tetrahedranes, such as $(HC)_4$ (−48.5 ppm)[60,61] and (tBuC)$_4$ (**4**, −45.0 ppm)[61] as well as for P_4 (−52.9 ppm).[58] Furthermore, the calculated NICS value of (tBuCP)$_2$ (**24**, −50.3 ppm), along with evidence of magnetically induced ring currents, confirms its stabilisation by spherical aromaticity.[49] Although NICS values have not yet been reported for other phosphatetrahedranes, similarly negative values, and thus a significant aromatic stabilisation, can reasonably be anticipated.

Additionally, the substituents attached to core atoms in tetrahedranes plays a significant role in the stabilisation. Maier and co-workers attributed the exceptional stability of (tBuC)$_4$ to the steric

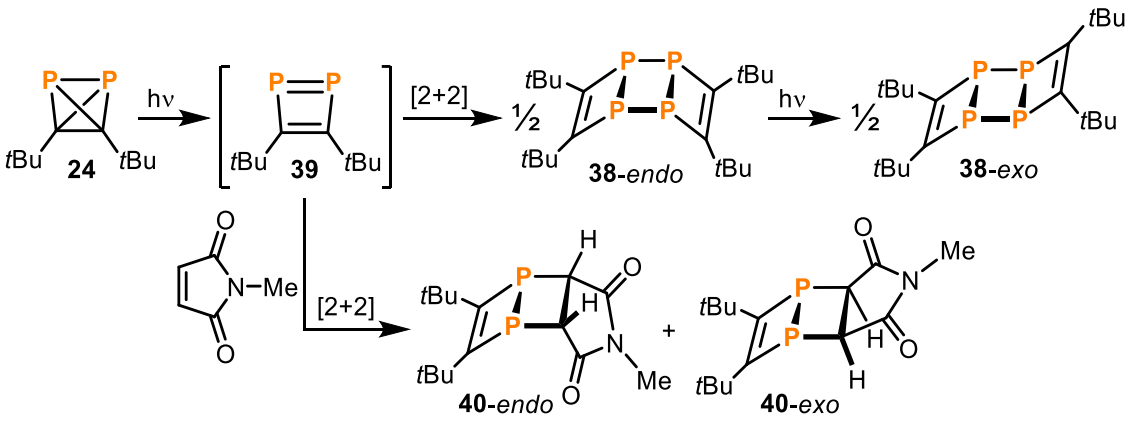
shielding provided by the four bulky *tert*-butyl groups. Additionally, they suggested that these substituents tend to orient themselves as far apart as possible, favouring a tetrahedral geometry, a phenomenon Maier and co-workers dubbed "corset effect".[6,7] Indeed, several attempts to isolate carbon-based tetrahedranes with smaller substituents were unsuccessful, highlighting the importance of steric bulk.[62] Nevertheless, Sekiguchi and co-workers succeeded in isolating stable tetrahedranes bearing smaller groups, attributing their stability to $SiMe_3$ substituents.[10,12,63] These groups act both as σ-donors and π-acceptors, delocalising electron density away from the strained tetrahedral core.[9,64]

Bader and co-workers introduced the concept of attractive hydrogen-hydrogen bonds, identifying up to 18 such interactions in $(t\text{BuC})_4$.[65] These contribute to the stability of the compound through London dispersion interactions. Similarly, in $(t\text{BuC})_3\text{P}$ (**25**), nine H···H interactions were identified between *tert*-butyl groups, with their stabilisation outweighing repulsive effects, such as Pauli repulsion, present in the system.[66] Furthermore, an even more significant stabilising factor was identified: electron delocalisation from C–C and C–P bonding orbitals within the tetrahedral core to $C–CMe_3$ antibonding orbitals.[66,67] This delocalisation substantially enhances the overall stability of the tetrahedrane.

In summary, although phosphatetrahedranes are inherently strained molecules, several factors contribute to their stability: ring strain reduction through σ-relaxation, spherical aromaticity, and, in some cases, stabilising ligand effects. Understanding these factors is not only crucial for the design of new phosphatetrahedranes but also for exploring their reactivity.

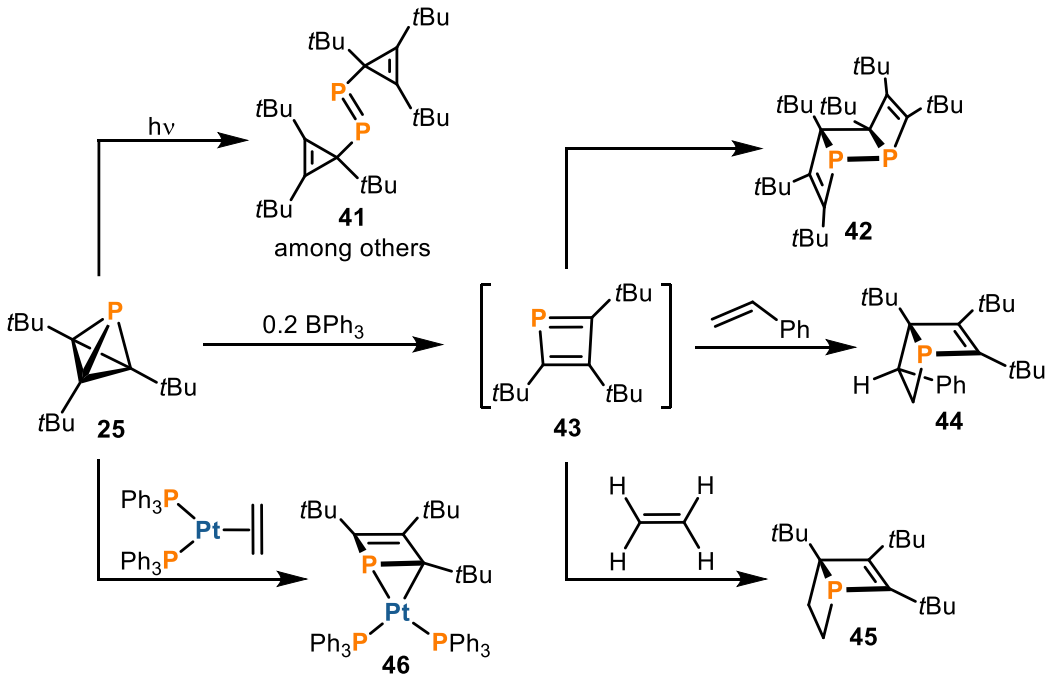
1.2.3 Reactivity

The relatively high-yielding, catalytic synthesis of $(t\text{BuCP})_2$ (**24**) allowed a systematic investigation of its stability and reactivity.[41] Compound **24** remains stable in dilute solutions for at least 15 h at ambient temperature. However, when exposed to elevated temperatures (>40 °C), it dimerises the ladderane $(t\text{BuCP})_4$ **38**.[41,49,68] This dimerisation reaction is also observed upon exposure to near UV light.[49] The process was analysed in detail using multinuclear NMR spectroscopy, stationary and transient UV/Vis absorption spectroscopy, and quantum chemical calculations. These studies led to the conclusion that the initial step involves a light-induced isomerisation of **24** to the planar 1,2-diphosphacyclobutadiene **39** (Scheme 9). Then **39** undergoes a [2+2] cycloaddition to form the transient ladderane **38**-*endo*, which subsequently isomerises to the more stable **38**-*exo* isomer. The diphosphacyclobutadiene **39** has been trapped with *N*-methylmaleimide, yielding the novel organophosphorus compounds **40**-*endo* and **40**-*exo* (Scheme 9).



Scheme 9. Light-driven isomerisation of **24** and subsequent [2+2] cycloaddition reactivity.

In fact, photochemical isomerisation is a key feature of related tetrahedranes and is observed in compounds such as (*t*BuC)$_4$, P$_4$ and (*t*BuC)$_3$P (**25**).[7,42,49,69] However, for **25** this process lacks selectivity, leading to a variety of mostly unidentified products, with the only identified reaction product so far being the diphosphene **41**, a dimerisation product of **25** (Scheme 10).[42]

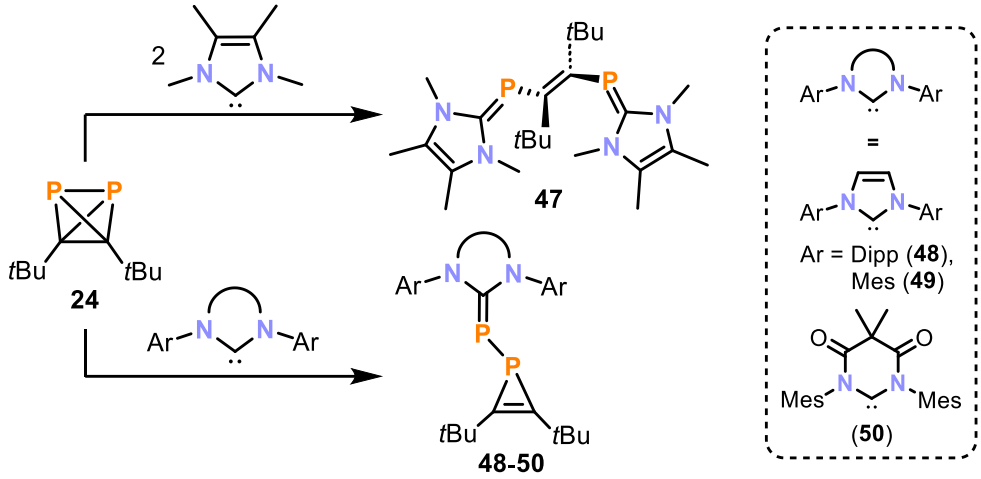


Scheme 10. Dimerisation and isomerisation of **25**.

More controlled dimerisation of **25** can be achieved upon reaction with Lewis acids.[42,47] Substochiometric amounts of triphenyl borane are sufficient to trigger the dimerisation of **25** to ladderane **42** (Scheme 10) similar to **38**-*exo*, a compound formed upon dimerisation of (*t*BuCP)$_2$ (**24**).[41,47] Quantum chemical calculations on the DLPNO-CCSD(T)/cc-pVTZ//B3LYP-D3BJ/def2-TZVP(-f) level of theory indicate that in an initial step, the Lewis acid induces isomerisation to the intermediary tri-*tert*-butylphosphacyclobutadiene (**43**), which is susceptible to [2+2] cycloaddition reaction, forming the observed ladderane **42**.[47] This proposed mechanism was further supported by the successful trapping of **43** in [2+2] reactions with alkenes (styrene and ethylene) to form **44** and **45**, respectively. Notably, reaction with (Ph$_3$P)$_2$Pt(C$_2$H$_4$) also leads

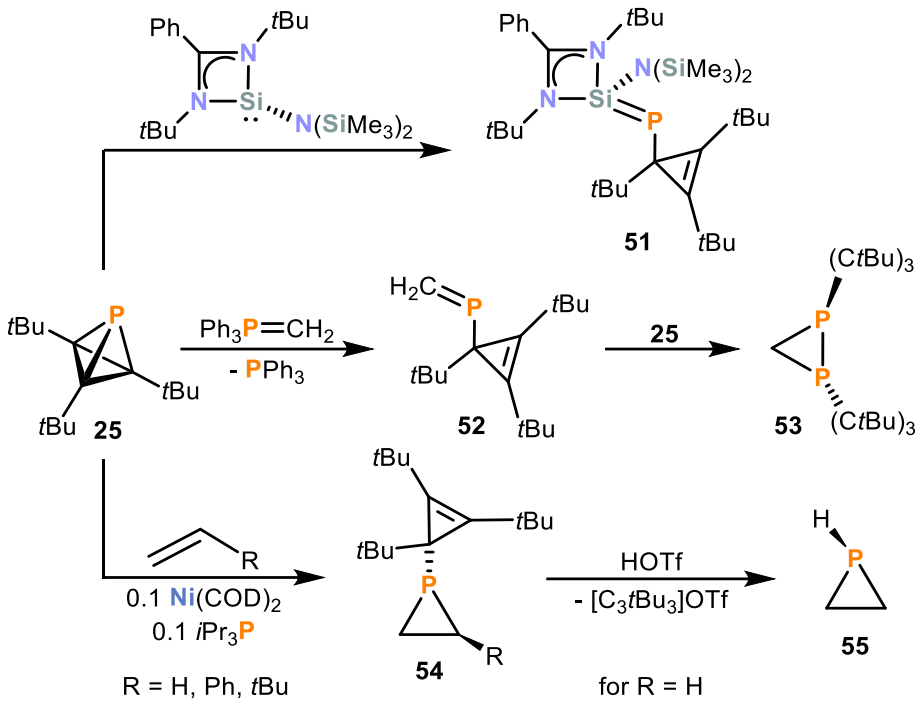
to isomerisation of **25** to **43**, which then coordinates to the platinum via a P−C bond in an η^2-fashion in the complex **46**.

The reactivity of **24** with main group compounds was also investigated. Reactions with N-heterocyclic carbenes (NHCs) produce two distinct types of unsaturated organophosphorus compounds, depending on the steric and electronic properties of the NHC.[51] The vinyl-bridged bis(phosphaalkyne) **47** is selectively formed when **24** reacts with 2,3,4,5-tetramethylimidazolin-2-ylidene (TMC, Scheme 11). This represents a rare instance of P−P bond cleavage in **24**, as most other reactions involve P−C bond scission.[41,49,51,70,71] In contrast, reactions of **24** with bulkier NHCs, such as IMes, IPr or ^{Mes}DAC, result in the formation of 1*H*-phosphirenes **48**-**50**, which arise from P−C bond cleavage (Scheme 11). The reactivity of these bulkier NHCs with **24** mirrors their reactivity with tetrahedral molecules like P_4 and $(t\text{BuC})_4$.[72]



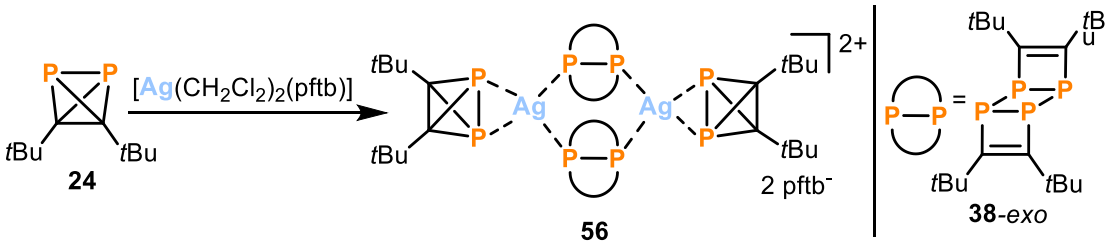
Scheme 11. Reactivity of **24** towards N-heterocyclic carbenes (NHCs).

In contrast, **25** does not react with either IMes or IPr.[73] However, treatment with a base-stabilises silylene results in a cyclopropene-type phosphasilylene (**51**, Scheme 12), resembling the 1*H*-phosphirenes **48**-**50**. Compound **52** with a similar structural motif was obtained by reacting **25** with the Wittig reagent Ph_3PCH_2. Further reaction of **52** with a second equivalent of **25** produced the diphosphirane **53**. The facile twofold P−C bond cleavage in **25** was also exploited in a catalytic regime, where substochiometric amounts of $Ni(cod)_2$ and $i\text{Pr}_3\text{P}$, along with excess ethylene, styrene, neohexene, or 1,3-cyclohexadiene, were added to **25**, resulting in the formation of phosphiranes such as **54**. The parent phosphirane **55** is formed upon HOTf-induced cleavage of the $(t\text{BuC})_3$ group from **54**-H, demonstrating that **25** can serve as a P_1 source. Overall, the reactivity of **25** towards main group compounds is characterised by strain release, which is facilitated by isomerisation, most prominently the formation of transient tri-*tert*-butylphosphacyclobutadiene (**43**), or twofold P−C bond cleavage, yielding a $(t\text{BuC})_3$–P building block in a variety of reactions (Scheme 12).[42,47,73]



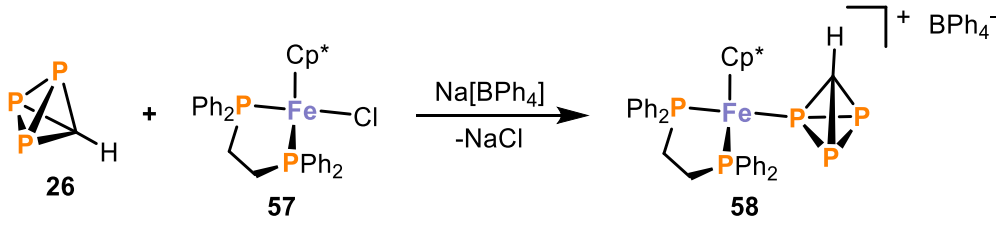
Scheme 12. Compound **25** acting as a P_1 building block.

Following these observations, and drawing on the extensive coordination chemistry of the P_4 molecule,[26–30] significant attention was given to the coordination behaviour of **24**. Treatment with the weakly coordinating aluminate salt $[Ag(CH_2Cl_2)_2(pftb)]$ (pftb=$Al\{OC(CF_3)_3\}_4$) gave the silver(I) complex **56** (Scheme 13). This compound demonstrates the ability of **24** to coordinate side-on to valence electron-rich (d^{10}) transition metals.[41] While similar side-on coordination has been observed in a few P_4 complexes, this coordination motif remains relatively rare.[74]



Scheme 13. Transition metal complex containing the intact diphosphatetrahedrane **24**.

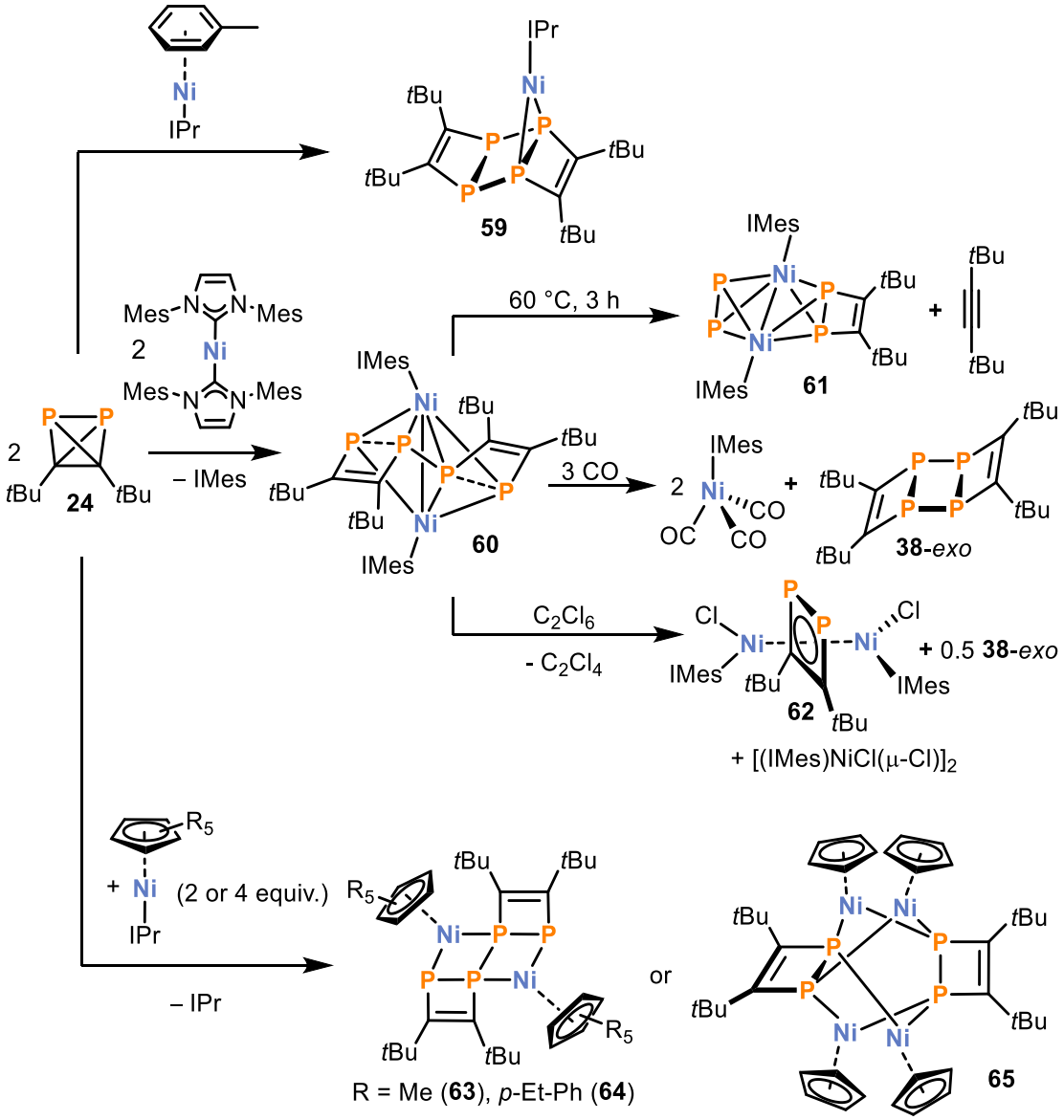
So far, an η^1-coordination of **24** has not been observed, although this coordination mode has been reported in a few P_4 complexes, such as in reaction with (dppe)Fe(Cp*)Cl. (**57**).[75] When this complex is treated with (HCP_3) (**26**) in the presence of $Na[BPh_4]$, it forms the iron-triphosphatetrahedrane complex $[(dppe)Fe(Cp^*)(\eta^1\text{-}HCP_3)][BPh_4]$ (**58**, Scheme 14), which is, to date, the only reported complex containing a η^1-coordinated phosphatetrahedrane.[43]



Scheme 14. Synthesis of [(dppe)Fe(Cp*)(η^1-HCP_3)][BPh_4] (**58**).

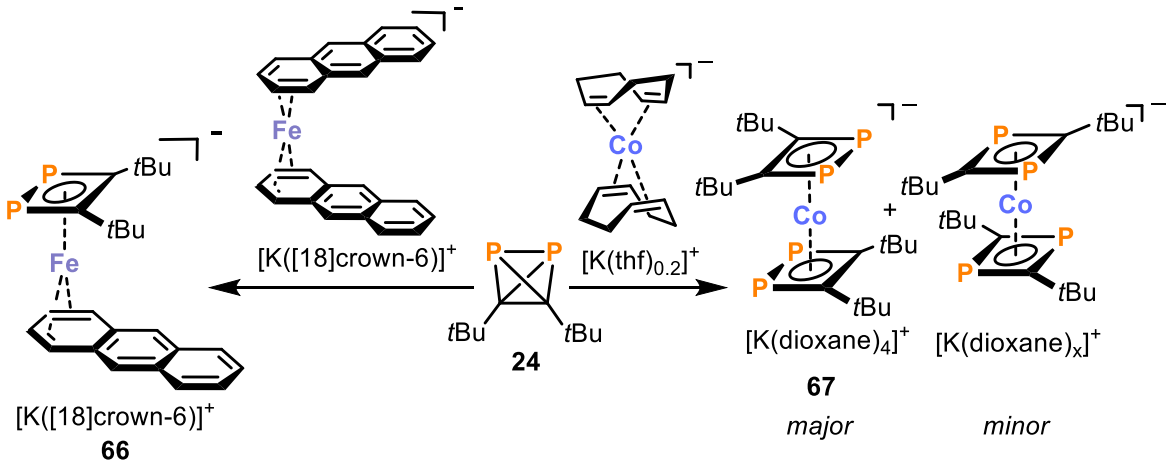
In contrast to the coordination of intact phosphatetrahedranes, reactions of **24** with Ni(0) and Ni(I) complexes lead to the formation of (*t*BuCP)$_n$-frameworks (n = 2, 4), resulting from P−C bond cleavage and, in some cases, the coupling of (*t*BuCP)$_2$ moieties (complexes **59**-**65**, Scheme 15).[71] When **24** reacts with the complexes [$(IPr)_2Ni$] and [(IPr)Ni(η^6-toluene)], which contain the sterically demanding NHC IPr, it dimerises to form the ladderane **38**-*exo*. Coordination of the ladderane, acting as a diphosphine ligand, to nickel results in the formation of complex **59**. In contrast, reaction with similar complexes containing the sterically less demanding NHC ligand IMes lead to a markedly different product. The resulting complex **60** is a dinuclear species featuring a (*t*BuCP)$_4$ unit with partially cleaved P−P bonds. Upon storage in solution or heating to 60 °C over 3 h, bis-*tert*-butylacetylene is eliminated, forming the P_2 complex **61**, which demonstrates that **24** can serve as a source of diphosphorus. Addition of CO gas or hexachloroethane to **60** causes the release of the (*t*BuCP)$_4$ framework. The latter also leads to the formation of the dinuclear [(IMes)NiCl(μ-Cl)]$_2$ and the chlorinated inverted sandwich complex **62**, which features a 1,2-diphosphacyclobutadiene ligand in a μ,η^4:η^4-coordination mode.

Ni(I) radicals of type [(Cp^R)Ni(IPr)] (Cp^R = C_5H_5, C_5Me_5, $C_5(4\text{-}EtC_6H_4)_5$) have been shown to react with P_4 upon homolytic cleavage of a P−P bond, leading to the formation of dinuclear complexes with a bridging, bicyclic P_4^{2-} ligand.[76] In contrast, similar reactions of these Ni(I) radical complexes with **24** result in the cleavage of two P−C bonds.[71] For radical complexes with bulky pentamethylcyclopentadienyl or pentaarylcyclopentadienyl ligands, the resulting complexes (**63** and **64**) feature a (*t*BuCP)$_4$ ligand like that in **60**. However, when the same reaction is carried out with a less sterically demanding cyclopentadienyl ligand, the tetranuclear complex **65** is formed, which contains two 1,2-diphosphacyclobutene-1,2-diide ligands coordinated by four (CpNi) moieties.



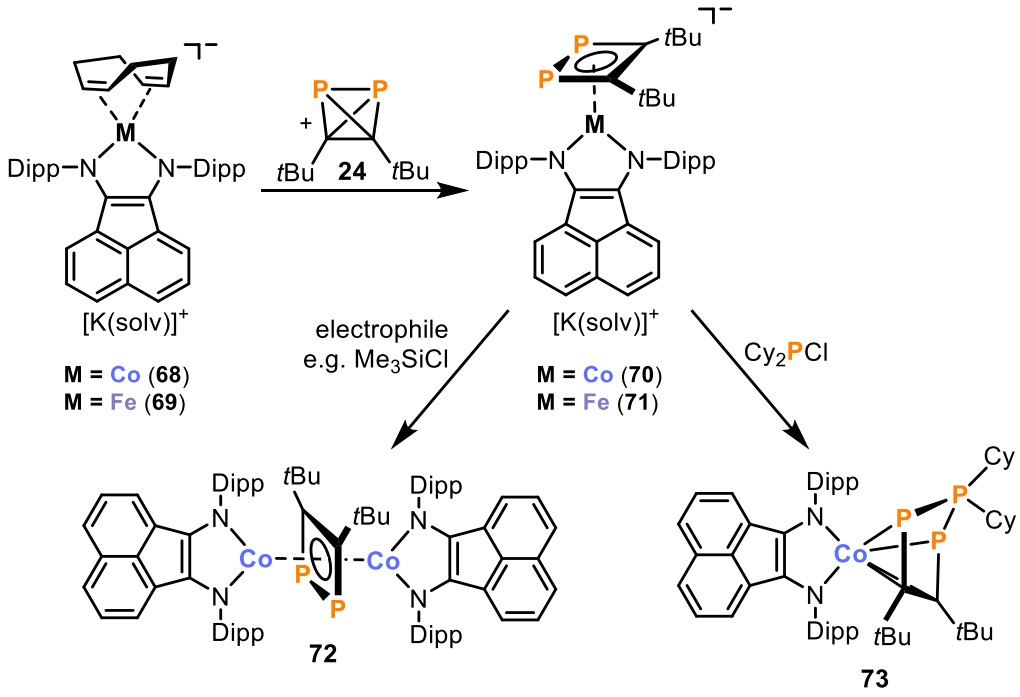
Scheme 15. Reactions of **24** with NHC-Ni(0) and NHC-Ni(I) complexes.

Subsequently, the reactivity of **24** towards low-valent cobaltate and ferrate anions was explored.[70] Reaction with [K([18]crown-6)][Fe(anthracene)$_2$] led to the formation of complex **66**, which features an η^4-coordinated 1,2-diphosphacyclobutadiene ligand that substitutes one of the anthracene ligands (Scheme 16). In contrast, when **24** reacts with [K(thf)$_{0.2}$][Co(η^4-cod)$_2$], the homoleptic sandwich complex **67** is formed as the main product. It is noteworthy that 1,2-diphosphacyclobutadiene ligands are relatively rare, with their 1,3-isomers being more commonly encountered, as seen in related reactions with *t*BuCP.[77]



Scheme 16. Reactions of **24** with low-valent ferrate and cobaltate complexes.

The reactions of the bis(aryl)acenaphthenequinonediimine-stabilised metalates **68** and **69** with **24** afforded similar 1,2-diphosphacyclobutadiene complexes (complexes **70** and **71**, Scheme 17) upon P–C bond cleavage of **24**.[70] Interestingly, reactions of **68** and **69** with *t*BuCP produced the corresponding 1,3-diphosphacyclobutadiene isomers, which can be converted to the 1,2-diphosphacyclobutadiene complexes upon heating.[70,78] The addition of electrophiles, such as HCl or Me_3SiCl, to **71** resulted in the dinuclear complex **72** featuring a 1,2-diphosphacyclobutadiene ligand in a μ:η^4,η^4-coordination mode, similar to **62**.[70,71] In contrast, treatment of **71** with Cy_2PCl led to the formation of **73** via insertion of the Cy_2P fragment into the P–P bond of the 1,2-diphosphacyclobutadiene ligand, yielding a unique η^4-coordinated $tBu_2C_2P_3Cy_2$-ligand (Scheme 17).[70] These results demonstrate that the diphosphatetrahedrane $(tBuCP)_2$ (**24**) serves as a reliable source of 1,2-diphosphacyclobutadiene ligands, which are challenging to obtain by other means and exhibit diverse reactivity.



Scheme 17. Reactivity of **24** towards low-valent ferrate and cobaltate anions.

1.3 Conclusion and Outlook

Tetrahedranes continue to captivate chemists due to their intriguing tetrahedral structure and their unusual bonding and reactivity. The first discovered tetrahedrane, white phosphorus (P_4), remains the most industrially relevant compound of its kind to date. Its reactivity and unique bonding continue to inspire investigations into related molecular frameworks. A major milestone in the field came in 1978 with the synthesis of *tert*-butyltetrahedrane, expanding the concept of tetrahedranes into the realm of organic chemistry.

Phosphatetrahedranes, which incorporate both phosphorus and carbon atoms into a tetrahedral framework, represent a novel and structurally unique subclass within organophosphorus and broader main group chemistry. Although predicted decades ago, they remained experimentally elusive until 2019, when di-*tert*-butyldiphosphatetrahedrane (tBuCP)$_2$ (**24**) was successfully synthesised. This breakthrough was followed by the preparation of tri-*tert*-butylphosphatetrahedrane (tBuC)$_3$P (**25**) and triphosphatetrahedrane (HCP_3) (**26**), catalysing a surge of interest and development in this emerging area.

Despite these achievements, phosphatetrahedrane chemistry remains in its infancy. With only three isolated representatives, the synthesis and study of mono-, di-, and triphosphatetrahedranes [(RC)$_3$P, (RCP)$_2$, and (RCP_3)] bearing diverse substituents remain attractive targets. Such efforts are expected to shed light on how steric and electronic factors influence the stability and reactivity of these compounds. Reactivity studies of **24**, **25**, and **26** have shown that the unique bonding situation in phosphatetrahedranes allows for the synthesis of otherwise inaccessible organophosphorus compounds. Nevertheless, in contrast to the extensively studied P_4, the broader reactivity of phosphatetrahedranes is still largely unexplored, offering opportunities for further insights into this compound class.

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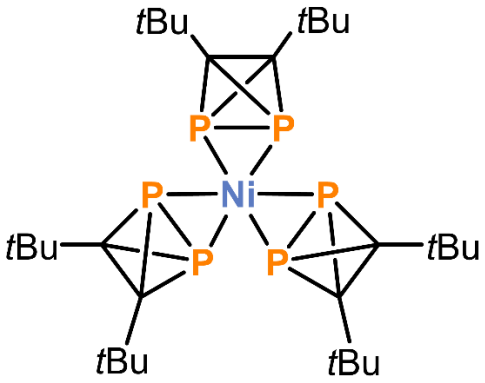
2 A Homoleptic Diphosphatetrahedrane Nickel(0) Complex[a,b]

Abstract: The stable diphosphatetrahedrane, (*t*BuCP)$_2$, was isolated only recently, and its coordination chemistry has been little explored so far. Herein we report the synthesis of [Ni{η^2-(*t*BuCP)$_2$}$_3$] (**1**) by CO substitution of Ni(CO)$_4$ with (*t*BuCP)$_2$. Single-crystal X-ray diffraction studies revealed that **1** features three intact diphosphatetrahedrane molecules coordinated via their P−P bonds to a single nickel(0) atom. Multinuclear NMR studies suggest that the structure of **1** is retained in solution. The bonding situation is analysed using quantum chemical methods. The coordination behaviour of (*t*BuCP)$_2$ is compared to the isoelectronic P$_4$ molecule, which scarcely forms complexes of intact P$_4$ tetrahedra.



[a] Reproduced from M. K. Uttendorfer, G. Hierlmeier, R. Wolf, *Z. Anorg. Allg. Chem.* **2022**, *648*, e202200124.

[b] Maria K. Uttendorfer performed all reactions and characterised the compounds. She performed and analysed the DFT calculations and wrote the manuscript. Gabriele Hierlmeier and Robert Wolf conceptualised the project and edited the manuscript. Robert Wolf supervised and directed the project.

2.1 Introduction

In 1970 *Ginsberg* and *Lindsell* reported the first transition metal complexes of white phosphorus (P_4) $[RhClL_2(\eta^2\text{-}P_4)]$ (L = PPh_3, P(*p*-Tol)$_3$, P(*m*-Tol)$_3$, $AsPh_3$; Tol = C_7H_8).[1] Since then, a wide variety of coordination compounds have been synthesised through coordination studies of P_4.[2] These complexes often contain reduced polyphosphide units resulting from a formal electron transfer from the metal atom to P_4. In many cases, this effects the cleavage of P–P bonds (as observed in the above-mentioned rhodium complexes),[3] which may be followed by a redistribution of the P atoms forming various polyphosphido ligands of the general composition P_n^{x-}. In contrast, the number of transition metal complexes featuring an intact, neutral P_4 tetrahedron has remained limited.

Figure 1a shows the structure of $[(np_3)Ni(\eta^1\text{-}P_4)]$ (**A**, np_3 = tris(2-diphenylphosphinoethyl)amine) reported by *Sacconi* and co-workers in 1979, the first structurally characterised transition metal complex in which the P_4 moiety coordinates end-on *via* a single phosphorus atom.[4] Further examples of this end-on coordination mode have been reported for a variety of transition metals, including as Fe, Ru, Os, Mn, and W.[5] In addition, several complexes with intact, side-on coordinated P_4 molecules have been reported.[3c,6] Such complexes are typically stabilised by different ancillary ligands, while the coinage metal complexes $[M(P_4)_2]X$ (**B**; M = Cu, Ag, X = $Al\{OC(CF_3)_3\}_4$; M = Au, X = $GaCl_4$) displayed in Figure 1a are the only isolated homoleptic P_4 complexes to the best of our knowledge.[3c,6a,b,d] These rare homoleptic complexes are stabilised by weakly coordinating anions. The coordinated P–P bonds are only slightly elongated by 0.10 to 0.20 Å with respect to those in the free P_4 molecule, indicating the presence of intact P_4 tetrahedra.

Phosphatetrahedranes comprised of phosphorus and carbon atoms were isolated only recently. We synthesised di-*tert*-butyldiphosphatetrahedrane (*t*BuCP)$_2$,[7] while Cummins and co-workers reported the related monophosphatetrahedrane tri-*tert*-butylphosphatetrahedrane (tBu_3C_3P) almost simultaneously and a triphosphatetrahedrane (HCP_3) soon afterwards.[8,9] Studies on the reactivity of these species are still scarce,[7-10] yet our preliminary investigations on the coordination behaviour of (*t*BuCP)$_2$ have revealed that this species easily undergoes P–C bond cleavage upon coordination to transition metal centres. Thus, reactions with anionic metalates of Fe and Co afforded η^4-coordinated diphosphacyclobutadiene complexes.[10a] Similar diphosphacyclobutenediide ligands were formed when reacting (*t*BuCP)$_2$ with Ni(0) and Ni(I) NHC complexes, showing planar $tBu_2C_2P_2^{2-}$ units which are σ-coordinated to Ni atoms.[10c] Only two complexes with intact phosphatetrahedrane moieties have been structurally characterised so far. The silver complex $[\{Ag(\eta^2\text{-}tBuCP)_2(\eta^2\text{-}tBuCP)_4\}_2][Al\{OC(CF_3)_3\}_4]_2$ (**C**, Figure 1b) was obtained by reacting (*t*BuCP)$_2$ with $[Ag(CH_2Cl_2)_2(Al\{OC(CF_3)_3\}_4)]$.[7] However, it was not possible to obtain a homoleptic complex in this case. In addition, Cummins and co-workers recently described the complexation of their triphosphatetrahedrane (HCP_3) to Fe in the complex $[Cp^*Fe(dppe)(\eta^1\text{-}HCP_3)][BPh_4]$ (**D**, Figure 1b, dppe = 1,2-bis(diphenylphosphino)ethane,

Cp* = C_6Me_6).[9] In the molecular structure of this complex, the triphosphatetrahedrane is end-on coordinated *via* a single phosphorus atom.

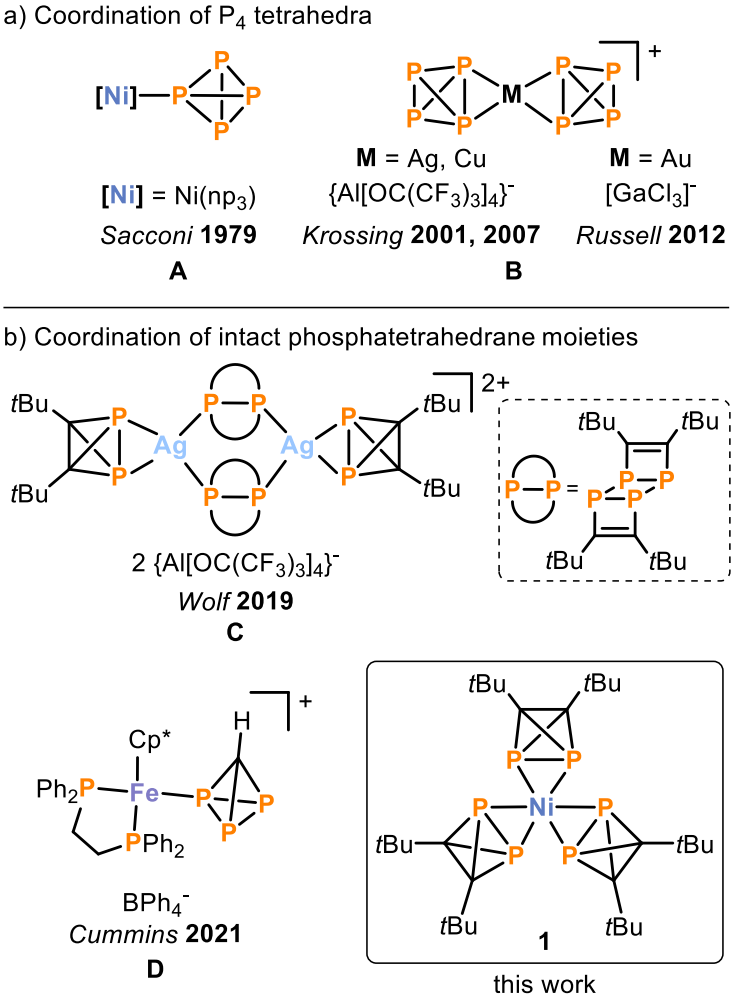
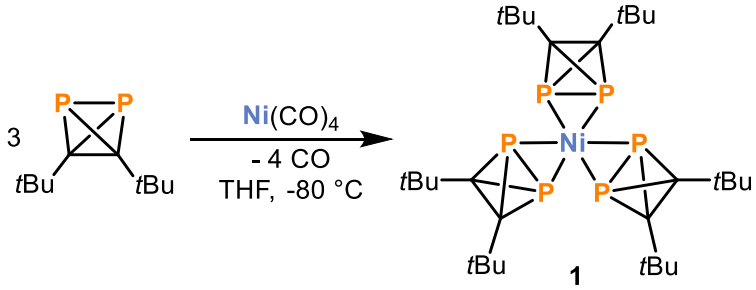


Figure 1. a) Selected examples of complexes featuring P_4 tetrahedra,[3c,4,6a,b] b) coordination of intact phosphatetrahedranes.[7,9]

These initial results promise a versatile coordination chemistry of phosphatetrahedranes, which is expected to be similar to that of P_4 and may also be comparable to the coordination behaviour of related low-coordinate organophosphorus compounds such as phosphaalkynes and phosphabenzenes.[2,11] However, in contrast to these well-investigated compound classes, reactivity studies of phosphatetrahedranes towards transition metal carbonyl complexes have not yet been reported. In extension to our recent studies of di-*tert*-butyldiphosphatetrahedrane towards NHC-stabilised Ni(0) complexes, we studied its reaction towards the highly reactive tetracarbonyl nickel(0) complex $Ni(CO)_4$. Herein, we report the isolation and characterisation of [Ni{η^2-(*t*BuCP)$_2$}$_3$] (**1**), which features three intact di-*tert*-butyldiphosphatetrahedrane moieties that coordinate to the Ni(0) core via their P–P bonds.

2.2 Results and Discussion

The reaction of three equivalents of di-*tert*-butyldiphosphatetrahedrane with $Ni(CO)_4$ (Scheme 1) was performed in toluene at −80 °C under exclusion of light to prevent the light-mediated dimerisation of (tBuCP)$_2$. After warming to 0 °C overnight, the reaction affords a deep blue solution. A $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture showed a new singlet resonance assigned to **1** at δ = −337.7 ppm (see Figures S4 and S5). In addition, signals for (tBuCP)$_2$ (δ = −469.0 ppm) and the ladderane-type compound (tBuCP)$_4$ (δ = −23.4 ppm) were observed. After work-up and crystallisation from a concentrated solution in *n*-hexane, indigo-coloured crystals of **1** suitable for single-crystal X-ray diffraction analysis were obtained. The structure was solved in the triclinic space group $P\bar{1}$, revealing a non-centrosymmetric molecular structure with the presence of two formula units of **1** per unit cell.



Scheme 1. Synthesis of [Ni{η^2-(tBuCP)$_2$}$_3$] (**1**).

The molecular structure of **1** is depicted in Figure 2. Three intact di-*tert*-butyldiphosphatetrahedrane units coordinate to a single nickel atom *via* their P–P bonds. Steric repulsion between the *tert*-butyl groups causes a propeller twist, resulting in a chiral complex, which crystallises as racemate with both enantiomers in the unit cell. Note that the classic alkene complex tris(ethylene)nickel(0) reported by *Wilke* and co-workers in 1973 shows a related structure, but this complex has a completely planar environment of the Ni atom due to electronic effects.[12,13]

The P–P bonds in compound **1** (2.3288(5) to 2.3319(5) Å) are elongated compared to (tBuCP)$_2$ (calculated gas-phase structure: P–P 2.203 Å).[7] The P–P bonds of the tetrahedral moieties in the only other well-characterised diphosphatetrahedrane complex [{Ag(η^2-tBuCP)$_2$(η^2-tBuCP)$_4$}$_2$][Al{OC(CF$_3$)$_3$}$_4$]$_2$ (2.308(3) Å) are slightly less elongated than in **1**.[7] This suggests a stronger interaction between the ligand and the metal atom of **1** compared to **C**. The P–C bonds in **1** (1.8418(16) to 1.8496(16) Å) are also slightly longer than in **C** (1.820(8) to 1.836(9) Å) yet similar to the structure of (tBuCP)$_2$ calculated by theoretical methods (1.852 Å).[7] The C–C bonds of the tetrahedral moieties in complex **1** (1.471(2) to 1.474(2) Å) are only very slightly elongated compared to (tBuCP)$_2$ (1.458 Å) and **C** (1.462(12) Å).[7] The Ni–P bonds of **1** (2.2947(4) to 2.3082(4) Å) are somewhat longer than those for Ni complexes with a bridging μ,η$^{2:2}$-P$_2$ moiety or a side-on coordinated μ,η$^{2:2}$-P$_4$ unit, e. g. 2.2354(7) to 2.2648(8) Å in [Ni$_2$(iPr$_2$Im)$_4$(μ,η$^{2:2}$-P$_2$)],[14] 2.241(1) to 2.250(1) Å in ((μ^2:η^2,η^2-P$_2$){Ni(IMes)(CO)}$_2$,[15] 2.255(4)

to 2.277(2) Å in [(^{Dipp}nacnac)Si(μ,$\eta^{2:2}$-P_4)Ni(nacnac)],[16] and 2.2657(6) to 2.2923(8) Å in [[(IPr)Ni{(μ-$\eta^{2:2}$-P_4)Si(^{Dipp}nacnac)}$_2$] (*i*Pr_2Im = 1,3-di(*iso*-propyl)imidazolin-2-ylidene, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene, nacnac = CH[C(Me)N(Dipp)]$_2$, ^{Dipp}nacnac = CH[C(Me)N(Dipp)][C(CH_2)N(Dipp)], Dipp = 2,6-di-*iso*-propylphenyl, IPr = 1,3-bis(2,6-di-*iso*-propylphenyl)imidazolin-2-ylidene).[17]

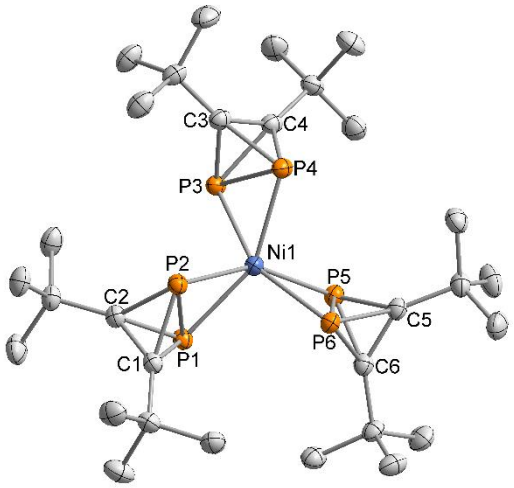


Figure 2. Solid-state molecular structure of [Ni{η^2-(*t*BuCP)$_2$}$_3$] (**1**). Displacement ellipsoids are drawn at the 50% probability level; H-atoms have been omitted for clarity; selected bond lengths [Å] and angles [°]: Ni1−P1 2.3082(4), Ni1−P2 2.3005(4), Ni1−P3 2.2962(4), Ni1−P4 2.3035(4), Ni1−P5 2.3074(4), Ni1−P6 2.2947(4), P1−P2 2.3288(5), P3−P4 2.3319(5), P5−P6 2.3302(5), P1−C1 1.8479(14), P1−C2 1.8495(15), P2−C1 1.8477(15), P2−C2 1.8471(15), P3−C3 1.8475(16), P3−C4 1.8429(15), P4−C3 1.8496(16), P4−C4 1.8427(15), P5−C5 1.8479(16), P5−C6 1.8418(16), P6−C5 1.8473(14), P6−C6 1.8451(15), C1−C2 1.473(2), C3−C4 1.474(2), C5−C6 1.471(2); C1−P1−P2 50.94(5), C2−P1−P2 50.91(5), C1−P1−C2 46.96(7), C1−P2−P1 50.94(4), C2−P2−C1 46.99(7), C2−P2−P1 51.00(5), P2−C1−P1 78.12(6), C2−C1−P1 66.58(8), C2−C1−P2 66.48(8), P2−C2−P1 78.10(6), C1−C2−P1 66.46(8), C1−C2−P2 66.52(8), P2−Ni1−P1 60.703(14), Ni1−P1−P2 59.486(14), P3−Ni1−P1 100.002(17), P4−Ni1−P1 152.359(18), P3−Ni1−P2 101.880(16), P2−Ni1−P4 101.526(16).

The Ni complex **1** was isolated in 23% yield as an indigo-coloured solid. The relatively low yield can likely be attributed to the thermal instability of **1** at room temperature. **1** is characterised by a $^{31}P\{^1H\}$ NMR singlet at −338.4 ppm, which is significantly shifted to low field in comparison to the resonance of free diphosphatetrahedrane (*t*BuCP)$_2$ ($\delta(^{31}P)$ = −468.2 ppm). The low-field shift is far less pronounced for the Ag complex **C** ($\delta(^{31}P)$ = −446.8 ppm).[7] Again, this points to a stronger interaction between metal core and ligand for **1**. The ^1H NMR spectrum of **1** displays the singlet of the *tert*-butyl groups at 1.33 ppm, while the $^{13}C\{^1H\}$ NMR spectrum shows three resonances at 29.7 ppm, 32.0 ppm, and 45.5 ppm. These are assigned to the quaternary carbon atoms of the *tert*-butyl groups, the methyl groups, and the carbon atoms in the tetrahedral core, respectively. The signal at 45.5 ppm shows the expected multiplet structure due to coupling with the ^{31}P nuclei. In conclusion, the multinuclear NMR spectra of **1** are fully consistent with the molecular structure observed in the solid state. The UV-Vis absorption spectrum of **1** dissolved

in *n*-hexane displays three absorption bands in the UV region at 225 nm, 280 nm and 315 nm in addition to two absorptions in the visible region at 415 nm and 680 nm, which presumably cause the blue colour of **1**.

While complex **1** can be isolated as a reasonably pure compound according to elemental analysis, it is noteworthy that it decomposes at ambient temperature, forming a clear brown mixture within 48 h which contains free (*t*BuCP)$_2$ and its dimerisation product, the ladderane (*t*BuCP)$_4$, according to $^{31}P\{^1H\}$ NMR monitoring.[7] The reaction proceeds without the formation of side products, as illustrated by the NMR spectra of the crude reaction mixture (see Figures S4 and S5); however, the thermal decomposition hampers the isolation of higher yields of **1**. The structurally comparable Ni(0) complex tris(ethylene)nickel(0) is also thermolabile, decomposing above 0 °C.[12]

The bonding situation in **1** was analysed by calculating intrinsic bond orbitals (IBOs) on the BP86/def2-TZVP level of theory.[18] Three filled orbitals forming 3-centre-2-electron bonds between Ni1/P1/P2, Ni1/P3/P4 and Ni1/P5/P6 could be identified (see Figure 3 for a representative IBO 175, IBOs 173 and 174 are similar and represent the other NiP_2 moieties; these orbitals and further relevant IBOs are displayed in Figure S7). Such 3-centre-2-electron bonds are also characteristic for olefin complexes as described by the Dewar-Chatt-Duncanson model, which describes the structure of tris(ethylene)nickel(0) well.[19] Indeed, calculations constructing IBOs for tris(ethylene)nickel(0) on the same level of theory confirmed the existence of three filled orbitals forming 3-centre-2-electron bonds between Ni1/C1/C2, Ni1/C3/C4 and Ni1/C5/C6 (see Figure S8 for a graphical representation of these orbitals). Similarly, the binding mode of η^2-coordinated intact P_4 tetrahedra is analogous to the Dewar-Chatt-Duncanson model.[6g] Moreover, a $3d^{10}$ configuration for the nickel could be derived from the IBO analysis of **1**, confirming the oxidation state Ni(0) (see Figure S7 for a depiction of the orbitals).

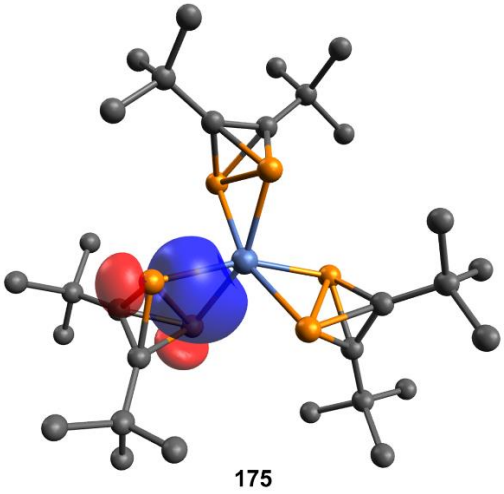


Figure 3. Intrinsic Bond Orbital of **1** showing a 3-centre-2-electron bond between the nickel core and the phosphorus atoms. Surface isovalue = 0.06. Hydrogen atoms have been omitted for clarity.

2.3 Conclusion

In summary, complex **1** is only the third reported example of coordination of an intact phosphatetrahedrane other than P_4 and the first homoleptic complex among these compounds. In the structure of **1**, diphosphatetrahedrane acts as a bidentate ligand coordinating in an η^2-fashion *via* the P–P bond to nickel. So far, mainly coinage metal cations stabilised by weakly coordinating anions have been reported to side-on coordinate intact tetrahedra of phosphatetrahedranes and the isoelectronic P_4 molecule. Prior to this work, only one example of the side-on coordination of an intact P_4 tetrahedron to a Ni-core was proposed, however, this compound was neither isolated nor confirmed by an X-ray structure.[6c] Quantum chemical calculations support the oxidation state Ni(0) in **1** and indicate the formation of 3-centre-2-electron bonds between the P atoms of $(t\text{BuCP})_2$ and the Ni-centre. The bonding situation appears to be comparable to that of tris(ethylene)nickel(0) and the few known examples in the literature showing side-on coordination of an intact P_4 tetrahedron.[6g,19] Further studies exploring the coordination chemistry of $(t\text{BuCP})_2$ and related molecules are currently underway in our laboratory.

2.4 Supporting Information

General: All reactions and manipulations were performed under an atmosphere of dry argon using standard Schlenk line techniques or in a MBraun UniLab glovebox under an atmosphere of dry argon. *n*-Hexane, and toluene were dried and degassed with an MBraun SPS-800 solvent purification system. Toluene was stored under argon over activated 3 Å molecular sieves and *n*-hexane was stored under argon over a potassium mirror. Deuterated toluene was purchased from Eurisotop and used as received. (tBuCP)$_2$ was prepared according to the previous reported procedure.[7] Ni(CO)$_4$ in toluene (c=1.2 M) was kindly provided by the group of Manfred Scheer.

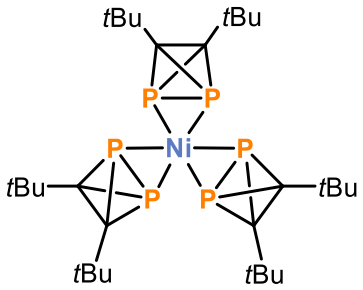
NMR spectroscopy: NMR spectra were recorded by the NMR department of the University of Regensburg on a Bruker Avance 400 spectrometer at 243 K and internally referenced to residual solvent resonances (toluene-d_8: ^{1}H NMR: 2.08 ppm, ^{13}C{^{1}H} NMR: 20.43 ppm). Chemical shifts (δ) are given in ppm referring to external standards of tetramethyl silane (^{1}H and ^{13}C{^{1}H}) and 85% phosphorus acid (^{31}P{^{1}H}). ^{13}C NMR signals were assigned based on 2D NMR spectra (^{1}H, ^{13}C-HMBC, ^{1}H, ^{13}C-HSQC).

Elemental analysis: The elemental analysis was determined by the analytical department of the University of Regensburg with a Micro Vario Cube (Elementar).

UV-Vis spectroscopy: The UV/Vis absorption spectrum was recorded on an Ocean Optics Flame Spectrometer with the corresponding light source (DH-2000-BAL/UV-Vis-NIR light source).

2.4.1 Synthesis of [Ni{η²-(*t*BuCP)₂}₃] (1)

The synthesis of **1** was carried out under the exclusion of light (flasks wrapped in aluminium foil) to prevent the decomposition of (*t*BuCP)$_2$. A colourless solution of Ni(CO)$_4$ in toluene (0.07 mL, 1.215 mol/L, 0.085 mmol, 1.0 eq.) was diluted with toluene (7 mL) and cooled to −80 °C. Subsequently, a colourless solution of (*t*BuCP)$_2$ in toluene (1.5 mL, 0.18 mol/L, 0.26 mmol, 3.0 eq.) was added. A deep blue mixture was formed, which was allowed to warm to 0 °C whilst stirring overnight. Volatiles were removed *in vacuo* to yield an indigo-coloured residue. This was extracted in *n*-hexane (6 mL). Storage of the extract in the freezer (−35 °C) for 21 days afforded indigo-coloured crystals which were isolated by filtration of the mother liquor and drying *in vacuo*. Single crystals suitable for X-ray analysis were grown from *n*-hexane at ambient temperature over 8 days. Complex **1** can be stored for prolonged periods in the freezer at −30 °C, but decomposes to a brown mixture upon storage at or below room temperature.



$C_{30}H_{54}NiP_6$, MW = 659.30 g/mol

Yield: 13.1 mg (23%).

^{1}H NMR (400.13 MHz, 243 K, toluene-d_8): δ/ppm = 1.33 (s, 54 H).

^{13}C{^{1}H} NMR (100.61 MHz, 243 K, toluene-d_8): δ/ppm = 29.7 (s, *C*(CH$_3$)$_3$), 32.0 (s, *C*H$_3$), 45.5 (m, P$_2$*C*$_2$).

^{31}P{^{1}H} NMR (161.98 MHz, 243 K, toluene-d_8): δ/ppm = −338.4 (s).

UV-Vis: (*n*-hexane, λ_{max}/nm, ε_{max}/L·mol^{-1}·cm^{-1}): 225 (36000), 280 (23000), 315 (16000), 415 (9000), 680 (2000).

Elemental analysis calcd. C 54.65, H 8.26; found C 54.83, H 8.16.

2.4.2 NMR Spectra

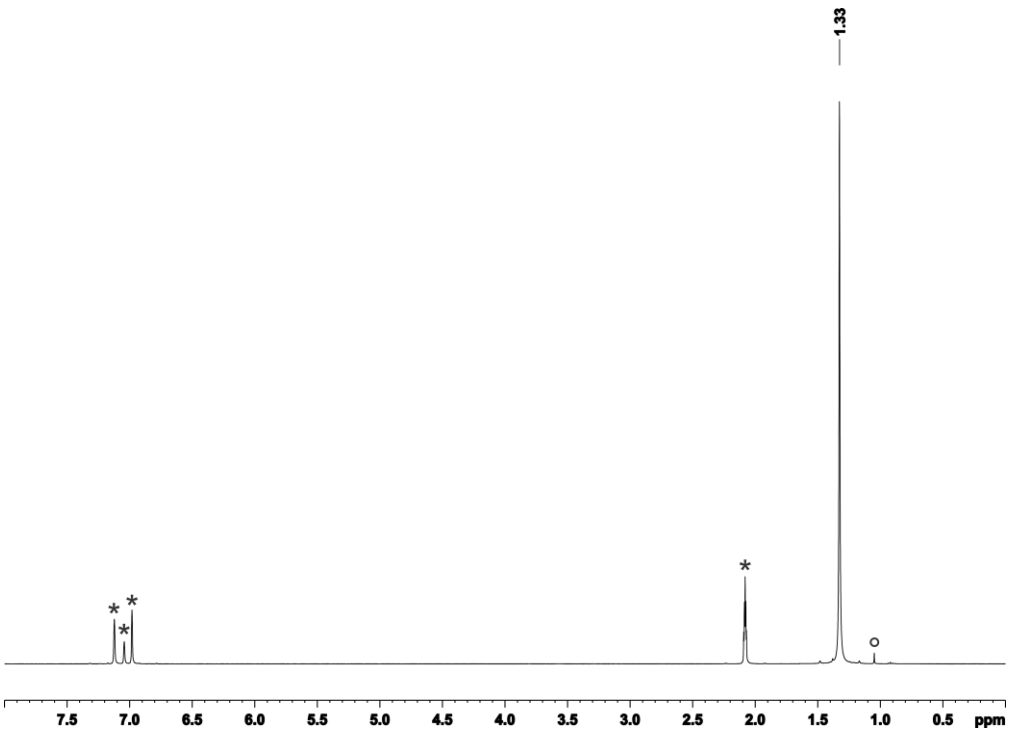


Figure S1. ^{1}H NMR spectrum (400 MHz, 243 K, toluene-d_8) of **1**. *Residual proton signals of toluene-d_8. ○ (tBuCP)$_2$.

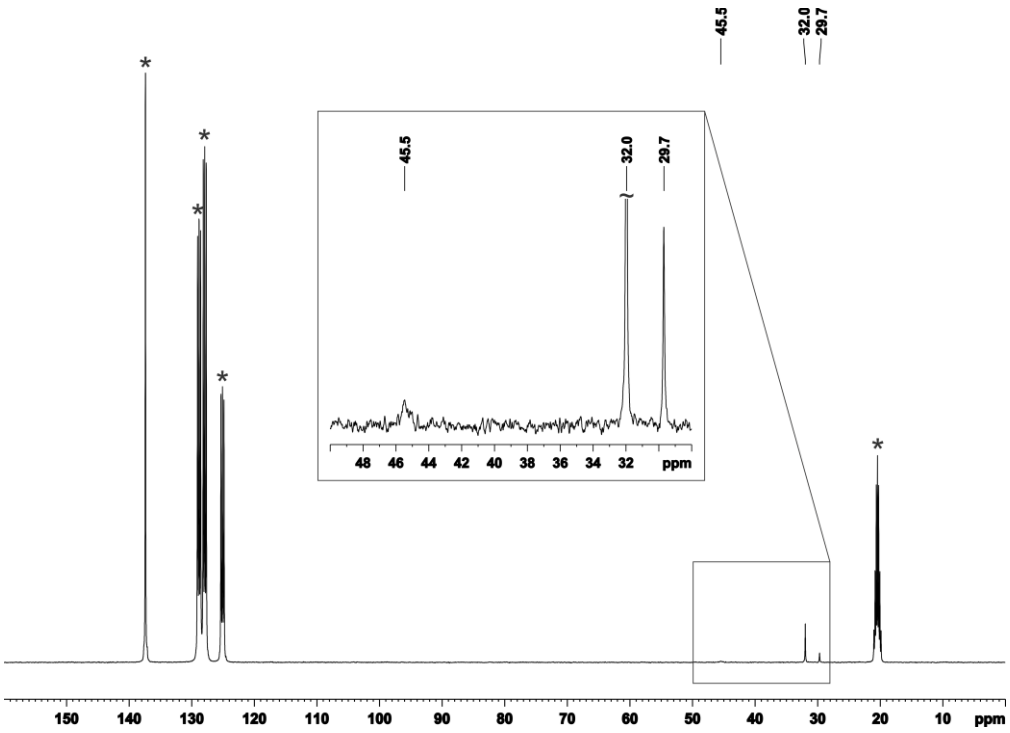


Figure S2. ^{13}C{^{1}H} NMR spectrum (100 MHz, 243 K, toluene-d_8) of **1**. *Toluene-d_8.

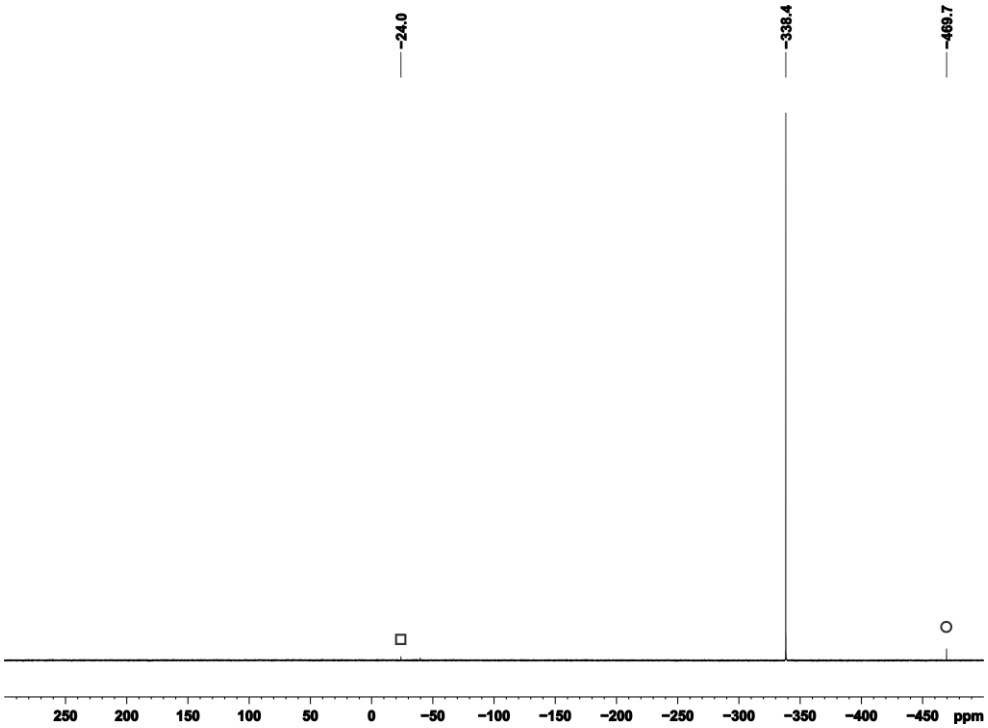


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 243 K, toluene-d_8) of **1**. ○ (tBuCP)$_2$, □ (tBuCP)$_4$.

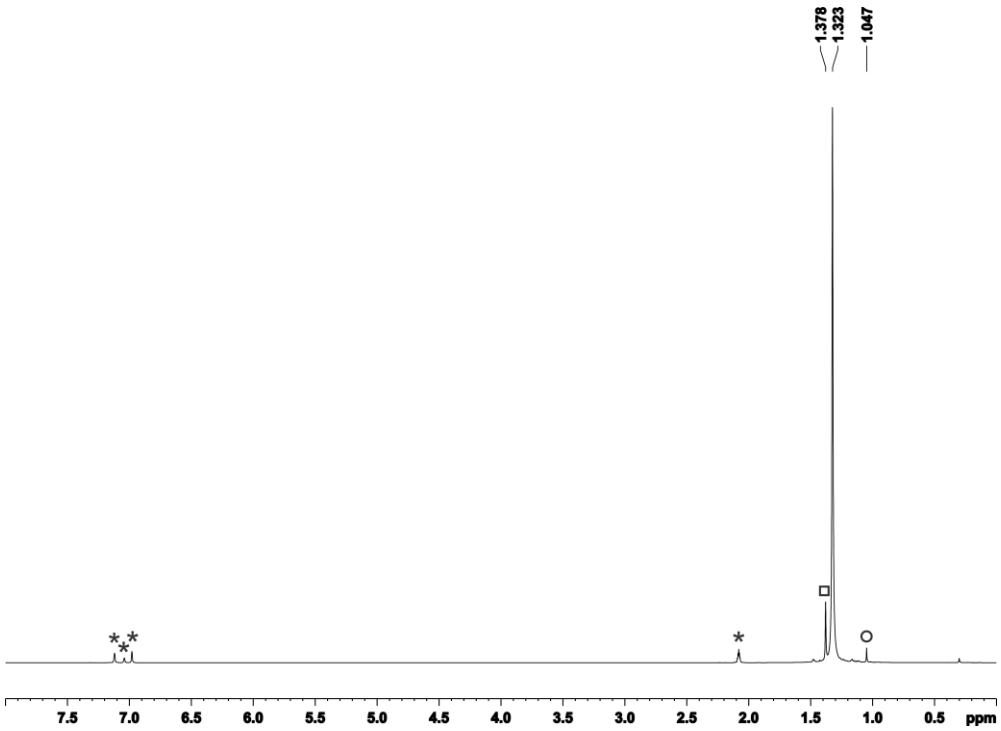


Figure S4. ^{1}H NMR spectrum (400 MHz, 243 K, toluene-d_8) of the crude reaction mixture of (tBuCP)$_2$ and Ni(CO)$_4$. *Toluene-d_8, ○ (tBuCP)$_2$, □ (tBuCP)$_4$.

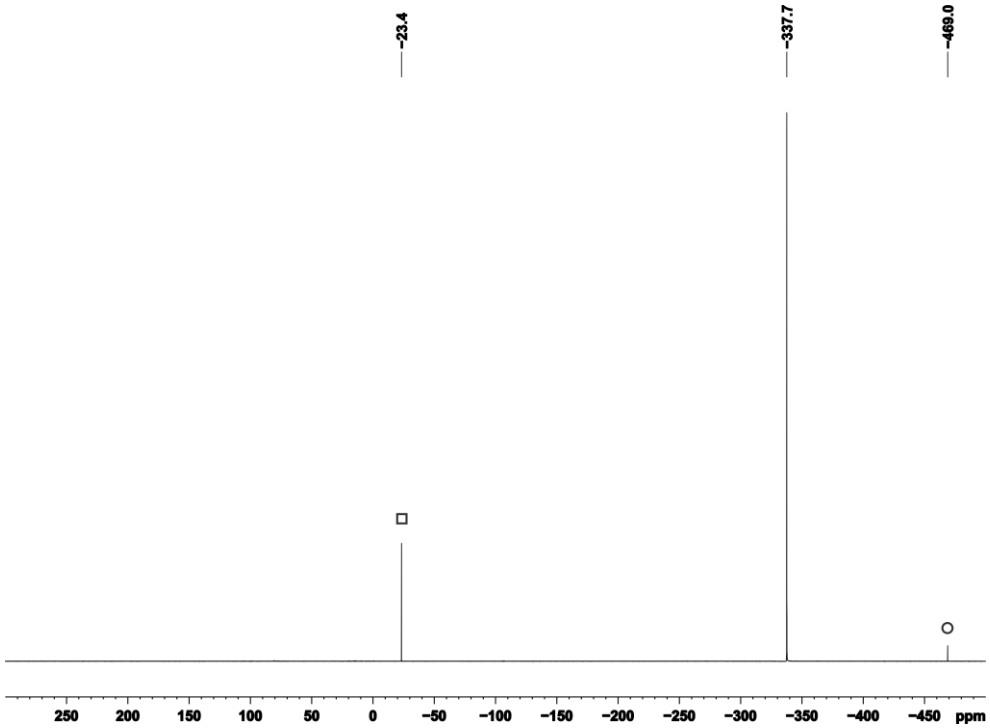


Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 243 K, toluene-d_8) the crude reaction mixture of (tBuCP)$_2$ and Ni(CO)$_4$. ○ (tBuCP)$_2$, □ (tBuCP)$_4$.

2.4.3 UV-Vis Spectrum

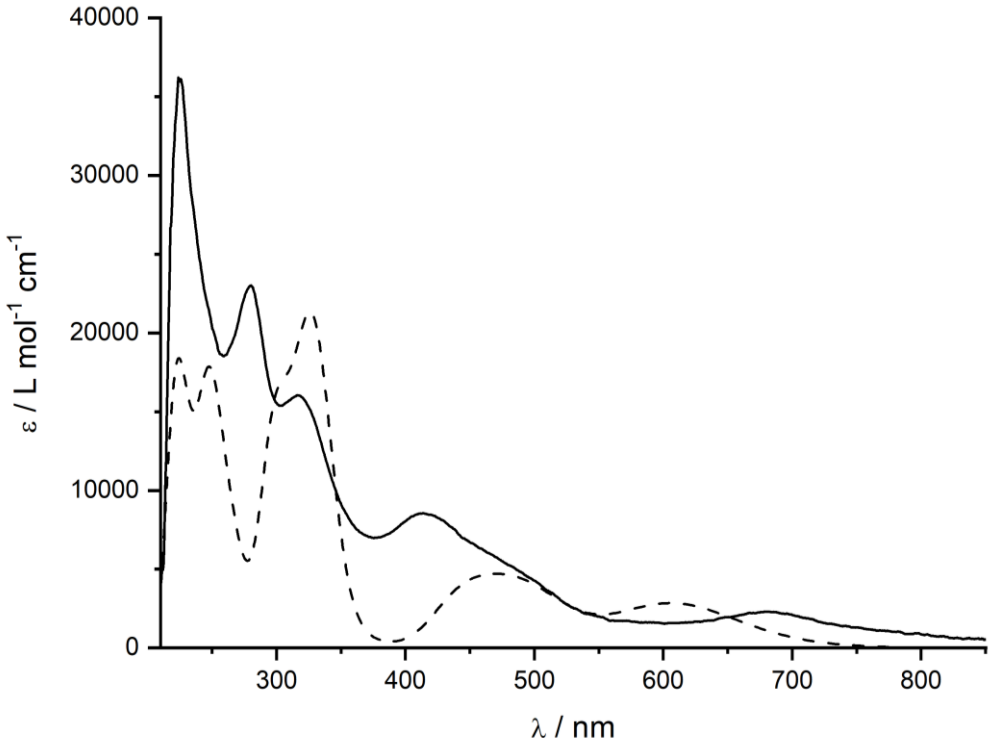


Figure S6. UV-Vis spectrum of **1** recorded in *n*-hexane (solid line). The UV-Vis spectrum calculated for **1** in the gas phase using TDDFT (BP86-D3BJ/def2-TZVP) is shown as a dashed for comparison.

2.4.4 Single-Crystal X-ray Diffraction Data

The single-crystal X-ray diffraction data was recorded on a Rigaku XtaLAB Synergy DW R (DW system, HyPix-Arc 150) diffractometer with microfocus Cu-Kα radiation (λ=1.54184 Å). Crystals were selected under mineral oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device. Either semi-empirical multi-scan absorption corrections[20] or analytical ones[21] were applied to the data. Using Olex2,[22] the structure was solved with the SHELXT[23] structure solution programme using Intrinsic Phasing and refined with the SHELXL[24] refinement package using Least Squares refinements on F^2. The hydrogen atoms were located in idealised positions and refined isotropically with a riding model. Crystallographic data for the structure in this paper has been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of this data can be obtained free of charge on quoting the depository number: 2158460 for compound **1**; E-mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk.

Table S1. Crystal data and structure refinement for **1**.

Compound	**1**
Empirical formula	$C_{30}H_{54}NiP_6$
Formula Weight	659.26
Temperature [K]	123(1)
Crystal System	triclinic
Space Group	$P\bar{1}$
a [Å]	11.85730(10)
b [Å]	13.1518(2)
c [Å]	13.2185(2)
α [°]	117.796(2)
β [°]	96.9280(10)
γ [°]	97.4380(10)
Volume [Å^3]	1769.25(5)
Z	2
ρ_{calc} [g/cm^3]	1.238
μ [mm^{-1}]	3.479
F(000)	704.0
Crystal Size [mm^3]	0.19 × 0.05 × 0.04
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection [°]	7.684 to 147.012
Index ranges	$-14 \leq h \leq 14$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$
Reflections collected	31861
Independent reflections	6870 [R_{int} = 0.0252, R_{sigma} = 0.0236]
Data / restraints / parameters	6870/0/352
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0265, wR_2 = 0.0688
Final R indexes [all data]	R_1 = 0.0310, wR_2 = 0.0707
Largest diff. peak/hole [e Å^{-3}]	0.29/−0.30
CCDC number	2158460

2.4.5 Quantum Chemical Calculations

General Methods

All calculations were performed with the ORCA programme package version 4.2.1 in the gas phase.[18c-e] Frequency calculations were carried out to confirm the nature of stationary points found by geometry optimisations. The RI[18f] approximation was used for GGA calculations. Geometry optimisations have been carried out at the BP86-D3BJ/def2-TZVP[18a,b,h-k] level of theory. The UV-vis spectrum of **1** was calculated at the same level using the TDDFT method. The input file of this calculation is given further below.

Intrinsic bond orbitals (IBOs) have been constructed from the occupied BP86 orbitals according to Knizia *et al*.[18l] To estimate the electron count within the complex, the composition and shape of the respective IBOs was analysed. Thereby, IBOs with a Ni contribution greater than 70% are identified as occupied 3d orbitals. Orbitals with a comparably low Ni contribution (70% to 80%) may indicate back-bonding from Ni in C-based orbitals (for $[Ni(\eta^2\text{-}C_2H_4)_3]$), offering additional stabilisation.

Orbital Pictures and Compositions

[Ni{η^2-(*t*BuCP)$_2$}$_3$] (**1**)

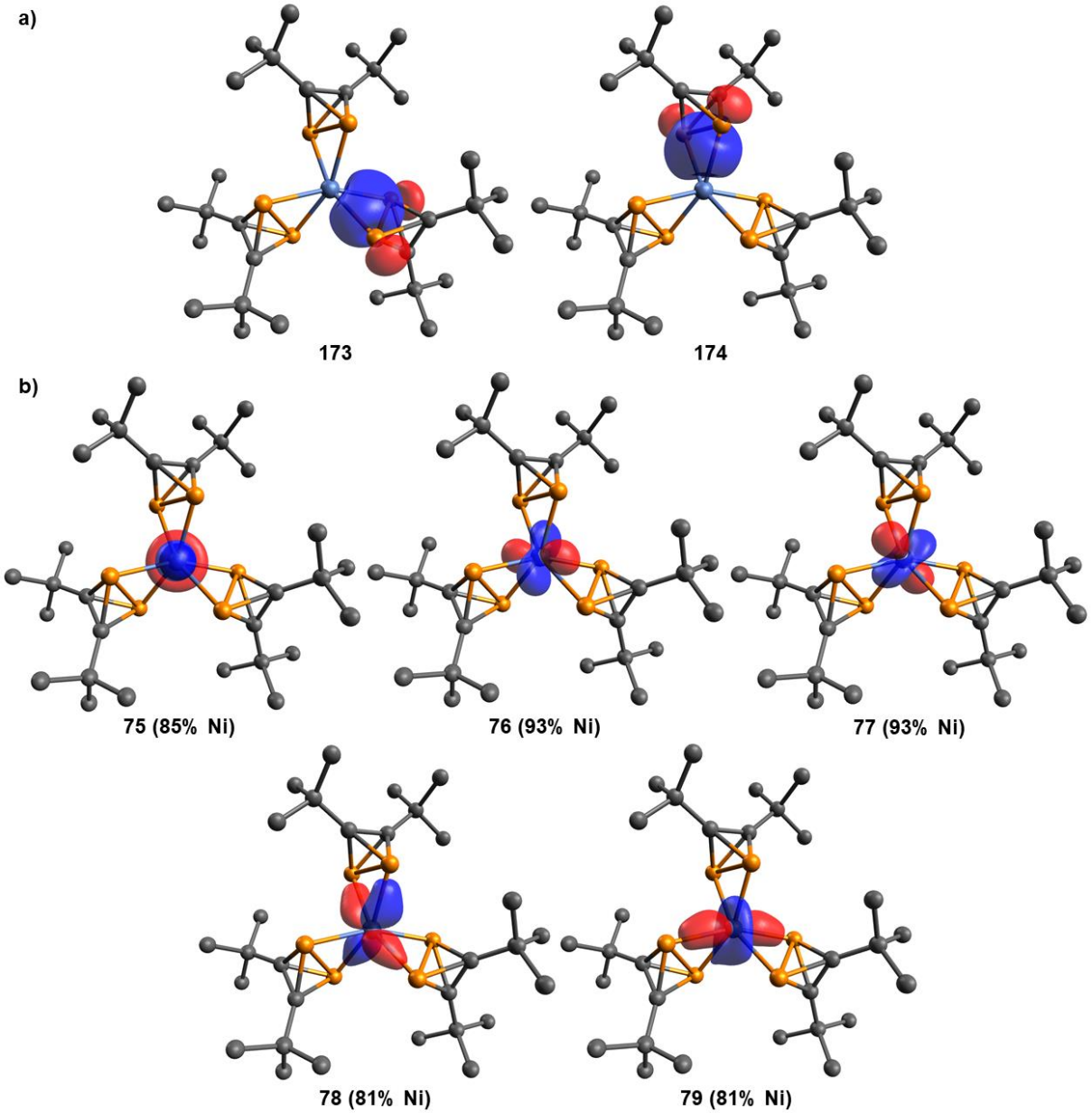


Figure S7. Intrinsic bond orbitals of **1** showing a) 3-centre-2-electron bonds between the nickel core and the phosphorus atoms and b) the filled 3d-orbitals at the Ni atom (contribution of the Ni atom is given in parentheses). Surface isovalue = 0.06. Hydrogen atoms have been omitted for clarity.

$[Ni(\eta^2\text{-}C_2H_4)_3]$

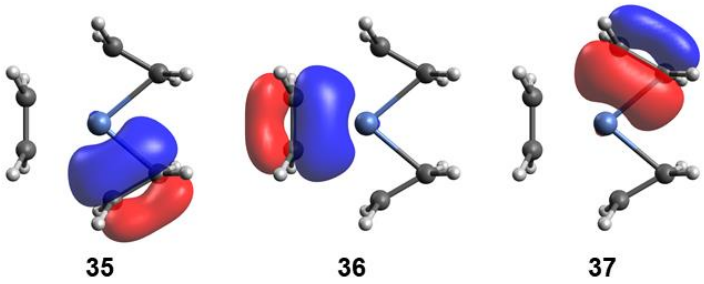


Figure S8. Intrinsic Bond orbitals of $[Ni(\eta^2\text{-}C_2H_4)_3]$ showing 3-centre-2-electron bonds between the nickel core and the carbon atoms. Surface isovalue = 0.06.

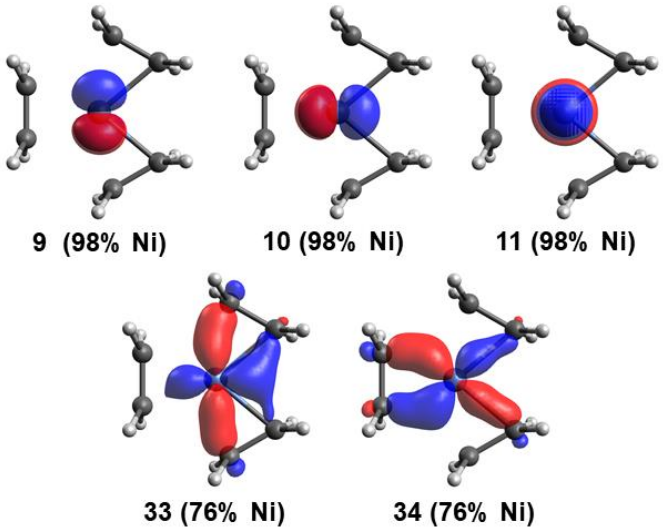


Figure S9. Intrinsic bond orbitals of $[Ni(\eta^2\text{-}C_2H_4)_3]$ showing the filled 3d-orbitals at the Ni atom (contribution of the Ni atom is given in parentheses). Surface isovalue = 0.06.

Cartesian Coordinates of the Optimised Structures

[Ni{η^2-(*t*BuCP)$_2$}$_3$] (1)

Ni	7.21384490279453	3.32270076731971	5.82099520456719
P	6.22508534088134	1.68395501573496	7.09266905416472
P	8.15744203924195	1.86626133267676	4.31475740001926
P	6.27394263008827	5.25574007260256	6.63574718931159
P	8.22357477450653	2.73798323033385	7.80009282852145
P	8.22686839363413	5.31729027306116	5.29870807674120
P	6.19333369276026	3.07293204959515	3.77769560637832
C	8.23844175743959	-0.35507295604898	8.26949571183108
C	7.55881629387822	2.48447606150023	2.67047225487549
C	6.86076576091984	6.56086829781032	5.45345121655956
C	8.35270627132540	7.27191356028335	7.73726520314311
C	6.83886060221906	2.03108453129948	8.80967713538863
C	7.62371631277294	1.00812423486811	8.10439399254081
C	6.23362343117416	2.36776193065442	10.14548741410689
C	7.68828702643301	6.45391615251210	6.66342758059634
C	6.74199928513002	1.39097254569910	3.21610202699727
C	6.08696872510992	0.08777111804496	2.84618618067803
C	9.00010465933702	-0.69040658351574	6.97632479275245
H	8.32011866605052	-0.66977339169096	6.11236944860973
H	9.45249497928522	-1.69104401164470	7.03991956799452
H	9.79712908241842	0.04375550776379	6.79250056760219
C	8.17679459928695	2.99577553914679	1.3974467451143
C	6.23599462887774	7.55680754685353	4.51435994424300
C	5.27619516813408	1.24573398903893	10.58127749898681
H	4.51380733357328	1.06247559133565	9.8103407836493 1
H	4.76409333049764	1.51934848879664	11.51569201052859
H	5.82133827757268	0.30765484470556	10.75484731187149
C	7.07080563250121	3.38397127612085	0.40090641653431
H	6.41333833816400	4.15195626828459	0.83312926135179
H	6.45122688297926	2.51718844706994	0.13442583594663
H	7.51277505766409	3.78624167497286	-0.52272330754221
C	7.33836474736787	8.34444240142368	3.78558553578267
H	7.99775672123981	7.66169290070363	3.23074990851368
H	7.95594824640795	8.91299563625072	4.49384844780341
H	6.89439413453053	9.05404429711250	3.07169097912627
C	5.28194744732957	-0.40053829913478	4.06213349198226
H	5.94085653974449	-0.53673855142753	4.93164869749302
H	4.79219430839962	-1.36087271661636	3.84317875692374
H	4.51078609363150	0.33233448727160	4.33778375103786
C	5.14562142713329	0.30041210546075	1.64858456333035
H	4.41560034150539	1.09413264728596	1.86344393455561
H	4.59453112358239	-0.62507381688684	1.42494157862959
H	5.70913909183646	0.58562568429758	0.74936973382624
C	7.13238175203808	-1.39987447966347	8.49667468325205
H	6.56745198269123	-1.18813766674253	9.41435838811775
H	7.56866463155686	-2.40572337951636	8.58689934459675
H	6.42528725362755	-1.40336963941599	7.65463462885594
C	9.01182808241310	4.24027033493786	1.74245620478939
H	9.46992077985034	4.66409969666194	0.83663217768707
H	9.81005810797354	3.98776015341009	2.45444085084260
H	8.38055770578740	5.01176058776179	2.20635102362036
C	9.13687951966643	6.31135953547279	8.64703583130671
H	8.46216807804740	5.56630012900826	9.09259577107255
H	9.63141186406609	6.86306361033137	9.46012181115427
H	9.90270164298980	5.76933594043747	8.07460859685044
C	7.34785081256112	2.54832618465836	11.19086573465418
H	7.91516882334468	1.61874242591675	11.33360756961005
H	6.91861499342867	2.83965325178188	12.16099700052558
H	8.05099266052045	3.33187898786924	10.87380792044499
C	9.21127959087430	-0.34531460733051	9.46079379684990
H	9.96740854622702	0.44363151671912	9.33876343016582
H	9.72971933724422	-1.31226027821555	9.54079973547250
H	8.67756210237857	-0.16670100732144	10.40449434399049
C	5.45735871347508	3.68677085694015	9.99496722177025
H	6.12724277092592	4.49298802961271	9.66312427009860
H	5.00538111547084	3.98240150529814	10.95325152090166
H	4.65866853373408	3.58623489876405	9.24666487092022
C	5.39908992549640	6.77758273312478	3.48609713103554
H	4.93702072178784	7.46383368575234	2.76115848810027
H	4.60370202574810	6.20639188262290	3.98510791169792
H	6.02894650411455	6.06332486034497	2.93643140413383
C	7.28633762792772	8.00389082884141	8.56999914250527
H	6.70821390738876	8.70456949849438	7.95273943969304
H	7.76139376343696	8.57391930923133	9.38217687496604
H	6.58471778158819	7.28451690543522	9.01632455479458
C	9.31516895661107	8.28645012421495	7.09721722069616
H	10.04193078291317	7.77653506675304	6.44850216195250
H	9.86895051688283	8.83328429707843	7.87474627131666
H	8.76829426185434	9.02083590818926	6.48985866419279
C	9.08237303581547	1.91229698457294	0.78765131565906
H	8.49532488223423	1.03825019617999	0.47318401421860
H	9.83445598809973	1.57783907352108	1.51671779608966
H	9.60781981424583	2.30428471418489	-0.09578748383853
C	7.16333893281300	-0.95421748989138	2.49597085652250
H	7.75975999392984	-0.63627080725857	1.63026314300664
H	6.69600969658638	-1.92032181100215	2.25404340371707
H	7.84619260973482	-1.10236199056357	3.34484886669479
C	5.33015306804371	8.51825550536820	5.30217448916023
H	5.91732274157611	9.13230462521899	5.99898393191501
H	4.58159083956644	7.95986203650056	5.88266117460213
H	4.80061812135149	9.19527709478399	4.61556216715243

[Ni(η^2-C$_2$H$_4$)$_3$]

Ni	0.00016638634385	-0.00000001491566	-0.00000003308907
C	1.56689728544881	1.32135742203062	-0.00000016523377
C	0.36105318520873	2.01761646103782	0.00000029134190
C	-1.92767130095814	-0.69622914358052	0.00000053221940
C	1.56689731916627	-1.32135743727206	0.00000021818291
C	0.36105323012629	-2.01761648188131	-0.00000048930718
C	-1.92767125040272	0.69622915796534	-0.00000038642486
H	-2.11842902234415	-1.24872054021038	-0.92147950755727
H	-2.11842876990676	-1.24871928793250	0.92148137234612
H	-2.11842879889458	1.24871933391660	-0.92148119561232
H	-2.11842878283962	1.24872054175737	0.92147968377677
H	2.14077624022135	-1.21029569107650	0.92147914668903
H	2.14077704911735	-1.21029528140411	-0.92147816845481
H	-0.02252858987509	-2.45849026275445	-0.92153581989433
H	-0.02252937834877	-2.45849088765653	0.92153421381662
H	2.14077637669922	1.21029566525601	-0.92147898787213
H	2.14077688366658	1.21029533328833	0.92147830856461
H	-0.02252881597265	2.45849032162046	0.92153550461289
H	-0.02252924645597	2.45849079181144	-0.92153451810452

(*t*BuCP)$_2$

P	-5.13935251918249	0.40796616296680	0.29640887514951
C	-3.37350644528157	-0.11745646412130	0.53086309642434
C	-3.53200368615679	0.91214265867323	-0.48583795054728
P	-3.51551749622253	1.59229292034246	1.24219806563405
C	-2.64596197981738	-1.38722049939028	0.87254299652275
C	-3.07017064948877	1.36337116977264	-1.84292271731738
C	-1.55533077489055	1.63350452548715	-1.81008198673246
C	-3.81789148865383	2.65787117201777	-2.20122467107412
C	-3.38907670095593	0.27607874035022	-2.88436983136682
C	-2.97981824321413	-2.47051329283992	-0.16849114836531
C	-3.10825970962510	-1.84917579496195	2.26396125270723
C	-1.12988063584308	-1.12372224833118	0.89096047111938
H	-4.19164310967426	-2.03542584792336	2.26973226208629
H	-2.88767642655097	-1.08256183728032	3.02029473496870
H	-2.59484823697046	-2.77821844222480	2.55112131121466
H	-0.76821126002146	-0.82353772306231	-0.10188912547609
H	-0.58804149419337	-2.03297628931143	1.19039922713605
H	-0.88305216391928	-0.32304121436455	1.60261366816783
H	-1.21496745361003	2.01610457816823	-2.78358497392297
H	-0.99319102078910	0.71586982069281	-1.58993991880344
H	-1.31003057959500	2.37859627014106	-1.03996177455801
H	-3.50438792204295	3.02219162009494	-3.19026854029801
H	-3.61008892308140	3.44297424904691	-1.46034372967774
H	-4.90324037286968	2.48481719869795	-2.22297598373818
H	-3.10031949949891	0.61457539690266	-3.89035757101945
H	-4.46437598746247	0.04773208599720	-2.89104980095819
H	-2.84299929114363	-0.65229667908762	-2.66821259509057
H	-2.63561132763437	-2.17842449689208	-1.16987946686950
H	-4.06451891286292	-2.64268702924058	-0.21557063228295
H	-2.48939568874758	-3.41867071032037	0.09696645696767

```
============================================================
                       INPUT FILE
============================================================
NAME = UVVis.inp
|  1> ! BP86 D3BJ def2-TZVP RI def2/J TightSCF
|  2> %maxcore 50000 # Memory settings often need to be modified when running
TDDFT. Check batching info in the TDDFT output.
|  3> %tddft
|  4> nroots 150   # Setting the number of roots (transitions) to be calculated.
|  5> maxdim 5 # Davidson expansion space = MaxDim * nroots. Use MaxDim 5-
10 for colable convergence. Note that the larger MaxDim is, the more disk space
is required
|  6> end
|  7>
|  8> %output
|  9> Print[ P_Basis ] 2
| 10> Print[ P_MOs ] 1
| 11> end
| 12>
| 13> %pal nprocs 1 end
| 14> %scf
| 15>  MaxIter 512
| 16> end
| 17>
| 18> * xyz 0 1
| 19> Ni        7.21385      3.32270      5.82099
| 20> P         6.22509      1.68396      7.09267
| 21> P         8.15744      1.86626      4.31476
| 22> P         6.27394      5.25574      6.63575
| 23> P         8.22358      2.73798      7.80009
| 24> P         8.22687      5.31729      5.29871
| 25> P         6.19333      3.07293      3.77770
| 26> C         8.23844     -0.35507      8.26950
| 27> C         7.55882      2.48448      2.67047
| 28> C         6.86077      6.56087      5.45345
| 29> C         8.35271      7.27191      7.73726
| 30> C         6.83886      2.03109      8.80968
| 31> C         7.62372      1.00812      8.10439
| 32> C         6.23362      2.36776     10.14549
| 33> C         7.68829      6.45392      6.66343
| 34> C         6.74200      1.39097      3.21610
| 35> C         6.08697      0.08777      2.84619
| 36> C         9.00010     -0.69041      6.97633
| 37> H         8.32012     -0.66977      6.11237
| 38> H         9.45250     -1.69104      7.03992
| 39> H         9.79713      0.04376      6.79250
| 40> C         8.17680      2.99578      1.39745
| 41> C         6.23600      7.55681      4.51436
| 42> C         5.27620      1.24573     10.58128
| 43> H         4.51381      1.06248      9.81034
| 44> H         4.76409      1.51935     11.51569
| 45> H         5.82134      0.30766     10.75485
| 46> C         7.07081      3.38397      0.40091
| 47> H         6.41334      4.15196      0.83313
| 48> H         6.45123      2.51719      0.13443
| 49> H         7.51278      3.78624     -0.52272
| 50> C         7.33836      8.34444      3.78559
| 51> H         7.99776      7.66169      3.23075
| 52> H         7.95595      8.91300      4.49385
| 53> H         6.89439      9.05404      3.07169
| 54> C         5.28195     -0.40054      4.06213
| 55> H         5.94086     -0.53674      4.93165
| 56> H         4.79219     -1.36087      3.84318
| 57> H         4.51079      0.33233      4.33778
| 58> C         5.14562      0.30041      1.64859
| 59> H         4.41560      1.09413      1.86344
| 60> H         4.59453     -0.62507      1.42494
| 61> H         5.70914      0.58563      0.74937
| 62> C         7.13238     -1.39987      8.49667
| 63> H         6.56745     -1.18814      9.41436
| 64> H         7.56867     -2.40572      8.58690
| 65> H         6.42529     -1.40337      7.65463
| 66> C         9.01183      4.24027      1.74246
| 67> H         9.46992      4.66410      0.83663
| 68> H         9.81006      3.98776      2.45444
| 69> H         8.38056      5.01176      2.20635
| 70> C         9.13688      6.31136      8.64704
| 71> H         8.46217      5.56630      9.09260
| 72> H         9.63141      6.86306      9.46012
| 73> H         9.90270      5.76934      8.07461
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| 75> H         7.91517      1.61874     11.33361
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| 77> H         8.05099      3.33188     10.87381
| 78> C         9.21128     -0.34531      9.46079
| 79> H         9.96741      0.44363      9.33876
| 80> H         9.72972     -1.31226      9.54080
| 81> H         8.67756     -0.16670     10.40449
| 82> C         5.45736      3.68677      9.99497
| 83> H         6.12724      4.49299      9.66312
| 84> H         5.00538      3.98240     10.95325
| 85> H         4.65867      3.58623      9.24667
| 86> C         5.39909      6.77758      3.48610
| 87> H         4.93702      7.46383      2.76116
| 88> H         4.60370      6.20639      3.98511
| 89> H         6.02895      6.06332      2.93643
| 90> C         7.28634      8.00389      8.57000
| 91> H         6.70821      8.70457      7.95274
| 92> H         7.76139      8.57392      9.38218
| 93> H         6.58472      7.28452      9.01633
| 94> C         9.31517      8.28645      7.09722
| 95> H        10.04193      7.77654      6.44850
| 96> H         9.86895      8.83328      7.87475
| 97> H         8.76829      9.02084      6.48986
| 98> C         9.08237      1.91230      0.78765
| 99> H         8.49532      1.03825      0.47318
|100> H         9.83446      1.57784      1.51672
|101> H         9.60782      2.30429     -0.09579
|102> C         7.16334     -0.95422      2.49597
|103> H         7.75976     -0.63627      1.63026
|104> H         6.69601     -1.92032      2.25404
|105> H         7.84619     -1.10236      3.34485
|106> C         5.33015      8.51826      5.30217
|107> H         5.91732      9.13231      5.99898
|108> H         4.58159      7.95986      5.88266
|109> H         4.80062      9.19528      4.61556**
****END OF INPUT****
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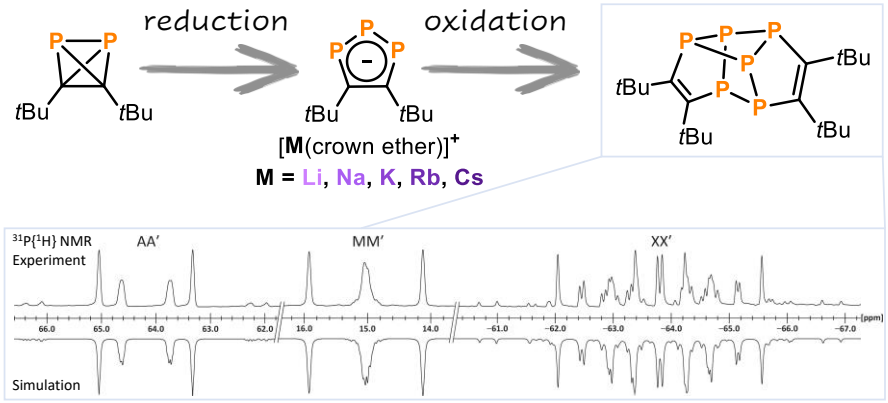
3 Access to 1,2,3-Triphospholide Ligands by Reduction of Di-*tert*-butyldiphosphatetrahedrane[a,b]

Abstract: Di-*tert*-butyldiphosphatetrahedrane (tBuCP)$_2$ (**A**) is a reactive tetrahedral molecule, which may serve as a source of new phosphaorganic molecules and ligands. However, the redox chemistry of this compound has not yet been investigated. Here, we show that the reduction of **A** with alkali metals (AM = Li, Na, K, Rb and Cs) affords 1,2,3-triphospholides [L$_n$AM][1,2,3-P$_3$C$_2$$tBu_2$] (**1-5**, [L$_n$AM] = [Li([12]crown-4)$_2$]$^+$, [Na([15]crown-5)$_2$]$^+$, [K([18]crown-6)]$^+$, [Rb([18]crown-6)]$^+$, and Cs$^+$) with 1,3-diphospholides [L$_n$AM][1,3-P$_2$C$_3$$tBu_3$] (**6-10**) formed as by-products. The potassium salt **3** was isolated on a preparative scale, allowing for reactivity studies. Transmetalation with iron(II) and ruthenium(II) chlorides yielded the sandwich complexes [Cp*M(η^5-1,2,3-P$_3$C$_2$$tBu_2$)] (**11**, M = Fe; **12**, M = Ru, Cp* = C$_5$Me$_5$) featuring η^5-coordinated triphospholide ligands. Treatment of **3** with [Cp$_2$Fe][BAr$_4^F$] or [H(Et$_2$O)$_2$BAr$_4^F$] (BAr$_4^F$ = B{C$_6$H$_3$(CF$_3$)$_2$}$_4$) afforded the polyphosphorus compound tBu$_4$C$_4$P$_6$ (**13**), which presumably results from the dimerisation of a 1,2,3-triphospholyl radical intermediate (1,2,3-P$_3$C$_2$$tBu_2$)$^\bullet$ (**3**$^\bullet$). Tetracyclic **13** is closely structurally related to an isomer of the hydrocarbon hypostrophene (C$_{10}$H$_{10}$).



[a] Reproduced from M. K. Uttendorfer, G. Hierlmeier, G. Balázs, R. Wolf, *Dalton Trans.* **2024**, *53*, 10113–10119.

[b] Maria K. Uttendorfer conducted all reactions and characterised the resulting compounds. She also performed and analysed the DFT calculations with input from Gábor Balázs and wrote the manuscript. Gabriele Hierlmeier and Robert Wolf conceptualised the project. Robert Wolf supervised and directed the project.

3.1 Introduction

Phosphatetrahedranes can be used to illustrate the diagonal relationship between carbon and phosphorus in the periodic table, and were postulated as stable compounds decades ago.[1,2] Surprisingly, the first representatives for this class of tetrahedral molecules were reported only recently.[3-5] We described the synthesis of di-*tert*-butyldiphosphatetrahedrane (tBuCP)$_2$ (**A**, Figure 1a) via the nickel-catalysed dimerisation of the phosphaalkyne tBuCP.[3] In parallel, Cummins and co-workers synthesised and explored the reactivity of tri-*tert*-butylphosphatetrahedrane (tBu$_3$C$_3$P) (**B**) and triphosphatetrahedrane (HCP$_3$) (**C**).[4,5] The phosphatetrahedranes **A**-**C** are isolobal to purely carbon-based tetrahedranes such as (tBuC)$_4$ (**D**), and the classical "inorganic tetrahedrane" P$_4$ (**E**, white phosphorus).[6,7] This has inspired the study of the reaction chemistry of **A**-**C**, which has revealed some similarities, but also differences with respect to the chemistry of white phosphorus in particular.[3-5,8-14]

Isomerisations of the phosphatetrahedrane scaffold have been observed in reactions with main group nucleophiles. Thus, *N*-heterocyclic carbenes (NHCs) effect P–C or P–P bond cleavage in **A**, giving bis(phosphaalkenes) or phosphirenes depending on the NHC (Figure 1b).[8] An isomerisation of **B** to intermediary (tri-*tert*-butylcyclopropenyl)phosphinidene has been proposed for various reactions, e.g. with triphenylmethylenephosphorane and a base-stabilised silylene.[9] The isomerisation to transient phosphacyclobutadienes is another predominant reaction path, which has been reported for the irradiation of **A** by UV or visible light and for the reaction of **B** with Lewis acids (Figure 1b).[10,11] Cyclobutadiene-type ligands are formed directly on the metal atom when **A** interacts with various low-valent Fe, Co and Ni complexes (Figure 1b).[12,13] Further studies have shown that, phosphatetrahedranes may alternatively retain their tetrahedral structure in selected coordination compounds.[3,5,14]

To the best of our knowledge, there are no reports on the synthesis of organophosphorus anions by reduction of phosphatetrahedranes. In contrast, the reduction chemistry of the closely-related compounds P$_4$ (**E**, white phosphorus) and *tert*-butylphosphaalkyne (tBuCP, the monomer of **A**) is well-investigated.[15-19] Reactions of P$_4$ with sodium afford pentaphospholide, tetraphospholide and 1,2,3-triphospholide anions (among other polyphosphide species),[15,16] while reduction of phosphaalkynes (RCP) with Na/Hg (and other alkali metal reductants) yields di- and 1,2,4-triphospholides.[17-19] These previous results inspired us to explore similar reductions of (tBuCP)$_2$ (**A**) (Figure 1c), with the aim to access anionic ligands. Here, we report the synthesis of 1,2,3-triphospholide salts [L$_n$AM][1,2,3-P$_3$C$_2t$Bu$_2$] (**1**-**5**, [L$_n$AM] = [Li([12]crown-4)$_2$]$^+$, [Na([15]crown-5)$_2$]$^+$, [K([18]crown-6)]$^+$, [Rb([18]crown-6)]$^+$, and Cs$^+$) from **A** and alkali metals. The utility of **3** as a suitable precursor for 1,2,3-triphospholide complexes is demonstrated by coordination to group 8 metal complexes. Furthermore, we report the synthesis and characterisation of the unusual polyphosphane (tBu$_4$C$_4$P$_6$) (**13**), which is an oxidation product of **3** with a remarkable structure built up by two fused 1,2,3-triphospholyl units. Our results

complement previous studies on the synthesis of 1,2,3-triphospholides via several other routes, including most prominently the reaction of polyphosphide anions with alkynes.[16,20-29]

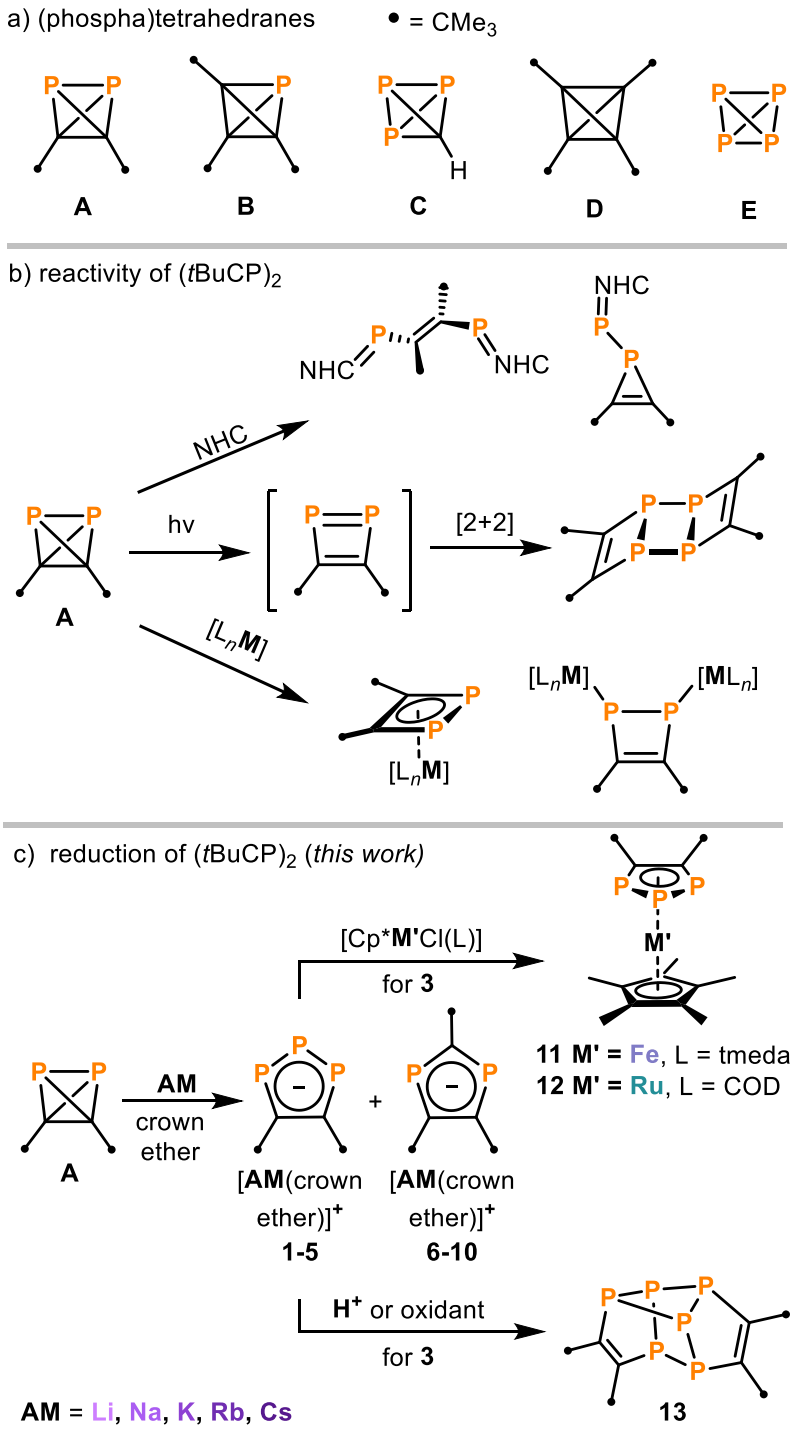


Figure 1. a) Tetrahedranes comprised of phosphorus and carbon atoms;[3-7] b) reactivity of **A** (NHC = N-heterocyclic carbene, M = Fe, Co, Ni; L e.g. 1,5-cyclooctadiene, anthracene, cyclopentadienyl),[8,11-13] c) alkali metal reduction of **A** and subsequent reactivity studies.

3.2 Results and Discussion

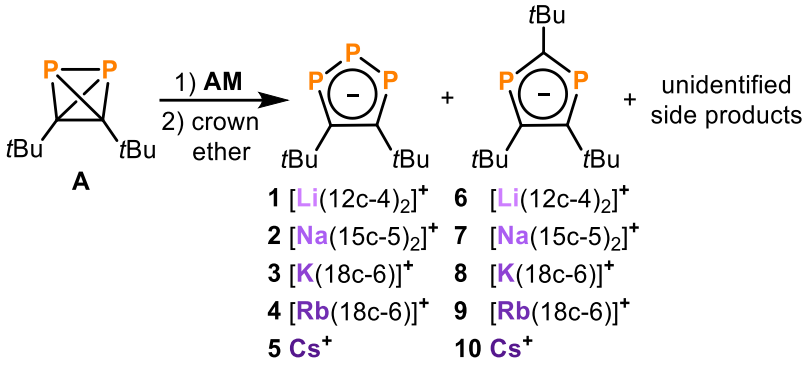
3.2.1 Reduction of A with alkali metals: Synthesis and characterisation of triphospholides 1-5

Initially, the redox properties of (tBuCP)$_2$ (**A**) were investigated by cyclic voltammetry in toluene/THF/[nBu$_4$N]PF$_6$. Surprisingly, no redox process was observed between −3.0 and +1.2 V vs. Fc/Fc$^+$ (Fc = Cp$_2$Fe, see Figure S47, section 3.4.6). The absence of any redox wave suggests that strong oxidants and reductants are required to react with **A**, while also indicating that oxidation and reduction is likely associated with a large overpotential on the platinum working electrode. DFT calculations on **A** show that the HOMO lies higher and the LUMO lower in energy compared to P$_4$.[11] This suggests that, in principle, **A** should be more easily reduced and oxidised. P$_4$ can be reduced at the potential $E_{1/2}$ = –1.55 V (vs. bottom mercury in DMF).[30] Therefore, the chemical reduction of **A** was pursued.

Different reducing agents were evaluated in experiments performed on an NMR scale. Unfortunately, **A** did not react with magnesium or zinc powder. Activated Rieke zinc and Rieke magnesium gave black and brown suspensions, respectively. The reaction with Rieke zinc is very unselective, leading to an array of unidentified products according to ^{31}P NMR spectroscopy. In contrast, the ladderane (tBuCP)$_4$ was observed as main product in the reaction with Rieke magnesium. (tBuCP)$_4$ is the dimerisation product of **A**, which can also be obtained by irradiation with UV or visible light (Figure 1b).[11,31]

The use of strongly reducing alkali metals gave more promising results. Analysis of the ^{31}P{^{1}H} NMR spectrum of the reaction of **A** with lithium chunks showed full consumption of **A** and two new species in a 2:1 ratio (see Figure S1). After the addition of [12]crown-4, these species were identified as [Li([12]crown-4)$_2$][1,2,3-P$_3$C$_2$$tBu_2$] (**1**) and [Li([12]crown-4)$_2$][1,3-P$_2$C$_3$$tBu_3$] (**6**, Scheme 1) based on the comparison of the NMR spectroscopic data with related compounds.[18,20-29] The major product **1** is characterised by two doublets of doublets at 224.0 ppm and 316.2 ppm ($^1J_{AX}$ = −463.8 Hz, $^1J_{A'X}$ = −465.5 Hz, $^2J_{AA'}$ = 4.3 Hz), while **6** gives rise to a singlet at 196.0 ppm (see Figure S6, SI). Subsequent investigations using heavier alkali metals (Na-Cs) gave similar mixtures of the tri- and diphospholide (Scheme 1).

Salts **1**-**10** clearly result from the initial reduction of **A**, followed by rearrangements that involve the exchange of P and tBuC units.‡ A similar process has been reported in the literature for the related reduction of tBuCP, but this yields mixtures of 1,2,4-triphospholides and 1,3-diphospholides.[18] 1,2,4-Triphospholides have been studied far more intensely than their 1,2,3-isomers due to the easier synthetic accessibility. The first 1,2,3-triphospholide salt was reported by Baudler and co-workers in 1990 as a side product in the reaction of P$_4$ with sodium in diglyme.[16] Since then several other 1,2,3-triphospholides have been reported, which contain aryl, alkyl, ester groups or hydrogen atoms as substituents.[20-29]



Scheme 1. Reduction of di-*tert*-butyldiphosphatetrahedrane (**A**) yielding the triphospholides **1**-**5** as the major products next to the diphospholides **6**-**10** and other unidentified side products (AM = Li, Na, K, Rb, Cs, 12c-4 = [12]crown-4, 15c-5 = [15]crown-5, 18c-6 = [18]crown-6). Conditions: THF, −80 °C → r.t., overnight.

It is interesting to note that the ratio of di- and triphospholide in this reaction mixture does not reflect the ratio of carbon and phosphorus atoms in the starting material **A**. Thus, several unidentified side products were detected in the ^{1}H NMR spectra of the reaction mixtures among them a singlet at 1.15 ppm which, likely can be attributed to the remaining *t*BuC fragments of this reaction (see Figure S11). Considering the similar solubilities of the di- and triphospholide salts, their clean isolation is hampered. Gratifyingly, salts **1** and **3** were isolated as crystalline materials in varying yield of up to 5% and 32%, respectively, whereas attempts to cleanly isolate **2**, **4** and **5** gave mixtures featuring the di- and triphospholide (see section 3.4 for further details).

The molecular structures of the di- and triphospholide salts are corroborated by single-crystal X-ray diffraction (sc-XRD) studies on crystals of **1**, **3**, **4** and **9** obtained from *n*-hexane/THF or *n*-hexane/toluene. The molecular structure of potassium salt **3** is shown as an example in Figure 2a. The similar structures of the lithium and rubidium salts **1** and **4** and the structure of the rubidium diphospholide **9** are shown in section 3.4.5. The salient feature of the structures of **1**, **3** and **4** are the planar five-membered P_3C_2 rings which are consistent with an aromatic 6 π-electron ring system with bond lengths in between typical single and double bonds (e.g. **3**: C−C (1.420(3) Å), C−P (1.780(2) Å), P−P (2.0740(8) Å and 2.0777(8) Å). This is well in line with related triphospholide structures.[16,20,23,25,26,29,32]

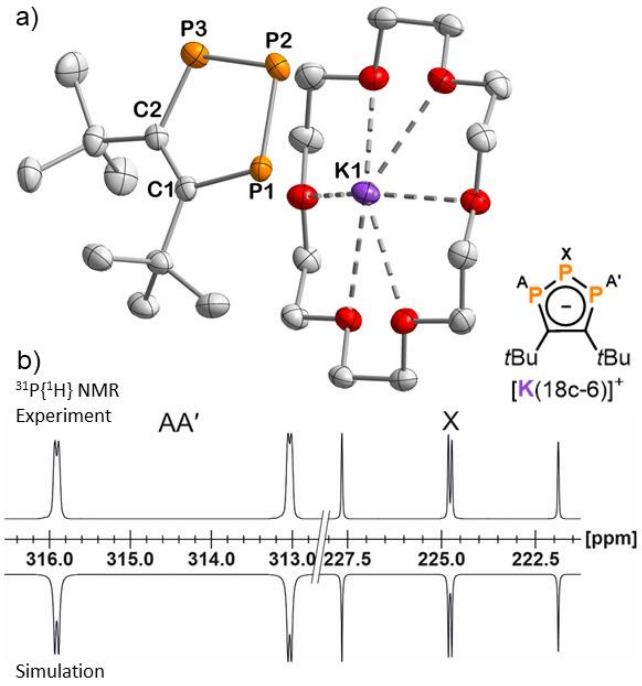


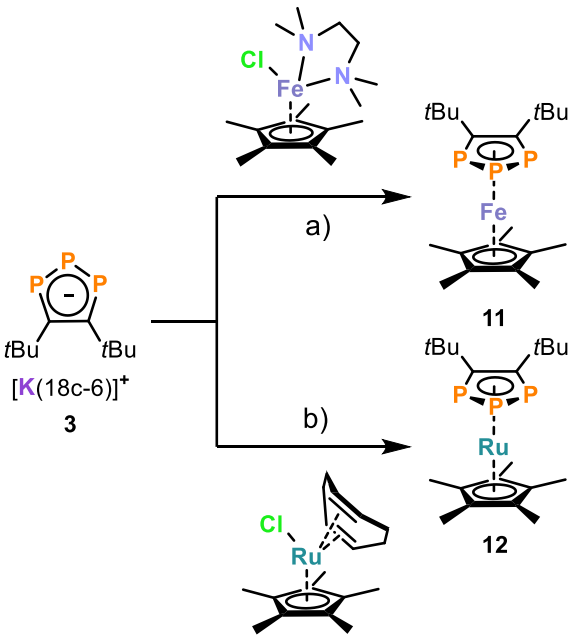
Figure 2. a) Solid-state molecular structure of **3**. Displacement ellipsoids are drawn at the 50% probability level; H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–P2 2.0777(8), P2–P3 2.0740(8), P1–C1 1.780(2), P3–C2 1.780(2), C1–C2 1.420(3), P1–P2–P3 97.24(3), C1–P1–P2 102.86(8), C2–P3–P2 103.02(7), C2–C1–P1 118.52(16), C1–C2–P3 118.35(15). b) Section of the $^{31}P\{^{1}H\}$ NMR spectrum of **3** with nuclei assigned to an AA′X spin system; experimental (top); simulation (bottom): $\delta(P_X)$ = 224.8 ppm, $\delta(P_{AA'})$ = 314.4 ppm, $^{1}J_{AX}$ = –465.6 Hz, $^{1}J_{A'X}$ = –467.5 Hz, $^{2}J_{AA'}$ = 4.3 Hz. The $^{31}P\{^{1}H\}$ NMR spectrum of **1** is similar (see Figure S7 and Table S1 for further details).

In contrast to other symmetrically substituted triphospholide salts,[16,20,25,27,29] the $^{31}P\{^{1}H\}$ NMR spectra of **1-5** do not display an A_2B spin system but an AA′X spin system. For example, the simulation of the spin system for **3** by an iterative fitting procedure gave the PP coupling constants: $^{1}J_{AX}$ = 465.6 Hz, $^{1}J_{A'X}$ = 467.5 Hz and $^{2}J_{AA'}$ = 4.3 Hz (Figure 2b). The magnetic inequivalence of the phosphorus atoms P^{A} and $P^{A'}$ is likely due to the proximity of the *t*Bu groups which cannot rotate independently and thus differentiates the two otherwise symmetrical halves of the 1,2,3-triphospholide anion (see Figure S44). The $^{31}P\{^{1}H\}$ NMR spectrum of **3** did not change significantly at elevated temperature (25, 40 and 60 °C), which may indicate that the *t*Bu-groups rotate in a concerted fashion (see Figure S19). The ^{1}H NMR spectrum of **3** (see Figure S15) gives two partly overlapping singlets for the *t*Bu groups at 1.75 ppm, similarly attributed to the non-equivalence of the 18 hydrogen atoms due to the hindered rotation of the *t*Bu groups. Another singlet at 3.57 ppm arises from the hydrogen atoms of the crown ether molecule. The signal of the carbon nuclei in the five membered P_3C_2 core of **3** appears as a multiplet centred at 184.4 ppm in the $^{13}C\{^{1}H\}$ NMR spectrum (see Figure S16), due to coupling to the phosphorus atoms. The multiplet detected at 38.9 ppm is assigned to the magnetically inequivalent methyl groups, while quaternary carbon atoms of the *t*Bu groups give rise to a multiplet centred at

40.5 ppm. Similar ^{13}C NMR data were recorded for **1** (see Figure S3). The UV-Vis absorption spectra of **1** and **3** dissolved in THF display two absorption bands in the UV region at 270 nm and 345 nm. The latter absorption tails into the visible region, causing the orange colour of **1** and **3** (see Figures S39 and S40).

3.2.2 Metal coordination of triphospholide 3: synthesis of iron and ruthenium complexes

Even though several 1,2,3-triphospholide salts were reported, the number of isolated 1,2,3-triphospholyl complexes is limited.[22-25,29,33] To test the utility of the newly synthesised triphospholide salts, we investigated the synthesis of triphosphaferrocenes using **3** (which was selected among **1**-**5** due to the superior isolated yield).[29,33] Dropwise addition of **3** to [Cp*FeCl(tmeda)] ((tmeda = tetramethylethylene-1,2-diamine) afforded the complex [Cp*Fe(η^5-1,2,3-P_3C_2tBu$_2$)] (**11**, Scheme 2a), which was isolated as a purple crystalline solid and was identified by its AA'X spin system with resonances at 116.3 ppm and at −17.8 ppm in the $^{31}P\{^1H\}$ NMR spectrum in C_6D_6. **11** was isolated as a purple powder in 54% yield after work-up. Similarly, the reaction of **3** with [Cp*RuCl(cod)] (cod = cycloocta-1,5-diene) led to the isolation of orange, crystalline **12** [Cp*Ru(η^5-1,2,3-P_3C_2tBu$_2$)] in 32% yield (Scheme 2b). Complex **12** can be identified by two multiplets (AA'X spin system) at 87.5 ppm and at −39.1 ppm in the $^{31}P\{^1H\}$ NMR spectrum.



Scheme 2. Synthesis of **11** and **12**. Reagents and conditions: a) THF, −30 °C, 1.5 h; b) THF, −30 °C, 1.5 h.

The structural and spectroscopic properties of **11** and **12** are broadly similar to related 1,2,3-triphosphaferrocenes.[29,33b-d] To our knowledge, only one 1,2,3-triphospholide ruthenium complex [K(2,2,2-crypt)][Ru(η^5-$P_3C_2H_2$){$CH_3C(CH_2)_2$}$_2$}] has been reported so far, which has not been crystallographically characterised.[23] In contrast to the previously reported examples,[29,33b,c] the (phospha-)cyclopentadienyl rings in the structures of **11** and **12** adopt a

staggered conformation (Figure 3), probably due to steric interactions between the Me groups of the Cp* ligands and the *tert*-butyl groups of the 1,2,3-triphospholyl ligands. It is noteworthy that the planes of the five membered ring ligands are slightly tilted with a plane-to-plane angle of 9°. In both complexes **11** and **12** the bonds in the five-membered ring of the triphospholide ligand are slightly elongated compared to the triphospholide salt **3** (**3**: P1−P2 = 2.0777(8) Å, C1−C2 = 1.420(3) Å, **11**: P1−P2 = 2.1056(7) Å, C1−C2 = 1.437(3) Å).

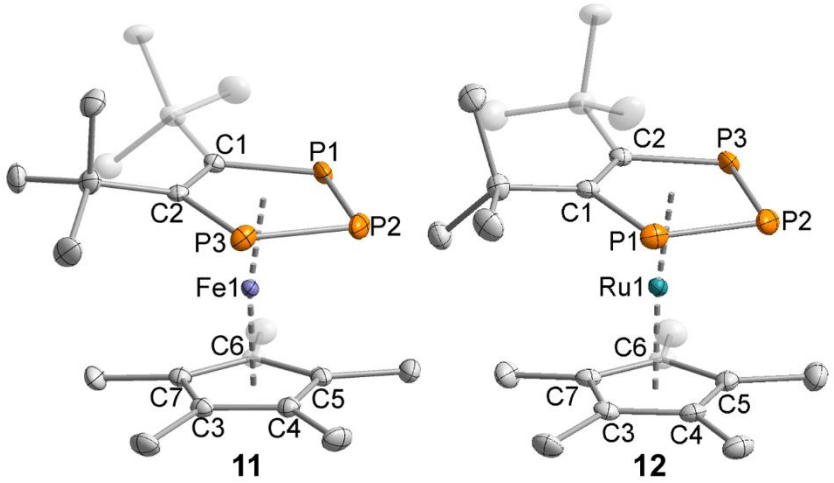


Figure 3. Solid-state molecular structure of **11** and **12**. Displacement ellipsoids are drawn at the 50% probability level; H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] for **11**: P1–P2 2.1054(7), P2–P3 2.1056(7), P1–C1 1.7999(19), P3–C2 1.8104(19), C1–C2 1.437(3), Fe1–$(P_3C_2)_{centroid}$ 1.6321(6), Fe1–$Cp^*_{centroid}$ 1.7116(9), P1–P2–P3 98.29(3), C1–P1–P2 101.85(6), C2–P3–P2 101.90(6), C1–C2–P3 118.53(13), C2–C1–P1 119.36(14), $Cp^*_{centroid}$–Fe1–$(P_3C_2)_{centroid}$ 172.02(4). **12**: P1–P2 2.1115(8), P2–P3 2.1093(8), P1–C1 1.808(2), P3–C2 1.814(2), C1–C2 1.435(3), Ru1–$(P_3C_2)_{centroid}$ 1.7595(6), Ru1–$Cp^*_{centroid}$ 1.8447(9), P1–P2–P3 98.25(3), C1–P1–P2 101.78(7), C2–P3–P2 101.95(7), C1–C2–P3 118.66(15), C2–C1–P1 119.33(15), $Cp^*_{centroid}$–Ru1–$(P_3C_2)_{centroid}$ 173.19(4).

Simulation of the $^{31}P\{^1H\}$ NMR spectra revealed an AA′X spin system for **11** and **12** (Figure 4). As reported for related complexes,[23,29,33] the ^{31}P and ^{13}C NMR resonances are shifted to lower frequency. The $^1J_{PP}$ coupling constants (**11**: $^1J_{AX}$ = 397.1 Hz, **12**: $^1J_{AX}$ = 393.4 Hz) are smaller compared to the signals of anionic **3** ($^1J_{AX}$ = 465.6 Hz, *vide supra*). The UV-Vis absorption spectrum of **11** displays two absorption bands in the UV region at 240 nm and 280 nm as well as two in the visible region at 470 nm and 575 nm (see Figures S41 and S42).

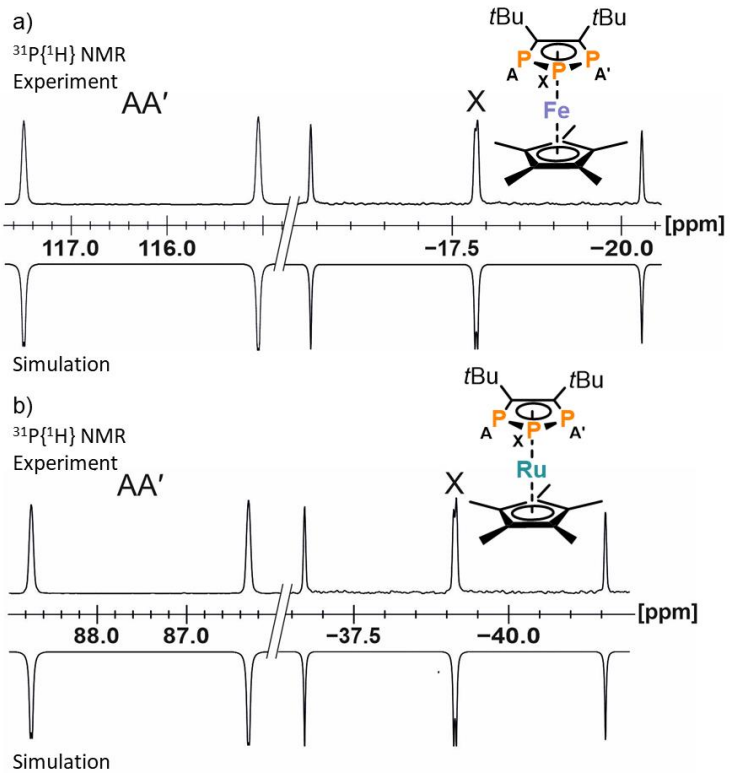
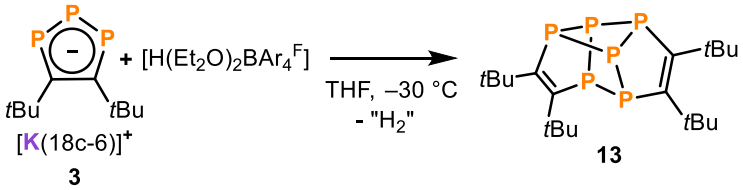


Figure 4. a) Section of the $^{31}P\{^{1}H\}$ NMR spectrum of **11** with nuclei assigned to an AA′X spin system; experimental (top); simulation (bottom): $\delta(P_X)$ = –17.8 ppm, $\delta(P_{AA'})$ = 116.3 ppm, $^{1}J_{AX}$ = –397.1 Hz, $^{1}J_{A'X}$ = –396.2 Hz, $^{2}J_{AA}$= 3.4 Hz. b) Section of the $^{31}P\{^{1}H\}$ NMR spectrum of **12** with nuclei assigned to an AA'X spin system; experimental (top); simulation (bottom): $\delta(P_X)$ = –39.1 ppm, $\delta(P_{AA'})$ = 87.5 ppm, $^{1}J_{AX}$ = –393.4 Hz, $^{1}J_{A'X}$ = –393.9 Hz.

3.2.3 Oxidation of 3 upon protonation: synthesis of hexaphosphane 13

Further reactivity studies of **3** with metal salts (e.g. $[(Ph_3P)_2NiCl_2]$, $[Cp_3Ni_2]BF_4$, $[(PPh_3)CuCl]$), oxidizing agents (e.g. $[Cp_2Fe]PF_6$), and organic electrophiles repeatedly revealed a set of three distinct multiplets at –63.8 ppm, 15.0 ppm and 64.2 ppm (1:1:1 integral ratio) in the $^{31}P\{^{1}H\}$ NMR spectra, which are assigned to a new product **13**. While this pattern was accompanied by further intractable products in most cases, reactions of **3** with $[Cp_2Fe][BAr_4^F]$ and $[H(Et_2O)_2BAr_4^F]$ (BAr_4^F = $B\{C_6H_3(CF_3)_2\}_4$) gave **13** in a selective fashion (see Figures S31 and S37). Isolation of crystalline **13** was possible from the reaction of **3** with $[H(Et_2O)_2BAr_4^F]$ by extraction of the crude reaction product with *n*-hexane and subsequent recrystallisation from *n*-pentane at −30 °C (22% yield, Scheme 3).



Scheme 3. Synthesis of **13**.

The determination of the molecular structure of **13** by sc-XRD revealed that this complex arises from the dimerisation of two 1,2,3-triphospholyl units, resulting in a tetracyclic structure

(Figure 5). The polycyclic framework of **13** represents a phosphorus-containing isomer of the hydrocarbon hypostrophene ($C_{10}H_{10}$) reported by Pettit and co-workers.[34] The P_6 core features a double-envelope arrangement with covalent P–P and P–C single bonds, while the adjacent C atoms each form a C=C double bond (C1–C2 1.364(3) Å, C3–C4 1.366(3) Å).[32] A similar double-envelope P_6 moiety has been reported for $[Cp''_2Th(\mu,\eta^3,\eta^3\text{-}P_6)ThCp''_2]$ ($Cp'' = \eta^5\text{-}1,3\text{-}t\text{Bu}_2C_5H_3$).[35] A related P_6 unit is also found in Jutzi's $P_6(C_5Me_5)_2$, which contains an additional P–P bond.[36]

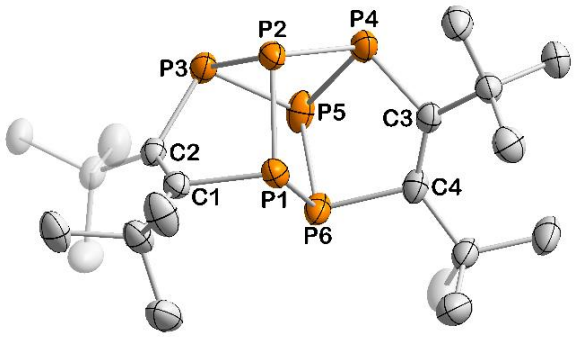


Figure 5. Solid-state molecular structure of **13**. Displacement ellipsoids are drawn at the 50% probability level; H atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–P2 2.1709(8), P1–P6 2.2380(8), P2–P3 2.2082(8), P2–P4 2.2571(8), P3–P5 2.2540(8), P4–P5 2.2054(9), P5–P6 2.1736(9), P1–C1 1.875(2), P3–C2 1.858(2), P4–C3 1.851(2), P6–C4 1.870(2), C1–C2 1.364(3), C3–C4 1.366(3), P1–P2–P3 90.50(3), C1–P1–P2 93.58(7), C2–P3–P2 99.04(7), C1–C2–P3 115.47(15), C2–C1–P1 116.22(15), P4–P5–P6 90.47(3), C3–P4–P5 98.78(7), C4–P6–P5 93.26(7), C3–C4–P6 115.92(15), C4–C3–P4 115.81(16), P1–P2–P4 87.60(3), P3–P2–P4 83.93(3), P4–P5–P3 84.07(3), P6–P5–P3 97.62(3).

The NMR spectroscopic data of **13** are fully consistent with the molecular structure, revealing two ^{1}H NMR singlets for the chemically inequivalent *t*Bu groups at 1.08 and 1.53 ppm and deshielded ^{13}C nuclei in the five-membered rings (165.0 ppm and 170.5 ppm) consistent with the C=C double bonds. An AA′MM′XX′ spin system is observed in the ^{31}P{^{1}H} NMR spectrum (Figure 6), confirming the presence of a covalently connected P_6 moiety. Note that $[Cp''_2Th(\mu,\eta^3,\eta^3\text{-}P_6)ThCp''_2]$ gives rise to a similar AA′MM′Q_2 spin system.[35]

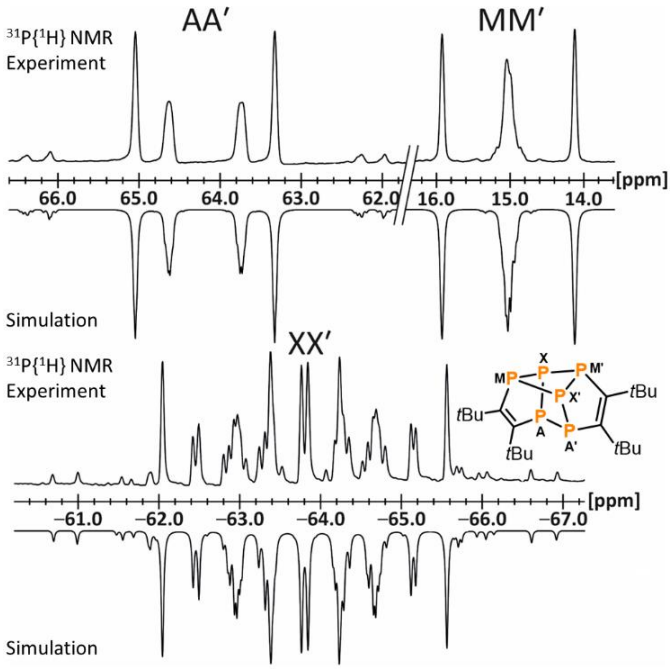
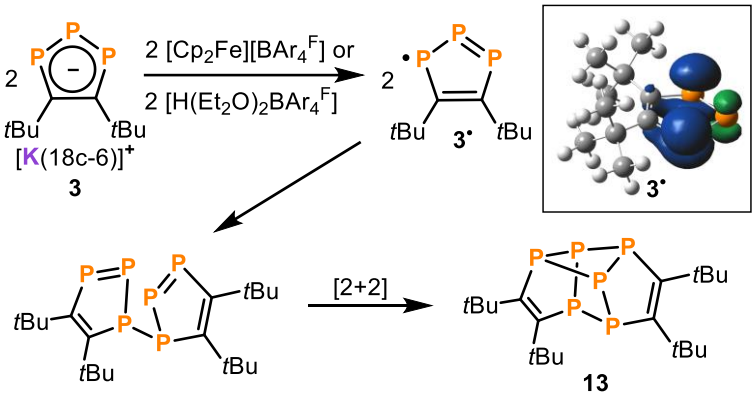


Figure 6. Section of the $^{31}P\{^{1}H\}$ NMR spectrum of **13** with nuclei assigned to an AA′MM′XX′ spin system; experimental (top); simulation (bottom): $\delta(P_{AA'}) = 64.2$ ppm, $\delta(P_{MM'}) = 15.0$ ppm, $\delta(P_{XX'}) = -63.8$ ppm, $^{1}J_{AA'} = -261.9$ Hz, $^{1}J_{AX} = {}^{1}J_{A'X'} = -293.9$ Hz, $^{1}J_{M'X} = {}^{1}J_{MX'} = -134.2$ Hz, $^{2}J_{AM} = {}^{2}J_{A'M'} = -3.2$ Hz, $^{2}J_{A'M} = {}^{2}J_{AM'} = 9.9$ Hz, $^{2}J_{MM'} = 24.9$ Hz, $^{2}J_{A'X} = {}^{2}J_{AX'} = 15.3$ Hz, $^{1}J_{MX} = {}^{1}J_{M'X'} = -157.7$ Hz, $^{2}J_{XX'} = 29.5$ Hz.

The possible mechanism of formation of **13** is shown in Scheme 4. We presume that $[H(Et_2O)_2BAr_4^F]$ acts as an oxidizing agent towards **3**, forming the radical $(1,2,3\text{-}P_3C_2tBu_2)^{\bullet}$ (**3**$^{\bullet}$) and dihydrogen (H_2) as a by-product.§ Subsequently, the presumed intermediate **3**$^{\bullet}$ dimerises under P–P bond formation, which is followed by a [2+2] cycloaddition to generate **13** (Scheme 4). The proposed mechanism is corroborated by DFT calculations (ωB97XD/def2-TZVPPD level of theory, see section 3.4.7) on the radical **3**$^{\bullet}$, which show that the calculated spin density is mainly located on the terminal P atoms (P1/P3) of the P_3 chain and to a lesser extent on the central P atom (P2). An alternative pathway might be the protonation of **3** to form $(1,2,3\text{-}P_3C_2tBu_2H)$ (**3-H**) that would be prone to cycloaddition, followed by dihydrogen elimination (Scheme S1).§§ However, the pathway proposed in Scheme 4 is considered more likely given that **13** from **3** is also formed with aprotic oxidizing agents such as $[Cp_2Fe]PF_6$ (see section 3.4.2).



Scheme 4. Proposed mechanism for the formation of **13** by reduction of **3**; the inset shows the calculated spin density distribution of **3**• drawn at a surface isovalue at 0.05.

3.3 Conclusion

The reduction of di-*tert*-butyldiphosphatetrahedrane (**A**) offers a new route to 1,2,3-triphospholide salts **1-5**, which are obtained as mixtures with 1,3-diphospholides **6-10**. This contrasts with the direct reduction of *t*BuCP with alkali metals which yields the related 1,2,4-triphospholides in addition to the 1,3-isomers. These findings echo the results of earlier investigations where **A** and *t*BuCP have formed isomeric reaction products.[11] The synthesis of [Cp*M(η^5-1,2,3-$P_3C_2tBu_2$)] (**11,** M = Fe; **12**, M = Ru) from the isolated potassium salt **3** complements earlier studies,[29,33] demonstrating the potential of **3** for transition metal coordination. Furthermore, reactions of **3** with [Cp_2Fe][BAr_4^F] and [$H(Et_2O)_2BAr_4^F$] resulted in an oxidation and dimerisation, forming the hexaphosphane $tBu_4C_4P_6$ (**13**). This compound has a remarkable molecular structure, which is closely related to a hypostrophene ($C_{10}H_{10}$) isomer. These results once more illustrate the potential utility of diphosphatetrahedranes as building blocks in organophosphorus chemistry. Further investigations into the reduction and oxidation of diphosphatetrahedrane **A** are in hand.

3.4 Supporting Information

General: All reactions and product manipulations were carried out in flame-dried glassware under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques (maintained at <0.1 ppm H_2O and <0.1 ppm O_2). (*t*BuCP)$_2$ (**A**).[3] [Cp*FeCl(tmeda)][37], [Cp*RuCl(cod)][38] and [H(Et$_2$O)$_2$BAr$^F_4$][39] were prepared according to procedures previously reported (tmeda = tetramethylethylenediamine, cod = cycloocta-1,5-diene, BAr_4^F = B{$C_6H_3(CF_3)_2$}$_4$). We thank the group of Nikolaus Korber for the generous donation of rubidium and caesium.

Solvents except DME were dried and degassed with a MBraun SPS800solvent purification system. DME was distilled from a sodium/benzophenone mixture. All dry solvents except *n*-hexane and *n*-pentane were stored under argon over activated 3 Å molecular sieves in gas-tight ampules. *n*-Hexane and *n*-pentane were stored over potassium mirrors.

NMR spectroscopy: NMR spectra were all recorded on Bruker Avance 400 spectrometers except for the ^{1}H and ^{13}C{^{1}H} NMR spectra of **13**, which were recorded on a Bruker Avance III 600 HD spectrometer with a 5 mm TCI cryo probe. All spectra were recorded at 300 K, except when specified otherwise, and referenced to residual solvent resonances (^{1}H NMR: THF-d_8: 1.72 ppm, CD_3CN: 1.94 ppm, C_6D_6: 7.16 ppm, ^{13}C{^{1}H} NMR: THF-d_8: 25.31 ppm, CD_3CN: 118.26 ppm, C_6D_6: 128.06 ppm). Chemical shifts (δ) are given in ppm referring to external standards of tetramethylsilane (^{1}H, ^{13}C{^{1}H}), 85% phosphorus acid (^{31}P{^{1}H}) and 1.0 M solution of LiCl in D_2O (^{7}Li{^{1}H}). ^{13}C NMR signals were assigned based on 2D NMR spectra (^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC, ^{1}H,^{31}P-HSQC, ^{31}P,^{31}P-COSY).

Elemental analysis: The elemental analysis was determined by the analytical department of the University of Regensburg with a Micro Vario Cube (Elementar).

UV-Vis spectroscopy: The UV/Vis absorption spectrum was recorded on an Ocean Optics Flame Spectrometer with the corresponding light source (DH-2000-BAL/UV-Vis-NIR light source).

Mass spectrometry: Mass spectra were recorded on a Jeol AccuTOF GCX device by the analytical department of the University of Regensburg.

NMR simulation: For compound **1, 3, 11, 12** and **13** the ^{31}P{^{1}H} NMR spectrum was processed with the software gNMR by Cherwell Scientific.[40] The full line shape iteration procedure of gNMR was applied to obtain the best match of the fitted to the experimental spectrum. $^1J(^{31}P^{31}P)$ coupling constants were set to negative values and all other signs of the coupling constants were obtained accordingly. The designation of the spin system was performed by convention.

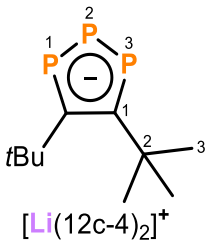
3.4.1 Synthesis of Compounds

[Li([12]crown-4)$_2$][1,2,3-P$_3$C$_2$*t*Bu$_2$] (1):

*Due to the light-sensitivity of **A**, the reaction was performed under the exclusion of light in a dark fume cupboard and with reaction flask wrapped in aluminium foil. No precautions for excluding light were taken during work-up.*

A piece of lithium (4.0 mg, 0.58 mmol, 1.0 eq.) in 2 mL THF was cooled to −80 °C and a solution of diphosphatetrahedrane **A** in toluene (1.56 mL, 0.55 mol/L, 0.87 mmol, 1.5 eq.) was added. The mixture was left to warm to room temperature whilst stirring overnight (^{31}P{^{1}H} NMR spectrum of the crude reaction mixture see Figure S1). The orange-red reaction mixture was filtered through a filter pipette in the glove box and [12]crown-4 (0.19 mL, 203 mg, 1.15 mmol, 2.0 eq.) was added. After stirring for 1.5 h at room temperature all volatiles were removed *in vacuo*. Subsequently, the orange solid was washed with *n*-hexane (1.5 mL) and toluene (2 x 0.5 mL). The dried residue was dissolved in THF (1.0 mL) and layered with diethyl ether (1.5 mL). Yellow needles were formed after 4 days at room temperature which were washed with diethyl ether (2 x 0.6 mL) and dried *in vacuo*.

Single crystals suitable for X-ray analysis were grown by slow diffusion of *n*-hexane in a concentrated THF solution at ambient temperature.



$C_{26}H_{50}LiO_8P_3$, MW = 590.54 g/mol

Yield: up to 16.8 mg (0.0284 mmol, 5%).

^{1}H NMR (400 MHz, 300 K, THF-d_8): δ = 1.74 (overlapping s, 18H, H_3C^3), 3.63 (s, 32H, $H^{(12c\text{-}4)}$) ppm.

^{13}C{^{1}H} NMR (100 MHz, 300 K, THF-d_8): δ = 38.9 (m, C^3), 40.6 (m, C^2), 70.1 (s, $C^{(12c\text{-}4)}$), 185.4 (m, C^1) ppm.

^{31}P{^{1}H} NMR (162 MHz, 300 K, THF-d_8): (AA'X spin system) δ = 224.0 ($^1J_{AX}$ = −463.8 Hz, $^1J_{A'X}$ = −465.5 Hz 1P, P^2), 316.2 ($^1J_{AX}$ = −463.8 Hz, $^1J_{A'X}$ = −465.5 Hz, $^2J_{AA'}$ = 4.3 Hz, 2P, $P^{1,3}$) ppm.

Coupling constants and chemical shifts are taken from the simulation (Figure S7 and Table S1).

^{7}Li{^{1}H} NMR (156 MHz, 300 K, THF-d_8): δ = −0.34 ppm.

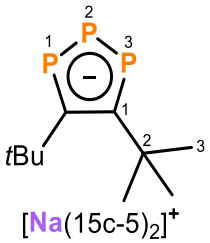
UV-Vis: (*n*-hexane, λ_{max} [nm], ε_{max} [L·mol^{-1}·cm^{-1}]): 270 (8000), 345 (3000).

Elemental analysis calcd. C 52.88, H 8.53; found C 53.17, H 8.00.

Mixture of [Na([15]crown-5)$_2$][1,2,3-P$_3$C$_2$*t*Bu$_2$] (2) and [Na([15]crown-5)$_2$][1,3-P$_2$C$_3$*t*Bu$_3$] (7): *Due to the light-sensitivity of **A**, the reaction was performed under the exclusion of light in a dark fume cupboard and with reaction flask wrapped in aluminium foil. No precautions for excluding light were taken during work-up.*

A piece of sodium (6.8 mg, 0.39 mmol, 1.0 eq.) in 1 mL THF was cooled to −80 °C and a solution of diphosphatetrahedrane **A** in toluene (1.0 mL, 0.43 mol/L, 0.44 mmol, 1.5 eq.) was added. The mixture was left to warm to room temperature whilst stirring overnight. The orange reaction mixture was filtered through a filter pipette in the glove box and [15]crown-5 (0.12 mL, 130 mg, 0.59 mmol, 2.0 eq.) was added. After stirring for 1.8 h at room temperature all volatiles were removed *in vacuo*. The orange solid was taken up in 0.5 mL toluene and 0.2 mL THF. *n*-Hexane (4 mL) was added to facilitate precipitation. The supernatant was decanted, and the residue washed with 2 mL of diethyl ether. 92.6 mg of orange solid were afforded after drying *in vacuo*.

Analytical data for **2**:

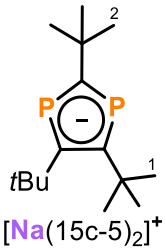


$C_{30}H_{58}NaO_{10}P_3$, MW = 694.70 g/mol

^{1}H NMR (400 MHz, 300 K, MeCN): δ = 1.68 (overlapping s, 18H, H_3C^3), 3.54 (s, 20H, $H^{(15c\text{-}5)}$) ppm.

^{31}P{^{1}H} NMR (162 MHz, 300 K, THF-d_8): δ = 224.8 ($^1J_{PP}$ = 458.8 Hz, $^1J_{PP}$ = 473.8 Hz, 1P, P^2), 314.9 ($^1J_{PP}$ = 466.7 Hz, $^2J_{PP}$ = 6.8 Hz, 2P, $P^{1,3}$) ppm.

Analytical data for **7**:[18b,c]



$C_{35}H_{67}NaO_{10}P_2$, MW = 732.85 g/mol

^{1}H NMR (400 MHz, 300 K, THF-d_8): δ = 1.38 (s, 9H, H_3C^2), 1.52 (s, 18H, H_3C^1), 3.54 (s, 20H, $H^{(15c\text{-}5)}$) ppm.

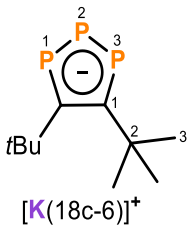
^{31}P{^{1}H} NMR (162 MHz, 300 K, THF-d_8): δ = 186.1 (s, 2P).

Mixture of [K([18]crown-6)][1,2,3-P_3C_2*t*Bu_2] (3) and [K([18]crown-6)][1,3-P_2C_3*t*Bu_3] (8):

*Due to the light-sensitivity of **A**, the reaction was performed under the exclusion of light in a dark fume cupboard and with reaction flask wrapped in aluminium foil. No precautions for excluding light were taken during work-up.*

A piece of potassium (21.8 mg, 0.56 mmol, 1.0 eq.) in 2.6 mL THF was cooled to −80 °C and a solution of diphosphatetrahedrane **A** in toluene (1.8 mL, 0.48 mol/L, 0.84 mmol, 1.5 eq.) was added. The mixture was left to warm to room temperature whilst stirring overnight. The orange reaction mixture was filtered through a filter pipette in the glove box and [18]crown-6 (148 mg, 0.56 mmol, 1.0 eq.) was added. After stirring for 1.8 h at room temperature all volatiles were removed *in vacuo*. The orange solid was taken up in 0.5 mL toluene and 0.3 mL THF. *n*-Hexane (4 mL) was added to facilitate precipitation. The supernatant was decanted, and the residue washed with diethyl ether (2 x 1 mL). 130 mg of orange solid were afforded after drying *in vacuo*.

Analytical data for **3**:



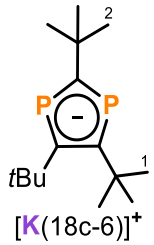
$C_{22}H_{42}KO_6P_3$, MW = 534.59 g/mol

^{1}H NMR (400 MHz, 300 K, CD_3CN): δ = 1.93 (overlapping s, 18H, H_3C^3), 3.76 (s, 36H, $H^{(18c\text{-}6)}$) ppm.

^{31}P{^{1}H} NMR (162 MHz, 300 K, CD_3CN): (AA'X spin system) δ = 226.6 ($^1J_{AX}$ = −465.6 Hz, $^1J_{A'X}$ = −467.5 Hz 1P, P^2), 317.2 ($^1J_{AX}$ = −465.6 Hz, $^1J_{A'X}$ = −467.5 Hz, $^2J_{AA'}$ = 4.3 Hz, 2P, $P^{1,3}$) ppm.

Coupling constants and chemical shifts are taken from the simulation (Figure S18 and Table S2).

Analytical data for **8**:



$C_{27}H_{51}KO_6P_2$, MW = 572.74 g/mol

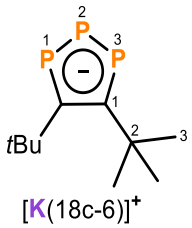
^{1}H NMR (400 MHz, 300 K, CD_3CN): δ = 1.60 (s, 9H, H_3C^2), 1.75 (s, 18H, H_3C^1), 3.76 (s, 36H, $H^{(18c\text{-}6)}$) ppm.

^{31}P{^{1}H} NMR (162 MHz, 300 K, CD_3CN): δ = 186.6 (s, 2P).

[K([18]crown-6)][1,2,3-$P_3C_2tBu_2$] (3):

*Due to the light-sensitivity of **A**, the reaction was performed under the exclusion of light in a dark fume cupboard and with reaction flask wrapped in aluminium foil. No precautions for excluding light were taken during work-up.*

A piece of potassium (20.5 mg, 0.52 mmol, 1.0 eq.) in 2.6 mL THF was cooled to −80 °C and a solution of diphosphatetrahedrane **A** in toluene (2.0 mL, 0.39 mol/L, 0.79 mmol, 1.5 eq.) was added. The mixture was left to warm to room temperature whilst stirring overnight. The orange reaction mixture was filtered through a filter pipette in the glove box and [18]crown-6 (138 mg, 0.52 mmol, 1.0 eq.) was added. After stirring for 1.3 h at room temperature all volatiles were removed *in vacuo*. Subsequently, the orange solid was washed with *n*-hexane (1.5 mL) and toluene (3 x 0.3 mL). The dried residue was dissolved in THF (0.5 mL) and layered with diethyl ether (1.0 mL). Yellow needles were formed after 7 days at room temperature, which were dried *in vacuo*. A second crop of crystals was obtained by removing the solvent from the toluene extract, redissolving the residue in THF (0.5 mL) and layering the solution with diethyl ether (1.0 mL). Single crystals suitable for X-ray analysis were grown by slow diffusion of *n*-hexane in a concentrated toluene solution at ambient temperature.



$C_{22}H_{42}KO_6P_3$, MW = 534.59 g/mol

Yield: up to 114 mg (two crops of crystals, 0.213 mmol, 32%).

Isolated yields varied due to the crystallisation properties of the compound.

^{1}H NMR (400 MHz, 300 K, CD_3CN): δ = 1.75 (overlapping s, 18H, H_3C^3), 3.57 (s, 36H, $H^{(18c\text{-}6)}$) ppm.

^{13}C{^{1}H} NMR (100 MHz, 300 K, THF-d_8): δ = 38.9 (m, C^3), 40.5 (m, C^2), 71.2 (s, $C^{(12c\text{-}4)}$), 183.4 (m, C^1) ppm.

^{31}P{^{1}H} NMR (162 MHz, 300 K, THF-d_8): (AA'X spin system) δ = 224.8 ($^1J_{AX}$ = −465.6 Hz, $^1J_{A'X}$ = −467.5 Hz 1P, P^2), 314.5 ($^1J_{AX}$ = −465.6 Hz, $^1J_{A'X}$ = −467.5 Hz, $^2J_{AA'}$ = 4.3 Hz, 2P, $P^{1,3}$) ppm.

Coupling constants and chemical shifts are taken from the simulation (Figure S18 and Table S2).

UV-Vis: (*n*-hexane, λ_{max} [nm], ε_{max} [$L \cdot mol^{-1} \cdot cm^{-1}$]): 270 (10000), 345 (4000).

Elemental analysis calcd. C 49.43, H 7.92; found C 50.15, H 7.85.

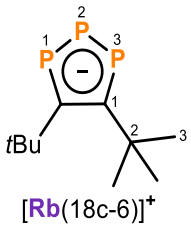
Mixture of [Rb([18]crown-6)][1,2,3-$P_3C_2tBu_2$] (4) and [Rb([18]crown-6)][1,3-$P_2C_3tBu_3$] (9):

*Due to the light-sensitivity of **A**, the reaction was performed under the exclusion of light in a dark fume cupboard and with reaction flask wrapped in aluminium foil. No precautions for excluding light were taken during work-up.*

A piece of rubidium (63.0 mg, 0.74 mmol, 1.0 eq.) in 3 mL THF was cooled to −80 °C and a solution of diphosphatetrahedrane **A** in toluene (1.3 mL, 0.85 mol/L, 1.1 mmol, 1.5 eq.) was added. The mixture was left to warm to room temperature while stirring overnight. The orange reaction mixture was filtered through a filter pipette in the glove box and [18]crown-6 (195 mg, 0.74 mmol, 1.0 eq.) was added. After stirring for 30 min at room temperature all volatiles were removed *in vacuo*. The orange solid was washed with 1 mL *n*-hexane, taken up in 0.5 mL THF and crystalised over 2 weeks to give 5 mg of yellow crystals which were washed with toluene (4 x 0.5 mL) and dried *in vacuo*.

Single crystals suitable for X-ray analysis of both **4** and **9** were obtained from the same batch, grown by slow diffusion of *n*-hexane (2 mL) in a concentrated THF solution at ambient temperature.

Analytical data for **4**:

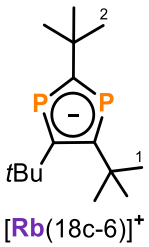


$C_{22}H_{42}RbO_6P_3$, MW = 580.96 g/mol

^{1}H NMR (400 MHz, 300 K, CD_3CN): δ = 1.77 (overlapping s, 18H, H_3C^3), 3.58 (s, 36H, $H^{(18c\text{-}6)}$) ppm.

^{31}P{^{1}H} NMR (162 MHz, 300 K, CD_3CN): δ 236.6 ($^1J_{PP}$ = 457.4 Hz, $^1J_{PP}$ = 471.2 Hz, 1P, P^2), 323.0 ($^1J_{PP}$ = 466.6 Hz, $^2J_{PP}$ = 4.8 Hz, 2P, $P^{1,3}$) ppm.

Analytical data for **9**:



$C_{27}H_{51}RbO_6P_2$, MW = 619.11 g/mol

^{1}H NMR (400 MHz, 300 K, CD_3CN): δ = 1.46 (s, 9H, H_3C^2)1.61 (s, 18H, H_3C^1), 3.58 (s, 36H, $H^{(18c\text{-}6)}$) ppm.

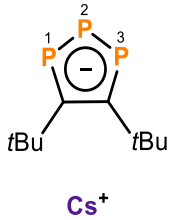
^{31}P{^{1}H} NMR (162 MHz, 300 K, CD_3CN): δ 193.6 (s, 2P).

Mixture of Cs[1,2,3-$P_3C_2tBu_2$] (5) and Cs[1,3-$P_2C_3tBu_3$] (10):

*Due to the light-sensitivity of **A**, the reaction was performed under the exclusion of light in a dark fume cupboard and with reaction flask wrapped in aluminium foil. No precautions for excluding light were taken during work-up.*

Caesium (19.5 mg, 0.15 mmol, 1.0 eq.) in 1 mL THF was cooled to −80 °C and a solution of diphosphatetrahedrane **A** in toluene (0.26 mL, 0.85 mol/L, 0.22 mmol, 1.5 eq.) was added. The mixture was left to warm to room temperature while stirring overnight. An orange reaction mixture was formed whose $^{31}P\{^1H\}$ NMR signals indicate the formation of **5** and **10.**

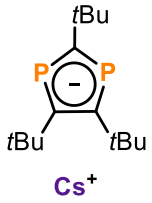
Analytical data for **5**:



$C_{10}H_{18}CsP_3$, MW = 354.08 g/mol

$^{31}P\{^1H\}$ NMR (162 MHz, 300 K, THF with C_6D_6 capillary): δ = 238.8 ($^1J_{PP}$ = 455.7 Hz, $^1J_{PP}$ = 467.8 Hz, 1P, P^2), 328.6 ($^1J_{PP}$ = 461.3 Hz, $^2J_{PP}$ = 4.3 Hz, 2P, $P^{1,3}$) ppm.

Analytical data for **10**:



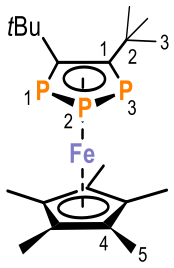
$C_{10}H_{18}CsP_3$, MW = 402.23 g/mol

$^{31}P\{^1H\}$ NMR (162 MHz, 300 K, THF with C_6D_6 capillary): δ 198.8 (s, 2P).

[Cp*Fe(η^5-1,2,3-P$_3$C$_2$*t*Bu$_2$)] (11):

A solution of triphospholide **3** (20.0 mg, 0.037 mmol, 1.0 eq.) in THF (0.8 mL) at −30 °C was added dropwise to a cooled (−30 °C) solution of [Cp*FeCl(tmeda)] (13.4 mg, 0.037 mmol, 1.0 eq.) in THF (0.8 mL). The mixture turned brown immediately and was left to warm to room temperature while stirring for 1.5 h. The volatiles were removed *in vacuo* and the residue extracted in *n*-hexane to give a purple solution. The mixture was filtered through a pad of silica gel (1 cm) and washed with *n*-hexane (3 x 1 mL). The solvent was removed and the purple solid dried *in vacuo*.

Single crystals suitable for X-ray analysis were grown from *n*-hexane at ambient temperature.



$C_{22}H_{39}FeP_3$, MW = 453.32 g/mol

Yield: 9.1 mg (0.020 mmol, 54%).

^{1}H NMR (400 MHz, 300 K, C_6D_6): δ = 1.65 & 1.66 (overlapping s, 18H, H_3C^3), 1.68 (s, 15H, H_3C^5) ppm.

^{13}C{^{1}H} NMR (100 MHz, 300 K, C_6D_6): δ = 12.6 (m, C^5), 38.4 (m, C^3), 39.2 (m, C^2), 86.8 (s, C^4), 134.6 (m, C^1) ppm.

^{31}P{^{1}H} NMR (162 MHz, 300 K, C_6D_6): (AA'X spin system) δ = −17.8 ($^1J_{AX}$ = −397.1 Hz, $^1J_{A'X}$ = −396.2 Hz 1P, P^2), 116.3 ($^1J_{AX}$ = −397.1 Hz, $^1J_{A'X}$ = −396.2 Hz, $^2J_{AA'}$ = 3.4 Hz, 2P, $P^{1,3}$) ppm.

Coupling constants and chemical shifts are taken from the simulation (Figure S26 and Table S3).

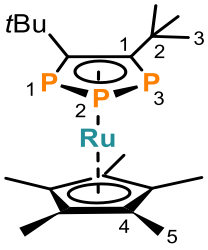
UV-Vis: (*n*-hexane, λ_{max} [nm], ε_{max} [L·mol^{-1}·cm^{-1}]): 240 (14000), 280 (16000), 470 (200), 575 (200).

Elemental analysis calcd. C 56.89, H 7.88; found C 56.76, H 7.82.

[Cp*Ru(η^5-1,2,3-P$_3$C$_2$*t*Bu$_2$)] (12):

A solution of triphospholide **3** (20.0 mg, 0.037 mmol, 1.0 eq.) in THF (0.8 mL) at −30 °C was added dropwise to a cooled (−30 °C) solution of [Cp*RuCl(cod)] (14.8 mg, 0.037 mmol, 1.0 eq.) in THF (0.8 mL). The mixture was left to warm to room temperature while stirring for 1 h. A colour change from yellow to red was observed. The volatiles were removed *in vacuo* and the residue extracted in *n*-hexane. Orange red crystals were formed upon storing at room temperature for 13 days. These were taken up in *n*-hexane (0.2 mL). Subsequently, the mixture was filtered through a pad of silica gel (1 cm) and washed with *n*-hexane (3 x 1 mL). The solvent was removed and the orange solid dried *in vacuo*.

Single crystals suitable for X-ray analysis were grown from *n*-hexane at ambient temperature.



$C_{22}H_{39}RuP_3$, MW = 497.55 g/mol

Yield: up to 5.9 mg (0.012 mmol, 32%).

^{1}H NMR (400 MHz, 300 K, C_6D_6): δ = 1.59 (s, 18H, H_3C^3), 1.78 (s, 15H, H_3C^5) ppm.

^{13}C{^{1}H} NMR (100 MHz, 300 K, C_6D_6): δ = 12.4 (m, C^5), 38.3 (m, C^3), 38.8 (m, C^2), 93.8 (s, C^4), 130.5 (m, C^1) ppm.

^{31}P{^{1}H} NMR (162 MHz, 300 K, C_6D_6): (AA'X spin system) δ = −39.1 ($^{1}J_{AX}$ = −393.4 Hz, $^{1}J_{A'X}$ = −393.9 Hz 1P, P^2), 87.5 ($^{1}J_{AX}$ = −393.4 Hz, $^{1}J_{A'X}$ = −393.9 Hz, $^{2}J_{AA'}$ = 0.6 Hz, 2P, $P^{1,3}$) ppm.

Coupling constants and chemical shifts are taken from the simulation (Figure S30 and Table S4).

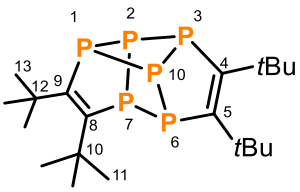
UV-Vis: (*n*-hexane, λ_{max} [nm], ε_{max} [$L \cdot mol^{-1} \cdot cm^{-1}$]): 230 (37000).

Elemental analysis calcd. C 51.39, H 7.12; found C 51.60, H 7.15.

tBu$_4$C$_4$P$_6$ (13):

To a solution of triphospholide **3** (83.0 mg, 0.155 mmol, 1.0 eq.) in THF (1.5 mL) at −30 °C was added a solution of $[H(Et_2O)_2BAr^F{}_4]$ (176 mg, 0.174 mmol, 1.1 eq.) in THF (1.5 mL). The mixture was left to warm to room temperature whilst stirring for 3 h and turned from colourless to pale yellow. The solvent was removed *in vacuo*, and the product was extracted with *n*-hexane (10x1 mL) and filtered. The compound was recrystallised from *n*-pentane (0.4 mL). Pale yellow crystals of **13** were obtained by storing the solution at −30 °C for twelve days. A second batch of crystals was isolated after storage of the supernatant at −30 °C for three weeks.

Crystals suitable for X-ray analysis were grown from *n*-pentane at −30 °C.



$C_{20}H_{36}P_6$, MW = 462.12 g/mol

Yield: 7.8 mg (two crops of crystals, 0.017 mmol, 22%).

^{1}H NMR (600 MHz, 300 K, C_6D_6): δ = 1.08 (s, 18H, H_3C^{13}), 1.53 (s, 18H, H_3C^{11}) ppm.

^{13}C{^{1}H} NMR(151 MHz, 300 K, C_6D_6): δ = 32.1 (t, J_{CP} = 5.4 Hz, C^{13}), 34.2 (t, J_{CP} = 6.6 Hz, C^{11}), 41.5 (m, C^{12}), 41.7 (m, C^{10}), 165.0 (m, C^9), 170.5 (m, C^8), ppm.

$^{31}P\{^{1}H\}$ NMR (162 MHz, 300 K, C_6D_6): (AA'MM'XX' spin system) δ = 64.2 ($^{1}J_{AA'}$ = –261.9 Hz, $^{2}J_{AM}$ = $^{2}J_{A'M'}$ = –3.2 Hz, $^{2}J_{A'M}$ = $^{2}J_{AM'}$ = 9.9 Hz, $^{1}J_{AX}$ = $^{1}J_{A'X'}$ = –293.9 Hz, $^{2}J_{A'X}$ = $^{2}J_{AX'}$ = 15.3 Hz, 2P, $P^{6,7}$), 15.0 ($^{2}J_{AM}$ = $^{2}J_{A'M'}$ = –3.2 Hz, $^{2}J_{A'M}$ = $^{2}J_{AM'}$ = 9.9 Hz, $^{2}J_{MM'}$ = 24.9 Hz, $^{1}J_{MX}$ = $^{1}J_{M'X'}$ = –157.7 Hz, $^{1}J_{M'X}$ = $^{1}J_{MX'}$ = –134.2 Hz, 2P, $P^{1,3}$), −63.8 ($^{2}J_{AX}$ = $^{2}J_{A'X'}$ = –293.9 Hz, $^{1}J_{A'X}$ = $^{1}J_{AX'}$ = 15.3 Hz, $^{1}J_{MX}$ = $^{1}J_{M'X'}$ = –157.7 Hz, $^{1}J_{M'X}$ = $^{1}J_{MX'}$ = –134.2 Hz, $^{2}J_{XX'}$ = 29.5 Hz, 2P, $P^{2,10}$) ppm.

Coupling constants and chemical shifts are taken from the simulation (Figure S35 and Table S5). HRMS (EI, toluene): m/z (%) calculated for $C_{20}H_{36}P_6$: 462.1237; found: 462.1233.

3.4.2 Additional Experiments

To an orange solution of triphospholide **3** and diphospholide **8** (combined 10 mg, approx. 0.04 mmol, 1.0 eq.) in DME (0.5 mL) at −30 °C was dropwise added a blue solution of $[Cp_2Fe]BAr^F_4$ (41 mg, 0.04 mmol, 1.0 eq.) in DME (0.5 mL). The mixture was left to warm to room temperature whilst stirring for 2.5 h and turned forest green. The solvent was removed *in vacuo*, and the product was extracted with *n*-hexane (5x0.5 mL) and filtered. The $^{31}P\{^{1}H\}$ NMR spectrum shows **13** as the main product (see Figure S37), side products can be attributed to the reaction of **8** with $[Cp_2Fe]BAr^F_4$ as they are similarly seen in the reaction of the mixture of **3** and **8** with $[H(Et_2O)_2BAr^F_4]$ (Figure S38). Nevertheless, the isolation of **13** is hampered due to the similar solubilities of **13** and Cp_2Fe as can be seen in the ^{1}H NMR spectrum (Figure S36).

Reactions of triphospholide **3** with $[IPrNi(vtms)_2]$, [Cp*RuCl(diphos)], $[FeCl_2(tmeda)]_2$, $[(Ph_3P)_2NiCl_2]$, $[Cp_3Ni_2]BF_4$, $[Cp_2Fe]PF_6$, $[(PPh_3)CuCl]$ and MeI were conducted according to the same procedure, yielding the characteristic $^{31}P\{^{1}H\}$ NMR signals of **13** among other, so far unidentified reaction products.

3.4.3 NMR Spectra

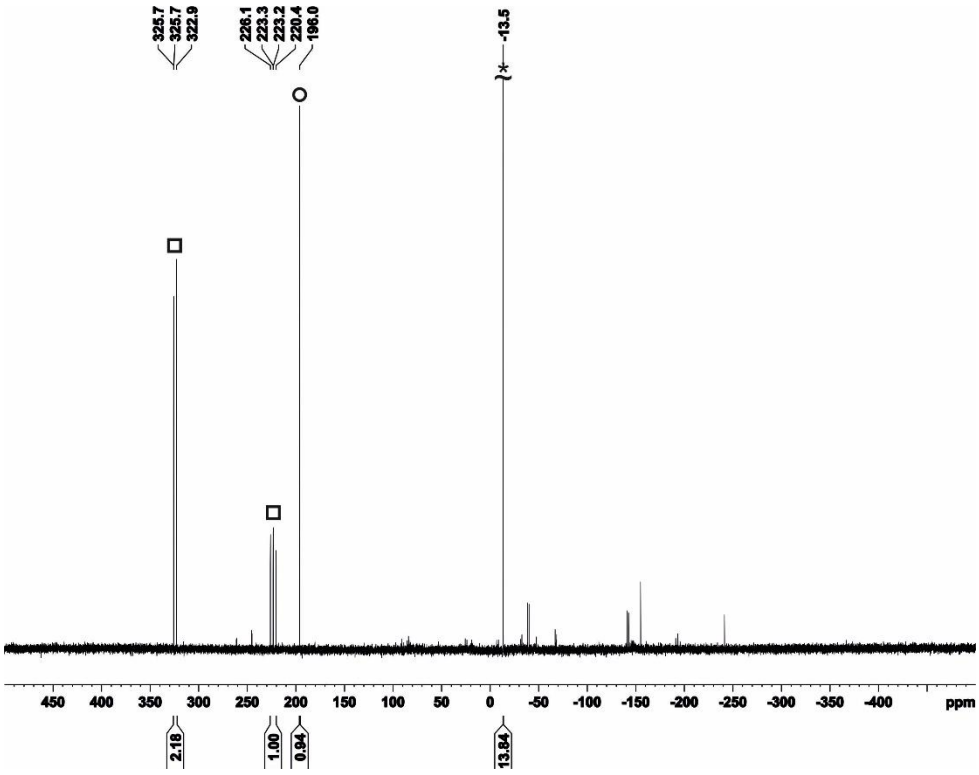


Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, THF with C_6D_6 capillary) of the reaction mixture of 1 eq. Li with 1.5 eq. **A**. **1** (□) and **6** (○). * = (*t*BuCP)$_4$.

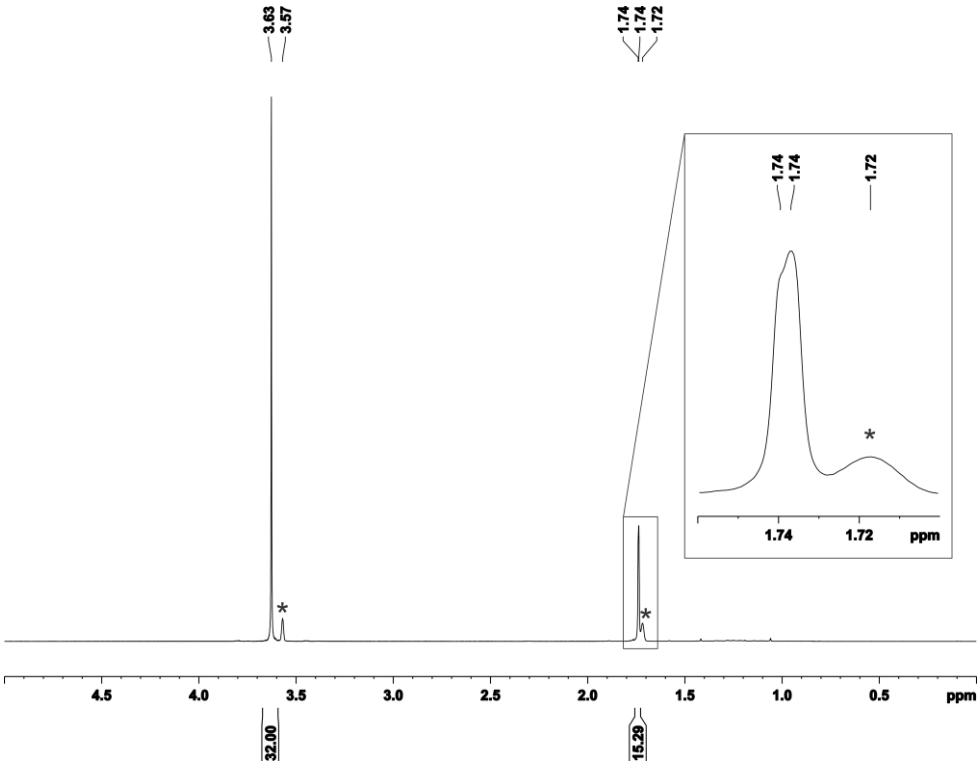


Figure S2. ^{1}H NMR spectrum (400 MHz, 300 K, THF-d_8) of **1**. *Residual proton signals of THF-d_8.

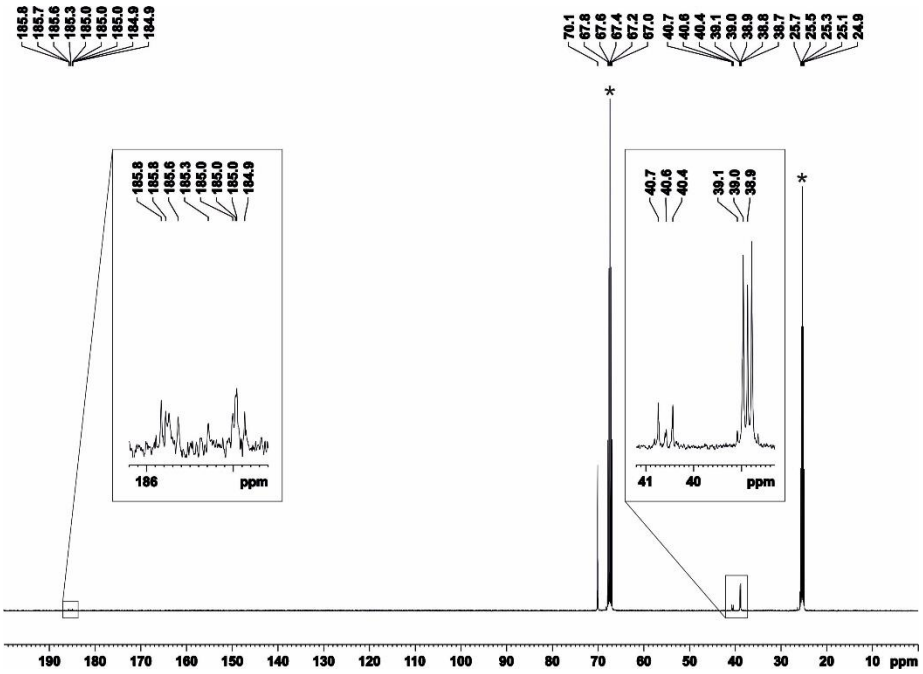


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, THF-d_8) of **1**. * = THF-d_8.

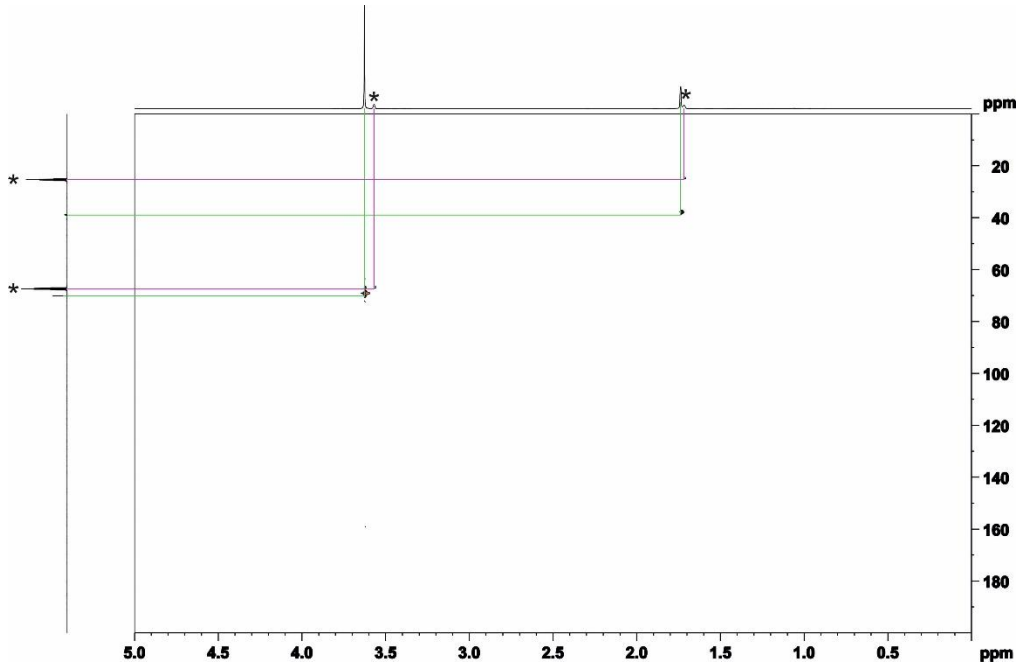


Figure S4. ^{1}H -^{13}C-HSQC NMR spectrum (100 MHz, 300 K, THF-d_8) of **1**, lines in green. * = THF-d_8, lines in purple.

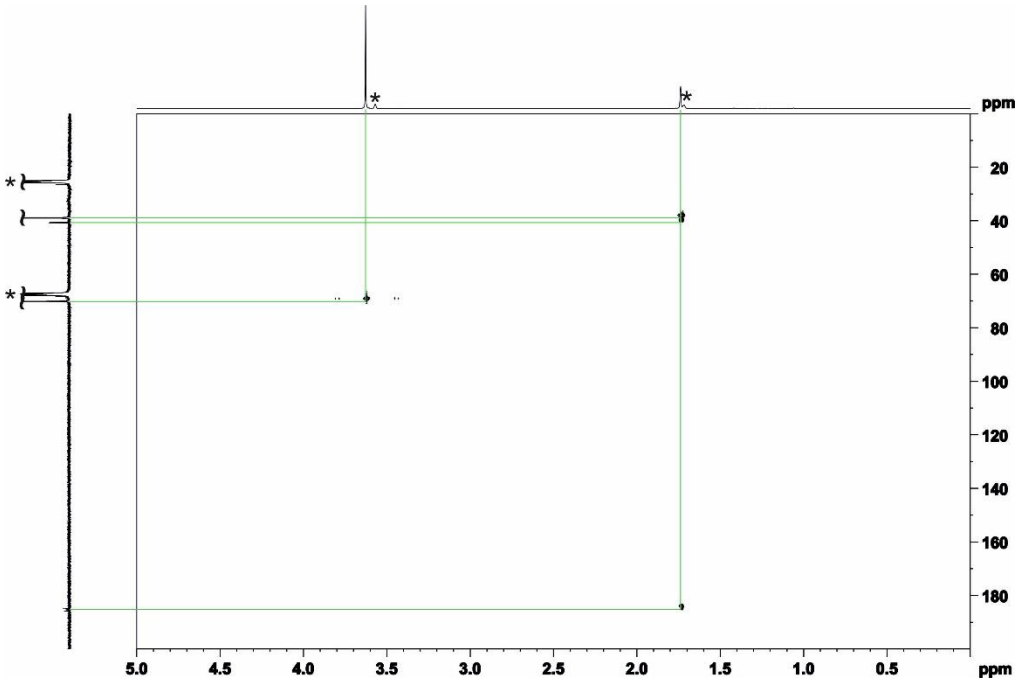


Figure S5. ^{1}H -^{13}C-HMBC NMR spectrum (100 MHz, 300 K, THF-d_8) of **1**, lines in green. * = THF-d_8.

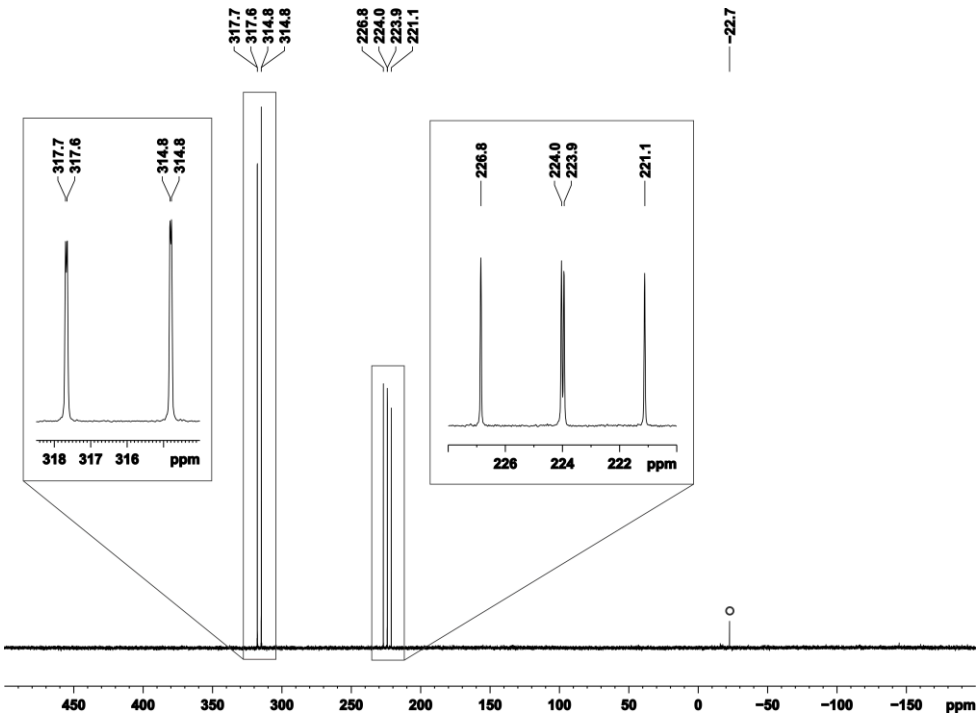


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, THF-d_8) of **1**. ○ = (tBuCP)$_4$.

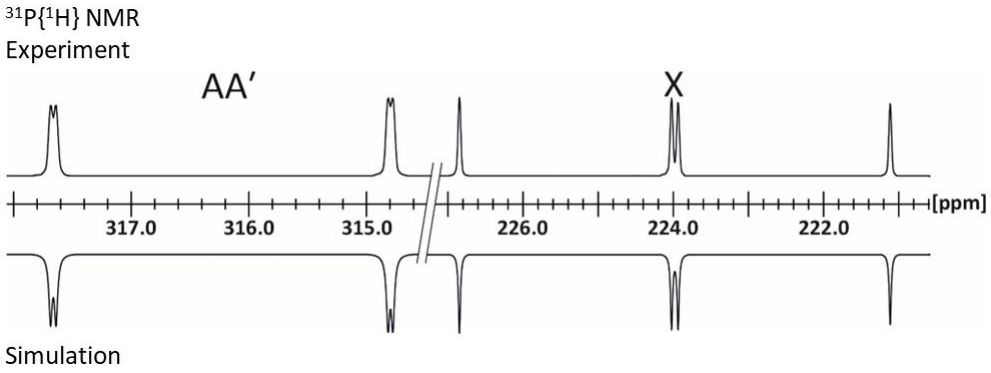
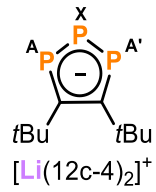


Figure S7. Section of the $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, THF-d_8) of **1**; experimental (upwards) and simulation (downwards).

Table S1. Coupling constants from the iterative fit of the AA′X spin system and representation of **1**.

	$\delta(P_{AA'}) = 316.2$ ppm $\delta(P_X) = 224.0$ ppm $^{1}J_{AX} = -463.8$ Hz $^{1}J_{A'X} = -465.5$ Hz $^{2}J_{AA'} = 4.3$ Hz

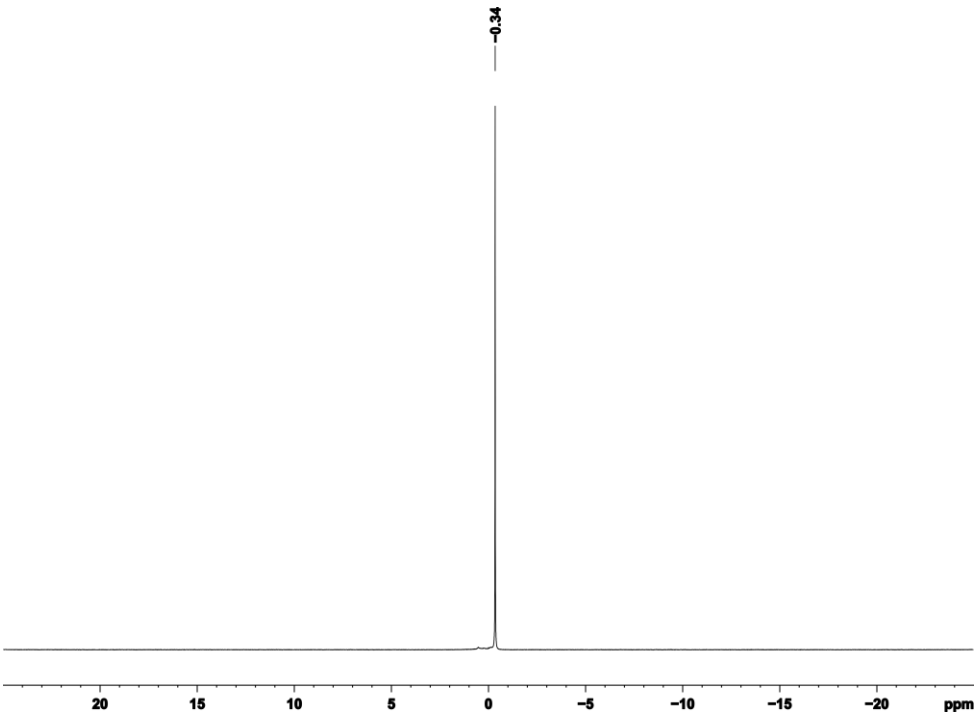


Figure S8. $^{7}Li\{^{1}H\}$ NMR spectrum (156 MHz, 300 K, THF-d_8) of **1**.

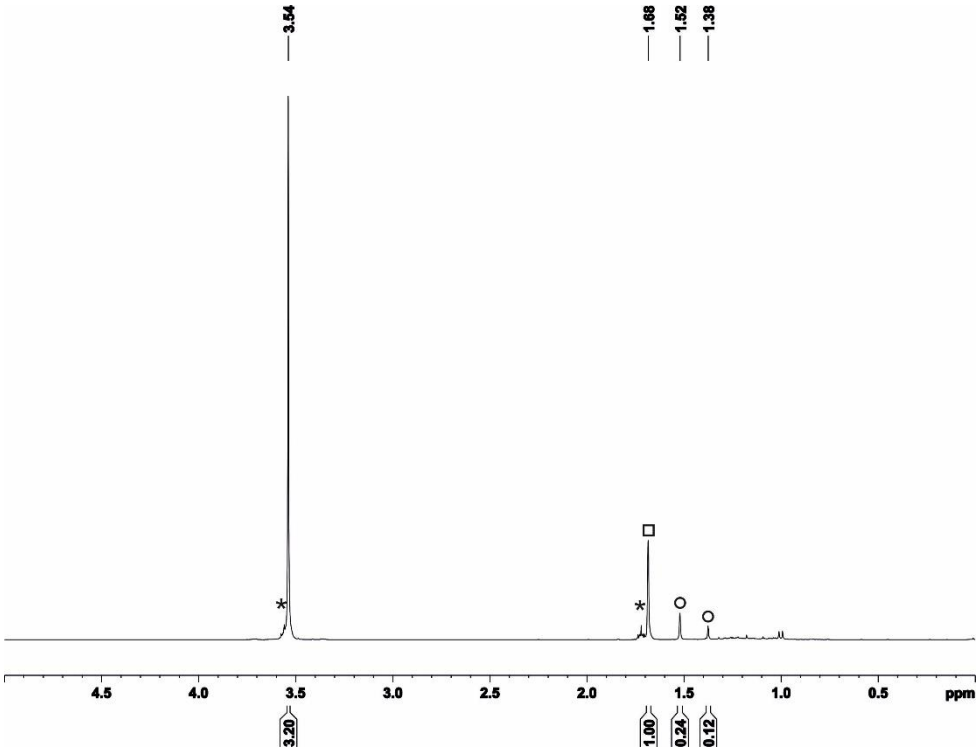


Figure S9. ^{1}H NMR spectrum (400 MHz, 300 K, THF-d_8) of the mixture of **2** (□) and **7** (○). * = Residual proton signals of THF-d_8.

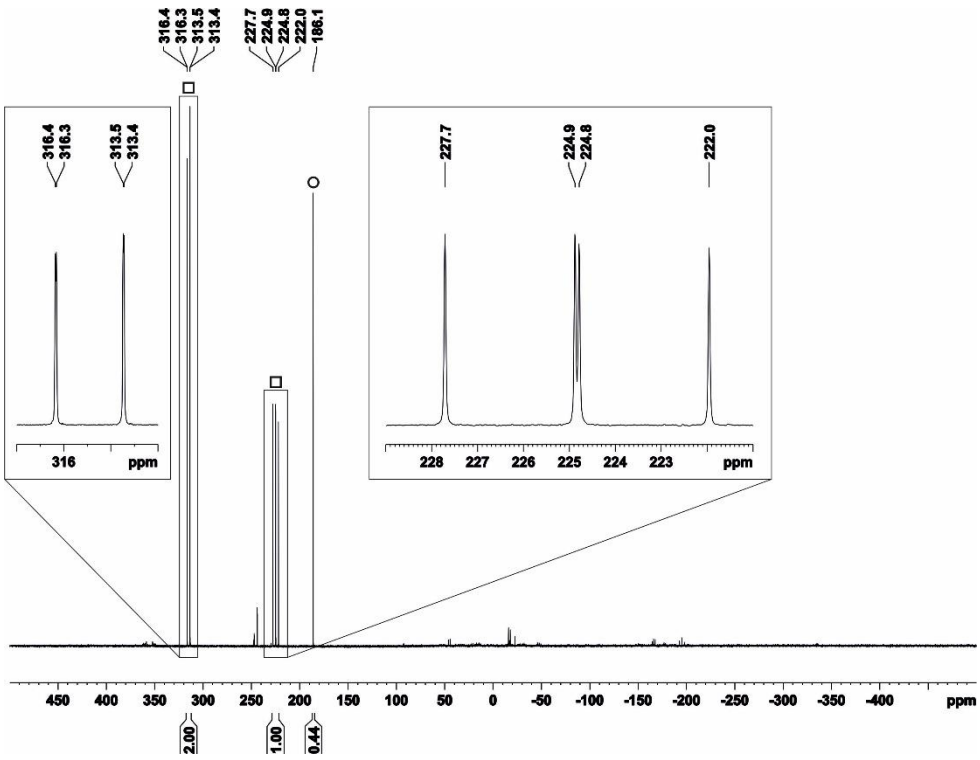


Figure S10. ^{31}P{^{1}H} NMR spectrum (162 MHz, 300 K, THF-d_8) of the mixture of **2** (□) and **7** (○).

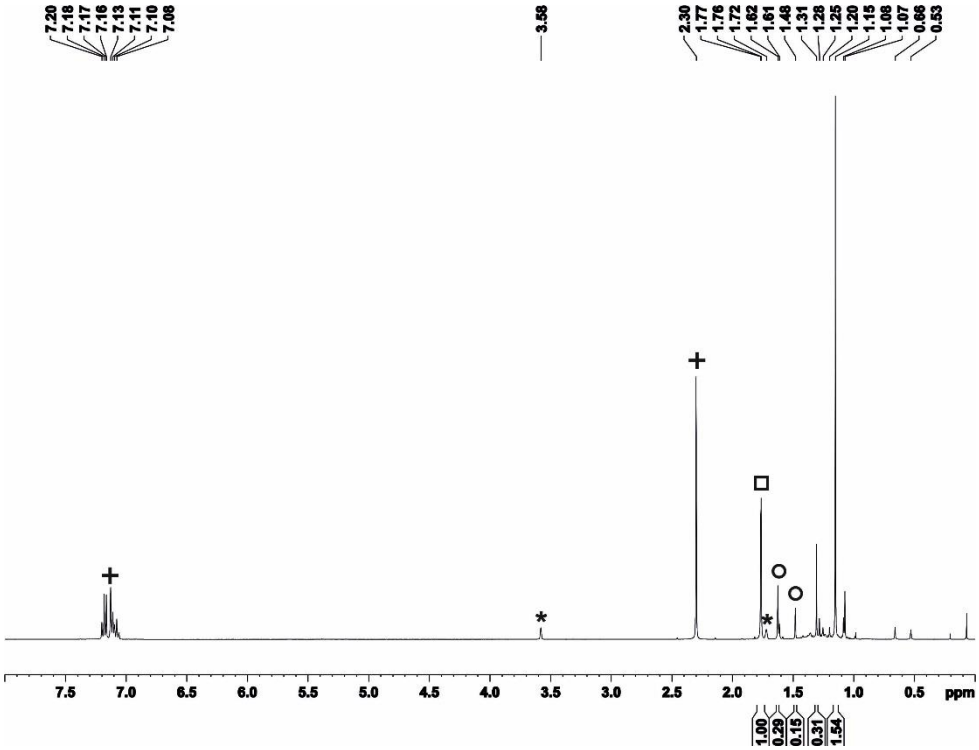


Figure S11. ^{1}H NMR spectrum (400 MHz, 300 K, THF-d_8) of the crude reaction mixture of 1.5 eq. of **A** and 1 eq. of K in THF-d_8. **3** (□) and **8** (○). * = Residual proton signals of THF-d_8. + = toluene in which **A** is dissolved.

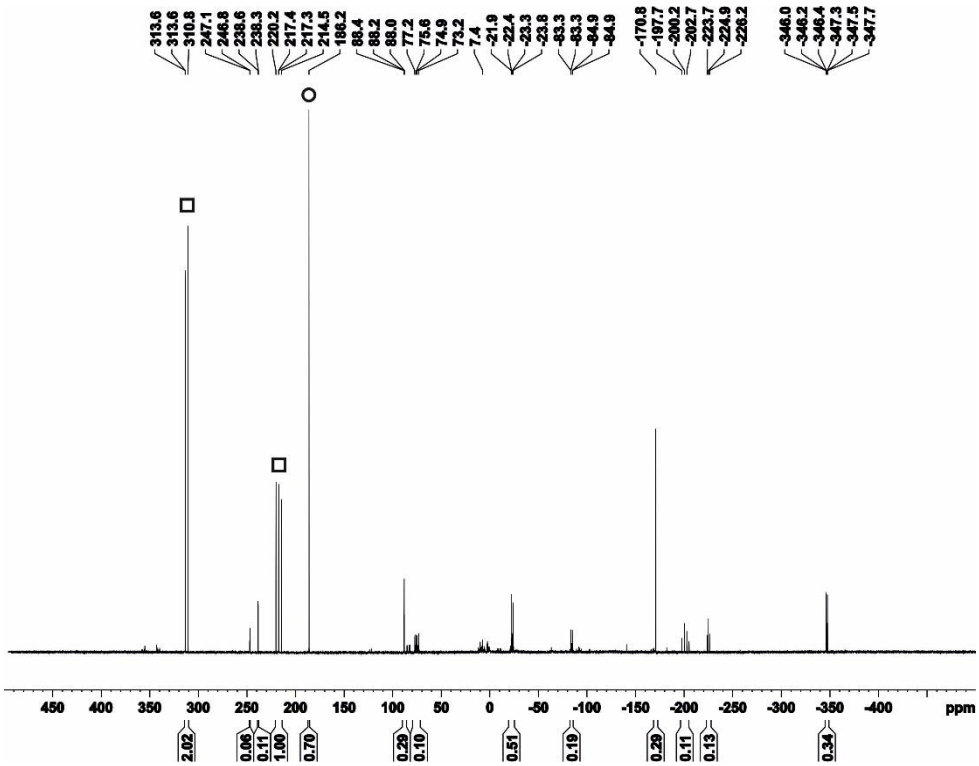


Figure S12. ^{31}P{^{1}H} NMR spectrum (162 MHz, 300 K, THF-d_8) of the crude reaction mixture of 1.5 eq. of **A** and 1 eq. of K in THF-d_8. **3** (□) and **8** (○).

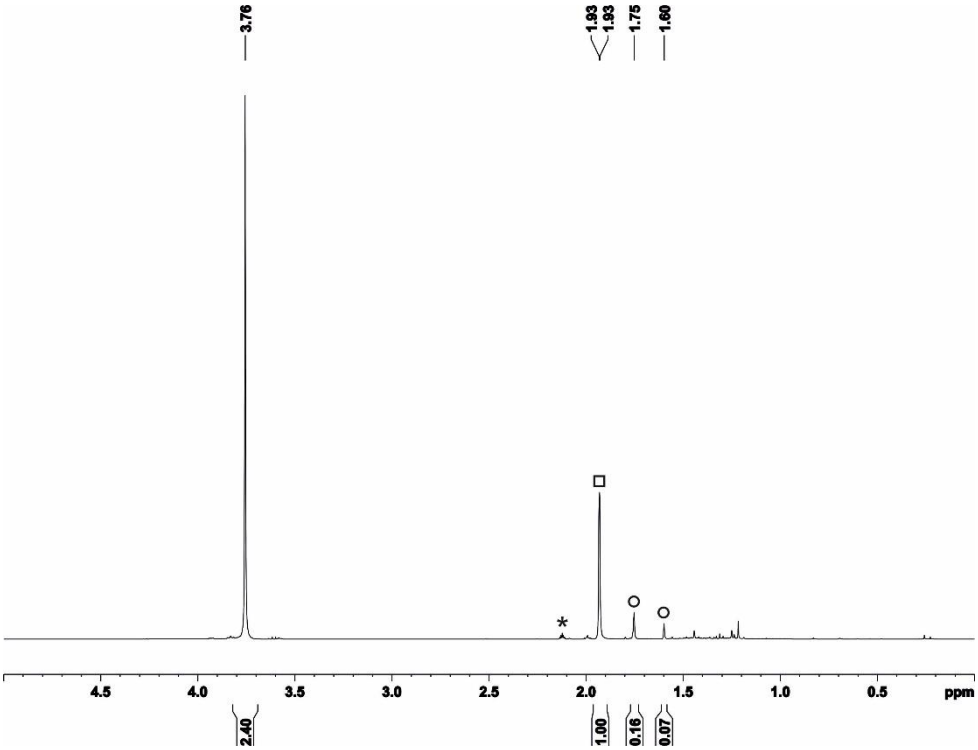


Figure S13. ^{1}H NMR spectrum (400 MHz, 300 K, CD_3CN) of the mixture of **3** (□) and **8** (○). * = Residual proton signals of CD_3CN.

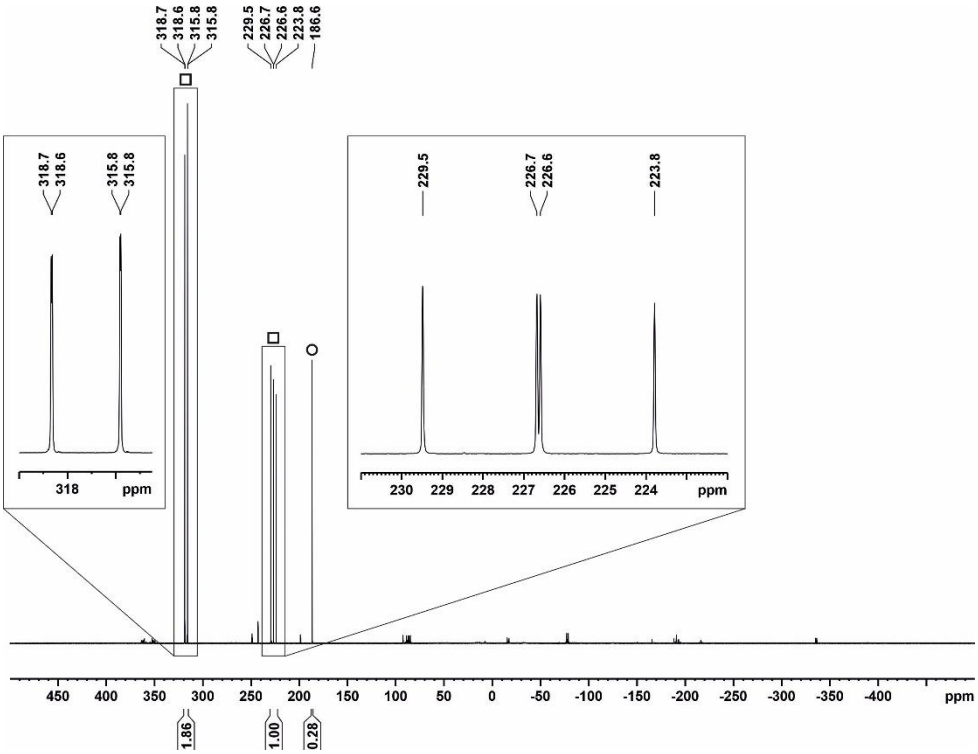


Figure S14. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, CD_3CN) of the mixture of **3** (□) and **8** (○).

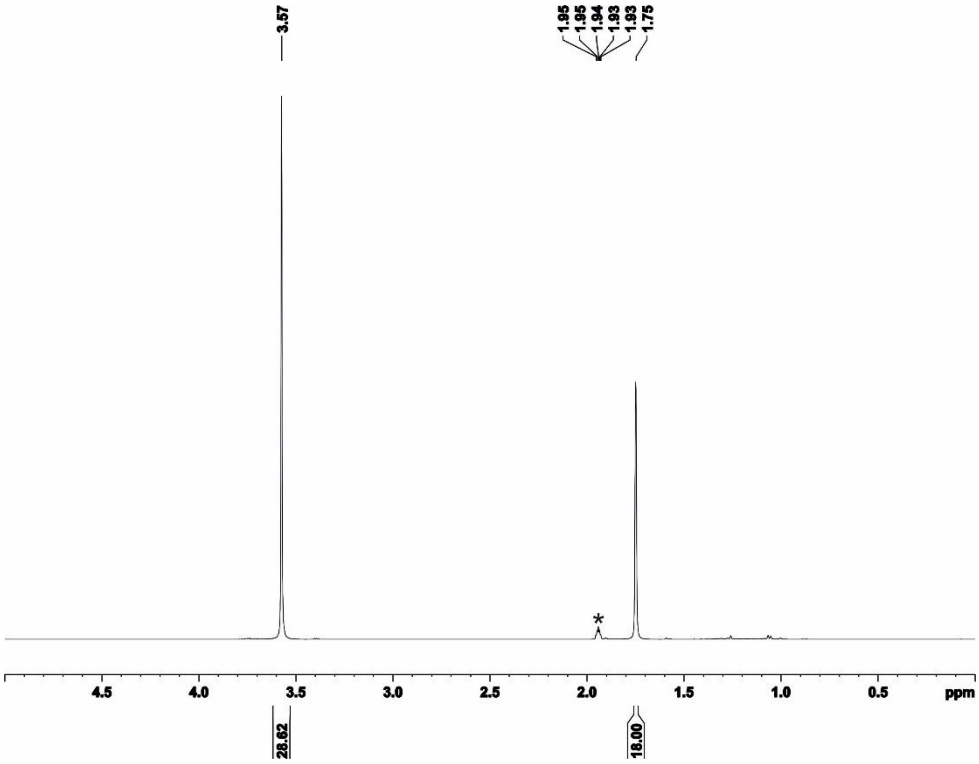


Figure S15. ^{1}H NMR spectrum (400 MHz, 300 K, CD_3CN) of **3**. * = Residual proton signals of CD_3CN.

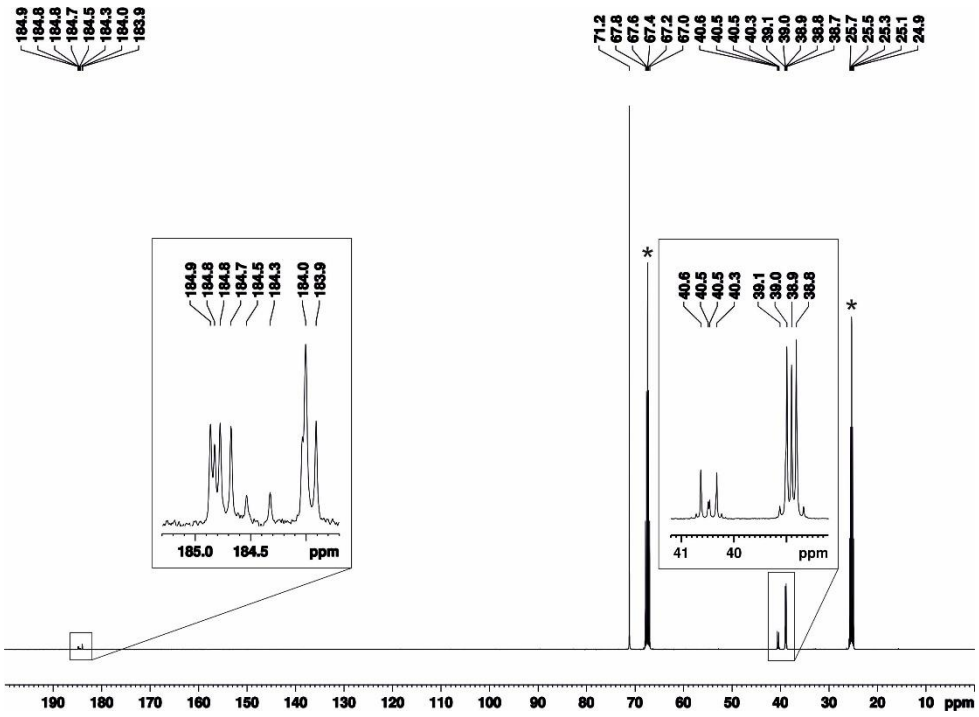


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, THF-d_8) of **3**. * = THF-d_8.

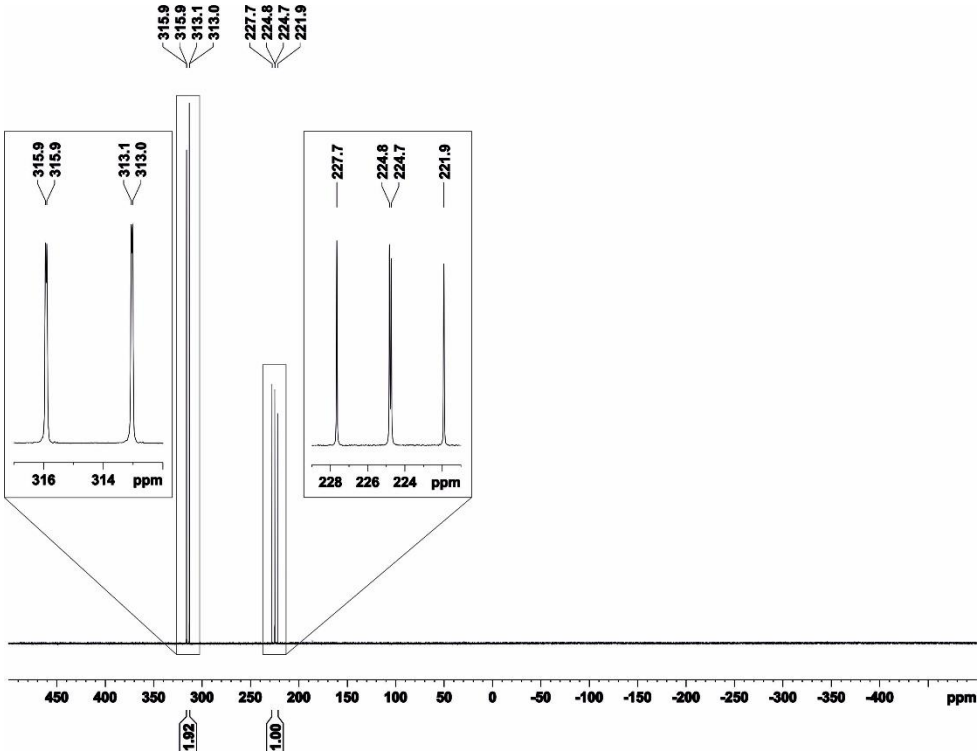


Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, THF-d_8) of **3**.

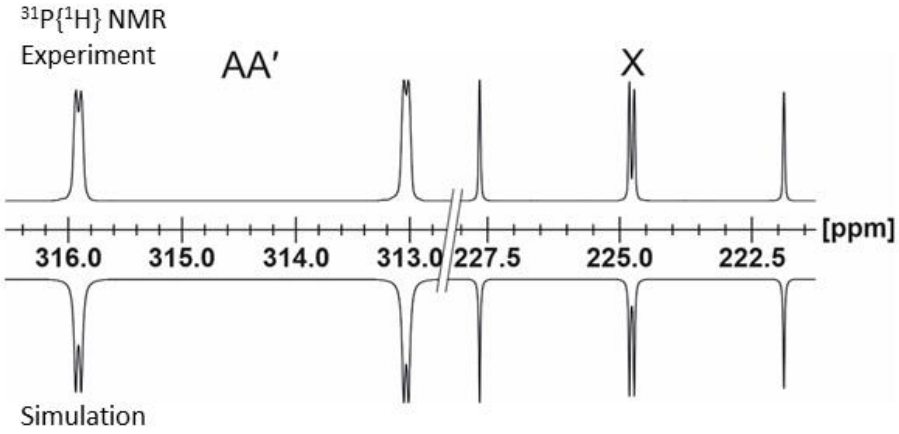
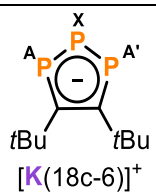


Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, THF-d_8) and simulation of **3**.

Table S2. Coupling constants from the iterative fit of the AA′X spin system and representation of **3**.

	$\delta(P_{AA'})$ = 314.4 ppm
	$\delta(P_X)$ = 224.8 ppm
	$^{1}J_{AX}$ = −465.6 Hz
	$^{1}J_{A'X}$ = −467.5 Hz
	$^{2}J_{AA'}$ = 4.3 Hz

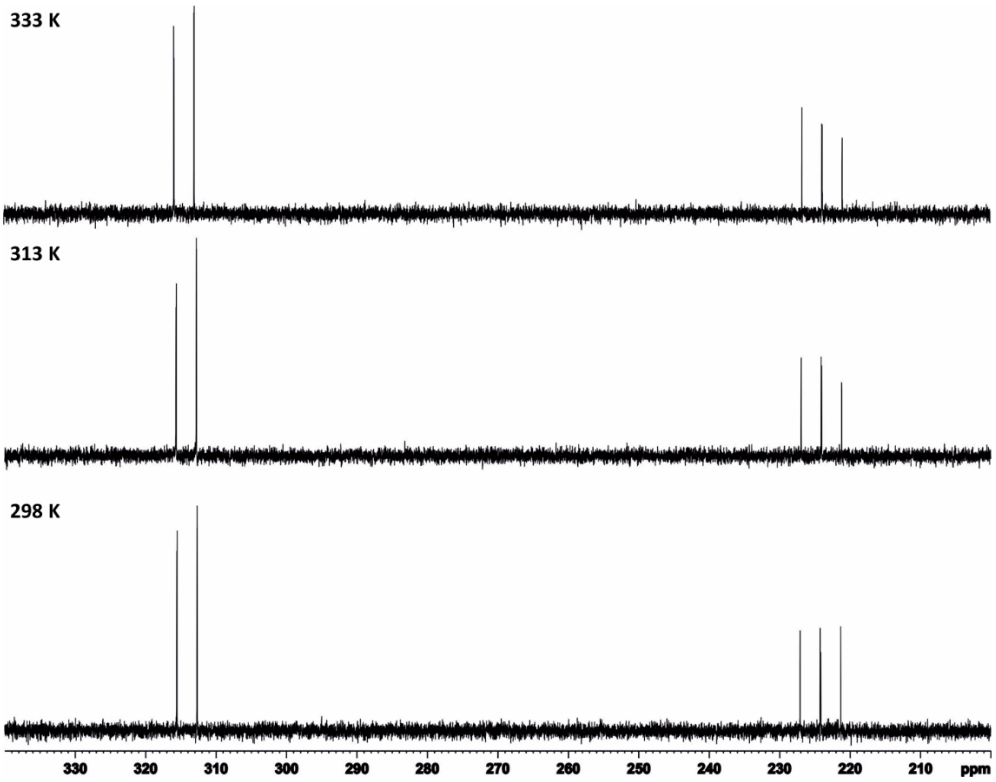


Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, THF-d_8) of **3** at different temperatures depicted from 200 to 340 ppm.

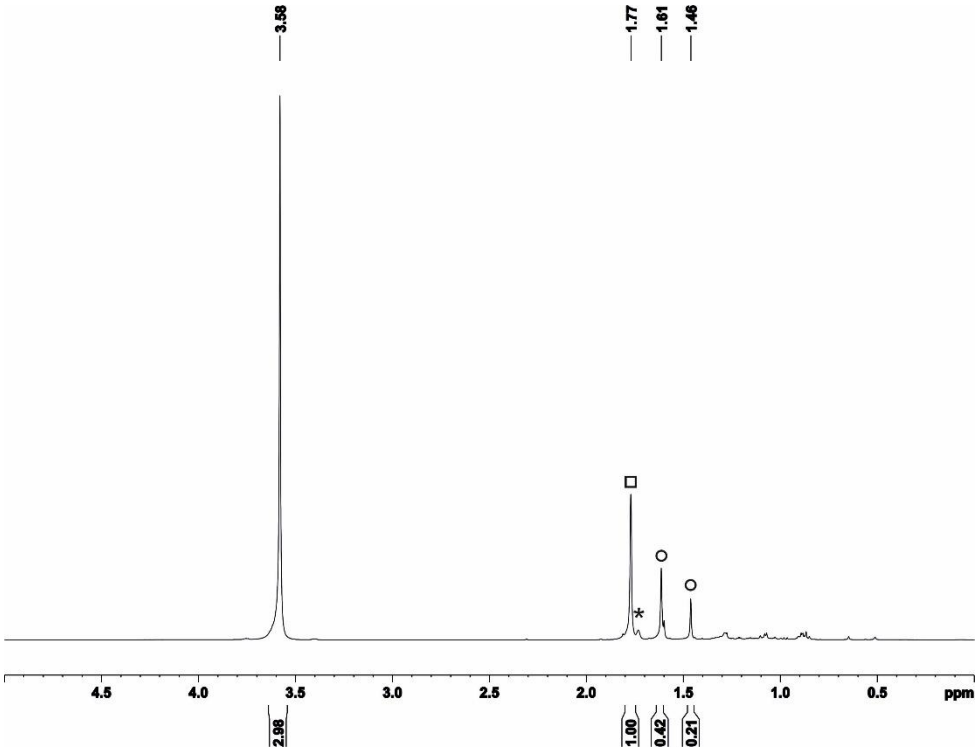


Figure S20. ^{1}H NMR spectrum (400 MHz, 300 K, CD_3CN) of the mixture of **4** (□) and **9** (○). * = Residual proton signal of THF-d_8, the other overlaps with the product signal at 3.58 ppm.

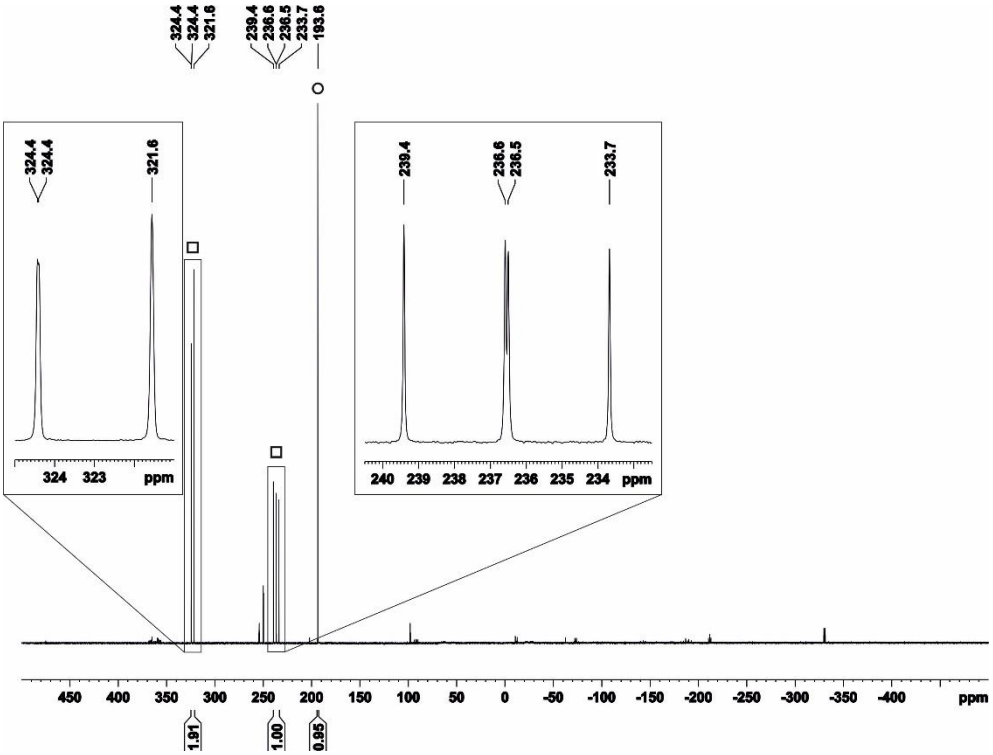


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, THF-d_8) of the mixture of **4** (□) and **9** (○).

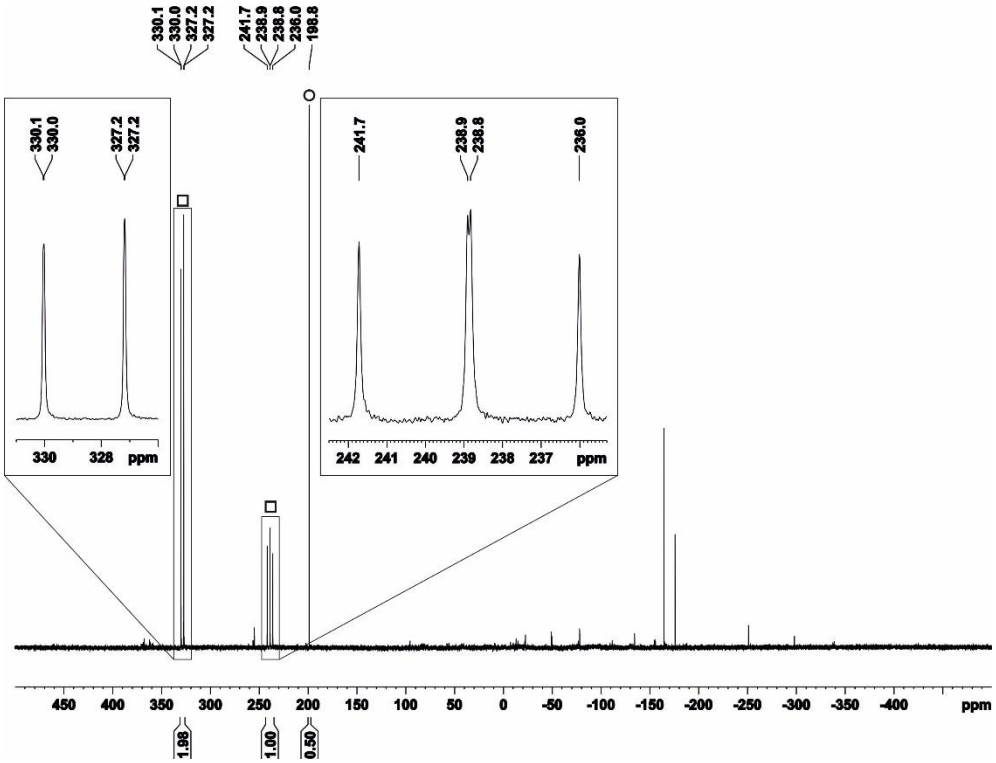


Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, THF with C_6D_6 capillary) of the reaction of **A** with Cs yielding **5** (□) and **10** (○).

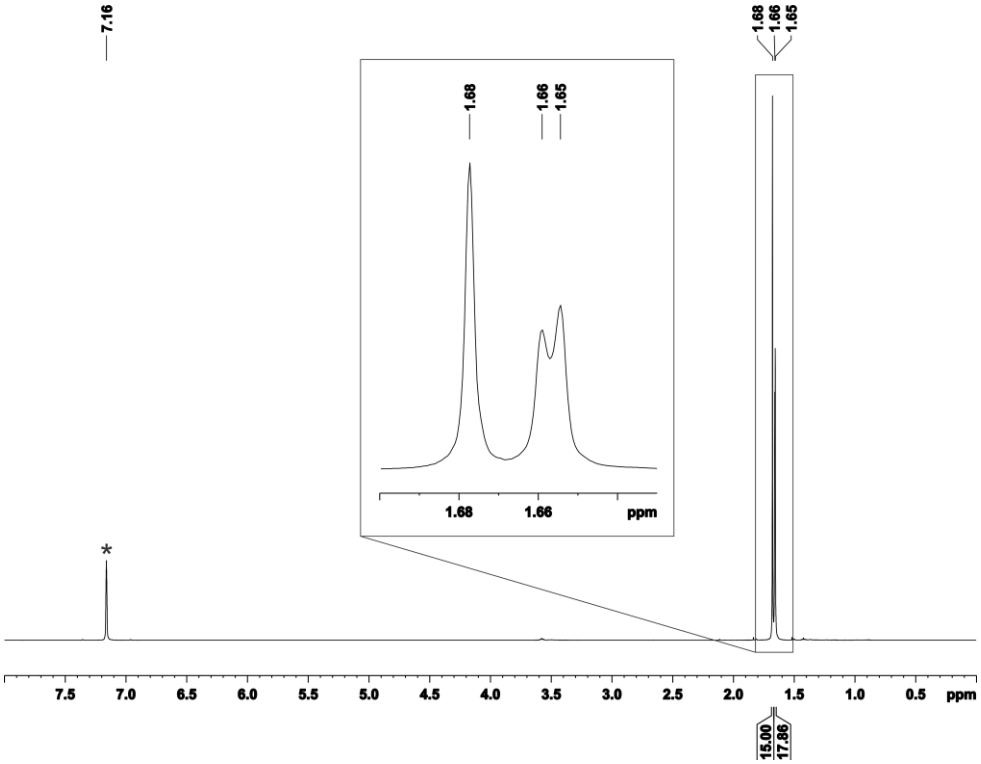


Figure S23. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **11**. * = Residual proton signals of C_6D_6.

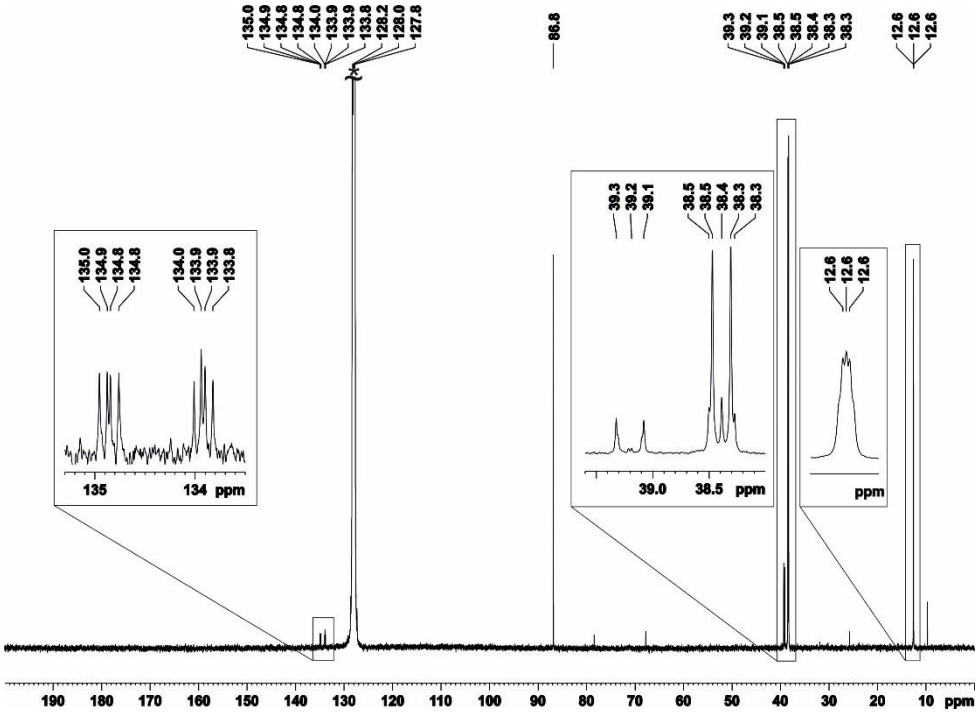


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **11**. * = C_6D_6.

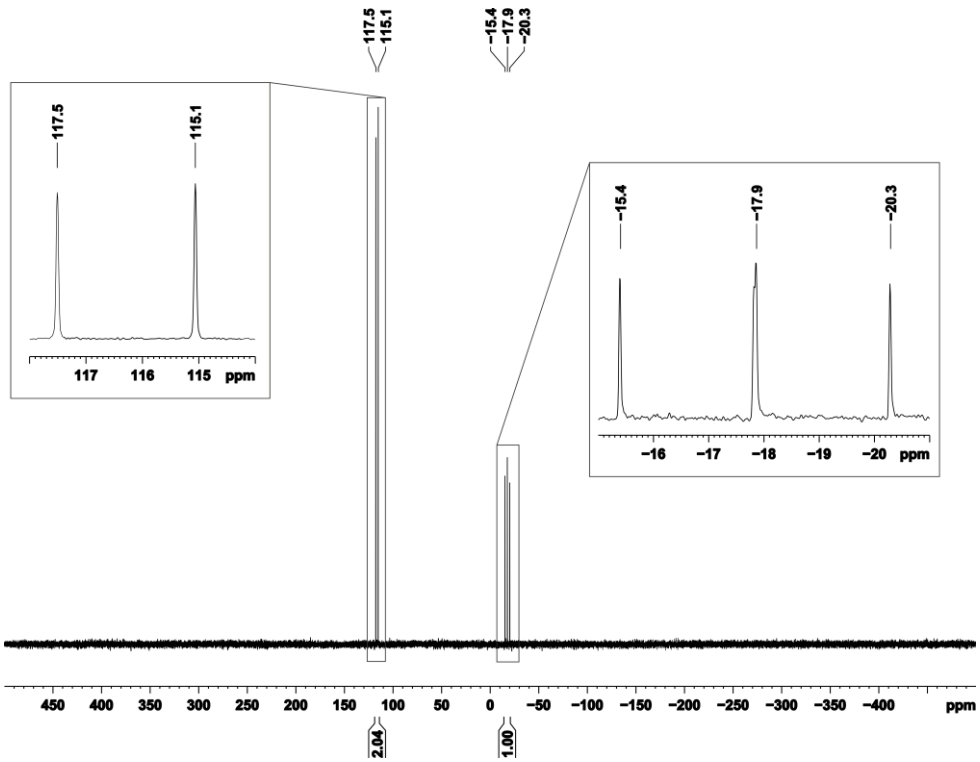


Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **11**.

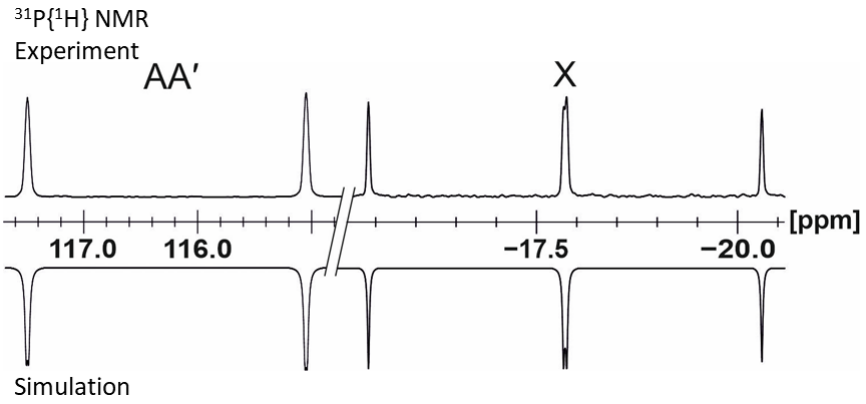
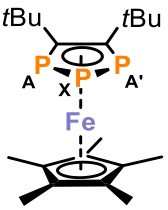


Figure S26. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) and simulation of **11**.

Table S3. Coupling constants from the iterative fit of the AA′X spin system and representation of **11**.

	$\delta(P_{AA'})$ = 116.3 ppm $\delta(P_X)$ = −17.8 ppm $^{1}J_{AX}$ = −397.1 Hz $^{1}J_{A'X}$ = −396.2 Hz $^{2}J_{AA'}$ = 3.4 Hz

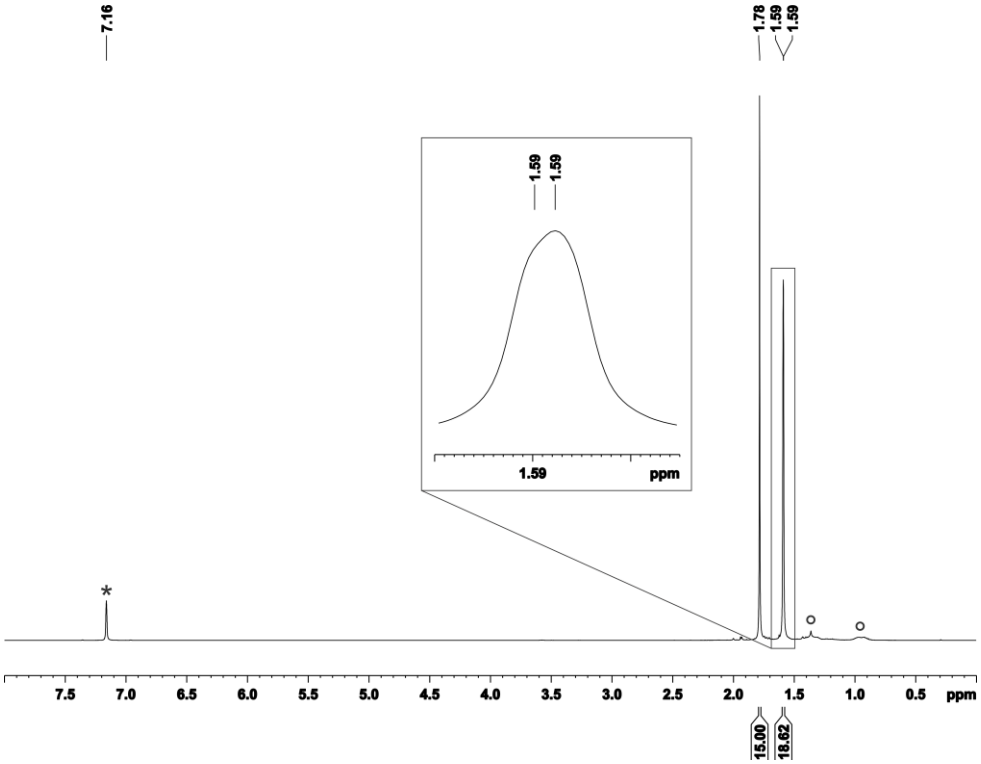


Figure S27. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **12**. * = Residual proton signals of C_6D_6 and ○ = *n*-hexane.

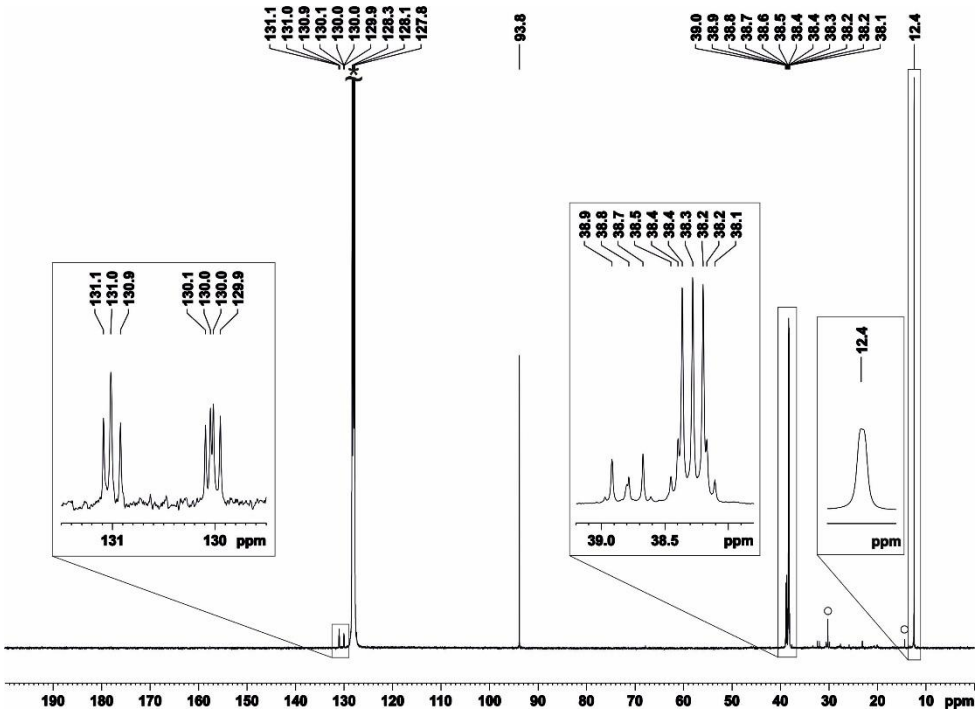


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **12**. * = C_6D_6 and ○ = *n*-hexane.

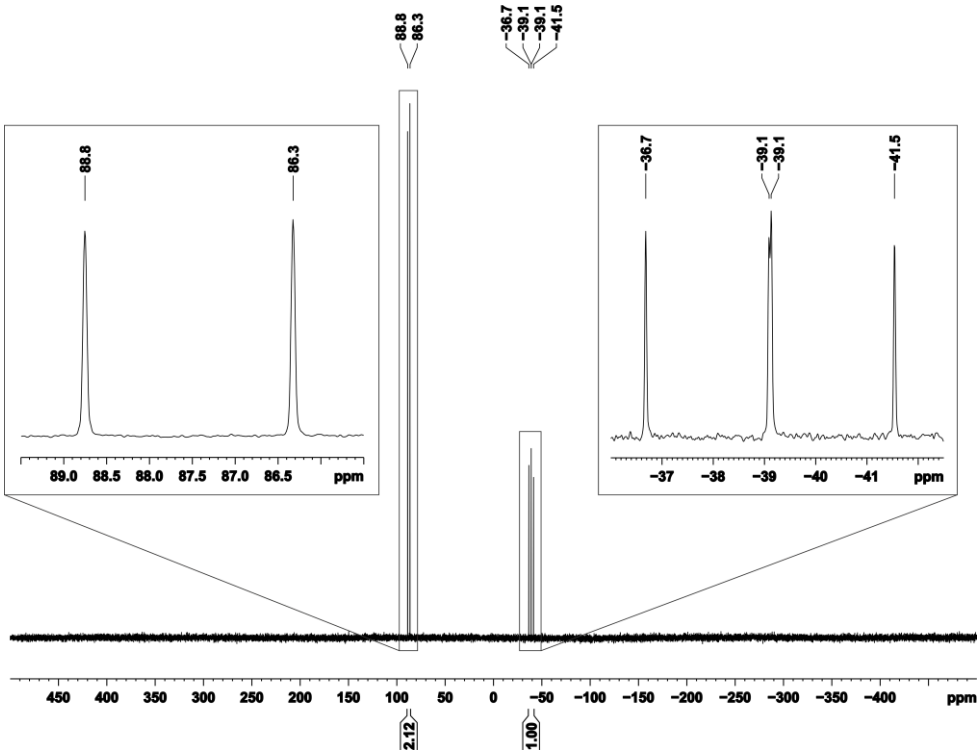


Figure S29. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **12**.

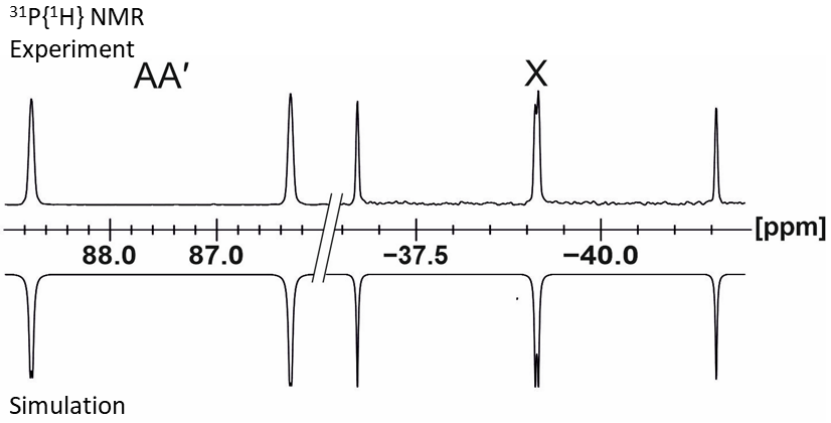
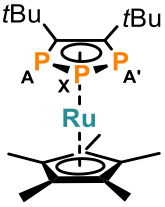


Figure S30. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) and simulation of **12**.

Table S4. Coupling constants from the iterative fit of the AA′X spin system and representation of **12**.

	$\delta(P_{AA'})$ = 87.5 ppm $\delta(P_X)$ = −39.1 ppm $^{1}J_{AX}$ = −393.4 Hz $^{1}J_{A'X}$ = −393.9 Hz $^{2}J_{AA'}$ = 0.6 Hz

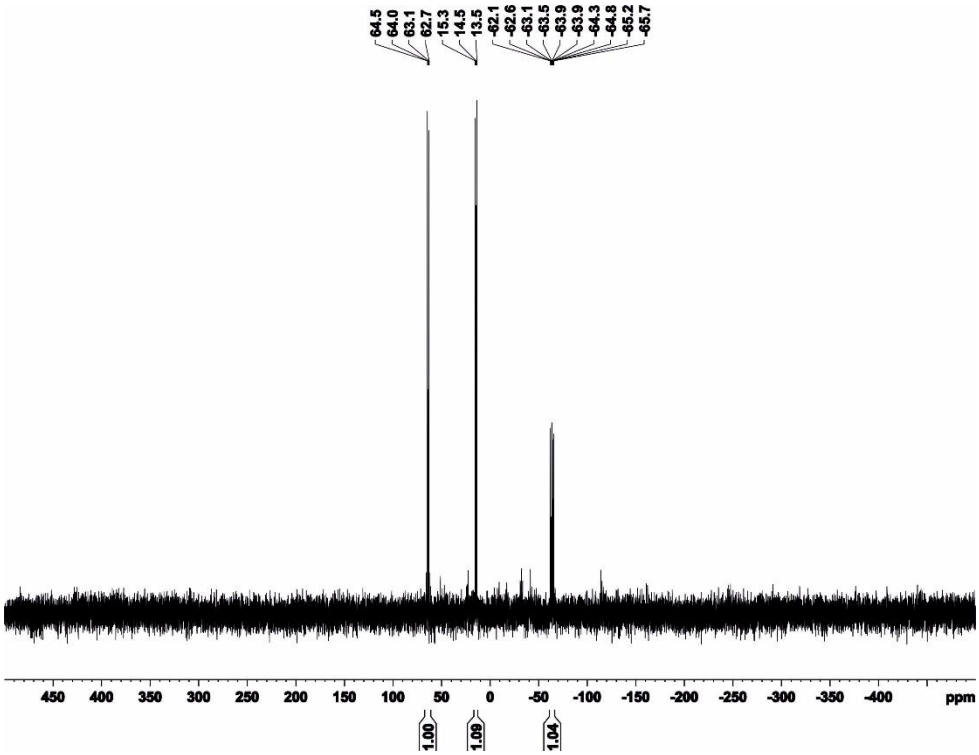


Figure S31. ^{31}P NMR spectrum (162 MHz, 300 K, THF with C_6D_6 capillary) of the crude reaction mixture of **3** and $[H(Et_2O)_2BAr^F{}_4]$.

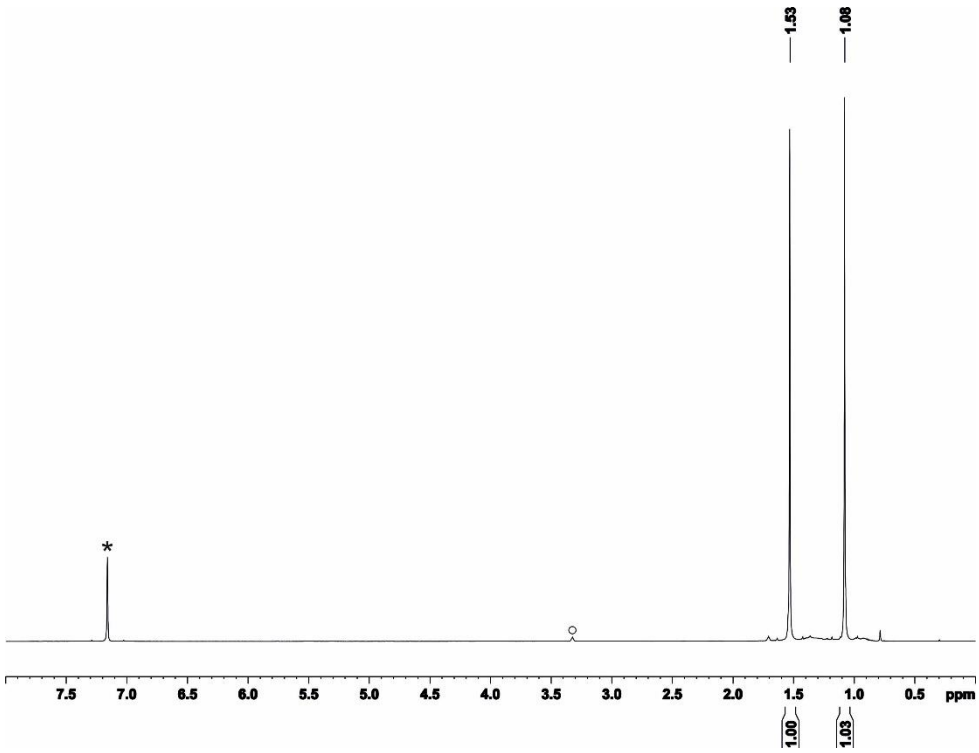


Figure S32. ^1H NMR spectrum (600 MHz, 300 K, C_6D_6) of **13**. * = Residual proton signals of C_6D_6 and O = [18]crown-6.

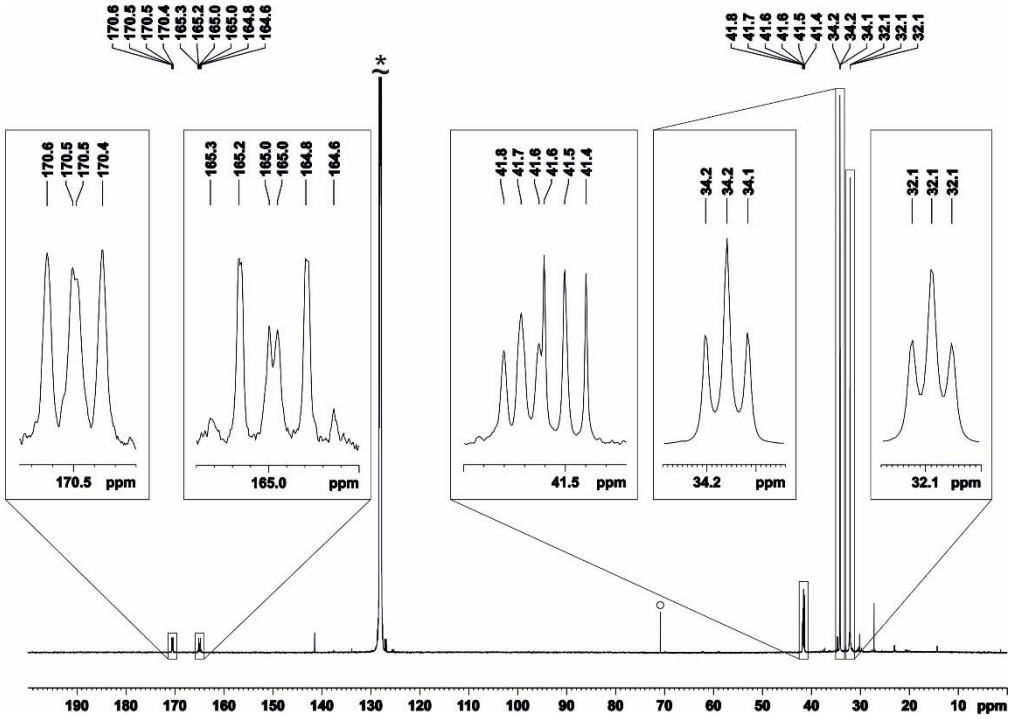


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, 300 K, C_6D_6) of **13**. * = C_6D_6 and O = [18]crown-6.

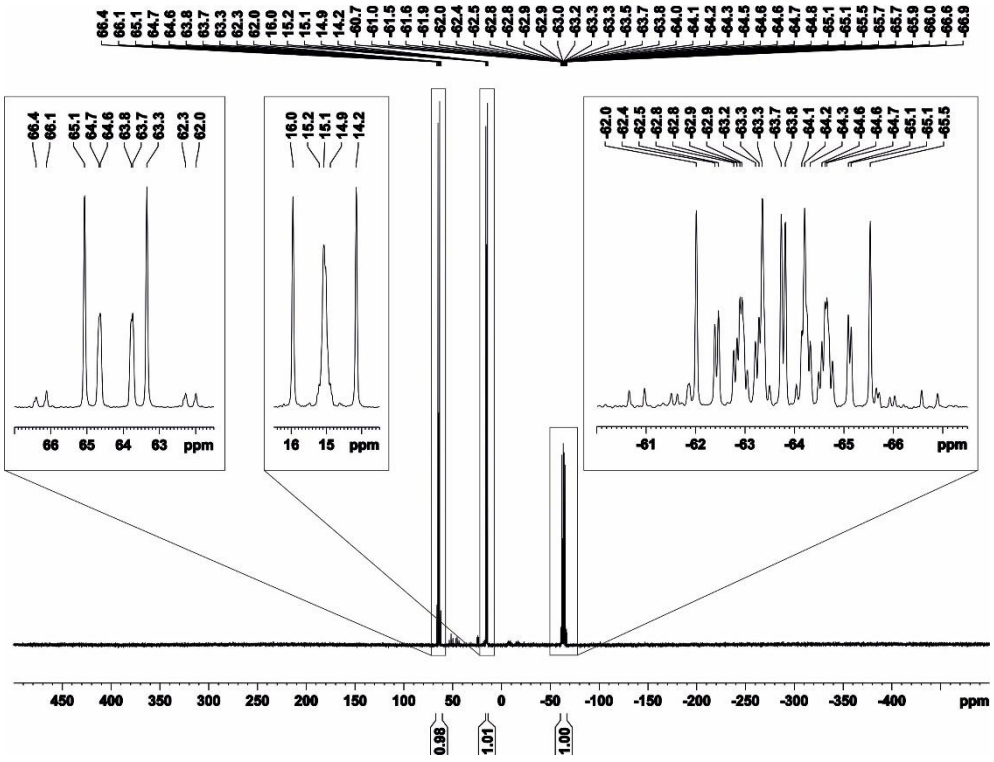


Figure S34. ^{31}P NMR spectrum (162 MHz, 300 K, C_6D_6) of **13**.

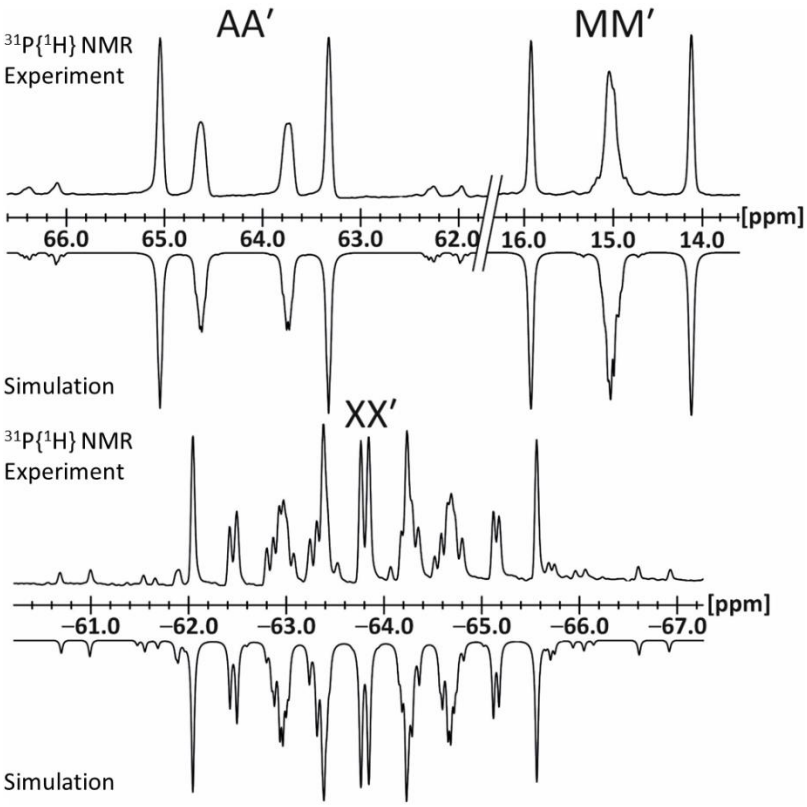
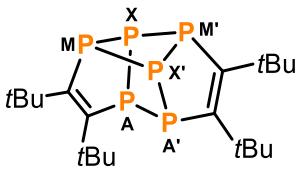


Figure S35. ^{31}P{^{1}H} NMR spectrum (162 MHz, 300 K, C_6D_6) and simulation of **13**.

Table S5. Coupling constants from the iterative fit of the AA′MM′XX′ spin system and representation of **13**.



$\delta(P_{AA'}) = 64.2$ ppm
$\delta(P_{MM'}) = 15.0$ ppm
$\delta(P_{XX'}) = -63.8$ ppm
$^{1}J_{AA'} = -261.9$ Hz
$^{2}J_{AM} = {}^{2}J_{A'M'} = -3.2$ Hz
$^{2}J_{A'M} = {}^{2}J_{AM'} = 9.9$ Hz
$^{2}J_{MM'} = 24.9$ Hz
$^{1}J_{AX} = {}^{1}J_{A'X'} = -293.9$ Hz
$^{2}J_{A'X} = {}^{2}J_{AX'} = 15.3$ Hz
$^{1}J_{MX} = {}^{1}J_{M'X'} = -157.7$ Hz
$^{1}J_{M'X} = {}^{1}J_{MX'} = -134.2$ Hz
$^{2}J_{XX'} = 29.5$ Hz

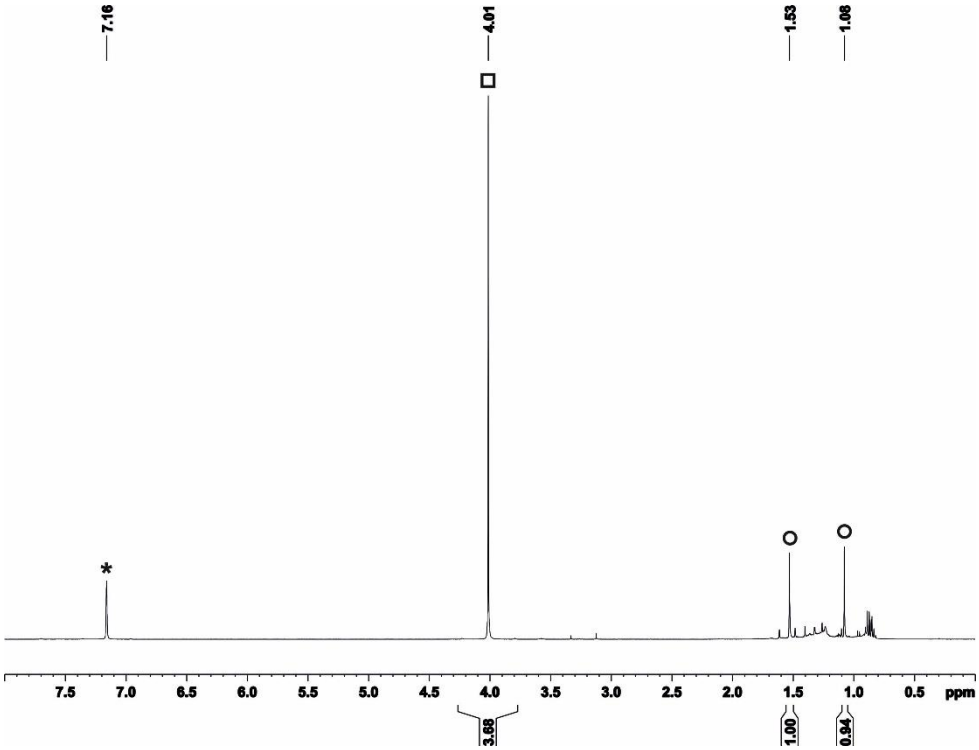


Figure S36. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of the reaction mixture of a mixture of **3** and **8** with $[Cp_2Fe]BAr^{F}_4$ after extraction. **13** (○) and Cp_2Fe (□). * = Residual proton signals of C_6D_6.

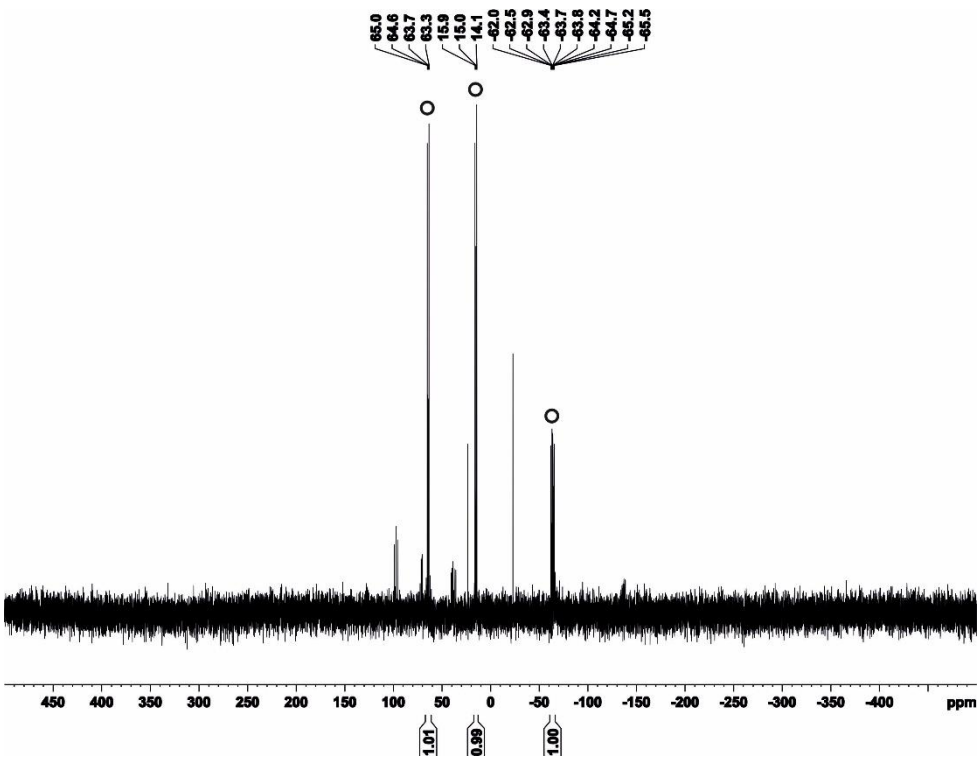


Figure S37. ^{31}P{^{1}H} NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction mixture of a mixture of **3** and **8** with $[Cp_2Fe]BAr^{F}_4$ after extraction. **13** (○).

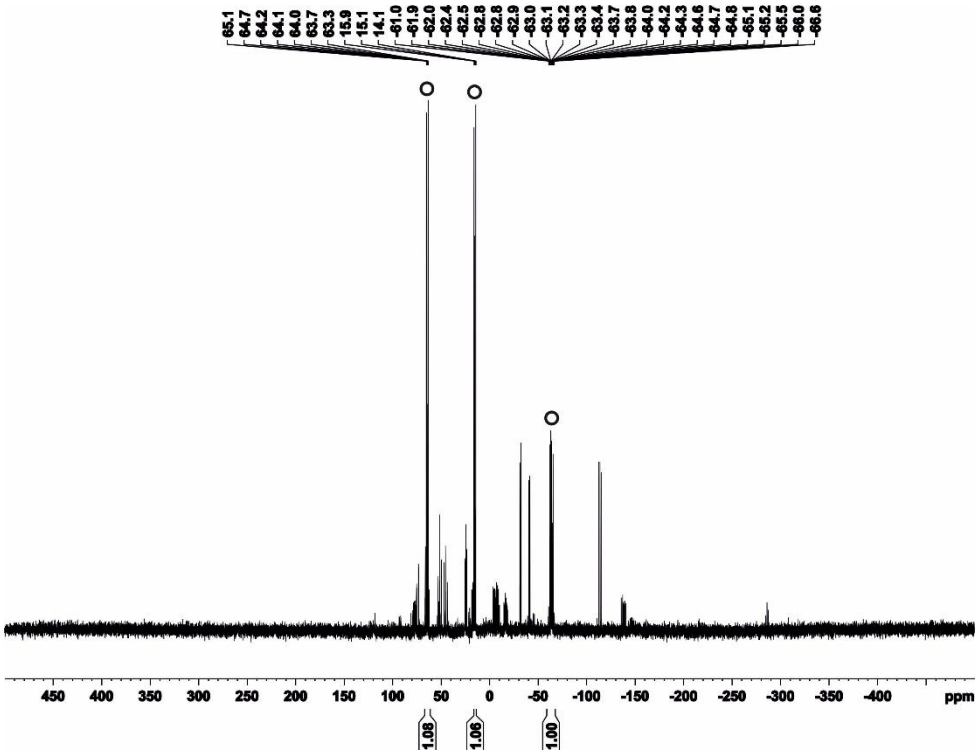


Figure S38. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction mixture of a mixture of **3** and **8** with $[H(Et_2O)_2BAr^F{}_4]$ after extraction with *n*-hexane. **13** (O).

3.4.4 UV-Vis Spectra

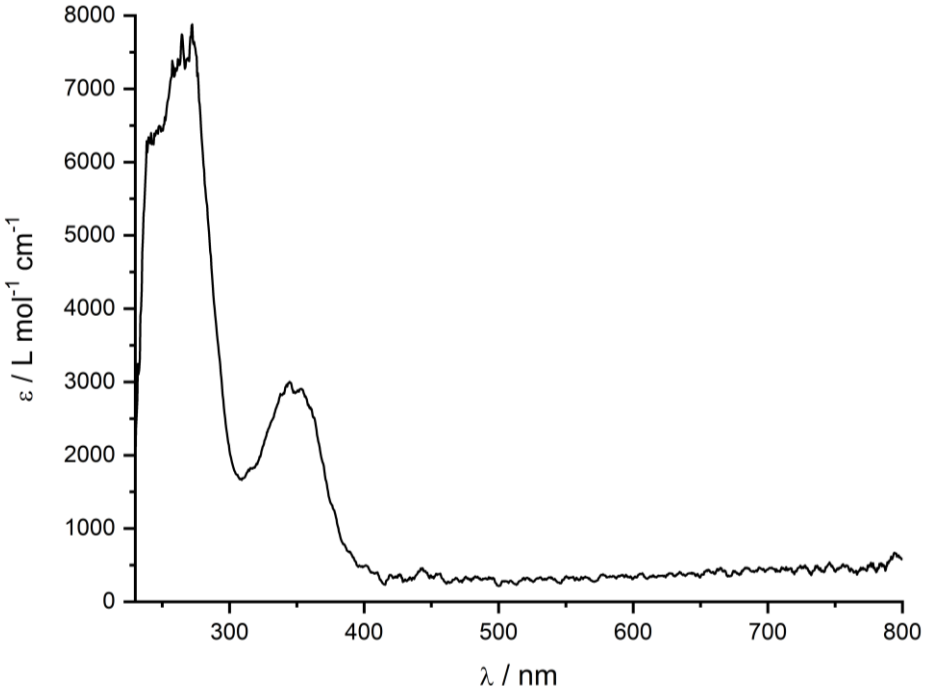


Figure S39. UV-Vis spectrum of **1** in THF.

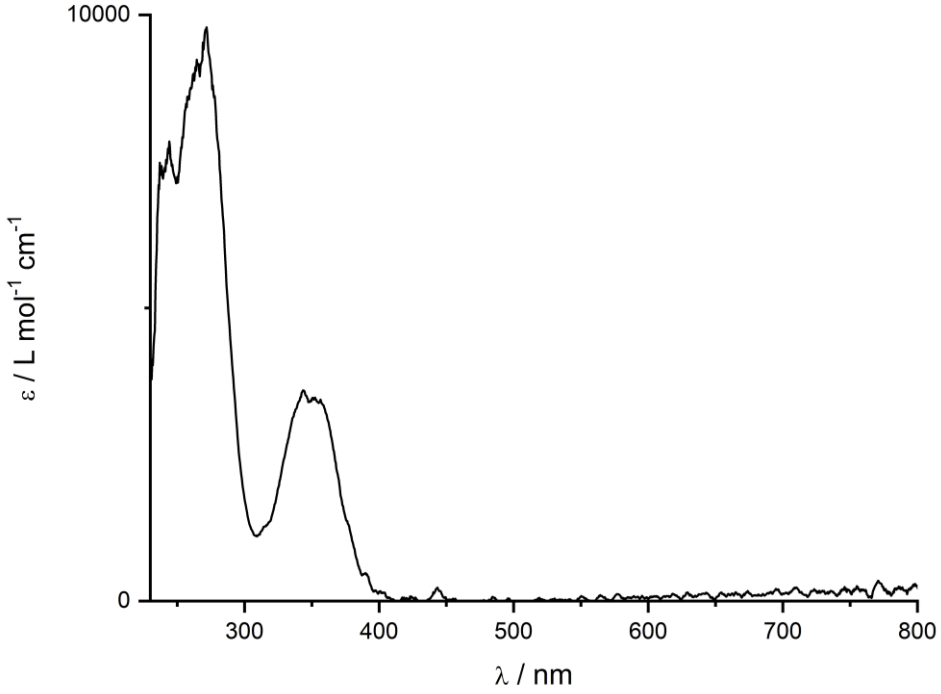


Figure S40. UV-Vis spectrum of **3** in THF.

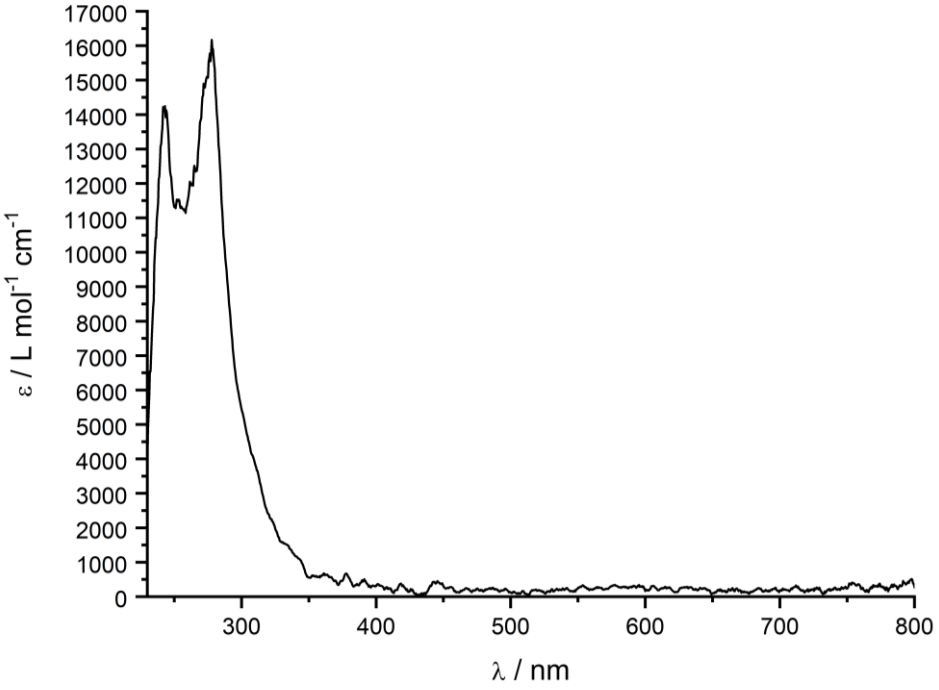


Figure S41. UV-Vis spectrum of **11** in *n*-hexane.

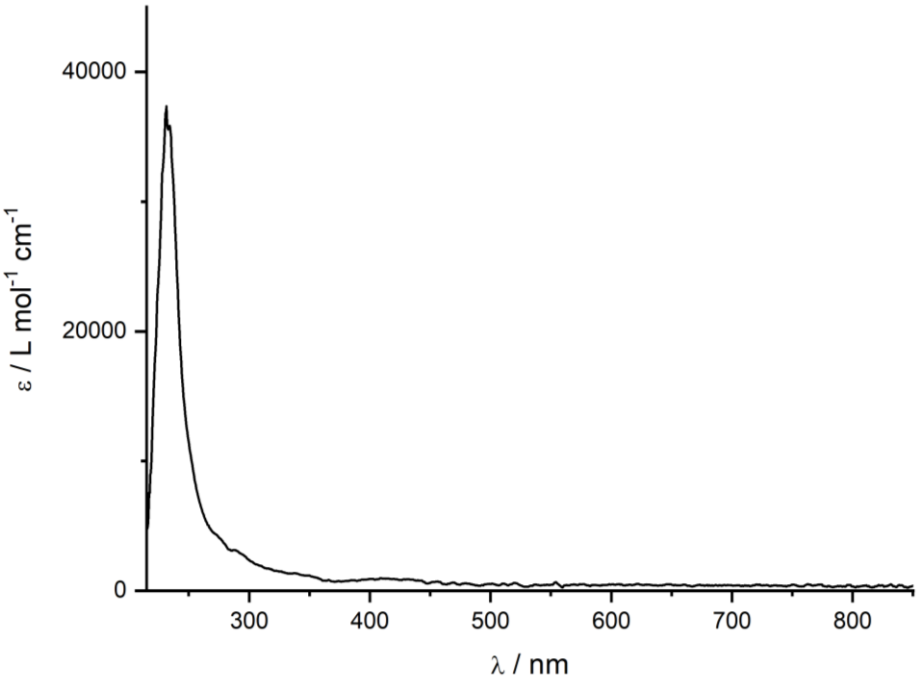


Figure S42. UV-Vis spectrum of **12** in *n*-hexane.

3.4.5 Single-Crystal X-ray Diffraction Data

The single-crystal X-ray diffraction data were recorded on Rigaku XtaLAB Synergy DW R (DW system, HyPix-Arc 150) or GV1000 Titan diffractometers with microfocus Cu-Kα radiation (λ = 1.54184 Å). Crystals were selected under mineral oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device. Either semi-empirical multi-scan absorption corrections[41] or analytical ones[42] were applied to the data. Using Olex2,[43] the structure was solved with the SHELXT[44] structure solution programme using Intrinsic Phasing and refined with the SHELXL[45] refinement package using Least Squares refinements on F^2. The hydrogen atoms were located in idealised positions and refined isotropically with a riding model.

1 crystallises in the orthorhomic space group *Pbca* with two formula units and two THF molecules in the asymmetric unit. One of these could be modelled, the other one, which is disordered over a symmetry element, was accounted for with the help of a solvent mask. The disorder of one crown ether in the crystal structure of **1** was refined with restraints (DFIX and SIMU).

CCDC 2346026 to 2346032 contain the supplementary crystallographic data for this publication. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html.

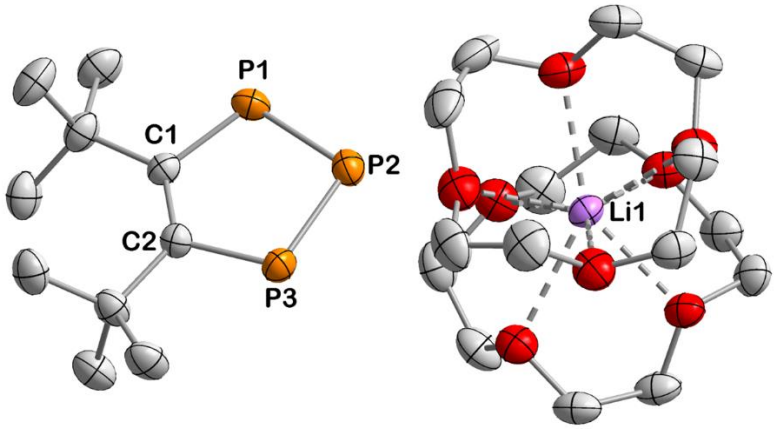


Figure S43. Solid-state molecular structure of **1**. Displacement ellipsoids are drawn at the 50% probability level; H atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–P2 2.0748(6), P2–P3 2.0763(6), P1–C1 1.7807(14), P3–C2 1.7819(14), C1–C2 1.418(2), P1–P2–P3 97.29(2), C1–P1–P2 102.96(5), C2–P3–P2 102.79(5), C2–C1–P1 118.32(10), C1–C2–P3 118.54(10).

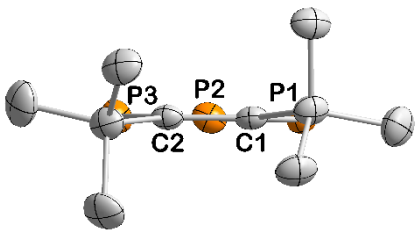


Figure S44. Solid-state molecular structure of **3**. Displacement ellipsoids are drawn at the 50% probability level; H atoms and cation have been omitted for clarity. View from the C1–C2 bond.

4 crystallises in the monoclinic space group $P2_1/n$ with one formula unit in the asymmetric unit.

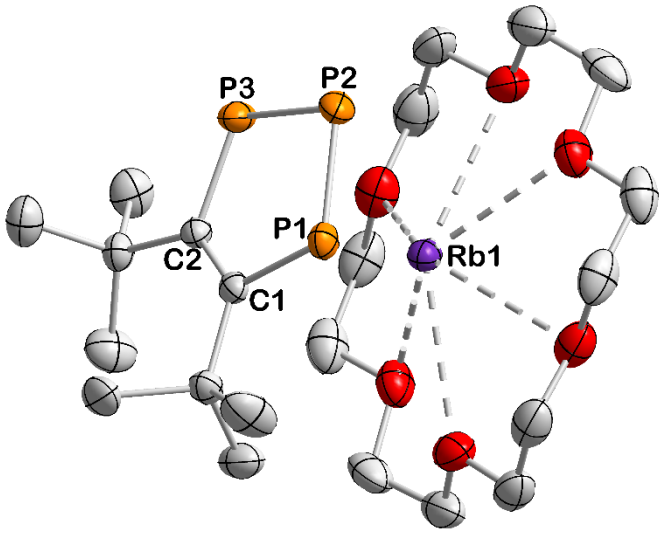


Figure S45. Solid-state molecular structure of **4**. Displacement ellipsoids are drawn at the 50% probability level; H atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–P2 2.0789(12), P2–P3 2.0779(12), P1–C1 1.783(3), P3–C2 1.787(3), C1–C2 1.414(4), P1–P2–P3 97.06(5), C1–P1–P2 102.90(11), C2–P3–P2 103.11(11), C2–C1–P1 118.8(2), C1–C2–P3 118.1(2).

9 crystallises in the triclinic space group $P\bar{1}$ with one formula unit in the asymmetric unit.

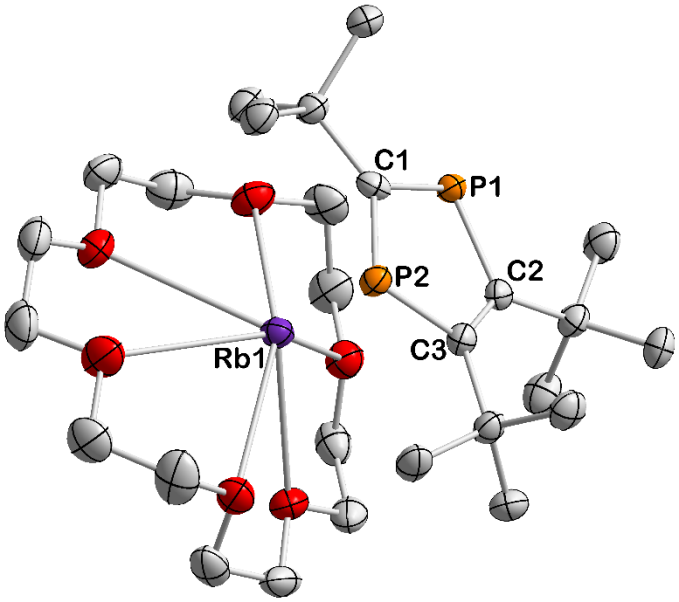


Figure S46. Solid-state molecular structure of **9**. Displacement ellipsoids are drawn at the 50% probability level; H atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.760(4), P2–C1 1.747(4), P1–C2 1.789(4), P2–C3 1.786(4), C2–C3 1.419(6), P1–C1–P2 112.6(2), C1–P1–C2 98.91(18), C1–P2–C3 98.93(19), P1–C2–C3 114.4(3), P2–C3–C2 115.2(3).

Table S6. Crystal data and structure refinement for **1** and **3**.

Compound	**1**	**3**
Empirical formula	$C_{28}H_{54}LiO_{8.5}P_3$	$C_{22}H_{42}KO_6P_3$
Formula Weight	662.61	534.56
Temperature [K]	123	123
Crystal System	orthorhombic	orthorhombic
Space Group	*Pbca*	$P2_12_12_1$
a [Å]	37.25924(16)	9.58810(10)
b [Å]	12.33778(5)	17.15960(10)
c [Å]	31.13083(16)	17.26040(10)
α [°]	90	90
β [°]	90	90
γ [°]	90	90
Volume [Å³]	14310.72(11)	2839.82(4)
Z	16	4
ρ_{calc} [g/cm³]	1.230	1.250
μ [mm^{-1}]	1.914	3.503
F(000)	5728.0	1144.0
Crystal Size [mm³]	0.322 × 0.181 × 0.167	0.419 × 0.287 × 0.253
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection [°]	4.744 to 143.892	7.264 to 133.652
Index ranges	$-45 \le h \le 45$, $-15 \le k \le 10$, $-38 \le l \le 38$	$-11 \le h \le 11$, $-20 \le k \le 20$, $-20 \le l \le 18$
Reflections collected	263626	53964
Independent reflections	13906 [R_{int} = 0.0529, R_{sigma} = 0.0188]	5040 [R_{int} = 0.0493, R_{sigma} = 0.0178]
Data / restraints / parameters	13906/352/851	5040/0/295
Goodness-of-fit on F^2	1.042	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0413, wR_2 = 0.1143	R_1 = 0.0236, wR_2 = 0.0632
Final R indexes [all data]	R_1 = 0.0461, wR_2 = 0.1178	R_1 = 0.0238, wR_2 = 0.0634
Largest diff. peak/hole [e Å^{-3}]	0.44/−0.27	0.32/−0.13
Flack parameter		−0.001(3)
CCDC number	2346026	2346027

Table S7. Crystal data and structure refinement for **4** and **9**.

Compound	**4**	**9**
Empirical formula	$C_{22}H_{42}O_6P_3Rb$	$C_{27}H_{51}O_6P_2Rb$
Formula Weight	580.93	619.08
Temperature [K]	123(1)	123(1)
Crystal System	monoclinic	triclinic
Space Group	$P2_1/n$	P-1
a [Å]	10.31930(10)	9.3862(2)
b [Å]	16.00110(10)	10.5727(2)
c [Å]	17.6998(2)	16.3426(4)
α [°]	90	90.511(2)
β [°]	106.4890(10)	98.341(2)
γ [°]	90	101.542(2)
Volume [Å³]	2802.40(5)	1570.099(6)
Z	4	2
ρ_{calc} [g/cm^3]	1.377	1.309
μ [mm^{-1}]	4.320	3.418
F(000)	1216.0	656.0
Crystal Size [mm³]	0.405 × 0.235 × 0.192	0.27 × 0.25 × 0.17
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection [°]	8.976 to 133.562	8.542 to 133.38
Index ranges	$-12 \le h \le 11$, $-18 \le k \le 18$, $-14 \le l \le 21$	$-11 \le h \le 11$, $-12 \le k \le 12$, $-18 \le l \le 19$
Reflections collected	42970	42737
Independent reflections	4954 [R_{int} = 0.0518, R_{sigma} = 0.0184]	5528 [R_{int} = 0.0608, R_{sigma} = 0.0226]
Data / restraints / parameters	4954/9/295	5528/0/334
Goodness-of-fit on F^2	1.028	1.152
Final R indexes [I>=2σ (I)]	R_1 = 0.0445, wR_2 = 0.1143	R_1 = 0.0518, wR_2 = 0.1228
Final R indexes [all data]	R_1 = 0.0450, wR_2 = 0.1148	R_1 = 0.0523, wR_2 = 0.1230
Largest diff. peak/hole [e Å^{-3}]	1.13/−0.35	1.06/−0.47
CCDC number	2346028	2346029

Table S8. Crystal data and structure refinement for **11** and **12**.

Compound	**11**	**12**
Empirical formula	$C_{20}H_{33}P_3Fe$	$C_{20}H_{33}P_3Ru$
Formula Weight	422.22	467.44
Temperature [K]	123.0(2)	123.0(1)
Crystal System	monoclinic	monoclinic
Space Group	$P2_1/c$	$P2_1/c$
a [Å]	10.1779(2)	10.2485(5)
b [Å]	12.7916(2)	13.0851(5)
c [Å]	16.4260(2)	16.3300(9)
α [°]	90	90
β [°]	107.870(2)	107.637(5)
γ [°]	90	90
Volume [Å³]	2035.35(6)	2086.96(18)
Z	4	4
ρ_{calc} [g/cm³]	1.378	1.488
μ [mm^{-1}]	8.148	8.234
F(000)	896.0	968.0
Crystal Size [mm³]	0.211 × 0.13 × 0.13	0.23 × 0.19 × 0.12
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection [°]	8.932 to 133.578	8.83 to 134.134
Index ranges	$-11 \le h \le 12$, $-15 \le k \le 14$, $-14 \le l \le 19$	$-12 \le h \le 12$, $-15 \le k \le 15$, $-19 \le l \le 15$
Reflections collected	12907	17208
Independent reflections	3510 [R_{int} = 0.0363, R_{sigma} = 0.0268]	3671 [R_{int} = 0.0526, R_{sigma} = 0.0265]
Data / restraints / parameters	3510/0/229	3671/0/229
Goodness-of-fit on F^2	1.073	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0280, wR_2 = 0.0772	R_1 = 0.0259, wR_2 = 0.0685
Final R indexes [all data]	R_1 = 0.0298, wR_2 = 0.0783	R_1 = 0.0264, wR_2 = 0.0690
Largest diff. peak/hole [e Å^{-3}]	0.40/−0.30	0.66/−0.43
CCDC number	2346030	2346031

Table S9. Crystal data and structure refinement for **13**.

Compound	**13**
Empirical formula	$C_{20}H_{36}P_6$
Formula Weight	462.31
Temperature [K]	123.0(1)
Crystal System	monoclinic
Space Group	*C2/c*
a [Å]	19.2177(5)
b [Å]	12.5176(3)
c [Å]	22.1442(6)
α [°]	90
β [°]	112.755(3)
γ [°]	90
Volume [Å^3]	4912.4(2)
Z	8
ρ_{calc} [g/cm^3]	1.250
μ [mm^{-1}]	4.088
F(000)	1968.0
Crystal Size [mm^3]	0.097 × 0.072 × 0.029
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection [°]	8.648 to 150.8
Index ranges	$-23 \le h \le 24$, $-15 \le k \le 15$, $-27 \le l \le 27$
Reflections collected	39101
Independent reflections	5007 [R_{int} = 0.0389, R_{sigma} = 0.0281]
Data / restraints / parameters	5007/0/247
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0411, wR_2 = 0.1128
Final R indexes [all data]	R_1 = 0.0471, wR_2 = 0.1174
Largest diff. peak/hole [e Å^{-3}]	0.95/−0.34
CCDC number	2346032

3.4.6 Cyclic Voltammogram of Di-*tert*-butyldiphosphatetrahedrane (A)

Cyclic voltammetry experiments were performed in a single-compartment cell inside a nitrogen-filled glovebox using a CH Instruments CHI600E potentiostat. The cell was equipped with a platinum disc working electrode (2 mm diameter) polished with 0.05 µm alumina paste, a platinum wire counter electrode, and a silver/silver nitrate reference electrode. The supporting electrolyte, tetra-*n*-butylammonium hexafluorophosphate, (nBu$_4$NPF$_6$), was dried in vacuo at 110 °C for three days. All redox potentials are reported versus the ferrocenium/ferrocene (Fc^+/Fc) couple. The scan rate is v = 100 mV·s^{-1}. To mimic the reaction conditions in the experimental setup, 29 µL of a solution of **A** in toluene (c = 0.4339 mol/L, n = 0.0126 mmol) were diluted with 10 mL THF. Similar cyclic voltammograms without any visible redox process were obtained with higher concentrations of **A**. Please note that P_4 can be reduced at the potential $E_{1/2}$ = –1.55 V (vs. bottom mercury in DMF).§§§[46]

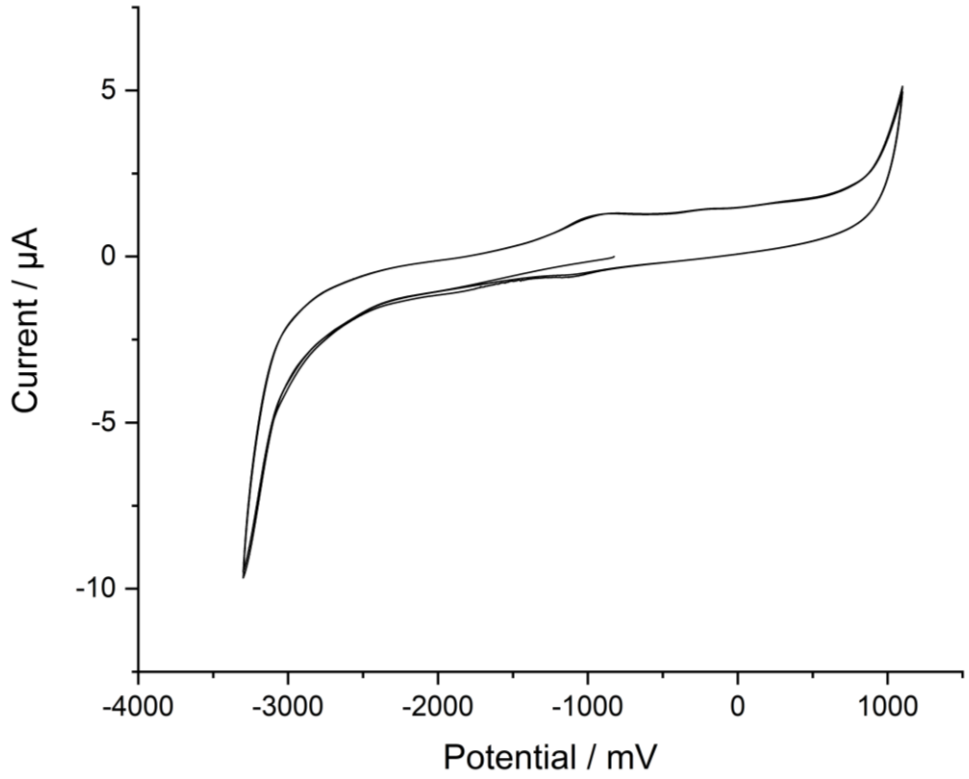


Figure S47. Cyclic voltammogram of di-*tert*-butyldiphosphatetrahedrane (**A**) in toluene/THF/nBu$_4$NPF$_6$; the potential is referenced vs. Cp_2Fe/Cp_2Fe^+.

3.4.7 Quantum Chemical Calculations

General Methods

All calculations were carried out with Gaussian09.[47] Geometry optimisations and frequency calculations were performed at the ωB97XD/def2-TZVPPD level of theory for all compounds except **13**, as SCF convergence could not be achieved with the diffuse function in the basis set. Thus, to calculate the thermodynamic parameters, the energies of the previously optimised geometries (at the ωB97XD/def2-TZVPPD level of theory) were calculated as single point calculations at the ωB97XD/def2-TZVPP level of theory. For compound **13**, geometry optimisation and frequency calculations were performed at the ωB97XD/def2-TZVPP level of theory.[48] In all calculations, the solvent effects have been incorporated via the CPCM model using tetrahydrofuran as solvent.[49] Frequency calculations were carried out to confirm the nature of the stationary points found by geometry optimisations. All optimised geometries show no imaginary frequencies.

Spin Density Distribution of (1,2,3-P_3C_2*t*Bu_2)$^{\bullet}$ (**3**$^{\bullet}$)

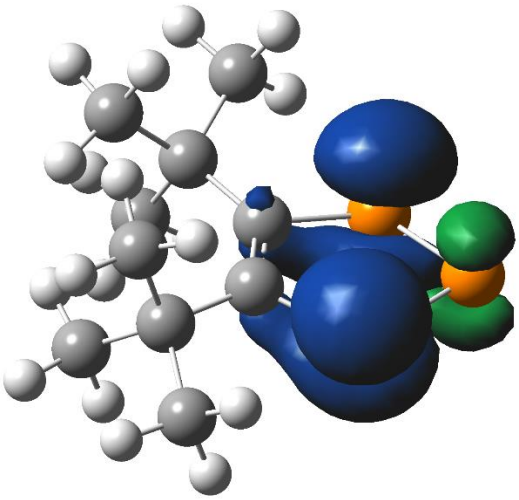
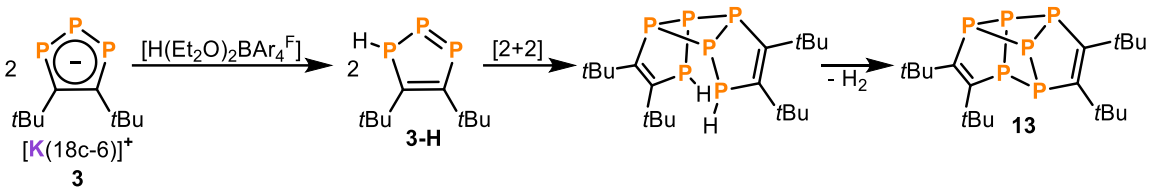


Figure S48. Calculated spin density distribution of **3**$^{\bullet}$. Surface isovalue at 0.05.

Table S10. Mulliken spin densities for selected atoms of the radical **3**$^{\bullet}$.

P1	0.597
P2	−0.135
P3	0.627
C1	−0.005
C2	−0.078

Proton Affinity



Scheme S1. Alternative proposed outline mechanisms for the formation of **13** by protonation of **3**.

Table S11. Proton affinity of selected atoms of $(1,2,3\text{-}P_3C_2t\text{Bu}_2)^-$.

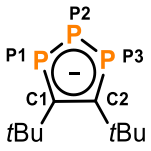
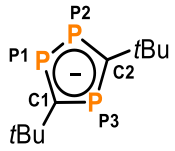
	P1 / P3	P2	C1 / C2	
Proton Affinity [kcal/mol]	200.2	191.1	199.5	

Table S12. Proton affinity of selected atoms of $(1,2,4\text{-}P_3C_2t\text{Bu}_2)^-$.

	P3	P1 / P2	C1 / C2	
Proton Affinity [kcal/mol]	196.5	197.6	200.3	

Reaction Energies

Table S13. Reaction energies for the formation of **13** from $(1,2,3\text{-}P_3C_2t\text{Bu}_2)^-$.

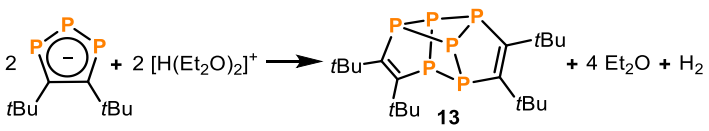
ΔE = −65.2 kcal/mol	
ΔH = −74.5 kcal/mol	
ΔS = 0.0645 kcal/mol	
ΔG = −93.7 kcal/mol	

Table S14. Reaction energies for the formation of **13** from **3**-H.

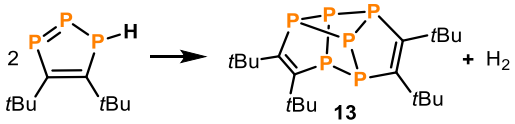
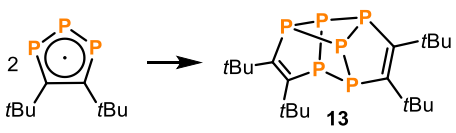
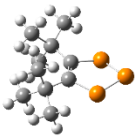
ΔE = −28.7 kcal/mol	
ΔH = −30.9 kcal/mol	
ΔS = −0.0236 kcal/mol	
ΔG = −23.9 kcal/mol	

Table S15. Reaction energies for the formation of **13** from **3**•.

ΔE = −77.8 kcal/mol	
ΔH = −76.5 kcal/mol	
ΔS = −0.0583 kcal/mol	
ΔG = −59.1 kcal/mol	

Cartesian Coordinates of Optimised Structures

3$^{\bullet}$

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ωB97XD/def2-TZVPP
E = −1415.96701614 Eh

0 2

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P	0.60934300	2.99750500	-0.16359300
P	1.76899100	1.33162100	0.23769000
C	0.67193400	-0.09201100	0.00672000
C	1.48027900	-1.42119300	-0.03327500
C	-1.91290000	-0.76339900	0.01150600
C	-0.67508200	0.18052500	0.00413300
C	0.91113200	-2.46950400	-1.00002200
H	-0.05514500	-2.86439800	-0.71750500
H	1.60141000	-3.31274900	-1.04125200
H	0.83289700	-2.05578600	-2.00596800
C	-1.78393600	-1.91858500	1.01457100
H	-0.99668000	-2.62346300	0.78476600
H	-2.72080100	-2.47710300	1.03543900
H	-1.60706400	-1.52682400	2.01721700
C	2.90972800	-1.16704200	-0.56371800
H	2.89499200	-0.68434900	-1.54285100
H	3.41530400	-2.12667200	-0.67545200
H	3.51491100	-0.56454000	0.11136700
C	-3.19934400	-0.02662000	0.44423100
H	-3.10550300	0.41032800	1.43922100
H	-4.01354200	-0.75157500	0.46970700
H	-3.48820400	0.76108800	-0.25010500
C	1.62966900	-1.99058100	1.38764600
H	2.17400700	-1.28862400	2.02139200
H	2.19897000	-2.92141300	1.35170800
H	0.67405200	-2.19294700	1.86143800
C	-2.18334100	-1.26121600	-1.41986500
H	-2.41460500	-0.41667300	-2.07133800
H	-3.04774300	-1.92801600	-1.41701300
H	-1.34530100	-1.79311600	-1.85457800

H^{+}
ωB97XD/def2-TZVPPD
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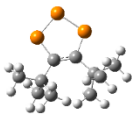
1 1

H	0.00000000	0.00000000	0.00000000

(1,2,3-P$_3$C$_2$*t*Bu$_2$)$^{-}$

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ωB97XD/def2-TZVPP
E = −1416.13002472 Eh

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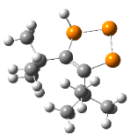
P	0.00115100	3.03702300	0.00003300
P	1.54730000	1.66499500	-0.09070800
C	0.70749000	0.10723300	-0.03685300
C	1.70778200	-1.09822000	0.02453600
C	-1.70861300	-1.09695500	-0.02453100
C	-0.70742700	0.10776400	0.03683400
C	1.39792100	-2.24905900	-0.94773800
H	0.46044400	-2.75660200	-0.76936200
H	2.18857800	-2.99898100	-0.87738800
H	1.38641200	-1.87618900	-1.97358900
C	-1.39955100	-2.24804300	0.94770300
H	-0.46249500	-2.75632500	0.76921900
H	-2.19081200	-2.99733500	0.87743300
H	-1.38763600	-1.87518800	1.97355400
C	3.14970200	-0.69614200	-0.36208800
H	3.20433800	-0.30570100	-1.37891100
H	3.78140700	-1.58554700	-0.30594800
H	3.56915700	0.05060900	0.30835200
C	-3.15023400	-0.69386000	0.36215300
H	-3.20452300	-0.30320800	1.37891400
H	-3.78251800	-1.58286700	0.30622400
H	-3.56926100	0.05304700	-0.30838000
C	1.81529600	-1.59439900	1.48039000
H	2.27970300	-0.81937100	2.09233300
H	2.44384600	-2.48765700	1.53166100
H	0.85555000	-1.82516900	1.92805000
C	-1.81654700	-1.59303600	-1.48038800
H	-2.28048000	-0.81769000	-2.09228800
H	-2.44568900	-2.48587800	-1.53163500
H	-0.85698400	-1.82443600	-1.92811300

(3-H-1,2,3-P$_3$C$_2$*t*Bu$_2$)

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ωB97XD/def2-TZVPP
E = −1416.59455789 Eh

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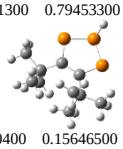
P	1.02079500	2.88419000	0.11088600
C	-0.64188600	0.24281100	0.01774100
C	-1.98903100	-0.53580800	0.03342000
C	1.28448900	-1.60905300	-0.01249200
C	0.67294200	-0.17095100	-0.01605400
C	-2.01634300	-1.68900700	1.04628100
H	-1.33328600	-2.49696300	0.82371500
H	-3.02077100	-2.11329900	1.06721200
H	-1.79105700	-1.31849300	2.04708900
C	0.58578500	-2.59858100	-0.95506600
H	-0.44047200	-2.81942700	-0.69745500
H	1.12941300	-3.54402300	-0.93778200
H	0.60625200	-2.22304500	-1.97914800
C	-3.16441300	0.36919400	0.46370900
H	-3.02384300	0.77442200	1.46600700
H	-4.07406300	-0.23118200	0.47345500
H	-3.33951500	1.19103300	-0.23056300
C	2.75182700	-1.61473200	-0.49979800
H	2.84950900	-1.19023200	-1.50021100
H	3.09445900	-2.64937200	-0.53903400
H	3.42294000	-1.07539200	0.16503200
C	-2.33561000	-1.00855500	-1.39105200
H	-2.46293800	-0.14728500	-2.04840200
H	-3.27777900	-1.55957600	-1.37223100
H	-1.57596400	-1.64663600	-1.82685800
C	1.32323200	-2.13082900	1.43521500
H	1.93599300	-1.47244800	2.05344100
H	1.77605300	-3.12411100	1.45542500
H	0.34199100	-2.19472000	1.89336100
P	-0.86070400	2.00881400	-0.24962400
H	-1.66972600	2.48151300	0.79453300

(2-H-1,2,3-P$_3$C$_2$*t*Bu$_2$)

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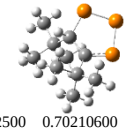
0 1

P	-1.42860700	1.76340400	0.15646500
P	1.73846600	1.40701900	-0.39035400
C	0.72612800	0.03634500	-0.11584500
C	1.57102200	-1.26798600	0.07994600
C	-1.81604200	-0.91636200	-0.06409000
C	-0.72546300	0.19914600	0.02660000
C	1.16023500	-2.48561000	-0.76627800
H	0.16048600	-2.85518100	-0.59291600
H	1.84685300	-3.30321200	-0.54375100
H	1.25850200	-2.25711900	-1.82846700
C	-1.68217800	-2.03033100	0.98736300
H	-0.77510000	-2.61330200	0.92344200
H	-2.51865600	-2.72199200	0.87721400
H	-1.73705000	-1.60122100	1.98912500
C	3.05642400	-1.06722400	-0.29416800
H	3.18258200	-0.80109900	-1.34470500
H	3.57624300	-2.01128100	-0.12749500
H	3.54943500	-0.31224900	0.31518100
C	-3.24193700	-0.37164700	0.16785600
H	-3.37174800	0.03380600	1.17146900
H	-3.94210200	-1.19937800	0.04719100
H	-3.52462200	0.39474700	-0.55299900
C	1.57425100	-1.59013500	1.58895400
H	2.10175700	-0.80219500	2.12821500
H	2.09806200	-2.53195400	1.76344200
H	0.58144300	-1.66915300	2.01796800
C	-1.83080100	-1.44943900	-1.51252100
H	-2.24212000	-0.68547200	-2.17375400
H	-2.46984900	-2.33221600	-1.57690900
H	-0.85115000	-1.70841200	-1.89395600
P	0.36231000	2.88295900	0.20949000
H	0.24465800	3.83561300	-0.81920200

(1,2,3-P$_3$HC$_2$*t*Bu$_2$)

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0 1

P	0.43404200	-1.89952500	0.70210600
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P	-1.99823700	-0.70646900	-0.95914000
C	-1.01368600	1.63361900	0.22732000
C	2.12957700	0.08091100	-0.19570700
C	0.66541400	-0.40900300	-0.05541300
C	-0.11458700	2.85348000	0.00421400
H	0.90621200	2.70691200	0.33607000
H	-0.51950100	3.69516900	0.56812000
H	-0.09777700	3.13822000	-1.04910100
C	2.60608700	0.77932100	1.09153300
H	1.99240800	1.62871800	1.37646900
H	3.62779000	1.13740400	0.95415200
H	2.59942700	0.07383800	1.92296500
C	-2.41385400	2.07617000	-0.23652400
H	-2.46208200	2.20176800	-1.31952400
H	-2.64466600	3.03907800	0.22101900
H	-3.19362300	1.37645500	0.06170100
C	3.07952700	-1.11413100	-0.41835100
H	3.08914200	-1.79570900	0.43105200
H	4.09555500	-0.74079900	-0.55655800
H	2.79744800	-1.67913700	-1.30737700
C	-1.07809000	1.30094700	1.71685700
H	-1.68607000	0.41415000	1.90288000
H	-1.53221100	2.13583800	2.25274900
H	-0.09024300	1.12560400	2.13961500
C	2.31387000	0.99049400	-1.41886000
H	2.00461700	0.47641200	-2.33047200
H	3.37175000	1.23435800	-1.52261200
H	1.76763200	1.92502900	-1.35419800
C	-0.50402400	0.36211700	-0.62428300

H	-0.22816300	0.76997900	-1.60235300

(1,2,4-$P_3C_2tBu_2$)$^-$
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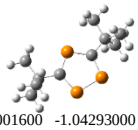

-1 1

P	-1.78545200	-0.00001600	-1.04293000
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C	-0.07315800	-0.00012300	-1.35175200
C	0.44072400	0.00000600	-2.80397900
C	1.97198600	0.00017800	-2.89002900
C	-0.06647200	-1.24928700	-3.54220100
H	0.30440700	1.26236100	-4.57038100
H	0.27776500	-2.15583100	-3.04159400
H	2.40134200	0.88262700	-2.41386300
H	-1.15653300	1.27386500	-3.57172900
H	0.27732000	2.15583200	-3.04137900
H	-1.15625500	-1.27410500	-3.57189200
H	0.30470700	-1.26220500	-4.57050700
H	2.27764200	0.00029700	-3.93905100
H	2.40153200	-0.88225700	-2.41400800
P	1.01491100	-0.00007900	0.00000000
P	-1.78545200	-0.00001600	1.04293000
C	-0.06674300	1.24926700	3.54206700
C	-0.07315800	-0.00012300	1.35175200
C	0.44072400	0.00000600	2.80397900
C	1.97198600	0.00017800	2.89002900
C	-0.06647200	-1.24928700	3.54220100
H	0.30440700	1.26236100	4.57038100
H	0.27776500	-2.15583100	3.04159400
H	2.40134200	0.88262700	2.41386300
H	-1.15653300	1.27386500	3.57172900
H	0.27732000	2.15583200	3.04137900
H	-1.15625500	-1.27410500	3.57189200
H	0.30470700	-1.26220500	4.57050700
H	2.27764200	0.00029700	3.93905100
H	2.40153200	-0.88225700	2.41400800

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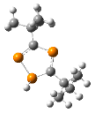

0 1

P	-1.13741900	1.81806800	-0.12494600
C	-3.87220700	0.59060400	-0.17146100
C	-1.36988000	0.14243200	-0.03913400
C	-2.77875800	-0.46619800	0.00503100
C	-2.92938100	-1.50467700	-1.11872100
C	-2.98092700	-1.15345900	1.36604900
H	-4.85045000	0.10879100	-0.14445700
H	-2.25308900	-1.95052800	1.52278400
H	-2.78987500	-1.03973000	-2.09575500
H	-3.84536800	1.33680800	0.62366700
H	-3.77827400	1.10590100	-1.12900600
H	-2.87923300	-0.43302500	2.17881000
H	-3.97917600	-1.59192900	1.41734800
H	-3.92907700	-1.94064600	-1.08520200
H	-2.20777300	-2.31606900	-1.02127100
P	0.01017400	-1.00691300	0.00268400
C	3.66988900	0.45204500	-0.89276400
C	1.34094000	0.03321500	-0.03485700
C	2.78948700	-0.45960800	-0.02671000
C	2.89228600	-1.89060500	-0.56656300
C	3.31731300	-0.44107200	1.41883500
H	4.68379200	0.05193300	-0.93477800
H	2.72709300	-1.10414300	2.05208600
H	2.51861500	-1.95515500	-1.58939200
H	3.73325700	1.46104200	-0.48189800
H	3.28598300	0.51755900	-1.91164800
H	3.27458300	0.56259500	1.84310900
H	4.35567900	-0.77705200	1.43847600
H	3.93641900	-2.20660800	-0.56295700
H	2.32802400	-2.59321000	0.04711700
P	0.97265500	1.75702200	0.19646200
H	1.51515600	2.42475200	-0.91825600

(4-H-1,2,4-$P_3C_2tBu_2$)
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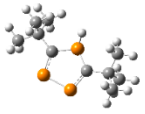
E = −1416.60293813 Eh



0 1

P	1.24766300	1.5[illegible]	[illegible]
C	3.33604500	-1.27132500	0.39871000
C	1.40186700	0.25707600	-0.00929400
C	2.75040500	-0.21855900	-0.55891800
C	2.58551900	-0.84643500	-1.94885600
C	3.73218500	0.95384700	-0.66779300
H	4.28779400	-1.63769900	0.00935900
H	3.35201100	1.72205700	-1.34230600
H	1.97335700	-1.74974200	-1.91649800
H	3.50688600	-0.84094900	1.38566900
H	2.66044400	-2.12060700	0.50704900
H	3.92006500	1.41340400	0.30265800
H	4.68494100	0.59506500	-1.05987500
H	3.56242500	-1.13116500	-2.34161800
H	2.13101500	-0.14381800	-2.64869600
P	-0.88476500	1.51425800	1.44510800
C	-3.77104200	0.51290700	1.14317700
C	-1.36472600	0.27158400	0.39168200
C	-2.82418200	-0.07997100	0.09602400
C	-3.02941200	-1.60127900	0.06120500
C	-3.18379800	0.50800800	-1.28086700
H	-4.80153400	0.26219400	0.88775300
H	-2.56109200	0.08719400	-2.07096000
H	-2.75461600	-2.05608300	1.01340500
H	-3.69355500	1.59981100	1.18822100
H	-3.55929700	0.11423500	2.13619800
H	-3.05325800	1.59052800	-1.28379100
H	-4.22637300	0.28579700	-1.51502200
H	-4.07927200	-1.82385400	-0.13491800
H	-2.43961100	-2.07368100	-0.72607300
P	-0.05466500	-0.69667000	-0.27100500
H	-0.27001700	-0.79629700	-1.65576000

(1,2,4-$P_3HC_2tBu_2$)
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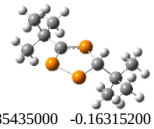
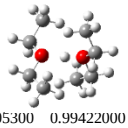
E = −1416.60887254 Eh



0 1

P	-1.03324300	-1.85435000	-0.16315200
C	-2.61657400	0.55707000	1.61671100
C	-2.73243000	0.46722100	0.09269000
C	-3.03619200	1.85736000	-0.47976600
C	-3.89527700	-0.46083400	-0.27551600
H	-3.54766000	0.93210100	2.04432600
H	-3.98085300	-0.57707300	-1.35757200
H	-2.27711700	2.58889000	-0.20293700
H	-2.41680300	-0.42114000	2.05835400
H	-1.81606900	1.23655900	1.91576700
H	-3.78132000	-1.45155400	0.16499800
H	-4.83168200	-0.03967800	0.09355300
H	-3.99392900	2.21290400	-0.09603200
H	-3.09999200	1.82767800	-1.56919700
P	0.04376600	1.05659300	-0.36634900
P	0.96564400	-1.78757100	0.06683800
C	3.30410300	-0.02847700	1.41586300
C	1.29983900	-0.01528000	-0.08107600
C	2.75718200	0.43699700	0.05689000
C	2.90349300	1.95893700	-0.02627900
C	3.58867700	-0.19526700	-1.07111600
H	4.34376500	0.28511800	1.52310700
H	3.21742400	0.11991300	-2.04723200
H	2.34381300	2.45802900	0.76643400
H	3.27128300	-1.11421200	1.51531000
H	2.72896800	0.40686500	2.23433600
H	3.55916700	-1.28490200	-1.02853400
H	4.63056600	0.11651300	-0.98118500
H	3.95500200	2.22769400	0.08463700
H	2.55623400	2.34599900	-0.98522600
C	-1.39962600	-0.07505800	-0.51242600
H	-1.54244800	-0.10580000	-1.60879600

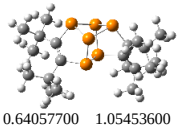
[H(Et_2O)$_2$]$^+$
ωB97XD/def2-TZVPP
E = −467,808338514 Eh



1 1

C	1.51989500	2.03105300	0.99422000
H	0.53322700	1.95887200	1.44930300
H	1.46412900	2.67038200	0.11493900
H	2.19350200	2.49217600	1.71478400
C	2.06428400	0.67399600	0.63936400
H	2.11239700	0.00312900	1.49702200
H	3.04278600	0.73447300	0.16974300
O	1.19182300	0.05699600	-0.35774100
C	1.64475800	-1.21862900	-0.90196000
H	2.59705400	-1.00946600	-1.38228300
C	0.61717100	-1.72552800	-1.87805300
H	0.43704400	-0.99756000	-2.66741800
H	0.99524800	-2.63917400	-2.33306500
H	-0.32478000	-1.96423900	-1.38528500
H	1.80354100	-1.90467200	-0.06971700
C	-0.63913100	-1.28902500	2.18255100
H	-0.33868400	-0.41547200	2.76049900
H	0.24260500	-1.73661800	1.72260200
H	-1.05464000	-2.02401300	2.86986100
C	-1.67949700	-0.92448300	1.15399400
H	-2.58029900	-0.53112100	1.62650900
H	-1.95812900	-1.78648700	0.54224900
O	-1.15936800	0.10458600	0.29911600
C	-2.07496000	0.55272700	-0.71450500
H	-2.26267300	-0.27129400	-1.40757300
C	-1.49234300	1.75163400	-1.41983400
H	-0.56438900	1.50466500	-1.93494300
H	-2.20459900	2.10641700	-2.16313700
H	-1.30012500	2.55886200	-0.71421100
H	-3.01204100	0.80521300	-0.21719100
H	0.15812400	0.04280400	-0.05835300

***t*$Bu_4C_4P_6$ (13)**:
ωB97XD/def2-TZVPP
E = −2832.05804382 Eh



0 1

P	0.35221900	0.64057700	1.05453600
P	0.14969900	-1.46220100	1.56848700
P	-0.35219800	0.64061300	-1.05448900
P	1.46954500	-1.99403600	-0.10998600
P	-1.46956400	-1.99401900	0.10994900
P	-0.14971100	-1.46215100	-1.56850800
C	2.18432200	0.52053600	0.69164900
C	2.56769100	-0.50628300	-0.11019600
C	-3.79517400	-0.69887900	1.03700600
C	3.79513600	-0.69886500	-1.03704600
C	-2.56769100	-0.50624900	0.11021200

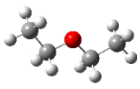
C	-2.18430000	0.52059400	-0.69159300
C	4.91894700	-1.45753700	-0.31575300
H	5.30104300	-0.91789900	0.54590600
H	5.74612000	-1.63140300	-1.00655900
H	4.55954500	-2.42862000	0.02913000
C	-2.98420100	1.69374500	-1.31074000
C	-4.91894100	-1.45754600	0.31563700
H	-5.30099900	-0.91789200	-0.54602800
H	-5.74614600	-1.63143900	1.00639700
H	-4.55951000	-2.42861600	-0.02925200
C	2.98424500	1.69367400	1.31079200
C	-3.37961200	-1.55412400	2.25513300
H	-3.07311400	-2.56340100	1.98062300
H	-4.23489900	-1.65024400	2.92406300
H	-2.57359100	-1.08076900	2.81818100
C	3.37952500	-1.55407600	-2.25518000
H	3.07303600	-2.56335900	-1.98068200
H	4.23478400	-1.65017900	-2.92414800
H	2.57348000	-1.08070600	-2.81818300
C	-4.44410800	1.33947100	-1.62537200
H	-4.48636500	0.47882200	-2.29460600
H	-4.90907200	2.18331000	-2.13654800
H	-5.05140200	1.11963900	-0.75851900
C	-4.29620700	0.61104800	1.66153100
H	-3.47608100	1.12256400	2.16718500
H	-5.05646800	0.37748900	2.40785900
H	-4.74029400	1.30295200	0.95895000
C	4.29611400	0.61109800	-1.66154100
H	3.47595400	1.12262200	-2.16713300
H	5.05634400	0.37758700	-2.40791600
H	4.74021900	1.30298100	-0.95895100
C	2.38138400	2.04744300	2.68997500
H	1.40174100	2.51237900	2.61212500
H	3.04438200	2.75294800	3.19192500
H	2.29317700	1.16240400	3.32320500
C	4.44415900	1.33939300	1.62537600
H	4.48643500	0.47872600	2.29458500
H	4.90913600	2.18321900	2.13656100
H	5.05142900	1.11958500	0.75849900
C	-2.38129400	2.04752600	-2.68989800
H	-1.40163400	2.51242000	-2.61201100
H	-3.04425200	2.75307200	-3.19184300
H	-2.29310700	1.16250200	-3.32315100
C	-2.88030400	2.94964200	-0.43261600
H	-3.34903400	2.81852700	0.53866500
H	-3.36066200	3.79178300	-0.93446900
H	-1.83379600	3.21300000	-0.26648500
C	2.88033600	2.94957600	0.43267900
H	3.34903000	2.81845800	-0.53862000
H	3.36072500	3.79170900	0.93451700
H	1.83382700	3.21295200	0.26658400

H_2
ωB97XD/def2-TZVPP
E = −1,17672716964 Eh

0 1

H	0.00000000	0.00000000	0.37187400
H	0.00000000	0.00000000	-0.37187400

Et_2O
ωB97XD/def2-TZVPP
E = −233.686444447 Eh



0 1

C	-2.37771500	0.40321800	0.00001400
H	-2.37860800	1.04025700	-0.88465700
H	-2.37864600	1.04011500	0.88478700
H	-3.29524000	-0.18537300	-0.00005200
C	-1.17477600	-0.51074400	-0.00003500
H	-1.18751300	-1.16208600	-0.88391200
H	-1.18751300	-1.16217800	0.88377300
O	0.00000000	0.26860400	0.00000500
C	1.17477600	-0.51074400	0.00001300
H	1.18751200	-1.16212400	0.88386100
C	2.37771500	0.40321800	0.00000400
H	2.37862100	1.04020300	0.88471500
H	3.29524000	-0.18537300	0.00002100
H	2.37863300	1.04016900	-0.88473000
H	1.18751400	-1.16214000	-0.88382300

3.5 Notes and references

‡ Note that the ladderane (tBuCP)$_4$ (i.e. the dimer of **A**) does not react with alkali metals under the conditions described in Scheme 1.

§ We could not unambiguously detect the formation of H_2 by ^{1}H NMR spectroscopy. Nevertheless, the well-documented ability of metal phosphides to catalyse hydrogen evolution reactions in acidic media supports the proposed pathway.[50]

§§ Such a pathway has been proposed by Nixon and co-workers for the protonation of Li[1,2,4-P_3C_2tBu$_2$] with an EtOH/$MeCO_2H$ mixture, leading to a tricyclic compound containing a P_5 chain and an isolated P atom.[51] Indeed, our DFT calculations for (1,2,3-P_3C_2tBu$_2$)$^-$ show that P1 and P3 have a slightly higher proton affinity than C1, C2 and P2. In contrast, the carbon atoms of (1,2,4-P_3C_2tBu$_2$)$^-$ have a higher proton affinity than the phosphorus atoms. The protonation of one P atom in (1,2,3-P_3C_2tBu$_2$)$^-$ leads to a localised P=P double bond which is prone to cycloaddition triggering the hydrogen elimination and formation of **13**. Both the dimerisation of **3$^\bullet$** to **13** and of protonated **3-H** to **13** are exergonic with −59.1 kcal·mol^{-1} and −23.9 kcal·mol^{-1}, respectively (see section 3.4.7). A 1,2,4-triphospholide radical dimerisation has been reported by Ionkin and co-workers.[52]

§§§ The measurements were performed relative to the bottom mercury at r.t. Bottom mercury means that one of the electrodes is the mercury at the bottom of the CV cell.[49]

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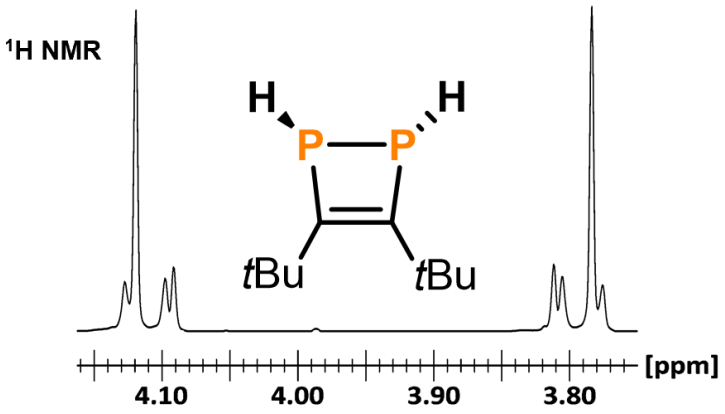
4 A Radical Path to 1,2-Diphosphacyclobutenes[a,b]

Abstract: Reactions of di-*tert*-butyldiphosphatetrahedrane (tBuCP)$_2$ with Mes*O**•**,** (PhSe)$_2$, and I_2 produce 1,2-diphosphacyclobutene derivatives (tBuCPR)$_2$ (R = OMes* (**1**), SePh (**2**), I (**3**); Mes* = 2,4,6-tri-*tert*-butylphenyl). Reaction of **3** with $LiAlH_4$ affords the elusive 1,2-dihydro-1,2-diphosphacyclobutene (tBuCPH)$_2$ (**4**).



[a] Reproduced from Maria K. Uttendorfer, Lisa M. Schneider, Lukas S. Diener, Gabriele Hierlmeier, Gábor Balázs, Robert Wolf, *Chem. Commun.* **2025**, *61*, 17464–17467.

[b] Maria K. Uttendorfer conducted all reactions and the characterisation of the compounds. She performed and analysed the DFT calculations and wrote the manuscript. Lukas S. Diener and Lisa M. Schneider conducted the synthesis and initial characterisation of compounds **1** and **2** as part of their B.Sc. theses under the supervision of Maria K. Uttendorfer. Gabriele Hierlmeier and Robert Wolf conceptualised the project. Robert Wolf supervised and directed the project. Gábor Balázs contributed to the analysis of the experimental and theoretical data.

4.1 Introduction

The reaction of white phosphorus (P_4) with p-block-element centred radicals is a well-known strategy to functionalise the P_4 molecule (**A**, Figure 1a).[1-4] Pioneering studies by Barton and Zhu as well as Cummins and Cossairt demonstrated the formation of phosphonic acids and tertiary phosphines from reactions of P_4 with alkyl, aryl and heavier group 14 element radicals.[1,5] Nonetheless, examples for selective P_4 functionalisation using radicals have remained limited.[6] The addition of radicals to P_4 typically results in the cleavage of a P–P bond and the formation of a P-centred radical. This radical then combines with another radical to form the butterfly-type species **B**.[6] Using very bulky substituents, such as in (*i*Pr$_2$N){(Me$_3$Si)$_2$N}P·, compounds of type **B** (e.g., [(*i*Pr$_2$N){(Me$_3$Si)$_2$N}P]$_2$P$_4$) have been isolated.[7] Further radical additions are generally energetically favourable.[6,8] However, while all P–P bonds are equivalent in the first radical addition step (leading to only one product), the following step is more complex and can lead to either a cyclo-P_3 (**C**) or a cyclo-P_4 species (**D**).[6,8] Subsequent degradation steps result in the formation of tertiary phosphines (PR_3, **E**).[6,8,9] As shown for the reactivity of R_3Sn· radicals with P_4, all these steps are energetically favourable, and the final product of the reaction is PR_3.[8]

Unlike P_4, phosphatetrahedranes, which are comprised of carbon and phosphorus atoms, were only recently synthesised. However, their reactivity with p-block radicals remains, to our knowledge, unexplored. In 2019, we reported the nickel-catalysed dimerisation of the phosphaalkyne *t*BuC≡P, resulting in the formation of di-*tert*-butyldiphosphatetrahedrane (*t*BuCP)$_2$ (**F**, Figure 1b).[10] Cummins and co-workers reported the syntheses of tri-*tert*-butylphosphatetrahedrane (*t*Bu$_3$C$_3$P) (**G**) and triphosphatetrahedrane (HCP_3) (**H**) almost simultaneously.[11,12] These phosphatetrahedranes display some striking similarities with P_4 and purely organic tetrahedranes.[10-21] The isolobal nature of the frontier orbitals of **A** and **F** was revealed by DFT calculations.[21] Nonetheless, the lower symmetry of **F** generally enables more complex reaction pathways. In particular, because **F** contains three types of bonds in its tetrahedral core (P–P, P–C and C–C), the selectivities for radical-induced bond cleavage are difficult to predict, but could give access to novel phosphaorganic frameworks. Earlier reactivity studies on **F** show a preferential cleavage of the P–C bonds.[14,17,19-21] Herein, we show that the reaction of **F** with the stable bulky aryloxy radical Mes*O· furnished the 1,2-diphosphacyclobutene (*t*BuCPOMes*)$_2$ (**1**, Figure 1c). Similar derivatives **2** and **3** were obtained by the reaction of **F** with Ph_2Se_2 and I_2. Furthermore, we analyse the structural and spectroscopic properties of **1** – **3** and demonstrate that the 1,2-dihydro derivative **4** can be obtained through the reaction of **3** with $LiAlH_4$. Our results show that the reaction products of **F** with aryloxy radicals and the formal radical sources Ph_2Se_2 and I_2 differ significantly from those observed with P_4.

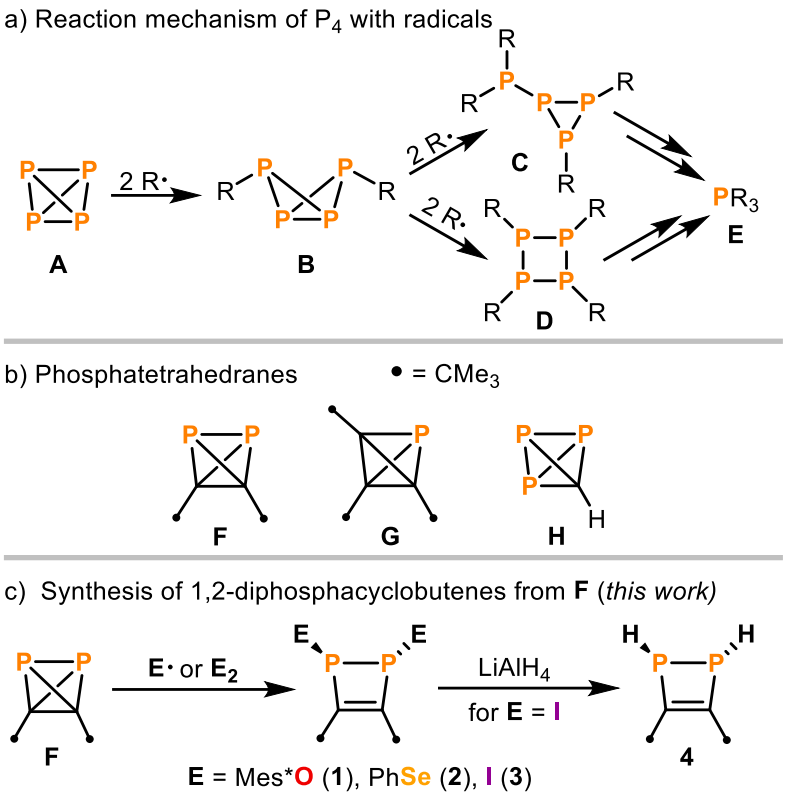
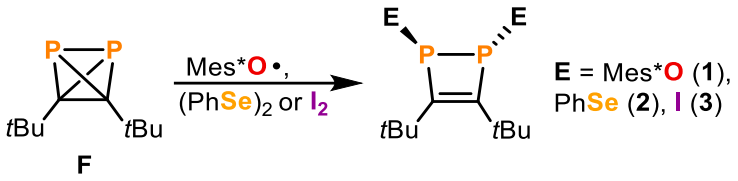


Figure 1. a) Mechanism for the reactivity of P_4 towards radicals, b) tetrahedranes comprised of phosphorus and carbon atoms, c) 1,2-diphosphacyclobutene derivatives synthesised in reactions of **F**.

4.2 Results and Discussion

Addition of **F** to a deep blue solution of the stable radical Mes*O· in toluene in the absence of light (Scheme 1) caused a colour change from deep to light blue, indicating that Mes*O· was consumed. The ^{31}P NMR spectrum of the reaction mixture displayed a singlet at 57.8 ppm, suggesting the formation of a new species with equivalent phosphorus atoms. Single-crystal X-ray diffraction analyses (SCXRD) on crystals obtained from a concentrated *n*-hexane solution at ambient temperature revealed the formation of 1,2-diphosphacyclobutene **1**. Analogous reactions of **F** with $(PhSe)_2$ and I_2 resulted in the formation of **2** and **3** (Scheme 1), which are identified by ^{31}P NMR singlet resonances at −15.4 ppm and −21.5 ppm. Compound **3** was previously synthesised via iodination of $[Cp_2Zr\{P_2C_2tBu_2\}]$, and its identity was confirmed by comparing the spectroscopic data and cell parameters of single crystals with literature data.[22] In contrast to $(PhSe)_2$, $(PhS)_2$ reacts with **F** only upon irradiation or heating (60 °C to 80°C for 5 h). In the ^{31}P NMR spectrum of the reaction solution, a singlet at −7.5 ppm is observed, indicating the formation of the sulphur derivative of **2**. Despite several attempts, this compound could not be isolated from the reaction mixture.



Scheme 1. Reaction of di-*tert*-butyldiphosphatetrahedrane (**F**) with Mes*O·, $(PhSe)_2$ and I_2, yielding the 1,2-disubstituted 1,2-diphosphacyclobutene derivatives **1** – **3**. Conditions: toluene, −80 °C → r.t., overnight.

Single crystals suitable for SCXRD of **2** and **3** were obtained from concentrated *n*-hexane solutions at room temperature. The solid-state molecular structures of **1** – **3** exhibit C2 symmetry with a slightly twisted C_2P_2 ring (P1'–P1–C1–C1' dihedral angles of −24.42(13) °, −14.90(19) ° and 17.144(7) ° for **1**, **2**, and **3**, respectively).[22] The substituents on the phosphorus atoms are in a trans arrangement.[22] Each structure features a C1–C1' double bond (1: 1.372(3) Å, 2: 1.368(5) Å, 3: 1.334(12) Å, Figure 2).[22] In comparison, the C–C bond length in **F** (1.458(2) Å)[21] is considerably longer and corresponds to a single bond.

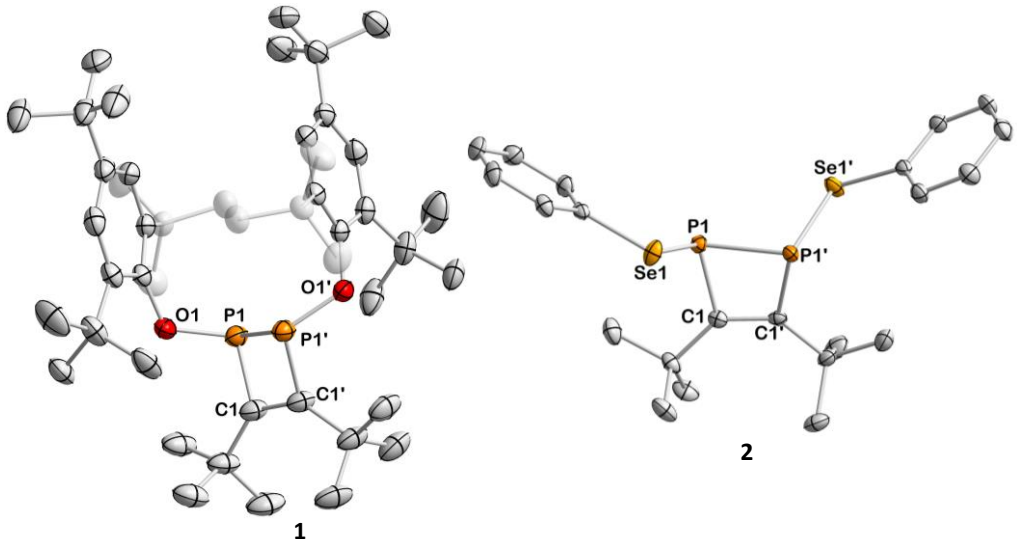


Figure 2. Molecular structures of **1** and **2** in the solid state. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for 1: P1–P1' 2.2322(7), P1–C1 1.8163(14), P1–O1 1.6785(10), C1–C1' 1.372(3), C1–P1–P1' 74.31(5), C1–P1–O1 105.86(6), P1'–P1–O1 108.96(4), P1–C1–C1' 100.51(6), P1'–P1–C1–C1' −24.42(13). 2: P1–P1' 2.2021(13), P1–C1 1.841(2), P1–Se1 2.2664(7), C1–C1' 1.368(5), C1–P1–P1' 76.20(8), C1–P1–Se1 105.84(8), P1'–P1–Se1 100.78(4), P1–C1–C1' 101.95(8), P1'–P1–C1–C1' −14.90(19).

To gain insight into the possible origin of the selectivity of the reaction, we conducted DFT calculations (ωB97X V/def2-TZVP level of theory) using the phenoxy radical PhO· as a smaller model system.‡ These studies revealed that P–P bond cleavage (light red reaction profile, Figure 3) is kinetically and thermodynamically favoured compared to the P–C bond cleavage (dark red reaction profile, $\Delta\Delta G^{\ddagger}$ = 2.2 kcal·mol^{-1} and $\Delta\Delta G$ = 7.2 kcal·mol^{-1}).§ However, the formation of the diphosphacyclobutene by addition of a second PhO· radical is

thermodynamically preferred by 6.5 kcal·mol^{-1} over the formation of the [1.1.0]bicyclobutane product ("butterfly-structure", Figure 3). In contrast, calculations with the bulkier Mes*O· show that the intermediate formed via P–C bond cleavage (dark blue reaction profile, Figure 3) is more stable than that from P–P bond cleavage (light blue reaction profile, Figure 3, $\Delta\Delta G = 5.8$ kcal·mol^{-1}). Previous computational studies on the addition of methyl and Ni(I) radicals have indicated that the 1,2-diphosphacyclobutene structure is energetically more favourable than the "butterfly-structure" despite the generally higher bond energy of P–C bonds with respect to P–P bonds.[20] In line with these findings, reactions of **F** with nickel(I) radicals [Cp^{R}Ni(IPr)] [Cp^{R} = C_5H_5, C_5Me_5, C_5(*p*-Et-C_6H_4)$_5$; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene)] afforded 1,2-diphosphacyclobutenediide ligands (tBu$_2$C$_2$P$_2$)$_n^{2-}$ (n = 1, 2).[20] In contrast, similar reactions of [Cp^{R}Ni(IPr)] with P_4 gave butterfly-P_4 complexes of type **B** (Figure 1a).[23]

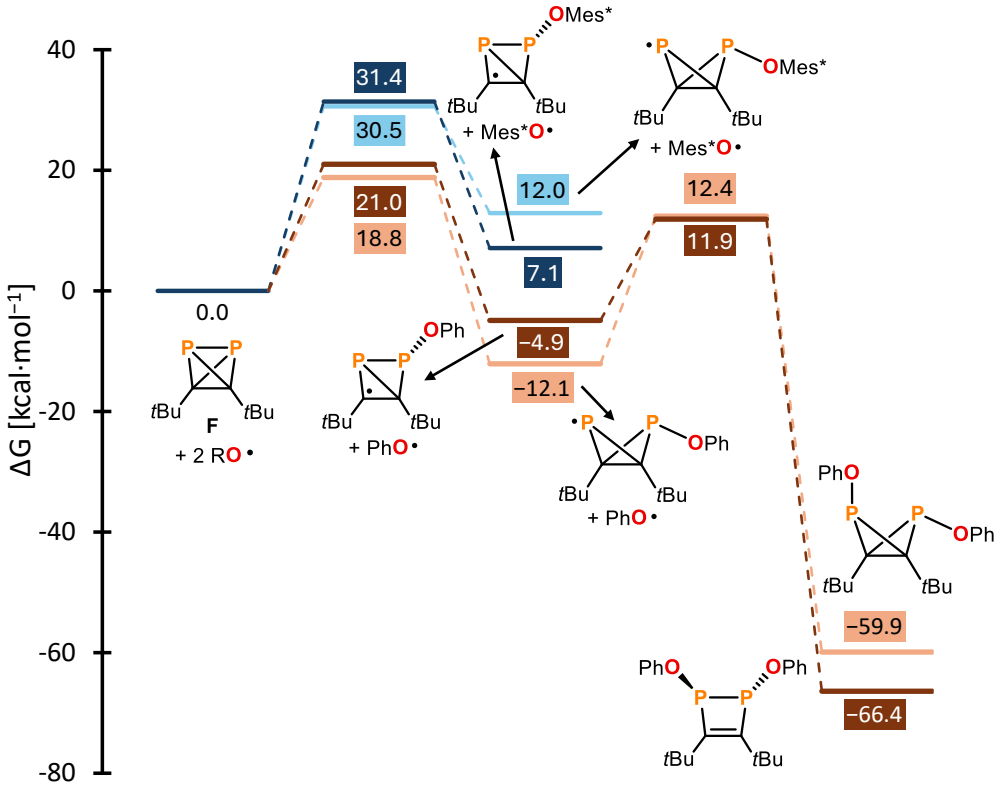
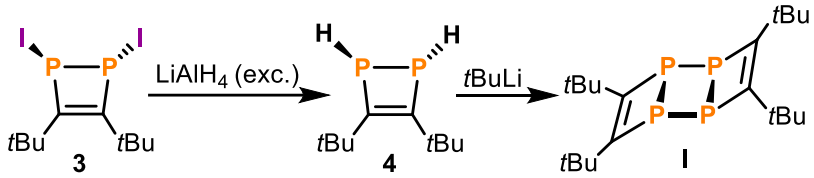


Figure 3. Mechanism of the reaction of (tBuCP)$_2$ (**F**) with two equivalents of RO· leading to P–P bond cleavage (for R = Ph light red and for R = Mes* light blue) or P–C bond cleavage (for R = Ph dark red and for R = Mes* dark blue) in **F**. Calculated on the ωB97X-V/def2-TZVP level of theory.

In analogy to the reaction of Mes*O·, the reaction mechanism of (PhSe)$_2$ likely involves PhSe· radicals formed by the dissociation of (PhSe)$_2$ under ambient conditions.[24] The more sluggish reactivity of (PhS)$_2$ towards **F** conforms with the higher bond dissociation energy of RS–SR bonds compared to RSe–SeR bonds.[25] Note that P_4 does not react with (PhSe)$_2$ or (PhS)$_2$ at ambient temperature; the formation of (PhS)$_3$P and (PhSe)$_3$P can be observed only upon heating or addition of base.[26-29]§§

To demonstrate the synthetic utility of the readily accessible compound **3**, we examined its potential for synthesising of other organophosphorus compounds. Gratifyingly, treatment of **3** with $LiAlH_4$ yielded the 1,2-dihydro compound **4** (Scheme 2), which was isolated in low yield as a colourless liquid through condensation.



Scheme 2. Reaction of **3** with $LiAlH_4$ yielding **4**. Conditions: Et_2O, −80 °C ⟶ r.t., overnight. Subsequent addition of 2 equivalents of *t*BuLi to isolated **4** forms **I**. Conditions: *n*-hexane, −80 °C → r.t., overnight.

While numerous 1,2-dihydrodiphosphacyclobutenes (also known as 1,2-dihydrodiphosphetes) and their metal complexes have been reported, compound **4** appears to be the first isolated example with two hydrogen substituents on the P atoms.[29,30] The multinuclear NMR data of **4** are in full agreement with the molecular structure. The $^{31}P\{^{1}H\}$ NMR spectrum of **4** shows a singlet at −144.8 ppm, which splits into an AA'XX' spin system in the proton coupled ^{31}P NMR spectrum. In the ^{1}H NMR spectrum, the X-part of the AA'XX' spin system is detected as a multiplet at 3.95 ppm. Simulation of the AA'XX' spin system by an iterative fitting procedure yields the coupling constants $^{1}J_{PH}$ = 162.4 Hz, $^{2}J_{PH}$ = 5.7 Hz, $^{1}J_{PP}$ = −14.1 Hz and $^{3}J_{HH}$ = 3.9 Hz (Figure 4). The remarkably small $^{1}J_{PP}$ coupling is consistent with a trans-configuration of the hydrogen substituents. Comparable ^{31}P NMR data have been reported for 1,2-disubstituted 1,2-diphosphete complexes. [30d,e]

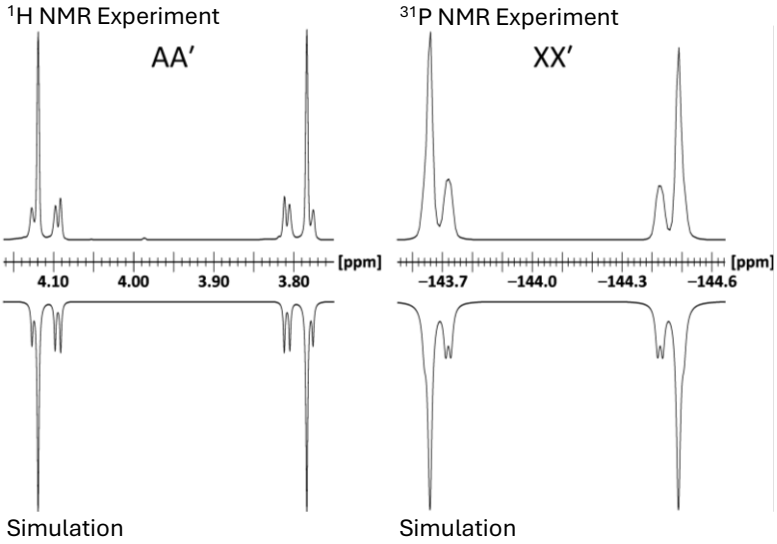


Figure 4. Section of the ^{1}H NMR (left, 500 MHz, 300 K, C_6D_6) and ^{31}P NMR spectra (right, 202 MHz, 300 K, C_6D_6) of **4**; experimental (upwards) and simulation (downwards).

An attempt to synthesise the elusive 1,2-diphosphacyclobutadienediide anion $(1,2\text{-}P_2C_2t\text{Bu}_2)^{2-}$ by deprotonation with 2 equivalents of *t*BuLi at −80 °C unfortunately failed to give the target compound.[31] The ^{31}P NMR spectrum of the reaction mixture showed formation of the ladderane $(t\text{BuCP})_4$ (**I**) instead.[21] Similarly, treating **3** with an excess of KC_8 also furnished **I**. Presumably, the intermediary 1,2 diphosphabutadiene $1,2\text{-}P_2C_2t\text{Bu}_2$ quickly dimerises to **I**.

4.3 Conclusion

In summary, we have demonstrated that the (formal) addition of radicals to di-*tert*-butyldiphosphatetrahedrane **F** efficiently generates 1,2-diphosphacyclobutenes. The addition of two aryloxy radicals Mes*O· to **F** generates **1** by oxidative P–C bond cleavage. This finding aligns with earlier computational results, which indicate that P–C bond cleavage in **F** by metalloradicals is more energetically favourable than P–P bond cleavage.[20] Analogous products **2** and **3** were obtained with $(PhSe)_2$ and I_2. These reactions highlight key differences between the chemistry of diphosphatetrahedrane **F** and P_4, which tends to form [1.1.0]bicyclobutanes ("butterfly species") upon the addition of radicals. The reduction of **3** unexpectedly led to the formation of the ladderane $(t\text{BuCP})_4$ (**I**). However, nucleophilic substitution of iodine atoms with hydrides produced the 1,2-dihydro-1,2-diphosphete **4**. Our work provides the first insights into the reactivity of diphosphatetrahedrane **F** with persistent radicals such as Mes*O· and other formal radical sources such as $(PhSe)_2$ and I_2. 1,2-Dihydrocyclobutene derivatives are the main reaction products with all three reagents. Given the widespread availability of main group element radicals,[32] many additional derivatisation reactions of diphosphatetrahedrane **F** and possibly other phosphatetrahedranes are conceivable. These investigations may uncover additional unusual organophosphorus compounds and identify potential applications as ligands in catalytically active transition metal complexes.[33]

4.4 Supporting Information

General: All reactions and product manipulations were carried out in flame-dried glassware under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques (maintained at <0.1 ppm H_2O and <0.1 ppm O_2). (*t*BuCP)$_2$ (**F**),[10] Mes*O· (Mes* = 2,4,6-tri-*tert*-butylphenyl),[34] and (*t*BuCP)$_4$ (**I**)[21] were prepared according to procedures previously reported in the chemical literature. $LiAlH_4$ was purified by extraction with diethylether. All other chemicals were purchased from commercial suppliers and used without further purification. All reactions with **F** were performed in the dark, e.g. by wrapping flasks in aluminium foil. Solvents were dried and degassed with a MBraun SPS800solvent purification system. All dry solvents except *n*-hexane were stored under argon over activated 3 Å molecular sieves in gas-tight ampules. *n*-Hexane was stored over a potassium mirror. $LiAlH_4$ was kindly provided by Robert Szlosek (group of Manfred Scheer, Universität Regensburg).

NMR spectroscopy: NMR spectra were recorded on Bruker Avance 400 and 500 spectrometers except for the ^{1}H and ^{13}C{^{1}H} NMR spectra of **1**, which were recorded on a Bruker Avance III 600 HD spectrometer with a 5 mm TCI cryo probe. All spectra were recorded at 300 K and internally referenced to residual solvent resonances (^{1}H NMR: C_6D_6: 7.16 ppm, ^{13}C{^{1}H} NMR: C_6D_6: 128.06 ppm). Chemical shifts (δ) are given in ppm referring to external standards of tetramethylsilane (^{1}H, ^{13}C{^{1}H}), 85% phosphorus acid (^{31}P{^{1}H}) and Me_2Se (^{77}Se{^{1}H}). ^{13}C NMR signals were assigned based on 2D NMR spectra (^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC).

For compound **2** and **4**, the ^{31}P{^{1}H} NMR spectrum was transferred to the software gNMR by Cherwell Scientific.[35] The full line shape iteration procedure of gNMR was applied to obtain the best match of the fitted to the experimental spectrum. $^1J(^{31}P^{31}P)$ coupling constants were set to negative values and all other signs of the coupling constants were obtained accordingly. The designation of the spin system was performed by convention.

Elemental analysis: The elemental analysis was determined by the analytical department of the University of Regensburg with a Micro Vario Cube (Elementar).

UV-Vis spectroscopy: The UV/Vis absorption spectrum was recorded on an Ocean Optics Flame Spectrometer with the corresponding light source (DH-2000-BAL/UV-Vis-NIR light source).

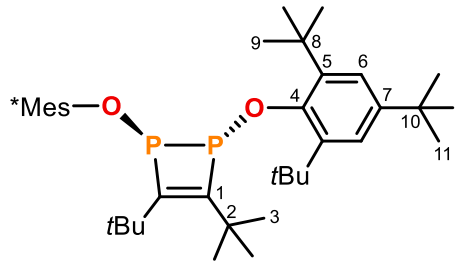
Mass spectrometry: Mass spectra were recorded on a Jeol AccuTOF GCX device by the analytical department of the University of Regensburg.

4.4.1 Synthesis of Compounds

(*t*BuCPOMes*)$_2$ (1):

The deep blue solution of Mes*O· (318 mg (containing 39% w/w Mes*OH as impurity), 0.74 mmol (Mes*O·), 2.0 eq.) in toluene (3.5 mL) was cooled to −80 °C and a solution of (*t*BuCP)$_2$ (**F**, 1.3 mL, 0.28 mol/L in toluene, 0.38 mmol, 1.0 eq.) was added under exclusion of light. The mixture was left to slowly warm to room temperature whilst stirring overnight. All volatiles were removed *in vacuo* from the light blue solution, and ^{31}P NMR spectroscopy revealed the formation of **1** (Figure S1). Since the side products and **1** have similar solubilities, extensive washing with acetonitrile (14 x 1 mL) was necessary, which negatively affected the final yield. The residue was taken up in toluene (0.5 mL) and left to crystallise at −30 °C for 14 days. The product was obtained as colourless crystals.

Single crystals suitable for X-ray analysis were obtained as colourless plates from a concentrated solution in *n*-hexane at ambient temperature.



$C_{46}H_{76}O_2P_2$, MW = 723.06 g/mol

Yield: 4.9 mg (0.0068 mmol, 1.8%).

^{1}H NMR (600 MHz, 300 K, C_6D_6): δ = 1.36 (s, 18H, HC^9), 1.41 (s, 18H, HC^{11}), 1.49 (s, 18H, HC^3), 1.54 (s, 18H, HC^9), 7.28 (s, 4H, H^6) ppm.

^{13}C{^{1}H} NMR (151 MHz, 300 K, C_6D_6): δ = 31.8 (s, 6C, C^9), 32.0 (s, 6C, C^{11}), 32.0 (s, 6C, C^3), 33.2 (s, 6C, C^9), 34.7 (s, 2C, C^{10}), 35.9 (s, 2C, C^8), 36.3 (s, 2C, C^8), 36.9 (t, *J* = 7.4 Hz, 2C, C^2), 122.8 (s, 2C, C^6), 124.8 (s, 2C, C^6), 140.7 (s, 2C, C^5), 141.3 (s, 2C, C^5), 143.3 (s, 2C, C^7), 150.3 (s, 2C, C^4), 159.1 (s, 2C, C^1) ppm.

^{31}P{^{1}H} NMR (202 MHz, 300 K, C_6D_6): δ = 57.8 (s, 2P) ppm.

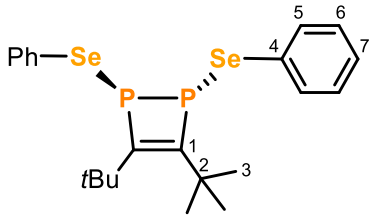
HRMS (FD-MS, toluene): m/z (%) = 722.5315 (100%) (*t*BuCPOMes*)$_2^+$ (M^+), 461.3311 (11%) [(*t*BuCP)$_2$OMes*]$^+$.

(*t*BuCPSePh)$_2$ (2):

A yellow solution of (PhSe)$_2$ (62 mg, 0.2 mmol, 1.0 eq.) in toluene (2 mL) was cooled to −80 °C and a solution of (*t*BuCP)$_2$ (**F**, 0.28 mL, 0.71 mol/L in toluene, 0.2 mmol, 1.0 eq.) was added under exclusion of light. The mixture was left to warm to room temperature whilst stirring overnight. All volatiles were removed *in vacuo*, and the resulting residue was washed with

n-hexane (3 x 0.3 mL and 3 x 0.5 mL) until the washing solution was colourless. The product was obtained as a white powder after drying under vacuum.

Single crystals suitable for X-ray analysis were obtained as colourless plates from a concentrated solution in *n*-hexane at ambient temperature.



$C_{22}H_{28}P_2Se_2$, MW = 512.36 g/mol

Yield: 40.9 mg (0.079 mmol, 40%).

^{1}H NMR (400 MHz, 300 K, C_6D_6): δ = 1.24 (s, 18H, HC^3), 6.93-6.97 (m, 6H, $H^{6,7}$), 7.64-7.67 (m, 4H, H^5) ppm.

^{13}C{^{1}H} NMR (100 MHz, 300 K, C_6D_6): δ = 31.4 (t, *J* = 4.0 Hz, 6C, C^3), 38.3 (t, *J* = 7.7 Hz, 2C, C^2), 127.5 (s, 2C, C^7), 129.4 (s, 4C, C^6), 130.8 (t, *J* = 8.6 Hz, 2C, C^4), 134.1 (t, *J* = 2.8 Hz, 4C, C^5), 158.3 (t, *J* = 4.3 Hz, 6C, C^1) ppm.

^{31}P{^{1}H} NMR (162 MHz, 300 K, C_6D_6): (AA'XX' spin system; X = Se) δ = −15.4 ppm ($^1J_{AA'}$ = −79.9 Hz, $^1J_{AX}$ = $^1J_{A'X'}$ = −210.0 Hz, $^2J_{A'X}$ = $^2J_{AX'}$ = 68.9 Hz).

^{77}Se{^{1}H} NMR (76 MHz, 300 K, C_6D_6): (AA'XX' spin system; X = P) δ = 302.9 ppm ($^1J_{AX}$ = $^1J_{A'X'}$ = −210.0 Hz, $^2J_{A'X}$ = $^2J_{AX'}$ = 68.9 Hz).

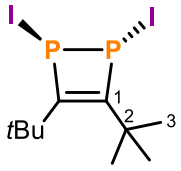
Coupling constants and chemical shifts are taken from the simulation (Figure S5, Figure S6 and Table S1).

Elemental Analysis calcd. C 51.57, H 5.51; found C 51.73, H 5.51.

UV-Vis: (*n*-hexane, λ_{max} [nm], ε_{max} [L·mol^{-1}·cm^{-1}]): 230sh (26 000), 240 (30 000).

(*t*BuCPI)$_2$ (3):

A purple solution of iodine (150 mg, 0.59 mmol, 1.2 eq.) in 5 mL toluene was cooled to −80 °C, and a solution of (*t*BuCP)$_2$ (**F**, 1.8 mL, 0.28 mol/L in toluene, 0.49 mmol, 1.0 eq.) was added under exclusion of light. The mixture turned yellow immediately and was left to warm to room temperature whilst stirring overnight. The volatiles were removed *in vacuo* to give the pure compound as a yellow solid.



$C_{10}H_{18}I_2P_2$, MW = 454.01 g/mol

Yield: 194 mg (0.42 mmol, 87%).

The analytical data are similar to literature values.[22]

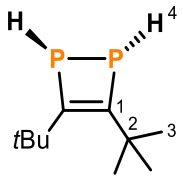
^{1}H NMR (500 MHz, 300 K, C_6D_6): δ = 1.11 (s, 18H) ppm.

^{13}C{^{1}H} NMR (126 MHz, 300 K, C_6D_6): δ = 30.1 (t, *J* = 4.4 Hz, 6C, C^3), 39.4 (t, *J* = 5.5 Hz, 2C, C^2), 153.5 (dd, *J* = 10.2 Hz, *J* = 11.9 Hz, 2C, C^1) ppm.

^{31}P{^{1}H} NMR (202 MHz, 300 K, C_6D_6): δ = −21.6 (s, 2P) ppm.

(*t*BuCPH)$_2$ (4):

A yellow solution of **3** (128 mg, 0.282 mmol, 1.0 eq.) in 10 mL Et_2O was cooled to −80 °C, and a solution of $LiAlH_4$ (64 mg, 1.69 mmol, 6.0 eq.) in Et_2O (20 mL) was added. The mixture turned colourless immediately and was left to warm to room temperature whilst stirring overnight. The volatiles were removed *in vacuo*. The product was isolated as a colourless oil by condensation into a receiving flask cooled with liquid N_2 (slowly heating up, 10 min at each temperature: room temperature, 40 °C, 60 °C, 80 °C, 10^{-3} bar).



$C_{10}H_{20}P_2$, MW = 202.22 g/mol

Yield: 34 mg (0.168 mmol, 60%).

^{1}H NMR (500 MHz, 300 K, C_6D_6): δ = 1.09 (s, 18 H, HC^3), 3.95 (AA'XX' spin system, $^1J_{AX} = {}^1J_{A'X'} = 162.4$ Hz, $^2J_{A'X} = {}^2J_{AX'} = 5.7$ Hz, $^3J_{AA'} = 3.9$ Hz, 2 H^4, HP) ppm.

^{13}C{^{1}H} NMR (126 MHz, 300 K, C_6D_6): δ = 30.4 (t, *J* = 3.5 Hz, 6C, C^3), 37.2 (t, *J* = 8.0 Hz, 2C, C^2), 153.5 (dd, *J* = 16.9 Hz, *J* = 21.9 Hz, 2C, C^1) ppm.

^{31}P{^{1}H} NMR (202 MHz, 300 K, C_6D_6): δ = −144.1 (s) ppm.

^{31}P NMR (202 MHz, 300 K, C_6D_6): (AA'XX' spin system) δ = −144.1 ppm ($^1J_{AX} = {}^1J_{A'X'} = 162.4$ Hz, $^1J_{XX'} = -14.1$ Hz, $^2J_{A'X} = {}^2J_{AX'} = 5.7$ Hz).

Coupling constants and chemical shifts are taken from the simulation (Figure S14, Figure S15 and Table S2.

HRMS (EI, *n*-hexane): m/z (%) = 202.1032 (50%) (*t*BuCPH)$_2^+$ (M^+), 113.0517 (38%) (*t*BuC$_2$PH)$^+$, 81.0704 (36%) (*t*BuC$_2$)$^+$, 57.0712 (100%) (*t*Bu)$^+$, 41.0393 (48%) (C_3H_5)$^+$ (and more fragments with less intensity).

4.4.2 Additional Experiments

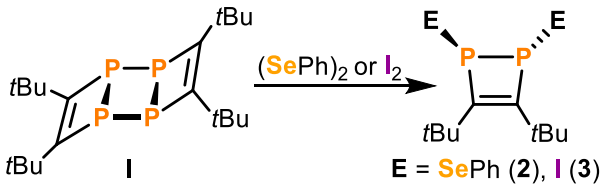
Reaction of (*t*BuCP)$_2$ (F) with (PhS)$_2$

To a solution of (PhS)$_2$ (22 mg, 0.1 mmol, 1.0 eq.) in toluene (0.5 mL) at −80 °C a solution of (*t*BuCP)$_2$ (**F**, 0.1 mL, 0.94 mol/L in toluene, 0.1 mmol, 1.0 eq.) was added. The reaction mixture was allowed to warm to room temperature while stirring overnight. Analysis by $^{31}P\{^1H\}$ NMR spectroscopy (see Figure S20) revealed signals of unreacted **F** and the ladderane **I**. Subsequently, the reaction mixture was irradiated (365 nm, 3 W, 2 h, Figure S21) or heated (60 °C for 4 h and 80 °C for 45 min, Figure S22). In each case, the reaction mixture was analysed by $^{31}P\{^1H\}$ NMR spectroscopy.

Reaction of (*t*BuCP)$_4$ (I) with Mes*O·

To a deep blue solution of Mes*O· (52 mg, 0.20 mmol, 4.0 eq.) in toluene (1 mL) at −80 °C, a solution of (*t*BuCP)$_4$ (**I**, 20 mg, 0.050 mmol, 1.0 eq.) in toluene (0.5 mL) was added. The colour of the reaction mixture changed to pale yellow after letting the mixture warm to room temperature whilst stirring for 10 days. The $^{31}P\{^1H\}$ NMR spectrum of the reaction solution (see Figure S23) shows only signals corresponding to unreacted **I**.

Reaction of (*t*BuCP)$_4$ (I) with (PhSe)$_2$ and I$_2$



Scheme S1. Reaction of **1** with (SePh)$_2$ and I$_2$ to generate **2** and **3**, respectively. Conditions: toluene, −80 °C.

Reaction of (*t*BuCP)$_4$ (I) with (PhSe)$_2$

To a solution of (PhSe)$_2$ (31 mg, 0.1 mmol, 2.0 eq.) in toluene (0.5 mL) at −80 °C a solution of (*t*BuCP)$_4$ (**I**, 20 mg, 0.05 mmol, 1.0 eq.) in toluene (0.5 mL) was added. After letting the reaction mixture warm to room temperature while stirring overnight, the mixture was analysed by $^{31}P\{^1H\}$ NMR spectroscopy (see Figure S24), revealing the selective formation of (*t*BuCPSePh)$_2$ (**2**).

Reaction of (*t*BuCP)$_4$ (I) with I$_2$

To the violet solution of I$_2$ (46 mg, 0.18 mmol, 2.0 eq.) in toluene (2 mL) at −80 °C (*t*BuCP)$_4$ (**I**, 37 mg, 0.091 mmol, 1.0 eq.) was added. The colour of the reaction mixture changed to orange. After letting the reaction mixture warm to room temperature while stirring overnight, the mixture was analysed by $^{31}P\{^1H\}$ NMR spectroscopy (see Figure S25). Subsequently, the volatiles were removed *in vacuo*, yielding (*t*BuCPI)$_2$ (**3**, 60 mg, 0.13 mmol, 73%).

Reaction of (*t*BuCPI)$_2$ (3) with KC$_8$

To a suspension of KC_8 (12 mg, 0.088 mmol, 2.0 eq.) in toluene (2 mL) at −80 °C a yellow solution of (*t*BuCPI)$_2$ (**3**, 20 mg, 0.044 mmol, 1.0 eq.) in toluene (2 mL) was added, leading to the immediate formation of a black solid (graphite). The reaction mixture was allowed to warm to room temperature while stirring overnight. Analysis by $^{31}P\{^1H\}$ NMR spectroscopy (see Figure S26) showed signals corresponding to unreacted **3** and the ladderane compound **I**. Addition of more KC_8 (additional 12 mg, 0.088 mmol, 2.0 eq.) in toluene (2 mL) at −80 °C led to a higher conversion to **I** as elucidated by $^{31}P\{^1H\}$ NMR spectroscopy (see Figure S27).

Reaction of (*t*BuCPH)$_2$ (4) with *t*BuLi

To a yellowish solution of (*t*BuCPH)$_2$ in THF (**5**, 1.0 mL, 0.016 mol/L, 0.016 mmol, 1.0 eq.) at −80 °C, a solution of *t*BuLi in *n*-hexane (1.1 mL, 0.028 mol/L, 0.032 mmol, 2.0 eq.) was added. The reaction mixture was allowed to warm to room temperature while stirring overnight. Analysis of the reaction mixture by ^{31}P NMR spectroscopy (see Figure S28) showed the formation of ladderane **I** as the main product.

4.4.3 NMR Spectra

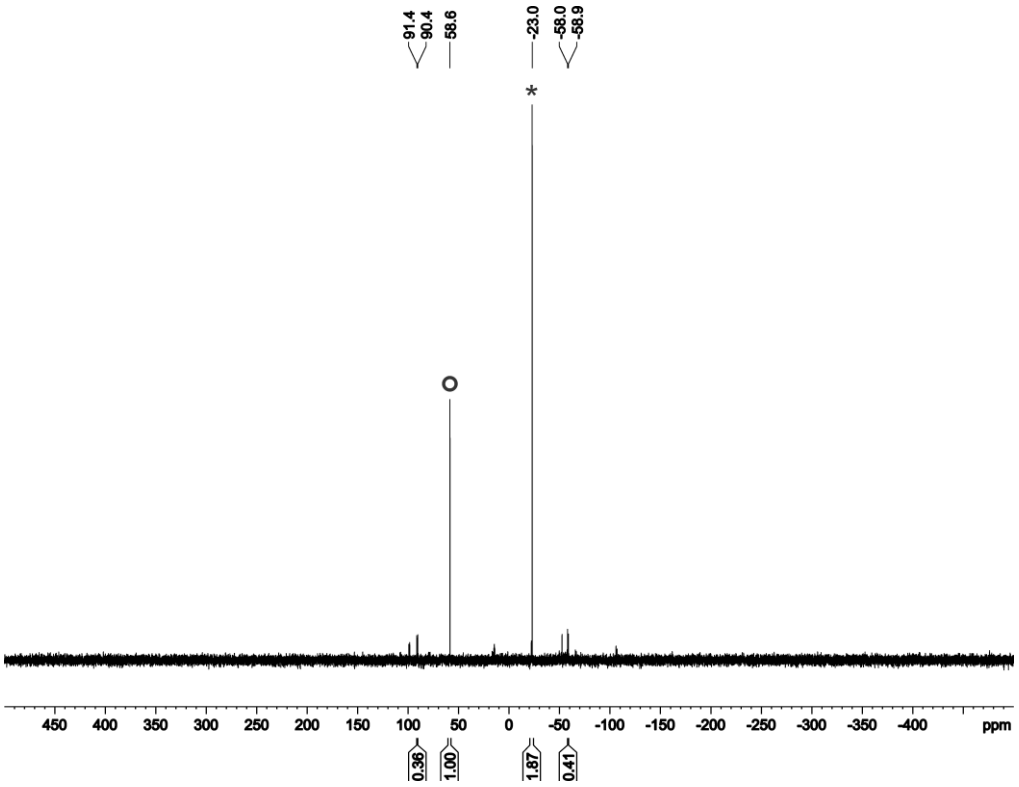


Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction mixture of Mes*O· and (*t*BuCP)$_2$ (**F**). (*t*BuCPOMes*)$_2$ (**1**, O). (*t*BuCP)$_4$ (**I**,*).

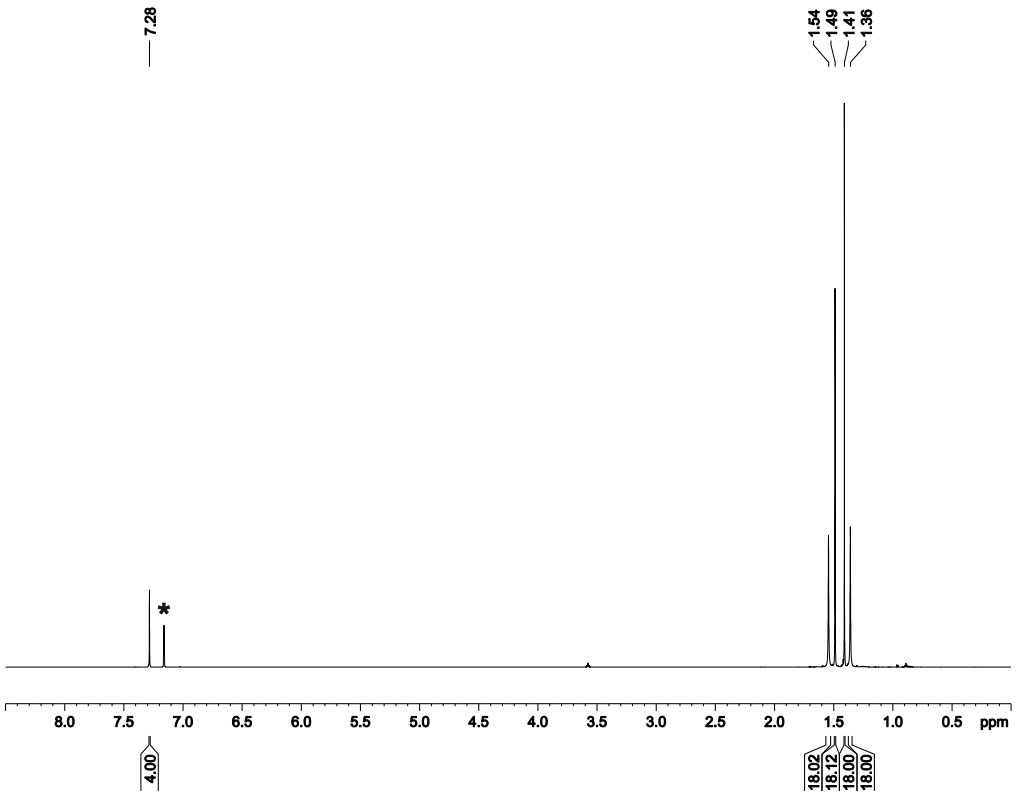


Figure S2. ^{1}H NMR spectrum (600 MHz, 300 K, C_6D_6) of **1**. *C_6D_5H.

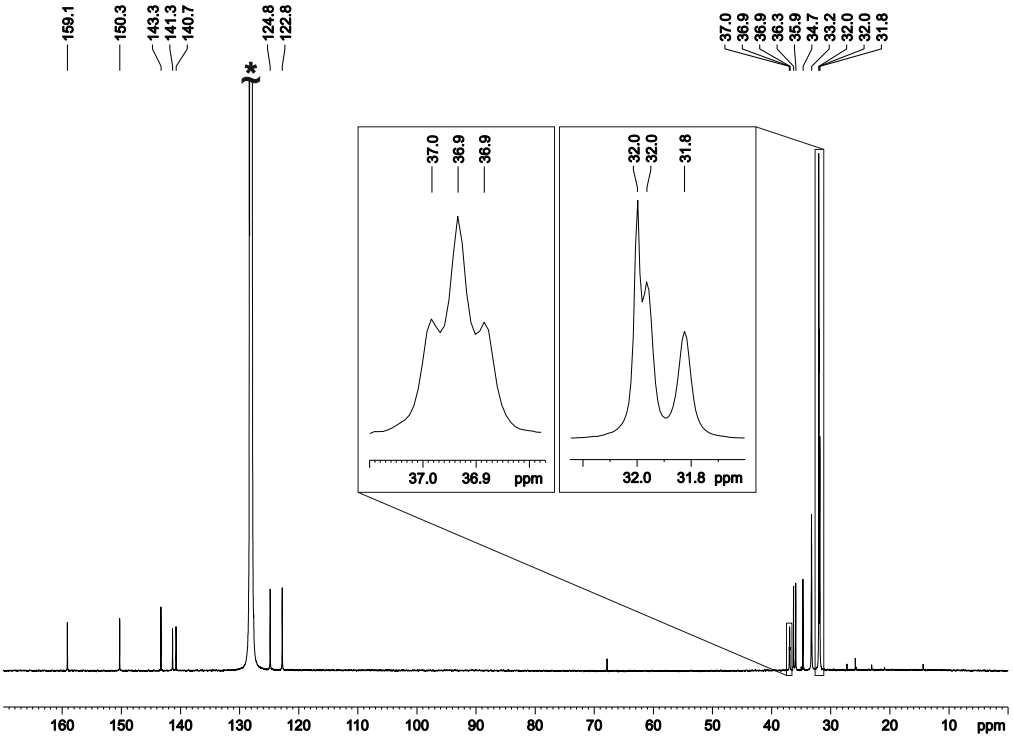


Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, 300 K, C_6D_6) of **1**. *C_6D_6.

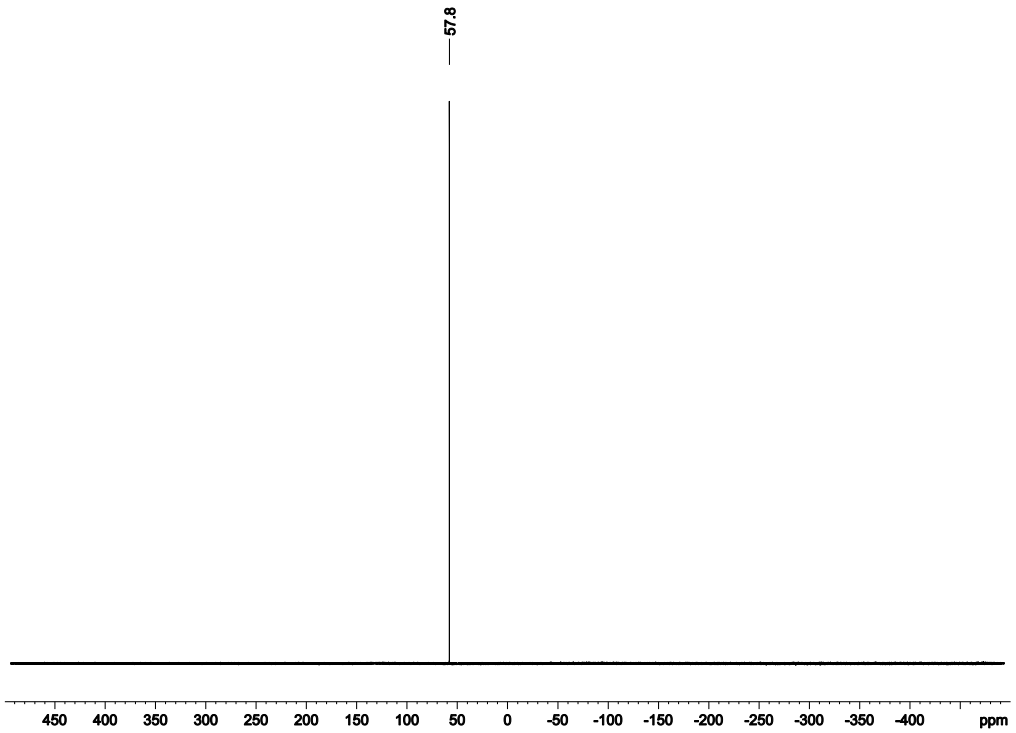


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of **1**.

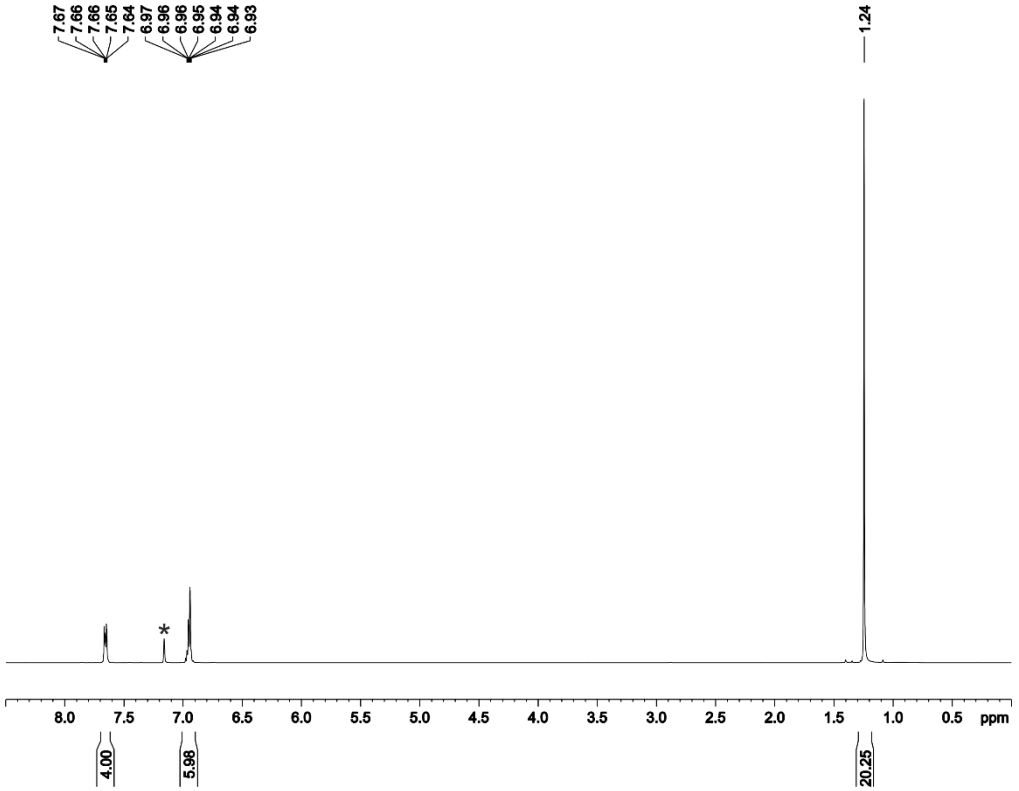


Figure S5. ^{1}H NMR spectrum (400 MHz, 300 K, C_6D_6) of **2**. *C_6D_5H.

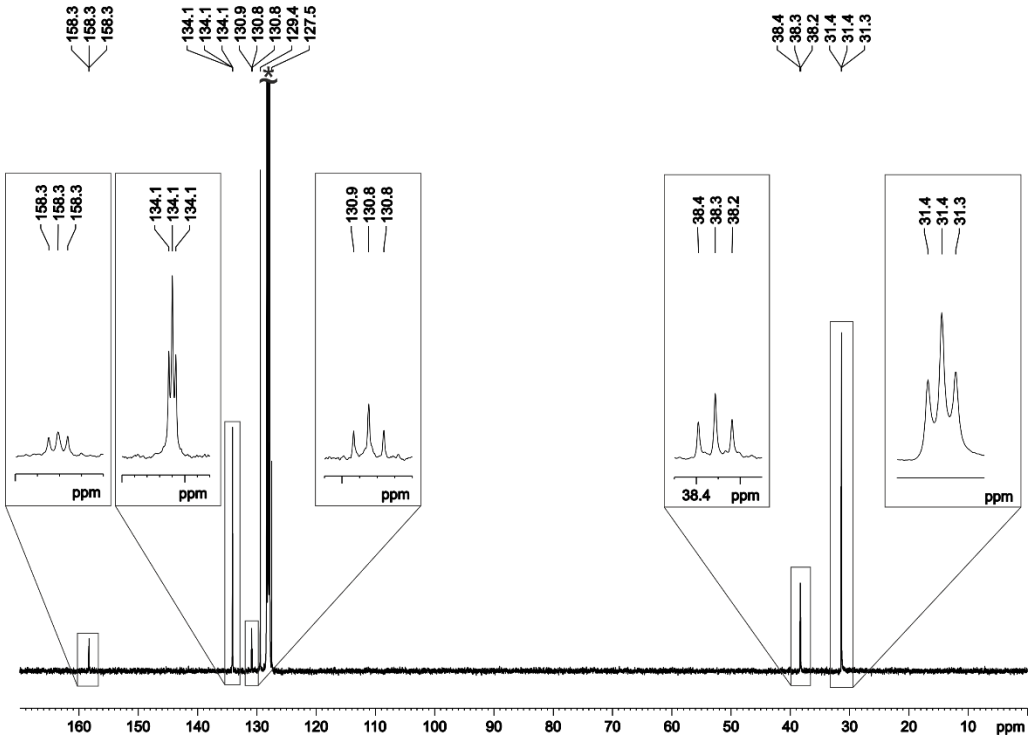


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, 300 K, C_6D_6) of **2**. *C_6D_6.

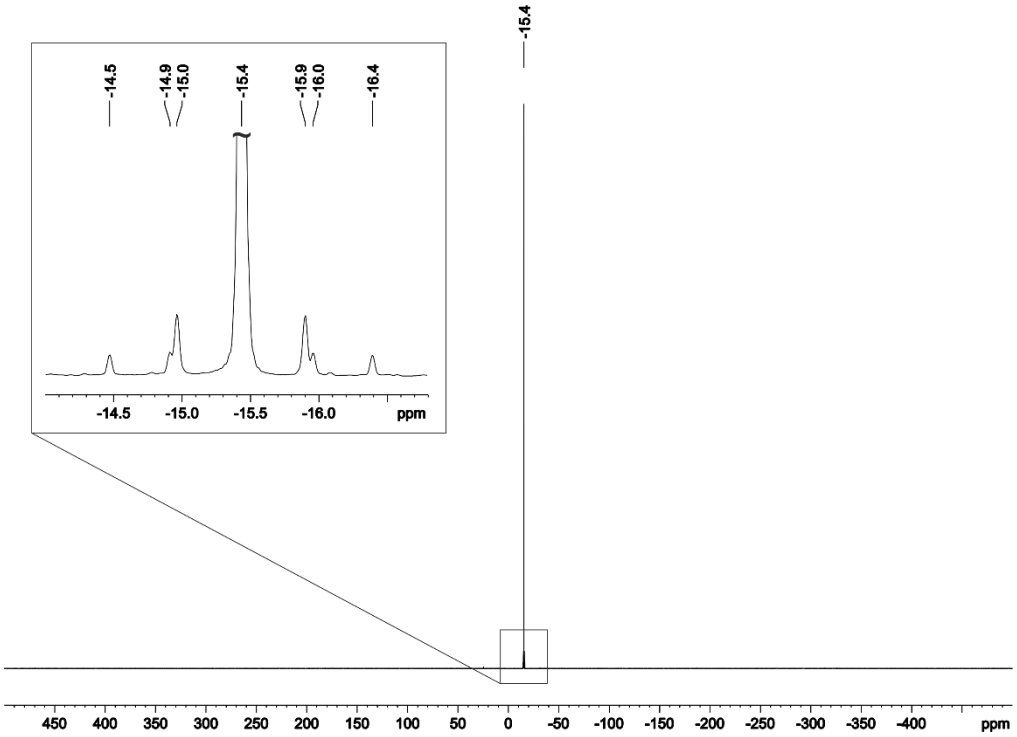


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **2**.

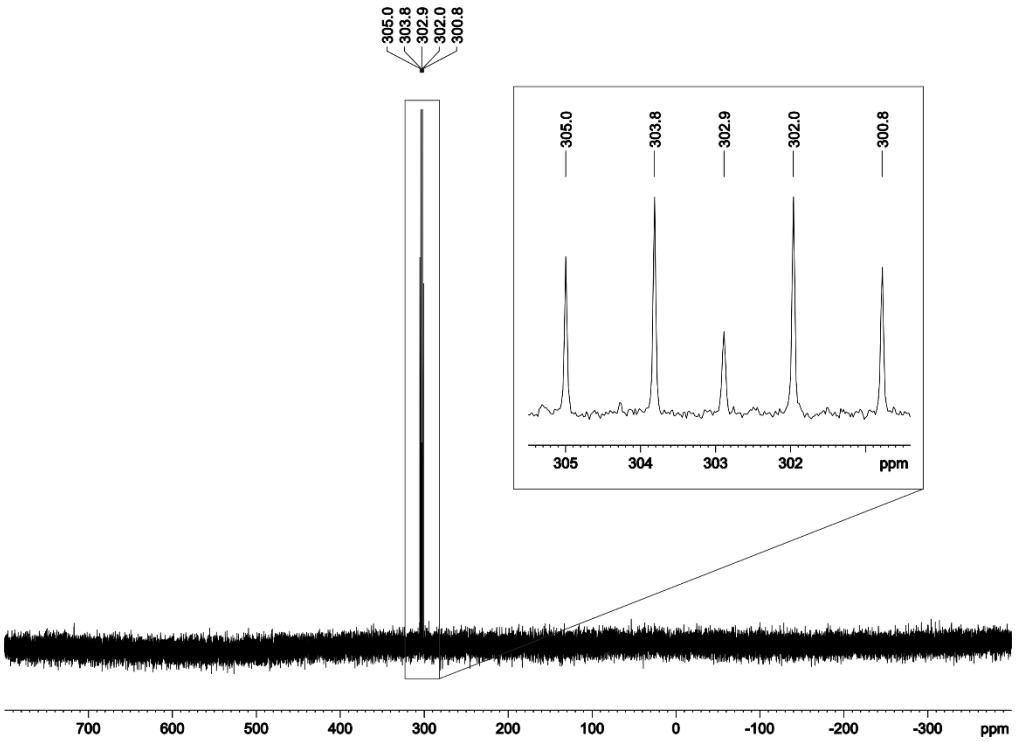


Figure S8. $^{77}Se\{^{1}H\}$ NMR spectrum (76 MHz, 300 K, C_6D_6) of **2**.

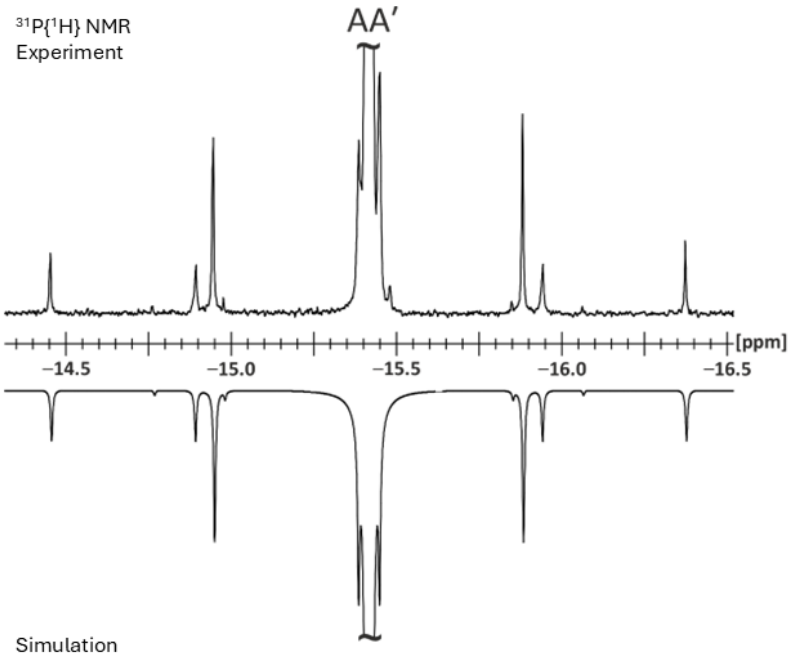


Figure S9. Section of the $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of **2**; experimental (upwards) and simulation (downwards).

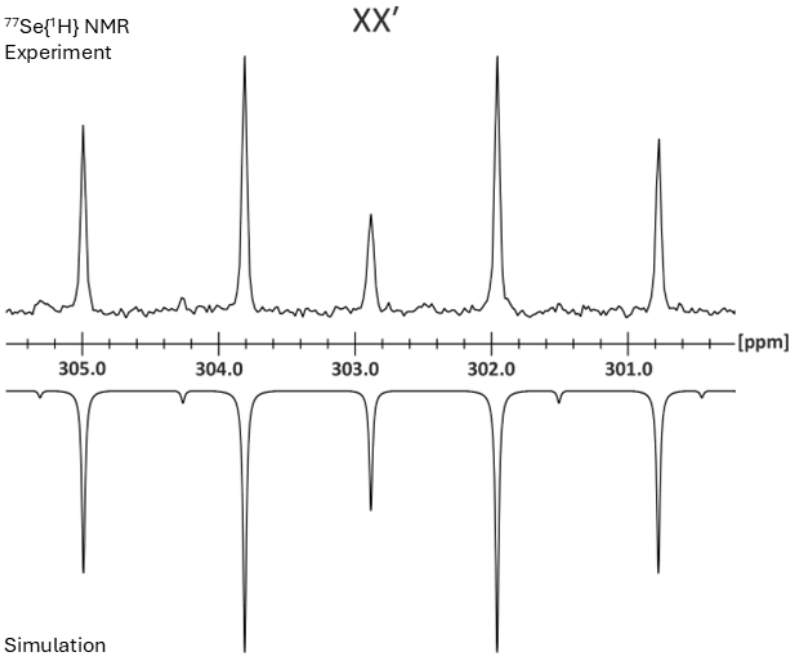


Figure S10. Section of the $^{77}Se\{^{1}H\}$ NMR spectrum (76 MHz, 300 K, C_6D_6) of **2**; experimental (upwards) and simulation (downwards).

Table S1. Coupling constants from the iterative fit of the AA′XX′ spin system and representation of **2**.

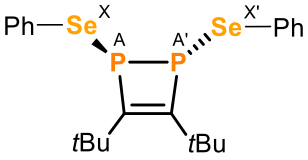
	$\delta(Se_{XX'})$ = 302.9 ppm $\delta(P_{AA'})$ = −15.4 ppm $^1J_{AX} = {}^1J_{A'X'}$ = −210.0 Hz $^1J_{AA'}$ = −79.9 Hz $^2J_{A'X} = {}^2J_{AX'}$ = 68.9 Hz $^3J_{XX'}$ = 0.0 Hz

Figure S11. ^{1}H NMR spectrum (500 MHz, 300 K, C_6D_6) of **3**. *C_6D_5H.

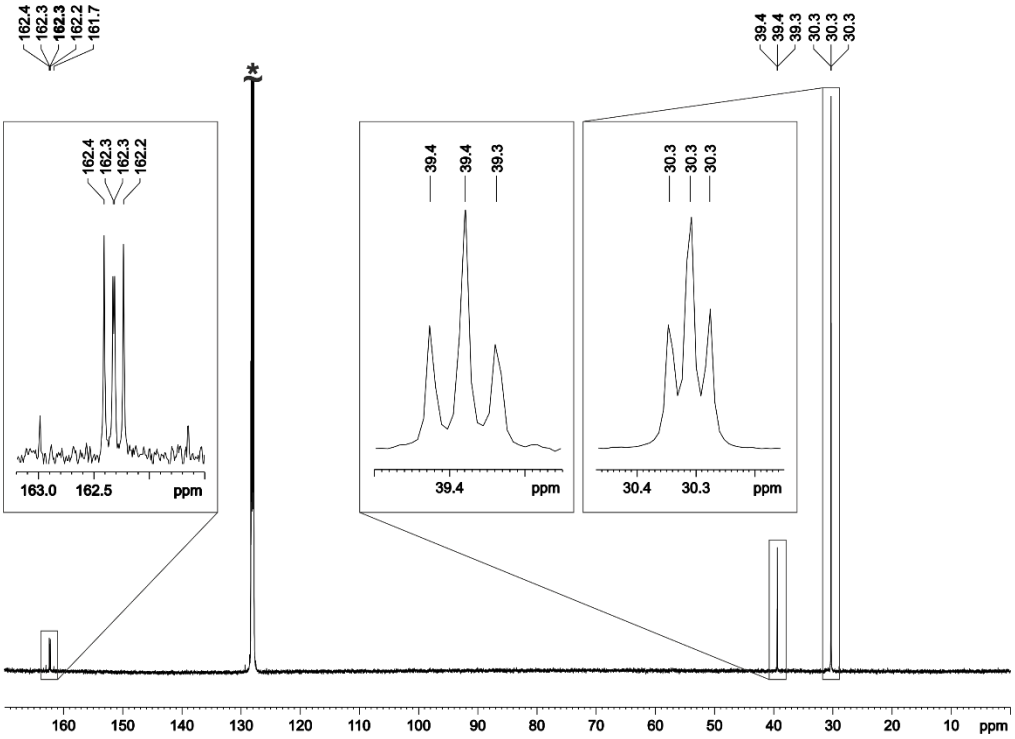


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, 300 K, C_6D_6) of **3**. *C_6D_6.

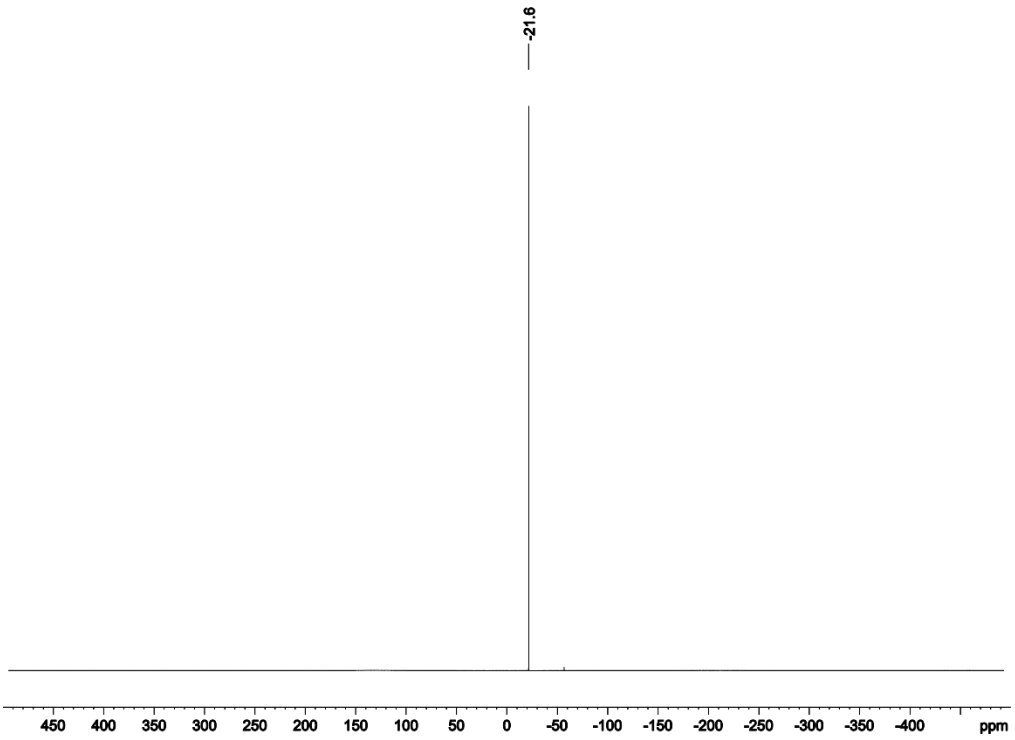


Figure S13. ^{31}P NMR spectrum (202 MHz, 300 K, C_6D_6) of **3**.

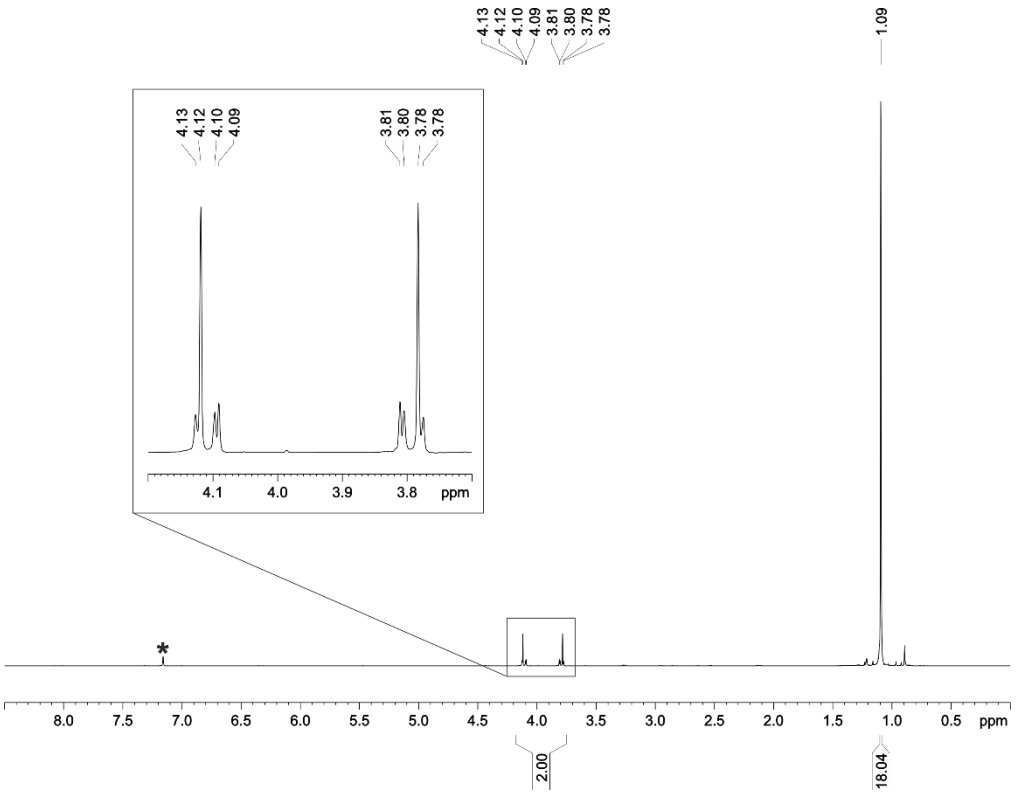


Figure S14. ^{1}H NMR spectrum (500 MHz, 300 K, C_6D_6) of **4**. *C_6D_5H.

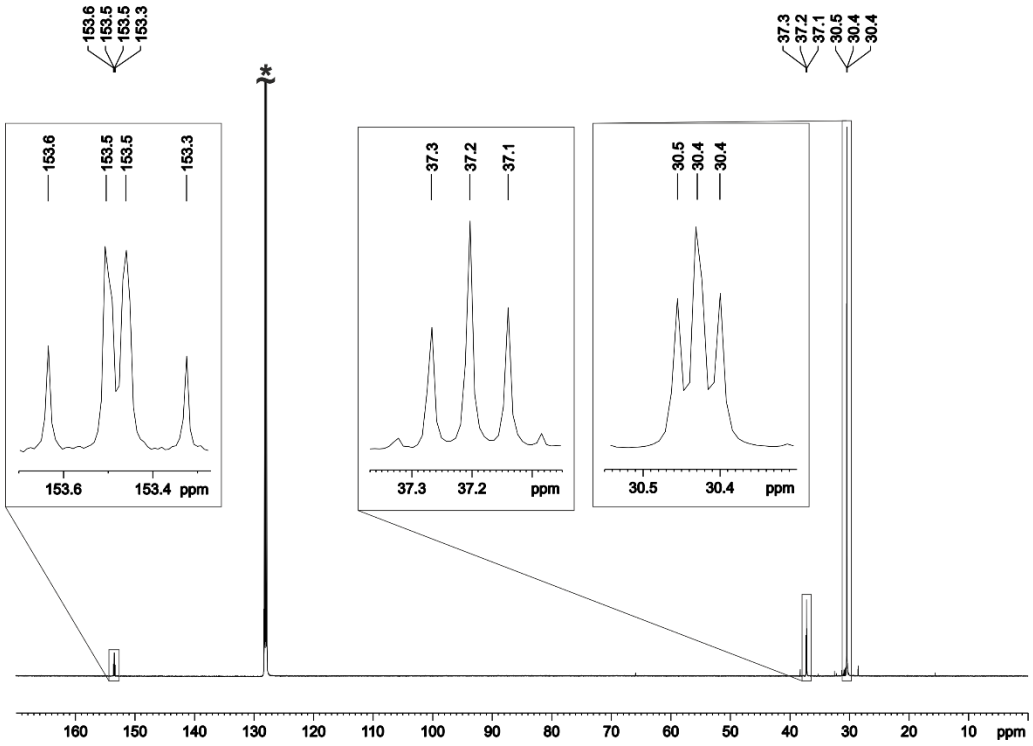


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, 300 K, C_6D_6) of **4**. *C_6D_6.

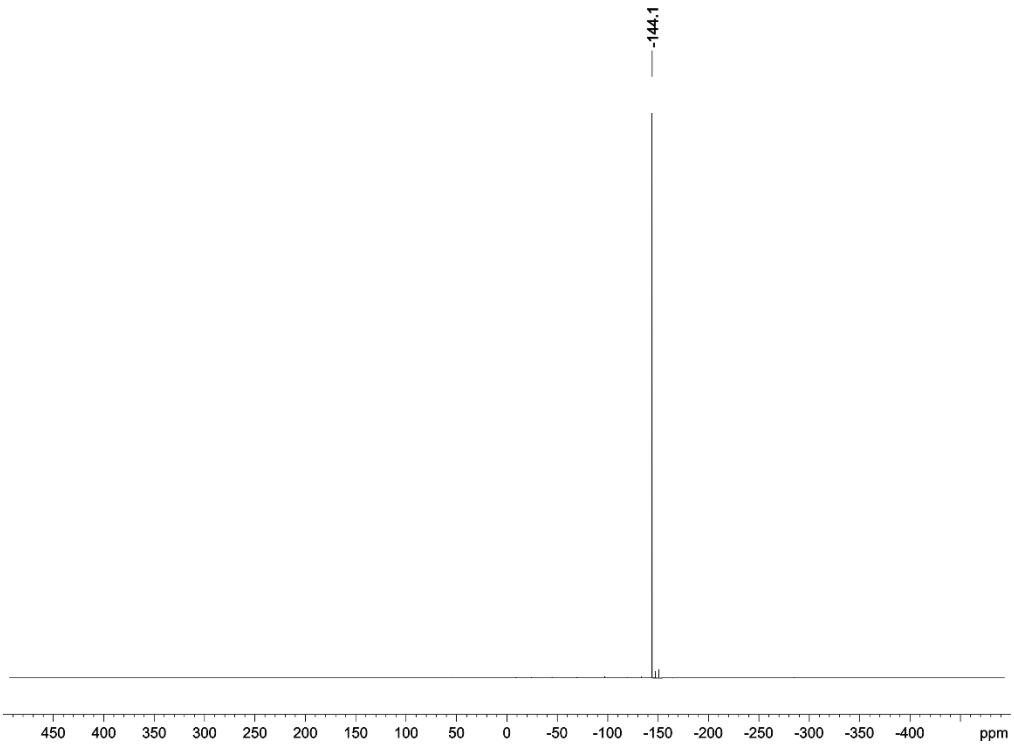


Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of **4**.

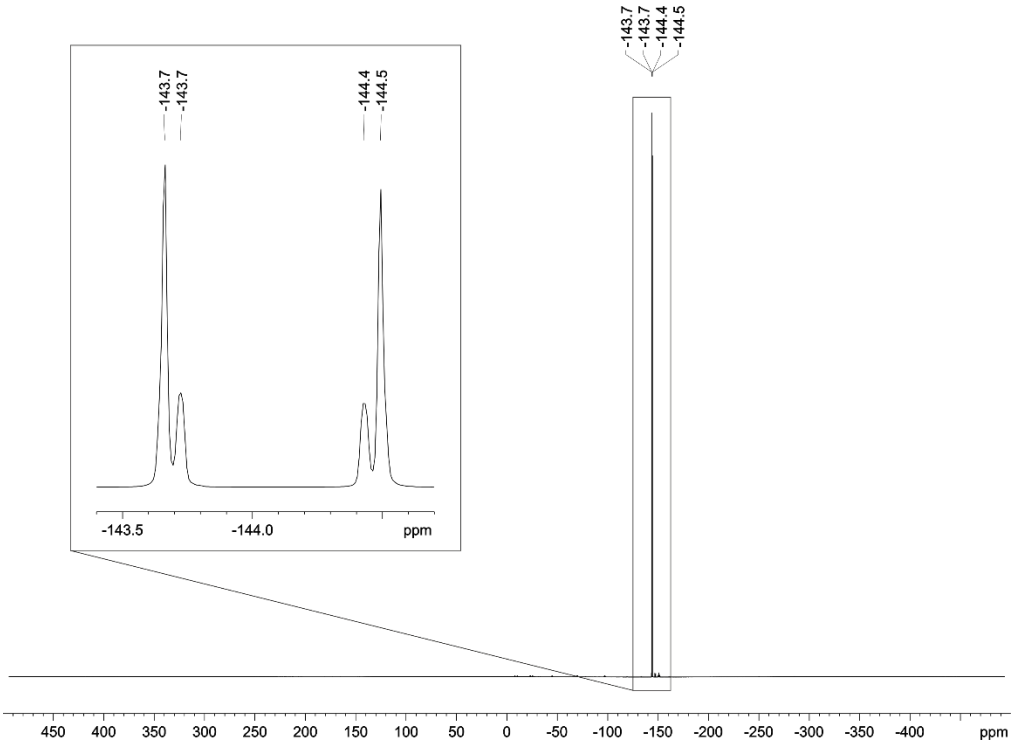


Figure S17. ^{31}P NMR spectrum (202 MHz, 300 K, C_6D_6) of **4**.

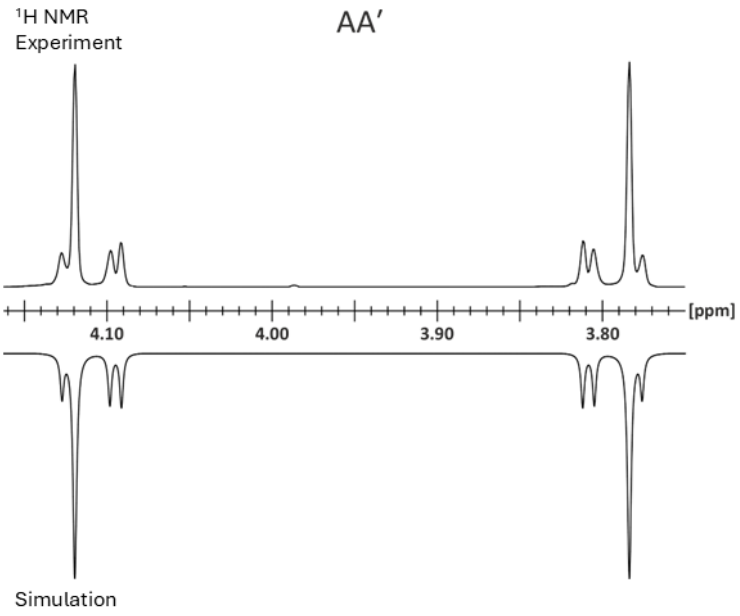


Figure S18. Section of the ^{1}H NMR spectrum (500 MHz, 300 K, C_6D_6) of **4**; experimental (upwards) and simulation (downwards).

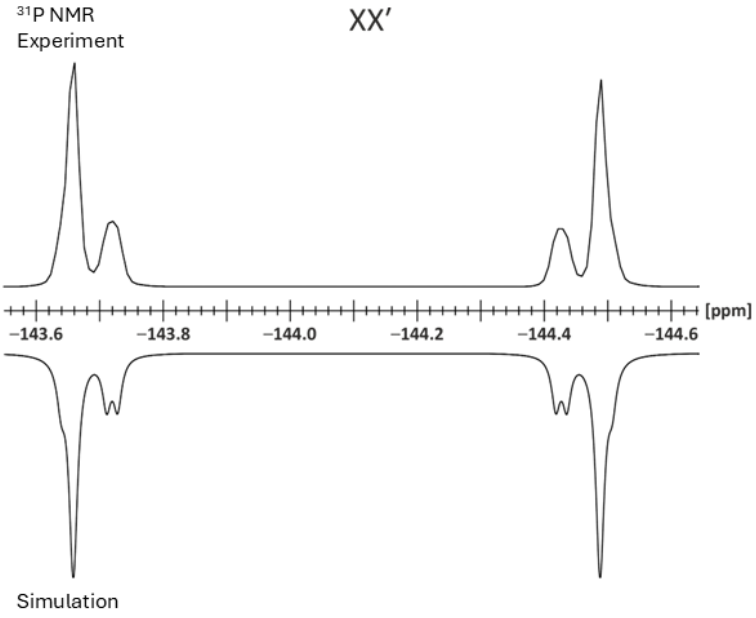
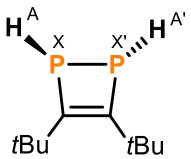


Figure S19. Section of the ^{31}P NMR spectrum (202 MHz, 300 K, C_6D_6) of **4**; experimental (upwards) and simulation (downwards).

Table S2. Coupling constants from the iterative fit of the AA′XX′ spin system and representation of **4**.

	$\delta(H_{AA'}) = 3.95$ ppm
	$\delta(P_{XX'}) = -144.1$ ppm
	$^1J_{AX} = {}^1J_{A'X'} = 162.4$ Hz
	$^1J_{XX'} = -14.1$ Hz
	$^2J_{A'X} = {}^2J_{AX'} = 5.7$ Hz
	$^3J_{AA'} = 3.9$ Hz

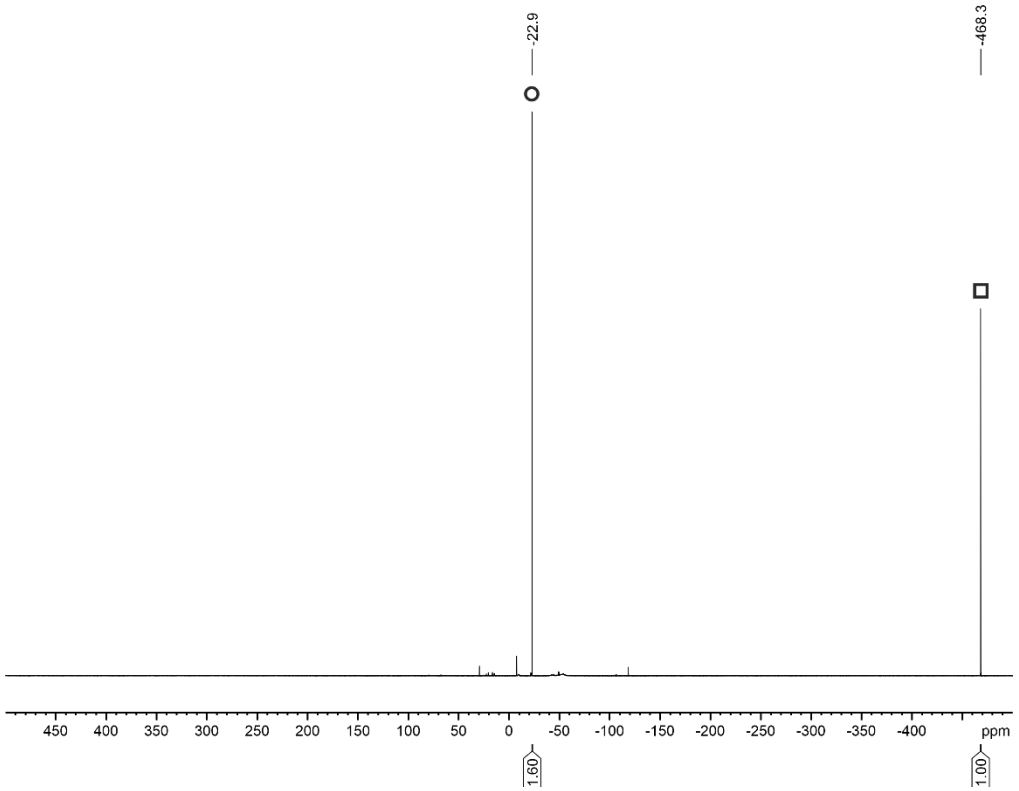


Figure S20. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, toluene with C_6D_6 capillary) of the reaction mixture of 1 eq. (tBuCP)$_2$ (**F**, □) with 1 eq. (PhS)$_2$. (tBuCP)$_4$ (**I**, ○).

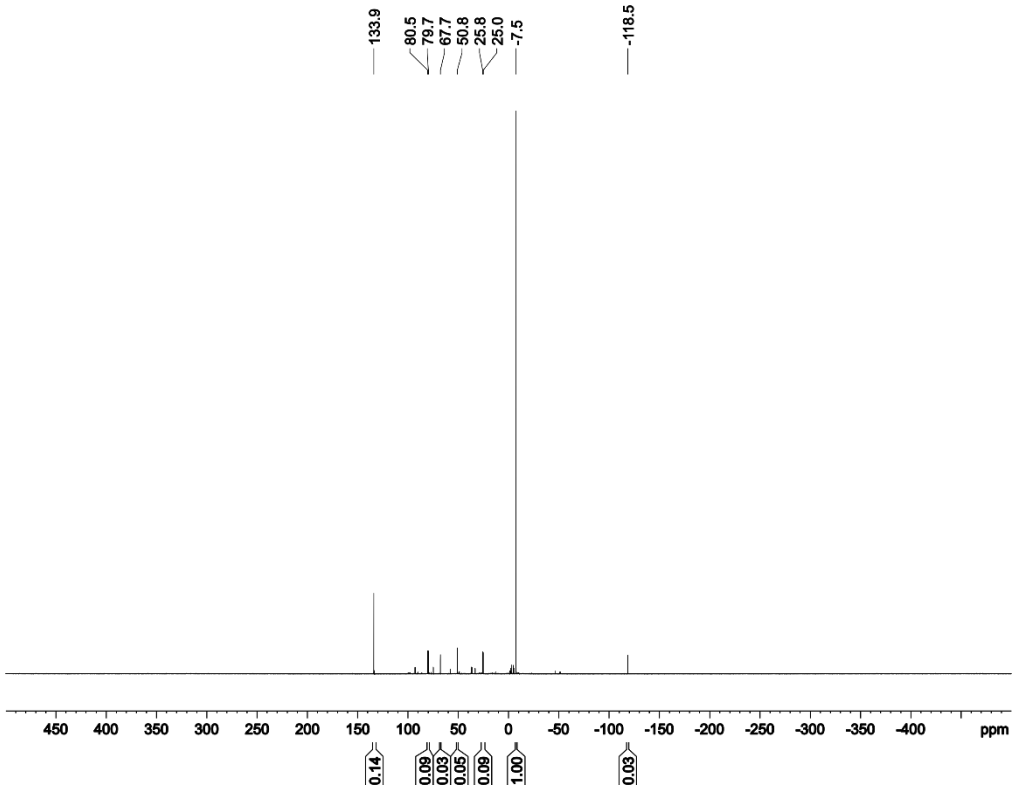


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, toluene with C_6D_6 capillary) of the reaction mixture of 1 eq. (tBuCP)$_2$ (**F**) with 1 eq. (PhS)$_2$ upon irradiation.

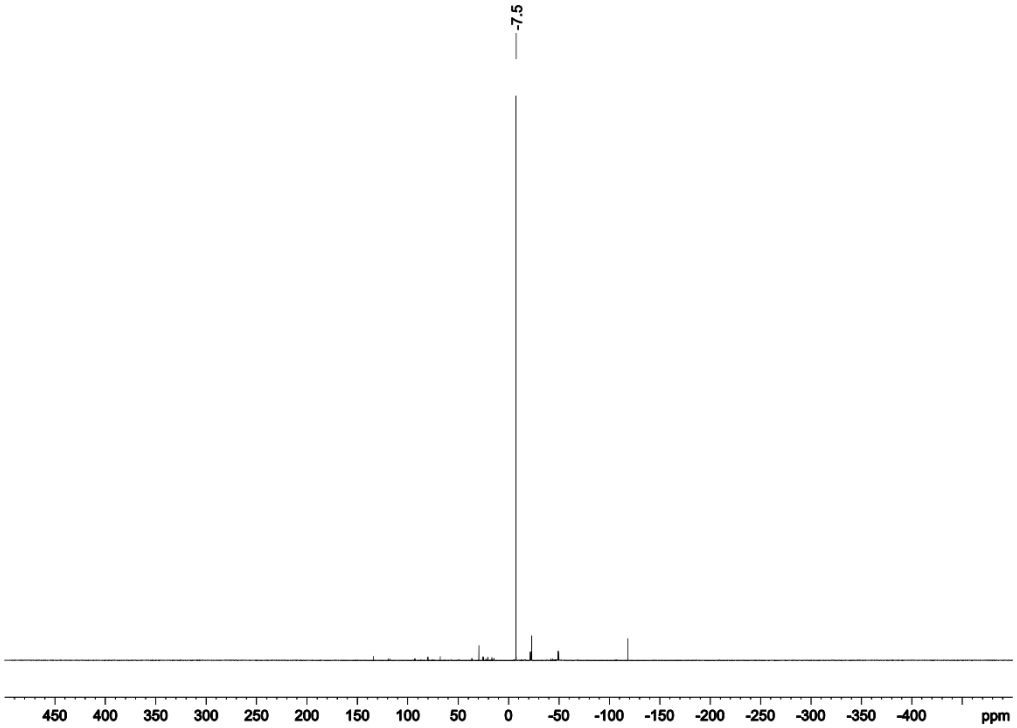


Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, toluene with C_6D_6 capillary) of the reaction mixture of 1 eq. (tBuCP)$_2$ (**F**) with 1 eq. (PhS)$_2$ upon heating for 4 h to 60 °C and 45 min to 80 °C.

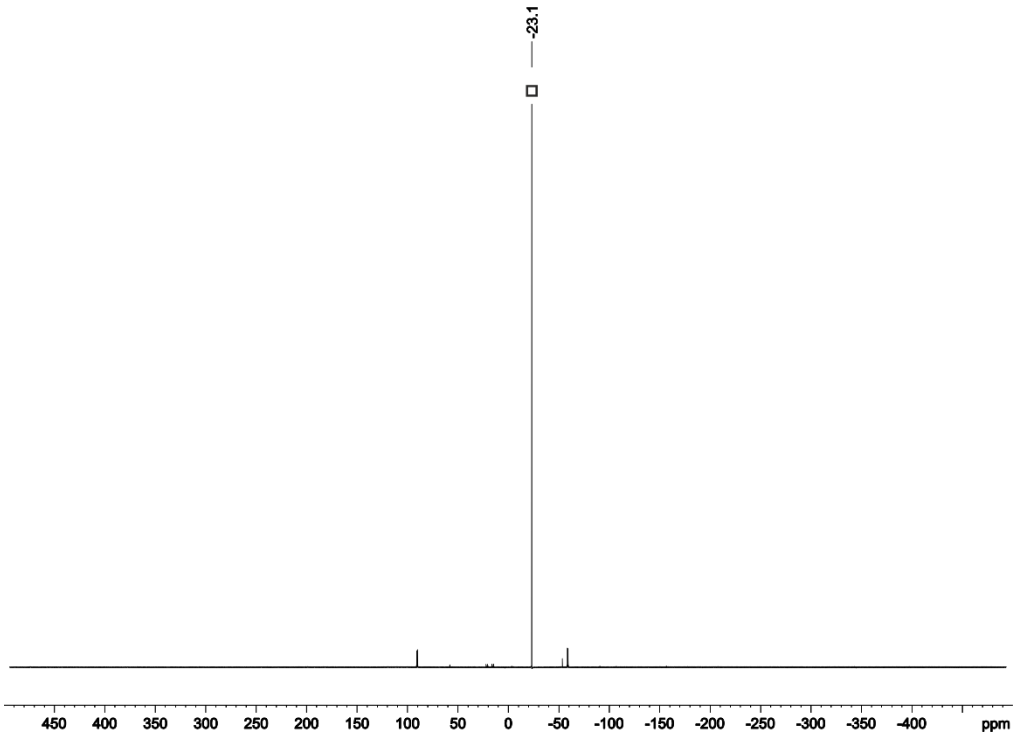


Figure S23. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, C_6D_6) of the reaction mixture of 1 eq. (tBuCP)$_4$ (**I**, □) with 4 eq. Mes*O·.

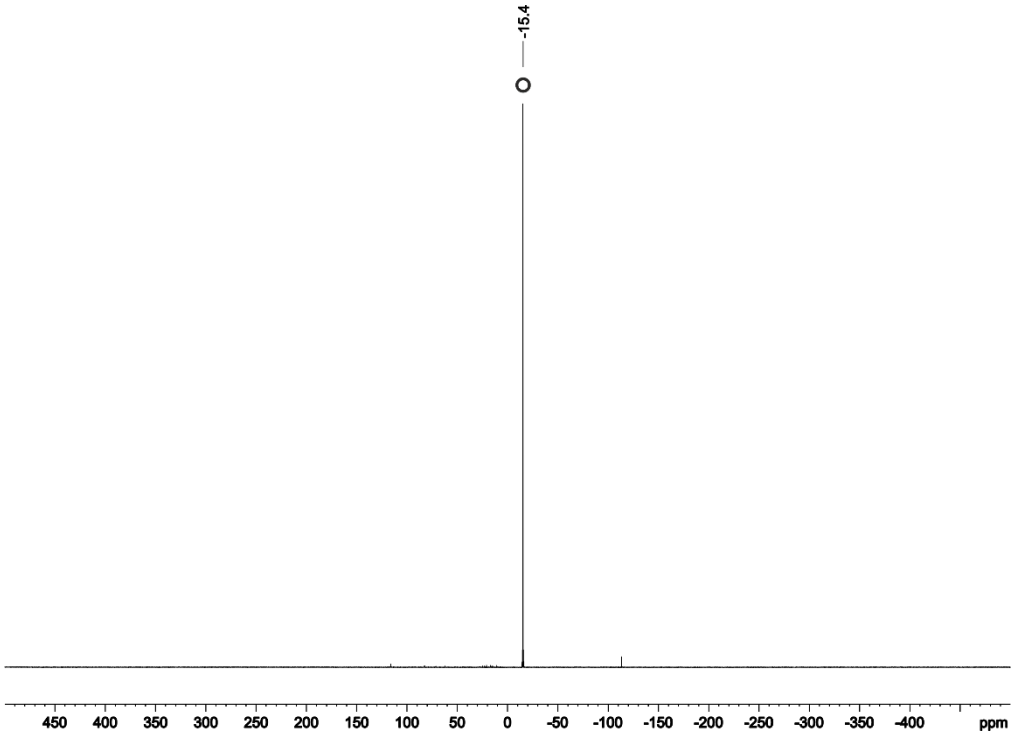


Figure S24. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, toluene with C_6D_6 capillary) of the reaction mixture of 1 eq. (tBuCP)$_4$ (**I**) with 2 eq. $(PhSe)_2$ forming (tBuCPSePh)$_2$ (**2**, ○).

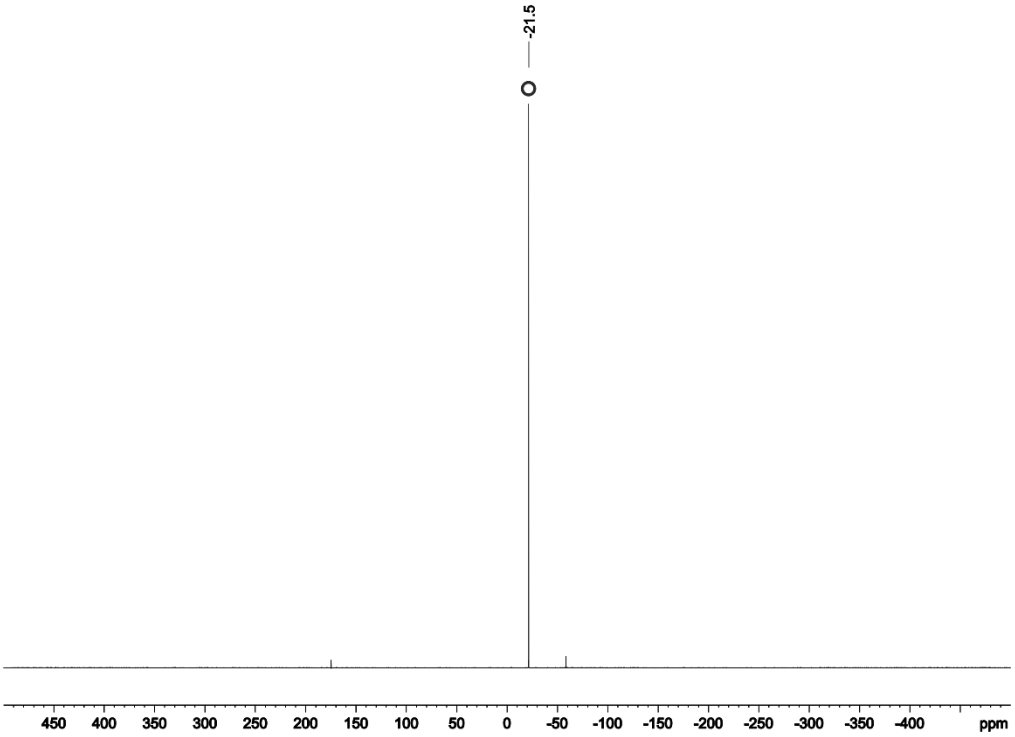


Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, toluene with C_6D_6 capillary) of the reaction mixture of 1 eq. (tBuCP)$_4$ (**I**) with 2 eq. I_2 forming (tBuCPI)$_2$ (**3**, ○).

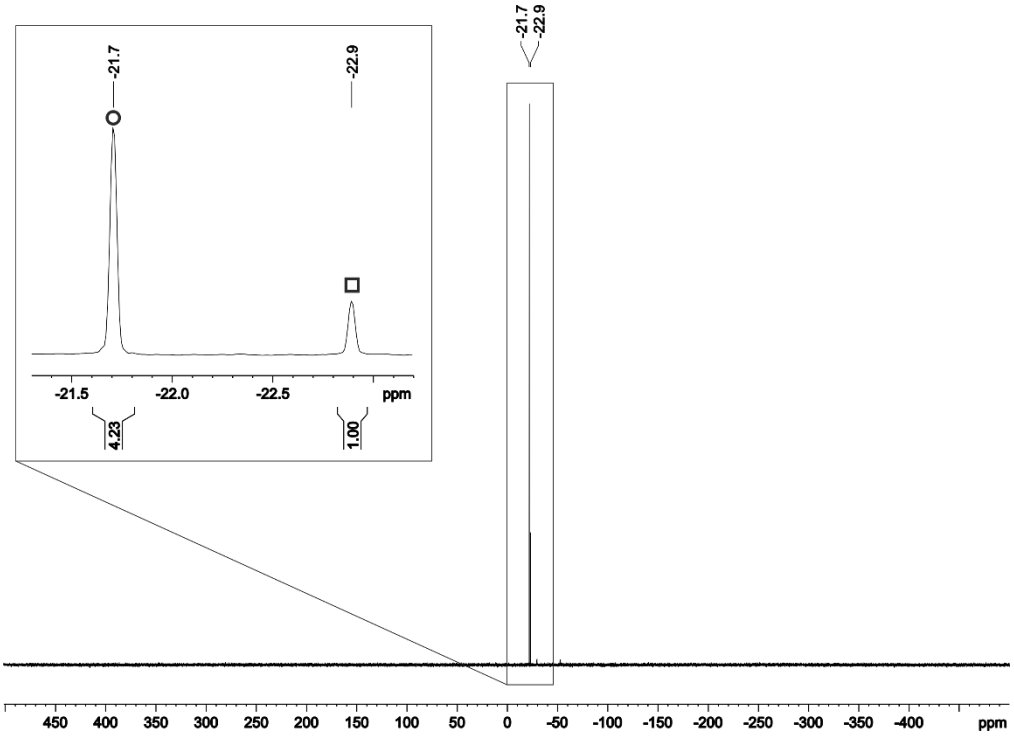


Figure S26. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, toluene with C_6D_6 capillary) of the reaction mixture of 1 eq. (*t*BuCPI)$_2$ (**3**, ○) with 2 eq. KC_8 forming (*t*BuCP)$_4$ (**I**, □).

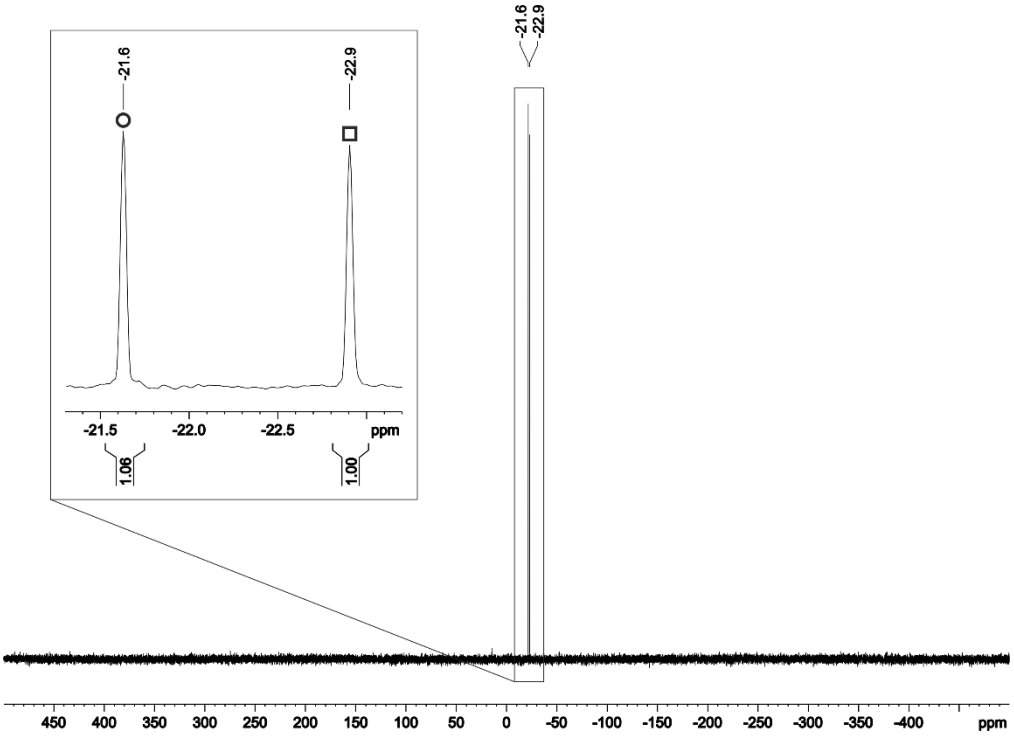


Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K, toluene with C_6D_6 capillary) of the reaction mixture of 1 eq. (*t*BuCPI)$_2$ (**3**, ○) with 4 eq. KC_8 forming (*t*BuCP)$_4$ (**I**, □).

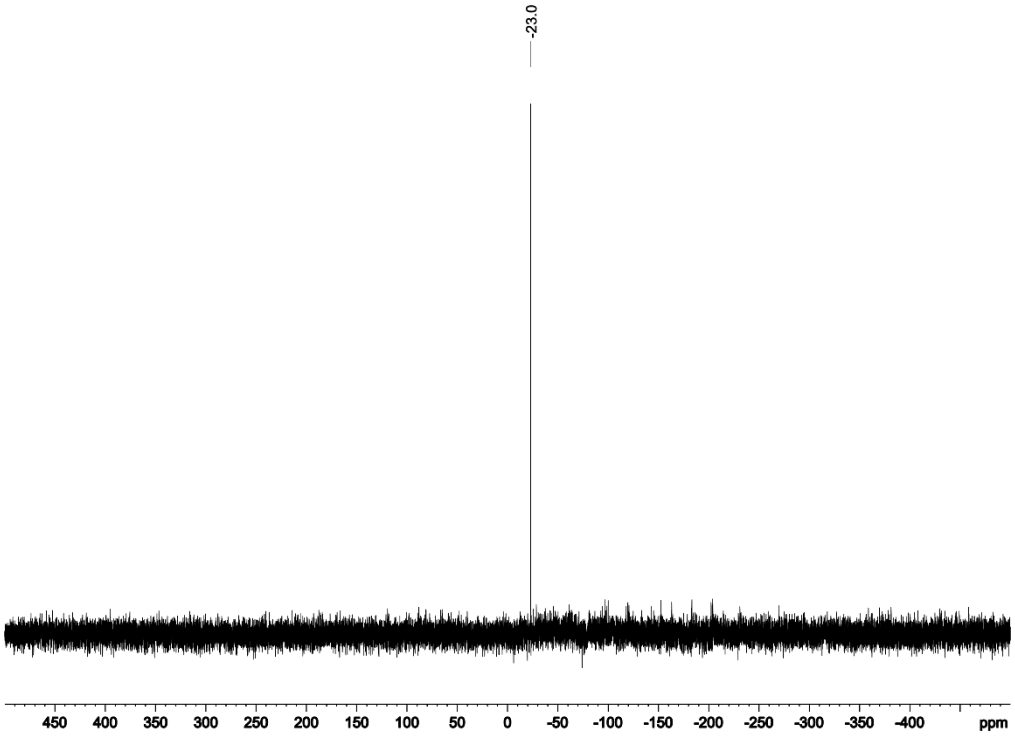


Figure S28. ^{31}P NMR spectrum (162 MHz, 300 K, THF/*n*-hexane with C_6D_6 capillary) of the reaction mixture of 1 eq. (*t*BuCPH)$_2$ (**4**) with 2 eq. *t*BuLi.

4.4.4 UV-Vis Spectrum

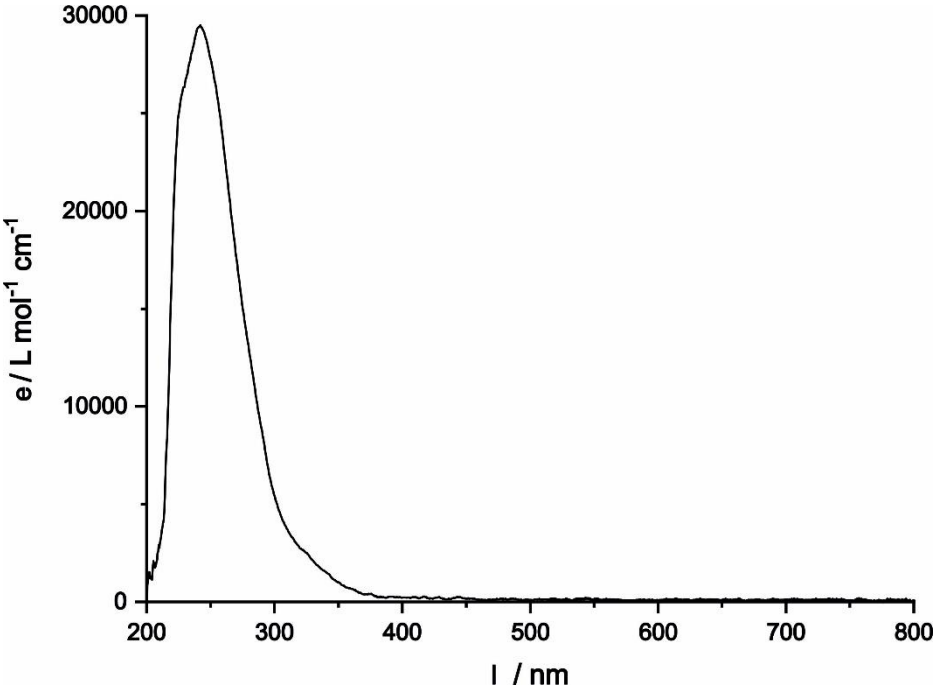


Figure S29. UV-Vis spectrum of **2** in *n*-hexane.

4.4.5 Single-Crystal X-ray Diffraction Data

The single-crystal X-ray diffraction data were recorded on Rigaku XtaLAB Synergy DW R (DW system, HyPix-Arc 150) or GV1000 Titan diffractometers with microfocus Cu-Kα radiation (λ = 1.54184 Å). Crystals were selected under mineral oil, mounted on micromount loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device. Either semi-empirical multi-scan absorption corrections[36] or analytical ones[37] were applied to the data. Using Olex2,[38] the structure was solved with the SHELXT[39] structure solution programme using Intrinsic Phasing and refined with the SHELXL[40] refinement package using Least Squares refinements on F2. The hydrogen atoms were located in idealised positions and refined isotropically with a riding model.

CCDC 2484370-2484371 contain the supplementary crystallographic data for this publication. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/conts/retrieving.html.

Table S3. Crystal data and structure refinement for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{46}H_{76}O_2P_2$	$C_{22}H_{28}P_2Se_2$
Formula Weight	723.00	512.30
Temperature [K]	122.99(10)	123.0(1)
Crystal System	monoclinic	monoclinic
Space Group	C2/c	*I2/a*
a [Å]	15.8760(2)	14.9890(2)
b [Å]	14.46840(10)	8.32050(10)
c [Å]	20.2954(2)	18.1480(2)
α [°]	90	90
β [°]	104.3860(10)	95.0240(10)
γ [°]	90	90
Volume [Å^3]	4515.68(8)	2254.65(5)
Z	4	4
ρ_{calc} [g/cm^3]	1.063	1.509
μ [mm^{-1}]	1.112	5.456
F(000)	1592.0	1032.0
Crystal Size [mm^3]	0.312 × 0.227 × 0.056	0.275 × 0.186 × 0.146
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection [°]	8.39 to 150.426	9.786 to 133.536
Index ranges	-18 ≤ h ≤ 19, -18 ≤ k ≤ 18, -24 ≤ l ≤ 25	-17 ≤ h ≤ 17, -9 ≤ k ≤ 9, -19 ≤ l ≤ 21
Reflections collected	48145	12025
Independent reflections	4626 [R_{int} = 0.0268, R_{sigma} = 0.0114]	2000 [R_{int} = 0.0476, R_{sigma} = 0.0201]
Data / restraints / parameters	4626/0/238	2000/0/121
Goodness-of-fit on F^2	1.062	1.091
Final R indexes [I>=2σ (I)]	R_1 = 0.0414, wR_2 = 0.1167	R_1 = 0.0319, wR_2 = 0.0858
Final R indexes [all data]	R_1 = 0.0438, wR_2 = 0.1185	R_1 = 0.0321, wR_2 = 0.0860
Largest diff. peak/hole [e Å^{-3}]	0.66/-0.36	1.21/-0.42
CCDC number	2484370	2484371

4.4.6 Quantum Chemical Calculations

General Methods

All calculations were carried out with the ORCA 5.0.4 programme package.[41] All calculations were carried out on isolated molecules (in the gas phase) at 298 K. All geometries were optimised at the ωB97X-V/def2-TZVP level of theory. The RIJCOSX[42] approximation was used for hybrid-GGA DFT calculations. Numerical frequency calculations were carried out to confirm the nature of the stationary points found by geometry optimisations. All optimised ground state geometries show no imaginary frequencies, while the optimised transition state geometries show one imaginary frequency which coincides with the desired transition. Approximate transition states were found by relaxed surface scans, followed by saddle-point optimisation. Pictures were rendered with the software Avogadro.[43]

The reaction of (*t*BuCP)$_2$ (F) with phenoxy radicals in a model system

DFT calculations were performed on the reaction of (*t*BuCP)$_2$ (**F**) with phenoxy radicals (PhO·), considering both P–P and P–C bond cleavage pathways (Figure S30).

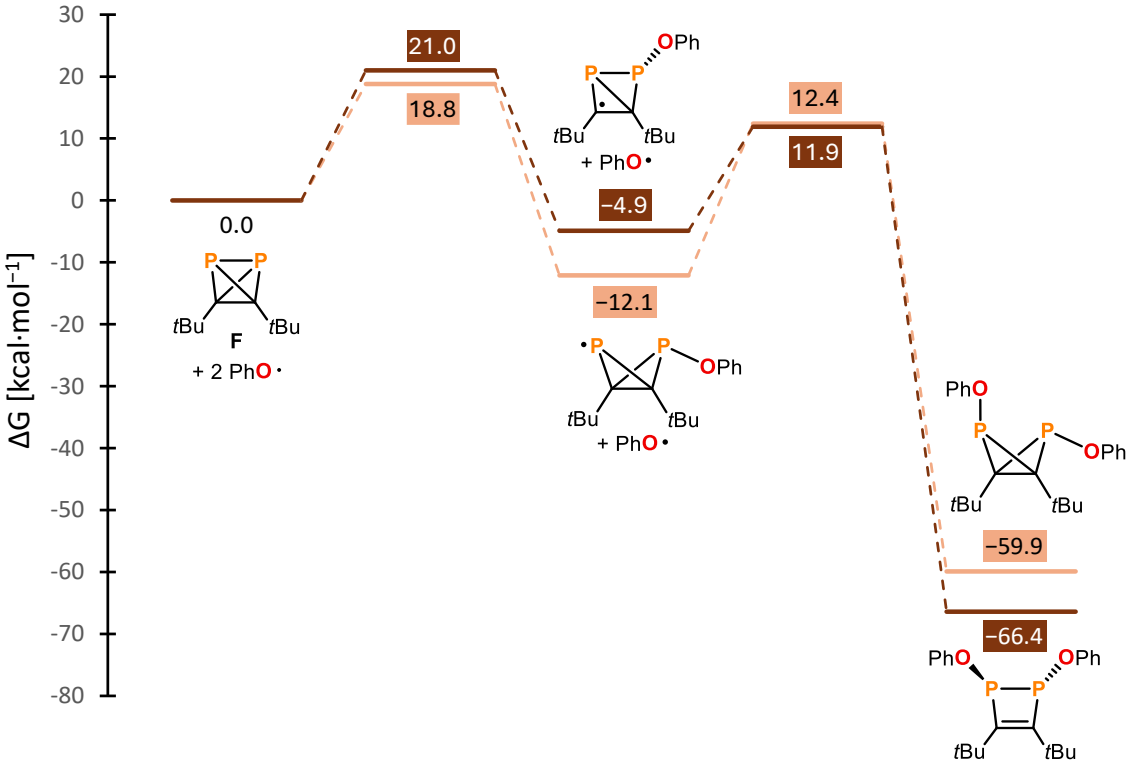


Figure S30. Mechanism of the reaction of 2 eq. PhO· with (*t*BuCP)$_2$ (**F**) leading to P–P bond cleavage (light blue) or P–C bond cleavage (dark blue) in **F**. Calculated on the ωB97X-V/def2-TZVP level of theory.

The initial addition of a PhO· radical to **F** leads to P–P bond cleavage, forming a butterfly intermediate featuring a PhO moiety in *exo*-orientation. A second PhO· addition yields either an *exo-exo* or an *endo-exo* butterfly, with the latter being 8.8 kcal/mol more stable. Alternatively, cleavage of the P–C bond generates an intermediate, which is 7.2 kcal/mol less stable than the

butterfly intermediate. However, subsequent addition of PhO· to the intermediate resulting from P–C cleavage gives a diphosphacyclobutene structurally analogous to (*t*BuCPOMes*)$_2$ (**1**), which is 6.5 kcal/mol more stable than the *endo-exo* butterfly.

Calculations on the reaction of (*t*BuCP)$_2$ (F) with Mes*O·

To evaluate whether these results translate to the experimental conditions, analogous calculations were performed using the bulkier Mes*O· radical. In contrast to the results obtained with the PhO· radical, P–P bond cleavage upon reaction of **F** with Mes*O· yields a butterfly intermediate, which is 5.8 kcal/mol less stable than the intermediate resulting from P–C bond cleavage (Figure S31). This aligns with the observed formation of **1**, which is obtained upon cleavage of two P–C bonds in **F**. Due to computational cost, the addition of a second Mes*O· and subsequent formation of **1** was not calculated.

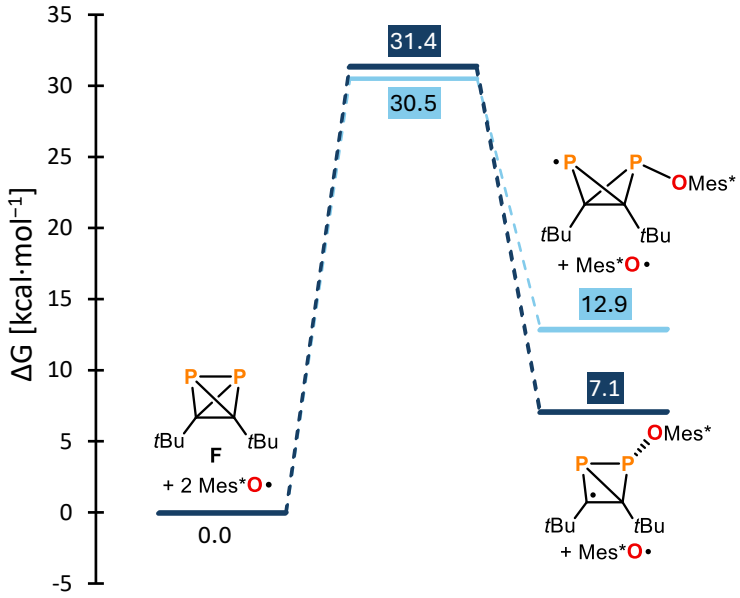
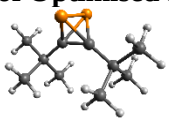


Figure S31. Mechanism of the reaction of 2 eq. Mes*O· with (*t*BuCP)$_2$ (**F**) leading to P–P bond cleavage (light blue) or P–C bond cleavage (dark blue) in **F**. Calculated on the ωB97X-V/def2-TZVP level of theory.

Cartesian Coordinates of Optimised Structures

(*t*BuCP)$_2$

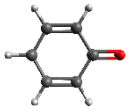


E = −1074.52856669 Eh
G = −1074.30864139 Eh

0 1

P	-5.10679169631724	0.42830853106350	0.34959971743013
C	-3.36734846010731	-0.08820659490253	0.56477287648583
C	-3.55083087093043	0.92091494546830	-0.47540739227225
P	-3.50920558686926	1.61520638995554	1.21427707559756
C	-2.59932368280345	-1.33891431045259	0.90215932733844
C	-3.12174522732436	1.32052245985780	-1.86284570911898
C	-1.59163259301453	1.39328204153349	-1.93511631954359
C	-3.72019725892122	2.69729425147006	-2.17172035616987
C	-3.64196311476361	0.30043938888706	-2.88479319237237
C	-2.73383165344874	-2.35200996922180	-0.24100450538918
C	-3.18055135705650	-1.93544228044048	2.18876604338575
C	-1.12054219965527	-0.99392792371750	1.12404479685459
H	-4.22168890081494	-2.23795981642193	2.04132230967408
H	-3.14755573065207	-1.20525740612116	3.00382820351434
H	-2.60510896716053	-2.81558818483136	2.49369624759975
H	-0.68501894412013	-0.51883238624454	0.24041920722687
H	-0.54843406617353	-1.90273057208477	1.33868764461440
H	-1.00711613244541	-0.30895884623554	1.96977436653335
H	-1.27648754405961	1.77142532597122	-2.91313392682939
H	-1.14439572710208	0.40414745494656	-1.79715559215700
H	-1.19496860993897	2.06258247502825	-1.16476947022589
H	-3.46397605810544	3.00455478126948	-3.19083036283842
H	-3.33883122596702	3.45179493201958	-1.47711734896832
H	-4.81124087583615	2.67175767012061	-2.08568989474158
H	-3.32932520828908	0.58578868995112	-3.89475510753174
H	-4.73507816267780	0.25483601264657	-2.86349504017526
H	-3.25484504088452	-0.70156988535639	-2.68119902663926
H	-2.24379817078925	-1.98697674714072	-1.14846705182438
H	-3.78688373657441	-2.54502987017809	-0.47036663583247
H	-2.26465319719704	-3.30129055683977	0.03761911637488

PhO·

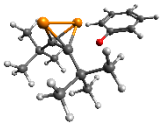


E = −306.84576548 Eh
G = −306.78338714 Eh

0 2

H	1.48140890508148	0.17771770079447	2.10515407297746
C	0.92298482336571	0.09777045343591	1.17765443908506
C	1.61751196210775	0.01993940968415	-0.04255928435003
H	2.70263798894474	0.04085258111561	-0.04393381378564
C	0.92331012920304	-0.08452026895150	-1.26090808676953
H	1.48203300814599	-0.14258395481194	-2.18985851951724
C	-0.44653536195010	-0.11224642935690	-1.27494167954780
H	-1.01455828804526	-0.19179877124913	-2.19601290042682
C	-1.20360220908511	-0.03439734702829	-0.03883456125538
C	-0.44688085419834	0.07266531348528	1.19525406985023
H	-1.01501980240818	0.13029915904587	2.11788350382868
O	-2.44856030116173	-0.05794784616354	-0.03727724008900

TS: PhO· + (*t*BuCP)$_2$ – P–P bond cleavage



E = −1381.36547849 Eh
G = −1381.06203645 Eh
im. freq. = −693.09 cm^{-1}

0 2

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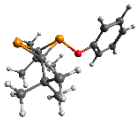
C	-1.03468218261920	2.08259892341167	4.68461623495732
H	-0.26031978728710	2.45122322193963	5.34975879892191
C	-0.80035571567563	0.94820983402658	3.90453043298464
H	0.15680269372959	0.43953274745382	3.96466932220422
C	-1.78558238691157	0.46738361406234	3.06393367749059
H	-1.63230059288158	-0.41634743872673	2.45241901011476
C	-3.03131649998693	1.13350645768809	2.96803150174315
C	-3.25527981025915	2.27673627117995	3.77427596639530
H	-4.22006022078855	2.77026240208939	3.70838982624126
O	-3.94495833509964	0.70972579000953	2.13713853313891
H	-7.22988945148458	-3.24618928964127	0.05775162421969
H	-9.43057739292598	0.13558316768206	0.78872469566854
H	-6.45725516453795	-2.80305362517381	-1.47823106432330
H	-9.33239101175244	1.80322461435724	0.19234969025682
H	-7.66641869901124	-1.73066539819147	-0.75035559465607
C	-6.83758494712759	-2.41046162302568	-0.52924458029846
C	-8.74104592444762	0.92514357126990	0.47155996403606
H	-8.20786653450218	0.57929816893505	-0.41913603498600
P	-7.51640644558700	-1.58752879888514	2.74175766538546
H	-9.29089106126812	1.09815044751777	3.14038760908819
H	-5.01536603369748	-3.45924848346630	1.28691521305137
H	-9.05710910748783	2.75252419809558	2.53936463042833
C	-8.54308688963018	1.82254140446098	2.80324237297189
C	-7.02167725200849	0.04408658732189	2.03239553392591
C	-6.27594826248223	-1.10265145608083	1.50519248943607
C	-7.76401624060797	1.28181039405756	1.59845733644550
C	-5.71548825446889	-1.68895159598356	0.23053947038539
H	-4.24380474852343	-3.19983141378690	-0.28946628134405
C	-4.62289305875509	-2.69651062965115	0.60600783785602
H	-7.86699201069410	2.03011993992011	3.63914984244683
H	-3.78901833343856	-2.18897849431198	1.10023485083590
P	-5.63657796764860	-0.43086305282512	3.08608923099749
C	-5.12020801628593	-0.58752890897613	-0.65662342315755
H	-5.90035658663746	0.09369886627533	-1.01010463871859
C	-6.77194901903782	2.34835649414873	1.11482840480092
H	-6.16985711597934	1.98661108552361	0.27785626914739
H	-4.64659424886148	-1.03731477187143	-1.53597895953336
H	-7.31535227351111	3.24243282618795	0.79085906579795
H	-4.37186713314538	-0.00823726908759	-0.11147538835153
H	-6.08517984912802	2.63013136464500	1.91730415423349

GS: PhOP(*t*BuC)$_2$P· – P–P bond cleavage

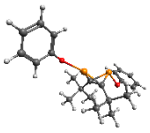


E = −1381.41914011 Eh
G = −1381.11136891 Eh

0 2

H	-1.53269190024897	3.88768280669731	2.88039163264962
C	-1.86087949556484	2.92752346034334	3.26671420159967
C	-1.31427028190601	2.42550099649619	4.44247731737979
H	-0.55990525949938	2.99015540029394	4.98023579657972
C	-1.73803870667162	1.19146047999809	4.91924442358617
H	-1.31152250492899	0.78488806311827	5.83109609699874
C	-2.70090870766374	0.45888735118757	4.23472747030872
H	-3.01892032431069	-0.51032548815025	4.60371248793644
C	-3.25327157470365	0.97840732742355	3.06660755998401
C	-2.83067661226119	2.21120167713515	2.57799876374698
H	-3.26406482958680	2.59116840014869	1.65901817060012
O	-4.19231769192871	0.29089687740293	2.32831632938189
H	-7.28054574778845	-3.44902804361318	0.22554014824285
H	-9.13867056648320	0.30045307640944	0.60504646427313
H	-6.39149574822959	-3.09691560753807	-1.26825235251418
H	-8.74447576431334	1.91343121813878	-0.01698841464327
H	-7.56097723820292	-1.92612051129887	-0.63376569544194
C	-6.79556467088717	-2.65580217944658	-0.35114511726234
C	-8.31558364804332	0.97744582050587	0.35550212342261
H	-7.73554718447140	0.52637428951701	-0.45490911215773
P	-7.85452795149916	-1.55970205048972	2.48348035253888
H	-9.14251429198109	1.29327516192627	2.94290065187923
H	-5.14206862758214	-3.79395073210131	1.56721486621599
H	-8.67012621951214	2.88708601824623	2.32142345241498
C	-8.28878478191570	1.92286185671275	2.67296801315132
C	-6.91566380655221	-0.04868509423943	2.16265612021404
C	-6.23029484431158	-1.34977604642282	1.71348075890306
C	-7.43809458295147	1.25656183286555	1.58202211683909
C	-5.66645926982205	-1.99626740974085	0.45133035315947
H	-4.27930743148274	-3.61517638681384	0.02665835379467
C	-4.66570905309348	-3.07248888626456	0.89551898056365
H	-7.69473349956326	2.09813493170907	3.57563853256460
H	-3.81702945115104	-2.62326919884124	1.42136114119448
P	-5.43627239831307	-0.51847708443148	3.11426544014322
C	-4.95212815269306	-0.97714351253305	-0.44777177900676
H	-5.65012861236560	-0.22165648550282	-0.82032849546380
C	-6.30328447597117	2.21132138707782	1.19052298912749
H	-5.61798288667146	1.75403364692520	0.47268364080552
H	-4.52780672462697	-1.49488766971006	-1.31474095622376
H	-6.72889685334653	3.11326498049203	0.73770124856587
H	-4.14531561470171	-0.46935147964591	0.08282535738836
H	-5.72396201219801	2.51425680601295	2.06710056655925

TS: PhO· + PhOP(*t*BuC)$_2$P· – P–P bond cleavage



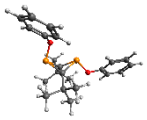
E = −1688.24980476 Eh
G = −1687.85571326 Eh
im. freq. = −501.39 cm^{-1}

0 3

H	-4.25225752535386	3.64348687154997	5.03421297030044
C	-3.87124680728300	2.86153044419553	4.38453342936028
C	-2.59268796760336	2.95919029186330	3.85392881520925
H	-1.96777241564241	3.81501952381236	4.08647734224534
C	-2.12070718746546	1.95125167862159	3.01794851786684
H	-1.12320212608429	2.01832040413272	2.59463071854509
C	-2.91360873782435	0.85265323368517	2.72244438368698
H	-2.55786952669730	0.05528173035944	2.07799187584166
C	-4.19448118504587	0.76166809656323	3.26036859389180
C	-4.68127717944716	1.76989184045037	4.08724191412610
H	-5.68569245522681	1.70715203537213	4.49560575143581
O	-4.94527546012271	-0.33410125914546	2.91160503964132
H	-7.81259226238261	-4.68967536813069	2.21996268360454
H	-10.08385908498409	-1.02767718455261	1.94169777598386
H	-7.13401095239939	-4.69468103192836	0.57993459351809
H	-9.87762972323025	0.31903196306737	0.80457567485323
H	-8.35023341760299	-3.48788210311999	1.03528500450943
C	-7.48331846390472	-4.05159127187385	1.39466431083227
C	-9.34765281829743	-0.45740955184872	1.36643919239398
H	-8.87312743796995	-1.13039472236882	0.64524773753732
P	-8.39470160535190	-2.29245866740177	3.95551463215671
H	-9.78346293855596	0.63229699636556	3.83939726577390
H	-5.51315028651347	-4.48619802623647	3.30452628601554
H	-9.49898617922787	1.95783063942137	2.68717757286348
C	-9.02074791524339	1.15239854509893	3.25482210403890
C	-7.64859881443702	-0.88955244125815	3.14699844991936
C	-6.84143497719476	-2.19201100801269	2.94395666283583
C	-8.30811893342649	0.18732966393440	2.29413470386423
C	-6.35338697357125	-3.11139235383537	1.83718705885753
H	-4.84526770433216	-4.66709820535293	1.66985227902288
C	-5.19537077041133	-3.94044552529221	2.41032893472472
H	-8.30651750228945	1.60726275220257	3.94990212811539
H	-4.35364822814761	-3.29578833994850	2.68292452910345
P	-6.02676210690271	-0.99146694651891	4.01454149535467
C	-5.86099766501501	-2.32424354043645	0.61260483756440
H	-6.68424699983828	-1.78488265981699	0.13581762760613
C	-7.30158733468726	0.98580946470324	1.45530155329149
H	-6.70239565914494	0.34391289585925	0.80663923819855
H	-5.44893551338863	-3.02273140762960	-0.12362011422307
H	-7.84802217695986	1.69618266104916	0.82565842695506

H	-5.08638046140622	-1.60532622349801	0.88383360110918
H	-6.61783889787156	1.55929154667977	2.08595219096723
C	-11.03471227478515	-2.58559091570003	5.20412420978352
C	-12.78924547274200	-4.49290040262155	6.23199974925069
C	-10.92247270937207	-3.00228026530977	6.54226299272564
C	-11.80077084920637	-3.94495947352244	7.04864422511641
C	-12.02529558017200	-3.15201676310405	4.38320632040528
H	-13.47326665482349	-5.23410009522021	6.63289427448501
H	-12.08649579403618	-2.82722525755725	3.34907884675072
H	-10.14101893793735	-2.56462506485023	7.15548818908185
C	-12.89847846292528	-4.09336171813587	4.90061328829353
O	-10.22790053844728	-1.64386302569863	4.72326103752688
H	-11.71799191526186	-4.26132176876934	8.08379248340206
H	-13.66771843180544	-4.52422069029143	4.26730659367907

GS: (*t*BuCPOPh)$_2$ – P–P bond cleavage (*endo*,*exo*)

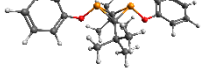


E = −1688.36881398 Eh
G = −1687.97085366 Eh

0 1

H	-2.79476589129764	3.31163822357901	3.41298947944690
C	-3.29273562302344	2.46482050054705	3.87518329386698
C	-2.89590246655585	2.02355293308302	5.13330776772607
H	-2.08827638192011	2.52258265647983	5.65821624953142
C	-3.53849346772025	0.93594305231873	5.71048303601335
H	-3.23177029868177	0.57953796027144	6.68898967366191
C	-4.57007250361904	0.28503713662384	5.04237288197609
H	-5.06127137063286	-0.57345606560632	5.48957016481935
C	-4.96555535575434	0.74213126352811	3.78888940683946
C	-4.32711513655800	1.83073499300356	3.20199241559465
H	-4.64870366748024	2.16103290171640	2.21958533036887
O	-5.94790215186139	0.12222098598111	3.05496918043917
H	-8.25152082276448	-4.45477336597472	2.08918956095660
H	-10.19547048502080	-0.82716559967338	0.23228150397687
H	-6.99057524958772	-4.64173003140977	0.85421992350870
H	-9.50735675664763	0.41458947112823	-0.82745641718072
H	-8.33764397232829	-3.52259402665247	0.58587979983560
C	-7.65421727554325	-3.92115081951554	1.34348558534610
C	-9.27977973327171	-0.28026125018252	-0.01260682198833
H	-8.54141546136118	-0.99874429927596	-0.38064426407908
P	-9.54039377941369	-1.82812320645369	2.84468500349869
H	-10.74574702318907	0.95128064425982	1.95741131670998
H	-6.53474138756007	-3.87315980373689	3.86742401776548
H	-10.06678704912274	2.19587834035044	0.88952081492164
C	-9.82717473116151	1.47904182541121	1.68190823216136
C	-8.48572361157196	-0.46194635632918	2.36260668462710
C	-7.75069690458069	-1.79560008079358	2.67285329763662
C	-8.75033111407072	0.49481872401034	1.20140349154543
C	-6.82395296232228	-2.80500467205141	1.99061591332544
H	-5.28528029150795	-4.19206207998402	2.64972664348672
C	-5.92879500142532	-3.41636619101484	3.07765322867536
H	-9.48069699686745	2.03820460876700	2.55688191520234
H	-5.28482611110218	-2.65434028080037	3.52987324601818
P	-7.35706775266687	-0.41639935846541	3.78340317150703
C	-5.94341076087069	-2.16013758361314	0.91101132932203
H	-6.55163286199525	-1.74618058568746	0.10200928266717
C	-7.50719282409005	1.29243192226235	0.78657043100956
H	-6.68473861370802	0.63843554268757	0.48821189959569
H	-5.28662884525845	-2.92162152924121	0.47630623065124
H	-7.76138529547501	1.93653589328006	-0.06200869783936
H	-5.32378152679328	-1.36116790074547	1.32062488065806
H	-7.15543161459412	1.92862321101001	1.60268130345480
C	-10.13018822328623	-2.69070619525177	5.22282418896667
C	-10.56216718273203	-4.94326039770154	6.78412900996949
C	-9.05786419502816	-3.29408300643834	5.86979124101701
C	-9.28009809667195	-4.42149105361137	6.65134933642659
C	-11.41603817842883	-3.20150958787958	5.35023083623661
H	-10.73136548205169	-5.82395804047373	7.39500765379218
H	-12.23509895515804	-2.70827076296065	4.83672727339433
H	-8.06593944740160	-2.86646515852448	5.76009482483433
C	-11.62705680023365	-4.32936999311172	6.13416577910788
O	-9.91546824178721	-1.56037487775834	4.45733689232402
H	-8.44556142167035	-4.89369804525995	7.16063115928559
H	-12.63062264457213	-4.73058058412019	6.23636041738446

GS: (*t*BuCPOPh)$_2$ – P–P bond cleavage (*exo*,*exo*)

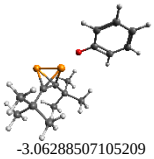


E = −1688.35638435 Eh
G = −1687.95683892 Eh

0 1

H	-3.08282203552142	3.27852499626344	3.94901122752871
C	-3.65918413196610	2.44938994072215	4.34777435605790
C	-3.68501835130466	2.21252709236956	5.71784873005638
H	-3.13196255974364	2.85447819832829	6.39541774578940
C	-4.41933936256332	1.14141303413522	6.21036894698997
H	-4.44059358504111	0.94080525109739	7.27711426494127
C	-5.12764195512137	0.30925243780070	5.35067599750975
H	-5.68814966181662	-0.53330264305177	5.74063032076037
C	-5.10862733290522	0.56696624165030	3.98249902298826
C	-4.37104367084817	1.63403365026482	3.47879795426995
H	-4.35878854378141	1.80839922027924	2.40851404415713
O	-5.76087566713245	-0.23067878580944	3.06611852589875
H	-8.14336142846371	-3.96450641063088	0.16615820473301
H	-9.09035146458032	-0.32626345504436	-0.72942915081846
H	-6.56548160564085	-3.97507521300287	-0.63158175137370
H	-8.45340490715867	1.30492505070310	-1.02034904070171
C	-7.61868765576738	-2.55410669292978	-0.76340960178190
C	-7.27970166554996	-3.34584970873929	-0.09026001635469
C	-8.31965022063458	0.38724971791677	-0.43706001623565
H	-7.34381573168899	-0.03484570650119	-0.69491642663917
P	-9.36536599087984	-1.92184593181475	2.16876542586077
H	-10.57169931237341	0.63830343780754	1.11957026511220
H	-7.06864278175289	-4.50079586907649	2.40339704819470
H	-9.91167522209440	2.26005491285077	0.83678021097202
C	-9.76478857201920	1.32650184351440	1.38978418593776
C	-8.22086087601590	-0.52164757177499	1.92986617908655
C	-7.55038697921970	-1.88487673358449	1.95483762763240
C	-8.39252074833798	0.72281893712584	1.05976339461765
C	-6.59632853041190	-2.77301710458195	1.15935500771277
H	-5.51783888385505	-4.61777831848375	1.54998496247036
C	-6.18989614527136	-3.93356534454175	2.07807340562528
H	-9.84443812108898	1.54638168058413	2.45954364870141
H	-5.67141263154014	-3.56516419083674	2.96906172953576
P	-7.26130330946468	-0.86355907707375	3.44220586259383
C	-5.33570420665551	-2.01493838983943	0.71614221818657
H	-5.59000083368437	-1.11405189069848	0.14992474275366
C	-7.30573692938849	1.76023679336268	1.36907265668282
H	-6.31358677355383	1.37191630697620	1.12716177840014
H	-4.73678550454343	-2.66397841454485	0.06847130049498
H	-7.48032087612717	2.65917641802396	0.76858947034093
H	-4.72349281268048	-1.71530627473940	1.56683373963385
H	-7.31298911937667	2.05018318856037	2.42482004586778
C	-10.84795837615385	-3.01909871724006	0.28017662815984
C	-12.75136523873696	-4.89118593263979	-0.49999294567392
C	-11.78879716557402	-2.68747366353762	-0.69051637410800
C	-12.73347964842724	-3.62551298958015	-1.07868582931596
C	-10.85025729061234	-4.28409602471905	0.85915908900699
H	-13.49452739854012	-5.62090805083616	-0.80353617340421
H	-10.11071432649743	-4.54468327709747	1.61020823771606
H	-11.76420070024375	-1.69458393580853	-1.12805307269118
C	-11.80893155853249	-5.21275788354156	0.46694727258640
O	-9.91563287240091	-2.06056056896294	0.59676364617204
H	-13.46518101996108	-3.36383721304271	-1.83679038367973
H	-11.81059770675258	-6.19772636603013	0.92348166104156

TS: PhO· + (*t*BuCP)$_2$ – P–C bond cleavage

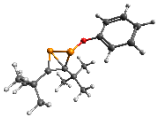


E = −1381.36236905 Eh
G = −1381.05852889 Eh
im. freq. = −735.78 cm^{-1}

0 2

H	-3.05558704005324	6.76093644513308	-3.06288507105209
C	-2.86111624051834	6.22727793013672	-2.13743375692164
C	-1.56246092381114	6.16646245489227	-1.63110568756225
C	-1.30697142105646	5.48321517501039	-0.44055401565085
H	-0.29437164484293	5.43639144155876	-0.05157422940834
C	-2.33726941552041	4.86904380556217	0.24526723878433
C	-3.66074504940233	4.92382547421062	-0.25230794816978
C	-3.89914298384128	5.60436428676134	-1.46909175079907
O	-4.65128117867868	4.37515770835561	0.40493012454316
H	-7.21430945881811	-1.35210396574406	1.71059816544843
H	-9.12093334483643	1.50139504735527	0.24715810329006
H	-7.12530719487875	-2.50918876078033	0.36839297553898
H	-9.54134798230883	2.15608696458446	-1.34563395072229
H	-8.01418956323156	-0.98939153065033	0.17091147211877
C	-7.12949401963379	-1.44412948505804	0.62344735306586
C	-8.74738232084080	1.67154013410278	-0.76804168257886
H	-8.53993483363678	0.70115082116864	-1.22862611415026
P	-6.11388657157709	1.74725427677857	1.94659196047543
H	-8.33447554647685	3.87130716047525	0.77099708397937
H	-4.68049271273463	-1.28202312952174	1.89647667463159
H	-8.58666153978873	4.42786398615664	-0.89524633259060
C	-7.87086566079466	3.95034059971691	-0.21739826020933
C	-6.45603775991179	1.94168549822868	0.14915686911081
C	-5.84781549331928	0.67892531571629	0.46774853034192
C	-7.49777883432246	2.56185369826562	-0.74911967318182
C	-5.83677905688651	-0.78244063986461	0.12236560219651
H	-4.62379793152024	-2.51415340674840	0.62118154395045
C	-4.63414979325474	-1.43654663660176	0.81357713068551
H	-6.98440414601330	4.58196084992430	-0.12915010456409
H	-3.69613147096714	-1.00989663998241	0.44640399852575
P	-4.64053634169331	2.13248764072623	0.44046144742893
C	-5.71474179795264	-0.94974238662229	-1.39771377870276
H	-6.59300264511069	-0.54794400628234	-1.91159829520570
C	-6.92440686032262	2.68894985304228	-2.16734622068374
H	-6.61946640619627	1.71488438653659	-2.56201143301489
H	-5.62719767064494	-2.01039782797424	-1.65457420575793
H	-7.67797450966246	3.10850362152731	-2.84224649907543
H	-4.82713428961463	-0.43168921582177	-1.77499769680645
H	-6.05038966848294	3.34758543989922	-2.17008211128721
H	-4.91670157827916	5.63773193826937	-1.84615153639097
H	-0.74949832600548	6.64934358381437	-2.16363799580971
H	-2.16135877255610	4.33537209374204	1.17416207618027

GS: PhOP(*t*BuC)$_2$P· – P–C bond cleavage



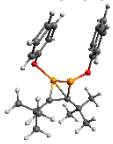
E = −1381.40749944 Eh
G = −1381.09981977 Eh

0 2

H	-2.97406921918793	8.34144558289858	0.34399366546808
C	-3.02829087035782	7.34829728313065	-0.09138136721594
C	-2.26432596018783	7.03497369392432	-1.21257412111823
C	-2.34902846083434	5.76259894445176	-1.76053993634927
H	-1.76296358451684	5.50810143854031	-2.63830207790183
C	-3.18792466559074	4.80301367049477	-1.20148691761202
C	-3.93670158667296	5.12345361112718	-0.07251024262572
C	-3.85948168360743	6.39856867389252	0.48215222383626
O	-4.80167303746818	4.23995525236977	0.51930412752364
H	-7.58815179694643	-0.94712401015274	2.03173846305400
H	-8.70939178697921	1.73582510274380	-0.34342778651615
H	-7.52117807716434	-2.39129183489024	1.00513682114432
H	-8.87148460451252	1.86186319674367	-2.10482023668396
H	-8.23566884182681	-0.89240331596907	0.38406824845012
C	-7.43504576154209	-1.29916770770520	1.00680774101120

C	-8.21504847985104	1.52275286263521	-1.29724352453173
H	-8.10122347029676	0.44093793814068	-1.39153093502038
P	-6.22183794297406	1.92655883858170	1.69411314526176
H	-7.54512244109279	4.08281452127349	-0.41493732801402
H	-5.09138195488245	-1.09600624161109	2.44106313987490
H	-7.83588170698033	4.00844708384026	-2.16565148562480
C	-7.12402429911035	3.76016759589854	-1.37157272149711
C	-5.97889337905172	1.82535574256219	-0.21912423877006
C	-5.87874424879843	0.60646992340430	0.53632940068244
C	-6.86740368141334	2.24768422037987	-1.38206297119946
C	-6.04509020537058	-0.88302768033943	0.49231296840959
H	-5.08955616926062	-2.58061923148316	1.46699749050095
C	-4.98242020442613	-1.49117372443291	1.42641599294201
H	-6.21017991961397	4.33071508687890	-1.54975689094238
H	-3.97436087245191	-1.25289390033996	1.07457975691294
P	-4.50018462020506	2.59118798754700	0.53734609612523
C	-5.83004907838978	-1.42481977564781	-0.92596033453322
H	-6.60841283302763	-1.08421415597847	-1.61323327847285
C	-6.14953067727223	1.87663717643249	-2.69002449189874
H	-5.94983441017158	0.80375434435168	-2.75143361575820
C	-5.85533105127803	-2.51936270507967	-0.91245126091761
H	-6.76708754999953	2.16151150623694	-3.54824838686657
H	-4.85899558883709	-1.10964499580336	-1.32079322503772
H	-5.19489478626294	2.40665407593315	-2.77184796441869
H	-4.45839773081680	6.62269452372179	1.35861128133614
H	-1.61160127212913	7.77952076732464	-1.65601247728713
H	-3.25666148863983	3.81303863397277	-1.64274274571978

TS: PhO· + PhOP(*t*BuC)$_2$P· – P–C bond cleavage

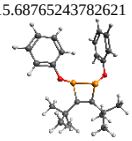


E = −1688.24894559 Eh
G = −1687.85648769 Eh
im. freq. = −616.72 cm^{-1}

0 3

P	3.79984981042590	12.06466483785208	14.32651001829156
O	4.10822769181170	11.36674316523500	12.84345237677990
C	4.00905994414859	9.99519739007858	12.72771620579354
C	2.81455208462505	9.33142157660706	12.98067868046308
C	5.13697350915545	9.29648752606411	12.31328984538190
C	3.87567925113732	7.24278442308596	12.39729029161349
C	2.75650582002001	7.95240110320619	12.81718177270426
H	1.82448055325480	7.43114572682495	13.01359191065467
C	4.35789101738824	13.76391922674646	14.15039704265569
C	5.06393804946587	7.92014942697380	12.14333822184691
H	5.94218411229925	7.37442471375418	11.81154747833801
H	1.94317462971360	9.89411570947845	13.30039263438881
C	4.50900862062690	14.72318261989564	12.98254093217494
H	6.05455866253235	9.84488605770874	12.12461674420447
H	3.82096583166959	6.16713347612404	12.26323427015068
C	4.99759381504090	14.00854885306690	11.71649626938653
H	5.94777765075683	13.49692542281022	11.89938724036809
H	5.14913365925011	14.74478894314076	10.92013561491996
H	4.27781597096552	13.26683921967545	11.36651157491596
C	5.51617303101588	15.81866296286251	13.35203304367700
H	5.18522686584093	16.39748959411669	14.21730483698522
H	5.64102993881042	16.50456792042777	12.50783771842435
H	6.49275295392454	15.38291902535190	13.58726628973957
C	3.13213332537036	15.34946657525917	12.69966379514608
H	2.40202299874073	14.57740373565422	12.43564881443304
H	3.20455759029308	16.05112250086182	11.86155453382345
H	2.75349766292724	15.89532086118800	13.56857794722462
P	5.71657646302519	12.70269433036079	15.15454153482254
O	5.87681645923651	11.36690626470272	16.84771349373027
C	5.13203201329524	10.29704716119699	16.74450421280547
C	5.54819064005358	9.20023864746557	15.95006279937280
C	3.89448317995412	10.20685025205799	17.42751041044306
C	3.56451651032824	7.98236235920470	16.56649597828262
C	4.77230928897095	8.06159342646133	15.86911400270543
H	5.09444515746640	7.23059276572385	15.25005407010305
C	4.62402233202359	14.01785262738767	15.58027023298268
C	3.13348721315039	9.05471142987494	17.34731047957958
H	2.19315154308994	8.98886461779941	17.88593741136599
H	6.48855987147078	9.28522930951120	15.41385324281549
C	3.88081156441652	14.60552903158673	16.75115730286985
H	3.57671401416094	11.05294223843557	18.02844188474317
H	2.95761833392011	7.08526251058644	16.49415949594457
C	4.64722246032693	14.29470832629715	18.04171017327101
H	4.77252735344124	13.21846736765061	18.17823304831161
H	4.11384874874049	14.70535025303201	18.90562968605310
H	5.64595864782576	14.74196363619060	18.01216471132874
C	2.46110602449043	14.01435394358680	16.82596679003944
H	1.90311746639575	14.21524103110750	15.90543934949568
H	1.91514735380835	14.46390420658040	17.66297292298618
H	2.48874363875618	12.93096087476031	16.97342304077243
C	3.76839550948278	16.13148058030447	16.59420111389895
H	4.75899756869938	16.59380581299939	16.55093534920869
H	3.23236502729360	16.55302085216614	17.45144202874952
H	3.21995408196367	16.40299563391276	15.68765243782621

GS: (*t*BuCPOPh)$_2$ – P–C bond cleavage

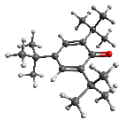


E = −1688.38171144 Eh
G = −1687.98122011 Eh

0 1

P	3.44904111343809	12.10641014555712	13.48949589907836
O	4.47556638924962	11.49547266368244	12.29840909081323
C	4.56389308606996	10.11801655067161	12.29486175498776
C	3.46074449995761	9.33002879492825	11.98035635121391
C	5.78030573553659	9.53315133698606	12.63083620931758
C	4.78993023450174	7.35083666982064	12.35293007978021
C	3.57907560307451	7.94541706182455	12.01616101134054
H	2.71814953230386	7.32936421992883	11.77572500283437
C	4.04059290925046	13.77467864783214	13.86972418014908
C	5.88964360268119	8.14843771662123	12.65280031314347
H	6.83863110696991	7.69076910666207	12.91464484129592
H	2.52113806475614	9.80534536802911	11.71695794677855
C	4.03537969928196	14.92439768597067	12.86215071245916
H	6.61960070328584	10.17334824392234	12.88189506072023
H	4.87806308378529	6.26941654548474	12.37667525632502
C	3.73070962187603	14.37357367928834	11.45842376818037
H	4.49416408820584	13.66478888577923	11.12975483889899
H	3.69724748856025	15.20002350720074	10.74192883422297
H	2.75815219281614	13.86929275747860	11.42891262478380
C	5.41922259169200	15.59012619262391	12.79686262135364
H	5.70823702371959	16.05272084059325	13.73907034528092
H	5.42008978185937	16.36434035004378	12.02193768865366
H	6.18112024221502	14.84924503873616	12.53491891530773
C	2.93036043244315	15.94102022358911	13.19401303604589
H	1.95200044668392	15.44927317435795	13.19897709083609
H	2.91153600118633	16.72542220578406	12.42976548203473
H	3.06703118271855	16.42156112812765	14.16248518439003
P	4.58968570315213	11.88433565218626	15.35305837778092
O	3.48528589222273	11.31356864818286	16.47374217737650
C	3.60161658569882	10.01761043072328	16.92289110692064
C	3.97290360682857	8.97668845165364	16.07687106158545
C	3.30356855974508	9.77115469704533	18.25922333031777
C	3.77818462099818	7.42977666510545	17.92084146138837
C	4.06500525803981	7.68589854926485	16.58647729958358
H	4.35851695371829	6.87730999966725	15.92368821765345
C	4.24195154805233	13.65911168357957	15.21904257709205
C	3.39163366235590	8.47705780719337	18.75227499870799
H	3.16112609962666	8.28640112323908	19.79594618652389
H	4.18223641207368	9.16209132353514	15.02711328549873
C	4.25542905215414	14.60434728537256	16.42184319741072
H	3.00724402840659	10.60034366811115	18.89380721809527
H	3.85014075388193	6.42007059648194	18.31150743187852
C	4.96623816108037	13.92244766004108	17.60443532029810
H	4.45844646034139	13.00530949918917	17.91085238490742
H	4.97855488170805	14.60144793214072	18.46260105031434
H	6.00358379014891	13.67732495599308	17.35302132891590
C	2.78852433252384	14.85971818891216	16.81390944689723
H	2.24658953001310	15.37675358910251	16.01745276021606
H	2.74598172060839	15.47607386711839	17.71856815449433
H	2.27556987696754	13.91443587914556	17.01617179598006
C	4.97858740368733	15.93694120563297	16.18839108343011
H	6.02707371352605	15.77149231505045	15.92236708737946
H	4.95773180101815	16.51551795331951	17.11785106527576
H	4.51684665030273	16.54793371648705	15.41446976284994

Mes*O·

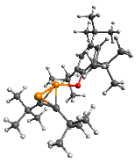


E = −778.67168409 Eh
G = −778.28651486 Eh

0 2

H	1.49120261019116	0.17601168381078	2.09772921021126
C	0.93411009536193	0.09863935875375	1.17485024520632
C	1.64810774403651	0.00765590316679	-0.02968814244870
C	3.17402706310805	0.01723532846705	-0.08141208145959
C	0.92657095023324	-0.08840501703392	-1.24072744649300
H	1.49252511111647	-0.15033350957406	-2.16180478953750
C	-0.44079225698859	-0.10559529429957	-1.29750774610509
C	-1.19539424055026	-0.21503318154341	-2.62341611817877
C	-1.19285992085990	-0.01695831394160	-0.03362047427236
C	-0.44188156185619	0.09238761761811	1.22615768810810
C	-1.19782946871306	0.19246488944326	2.55151006826107
O	-2.43687764985956	-0.03335442051450	-0.03244450022164
C	-0.23573878538256	-0.28040119799143	-3.81919812064021
C	-2.09942156656364	1.01745380641346	-2.81858856588692
C	-2.04779318116964	-1.49865210710591	-2.63894401714068
C	3.81124242549607	0.08189197735536	1.31111976163305
C	3.63703223572703	1.24680059496201	-0.88572160303272
C	3.66577583193739	-1.26721717102577	-0.77449047393631
C	-0.24049921971845	0.29124607368256	3.74714262415360
C	-2.06998636477712	-1.06178535488293	2.75508153679567
C	-2.08297084346537	1.45398057384150	2.55975835985585
H	3.29800322365785	2.17213437718786	-0.40949622895467
H	3.25038487809749	1.23326762708267	-1.90820188918893
H	4.73050421873399	1.26871708540536	-0.93894362237337
H	3.53466231674070	0.99730705996508	1.84334719266570
H	4.90077686288414	0.07294295894043	1.21220116622914
H	3.52713899385283	-0.77722097349110	1.92692176540715
H	0.40155982063031	-0.59171241608369	3.83264822416360
H	-0.82907565432253	0.36175199782497	4.66642884799524
H	0.39444951090880	1.18162795763139	3.69306430447879
H	-1.47215528593403	2.35466295835288	2.43473886737420
H	-2.59944495270964	1.52915670669437	3.52267495712447
H	-2.82845460820854	1.42182281180527	1.76560651798532
H	-1.50507538167074	1.93768351842693	-2.80997625283248
H	-2.85637252940097	1.08122156217742	-2.03756205269761
H	-2.60171257087405	0.95015797663136	-3.78960575143582
H	0.38468526382725	0.61879434495651	-3.89625811086226
H	-0.82170798892208	-0.35671983245111	-4.73968535422786
H	0.42049894774974	-1.15580560105627	-3.77287413181524
H	-1.45191007362518	-1.96631890977582	2.75240903923602
H	-2.82519620541744	-1.15039176173378	1.97477594918438
H	-2.57341855962277	-1.00087374862619	3.72593861021253
H	3.34425298436840	-2.15463112729991	-0.22035281350002
H	4.75968406605098	-1.26975189481810	-0.82049189624358
H	3.28778620800306	-1.35257810620483	-1.79655959145223
H	-1.41399157427034	-2.38431417719242	-2.52145241904246
H	-2.56506980221020	-1.58064425195129	-3.60090401733394
H	-2.79171111562051	-1.49059838199952	-1.84254672497329

TS: Mes*O· + (*t*BuCP)$_2$ – P–P bond cleavage



E = −1853.17596597 Eh
G = −1852.54660664 Eh
im. freq. = −783.02 cm^{-1}

0 2

H	-1.79990274023961	3.99521490781014	4.55065363433595
C	-1.81842892919076	2.93827030702801	4.33024062523579
C	-0.96284220399614	2.09989878223510	5.03388321543880
C	-0.02443870020973	2.60327891514424	6.13299575219440
C	-0.94161985658364	0.75085229007651	4.67472915445670
H	-0.23136835202557	0.10511617567652	5.17380435359364
C	-1.77109554837446	0.21096909230919	3.70597002757013
C	-1.58687997323385	-1.26082547698454	3.29073393060142
C	-2.73181264752694	1.07521830527436	3.08257354266437
C	-2.69628688813717	2.47681294378832	3.35324406429032
C	-3.57227364589254	3.49551174236491	2.60107199613617
O	-3.60672787764769	0.58016355738624	2.21244365972628
C	-0.37526111693835	-1.90522321179136	3.98327607002050
C	-1.31733133351067	-1.33404808430588	1.77591001542978
C	-2.80670668860902	-2.11815204556592	3.66307193143193
C	-0.22017061916613	4.09417505283048	6.42951910612262
C	1.43462680120798	2.38222368571877	5.69763274071877
C	-0.29159663616965	1.81862284816577	7.42920185347901
C	-3.07863145059817	4.93850819640482	2.80604221534330
C	-5.00771486377727	3.42827648529718	3.13920924099198
C	-3.55660850746453	3.24455072352054	1.08122491821350
H	1.65278013598797	2.93350288996114	4.77742193515198
H	1.64307565970252	1.32447980034661	5.51411836588969
H	2.11987216615296	2.73080594509668	6.47795857183520
H	0.00657989806096	4.71629413666126	5.55795986811536
H	0.45475695517471	4.39694675776328	7.23601270279664
H	-1.24412379723968	4.30968142945127	6.75163401063945
H	-3.18840604489363	5.27658559627098	3.84070367337586
H	-3.68211080323165	5.60633128346791	2.18374506234468
H	-2.03170268866015	5.05643817322680	2.50865523872333
H	-2.52972192811346	3.26951885092720	0.70043845572164
H	-4.12109878913375	4.03643896827464	0.57590543956813
H	-3.99120115088290	2.28173987551830	0.81915095139559
H	-0.38395302933169	-0.81614724760580	1.53118436261314
H	-2.12284144348307	-0.87726561516458	1.20231265321369
H	-1.21239396632756	-2.38020649677914	1.46612247244817
H	0.55153608185194	-1.35884987704556	3.78246773030097
H	-0.25237566907934	-2.92118213834230	3.59604628517866
H	-0.51050613155312	-1.98201386019032	5.06705593670786
H	-5.02903583891764	3.65417946565266	4.21087687345199
H	-5.43760725641368	2.43791379050030	2.99454529366003
H	-5.64388009382962	4.15683934484533	2.62233266372404
H	-1.33010827802264	1.94436065234922	7.75149654748292
H	0.36314981458983	2.17936144042499	8.22972452262626
H	-0.10510389352359	0.74892901882059	7.30077565213138
H	-3.05409022921609	-2.00655811374546	4.72376802362019
H	-2.58707647972323	-3.17504652494375	3.47356545807807
H	-3.68489720937758	-1.85629469211554	3.07670520345776
H	-7.43255384989890	-2.59170742932166	-0.27368685376335
H	-9.70968173538157	-0.26445973746617	1.71496600190065
H	-6.39652791850045	-2.36650810122980	-1.69639867348716
H	-9.97406038983811	1.13541175818177	0.65935985430009
H	-7.34474932165741	-1.00880055129824	-1.07759412808650
C	-6.76540855983021	-1.88854260833904	-0.78301883144204
C	-9.23814570391299	0.38800151568710	0.97390467385565
H	-8.97700921095644	-0.21700848553957	0.10221282441844
P	-7.15469652035192	-1.61555616794278	2.76606811482766
H	-8.83263169656329	1.18263743619244	3.57813220400626
H	-5.30505316875336	-3.51351808039893	0.89153621124415
H	-9.24341624555059	2.57340863667491	2.55825474530900
C	-8.44704587808151	1.86758084199691	2.81584039876355
C	-6.97362916256690	0.06872023449001	1.97356535338286
C	-6.10944642607960	-0.97974532200043	1.42981894485577
C	-8.00908212701329	1.09110695802789	1.56718786937445
C	-5.58003369130270	-1.49895371152647	0.11209628807438
H	-4.36776841646081	-3.15883170031671	-0.57326302980347
C	-4.72396030795419	-2.74262055082515	0.37484003305611
H	-7.61789149666982	2.43144435990304	3.24932738311667
H	-3.85250216990393	-2.49899451129773	0.98574048535944
P	-5.48291490861540	-0.15097205365360	2.97142760959148
C	-4.73855271203161	-0.43201107199025	-0.60000972303243
H	-5.32785085342430	0.46696806171224	-0.80280025019472
C	-7.42068067815491	2.05285066648878	0.52520347048453
H	-7.22376004952275	1.53449221990957	-0.41772199717847
H	-4.38134326417501	-0.82468478573650	-1.55816875117577
H	-8.13040690444818	2.86173693552437	0.32159589790910
H	-3.87767081167395	-0.14119851147288	0.00348436743503
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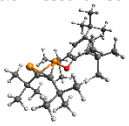
GS: Mes*OP(*t*BuC)$_2$P· – P–P bond cleavage



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G = −1852.57455294 Eh

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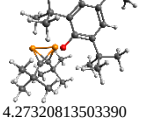
C	-1.06636949582437	2.06489219935903	5.03312454936814
C	-0.12366519250236	2.43887842742493	6.17957500194560
C	-1.03130433467776	0.78663138293137	4.49497834575448
H	-0.28956572759664	0.09639635298969	4.87384963445550
C	-1.89006408903655	0.34578141417582	3.49080385310659
C	-1.62615778310212	-1.05423066276893	2.89931371200590
C	-2.89558172392933	1.24113064013984	3.05730987546930
C	-2.85583215954800	2.59268152048445	3.45558668594254
C	-3.72378926958153	3.69324633937073	2.82366312855905
O	-3.93202715427405	0.80137065279141	2.20332903049413
C	-0.18975302500066	-1.53156236503605	3.19416586167295
C	-1.72532604728499	-1.00174341362709	1.36521373669252
C	-2.55880030274468	-2.10064101373466	3.53076504119987
C	-0.32189663534162	3.88644160748745	6.64214118768589
C	1.33588954670091	2.26809478487787	5.72597633906971
C	-0.39615072651224	1.51057714216089	7.37557748985950
C	-3.25117872393457	5.10619802569995	3.20847291920358
C	-5.16809912125070	3.57208001356171	3.32841957895004
C	-3.60591377870063	3.61929780532332	1.28903477849494
H	1.55533758409330	2.91759155941690	4.87251921829204
H	1.54681449034161	1.23714417396410	5.42772567774937
H	2.01983130864478	2.52836323833267	6.54105070388117
H	-0.09798103085152	4.60216817239741	5.84458946051302
H	0.35326377546529	4.09897472218470	7.47677338690600
H	-1.34599845551042	4.06200539035095	6.98719289765918
H	-3.39372757688938	5.32178053709254	4.27155442678377
H	-3.84664806074987	5.83383283666145	2.64803514948979
H	-2.19916010764841	5.26793517164416	2.95448638167963
H	-2.57232613926958	3.83319344322296	0.99620099899997
H	-4.24831609329846	4.37514394008565	0.82335567420500
H	-3.87218807546753	2.64213798506849	0.89117808724214
H	-0.97414410941135	-0.30699308874739	0.97364464277249
H	-2.69798998320980	-0.66685879749245	1.01761198555765
H	-1.52004000202432	-1.99022463867578	0.94018213902141
H	0.55525606238637	-0.78906821873720	2.89207670973683
H	-0.00591739855076	-2.44674841409293	2.62286582343051
H	-0.03366831020009	-1.77695730188149	4.24837392476524
H	-5.19607343144073	3.72993538452611	4.41189599160911
H	-5.59718029618688	2.59246089429647	3.12993742949272
H	-5.80773355688129	4.32787067728475	2.85772365416216
H	-1.43307192148944	1.60688001004994	7.71261026547852
H	0.26341042228417	1.76578214709625	8.21204094195299
H	-0.22274234106785	0.46185832943484	7.11766751844430
H	-2.40811870095592	-2.11740498596820	4.61517576784834
H	-2.33089442453362	-3.09840068581231	3.13886304957778
H	-3.61489525999435	-1.90452474301817	3.35090891695118
H	-7.33647247783298	-3.38319089059466	0.80694363796811
H	-9.20610382497727	-0.10828873963588	0.85117961123342
H	-6.72778204660878	-3.18960934719057	-0.84543246119530
H	-9.22011145742368	1.37930326745124	-0.11084336393841
H	-7.78634569878919	-1.95891276860272	-0.14026186850601
C	-6.97284923197865	-2.65301975957970	0.07762790263615
C	-8.57138368770936	0.61418909146333	0.32844266966260
H	-8.06187432882955	0.10313686603420	-0.49211988130147
P	-7.53765884830032	-1.21572487954837	2.85303219330857
H	-9.10486401327524	1.50569692563898	2.81012106595577
H	-5.07077291033957	-3.57421710664343	1.88187034288956
H	-8.91975279094975	2.92124399138530	1.75722141871829
C	-8.37549274242167	2.13023402893727	2.28415993494886
C	-6.78245695042104	0.24448304519756	2.07376509695448
C	-6.05643416481755	-1.07902627130489	1.81776450108093
C	-7.57170396398912	1.28770409455206	1.28117900963618
C	-5.71625968255937	-1.93766613662822	0.59891738183376
H	-4.60329683316884	-3.74361358632346	0.17936345336373
C	-4.71662145859269	-3.02827215208543	1.00104150462624
H	-7.73107804598589	2.59887353094512	3.03080608123925
H	-3.73654734963410	-2.61390648290156	1.22458061803958
P	-5.21221622125529	0.04355961464199	3.00803414011672
C	-5.12917372390667	-1.07470851752184	-0.52867641023503
H	-5.90660209938101	-0.46523306956394	-0.99790643098088
C	-6.66564274038770	2.19644195456984	0.44389211976700
H	-6.00911304736445	1.61708113556305	-0.21053911203126
H	-4.69606679146590	-1.71604363646619	-1.30371572628823
H	-7.28340443252017	2.84700221277908	-0.18505370861326
H	-4.34937938440264	-0.40187042340191	-0.16448810216182
H	-6.04445857793453	2.83021375468234	1.06955610363217

TS: Mes*O· + (*t*BuCP)$_2$ – P–C bond cleavage



E = −1853.17633835 Eh
G = −1852.54510665 Eh
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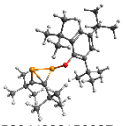
C	-1.06047994255739	2.07258449302044	5.02262538071468
C	-0.33482179368142	2.62328023558996	6.25369308084689
C	-1.03019869784184	0.70219687070029	4.75977144070800
H	-0.44569007983886	0.06997763216297	5.41599202328805
C	-1.70833620505970	0.12070393215063	3.69797323300406
C	-1.49562907820674	-1.36874753014486	3.36759147939144
C	-2.51118623152702	0.96568759377344	2.87567163903636
C	-2.45428204715715	2.37616748961341	3.03865626346643
C	-3.06378108096412	3.33762157206749	2.00003845527466
O	-3.31358574684205	0.42909252322293	1.95019883668470
C	-0.49771464467069	-2.02910259001554	4.33104379876880
C	-0.90003547769497	-1.47406902283348	1.95005407012288
C	-2.79164254089957	-2.19345176084149	3.43900934223716
C	-0.40320451488179	4.15216619664653	6.33586660925796
C	1.14814903862968	2.21549341882435	6.21759065587070
C	-0.99068327435967	2.04301886069954	7.51882602130202
C	-2.78395845516835	4.80792776625511	2.34671165188407
C	-4.58912986273949	3.19746514647455	1.87264719965278
C	-2.40922870768408	3.05767450052940	0.63363438163766
H	1.63309584836610	2.59697289846660	5.31342017251329
H	1.27246892250783	1.12933043921959	6.23485844990900
H	1.67267092857035	2.62548558502740	7.08753641199576
H	0.06698273927034	4.62535524839832	5.46763527308097
H	0.12869086143383	4.49271434289785	7.22986455360525
H	-1.43583601759243	4.50807930849508	6.40716572271610
H	-3.26486318181495	5.10657990124336	3.28423167646723
H	-3.18800525300309	5.44114473194159	1.55083700224403
H	-1.71252301295696	5.01595325618771	2.42232449451029

H	-1.33225241763099	3.25088277460837	0.67924457809340
H	-2.84063238996092	3.71308730042071	-0.13185084603295
H	-2.55950781609531	2.02044053518284	0.32972434805924
H	0.06925680581321	-0.96672932257734	1.90241588572171
H	-1.56190951955059	-1.02146781699083	1.20949506215585
H	-0.74626926946688	-2.52673440417067	1.68603165603888
H	0.47489360392783	-1.52767665155435	4.32439031002076
H	-0.33840770603610	-3.06522646704877	4.01733019139020
H	-0.87395959858052	-2.04971430656335	5.35940020694758
H	-5.07603498692056	3.25898950647722	2.85251401633569
H	-4.86455759016142	2.25541138516056	1.40052608347544
H	-4.97936263939018	4.01023982132411	1.24868090647587
H	-2.04604478841024	2.32906088160242	7.57308758408715
H	-0.48585111018111	2.41793823904343	8.41611379602242
H	-0.93757766915035	0.95057189772056	7.53132843492327
H	-3.30659318882768	-2.04093590751578	4.39337873415856
H	-2.55079026005609	-3.25898464953965	3.35066456699422
H	-3.47245918816381	-1.93831011156242	2.62882131505724
H	-7.29190075970682	-2.42777260711200	-0.29143138060269
H	-9.53936033113390	-0.87268319861558	2.58613802915638
H	-6.66532227030629	-1.78748315371853	-1.82227396981945
H	-10.32801245331144	0.48409671898012	1.75822625359120
H	-7.72682785845371	-0.78770724371278	-0.81892462834006
C	-6.92018216088621	-1.52655543796319	-0.79013681792711
C	-9.40479764968357	-0.10128572885951	1.82212517937377
H	-9.25005494866702	-0.59661740434242	0.85953381813141
P	-6.49763453454041	-1.69388263003894	2.82984575988853
H	-8.47250962277323	0.63896795384455	4.32966785896218
H	-4.82857259561800	-2.92983382983586	0.34382805777860
H	-9.39924063640453	1.96343458884577	3.59850255217379
C	-8.44766300700151	1.42318426410770	3.56591663078286
C	-6.95095414180795	0.01883575061068	2.19958660109891
C	-6.03905264652560	-0.72143883967827	1.36866165556975
C	-8.22736657778277	0.81964273363945	2.17433886648738
C	-5.68036164437837	-0.96835470200252	-0.07550812351351
H	-4.29156666234926	-2.20578219431055	-1.18525900310032
C	-4.54118522699309	-1.99081128697682	-0.14116029299951
H	-7.64451543825776	2.12210108573640	3.81867855828919
H	-3.64962947262750	-1.59931460137205	0.35426687458656
P	-5.25045534113149	0.08342844798907	2.89414383287488
C	-5.23310820744133	0.33362064907407	-0.75303714562567
H	-6.00733535595825	1.10407149448454	-0.69465455858794
C	-8.12513185941497	1.94268780253480	1.13435129554763
H	-8.04498401056756	1.53594053364495	0.12212515282326
H	-5.02532793632946	0.14352915236306	-1.81131705489818
H	-9.02258133342323	2.56830543678245	1.17674310135970
H	-4.32423437021101	0.71518777738605	-0.28371199861375
H	-7.25584923885548	2.57853034585977	1.32373857190537

GS: Mes*OP(*t*BuC)$_2$P· – P–C bond cleavage



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G = −1852.58381872 Eh

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C	-0.94953307805334	1.85813320160192	5.29880448022257
C	0.24239859881650	2.39385012656837	6.09756427025086
C	-0.72555376548353	1.08792725306412	4.16227810380215
H	0.29822542163442	0.87751845899999	3.88497463762674
C	-1.74937859595026	0.56006700614172	3.38441560851426
C	-1.38733911334387	-0.40801169041211	2.23716613278704
C	-3.07622402278175	0.87793626273538	3.75939969531904
C	-3.35678050347911	1.57760934860481	4.94556949167254
C	-4.77265018909285	1.84862135676299	5.50301703880177
O	-4.12689721578543	0.41186645905463	2.96487680100443
C	0.12321846524418	-0.69572628715833	2.18557108772752
C	-1.75261261393940	0.15242905120892	0.85227436152057
C	-2.07528678368105	-1.76161655516658	2.48890792512485
C	-0.19444665571274	3.19133501726167	7.33102947848962
C	1.08466869126988	3.31532811711856	5.19964176230038
C	1.10950631675320	1.21542096069715	6.57398408081962
C	-4.73087555567309	2.13653335009246	7.01749397340176
C	-5.71083855763451	0.63793507175342	5.34436852977557
C	-5.36090146225850	3.10271396599800	4.83359488433844
H	0.49242552803818	4.16991866558021	4.85737287970219
H	1.45470391416790	2.78720056323454	4.31611296899227
H	1.95055413424046	3.69629864413737	5.75190129851124
H	-0.80347390538532	4.05920506977526	7.05849175460996
H	0.69075991444454	3.55912304008001	7.85919420319834
H	-0.76609437374585	2.57277719684039	8.03046582415527
H	-4.22545039015487	1.33708849770639	7.56855188592849
H	-5.75801484558158	2.20637078652056	7.38743781379817
H	-4.24422056406654	3.08618378238880	7.25485902072267
H	-4.74009101813026	3.97565436262177	5.06127281759217
H	-6.37216515214929	3.29328041704336	5.21082787752598
H	-5.41942180798787	3.01167792155951	3.74883528047058
H	-1.32731893911749	1.15171279558836	0.71443863374249
H	-2.82583290713288	0.22062590491009	0.68335012800966
H	-1.34593937892208	-0.50199376959384	0.07293807564804
H	0.70669881903986	0.19592972240896	1.93449685427361
H	0.30683018057676	-1.43834288743423	1.40332759610548
H	0.49690690759082	-1.10782743111750	3.12764515214092
H	-5.26590158851206	-0.25030964352955	5.80656857287501
H	-5.93743284451009	0.39332073345751	4.31048615101378
H	-6.65620908250911	0.84768778944596	5.85547150483441
H	0.52579774373024	0.53580397058176	7.20317719855840
H	1.95899726085026	1.58258110267783	7.15992648878694
H	1.50687999356279	0.63936143331448	5.73353540918250
H	-1.70324493791782	-2.20214734911242	3.41980242372746
H	-1.84980720697005	-2.45668936549518	1.67207167124824
H	-3.15609198589722	-1.66320924208216	2.57129000927178
H	-8.26010056128661	-1.08681409642240	0.49273791416017
H	-8.94197407663567	2.29337691495735	-0.94497012898016
H	-7.56832288311314	-2.61681413299932	-0.08023268894145
H	-8.30846676081957	2.43519979141733	-2.59687482587217
H	-7.37286083173370	-1.14148125883575	-1.04150326404350
C	-7.40421437680925	-1.53590571515369	-0.02162573413045
C	-8.21251730005754	1.88776500563784	-1.65276150189497
H	-8.46344723477724	0.83924236423641	-1.83664611686029
P	-6.97514083005390	1.47409814703505	1.94266839058272
H	-7.17119385201570	3.95590265077342	-0.15845669857551
H	-7.04676976445739	-1.61048250207154	2.65070150337306
H	-6.57903429592185	4.06773213877831	-1.82825431960334
C	-6.47772711453930	3.52053604809099	-0.88470628759244
C	-6.67300785406355	1.31826874185955	0.21885950042517
C	-5.93424191958047	0.26012020937496	0.88580966647944
C	-6.78379423396455	2.02879923297134	-1.09834745276474
C	-6.09816253361974	-1.25093234699666	0.72872204374245
H	-6.21337371958143	-3.02269343150609	1.97143479792719
C	-6.15811726171515	-1.93629947187275	2.10021236010650
H	-5.45911887738331	3.65999316464622	-0.50964239806998
H	-5.28290057131002	-1.70376588073178	2.70894029628189
P	-4.75599515279894	1.34654083684714	1.73232189963593
C	-4.92018218213943	-1.80823961284303	-0.08333238482874
H	-4.82907137993465	-1.30054303123576	-1.04869761435131
C	-5.77852083269811	1.43516703715408	-2.09296639318193
H	-5.99896198424636	0.38272924361022	-2.29609746329658
H	-5.07125663543708	-2.87642102879441	-0.27252422869159
H	-5.82099797108685	1.97819398636952	-3.04283015622540
H	-3.97697013165909	-1.69269337587642	0.45343875574975
H	-4.75749757039598	1.50412579346610	-1.70311054718514

4.4.7 Mass Spectra

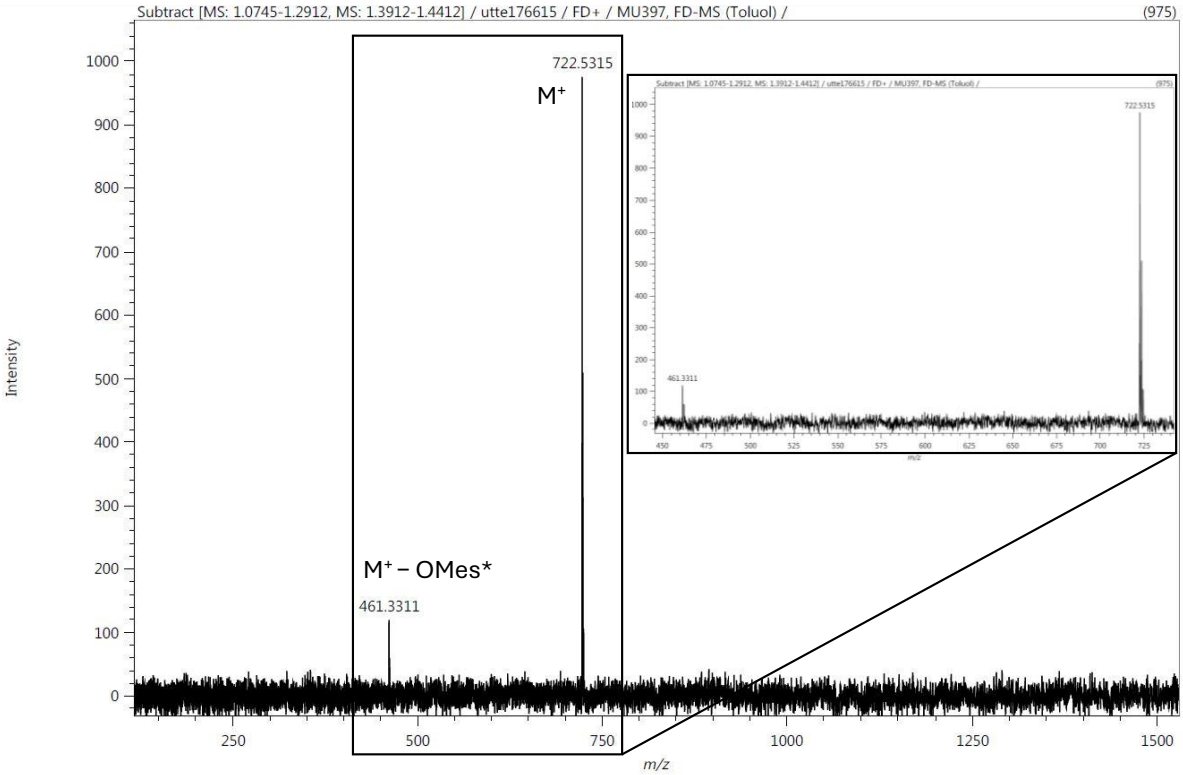

Figure S32. Field desorption mass spectrum of **1**.

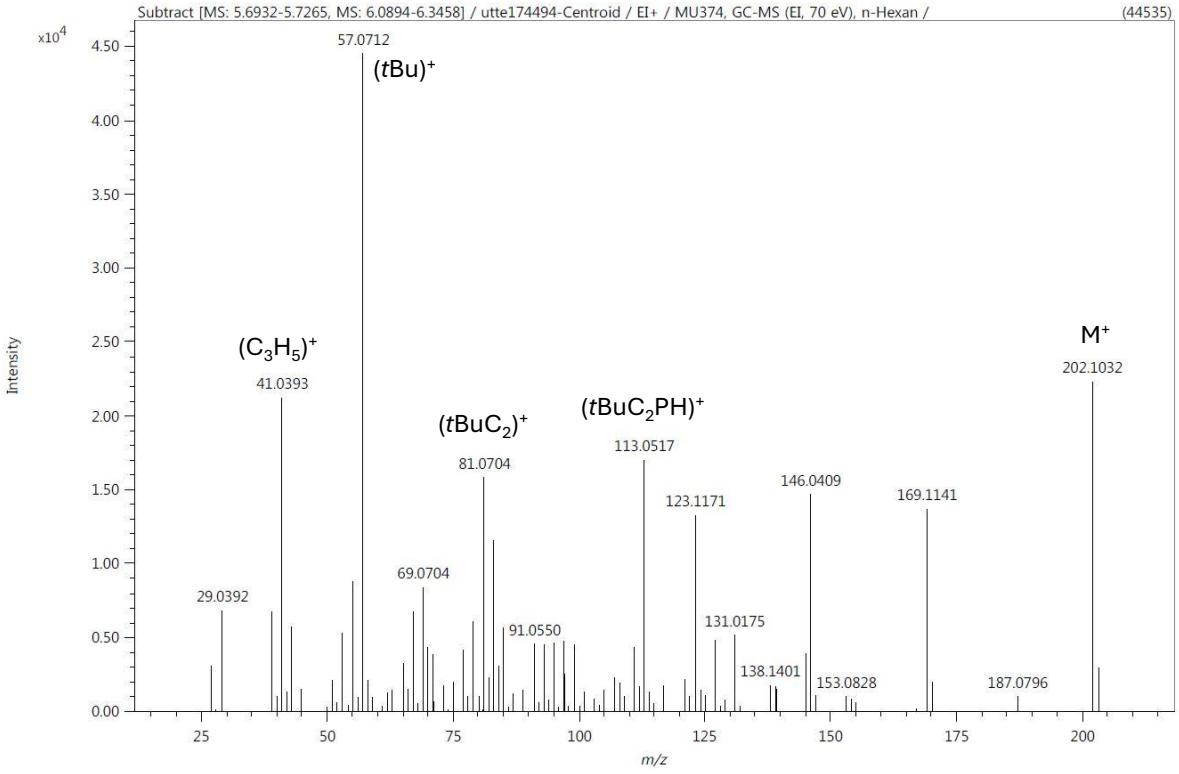

Figure S33. Electron ionisation mass spectrum of **4**. The strong fragmentation is due to the ionisation method (EI, 70 eV).

4.5 Notes and references

‡ Considering that the reaction of **F** with radicals was observed in the absence of light, photo-isomerisation of **F** to its 1,2-diphosphacyclobutadiene isomer and subsequent radical addition can be excluded as a possible mechanism.[21]

§ The reaction mechanism of **F** and I_2 forming **3** is currently unknown. However, based on previously reported quantum chemical calculations on the reaction of P_4 with I_2, it is plausible that this reaction occurs through closed-shell species and involves the concerted reaction of I_2 with **F** as the initial step.[44] However, the formation of an electron donor-acceptor complex between **F** and I_2, which might induce a single electron transfer, cannot be ruled out.

§§ Compounds **2** and **3** are also formed by reactions of the ladderane (tBuCP)$_4$ (**I**) with $(SePh)_2$ and I_2, respectively.

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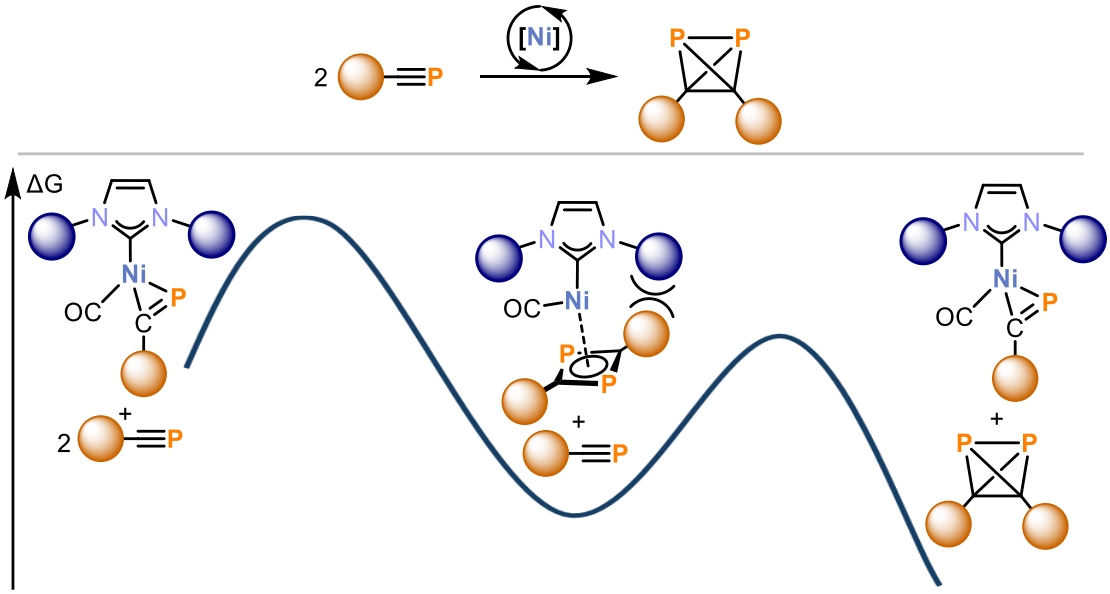
5 Synthesis of Diphosphatetrahedranes: Quantum Chemical and Experimental Investigations on the Mechanism[a]

Abstract: Di-*tert*-butyldiphosphatetrahedrane (*t*BuCP)$_2$, the only isolated diphosphatetrahedrane to date, is accessible via the N-heterocyclic carbene (NHC) Ni-catalysed dimerisation of *tert*-butylphosphaalkyne. To gain a deeper understanding of the steric effects on the formation of diphosphatetrahedranes from phosphaalkynes catalysed by (NHC)Ni(CO)(RCP), we investigated a variety of substituents on both the phosphaalkyne and NHC ligand by means of density functional theory (DFT) calculations, combined with experimental studies. Two competing steric effects were identified, indicating that for both very bulky and very small substituents on phosphaalkyne and NHC, product formation is kinetically or thermodynamically hindered. These findings indicate that only a narrow steric window allows productive catalysis.



[a] All experiments and DFT calculations were conducted by Maria K. Uttendorfer. Andreas W. Ehlers supervised the theoretical study. Robert Wolf conceptualised, supervised, and directed the project. Maria K. Uttendorfer wrote the manuscript, which was edited by Andreas W. Ehlers, Gábor Balázs and Robert Wolf.

5.1 Introduction

Tetrahedranes, molecules featuring a tetrahedral core of four atoms, have long captivated chemists due to their inherent ring strain, high symmetry, and challenging syntheses.[1] The first carbon-based tetrahedrane, tetra-*tert*-butyltetrahedrane, was isolated in 1978 by Maier and co-workers,[2] paving the way for a range of related compounds.[3] However, the earliest isolation of a tetrahedrane, white phosphorus (P_4), dates back to 1668.[4] Owing to the isolobal relationship between the HC unit and phosphorus, mixed tetrahedranes were envisioned and predicted to be stable.[5] In 2019, our group reported the synthesis of di-*tert*-butyldiphosphatetrahedrane, (tBuCP)$_2$ (**1**, Figure 1a), via the nickel catalysed dimerisation of *tert*-butylphosphaalkyne.[6] Almost simultaneously, Cummins and co-workers reported the synthesis of tri-*tert*-butylphosphatetrahedrane ((tBuC)$_3$P),[7] and, shortly thereafter, phosphatetrahedrane (HCP_3).[8] Reactivity studies on these have demonstrated their potential to form a variety of organo(metallic) phosphorus compounds. Coordination of phosphatetrahedranes to metal centres can either lead to retention of the tetrahedral shape,[6,8,9] or isomerisation to diphosphacyclobutadiene ligands (Figure 1b, top, examples of **1**).[10]

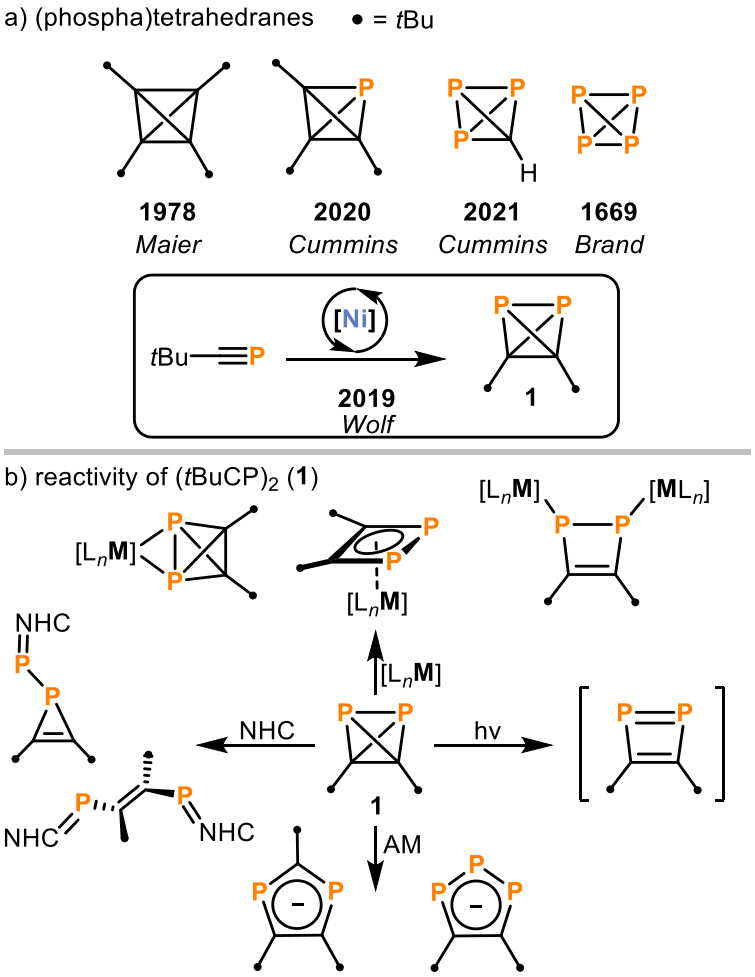


Figure 1. a) Selected (phospha)tetrahedranes, b) reactivity of di-*tert*-butyldiphosphatetrahedrane (**1**) towards [ML_n] (top, M = Fe, Co, Ni; L *e.g.* 1,5-cyclooctadiene, anthracene, cyclopentadienyl), irradiation (right), alkali metals (bottom, AM = Li, Na, K, Rb, Cs), and N-heterocyclic carbenes (NHC, left).[6]

Isomerisation of **1** to diphosphacyclobutadiene as a transient species can also be achieved upon UV or visible light irradiation (Figure 1b, right).[11] Similarly (tBuC)$_3$P isomerises to phosphacyclobutadiene upon reaction with Lewis acids.[12] Reduction of **1** with alkali metals leads to 1,2,3-triphospholides and 1,2-diphospholides (Figure 1b, bottom),[13] while reaction with N-heterocyclic carbenes leads to the formation of phosphirenes or bis(phosphaalkenes), depending on the steric requirements of the NHC (Figure 1b, left).[14] In reactions with base-stabilised silylenes or Ph_3PCH_2, (tBuC)$_3$P functions as a synthon of (tri-*tert*-butylcyclopropenyl)phosphinidene, leading to phosphasilene and diphosphirane, respectively.[15] These studies show that phosphatetrahedranes serve as precursors for a variety of different compounds. However, to date, only three phosphatetrahedrane representatives could be isolated, *i.e.* (tBuC)$_3$P, (tBuC)$_2$P$_2$ and HCP$_3$.[6-8] Except for the latter, only representatives with tBu substituents are known. This can be attributed to the stabilizing influence of bulky substituents on tetrahedral molecules, a phenomenon dubbed "corset effect" by Maier and co-workers.[16] Subsequent investigations by Cummins and co-workers identified hydrogen-hydrogen bonds between the tBu-groups as the primary stabilizing factor.[17] Since the diphosphatetrahedrane (tBuCP)$_2$ (**1**) was synthesised via a catalytic reaction starting from *tert*-butylphosphaalkyne, we aimed to investigate whether a library of diphosphatetrahedranes (**A**) can be synthesised by this method, considering that various differently substituted phosphaalkynes have been reported.[18]

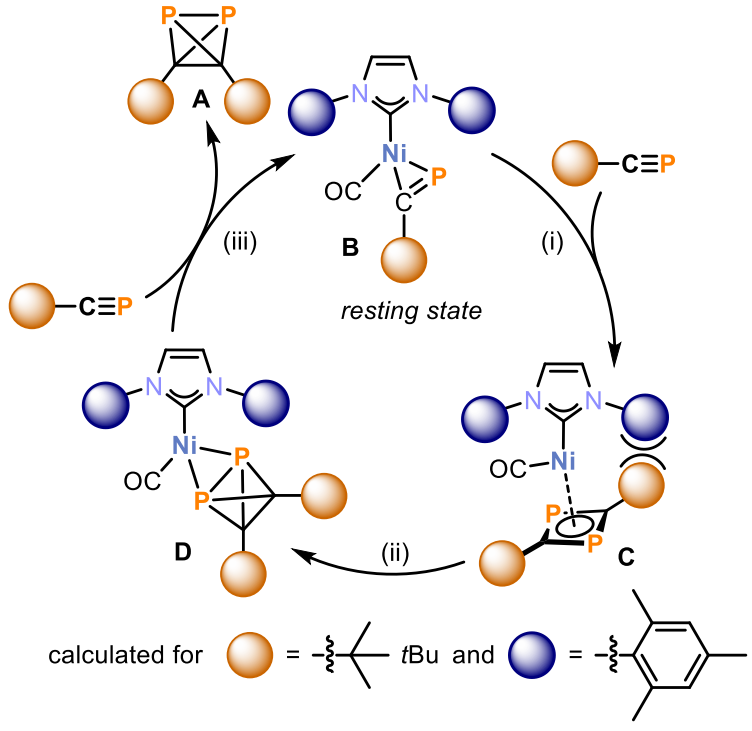


Figure 2. Proposed mechanism for the formation of di-*tert*-butyldiphosphatetrahedrane (**1**).[6]

Initial investigations into the mechanism of the formation of **1**, conducted by ^{31}P NMR spectroscopic reaction monitoring and DFT calculations, suggest that the precatalyst (IMes)Ni(CO)$_3$ forms the active species **B** upon substitution of two CO ligands by an

η^2-coordinating phosphaalkyne (Figure 2, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene).[6] Subsequent coordination of a second phosphaalkyne generates the diphosphacyclobutadiene complex **C**, which, due to steric repulsion between the bulky N-heterocyclic carbene (NHC) ligand and the phosphaalkyne, rearranges to the diphosphatetrahedrane complex **D**. **1**, being a weak ligand, is easily substituted by a phosphaalkyne leading to the regeneration of **B**, which also represent the resting state. While these initial investigations have outlined the general catalytic cycle, a more in-depth study of the mechanism, especially regarding activation barriers, is needed to fully understand the catalytic dimerisation process and to assess how the steric bulk of the phosphaalkyne and NHC affects it. This will enable broader application to different phosphaalkynes and help predict the optimal NHC and phosphaalkyne combinations for producing the corresponding diphosphatetrahedranes. Herein, we report a combined computational and experimental investigation of the steric effects of NHC and phosphaalkyne on the formation of diphosphatetrahedranes.

5.2 Results and Discussion

5.2.1 Transformation from B to C (Figures 3 and 4)

The density functional theory (DFT) calculations were performed at the TPSS-D3BJ/def2-TZVP level of theory.[19] The focus was first to ascertain the influence of the steric bulk of the substituent R on the phosphaalkyne (R = H, Me, *t*Bu) on the transformation of the active catalyst **B** (here modelled as [(IXy)Ni(CO)(RCP)] with R = H, Me, *t*Bu; IXy = 1,3-bis(2,6-dimethylphenyl)imidazolin-2-ylidene) to the intermediate **C**. This process proceeds by the addition of a second phosphaalkyne to **B**, forming the first intermediate **Int1** (Figure 3). It is worth noting that in the initial investigation into the mechanism, only the thermodynamic process was calculated.[6] Although many factors influence the accuracy of the calculations of the transformation from **B** to **Int1**, it can be assumed that these factors do not have a decisive effect on the parameters and merely cause scaling. As could be expected, DFT calculations using uncorrected gas phase entropies overestimate the activation barrier.[20]

Subsequently, **Int1** isomerises to form the metalla-2,4-diphosphacyclopentadiene intermediate **Int2** over the transition state **TS1**. **TS1** is critical for the catalytic system, as no subsequent transition state exhibits a significantly higher energy (not more than +2 kcal·mol^{-1} compared to **TS1**, Figure 7), which suggests that this is the rate-determining step for the transformation **B** → **C**. The rearrangement of **Int2** to **C** proceeds via another intermediate (**Int3**, Figure 7, *vide infra*) and two transition states, which are of similar energies to **TS1** (see Figure 7 for details).

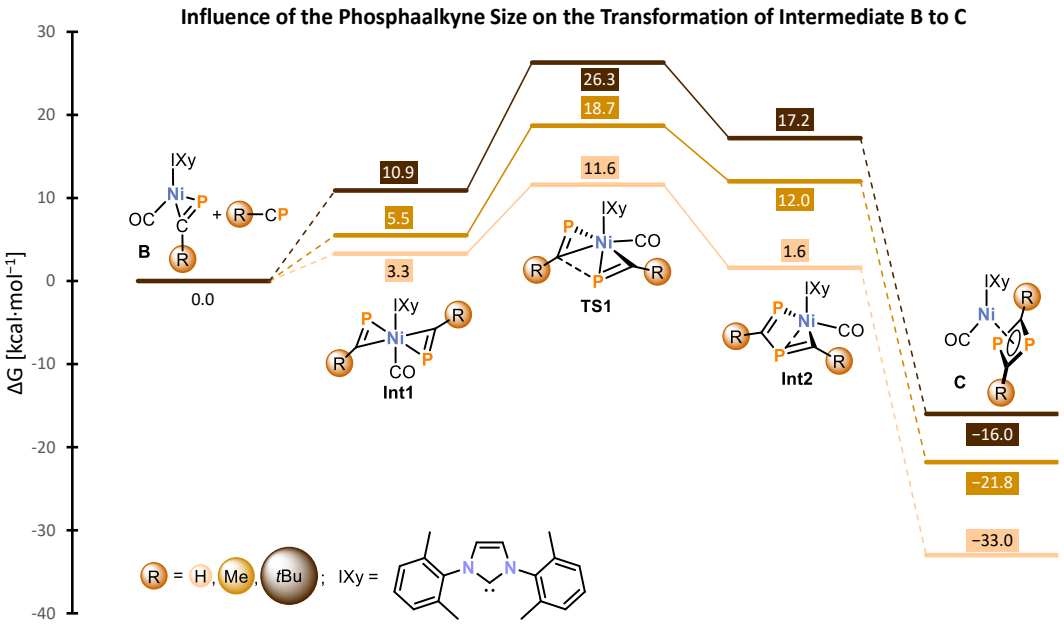


Figure 3. Calculated Gibbs free energy profiles for the transformation **B** → **C** with different phosphaalkyne substituents (R) at the TPSS-D3BJ/def2-TZVP level of theory and schematic drawings of intermediates and transition states. IXy = 1,3-bis(2,6-dimethylphenyl)imidazoline-2-ylidene. Gibbs free energies (in kcal·mol^{-1} at 298 K).

A clear trend is observed in the energies of the activation barriers ($\Delta G^{\ddagger}_1$) with the bulkiness of the substituent on the phosphaalkyne (R, Figure 3). While for the parent phosphaalkyne (R = H), the

activation barrier is rather low ($\Delta G^{\ddagger}_1$ = 11.6 kcal·mol^{-1}), for R = *t*Bu it is significantly higher ($\Delta G^{\ddagger}_1$ = 26.3 kcal·mol^{-1}). Methylphosphaalkyne, with moderate steric bulk, shows an intermediate value of 18.7 kcal·mol^{-1} (Figure 3). This indicates that increasing the steric bulk of R directly correlates with a higher activation barrier for **TS1**. The relative energy of **C** compared to **B** inversely correlates with the size of R, *i.e.* the Me derivative of **C** is considerably more stable (ΔG_C = −21.8 kcal·mol^{-1}) than the *t*Bu derivative (ΔG_C = −16.0 kcal·mol^{-1}; Figure 3).

These computational results agree with experimental outcomes. For the synthesis of **1**, the reaction mixture has to be heated to 60 °C for 18 h, which is consistent with an activation barrier of 26.3 kcal·mol^{-1}.[6] Extrapolating from the conducted calculations, it can be assumed that even bulkier phosphaalkynes lead to even higher activation barriers. Indeed, the reaction of 10 equivalents of bulky mesitylphosphaalkyne with the precatalysts (IMes)Ni(CO)$_3$ (see Figure S1), does not afford the corresponding tetrahedrane nor to the corresponding complex **C**, even after heating to 60 °C overnight. Higher temperatures lead to decomposition of **1** and were thus not investigated.[6] Additionally, minor decomposition of MesCP was detected under these reaction conditions (see Figure S2). The ^{31}P NMR spectra show significant amounts of unreacted phosphaalkyne, along with a so far unidentified signal at 132.8 ppm (see Figure S2), which tentatively can be assigned to a complex similar to **B**. These results suggest that the formation of **C** is hindered by a high-energy **TS1**.‡

Having explored the steric influence of R on the transformation from **B** to **C**, we next investigated the impact of the steric bulk of the NHC on this part of the catalytic cycle (Figure 4). The addition of *t*BuCP to the complexes [(NHC)Ni(CO)(*t*BuCP)] (**B**), forming **Int1**, its subsequent conversion to **Int2**, and the relative energies of **C** were investigated for the NHCs IH, IPh, IXy (IH = imidazoline-2-ylidene; IPh = 1,3-diphenylimidazoline-2-ylidene, Figure 4) possessing differently sized substituents R' on the imidazoline-2-ylidene. The calculated Gibbs free energy profile is very similar to that calculated for different substituents R on the phosphaalkynes, *i.e.* the transformation of **Int1** into **Int2**, over **TS1** is the rate-determining step. The relative energy of **TS1** increases with increasing R' ("parent system" R = R' = H: $\Delta G^{\ddagger}_1$ = 10.8 kcal·mol^{-1}; IH: $\Delta G^{\ddagger}_1$ = 19.7 kcal·mol^{-1}, IPh: $\Delta G^{\ddagger}_1$ = 22.9 kcal·mol^{-1}, IXy: $\Delta G^{\ddagger}_1$ = 26.3 kcal·mol^{-1}), indicating faster reactions for smaller NHCs. In addition, the steric demand of the NHC also influences the stability of **C**. As observed for phosphaalkynes, increased R' bulk leads to stronger repulsive interactions with the phosphaalkyne and greater destabilisation of C ("parent system" R = R' = H: ΔG_B = −33.3 kcal·mol^{-1}; IH: ΔG_B = −25.2 kcal·mol^{-1}, IPh: ΔG_B = −22.2 kcal·mol^{-1}, IXy: ΔG_B = −16.0 kcal·mol^{-1}).

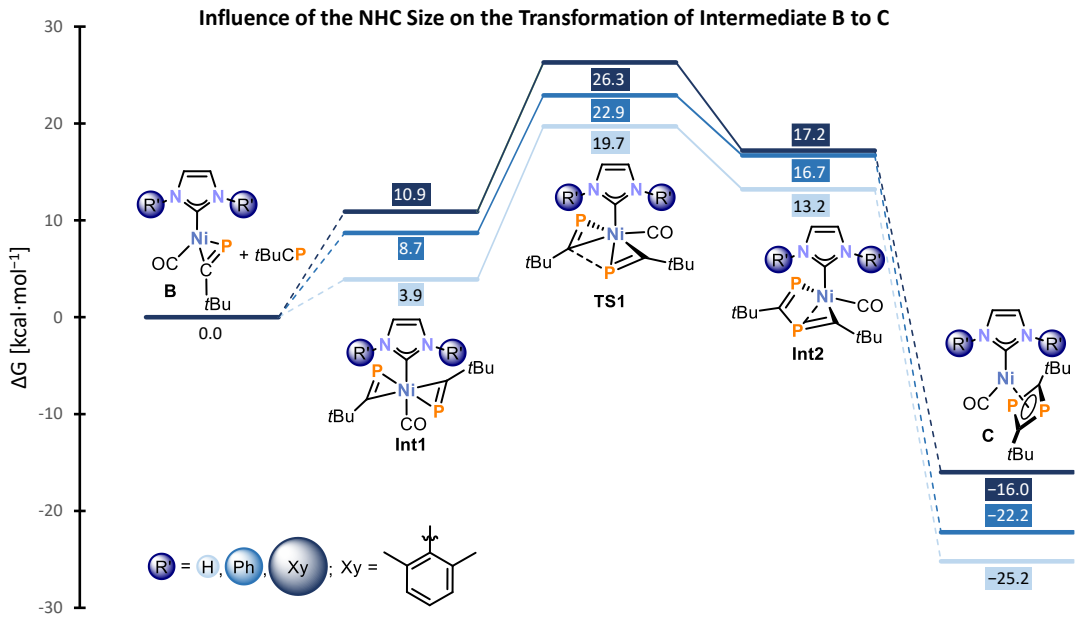


Figure 4. Calculated Gibbs free energy profiles for the transformation **B** → **C** with different NHC substituents (R') at the TPSS-D3BJ/def2-TZVP level of theory and schematic drawings of intermediates and transition states. Xy = 2,6-dimethylphenyl. Gibbs free energies (in kcal·mol^{-1} at 298 K).

Experimental data obtained from the catalyst screening for the synthesis of **1** validate the results from the calculations. The dimerisation of *t*BuCP catalysed by (IPr)Ni(CO)$_3$ is lower yielding than with the sterically slightly less demanding (IMes)Ni(CO)$_3$, *i.e.* 49% and 67% yield, respectively (IPr = 1,3-bis(2,6-di-*iso*-propylphenyl)imidazolin-2-ylidene). However, the difference is within the experimental error.[6] In comparison, recent experiments subjecting the even bulkier [(6-Dipp)Ni(CO)$_3$] to similar reaction conditions gave only minor amounts of **1** (3%), while significant amounts of unreacted phosphaalkyne remain (6-Dipp = :C({Dipp}NCH$_2$)$_2$CH$_2$, Dipp = 2,6-di(*iso*-propyl)phenyl). This confirms that, extrapolated from the conducted calculations, for very bulky NHCs the relative energy of **TS1** is too high (Figure 4). It is worth noting that **C** was detected by ^{31}P NMR spectroscopy only for one phosphaalkyne/NHC combination (R = *t*Bu, NHC = *i*Pr$_2$Im^{Me}; *i*Pr$_2$Im^{Me} = 1,3-di(*iso*-propyl)-4,5-di(methyl)imidazoline-2-ylidene). Therefore, the formation of tetrahedrane derivatives **A** must be considered instead.

Summing up, for the transformation of **B** to **C**, a clear trend emerges: Small substituents on phosphaalkyne (R) and NHC (R'), both lead to energetically low lying **TS1** and stabilise the intermediate **C**. While large substituents lead to higher transition states (**TS1**) and destabilise **C**.

5.2.2 Transformation of C to A and B (Figures 5 and 6)

Next, we examined the transformation of **C** to **D** and the formation of the final product (Figure 5). The diphosphacyclobutadiene complex **C** is a local minimum. It isomerises over the transition state **TS4** to the intermediate **Int4**, which then rearranges over **TS5** to form the tetrahedrane complex **D**. A ligand exchange of the formed tetrahedrane by phosphaalkyne releases **A** and regenerates **B**, closing the catalytic cycle.

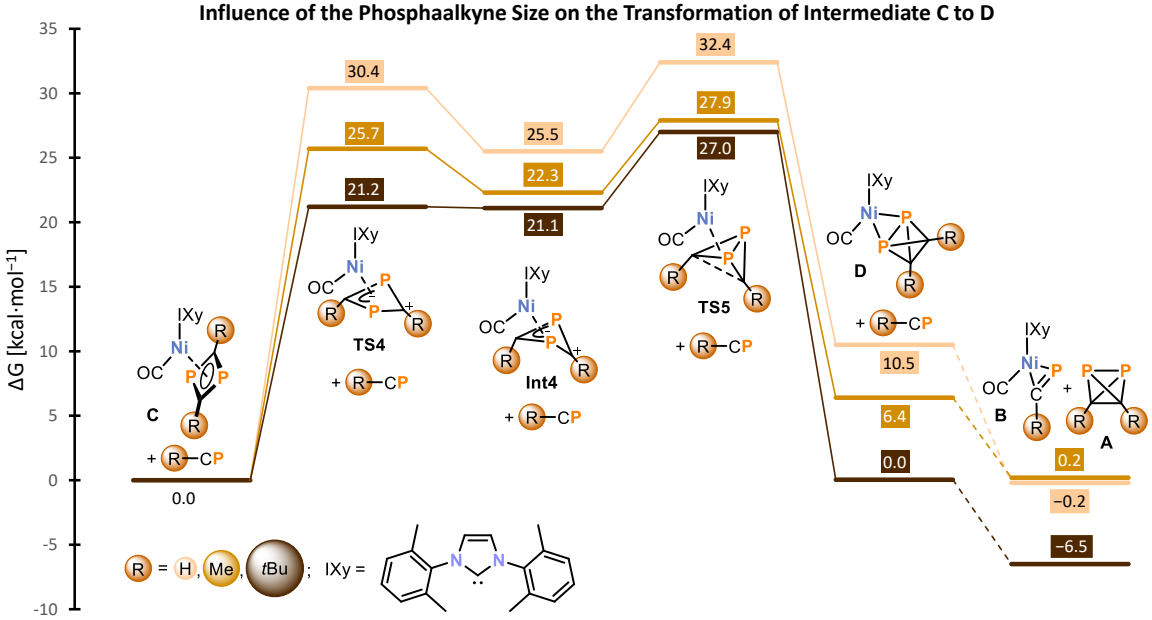


Figure 5. Calculated Gibbs free energy profiles for the transformation **C** → **A** + **B** for different phosphaalkyne substituent (R) at the TPSS-D3BJ/def2-TZVP level of theory and schematic drawings of intermediates and transition states. IXy = 1,3-bis(2,6-dimethylphenyl)imidazoline-2-ylidene. Gibbs free energies (in kcal·mol^{-1} at 298 K).

The relative energy of **TS4** is relatively high, but still in the chemically accessible range (Figure 5). The steric bulk of the phosphaalkyne substituent R has a strong influence on the energy, *i.e.* bulky substituents R lower the activation barrier (R = H: $\Delta G^{\ddagger}_4$ = 30.4 kcal·mol^{-1}, R = Me: $\Delta G^{\ddagger}_4$ = 25.7 kcal·mol^{-1}, R = *t*Bu: $\Delta G^{\ddagger}_4$ = 21.2 kcal·mol^{-1}), probably due to repulsion with the NHC substituents R' on the NHC, which destabilises **C**. The rate determining step of this transformation is the transition state **TS5**, which lies, for most combinations of substituents on phosphaalkyne (R) and NHC (R'), energetically slightly higher than **TS4** (Figure 5). Similarly to **TS4**, bulky phosphaalkyne substituents (R) lower the energy of **TS5**, rendering the conversion of **C** to **D** more feasible (R = H: $\Delta G^{\ddagger}_5$ = 32.4 kcal·mol^{-1}, R = Me: $\Delta G^{\ddagger}_5$ = 27.9 kcal·mol^{-1}, R = *t*Bu: $\Delta G^{\ddagger}_5$ = 27.0 kcal·mol^{-1}; Figure 5). The release of **A** from **D** is an exergonic process and does not play a significant role in this process. Most importantly, the energy balance of this transformation (**C** to **A** and **B**) is almost zero for the less bulky methyl- and parent phosphaalkyne (ΔG = ±0.2 kcal·mol^{-1}), but it is exergonic for the *tert*-butylphosphaalkyne (ΔG = −6.5 kcal·mol^{-1}, Figure 5). This shows that bulky R substituents are needed to render the formation of the corresponding tetrahedranes **A** exergonic.

To validate the calculated thermodynamic parameters, we investigated the reaction of MeCP with $(IMes)Ni(CO)_3$. Based on the results of the DFT calculations on the model system (R = *t*Bu and R' = Xy), the formation of the diphosphatetrahedrane **A** is energetically unfavourable, as the intermediate **C** is lower in energy ($\Delta\Delta G = 0.2$ kcal·mol^{-1}, Figure 5). The reaction of 10 equivalents of MeCP with $(IMes)Ni(CO)_3$ results in an orange solution with brown insoluble precipitate. In the ^{31}P NMR spectrum, no signal for the dimethyldiphosphatetrahedrane **A** could be detected, which is consistent with the DFT prediction. However, a singlet at 105.5 ppm was detected in the ^{31}P NMR spectrum. Attempts to assign this signal based on calculated ^{31}P NMR chemical shifts were inconclusive, due to the very similar values predicted for species **B** and **C** (see Table S1), and the fact that single crystals suitable for single-crystal X-ray diffraction have not yet been obtained.

The size of the NHC ligand has a similar effect as the bulk of the R substituent on the process **C** to **A** (*vide supra*, Figure 6). The larger the NHC ligand, the lower the activation barriers of **TS4** and **TS5** ("parent system" R = R' = H: $\Delta G^{\ddagger}_4 = 31.9$ kcal·mol^{-1}, $\Delta G^{\ddagger}_5 = 32.6$ kcal·mol^{-1}; NHC = IH: $\Delta G^{\ddagger}_5 = 36.8$ kcal·mol^{-1}; NHC = IPh: $\Delta G^{\ddagger}_4 = 31.3$ kcal·mol^{-1}, $\Delta G^{\ddagger}_5 = 34.1$ kcal·mol^{-1}; NHC = IXy: $\Delta G^{\ddagger}_4 = 21.2$ kcal·mol^{-1}, $\Delta G^{\ddagger}_5 = 27.0$ kcal·mol^{-1}; Figure 6). This enables a more facile transformation of **C** to **A**. Additionally, **B** plus **A** are lower in energy compared to **C**, with increasing size of the NHC substituent (R'). This is especially relevant as **A** plus **B** are less stable than **C** for small NHCs (NHC = IH: $\Delta G = 2.6$ kcal·mol^{-1}), preventing their formation. In contrast, for bulkier NHCs, the final product **A** is the global minimum of the mechanism (NHC = IMes: $\Delta G = -6.5$ kcal·mol^{-1}), thus allowing for the completion of the catalytic cycle.

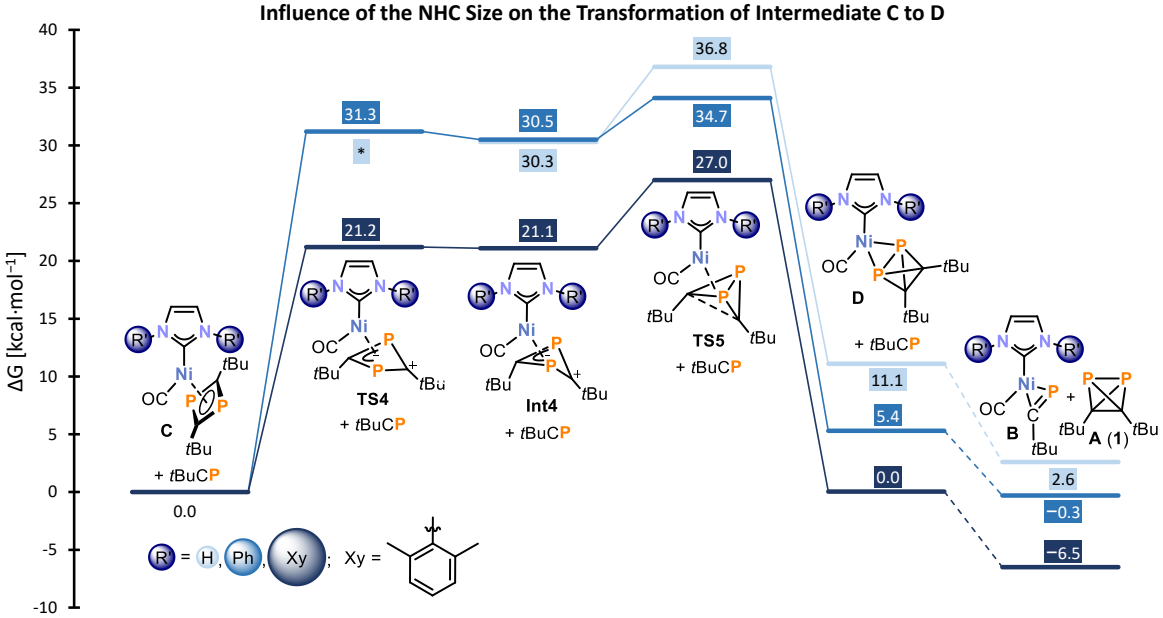


Figure 6. Calculated Gibbs free energy profiles for the transformation **C** → **A** + **B** for different NHC substituents (R') at the TPSS-D3BJ/def2-TZVP level of theory and schematic drawings of intermediates and transition states. Xy = 2,6-dimethylphenyl. Gibbs free energies (in kcal·mol^{-1} at 298 K). * **TS4** with R = H and R' = IXy could not be located, probably due to a flat energy hypersurface. It can be assumed that its energy lies relatively close to that of **Int4**.

The strong influence of the NHC on whether the reaction stops at intermediate **C** or proceeds to the diphosphatetrahedrane **A** had already been reported.[6] While nickel carbonyl complexes with the bulky NHCs IPr or IMes serve as precatalysts for the formation of **1**, using the less bulky NHC *i*Pr$_2$Im^{Me} leads only to the formation of minor amounts of the corresponding tetrahedrane **A** (3% yield). Instead, complex **C** was isolated, further supporting the results of the DFT calculations.[6] Indeed, computational analysis for the transformation of **C** to **A** and regeneration of **B** for the combination of R = *t*Bu and NHC = *i*Pr$_2$Im^{Me} predicts an endergonic process ($\Delta\Delta G$ = 3.0 kcal·mol^{-1}, see Section 5.4.3). Additional calculations indicate that the steric demand of phosphaalkyne and NHC has a significantly stronger influence on the catalytic formation of **A** when both compounds are at least moderately bulky (see Figures S7 to S12).

5.2.3 The full catalytic cycle (Figure 7)

With all the computational insights into the steric effects on the mechanism of the catalytic formation of diphosphatetrahedranes in mind, we revisit the entire catalytic cycle (Figure 7).§ The transition state **TS1** for the addition of a second phosphaalkyne ligand to **B** is highly dependent on the steric bulk of substituents on both phosphaalkyne (R) and NHC (R'): the bulkier both are, the higher the activation barrier ($\Delta G^{\ddagger}_1$). Conversely, small R and R' facilitate the formation of intermediate **C**, which is energetically more stable compared to systems with bulky R and R'. Now, the relative energy of **TS1** is decisive for the formation of **C**, while the relative energy of **C** is crucial for its transformation to the corresponding tetrahedrane **A**. If the relative energy of **TS1** is too high, the intermediate **C** is not formed. This might be the case for very bulky substituents. On the other hand, if the relative energy of **C** is too low, which is the case for sterically less demanding substituents, *i.e.* H or Me, the activation barrier ($\Delta G^{\ddagger}_5$) is too high, and **C** does not transform to the tetrahedrane **A**. This indicates that a specific combination of substituents is required for the formation of **A**. R and R' must be small enough to allow the formation of **C**, but large enough to prevent its excessive stabilisation.

The transformation of two phosphaalkynes to a diphosphatetrahedrane **A** catalysed by **B** is exergonic for all investigated combinations of substituents on phosphaalkyne (R) and NHC (R') combinations. However, if R or R' is small, the transformation of intermediate **C** with one phosphaalkyne to **A** and **B** can have a $\Delta\Delta G$ of approximately 0 kcal·mol^{-1}, meaning that the formation of **A** is not energetically advantageous (e.g. for R = H, R' = H, Figure 7; R = *t*Bu, R' = Ph, Figure 6; R = H or Me; R' = Xy, Figure 5). In certain cases, this process is endergonic (($\Delta\Delta G$ = 1.5 kcal·mol^{-1} for R = Me, R' = Ph, Figure 7; $\Delta\Delta G$ = 2.6 kcal·mol^{-1} for R = *t*Bu, R' = H, Figure 6), with **C** as the energetic minimum, thus preventing the formation of **A**. For sufficiently bulky NHCs and phosphaalkynes, the formation of **A** and the regeneration of **B** are energetically downhill, allowing for the closure of the catalytic cycle.

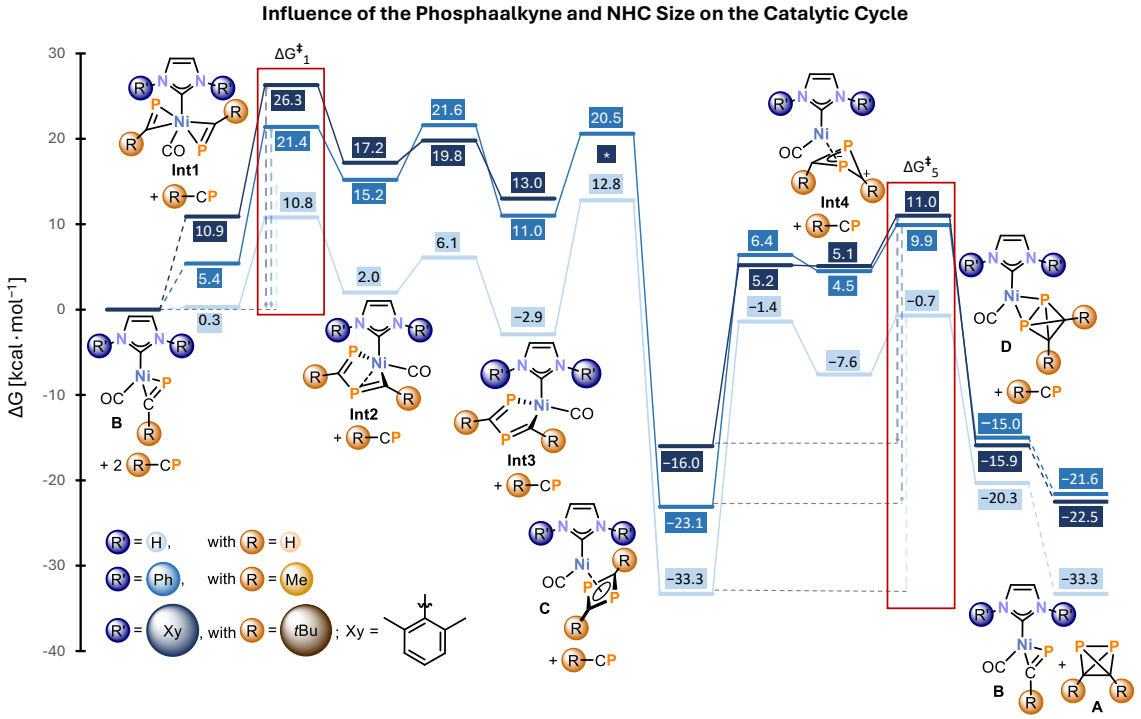


Figure 7. Calculated Gibbs free energy profiles for the transformation **B** + 2 equivalents of phosphaalkyne → **A** + **B** at the TPSS-D3BJ/def2-TZVP level of theory and schematic drawings of intermediates and transition states. Gibbs free energies (in kcal·mol^{-1} at 298 K). *** TS3** with R = *t*Bu and R' = IXy could not be located, probably due to a flat energy hypersurface. It can be assumed that its energy lies in the range of **TS3** calculated for other substituents on phosphaalkyne (R) and NHC (R').

5.3 Conclusion

This combined computational and experimental study of the nickel-catalysed dimerisation of phosphaalkynes to diphosphatetrahedranes highlights the critical role of steric effects from both the phosphaalkyne and NHC ligands in the successful product formation. The rate determining step, *i.e.* the formation of the metalla-2,4-diphosphacyclopentadiene **Int2**, shows a higher activation barrier with larger NHC and phosphaalkyne substituents. On the other hand, a steric clash between these groups is necessary to destabilise the diphosphacyclobutadiene intermediate **C**, which in less bulky systems acts as an energetic sink that prevents product formation. Experimental results across various NHC-phosphaalkyne combinations support these computational findings. To synthesise diphosphatetrahedranes with different substituents, a fine balance in the steric bulk of the catalyst and phosphaalkyne is essential. Ongoing work in our labs aims to identify suitable NHC-phosphaalkyne combinations to expand the range of accessible diphosphatetrahedranes.

5.4 Supporting Information

General: All reactions and product manipulations were carried out in flame-dried glassware under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques (maintained at <0.1 ppm H_2O and <0.1 ppm O_2). *t*BuCP,[21] MeCP,[22] MesCP,[23] [(NHC)Ni(CO)$_3$] (NHC = IMes, IPr, *i*Pr$_2$Im^{Me}; IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene, *i*Pr$_2$Im^{Me} = 1,3-di(*iso*-propyl)-4,5-di(methyl)imidazolin-2-ylidene),[6,24] [(NHC)Ni(CO)(*t*BuCP)] (NHC = IMes, IPr),[6] and 6-Dipp (:C({Dipp}NCH$_2$)$_2$CH$_2$; Dipp = 2,6-di(*iso*-propyl)phenyl).[25] were prepared according to procedures previously reported in the chemical literature. All other chemicals were purchased from commercial suppliers and used without further purification. All reactions were performed in the dark, as much as possible, *e.g.* by wrapping flasks in aluminium foil.

Solvents were dried and degassed with a MBraun SPS800solvent purification system. All dry solvents except *n*-hexane were stored under argon over activated 3 Å molecular sieves in gas-tight ampules. *n*-Hexane was stored over a potassium mirror.

NMR spectroscopy: NMR spectra were recorded on Bruker Avance 400 and 500 spectrometers. at 300 K and internally referenced to residual solvent resonances (^{1}H NMR: C_6D_6: 7.16 ppm, ^{13}C{^{1}H} NMR: C_6D_6: 128.06 ppm). Chemical shifts (δ) are given in ppm referring to the external standards of tetramethylsilane (^{1}H, ^{13}C{^{1}H}) and 85% phosphorus acid (^{31}P{^{1}H}). Spectroscopic yields of products obtained in the catalytic reaction of *t*BuCP with [(6-Dipp)Ni(CO)$_3$] were determined using quantitative ^{31}P{^{1}H} NMR (zgig30, D1 = 30 s, inverse gated decoupled) with PPh_3 as an internal standard.

5.4.1 Reactivity Studies

Reaction of MesCP with [(IMes)Ni(CO)$_3$]

To a slightly beige solution of [(IMes)Ni(CO)$_3$] (13.9 mg, 0.03 mmol, 1.0 eq.) in deuterated benzene (0.5 mL) mesitylphosphaalkyne (28.9 µL, 10.4 mol/L in toluene, 0.30 mmol, 10 eq.) was added. The reaction mixture turned yellow and was stirred at room temperature for 40 min. ^{31}P NMR spectroscopy revealed unreacted mesitylphosphaalkyne as the main signal and a so far unidentified compound at 132.8 ppm (Figure S1). Heating of the mixture to 60 °C for 20 h led to a darkening of the solution and formation of a tiny amount of precipitate. However, the subsequently recorded ^{31}P NMR spectrum was almost unchanged, only the intensity of the signal of mesitylphosphaalkyne decreased slightly, probably due to decomposition (Figure S2).

Reaction of MesCP with [(IPr)Ni(CO)$_3$]

To a slightly beige solution of [(IPr)Ni(CO)$_3$] (16.0 mg, 0.03 mmol, 1.0 eq.) in deuterated benzene (0.5 mL) mesitylphosphaalkyne (25.0 µL, 10.4 mol/L in toluene, 0.24 mmol, 8.7 eq.) was added. The reaction mixture turned yellow and was stirred at room temperature for 2 h. ^{31}P NMR spectroscopy revealed unreacted mesitylphosphaalkyne as the main signal and a so far unidentified compound at 139.4 ppm (Figure S3). Heating of the mixture to 60 °C for 23 h led to a darkening of the solution. However, the subsequently recorded ^{31}P NMR spectrum was almost unchanged, only the intensity of the signal of mesitylphosphaalkyne decreased slightly, probably due to decomposition (Figure S4).

Reaction of MesCP with [(*i*Pr$_2$Im^{Me})Ni(CO)$_3$]

To a solution of [(*i*Pr$_2$Im^{Me})Ni(CO)$_3$] (10.0 mg, 0.03 mmol, 1.0 eq.) in toluene (0.5 mL) mesitylphosphaalkyne (56 mg, 0.35 mmol, 12 eq.) was added. The reaction mixture was stirred at room temperature for 30 min. ^{31}P NMR spectroscopy revealed unreacted mesitylphosphaalkyne as the main signal and a so far unidentified compound at 185.7 ppm (Figure S5).

Reaction of *t*BuCP with [(6-Dipp)Ni(CO)$_3$]

To a solution of [(6-Dipp)Ni(CO)$_3$] (2.9 mg, 0.0052 mmol, 2 mol&) in *n*-hexane (0.5 mL) *tert*-butylphosphaalkyne (94 µL, 2.76 mol/L in (Me$_3$Si)$_2$O, 0.26 mmol, 1.0 eq.) was added. The reaction mixture was stirred at 60 °C for 18 h. PPh$_3$ (14 mg, 0.053 mol) was added as internal standard to 100 µL of the reaction solution. ^{31}P{^{1}H} NMR spectroscopy revealed unreacted *tert*-butylphosphaalkyne (0.12 mmol, 45%) and formation di-*tert*-butyldiphosphatetrahedrane (**1**, 0.004 mmol, 3%) next to the signal of the internal standard (Figure S6).

Reaction of MeCP with [(IMes)Ni(CO)$_3$]

To a slightly beige solution of [(IMes)Ni(CO)$_3$] (5.0 mg, 0.011 mmol, 1.0 eq.) in *n*-hexane (0.5 mL) methylphosphaalkyne (0.65 mL, 0.17 mol/L in toluene, 0.11 mmol, 10 eq.) was added. The reaction mixture was stirred at room temperature for 15 min while turning yellow to orange to brown upon brown precipitate formation. ^{31}P NMR spectroscopy of the reaction mixture revealed formation of a so far unidentified compound at 105.5 ppm (Figure S7). The precipitate was insoluble in *n*-hexane and acetonitrile and might stem from phosphaalkyne oligomerisation.

5.4.2 NMR Spectra

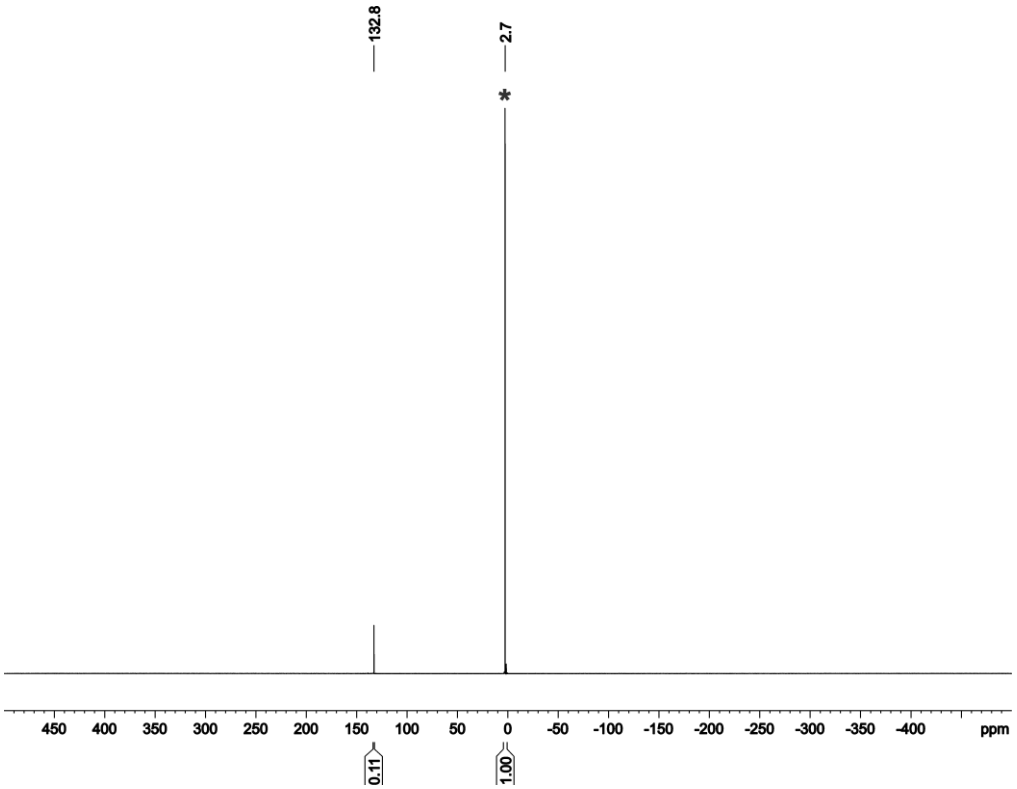


Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K C_6D_6) of the reaction mixture of 1 eq. [(IMes)Ni(CO)$_3$] with 10 eq. MesCP (*) after 40 min at r.t.

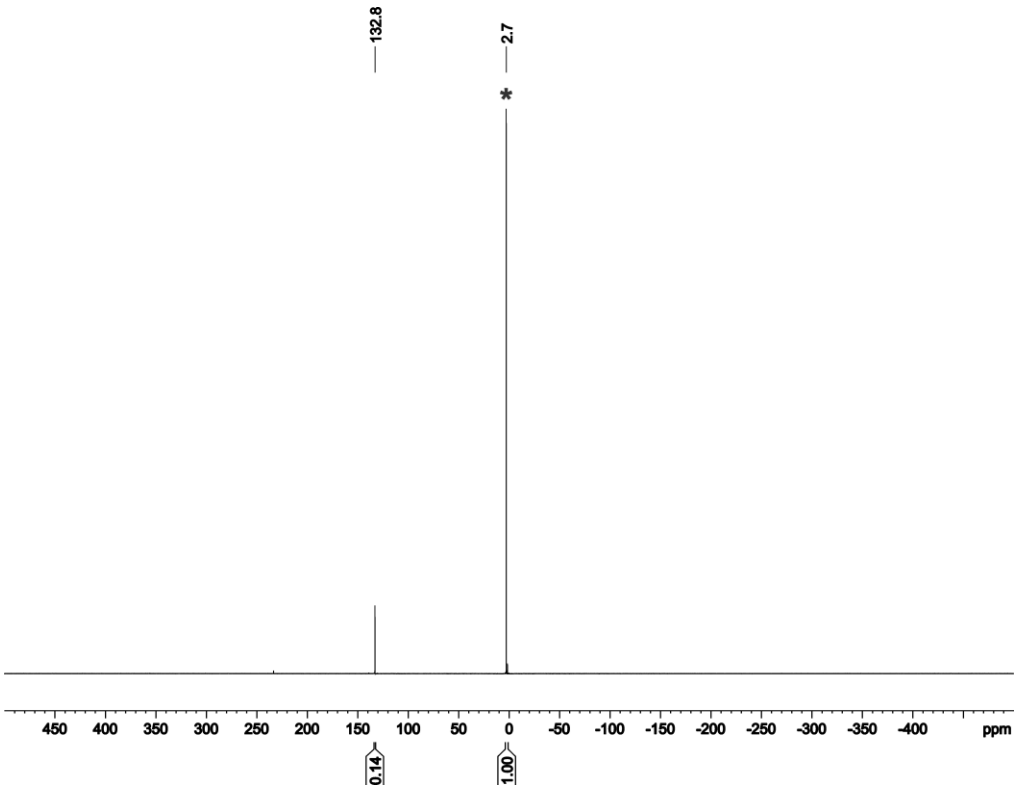


Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K C_6D_6) of the reaction mixture of 1 eq. [(IMes)Ni(CO)$_3$] with 10 eq. MesCP (*) after 20 h at 60 °C.

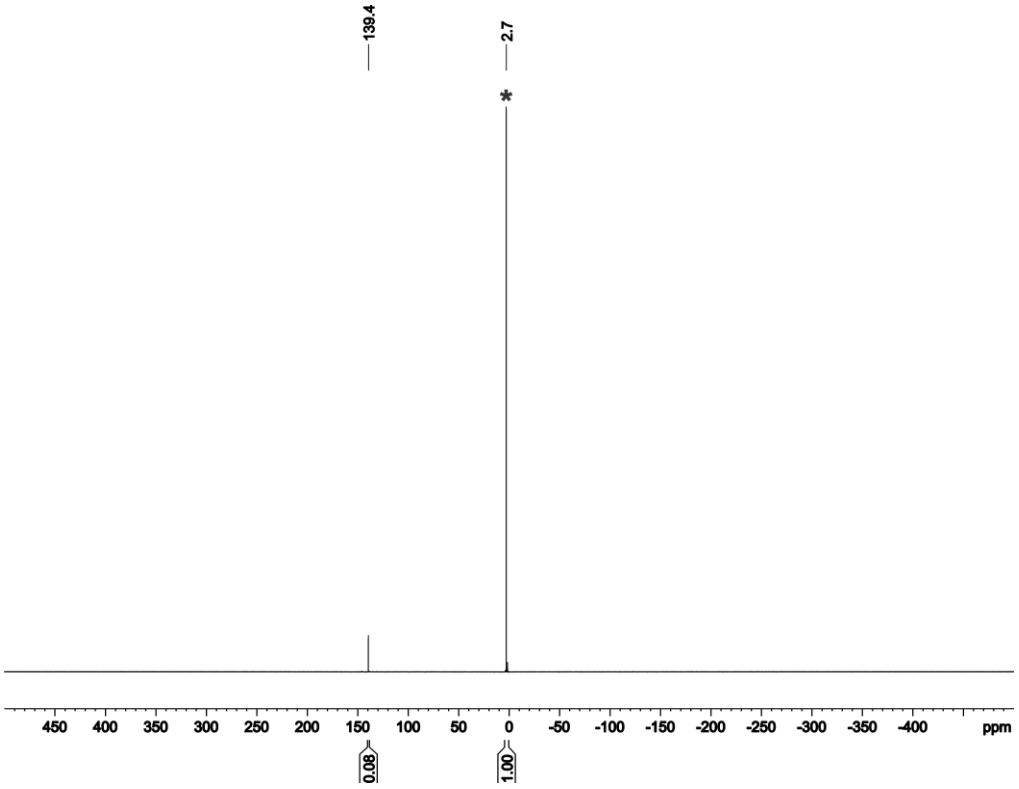


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K C_6D_6) of the reaction mixture of 1 eq. [(IPr)Ni(CO)$_3$] with 8.7 eq. MesCP (*) after 2 h at r.t.

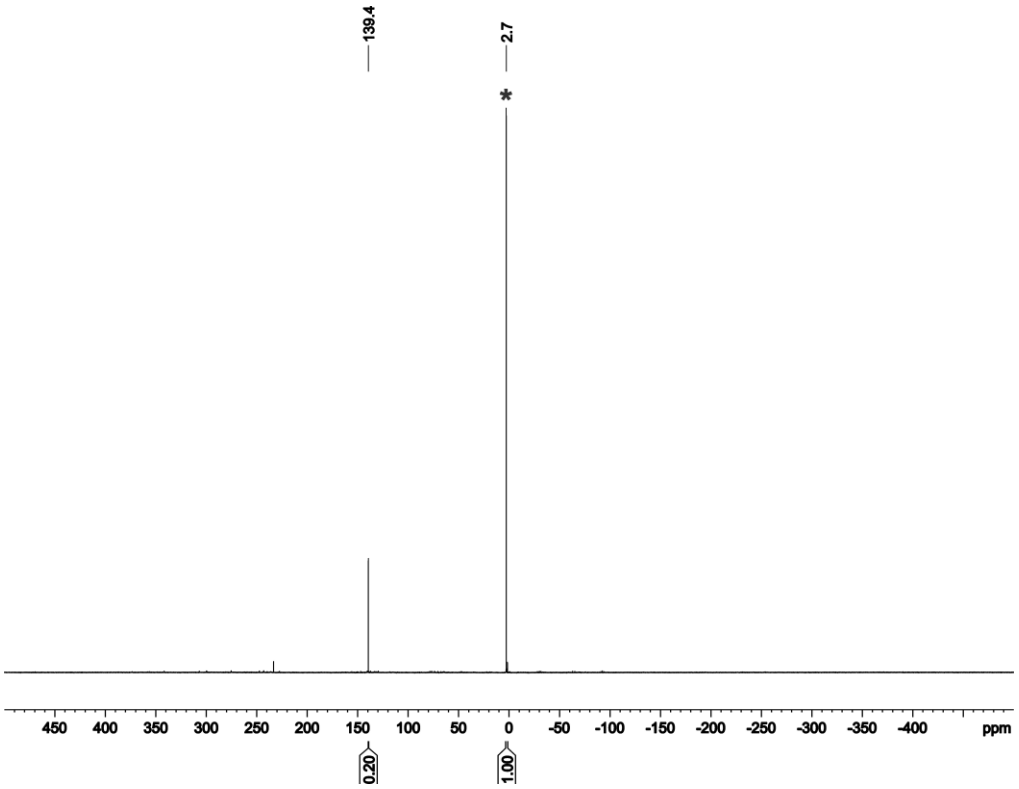


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K C_6D_6) of the reaction mixture of 1 eq. [(IPr)Ni(CO)$_3$] with 8.7 eq. MesCP (*) after 23 h at 60 °C.

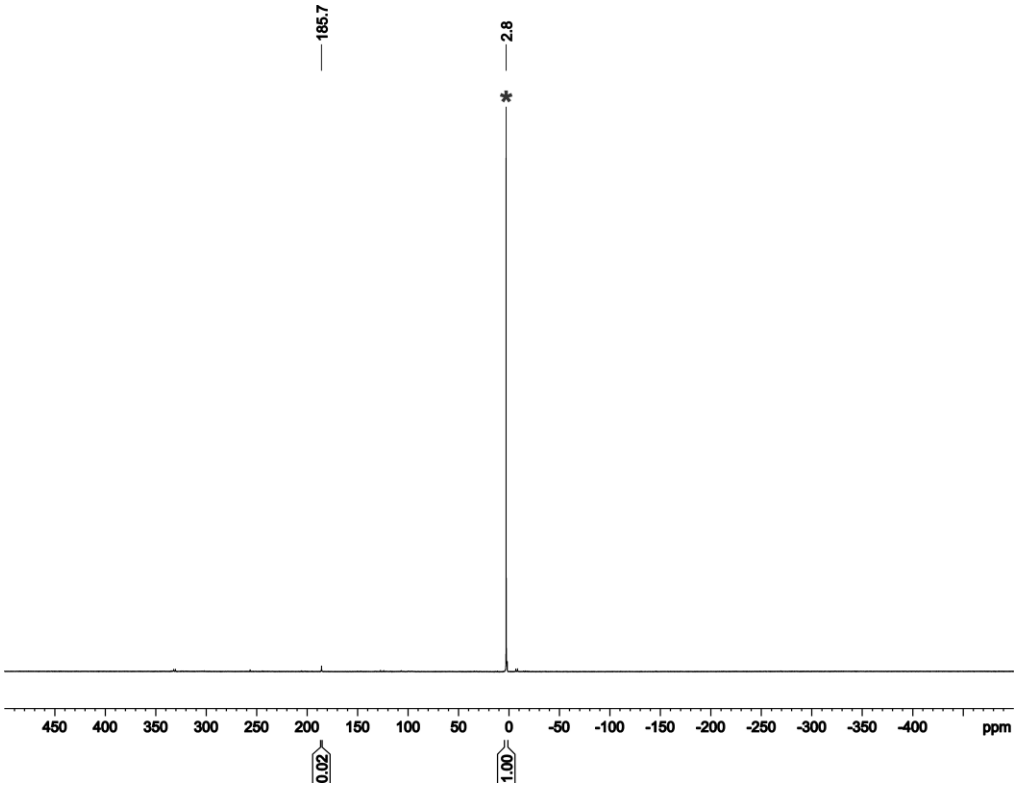


Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K C_6D_6) of the reaction mixture of 1 eq. [(*i*Pr_2Im^{Me})Ni$(CO)_3$] with 12 eq. MesCP (*) after 30 min at r.t.

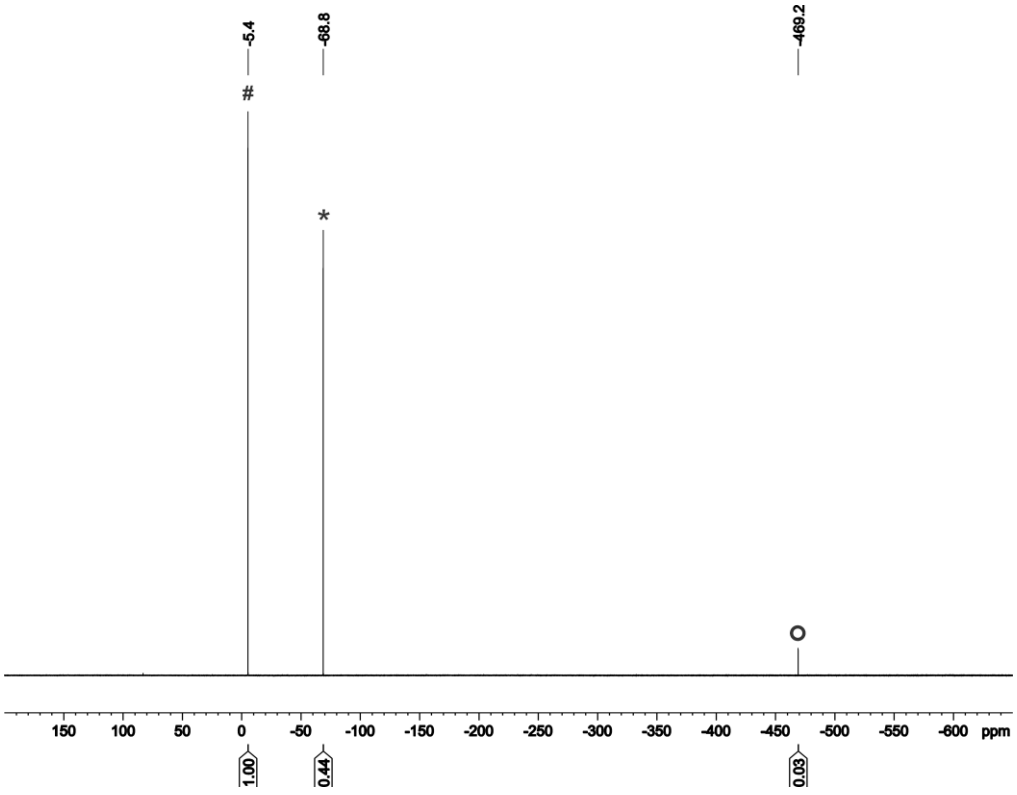


Figure S6. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of *t*BuCP (*) with catalytic amounts of [(6-Dipp)Ni$(CO)_3$] after 18 h at 60 °C. Internal standard PPh_3 (#). (*t*BuCP)$_2$ (**1**, ○).

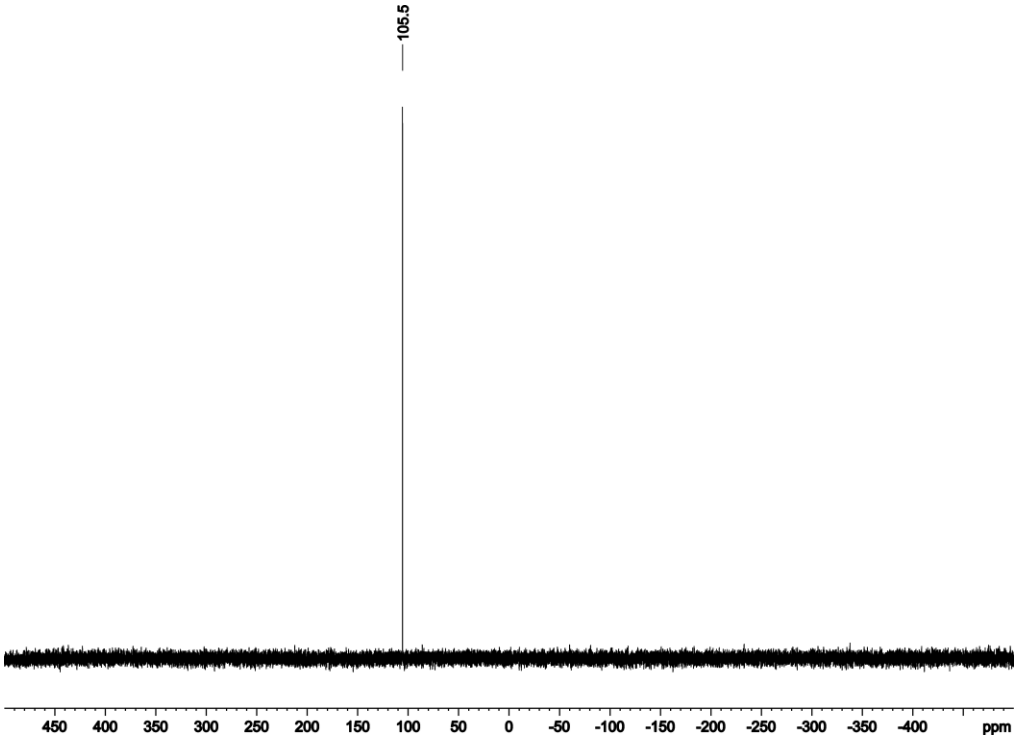


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum (162 MHz, 300 K C_6D_6) of the reaction mixture of 1 eq. [(IMes)Ni$(CO)_3$] with 10 eq. MeCP after 15 min at r.t.

5.4.3 Quantum Chemical Calculations

General Methods

All calculations were carried out with the ORCA 5.0 programme.[26] The calculations were carried out on isolated molecules (in the gas phase) at 298 K. Geometry optimisations were performed at the TPSS-D3BJ/def2-TZVP level of theory,[19] with the auxiliary basis set def2/J.[27] Density fitting techniques, also called resolution-of-identity approximation (RI)[28] and atom-pairwise dispersion corrections with the Becke-Johnson damping (D3BJ),[29] were used for all calculations. Numerical frequency calculations were carried out to confirm the nature of the stationary points found by geometry optimisations. All optimised ground state geometries show no imaginary frequencies, while the optimised transition state geometries show only one imaginary frequency with a vibration larger than −10 cm^{-1}, which coincide with the desired transitions. Approximate transition states were generated in correspondence to the initial report of the mechanism,[6] followed by saddle-point optimisation. In a few cases this did not lead to the desired transition state. For these, the nudged elastic band (NEB) method implemented in ORCA, was used to find approximate transition states which subsequently were subjected to saddle-point optimisations. Pictures were rendered with the software ChemCraft.[30]

Calculation of ^{31}P NMR shifts

NMR chemical shifts were computed at the TPSS-D3BJ/ pcSseg-3 level of theory with the with Gauge-Independent Atomic Orbital (GIAO) method.[26a,31,32] Comparison of the calculated ^{31}P NMR shift of **B** (R = *t*Bu, R' = IXy; δ = 107.1 ppm, Table S1.) with the measured value for **B** (R = *t*Bu, R' = IMes; δ = 91.2 ppm)[6] indicated, that a deviation of measured and calculated values of about ±16 ppm has to be expected. To assign the signal at 105.5 ppm obtained from the reaction of [(IMes)Ni(CO)$_3$] with 10 eq. of MeCP, the chemical shifts for **B** (R = Me, R' = IXy; δ = 118.3 ppm) and **C** (R = Me, R' = IXy; avg. due to fast exchange: δ = 98.3 ppm) were calculated. However, both calculated shifts are within the deviation of ±16 ppm and thus no unambiguous assignment of the signal can be made.

Table S1. Calculated ^{31}P NMR shifts for B (R = *t*Bu, R' = IXy), B (R = Me, R' = IXy), and C (R = Me, R' = IXy).

	δ [ppm] isotropic chemical shielding	δ [ppm] calculated with respect to reference PH_3
PH_3	581.848	
B (R = *t*Bu, R' = IXy)	234.798	107.050
B (R = Me, R' = IXy)	223.595	118.253
C (R = Me, R' = IXy)	232.083 255.111	109.765 86.737

Additional Calculations

Additional calculations with more NHC-phosphaalkyne combinations than described in the main manuscript were performed. In general, these confirm the insights discussed in the main manuscript. It shall only be noted, that for small phosphaalkynes as well as for small NHCs the effects are far less pronounced while the product of the reaction mixture is in none of these cases significantly more stable than intermediate **C**.

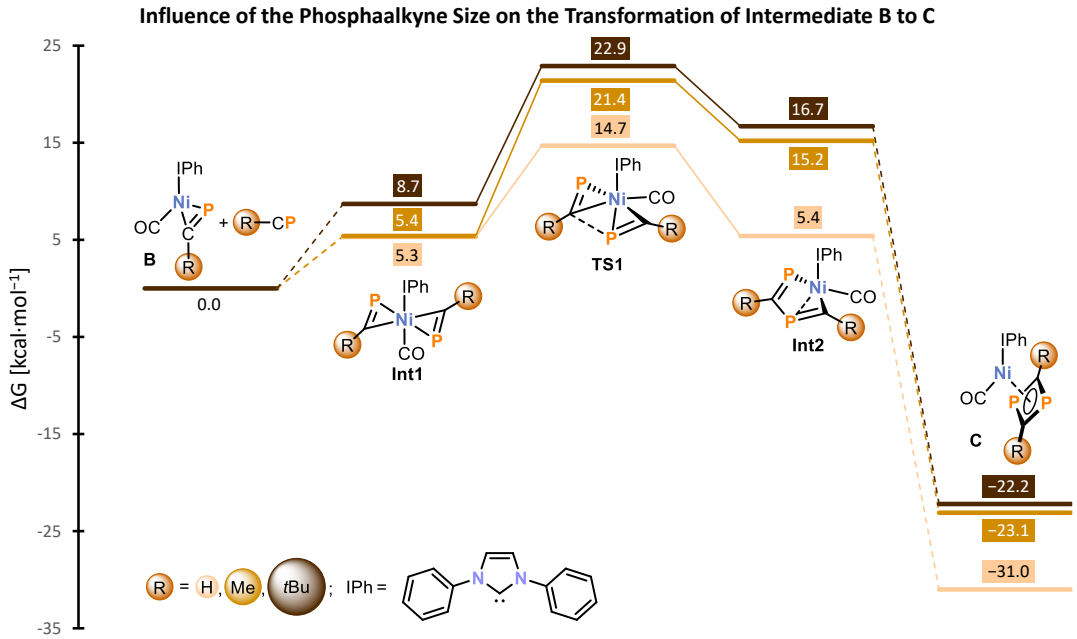


Figure S8. Calculated Gibbs free energy profiles for the transformation **B** → **C** for different phosphaalkyne substituents (R) at the TPSS-D3BJ/def2-TZVP level of theory and schematic drawings of intermediates and transition states. IPh = 1,3-diphenylimidazoline-2-ylidene. Gibbs free energies (in kcal·mol^{-1} at 298 K).

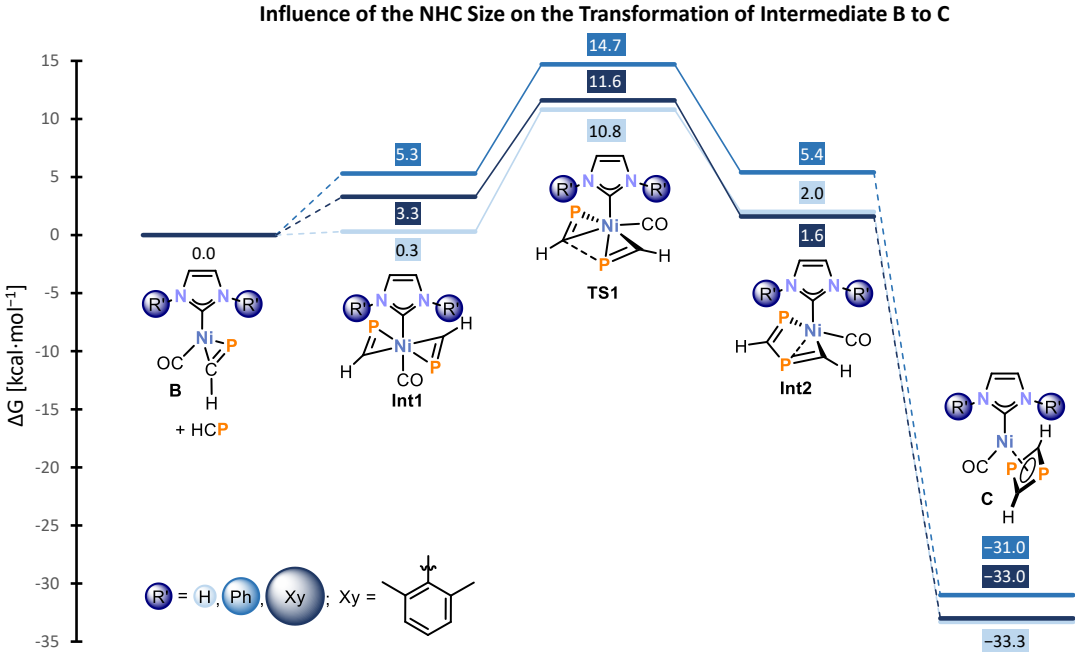


Figure S9. Calculated Gibbs free energy profiles for the transformation **B** → **C** for different NHC substituents (R') at the TPSS-D3BJ/def2-TZVP level of theory and schematic drawings of intermediates and transition states. Gibbs free energies (in kcal·mol^{-1} at 298 K).

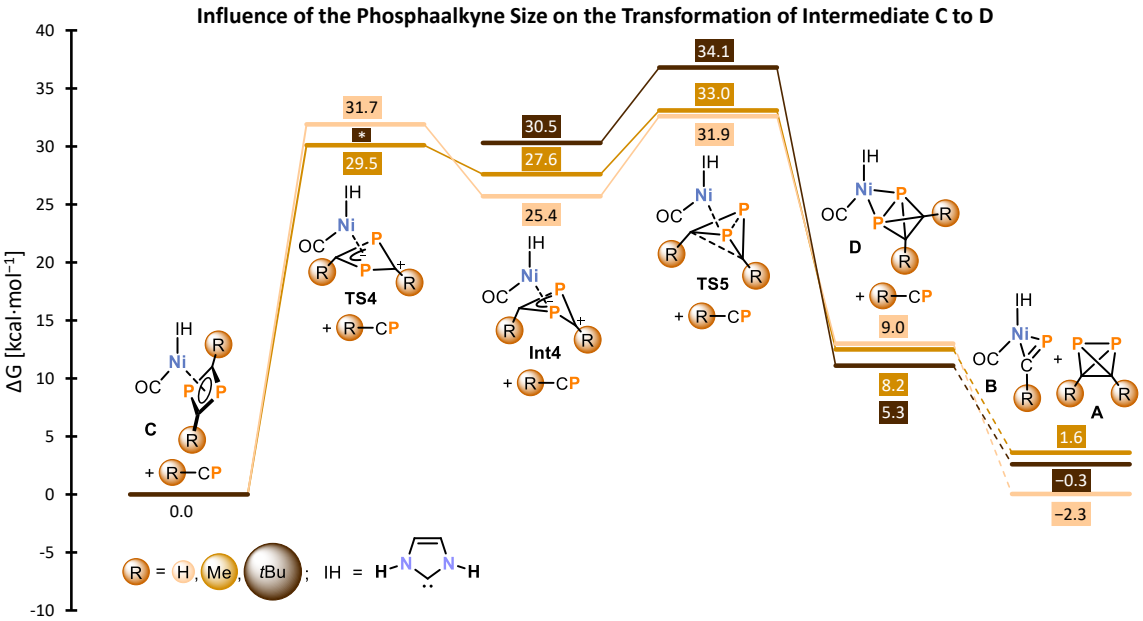


Figure S10. Calculated Gibbs free energy profiles for the transformation **C** → **A** + **B** for different phosphaalkynes (R) at the TPSS-D3BJ/def2-TZVP level of theory and schematic drawings of intermediates and transition states. IH = Imidazoline-2-ylidene. Gibbs free energies (in kcal·mol^{-1} at 298 K). * **TS4** with R = H and R' = IXy could not be located, probably due to a flat energy hypersurface. It can be assumed that its energy lies relatively close to that of **Int4**.

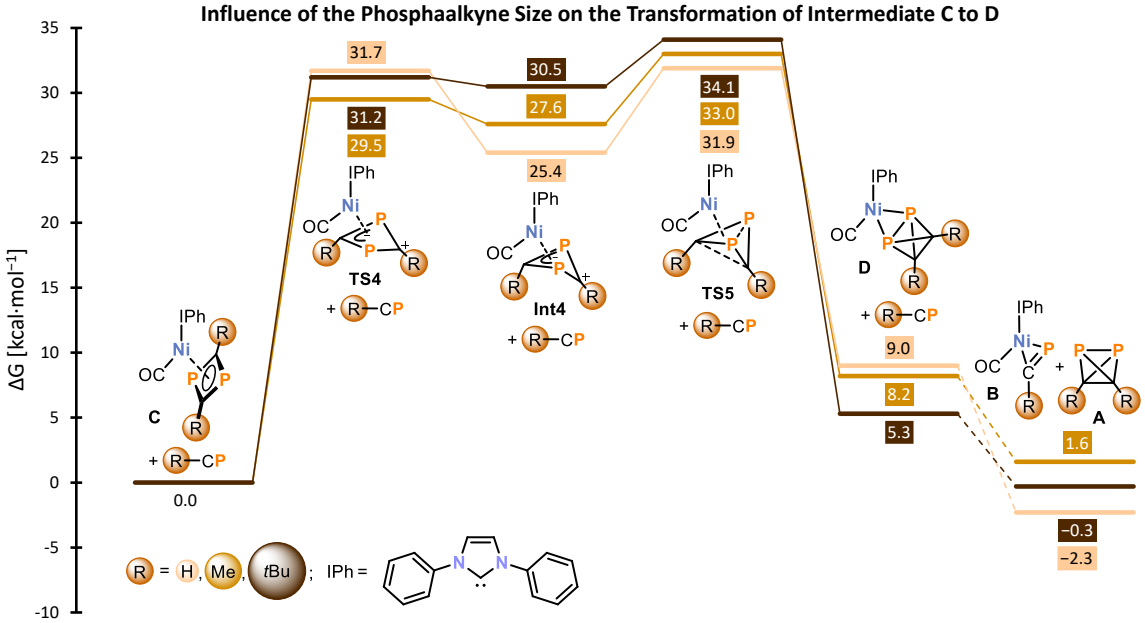


Figure S11. Calculated Gibbs free energy profiles for the transformation **C** → **A** + **B** for different phosphaalkyne substituents (R) at the TPSS-D3BJ/def2-TZVP level of theory and schematic drawings of intermediates and transition states. IPh = 1,3-diphenylimidazoline-2-ylidene. Gibbs free energies (in kcal·mol^{-1} at 298 K).

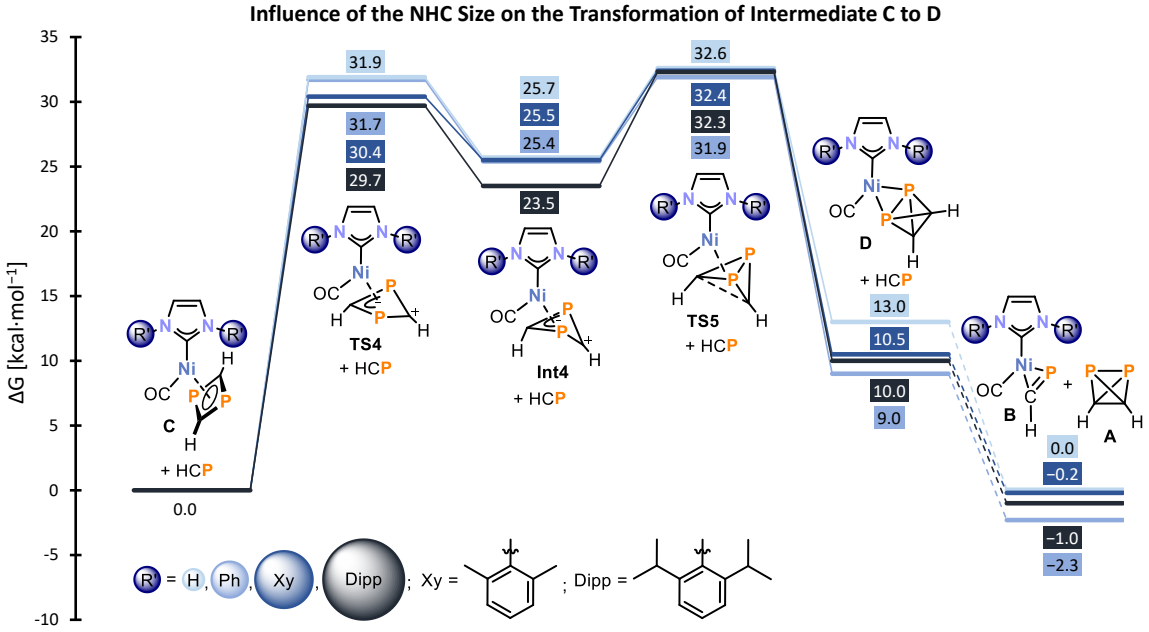


Figure S12. Calculated Gibbs free energy profiles for the transformation **C** → **A** + **B** for different NHC substituents (R') at the TPSS-D3BJ/def2-TZVP level of theory and schematic drawings of intermediates and transition states. Gibbs free energies (in kcal·mol^{-1} at 298 K).

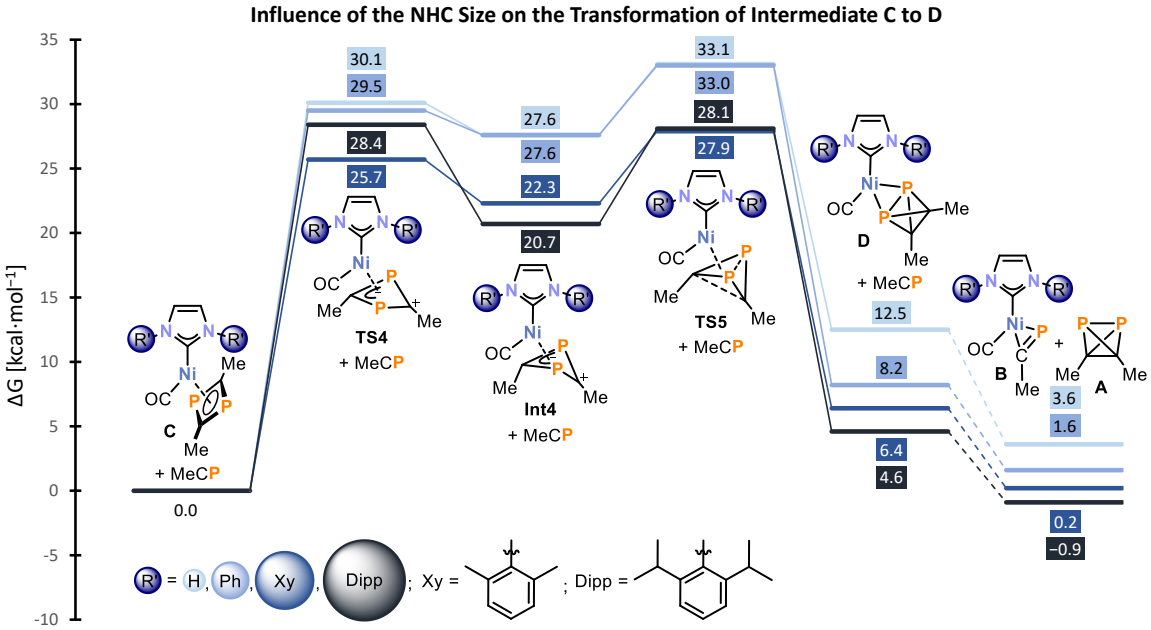


Figure S13. Calculated Gibbs free energy profiles for the transformation **C** → **A** + **B** for different NHC substituents (R') at the TPSS-D3BJ/def2-TZVP level of theory and schematic drawings of intermediates and transition states. Gibbs free energies (in kcal·mol^{-1} at 298 K).

Cartesian Coordinates of Optimised Structures

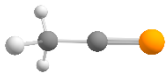
HC≡P

TPSS D3BJ/def2-TZVP
E = −380.05223020 Eh
G = −380.05924155 Eh

0 1

P	0.00000000270087	-0.00000000275634	0.53612189574936
C	-0.00000000540152	0.00000000551246	-1.00547952397174
H	0.00000000270065	-0.00000000275612	-2.08100637177762

MeC≡P

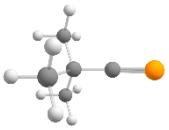


TPSS D3BJ/def2-TZVP
E = −419.40401031 Eh
G = −419.38749958 Eh

0 1

C	-1.75967251070778	-0.00005689381027	-0.00005979236195
C	-0.30159183145397	0.00006943821939	0.00007775038441
H	-2.15014372893083	-0.56099042639321	-0.85810021220544
H	-2.15036196121886	1.02341397839732	-0.05684123478567
H	-2.15034230790837	-0.46267934231686	0.91466180124561
P	1.24847034021982	0.00003924590363	0.00004568772305

***t*BuC≡P**



TPSS D3BJ/def2-TZVP
E = −537.41812928 Eh
G = −537.32429614 Eh

0 1

C	-0.72649101669288	0.00001066522140	0.00023033095093
C	0.73868401707964	0.00045972148640	0.00009852865891
C	-1.23670196755591	-1.26078091779180	-0.73987958679407
C	-1.23761593412675	1.27063958087010	-0.72212700815231
C	-1.23611719347810	-0.01052231598628	1.46233790780915
P	2.29072640240161	0.00074282649833	0.00037498257961
H	-0.88337422686881	-2.16898129136999	-0.24370852126083
H	-0.88243884479947	-1.26971653259463	-1.77442586562744
H	2.33257658790950	-1.26342605259975	-0.74236728781851
H	-0.88467047946404	2.17203563291377	-0.21344559564159
H	-2.33348636785836	1.27265318259070	-0.72429456832372
H	-0.88364798204898	1.29423406600371	-1.75655558678340
H	-0.88222321364386	0.87344095531272	2.00013739807174
H	-0.88112908156382	-0.90157010134052	1.98755686017895
H	-2.33200452347074	-0.01121841921418	1.46744301215257

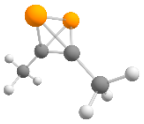
A $(HCP)_2$

TPSS D3BJ/def2-TZVP
E = −760.17726052 Eh
G = −760.17150131 Eh

0 1

P	-1.10600194078173	-0.43154962622350	0.00003995640514
C	-0.00000736373654	0.83720316764003	-0.73169079378586
C	0.00001603197301	0.83720117719423	0.73169292477953
P	1.10600141800308	-0.43155948429188	-0.00004129318956
H	0.00011148631269	1.55844373225203	1.53197218873814
H	-0.00008463177050	1.55844803342909	-1.53196798294739

A $(MeCP)_2$

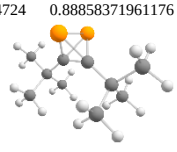


TPSS D3BJ/def2-TZVP
E = −838.86621496 Eh
G = −838.80940703 Eh

0 1

P	0.00004865397535	-0.96134336873510	-1.10738713779504
C	0.72984060249111	0.32363469617460	0.00000610200053
C	-0.72985048443102	0.32362211031422	-0.00005997509077
P	-0.00002770595558	-0.96151792477071	1.10712809391980
C	1.84167351225149	1.31504365382968	0.00008129599010
C	-1.84170657301050	1.31500208027127	0.00000196098115
H	-1.78703266779600	1.95535464276374	0.88849063424443
H	-2.81310487808162	0.81209530955371	-0.00010337541835
H	-1.78694344980327	1.95556298143286	-0.88833118438085
H	1.78688253169218	1.95562610874804	-0.88823468245749
H	2.81308348050125	0.81216239957046	-0.00004545160527
H	1.78698697816661	1.95537731084724	0.88858371961176

A (*t*BuCP)$_2$ (1)



TPSS D3BJ/def2-TZVP
E = −1074.89925853 Eh
G = −1074.68447482 Eh

0 1

P	-0.01332140712152	-1.62927977789934	1.10232372214062
C	-0.72949363195144	-0.33196865941615	-0.00892250960912
C	0.72949358261533	-0.33196845430294	0.00893246460907
P	0.01332163614084	-1.62929071089598	-1.10230103665648
C	-1.94965622188432	0.54960873155813	-0.02386828024440
C	1.94965619965034	0.54960909103828	0.02386863955620
C	1.96755129007167	1.43405848822458	-1.23695264114490
C	3.19591392148333	-0.35222454158643	0.03742944069480
C	1.93912730598304	1.43189499720666	1.28632269240840
C	-1.96755166905623	1.43407204787071	1.23694318582704
C	-3.19591396952021	-0.35222497356959	-0.03741949298349
C	-1.93912669079599	1.43188071090047	-1.28633207832980
H	-3.21476325894878	-0.99473863229619	0.84898615539002
H	-3.19857398295310	-0.99118442671419	-0.92660310634811
H	-4.10592029425429	0.25768176322522	-0.04454614224113
H	-1.08280642116062	2.11281906157295	-1.28434861843562
H	-2.85360289248377	2.03385559180105	-1.33162043434766
H	-1.88579146891009	0.81287893646777	-2.18784071446726
H	2.87600321709596	2.04652174316658	-1.25375639484109
H	1.10358026930639	2.10478107058117	-1.25945119255998
H	1.94831388389326	0.81616981810412	-2.14059319916651
H	4.10592029569102	0.25768222432753	0.04454571107831
H	3.21476102872395	-0.99475020576149	-0.84896755384573
H	3.19857595835664	-0.99117194158236	0.92662170213248
H	2.85360484831597	2.03386828703269	1.33160522551180
H	1.88578996818430	0.81290332824997	2.18783814008673
H	1.08280870648797	2.11283547521021	1.28433119134773
H	-1.10358224230645	2.10479699137423	1.25943345588560
H	-1.94831200287250	0.81619353114538	2.14059062755075
H	-2.87600495778071	2.04653343496695	1.25374104100171

B (R = H, R' = H)

TPSS D3BJ/def2-TZVP
E = −2228.32243561 Eh
G = −2228.26305480 Eh

0 1

Ni	-0.92783602048825	2.22712613508095	7.41423346546766
P	0.14848677558476	3.87111720826043	6.33995564340348
N	-2.73181528230283	4.44993156869786	8.23027794146082
N	-3.40326202785590	2.60697550357389	9.03452417932092
C	-2.40692060178385	3.12492951612306	8.25457220282626
H	-2.16764094463298	5.11240839829664	7.71496237969369
H	-3.44976438449599	1.62184179166616	9.25285570084696
C	-3.87295017075169	4.74628211943911	8.95718317899322
H	-4.27165957336226	5.74386179363312	9.04470601453761
C	-4.30425890966347	3.56505507286390	9.47357744619647
H	-5.15126434796240	3.33223192651280	10.09818295463679
H	1.34686921839377	1.60087021392723	5.97523199081919
C	0.61181611549070	2.30848836054817	6.33730911661666
O	-1.12930168755592	-0.58797051215162	8.15048212220212
C	-1.05614815861365	0.53008090352825	7.85524566297802

Int1 (R = H, R' = H)

TPSS D3BJ/def2-TZVP
E = −2608.39206216 Eh
G = −2608.32182078 Eh

0 1

C	2.33568166695578	-0.84342162672284	-0.71382047235984
C	0.70184157524016	1.42744955372188	-1.35443767729307
Ni	0.66417377265248	-0.01382018522466	0.04945231322777
N	-2.14862089958767	-1.14673800883248	0.29243660898609
N	-2.14141901192651	0.88579010447859	-0.30950875774415
C	-1.29232249888297	-0.12719283733893	0.00665968121444
C	-3.48332598247623	-0.78335286646003	0.15778142598121
H	-4.29827495316496	-1.46458142422333	0.34157919698531
C	-3.47647608833207	0.51975356763705	-0.22689336876864
H	-4.28559180459890	1.19816889095465	-0.44354578881795
O	1.25528453700771	-0.46884515477268	2.91747976694984
C	1.02564453145305	-0.30265111231557	1.79984847316403
P	1.07408040604744	2.32237834516350	-0.07978191681667
P	1.25687066240076	-1.89828500652013	-1.24902399337813
H	-1.81591430346692	-2.06400325659426	0.55299003077959
H	-1.77636498706436	1.79514932505626	-0.57219458116673
H	0.55419232470597	1.27330815939727	-2.41387324994189
H	3.34591305303724	-0.46831546740428	-0.63565169100120

TS1 (R = H, R' = H)

TPSS D3BJ/def2-TZVP
E = −2608.37542436 Eh
G = −2608.30515731 Eh
im. freq. = −128.53 cm^{-1}

0 1

C	1.84307906243693	-1.49963565719451	0.07606239145089
C	1.80525153271718	1.20247842223235	-1.85196996419892
Ni	1.38481451075989	0.37768853316810	0.23034380032478
N	-1.19488314828082	-0.96475871190305	-0.39045900056966
N	-1.56980404469469	0.74919471922483	0.79911960580523
C	-0.54263113549812	0.05707265356704	0.22791657095638
C	-2.57009278597459	-0.91528387145357	-0.21987055664431
H	-3.24166478974852	-1.64581867606164	-0.64108403799649
C	-2.81239353172478	0.18189873725808	0.54407502539339
H	-3.73501145951764	0.59575711110342	0.91771878861335
O	2.89289193922756	1.20458447350384	2.59867311502026
C	2.36326164233319	0.86831757863392	1.62438055510624
P	1.21695015762097	2.35648603421677	-0.89827538621247
P	2.13554655840117	-1.29243216771302	-1.50149869371665
H	-0.67621645996043	-1.65986248999090	-0.91633619978621
H	-1.41111376883331	1.58912300009765	1.33695212932686
H	2.25909772047149	1.02194054007134	-2.81372287818102
H	1.85291800026454	-2.22675022876063	0.87797473530835

Int2 (R = H, R' = H)

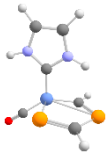
TPSS D3BJ/def2-TZVP
E = −2608.39213072 Eh
G = −2608.31906588 Eh

0 1

P	1.08192949691055	2.21107627903238	-0.52096690107226
C	0.80286518733157	0.89676187429054	-1.54308542954597

C	0.98736065018885	1.56142393618086	1.23616427092878
Ni	0.59873908701647	-0.51098542782103	-0.29585325692643
N	-2.06928187228129	0.71399838806736	-0.38840982208935
N	-2.20271583051157	-1.35030463897370	0.10869902152349
C	-1.29164187385338	-0.37941800919238	-0.18472817018137
C	-3.41826360068699	0.44708653418765	-0.22347174379254
H	-4.18141263636266	1.19768901353233	-0.34809556785264
C	-3.50769057047274	-0.87300242529018	0.08675668979761
H	-4.36154720731023	-1.50067841381234	0.28256952823086
O	2.86908248681163	-2.31880295269462	-0.47523252173513
C	2.01141037778165	-1.55056669068943	-0.37546276632466
P	0.69519890084031	0.03054134600607	1.88056641387431
H	-1.92819185047872	-2.29296727448314	0.34442932147487
H	-1.64325733492302	1.60485127192658	-0.62760285051779
H	0.79920995830234	1.03642023985494	-2.62352366840496
H	1.21155263169725	2.37861994987810	1.92580945261318

TS2 (R = H, R' = H)

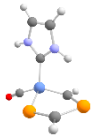


TPSS D3BJ/def2-TZVP
E = −2608.38576968 Eh
G = −2608.31251928 Eh
im. freq. = −170.95 cm^{-1}

0 1

C	0.78910209883951	-1.43443613546621	3.34603848508104
C	3.43093866053602	-2.17146994028380	3.54063823444088
Ni	1.76369662612267	0.20482225813127	3.24477577492831
C	2.14495024582083	1.50775233971174	4.38996756531607
N	2.01179156506423	-0.87284008184756	0.53413280203224
N	2.59172501734890	1.17458793718860	0.52211889335532
C	2.17739412611749	0.18693625251886	1.36589175692578
C	2.31777624015113	-0.57205104274649	-0.77793972805941
H	2.24060214436067	-1.29142124907863	-1.57687546940696
C	2.68124813379022	0.74069307086045	-0.79214338910555
H	2.97583052369835	1.38696428216287	-1.60295620437082
O	2.34101388173259	2.39299490797196	5.11014253087127
P	3.85019980283018	-0.54549428704003	3.40427426834221
P	1.75029161158000	-2.84801847011248	3.43244162885849
H	4.23421724113227	-2.89161581527172	3.71703631530130
H	-0.27196598200110	-1.65549302958192	3.18225513829136
H	2.83316724129038	2.09828416901278	0.85205813053302
H	1.73199082158560	-1.77453516612970	0.92142326666544

Int3 (R = H, R' = H)

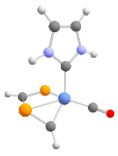


TPSS D3BJ/def2-TZVP
E = −2608.39979736 Eh
G = −2608.32698045 Eh

0 1

C	-0.98784758793966	-0.87188515492960	-1.24613730114762
C	-2.11189754508037	-1.00668043723652	1.01882366105209
Ni	-0.13110014072239	0.70659100916581	-0.75242823767299
C	-0.06183427401375	2.51258885201462	-0.91634957552703
N	2.77496754640032	0.37392956408278	0.09952120453063
N	1.63880399235023	-1.41738304885768	0.19588475200647
C	1.54066247627956	-0.12268273447269	-0.19443868092883
C	3.60849102098225	-0.57864343727767	0.66579025742320
H	4.62169321377764	-0.36700031252359	0.96675248595606
C	2.87435931097019	-1.72431986694495	0.72815496490414
H	3.12782197797909	-2.70629266172962	1.09340309188159
O	-0.09111518189723	3.65625718497472	-1.06352886755376
P	-1.55816150682777	0.59741924150426	0.87243907902439
P	-1.86369309067600	-2.07414935829623	-0.38931282868591
H	0.83103252520647	-2.03521150511835	0.09604669197839
H	3.02018807014286	1.34038884835084	-0.06214926290431
H	-0.77365438530825	-1.00571663882425	-2.31833416461725
H	-2.62970720262324	-1.32213954388184	1.92592973028074

TS3 (R = H, R' = H)

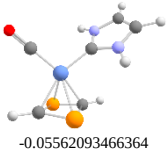


TPSS D3BJ/def2-TZVP
E = −2608.37419493 Eh
G = −2608.30184659 Eh
im. freq. = −112.39 cm^{-1}

0 1

C	-2.15906633858518	0.03977116678035	-0.84639481414795
C	-1.41409781757710	-2.01759154847373	0.80373086639971
Ni	-0.56997248624998	0.49191611155583	-0.16979522572190
N	1.91199172068282	-1.01724368581150	-0.60633186052792
N	2.37371632292076	0.79160672986739	0.40699829337192
C	1.31649740187180	0.09971898532896	-0.10566627357113
C	3.28526855008515	-1.02609026134454	-0.41664170155885
H	3.91720461702080	-1.83140727255424	-0.75351176811142
C	3.58271542292341	0.12954838245165	0.23221035043570
H	4.52290052085923	0.52808323128559	0.57666929695684
O	-0.90118720832874	3.43321489963389	-0.08966594527358
C	-0.74241420448232	2.29090903319036	-0.14219758422587
P	-0.96921498032244	-0.68476933605432	1.75051797952232
P	-1.46307799651154	-1.57140659455087	-0.95448810006298
H	1.36166526496553	-1.73718307723603	-1.06080057695281
H	2.26015902871470	1.68150381664626	0.87029260279294
H	-1.60146912639249	-3.02803653664586	1.17715764705339
H	-2.99330969159444	0.56514395593080	-1.30073718637842

C (R = H, R' = H)

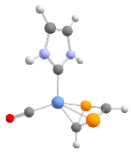


TPSS D3BJ/def2-TZVP
E = −2608.45193496 Eh
G = −2608.37538235 Eh

0 1

Ni	0.43330197488316	0.34055416692719	-0.05562093466364
N	-2.38858557009062	0.53900549863390	0.83287771735470
N	-2.11738101656095	-0.90961614175761	-0.69862237182912
C	-1.42232879036731	-0.00557728558954	0.04401544480324
C	-3.64301177792095	-0.00870757830890	0.59474410773384
H	-4.52679490436982	0.30118999624630	1.12783411127997
C	-3.46851555485726	-0.93379022017484	-0.38437747003277
H	-4.17175132826083	-1.58770153741175	-0.87337599506377
P	2.07524895405310	-0.31647092493363	1.41105687934633
O	0.44963176869512	3.18485624911297	-0.69291305262890
C	0.44898655637929	2.05654911998047	-0.44001269958502
C	0.95524384133459	-1.49520709708997	0.67175044097513
P	1.46551577500937	-1.44040643093753	-1.08776969912608
C	2.40205093676657	-0.08861870066394	-0.37558317870752
H	3.06326784005551	0.62124981374236	-0.86445645004657
H	0.21925224690247	-2.13444377743124	1.15259614430037
H	-2.17764671443896	1.24598627294948	1.52276249815165
H	-1.65242423721247	-1.46269242329373	-1.40757849226183

TS4 (R = H, R' = H)

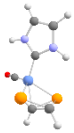


TPSS D3BJ/def2-TZVP
E = −2608.39791308 Eh
G = −2608.32454852 Eh
im. freq. = −280.60 cm^{-1}

0 1

Ni	-0.43239302768121	0.58628199163757	-0.06077224037501
N	1.94304191882117	-1.04888911182037	-0.70355085183961
N	2.43706838642095	0.48058230528461	0.68286845041154
C	1.37933122576699	-0.00638784569263	-0.02926708665542
C	3.29026956725543	-1.21458148060484	-0.41682447289874
H	3.89371306391737	-1.98915103729040	-0.86106350564423
C	3.60717747383889	-0.23576742774690	0.47002619810146
H	4.53976919436186	0.00888459526209	0.95160229016353
P	-1.57848241434496	-1.12056080411457	-1.33483194733472
O	-0.45945070697976	3.48742175685386	-0.31455399551783
C	-0.45805137570764	2.33125214745544	-0.21868459575957
C	-1.62038257765023	-1.96618451531083	0.24141612342200
P	-1.49608928365453	-0.79430852615472	1.57537100147308
C	-2.19223694255012	0.01677644575445	0.02561656964541
H	1.38948670207917	-1.61556002864167	-1.33169780101055
H	2.33979630158543	1.26843421273557	1.30676809829762
H	-3.23667440247100	0.32224428226844	0.02402244326984
H	-2.00300510300781	-2.98992195987510	0.36834832225119

Int4 (R = H, R' = H)

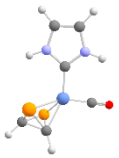


TPSS D3BJ/def2-TZVP
E = −2608.40890192 Eh
G = −2608.33445301 Eh

0 1

Ni	-0.42379316854175	0.58396642602129	0.01513758433079
N	1.81572118704856	-1.24463647311972	-0.53127455850935
N	2.45191587813144	0.48756274881929	0.52384291895855
C	1.33105051195541	-0.07794975547178	-0.01461274915545
C	3.17704352014514	-1.40510995340809	-0.31628919584697
H	3.72695509626284	-2.26628260440984	-0.65900719853718
C	3.58441696232025	-0.29861250800507	0.35717389910021
H	4.55770927832563	-0.00709944775990	0.71643638877374
P	-1.57675395607699	-0.79786909311207	-1.46159066269930
O	-0.10551863666903	3.51006016405029	0.05880220826859
C	-0.26165858720574	2.35956224727114	0.03982307709309
C	-1.95152912322642	-1.70764595228355	0.05855780460005
P	-1.37902862668785	-0.85683486166440	1.53870869759643
C	-2.27679105903785	-0.09166652630739	0.10336971773612
H	1.20518974717012	-1.89841352485071	-1.00046635990876
H	2.42029773034135	1.37870852028515	0.99787119154768
H	-2.74942454593196	-2.45508754395827	0.10022917619611
H	-3.27366626832315	0.33038802290363	0.17682207245564

TS5 (R = H, R' = H)

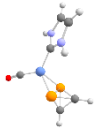


TPSS D3BJ/def2-TZVP
E = −2608.39828992 Eh
G = −2608.32336709 Eh
im. freq. = −238.32 cm^{-1}

0 1

Ni	-0.36170686359435	0.38288170363011	-0.10616864262841
N	2.56719268779061	0.59459092975689	-0.18647076376865
N	1.94318976017151	-1.35811397275218	0.38591893880965
C	1.43230935481892	-0.14982132064887	-0.00377287446230
C	3.72612530256119	-0.11388543852228	0.09515126592055
H	4.70935451940505	0.31950397007137	0.01239481572532
C	3.32833042602655	-1.35912602793629	0.46131190288570
H	3.89663990058578	-2.22434366531169	0.76078403562546
P	-1.13131980197414	-1.50602019753338	-0.99069511682335
O	0.05006201485462	3.29358626748421	-0.27334755670651
C	-0.11322252736118	2.14711478797468	-0.21692154634630
C	-2.48036810471824	-1.38968841267306	0.21867640798008
P	-2.16681117089212	0.07539091483673	1.26091039259928
C	-2.25780029911356	-0.10114288654858	-0.67056589901697
H	-2.98844680821982	0.34604780585348	-1.33183463018000
H	-3.42226344991718	-1.93188692874002	0.13251666954871
H	2.53310845753428	1.55708848903134	-0.48995778463070
H	1.34008060204207	-2.13069501797246	0.62784538546847

D (R = H, R' = H)



TPSS D3BJ/def2-TZVP
E = −2608.42693828 Eh
G = −2608.35472470 Eh

0 1

Ni	0.25083516079038	0.68755849972276	-0.06393788386338
N	-2.64491384705319	0.56747601800727	0.75761288419943
N	-2.19420657231734	-0.90563466469843	-0.69934893300204
C	-1.60237379854657	0.11636674352420	-0.00648392348511
C	-3.82182807632285	-0.13992316782477	0.55333286857851
H	-4.73880511097943	0.08125766186011	1.07495181029871
C	-3.53374425503678	-1.08009282600713	-0.38346290765920
H	-4.15197749623559	-1.83551863257958	-0.84049753819697
P	1.54410297967260	-0.63359040307755	1.19641787391132
O	1.37402814994464	3.38739558968761	-0.36074592213014
C	0.87225019884045	2.34898896391807	-0.23878084679276
C	1.68608202702485	-2.18352295962390	0.21036695717993
P	1.44190690474537	-0.89804700417263	-1.09320120682924
C	2.83462850497065	-1.26531651317819	0.04761543127104
H	-2.54157686684298	1.35080024983783	1.38576167437682
H	-1.66850505110897	-1.47447833203772	-1.34800164959833
H	1.57885098890958	-3.25131216072089	0.33793022466983
H	3.90867115954520	-1.37472806263706	0.00493408707160

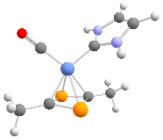
B (R = Me, R' = H)

TPSS D3BJ/def2-TZVP
E = −2267.66872265 Eh
G = −2267.58351250 Eh

0 1

Ni	-0.53391005334082	0.14955891966784	0.00043402121227
P	-1.21306466462548	-1.97946449065783	0.00005119196179
N	2.15131434262351	-1.13485040491703	-0.00016942440553
N	2.34070869577352	0.97640349288382	0.00050850920395
C	1.38743173903607	-0.00419918849578	0.00026170238824
C	3.51159697185604	-0.87618879670924	-0.00017891304082
H	4.25840810645013	-1.65346182656852	-0.00047906335945
C	3.63455162766129	0.47788281501589	0.00024299470383
H	4.50810050922795	1.10934935089813	0.00038121600584
C	-2.22950920463679	-0.69624094272230	0.00034369702301
O	-1.18938328332467	2.98880338101864	-0.00002714117403
C	-0.91574100532397	1.86136234991722	0.00030279217905
H	1.71877856174372	-2.04930853105368	-0.00043549726102
H	2.09480753349808	1.95599002089869	0.00084678240700
C	-3.63110827688766	-0.21099776416772	0.00062884678612
H	-4.35734666118690	-1.03150899586770	-0.00056192066611
H	-3.81342077133914	0.41756602488485	0.88086875689453
H	-3.81311916720488	0.41994958597472	-0.87795255085866

C (R = Me, R' = H)

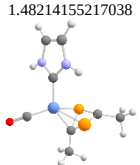


TPSS D3BJ/def2-TZVP
E = −2687.13922464 Eh
G = −2687.01122374 Eh

0 1

Ni	-0.28872509131807	0.40191590286708	-0.05474548614190
N	2.55437597868588	0.59211234085657	-0.90798854489066
C	2.34337471347216	-0.11910779614247	1.08238507397236
C	1.60298288517008	0.29794754769516	0.01966999597350
C	3.84363544542518	0.36223611683798	-0.44353910325331
H	4.72185112682407	0.53992311113730	-1.04240774808743
C	3.70760110162194	-0.09306135607339	0.82902213192020
H	4.44491365069802	-0.38983117415881	1.55681028350961
P	-1.68149281587570	-0.84415954942195	-1.39187021567180
O	-0.69158208435129	3.28915897323489	-0.14174511574875
C	-0.53736451986394	2.14280813748834	-0.10341358816491
C	-0.52337837480565	-1.63558181239419	-0.27291277208817
P	-1.22519474757769	-1.16293990398545	1.35257074597255
C	-2.23133252751546	-0.17881767158165	0.22459302201230
H	2.31156717572361	0.92445458282219	-1.83048822684533
H	1.89377323805636	-0.40101117920003	1.94441916836355
C	0.56318381817207	-2.62040067136660	-0.57820928898193
H	1.01474511016700	-2.43853225632230	-1.56028796643765
H	1.35725896562735	-2.60392102266756	0.17702847354608
H	0.14311085577062	-3.63450440490258	-0.58661474371968
C	-3.38195981741951	0.73264209778423	0.52410719891658
H	-3.51647985931024	1.48590649364533	-0.26011462619961
H	-4.30883187011998	0.14694388898638	0.58084077987403
H	-3.25248935725681	1.24788660486156	1.48214155217038

TS4 (R = Me, R' = H)

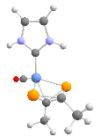


TPSS D3BJ/def2-TZVP
E = −2687.08856227 Eh
G = −2686.96320634 Eh
im. freq. = −123.89 cm^{-1}

0 1

Ni	-0.05943285349514	0.74014061035438	-0.06161622068708
N	-2.84834014149227	0.10844618886824	0.70153853196299
N	-2.11062925792646	-1.27527857464762	-0.72959110054310
C	-1.72901638278509	-0.16576080294226	-0.03252511343538
C	-3.87715632916451	-0.79724534133686	0.47850265165666
H	-4.83236480711385	-0.73275079539761	0.97353459415108
C	-3.40457411691686	-1.68245936606607	-0.43677056869640
H	-3.86885740544627	-2.53914312699362	-0.89733240570058
P	1.20864700097507	-0.45148593231494	1.50901113341320
O	-0.56797765620587	3.61494697888501	-0.20310081219818
C	-0.35726662158936	2.47331102703887	-0.15218505189250
C	2.58525191924707	-2.69749648575764	0.25795074190333
C	1.65972205899541	-1.51516976492971	0.14467975636061
H	2.58285740300468	-3.12138484739089	1.26617997082193
H	3.61036984448464	-2.38824046637902	0.01705034857144
H	2.30818550900845	-3.46719802901093	-0.47183459962846
P	1.31538362188729	-0.65447222299775	-1.40376986371287
C	1.81257946309167	0.49093019979827	-0.00868638323298
C	3.08090695443595	1.30151602218634	-0.01156498826578
H	3.09030370987762	1.98966001879320	0.83898078331528
H	3.15289182051224	1.87898482908129	-0.93815838313228
H	3.96525731829551	0.65769791826195	0.05883961478990
H	-2.88308827870903	0.88753683497923	1.34264308118160
H	-1.47435177297087	-1.71806587208186	-1.37827471700242

Int4 (R = Me, R' = H)

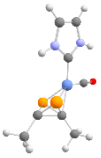


TPSS D3BJ/def2-TZVP
E = −2687.09260841 Eh
G = −2686.96720060 Eh

0 1

Ni	0.08875658599464	0.66134513708281	-0.06000162865261
N	2.08325862871117	-1.44462298099574	-0.54511890131420
N	2.91619230233135	0.18277342433770	0.53921595068749
C	1.74426310601596	-0.22464759331897	-0.03384404478307
C	3.40427261067880	-1.78784080905970	-0.29349348736169
H	3.84249984875690	-2.71410960474445	-0.62734141611526
C	3.93713510125320	-0.74808778343067	0.39837785480559
H	4.92990677899782	-0.59071251345849	0.78700876251072
P	-1.25353182257500	-0.59822601309982	-1.45689157709648
O	0.78214949585613	3.51787792820531	-0.16986337223278
C	0.48755302000058	2.39411788078093	-0.13111767086668
C	-1.82992565544312	-1.33885939404905	0.09714585642171
P	-1.09484757558838	-0.49223549200658	1.50972337923064
C	-1.86031726559586	0.35551777700985	0.02691501082065
H	1.40490277243231	-2.00338641248114	-1.04297375498396
H	2.99136186348951	1.06777994747714	1.01952119039408
C	-3.04558899375335	-2.23313108499828	0.19394217426568
H	-2.71262594017417	-3.27719036648414	0.16784118415913
H	-3.58934395014281	-2.07715675056742	1.13083411283883
H	-3.72326957272987	-2.07843642083731	-0.65177903552499
C	-3.08234972183549	1.24576013946532	0.05889090150891
H	-3.06310085743281	1.89051491505060	0.94139630738292
H	-3.11435447314240	1.87689120743034	-0.83288657233572
H	-4.00042928610510	0.64759486269175	0.08921177624111

TS5 (R = Me, R' = H)

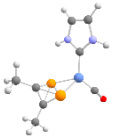


TPSS D3BJ/def2-TZVP
E = −2687.08436347 Eh
G = −2686.95848262 Eh
im. freq. = −190.96 cm^{-1}

0 1

Ni	0.11243769232785	0.46270635420908	0.02814290833719
N	3.04567071766028	0.39759672129317	-0.08925490254017
N	2.24073589324528	-1.56609297982543	0.06976672750456
C	1.84410876176919	-0.25924799023439	-0.03251303558363
C	4.13295183123036	-0.45951409825626	-0.00870238169675
H	5.15276235883212	-0.11165053074872	-0.03024585208830
C	3.62026071512787	-1.71226018255605	0.09424319511824
H	4.10519835065564	-2.67080210312041	0.17987748773983
P	-0.92138712072148	-1.21025147804951	-0.99815022918011
O	0.83322271451054	3.31526845197462	0.05547042601625
C	0.53652537114537	2.19289443684886	0.04391404984654
C	-3.54365880707894	-1.73231360793573	0.27456421800248
C	-2.17569146910907	-1.11100115726154	0.31227919805299
P	-1.60922395181107	0.16385219202050	1.48985763910614
C	-1.85974966404405	0.26934120279035	-0.44303995729001
C	-2.83036286180304	1.14915344320993	-1.19138952285707
H	-3.84588051563527	-2.00585910143474	-0.74405460368020
H	-3.55931573437304	-2.63790122842703	0.89019904666955
H	-4.28197644239484	-1.03489398887869	0.69076635545232
H	-2.56161259612431	1.21576121502759	-2.24941956522482
H	-2.83133358756778	2.15844121087783	-0.77385557984493
H	-3.84979682873181	0.75117840284647	-1.11482532524493
H	3.10298971002031	1.40204563190589	-0.17531661729286
H	1.56896146286986	-2.31471881627579	0.15397032067768

D (R = Me, R' = H)

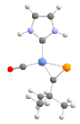


TPSS D3BJ/def2-TZVP
E = −2687.11603695 Eh
G = −2686.99128496 Eh

0 1

Ni	0.33457449219239	0.93647592519371	0.03922290844511
N	3.05840327177299	-0.01838040216210	-0.82621364053225
N	2.37087978692140	-1.07491537716870	0.87952281557992
C	1.99294489474918	-0.06632893294193	0.03304908273849
C	4.04439019320931	-0.95096028233722	-0.53107614681966
H	4.94959598357466	-1.05145452496093	-1.10759875274229
C	3.60573207018362	-1.62370961287055	0.56366023476732
H	4.05618562902687	-2.42255166250536	1.12997450190523
P	-1.26543444641078	-0.05497458084463	-1.17035328529795
O	-0.12991837482279	3.83249993813107	0.22525734561348
C	0.11670668496165	2.70169003538124	0.14570632160102
C	-1.75961706816102	-1.52363456251412	-0.15785050702907
P	-1.17394844402370	-0.31152551967093	1.11877676718111
C	-2.65489498592695	-0.36330257891330	0.01410122648507
H	3.10172915133789	0.64999488756280	-1.58111383539546
H	1.77073550289278	-1.38079052890438	1.63240164984968
C	-1.93776583388045	-2.99704329903228	-0.31172552492206
H	-2.53566752924081	-3.22425957622125	-1.20306946416085
H	-0.97146571760377	-3.50149443105899	-0.41454053301786
C	-2.45382706161521	-3.42022680914956	0.55911088586868
C	-4.12749555881268	-0.14143741606453	0.09971259879875
H	-4.62251847960143	-0.48469786113218	-0.81689561377528
H	-4.55429853754160	-0.69530910812045	0.94479948906003
H	-4.35587462318152	0.92003028030457	0.23519247579882

B (R = *t*Bu, R' = H)

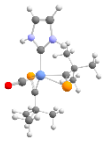


TPSS D3BJ/def2-TZVP
E = −2385.6854119 Eh
G = −2385.52084824 Eh

0 1

Ni	-0.22219811031000	0.17434844661658	0.00071152044118
P	0.50877256856621	-1.93652549925292	0.00048886085584
N	-2.85140341024557	-1.22090408296539	-0.00001738174514
N	-3.13133573284368	0.88037281074688	0.00053156690672
C	-2.13719713085551	-0.05860378654711	0.00054727997215
C	-4.22135313614866	-1.02109234996382	-0.00006757371756
H	-4.93390730221229	-1.82987333419605	-0.00042239632661
C	-4.40251796518535	0.32643451717797	0.00035199214564
H	-5.30234959057831	0.91984453690918	0.00042697997905
C	2.91100726617243	-0.14491558874106	0.00078147174620
C	1.49747547844909	-0.62914734140526	0.00067937283945
O	0.13818751195513	3.06546313879168	0.00203878618537
C	0.02009045770110	1.91034246690469	0.00139198382392
C	3.15311735992639	0.71553953571496	-1.25846478248866
C	3.88109791869492	-1.34506148197596	0.00059243996003
C	3.15308264056334	0.71512146584912	1.26031615063112
H	4.18840909730581	1.07637421022762	-1.26675979900901
H	2.48109438725387	1.57805919865806	-1.27321018436257
H	2.98016325370910	0.12840111809705	-2.16577681563994
H	4.92146487491905	-0.99846998976838	0.00067110217211
H	3.71810541363657	-1.96527887950750	-0.88619664579386
H	3.71807486551317	-1.96559328361084	0.88715590137090
H	4.18838740148276	1.07591479985245	1.26877820893615
H	2.98006479292212	0.12769692711189	2.16743093142027
H	2.48109548257163	1.57766579303848	1.27531545655333
H	-2.37889100336843	-2.11559198259656	-0.00027266466247
H	-2.92835938959491	1.86988363483425	0.00076723780638

Int1 (R = *t*Bu, R' = H)

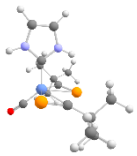


TPSS D3BJ/def2-TZVP
E = −2923.12220753 Eh
G = −2922.83895265 Eh

0 1

C	0.80673624858807	2.52718618508591	5.96814566809061
C	0.40469971582129	1.92016583734070	8.99401131491643
Ni	-0.71360997125313	2.21529786876423	7.30367939816537
N	-2.74718906131744	4.28065665291834	8.21096302267755
N	-2.60253440033818	2.63570286252504	9.54145419078514
C	-2.07842306829646	3.10921078889862	8.38052927691344
H	-2.55750873540388	4.88714639212236	7.42493640420104
H	-2.25480449423977	1.77190109166854	9.94455692214346
C	-3.64582149769556	4.54004498267431	9.23861702288143
H	-4.25946106769291	5.42563249921301	9.27286045466930
C	-3.55125503945010	3.48520880439219	10.09067789471429
H	-4.06767742440844	3.27254024930206	11.01262629186310
C	1.70556782378283	1.57427837993205	5.25686018464159
O	-2.59162263174492	0.81713180310282	5.49555776411792
C	-1.82520936956510	1.35009602703007	6.17389277859537
C	2.83273783573719	1.11698740928452	6.21132853692132
C	2.33110426003700	2.28701611597716	4.03667531232592
C	0.92413040340381	0.33196550876870	4.78342998175397
C	1.16067370143581	2.87310458925787	9.85754883189635
C	0.45515901597951	4.23778326079669	9.98428445744369
C	2.55655002878953	3.09908911099602	9.22840534406398
C	1.33199891120376	2.24900559026112	11.26069663941165
P	-0.04770794742005	0.40820055758055	8.65578757753223
P	0.30179915711271	4.03657627329574	6.22683357245894
H	1.84654157188104	1.28609952658649	11.19055033017836
H	0.35632466398352	2.08352645001568	11.72942113687313
H	1.91790331785361	2.91820470040337	11.90223370783902
H	2.46047514098920	3.54127788293035	8.23409228270655
H	3.09844277152456	2.15343602815190	9.14139518301954
H	3.13137570638689	3.77940235484960	9.86791578230199
H	3.48007873193763	0.40365662854067	5.68778667582333
H	2.41661356181466	0.63100647217288	7.09763044321900
H	3.43792043979871	1.96915874412553	6.53240613884320
H	3.01406873040675	1.60713833032548	3.51329865113858
H	2.89091099927074	3.17089116036523	4.35723113206675
H	1.55100624100061	2.60713482267764	3.33950801766469
H	1.60080206097968	-0.34583361015322	4.25034479391605
H	0.11205708347620	0.61428625180282	4.10663467368462
H	0.49520018562702	-0.19786511509825	5.63875086925522
H	0.29511074712946	4.67482943237593	8.99492928274403
H	1.07975828554039	4.91672249346029	10.57588107330121
H	-0.51353263266622	4.14071860527889	10.48385098224026

TS1 (R = *t*Bu, R' = H)

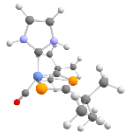


TPSS D3BJ/def2-TZVP
E = −2923.09565961 Eh
G = −2922.81382696 Eh
im. freq. = −112.66 cm^{-1}

0 1

C	0.46773457758094	-0.39892304952838	-1.25217992310960
C	0.45744928263810	0.00885639646472	2.12490719845612
Ni	-0.43251862038793	-1.28629999551384	0.20143496285763
N	-2.19280161422938	1.00695631809556	-0.37902344593612
N	-3.38577388510683	-0.71637754086946	-0.05182594034386
C	-2.08327467623671	-0.31583369935682	-0.08704550672362
H	-1.35484860732588	1.57329444652430	-0.48349999415189
H	-3.64557346178431	-1.66873245927819	0.16074439366105
C	-3.50711194516471	1.42397533772667	-0.51858541246517
H	-3.77930301702576	2.44080530114077	-0.75100485899999
C	-4.27387130043346	0.32109681171096	-0.31119790136036
H	-5.34348930974970	0.18782325921364	-0.32604574258879
C	0.43774829984696	-0.70735827840229	-2.71991177257468
O	0.07155754336324	-4.14191568649262	-0.11849181230317
C	-0.05086329640445	-2.99696612257159	0.03138896780704
C	1.43833135120060	-1.86171526008603	-2.97043931032536
C	0.87088635624019	0.52688133169689	-3.53894309344829
C	-0.96848653111112	-1.15600718692761	-3.16446622678485
C	1.39899947749917	0.90070917490415	2.89955665273134
C	1.16821620955078	2.39253425458143	2.57671463613655
C	2.87112345142506	0.51941239840960	2.63437004389254
C	1.10831556439066	0.68542571465447	4.40454619360241
P	-0.66291551780358	-1.12364662874306	2.44504719909675
P	1.19111814433003	0.63277385339274	-0.20106078273810
H	1.28027502502186	-0.35843156562693	4.68252910772157
H	0.06925718795036	0.93791633848288	4.63627323017357
H	1.76879534060576	1.32507803310701	5.00255800503600
H	3.14474390056651	0.68310806903093	1.58827920810141
H	3.03927480393709	-0.53483752261773	2.87351245031657
H	3.52479622760853	1.13370897193404	3.26481318508030
H	1.45551865161672	-2.09821084935799	-4.04077275133774
H	1.14491249167550	-2.75759177569955	-2.41822700250960
H	2.44518284792645	-1.57277714030057	-2.65565363842948
H	0.87077971083081	0.29345968846365	-4.61027447964495
H	1.87721224284945	0.84519705398097	-3.24911407332319
H	0.18397251875175	1.36207405298209	-3.36612095752451
H	-0.95713528412447	-1.41381248007782	-4.22998883580439
H	-1.70051889954654	-0.35663318146982	-3.01040650622044
H	-1.28824555252817	-2.02812500218422	-2.58773105093025
H	1.39610398434494	2.61790165383145	1.53171770082317
H	1.81756339723507	3.00741464070145	3.21070032214941
H	0.12686290297645	2.66779232407417	2.77291756193496

Int2 (R = *t*Bu, R' = H)

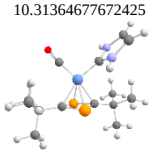


TPSS D3BJ/def2-TZVP
E = −2923.10745171 Eh
G = −2922.82412494 Eh

0 1

P	1.00019191814035	3.23750124439742	6.53467867198165
C	-0.12051038502421	1.96664653780823	6.46606552472726
C	1.38197945587477	3.69750545875662	8.34105223803595
Ni	-0.34680313604718	1.70347682024151	8.31927109018127
N	-2.09887664486436	3.99074180170387	7.75851113912853
N	-2.97348551366808	2.72236968417620	9.22534440228880
C	-1.86244038817261	2.84115619912690	8.44277740018603
H	-1.41684226273905	4.32979046923159	7.08443957667895
H	-3.08983911294384	1.96569055906603	9.88340612205250
C	-3.30603850844669	4.57787661098372	8.10007561127451
H	-3.65618274390990	5.49551000773169	7.65653827645425
C	-3.87087493420793	3.76696809578859	9.03252337260912
H	-4.80908912090958	3.83580007295928	9.55836763045796
C	-0.66121503019714	1.31776844510303	5.22314213757006
O	0.75969017402516	-0.88505441091972	9.04519514811352
C	0.38122885357228	0.16884101352408	8.74952052006813
C	-0.06839328751122	-0.11013077633600	5.15252447895580
C	-0.29756865112401	2.08057359442349	3.93285353544748
C	-2.19747726665182	1.20899965134305	5.33856311941294
C	2.46119327241349	4.81290400403563	8.35960335031687
C	1.94163726169295	6.04624450799178	7.59068769173917
C	3.75158054638773	4.29521340217415	7.68866082946579
C	2.79755573399290	5.24085045445105	9.79669247338256
P	0.74181775391108	3.03706446324688	9.76005429799721
H	-2.60165394619420	0.67792629375878	4.46860003470370
H	-2.65889179924103	2.20140210313880	5.38036258262832
H	-2.46989012820099	0.66593192845764	6.24863758803275
H	-0.71008957360294	1.56767218545032	3.05590505598938
H	0.78884274943902	2.14869971422775	3.81669716476075
H	-0.70009371681990	3.09880436525121	3.96030891840531
H	-0.46215963225419	-0.62662305580559	4.26909862872999
H	-0.33502611736871	-0.68176733459891	6.04572747059783
H	1.02254322772046	-0.07023390685547	5.08025250305967
H	3.56797015149323	4.00228625334321	6.64986500380708
H	4.13817305929523	3.42516429343525	8.22870222291782
H	4.51538029130805	5.08219790048940	7.69564023400739
H	1.70952867136061	5.79858872887869	6.54947960940220
H	2.70541552716058	6.83301481473113	7.59231467693221
H	1.03570271988996	6.43910332395440	8.06536775282994
H	3.55675478432860	6.03213981400930	9.77453557842143
H	3.19058568828938	4.39909151246879	10.37600955952324
H	1.91102005980372	5.62265315465605	10.31364677672425

C (R = *t*Bu, R' = H)



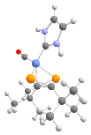
TPSS D3BJ/def2-TZVP
E = −2923.17085350 Eh
G = −2922.88523866 Eh

0 1

Ni	0.03663794275937	-0.62977994012213	-0.29767820612811
N	-2.75585996532469	-1.61647692493511	-0.68837148266052
N	-2.22149317370720	-1.38301478121549	1.35497870838075
C	-1.72415651810741	-1.20691811171804	0.10086926206039
C	-3.86596882047118	-2.01221385596721	0.04762335863360
H	-4.77619818537269	-2.36360089082342	-0.41001073505746
C	-3.52335495041969	-1.85831340506950	1.35363805884145
H	-4.08023230015058	-2.04562476459382	2.25700164238353
P	1.05088536498075	1.19121320673172	-1.25856839764821
O	0.89795037809341	-3.14344449827959	-1.49177627390160
C	0.61015032547585	-2.13079679314061	-1.00725382746841
C	-0.26101963131631	1.41960610802582	-0.07605488692734
P	0.55951489735288	0.77852308930791	1.45101133510459
C	1.78154185501409	0.36680502392055	0.21398702164999
H	-2.69409679231577	-1.60630006357271	-1.69635549808249
H	-1.66305848568328	-1.12769147984306	2.16123645885353

C	-1.49783042397301	2.27554503502250	-0.22501464926910
C	3.16915310064633	-0.19828659670183	0.39660251281666
C	-1.04834754520769	3.73484531434681	0.03960254604440
H	-0.28443375520596	4.03561071574536	-0.68355910730616
H	-1.90476815449923	4.41470153141094	-0.04507881835498
H	-0.62566312431857	3.83036698031438	1.04516300837096
C	-2.05469320033603	2.17219733836285	-1.65480939153616
H	-2.39917214162349	1.15322302601880	-1.85820998158837
H	-2.89611333379805	2.86144997369899	-1.79213107948879
H	-1.28275742733808	2.42169776077319	-2.39136820385414
C	-2.59537566158019	1.91725059185776	0.79144127368449
H	-2.18568681385859	1.86386814619232	1.80687236616082
H	-3.37932777108874	2.68302809149132	0.78111123384785
H	-3.05861786470919	0.95696650483222	0.55328496249952
C	4.06699470741308	0.97503418222214	0.86308612646271
H	3.70779228458278	1.37687212521885	1.81559792802418
H	5.10027638660679	0.63115441166322	0.99055988902617
H	4.05782487731624	1.78327894233803	0.12447696799869
C	3.72527176590929	-0.74550537442255	-0.92898037473967
H	4.77259683919447	-1.04369726925669	-0.80549489450511
H	3.15948680548052	-1.61728887015539	-1.26654582251304
H	3.67812254172605	0.01786488762300	-1.71378934990796
C	3.17188945304346	-1.29711720550516	1.47275473594654
H	2.57016856773181	-2.15160226542761	1.14866669447748
H	4.19414387325279	-1.63984992784728	1.67079898909247
H	2.74939007382566	-0.91984496852148	2.41129590057683

Int4 (R = *t*Bu, R' = H)

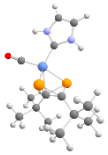


TPSS D3BJ/def2-TZVP
E = −2923.12195252 Eh
G = −2922.83702072 Eh

0 1

Ni	1.12786638747857	0.80586064965000	0.04806568396498
N	2.37425018221682	-1.86802530456812	0.11297794415472
N	3.82743492471449	-0.32893846067547	-0.07171331070057
C	2.47752114263004	-0.50831948391082	0.03691135848404
C	3.60284412730879	-2.50808744927691	0.04836713726706
H	3.70738137781038	-3.57990614148206	0.09350185857352
C	4.53338917269379	-1.52605887288433	-0.06870970109367
H	5.60727013172682	-1.57246717984016	-0.14594693306639
P	-0.26161378140608	-0.16005270482051	-1.48016143699991
O	.60938907480055	3.34185818216968	0.10813323025017
C	1.96215099182017	2.37322599545107	0.07996317411383
C	-0.97273689822611	-0.96446826454163	-0.01194952233287
P	-0.30887660373951	-0.18481954476632	1.48602693319138
C	-0.89400183349987	0.76576262285057	-0.00416013833987
C	-1.31367524939338	-3.34954646181022	0.23061008011875
H	-0.78874795058465	-3.32529240734225	1.19255489651518
H	-2.01427824141224	-4.19175953434821	0.24311543881909
H	-0.58610853249281	-3.52755243423891	-0.57064880277133
C	-2.81540672617642	-2.12626327674496	-1.35372749615165
H	-3.52048812691909	-2.96531111046744	-1.32606232931520
H	-3.37490114613294	-1.21472715271228	-1.57406992941327
C	-2.10974624632832	-2.29316909248546	-2.17352253085683
H	-3.08161171769030	-1.82826577477199	1.14255533694911
H	-3.64535367095371	-0.89917619331525	1.02303929499970
H	-3.79382407718941	-2.66120707212428	1.16030720043515
H	-2.56554421910438	-1.78488257335527	2.10627957767606
C	-3.20736474181130	1.44403998743271	-0.81312503799379
H	-2.94085703387540	1.12735609976307	-1.82648596509969
H	-3.72125523100889	0.61885010256726	-0.31326822562157
H	-3.90693062407921	2.28454364232740	-0.87973947518873
C	-1.32789388254554	3.08399774624362	-0.76814038949630
H	-2.06771647761139	3.88837379200443	-0.85261182025351
H	-0.45839275944751	3.45775031089089	-0.22284475614309
C	-1.00299786073691	2.79912165733884	-1.77449140109429
H	-2.33739406127038	2.29342493613729	1.39159997783338
H	-1.45020973882730	2.60526402481068	1.95248880057896
H	-3.04133141191976	3.13303461170098	1.36263886503383
H	-2.80567511426913	1.46186395074559	1.92804285829880
H	1.47198883500114	-2.31783717055417	0.19587716375585
H	4.23449059391498	0.59222262646911	-0.15058460968740
C	-1.95261902621705	1.87962682645605	-0.03778399570646
C	-2.07976395724747	-2.02575310397217	-0.00820330960714

TS5 (R = *t*Bu, R' = H)

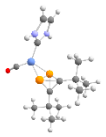


TPSS D3BJ/def2-TZVP
E = −2923.11116170 Eh
G = −2922.82655845 Eh
im. freq. = −182.52 cm^{-1}

0 1

Ni	-1.05917359313759	0.43316948681227	-0.21252553488781
N	-3.93026211868004	-0.03979463072221	0.08700307827169
N	-2.82568510338961	-1.81209324174213	0.49970708106578
C	-2.63915947232204	-0.49411184948138	0.17284379546996
C	-4.86849309032639	-1.03190978712978	0.32806891568343
H	-5.93030956456226	-0.85080517625271	0.29362824574813
C	-4.16509360179315	-2.16267383927482	0.59091220566654
H	-4.49295986312978	-3.16072965222453	0.83115337712034
P	0.22091975282997	-0.75033085099110	1.16645150422375
O	-2.30888847299438	2.93140443220218	-1.15029666446849
C	-1.79000252954847	1.97766020177399	-0.73431534992017
C	2.67549395610276	-1.71083959826222	-0.27141134370531
C	1.36969975224605	-0.92026345819290	-0.24803043579521
C	2.33485840550795	-3.01603106286059	-1.02552332972153
C	3.16196962709861	-2.07883301367750	1.14000179483704
C	3.77330961158778	-0.97070980684274	-1.05576513269787
P	0.59939728016967	-0.04723881619188	-1.65219869411579
C	0.99624162112598	0.57571626877469	0.18718926665084
C	1.76798496172674	1.81963060054342	0.63985233885053
C	0.79174153004432	2.76943386385375	1.35766569440962
C	2.37851931483867	2.54460343700246	-0.57176259636774
C	2.87708748857511	1.45234342262821	1.64458655812010
H	4.12485807544345	-0.08818853313299	-0.51560524344997
H	3.39230813146845	-0.64425733211255	-2.02892252560610
H	4.62916882777945	-1.63623746729201	-1.21542845940044
H	3.21389909535444	-3.66906025073626	-1.07085725078473
H	2.01081400033179	-2.79263654430160	-2.04715549795374
H	1.52747624400987	-3.55664858957497	-0.51889820597998
H	3.40821445462742	-1.19369872415007	1.73035610218514
H	4.05817202309470	-2.70621905414537	1.07332827989168
H	2.39216131270283	-2.64160165120712	1.67967899735175
H	2.90992265397584	3.44316098513649	-0.23612294378616
H	1.59448268590868	2.84243420355101	-1.27408425450936
H	3.07948514528273	1.89905796090798	-1.10719409931353
H	1.34029332722602	3.63747624515345	1.74185139383066
H	0.30283706766191	2.26304388774350	2.19673119060310
H	0.01426756078239	3.12166862907464	0.67561094379441
H	3.33813689547177	2.36797330521563	2.03141289873427
H	3.66288863389611	0.85225781408571	1.18088750315031
H	2.46095828634636	0.89112268650393	2.48801934327149
H	-2.04549677775599	-2.44135326643700	0.61784801930848
H	-4.14464053557817	0.92048876597311	-0.14043496577514

D (R = *t*Bu, R' = H)

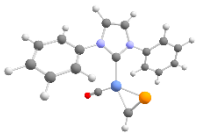


TPSS D3BJ/def2-TZVP
E = −2923.15034926 Eh
G = −2922.86759833 Eh

0 1

Ni	-1.24428079056275	-1.33315387976203	-0.01535483737758
N	-3.42536659094919	0.45740798751258	-1.01878904686820
N	-3.49082035142575	0.30537507651767	1.09663546157710
C	-2.80300395257573	-0.18793984534368	0.01812655349034
C	-4.44242992687548	1.30977869725283	-0.60506193257112
H	-5.03355775863404	1.89381418115359	-1.29141170714813
C	-4.48424347031473	1.21287720911827	0.74698138973131
H	-5.11900561695461	1.69558968244606	1.47200834325429
P	0.37934486870648	-0.30240627309576	-1.15915734294519
O	-0.86096387763992	-4.24520455954203	-0.05964067159888
C	-1.08873224801067	-3.10751320920229	-0.04386327347274
C	0.97714985463704	1.02803090081219	-0.01366169087957
P	0.36843963420915	-0.29273847702529	1.13642350281890
C	1.82439557495518	-0.18103020959680	-0.00461268180191
H	-3.14094885348852	0.31990305158259	-1.97715716472106
H	-3.27073743104065	0.02550721648111	2.04080799745508
C	1.02750062032927	2.53350606692580	-0.01359220186251
C	3.25420665276551	-0.65527720949878	-0.00509126588264
C	1.86430199010709	3.03547801988504	-1.20439130368647
H	1.82883971940706	4.12974070446791	-1.25894319303457
H	2.91120922358954	2.73353168804826	-1.10352495339428
H	1.47799623486104	2.62806091608660	-2.14473627295587
C	-0.41712173784576	3.05094668163734	-0.14518524010763
H	-1.03507143673212	2.67808304488421	0.67832271469002
H	-0.43650388443944	4.14672094347553	-0.12824971401421
H	-0.85990420190869	2.70746643552340	-1.08564313714089
C	1.63358670902265	3.04099164319699	1.30791374097744
H	2.66202374519482	2.68897854514342	1.43115117506650
H	1.64129995183752	4.13699701446208	1.32549237604231
H	1.04593134906629	2.68276872779769	2.15964860154385
C	4.01333379988461	-0.04478446620057	1.18703455313820
H	5.03005743342398	-0.45135099640663	1.23397958261101
H	4.08593971221031	1.04323419304511	1.09245467817989
H	3.50382183036108	-0.27659835641710	2.12826333556527
C	3.93962940603074	-0.25661623318018	-1.32533678448619
H	3.96816929407863	0.83069993501093	-1.44394334358331
H	4.96967307728145	-0.63071105935932	-1.34244641932002
H	3.40077954276804	-0.68128537228820	-2.17860201696235
C	3.23862339854467	-2.18984390539617	0.12155134732711
H	2.76118368186237	-2.49183872484423	1.05903440827731
H	2.67676975759342	-2.63695907595350	-0.70474232900123
H	4.26037206667012	-2.58580970935467	0.10457876307065

B (R = H, R' = Ph)



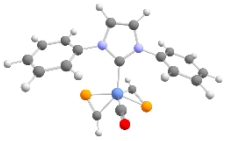
TPSS D3BJ/def2-TZVP
E = −2690.70820031 Eh
G = −2690.50172163 Eh

0 1

Ni	0.02588106319047	-1.30865692840864	0.09181132864338
P	-1.09125130908313	-1.89441463150637	-1.77162066286522
N	-1.06868980397598	1.48198981244590	0.06828246434583
N	1.07787772510191	1.47695531889423	-0.10090994482995
C	0.00534555542065	0.62467529510113	0.01850016423642
C	-2.42437751901830	1.05400324715370	0.18287328117017
C	-3.42231882124217	1.72409957662317	-0.52619753686599
C	-2.73610019061786	-0.04186427296442	0.98883462282170
C	2.43410380745746	1.04120571696956	-0.18321889290066
C	-0.67102989476978	2.81576060277632	-0.02088948155583
H	-1.37607789003715	3.62926362304652	0.02271553493480
C	0.67835685352161	2.81310427698991	-0.12318049181099
H	1.38212065307883	3.62139199481831	-0.23382483132996
C	-4.05739240807683	-0.47361539446452	1.07264724243165
H	-4.29829275419536	-1.33190517142348	1.69234018866802
C	-4.74351539927579	1.29209211791709	-0.42386915035880
H	-5.51928090708683	1.80735646418123	-0.98226178493231
C	-0.46574045739190	-2.95468866514510	-0.70853713570849
C	3.43092849103844	1.75718404929949	0.48157669746855
C	2.74700051219448	-0.10408533409333	-0.91753044708040
C	-5.06378238511736	0.19126199733616	0.37116432111217
O	1.56181567909637	-2.14453635001327	2.42710325168791
C	0.94044979492021	-1.80237374878153	1.51321464947603

C	5.07415127582450	0.16915878853559	-0.31100762068914
C	4.06905614570132	-0.53996063761019	-0.96988149126005
H	4.31173495256096	-1.43426060757602	-1.53576868799711
C	4.75257133712536	1.31987135662119	0.40941473316042
H	5.52757088823147	1.87137023187774	0.93319621831688
H	1.95572928934871	-0.63833945545327	-1.43550740248506
H	6.10327339277607	-0.17412054949064	-0.35653446660911
H	3.17086993393160	2.62924285877702	1.07395129690235
H	-3.16325376263465	2.55341510043570	-1.17734350167892
H	-1.94284112599823	-0.54718794018934	1.53241906649278
H	-6.09267163931840	-0.14866832104163	0.44064068670551
H	-0.32128008268070	-3.99555642163822	-0.44891640001658

Int1 (R = H, R' = Ph)

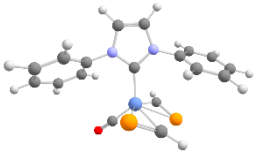


TPSS D3BJ/def2-TZVP
E = −3070.77013889 Eh
G = −3070.55252215 Eh

0 1

C	-1.10514803948077	-2.78481878187675	-0.64434450066293
C	1.19455984139992	-1.08353493261322	-1.75383386575050
Ni	0.02317672973038	-1.17674878664381	-0.06126738596920
N	-1.13177402046730	1.63150164506432	0.09675728399667
N	1.01331794205191	1.66904239734552	0.06716452521581
C	-0.04299798757853	0.78930246968438	0.09175122442951
C	-0.75842457786860	2.97348761055115	0.03620828665266
H	-1.48580525605521	3.76838254917084	0.05472442564735
C	0.59410324148383	2.99664939865362	0.01709127428339
H	1.29608329398546	3.81449926002128	0.01545850538805
O	0.23499382153092	-2.04925724383098	2.73805589901626
C	0.13812793664081	-1.71148322277219	1.63486790132640
P	2.11730182287272	-2.01928110890966	-0.85737434144412
P	-1.97264376089602	-1.63529498919829	-1.32471095918559
H	0.93973917593995	-0.53241822697956	-2.64523862074517
H	-0.89257750111974	-3.80874984504651	-0.37833284417687
C	2.39351298636415	1.29820356633901	0.14234069507876
C	2.83525692518795	0.52213752287993	1.21103901632071
C	3.27328541138277	1.72737745794721	-0.84849543648372
C	4.17566962367376	0.14627378821148	1.26767794377332
H	2.13021872603428	0.20797970920616	1.97149091731451
C	4.61647860300337	1.36192117399792	-0.77412987772115
H	2.89988944827698	2.31508496305623	-1.68162250873357
C	5.06660700275327	0.56429918566658	0.27735926653556
H	4.52308683759198	-0.47360482487632	2.08841941573325
H	5.30475727984505	1.68299097852679	-1.55007637903124
H	6.10969698742040	0.26650453053134	0.32500500029772
C	-2.49630506847775	1.21504885291146	0.17487369673979
C	-2.88180263552149	0.29270923898089	1.14726326333209
C	-3.42487150737412	1.74074693937178	-0.72232118478941
C	-4.21104889171704	-0.11856060491878	1.20568385331545
H	-2.13874834938417	-0.10442844281523	1.82847884680195
C	-4.75555653334012	1.33145851900292	-0.64802963518878
H	-3.10008518190434	2.43676816833935	-1.48984637459169
C	-5.14928208553083	0.39847233942163	0.31071733674221
H	-4.51152340963986	-0.84774122304745	1.95161410178785
H	-5.47907785647228	1.72890054194956	-1.35340331543504
H	-6.18327997434170	0.07047642669734	0.35722955017569

TS1 (R = H, R' = Ph)

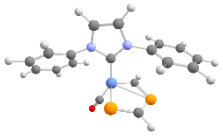


TPSS D3BJ/def2-TZVP
E = −3070.75473303 Eh
G = −3070.53747952 Eh
im. freq. = −135.11 cm^{-1}

0 1

P	2.49094636497309	0.74366104393834	-1.62265257095574
C	1.31355423212977	-0.31784721590847	-1.92548379271092
C	2.60877495782094	0.82487888909640	0.89383940049136
Ni	1.14018462685379	-0.68801571213325	-0.01766846539963
N	-1.36185768428328	1.02758107051332	-0.20675783305066
N	-1.68453180608292	-0.76188253344704	0.92781942197603
C	-0.70033355903041	-0.09150929472881	0.23716999592715
C	-0.73154473464189	2.09763840142626	-0.92259474164384
C	0.22709690650274	2.87163466954884	-0.27540184265187
C	-1.07599341957094	2.33619030949162	-2.25062735290127
C	-1.49269281927346	-2.00526604940687	1.61356390372960
C	-2.69904615870193	1.04583734801921	0.18544647239368
H	-3.35821964607277	1.85841311847687	-0.07379373938376
C	-2.90021647335139	-0.08208950487437	0.90818327758495
H	-3.77990608325875	-0.47488175202575	1.39149142240936
C	-0.44170130042762	3.36607470106206	-2.94498099501855
H	-0.69774677734527	3.55214931967719	-3.98367500265589
C	0.86695201475013	3.88871951430652	-0.98130432223470
H	1.62947317082320	4.48518434920789	-0.48962301039597
C	-1.18824043350274	-3.15355966312603	0.88654078360559
C	-1.62598743649067	-2.04578673759744	3.00036377663044
C	0.53319359465706	4.13773324194122	-2.31370213105704
O	2.09364795842964	-3.46891729963279	0.08720123679956
C	1.74752654613648	-2.36473823771903	0.02919301689813
C	-1.13189123997451	-4.41123149856961	2.95028261945845
C	-1.44739390509158	-3.25722510882125	3.66784991174943
H	-1.54096364961032	-3.29408194068461	4.74906932697991
C	-1.00235772091956	-4.35777461789958	1.56168063535047
H	-0.74846903867520	-5.25227654277774	1.00172692785701
H	-1.84609787832790	-1.13328033409171	3.54613869039556
H	-0.98231877173602	-5.35107570513428	3.47332809043261
H	-1.08679908231316	-3.08925188170078	-0.19080544062713
H	0.48764747515462	2.64978163388761	0.75310751189663
H	-1.81406682266080	1.70508051359966	-2.73618426551572
H	1.03673995714579	4.92910624781683	-2.86075472126701
P	1.83668191842931	-0.01291982286530	2.03403121967771
H	0.75609895810041	-0.77719501273384	-2.73117513140372
H	3.34539193943615	1.59846598386869	0.74232449662980

Int2 (R = H, R' = Ph)



TPSS D3BJ/def2-TZVP
E = −3070.77249444 Eh
G = −3070.55242487 Eh

0 1

P	2.30629376636815	-2.12073479337754	-0.02189130367425
C	1.27073951922795	-1.60169429983099	-1.24832868701004
C	1.43084243889312	-1.78292172844473	1.58064405458797
Ni	-0.28071310136687	-1.01028912014695	-0.31370096416408
N	0.86085667515219	1.76578369524919	-0.07210928297186
N	-1.29193936643866	1.69657190614198	-0.10138236588378
C	-0.17936659545875	0.88358696239531	-0.18109358334600
C	0.41525806719597	3.07644827989677	0.07810296043508
H	1.10458778834695	3.90047872906146	0.16315388604683
C	-0.93845737884241	3.03415396685037	0.05803690731229
H	-1.67547230195237	3.81910806901237	0.09900591171694
O	-1.91843743321318	-3.40663197089681	-0.52367608851552
C	-1.23553549411499	-2.48347317694014	-0.39619659068021
P	-0.11551022569723	-1.19509325532545	1.92974665067117
H	1.56679143353201	-1.75336868048887	-2.28657166352328
H	2.08035308863094	-2.03937716940399	2.42200639385658
C	2.25151546117855	1.40579423370303	-0.13008205552854
C	2.86403389054732	1.27873488331578	-1.37410642364083
C	2.95413389760727	1.18827978451044	1.05020854733851
C	4.21054780983854	0.92719600137287	-1.43597598645574
H	2.28083327182584	1.43642278084790	-2.27531089247582
C	4.29887787689746	0.82555319117198	0.97851568835899
H	2.44171808283636	1.26631439978349	2.00272668563376
C	4.92538674994798	0.69555014839880	-0.26091710470487
H	4.69489795891653	0.81690647811080	-2.40125075307066
H	4.85234700588534	0.63299635838504	1.89240931804524
H	5.97009050250832	0.40393381779903	-0.31069774159249
C	-2.62774336909824	1.20658999267740	-0.13512241508995
C	-3.58280407285299	1.72605312248644	0.73902538041538
C	-2.95521447385467	0.18662196353467	-1.02998908497908
C	-4.87920133579463	1.21481640104180	0.71520908234231
H	-3.30466192120436	2.49668843062368	1.45144860365965
C	-4.25017044587164	-0.32929312586636	-1.03321560857080
H	-2.20209999691159	-0.17136944367204	-1.72737623858722
C	-5.21303300392923	0.18320637297126	-0.16389520255037
H	-5.62273961357666	1.60987592929806	1.40075333458834
H	-4.50404057139585	-1.12992524166133	-1.72100408859436
H	-6.22100158376246	-0.22030789258473	-0.16998827939928

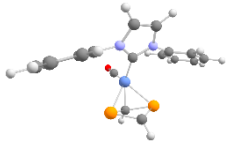
C (R = H, R' = Ph)

TPSS D3BJ/def2-TZVP
E = −3070.83334597 Eh
G = −3070.61036951 Eh

0 1

C	0.00048060418238	2.95916667742730	-0.47706957735253
C	0.00046492696046	1.10806820808901	-1.77378680321898
Ni	0.00008514857167	1.05856127965363	0.25439017527131
N	-1.07694169899443	-1.69065648871342	0.12663011632221
N	1.07598699734231	-1.69105231332038	0.12681875250181
C	-0.00033225074683	-0.84913890142188	0.23219860189211
C	-2.44688393717403	-1.27138128084144	0.12098063657779
C	-2.93082950734493	-0.46377078957012	1.14794141375359
C	-3.27364338911723	-1.68023438227918	-0.92375981867731
C	2.44608561274128	-1.27227681453455	0.12137330016721
C	-0.67797353230258	-3.01219322351638	-0.06303696706566
H	-1.39229326087712	-3.81560564091280	-0.13696367758744
C	0.67657123325087	-3.01243140195677	-0.06298514073718
H	1.39061454432388	-3.81609501092695	-0.13685166153557
C	-4.60726965859028	-1.27296136731591	-0.93875811705637
H	-5.25272082619338	-1.57925541481353	-1.75628543655700
C	-4.26329893753810	-0.06041218244647	1.12243454007685
H	-4.64404258917567	0.57352218412323	1.91711885325916
C	3.27277988701621	-1.68122324930711	-0.92338121408777
C	2.93024361989742	-0.46505737281080	1.14854013539806
C	-5.10188826088730	-0.46130294653936	0.08150694939103
O	-0.00008677564534	1.70078183009414	3.09781125398365
C	0.00004045562164	1.45321275927754	1.96560050535971
C	5.10138930027438	-0.46316887549169	0.08228516429112
C	4.26286420159639	-0.06218557625735	1.12322868539906
H	4.64377757112599	0.57144429790458	1.91807425316414
C	4.60655632741617	-1.27443457376095	-0.93818818599638
H	5.25196302954476	-1.58079899342933	-1.75572422405274
H	2.26755389222780	-0.16001531663536	1.94878999574494
H	6.13784915476968	-0.14006995408383	0.06446967297879
H	2.86742692045331	-2.28713600505404	-1.72833067978378
H	-2.26809233180696	-0.15880929410179	1.94818253953662
H	-2.86844805473280	-2.28645126530068	-1.72855949368738
H	-6.13822769679983	-0.13782609869431	0.06354059689444
P	-1.41131568191346	2.10751086377163	-1.23135118491172
P	1.41231608359818	2.10709397017534	-1.23088039682388
H	0.00048826521269	3.81312999260092	0.19581692431337
H	0.00043061371280	0.18396967091904	-2.34742998714528

TS4 (R = H, R' = Ph)



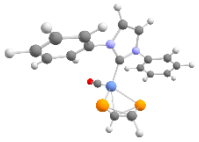
TPSS D3BJ/def2-TZVP
E = −3070.78043653 Eh
G = −3070.55990532 Eh
im. freq. = −297.93 cm^{-1}

0 1

Ni	-0.00091090292610	0.53709003796850	0.88055646546788
N	1.07746170964713	-1.93112335032106	-0.39284311398376
N	-1.07373659216258	-1.93380045349372	-0.39417574479211

C	0.00072355685762	-1.18721964018509	0.03171360075023
C	2.44640082076721	-1.56006241272101	-0.21369775574382
C	3.31237128191142	-1.60664894180637	-1.30507401761593
C	2.89679435504981	-1.15436552791967	1.04200679797517
C	-2.44383743210092	-1.56560910514150	-0.21814997150679
C	0.68065025955910	-3.07705292226190	-1.07893192222858
H	1.39415031168574	-3.79159730009586	-1.45522875623498
C	-0.67307606158655	-3.07856237001753	-1.08005553425256
H	-1.38419894778497	-3.79457814537109	-1.45812432028454
C	4.22871701060167	-0.77969792670725	1.19776607065002
H	4.58141242451026	-0.45622116139893	2.17241447451154
C	4.64693116335014	-1.23805985421497	-1.13661168491938
H	5.32150542424814	-1.26267547752350	-1.98714422524125
P	1.46243578173484	1.84586994383343	-0.50655392909525
C	-2.89797878987887	-1.16043584677093	1.03623429101538
C	-3.30735101643370	-1.61461140836570	-1.31139577843625
C	5.10541637659415	-0.81945613024881	0.11175932304246
O	-0.01309759979163	0.27915313686856	3.78077813609727
C	-0.00560985572145	0.39350463821469	2.62391274995068
C	-5.10524802742757	-0.83073033102015	0.10069506025702
C	-4.64310310360428	-1.24893448060348	-1.14623489738565
H	-5.31579161437265	-1.27571030617668	-1.99823955057605
C	-4.23103142427047	-0.78857543433398	1.18865259102975
H	-4.58659578405515	-0.46546633560201	2.16216132370706
H	-2.92819889559745	-1.90648472942766	-2.28613270298319
H	-6.14274414210466	-0.53549006681155	0.22459558027513
H	-2.20611855560449	-1.12891077237604	1.86910274249054
H	2.93585032223451	-1.89878528723544	-2.28088942629391
H	2.20283689493120	-1.12413593076886	1.87320014543484
H	6.14200892788832	-0.52195286931776	0.23827365290904
C	-0.00313329983411	2.03426198105598	-1.50831580717552
P	-1.46717547519766	1.84468520874603	-0.50378519152612
C	-0.00201714746113	2.36704763144963	0.53944406505988
H	-0.00099728434066	3.34671990450725	1.01333685175517
H	-0.00380620931419	2.51728440559445	-2.49694010210343

Int4 (R = H, R' = Ph)

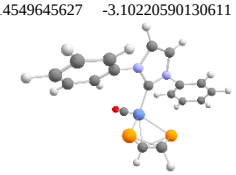


TPSS D3BJ/def2-TZVP
E = −3070.79223282 Eh
G = −3070.56987805 Eh

0 1

Ni	-0.00010784932434	-1.08821495754064	0.41327281443039
N	-1.07708921606169	1.64086219397313	0.07262536742799
N	1.07835338804163	1.64039159425038	0.07287079599865
C	0.00042705954397	0.79011073274169	0.19657432756348
C	-2.44856925643019	1.24182469187581	0.09607724331196
C	-3.30191118838934	1.68829079390355	-0.91265589599890
C	-2.91939483136963	0.41724535394225	1.11802880189052
C	2.44964805867733	1.24076887167648	0.09662257543928
C	-0.67522181743603	2.95817439484972	-0.14535373818038
H	-1.38704128304431	3.76232177897535	-0.23280765779562
C	0.67709602426784	2.95788448235863	-0.14518532953420
H	1.38926881822163	3.76174021457218	-0.23243331705481
C	-4.25646476920804	0.02803428438715	1.11610485123082
H	-4.62347721747394	-0.62021092017805	1.90596942853564
C	-4.64231038781306	1.30200435136712	-0.89890473062907
H	-5.30582713967918	1.64078576790136	-1.68884955006672
P	-1.50614703512584	-1.77749788591676	-1.22426118151766
C	2.91968392729348	0.41517763590749	1.11812704024003
C	3.30363731429543	1.68767307864354	-0.91137608621257
C	-5.12009161747378	0.46787572994423	0.11058184668979
O	-0.00255158098312	-1.63685953653989	3.30273623381091
C	-0.00109138529497	-1.44624787690442	2.15577920491504
C	5.12087000101762	0.46573351675751	0.11173229435812
C	4.64387518555710	1.30084449310769	-0.89731512007410
H	5.30788302605141	1.63998360017194	-1.68669399616799
C	4.25659931528978	0.02543336901788	1.11649959250697
H	4.62298581815904	-0.62358710154837	1.90601921457670
H	2.91412970582979	2.30781103464888	-1.71318501673244
H	6.16131687694932	0.15517812382272	0.11430873256559
H	2.23684967342378	0.07814931689916	1.88839969116850
H	-2.91177782428859	2.30766252912759	-1.71475395286494
H	-2.23707920898233	0.08060330859701	1.88892530466292
H	-6.16066191868569	0.15773270577901	0.11292461992281
C	-0.00056730366555	-2.02052398816678	-2.18262588798164
P	1.50534611252632	-1.77789162438208	-1.22464973242256
C	-0.00042568006663	-2.72236422653097	-0.68859524192336
H	-0.00055627761087	-3.79093733503524	-0.49980664478304
H	-0.00071951673833	-2.61314549645627	-3.10220590130611

TS5 (R = H, R' = Ph)

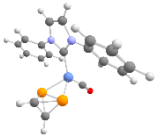


TPSS D3BJ/def2-TZVP
E = −3070.78170593 Eh
G = −3070.55946661 Eh
im. freq. = −175.49 cm^{-1}

0 1

Ni	-0.07540042200494	0.45996166442782	0.67105840267918
N	1.25211558656397	-1.77394434322613	-0.75753012383057
N	-0.87085374907284	-2.07763972008717	-0.55151689365755
C	0.11915919748911	-1.17151724718429	-0.26312083398046
C	2.56656330687512	-1.22266106743955	-0.66260752013643
C	3.36999177153444	-1.16801688174509	-1.80098756958250
C	3.02133222208673	-0.73686184962652	0.56381812228098
C	-2.25687861559739	-1.92048566151609	-0.21563213450281
C	0.96655635904866	-3.00716884609162	-1.34192894847135
H	1.73826462495343	-3.62636692372211	-1.76868565938475
C	-0.36601690188672	-3.20130905022102	-1.20325520950698
H	-1.00675454438032	-4.01085500661135	-1.51194400543092
C	4.29031663562728	-0.16642123338075	0.63771545415168
H	4.64588575302962	0.22352108102880	1.58657351769629
C	4.64663172192066	-0.61397755870504	-1.71027351783349
H	5.27294361525629	-0.56199181739321	-2.59561141772655
P	1.17554526855533	1.71542143644117	-0.70519135553446
C	-2.87144145340889	-2.88268136912423	0.58308069992806
C	-2.96404337672097	-0.82304938236485	-0.70248069324737
C	5.10361173531145	-0.10442243327967	-0.49546257147028
O	-0.71386442529363	-0.70744668854552	3.29423828729334
C	-0.43713863470806	-0.23791624069787	2.27224673838559
C	-4.94193695927477	-1.64826868296422	0.42192303197411
C	-4.31236744650457	-0.69154145655668	-0.37642620314548
H	-4.86984851072860	0.16383907683413	-0.74555760414759
C	-4.22356060558670	-2.74461329913751	0.89854931324477
H	-4.70802890002821	-3.48667326723890	1.52576251958672
H	-5.99236197324789	-1.53744107370763	0.67446385502627
H	6.09161976357717	0.34145955087911	-0.43131388392058
C	-0.15344706281711	2.94559586795808	-0.56928321261173
P	-1.48204750583027	2.28004358140776	0.47354462575787
C	0.43198825587489	2.40847130610774	0.80778002824180
H	-2.45332873210231	-0.08415390187746	-1.30744286636555
H	-2.29076966884952	-3.71625352805453	0.96683580281311
H	2.37233950130873	-0.78978782904035	1.43082876622290
H	2.98735019545295	-1.53104569797142	-2.75013242788322
H	0.89184401386087	3.01836774314996	1.57502352176903
H	-0.00038911028302	3.99138215927629	-0.83958999468108

D (R = H, R' = Ph)



TPSS D3BJ/def2-TZVP
E = −3070.81642027 Eh
G = −3070.59603733 Eh

0 1

Ni	0.00026228678305	0.95639288837009	0.54746859887847
N	1.07729433353722	-1.82167434070937	0.09902169788694
N	-1.07661067659081	-1.82169472217143	0.09875371967375
C	0.00030794896499	-0.98183824494013	0.29299859799945
C	2.43498499751022	-1.39431181706769	0.15317033239899
C	3.36711649252152	-1.93138362106360	-0.73673243518725
C	2.81763438284573	-0.42753927323881	1.08435732656755
C	-2.43433065340820	-1.39434274410152	0.15243941856869
C	0.67648422001384	-3.12080715101777	-0.21497822791629
H	1.38322503910233	-3.92139533341150	-0.35832417549542
C	-0.67569572975513	-3.12081900343463	-0.21514614447618
H	-1.38238850629181	-3.92141460991405	-0.35868549470964
C	4.13929292017651	0.00938130838058	1.11358907860218
H	4.43315832230356	0.76628881066730	1.83456354972641
C	4.69028819587737	-1.49555914883748	-0.69049603174283
H	5.41291389576600	-1.90724541146091	-1.38881663691819
P	1.15892109790114	1.94013804604609	-1.12232705373870
C	-2.81731466911590	-0.42755488395594	1.08347104415923
C	-3.36614682911849	-1.93144429694225	-0.73777426701305
C	5.07963304656888	-0.52221293913138	0.22985474304447
O	0.00100413018276	2.72963253166257	2.88912247954322
C	0.00092152265908	1.96404496404840	2.01689095686045
C	-5.07902355470880	-0.52229568023659	0.22820482423328
C	-4.68934647062017	-1.49565454942207	-0.69198948799083
H	-5.41172784821652	-1.90737614393782	-1.39054122740988
C	-4.13899074975954	0.00934454298252	1.11224016621283
H	-4.43311711538676	0.76625951194167	1.83310149540531
H	-3.05257388646476	-2.65994212575398	-1.47919704975544
H	-6.10849651010202	-0.17810824033893	0.25385046944817
H	-2.07475903498514	-0.02754029288693	1.76801817333019
H	3.05381052247637	-2.65987290030629	-1.47827617524855
H	2.07483916943024	-0.02755858641646	1.76867335061160
H	6.10908924624741	-0.17800187354064	0.25585513880478
C	-0.00192506021465	1.90940349959024	-2.54950384962152
P	-1.16090628770618	1.93965482605527	-1.12080372760922
C	-0.00170693405896	3.18985548850854	-1.80605009444360
H	-0.00254965878315	1.63179910762567	-3.59351291381392
H	-0.00208959558124	4.23588140835926	-2.07538716886544

B (R = Me, R' = Ph)

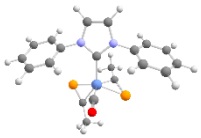
TPSS D3BJ/def2-TZVP
E = −2730.05411496 Eh
G = −2729.82202017 Eh

0 1

Ni	-0.02497979204032	1.11458957133754	0.13054405886947
P	1.06893472458916	1.71040262268076	-1.73795457069705
N	1.04531462366610	-1.68952058018599	0.04698492915557
N	-1.10110342891247	-1.66331148566074	-0.11903525933591
C	-0.02170636289708	-0.82213695753635	0.01930491605359
C	2.40433137149741	-1.27513975963364	0.16868387881308
C	3.39587761754543	-1.93812524388958	-0.55580872714872
C	2.72626542108379	-0.19895294183833	0.99692327363753
C	-2.45331596456858	-1.21428231767011	-0.19144261565124
C	0.63700420384198	-3.01768810801566	-0.07365221545564
H	1.33548638157132	-3.83768909409911	-0.05058935170069
C	-0.71240837743218	-3.00190043671069	-0.17376699025035
H	-1.42268824974320	-3.80175249328914	-0.30282203879230
C	4.05134391571076	0.21945489836053	1.08810695744459
H	4.30060479151486	1.06201324405826	1.72592301158775
C	4.72076820290661	-1.51932065146222	-0.44669114207213
H	5.49134101696831	-2.02891221956730	-1.01737001267246
O	0.28688545369330	4.19775346828724	-0.25205086704489
C	0.47742340031663	2.78344961247828	-0.65822460131224
C	-3.45665691519598	-1.93568290941381	0.45744656516624
C	-2.75602613045119	-0.05072189779739	-0.90113067153482
C	5.05135746240760	-0.43851176145817	0.37113721212234
O	-1.53210353496156	1.94170140049570	2.48454126503670
C	-0.91952867327333	1.59680417188740	1.56393631145217
C	-5.08580871997079	-0.31645873801553	-0.30025737752471
C	-4.07430416027975	0.39748132095746	-0.94405442221951

H	-4.30947669825860	1.30521397147425	-1.49156011400495
C	-4.77445793673802	-1.48526009254643	0.39501299195602
H	-5.55437121954903	-2.04124219004342	0.90666305363578
H	-1.95966389900842	0.48697552212425	-1.40797377808550
H	-6.11190525356303	0.03673262581694	-0.33838156417811
H	-3.20447674380468	-2.82307160393972	1.03017693135981
H	3.12903060336469	-2.75111014627972	-1.22417102515899
H	1.93773849090641	0.30139410448887	1.55201138616120
H	6.08316085092815	-0.10870956095196	0.44629294134032
H	-0.78127641858714	4.42145138976952	-0.14084238973603
H	0.71771668773996	4.89959856518945	-0.97530292272151
H	0.74677625898289	4.37872570059858	0.72728467350558

Int1 (R = Me, R' = Ph)

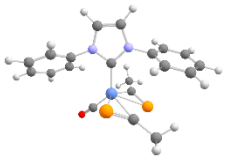


TPSS D3BJ/def2-TZVP
E = −3149.47130050 Eh
G = −3149.20084591 Eh

0 1

C	0.99163002264120	2.52454705040801	6.05573050587614
C	0.53663253791797	1.82885177236336	8.96343295770374
Ni	-0.63796125115143	2.18236083391205	7.28833771610297
N	-2.50484264378258	4.39020135223465	8.22841099344585
N	-2.60438842219276	2.68248643402807	9.52331682006657
C	-2.01400806197279	3.10972386201128	8.35645964719911
C	-2.24384767432714	5.26746268363702	7.13125085366621
C	-1.83867102592790	6.57738156180597	7.38182940627337
C	-2.40291683093633	4.80424102330340	5.82567054643353
C	-2.49532458858159	1.36152356876700	10.06292968215429
C	-3.32934258084979	4.74742698034065	9.29435134325594
H	-3.81730645959742	5.70719342173112	9.34022630872071
C	-3.39152580842155	3.67095500382016	10.11147582505367
H	-3.94357324067675	3.49332573834774	11.02002317278951
C	-2.13331827129504	5.66117434897931	4.76192749732779
H	-2.24205653636776	5.29895617205682	3.74434416009508
C	-1.58186377237877	7.43135368861114	6.30998744531723
H	-1.25340871045404	8.44840661390008	6.50156541870345
C	1.66396703826644	1.46344930832522	5.29015409741792
C	-2.85018203495588	0.27029371597118	9.27270474572769
C	-2.05318520276831	1.18888271366227	11.37229889035495
C	-1.72272514182675	6.97385087128521	5.00019546990663
O	-2.20873096113371	0.72021937482232	5.27608336096990
C	-1.58216349844541	1.30747161140560	6.05456947380894
C	-2.28165716930875	-1.20143822261155	11.10577060547072
C	-1.95044819334078	-0.09995152774909	11.89391551766934
H	-1.59447279534745	-0.24195584533344	12.90983091953635
C	-2.73264214309331	-1.01405456417932	9.79772790138949
H	-2.99190325915845	-1.86965869093240	9.18188279366949
H	-1.76769567395367	2.05406372801610	11.96304738781451
H	-2.18753890207340	-2.20524069474430	11.50893510510680
H	-3.19257092483698	0.43533416918738	8.25779563576726
H	-1.69424546898985	6.91206988563577	8.40469262753381
H	-2.71446593526125	3.78036239157281	5.65782391993071
H	-1.50857520641510	7.63652433129601	4.16716567963910
H	1.98197612068152	0.65623058040592	5.96380613706338
H	2.54294462304855	1.84431726038231	4.75637148804127
H	0.97434819565511	1.01645425978182	4.56224588982431
C	0.98749039605748	2.88113895156593	9.88636302927326
H	0.12879386550703	3.39234773770544	10.34113562260766
H	1.55431658451473	3.64403920663842	9.33611039763485
H	1.61991024911652	2.47682223621160	10.68582870137077
P	0.38520712370356	0.34396975241455	8.39455179748411
P	0.72129363271263	4.01552335900635	6.56564853480148

TS1 (R = Me, R' = Ph)

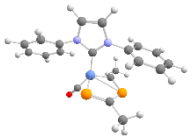


TPSS D3BJ/def2-TZVP
E = −3149.44565854 Eh
G = −3149.17544981 Eh
im. freq. = −184.05 cm^{-1}

0 1

P	2.43113671853745	0.70255222944220	-1.61156610447879
C	1.29361397250832	-0.43810365684184	-1.87527123995842
C	2.68957065953985	0.97064891201453	0.75052635233178
Ni	1.12983762709490	-0.71841139672139	0.03192546259456
N	-1.32345779962709	1.04666757261692	-0.16983445843159
N	-1.68594743801643	-0.75572234031663	0.93440119581014
C	-0.68556241987760	-0.09272503517927	0.25833274731808
C	-0.68528039187741	2.11667260964846	-0.88252152398413
C	0.19975361884133	2.95328307069306	-0.20752244335549
C	-0.97123387020547	2.30727695198830	-2.23203815166300
C	-1.52488741926047	-2.01925954661411	1.58794944888293
C	-2.65946013654279	1.08761813889155	0.22618954712414
H	-3.30116557545316	1.91731875798736	-0.02231554089987
C	-2.88578568833918	-0.04828288188203	0.92811135490436
H	-3.77525220438588	-0.43213900913218	1.40053309864319
C	-0.34642535197032	3.34452669514808	-2.92248760233753
H	-0.55382557126028	3.49047774985041	-3.97828649410564
C	0.82221498202095	3.98622028315725	-0.90651890756540
H	1.51836530114997	4.64013207638565	-0.39018327553084
C	0.55184366218962	-1.12970314535408	-2.95838686934998
C	-1.18275640556428	-3.14344530267628	0.83966785657755
C	-1.72792074839839	-2.10571683224749	2.96401358551261
C	0.55361069720649	4.18040332132763	-2.26203737871474
O	2.16356377718565	-3.45319808692318	0.27360792963806
C	1.81092885718635	-2.35163281031454	0.18994003761206
C	-1.23098751028387	-4.46903899699631	2.86072311853202
C	-1.58298318391465	-3.33897018017650	3.59898304394254
H	-1.73081750977135	-3.41146257082990	4.67232046496288
C	-1.03066764878309	-4.36953044106658	1.48309165309329
H	-0.74843615701677	-5.24534690679758	0.90736924581905
H	-1.97404569420195	-1.21129747419773	3.52830151555932
H	-1.10790143666345	-5.42594819952067	3.35911134327998
H	-1.02913032227967	-3.04392382975031	-0.22883670963238
H	0.41373478037032	2.77136516546879	0.83926470723601
H	-1.65767958163925	1.63370085245906	-2.73565627980631
H	1.04695116391739	4.98197455802663	-2.80356514349826
H	0.75495791546742	-2.20746595891757	-2.92062022193033
H	0.80937713884350	-0.75946964567244	-3.95763577156602
H	-0.52932826890264	-1.01353528460608	-2.80683189448926
C	3.74930589525166	2.01406506652909	0.60517566026065
H	3.40989718190250	2.83857989453545	-0.03433706145624
H	4.64402476431932	1.59433394023687	0.12820067614649
H	4.02854628498267	2.41269794264827	1.58661243432046
P	1.90970333591980	0.19381374387906	1.95210059275204

Int2 (R = Me, R' = Ph)



TPSS D3BJ/def2-TZVP
E = −3149.45731581 Eh
G = −3149.18536927 Eh

0 1

P	1.07760011450207	3.46768968273004	6.50035023463902
C	-0.13640595502670	2.31885034334331	6.21708938810796
C	1.33767826926979	3.66593469592400	8.34067953877103
Ni	-0.53220739812872	1.82182701316422	8.00230403086305
N	-2.59588346750476	4.01016572280262	8.21633156073689
N	-3.09381910880135	2.21856892981677	9.30131031072601
C	-2.12767836010283	2.74781994188397	8.46877924714355
C	-1.95036973860290	4.97477531268234	7.36941241575495
C	-1.09189307267895	5.91526157643530	7.93093213771719
C	-2.21178458391454	4.95773372945587	6.00207534354667
C	-3.02697304727110	0.91256334638260	9.86656012414183
C	-3.79731860913191	4.26197483189297	8.87592192743615
H	-4.30961146307521	5.20478767077298	8.77523533830917
C	-4.11106263424882	3.13509216161000	9.55770057207967
H	-4.96833072668592	2.88251727739833	10.15971574392463
C	-1.59314023082248	5.89510490796132	5.17834312750874
H	-1.78048653646486	5.88023466437274	4.10909702720711
C	-0.47591907356910	6.84976475769933	7.09906940985135
H	0.20328847661796	7.58232713526203	7.52419853468703
C	-0.57911365531299	1.88568891888009	4.85799205138983
C	-2.64172183980550	-0.16209951824643	9.06411914281507
C	-3.32980031764607	0.72645478498636	11.21535444401983
C	-0.72217400223994	6.83698121997183	5.72589574747836
O	0.93349265858437	-0.67910998965344	8.26805018055457
C	0.40621825794330	0.34558256009671	8.16530170359197
C	-2.84464182297099	-1.63108952369564	10.97486603134812
C	-3.24354647110991	-0.55195156974800	11.76476499970055
H	-3.46884712571808	-0.69893633463302	12.81673918354058
C	-2.54310572208670	-1.43316334574256	9.62717464446173
H	-2.23169606186542	-2.26880296740928	9.00808289839431
H	-3.59682613223135	1.57852936940258	11.83297368979673
H	-2.76629974750525	-2.62295021144725	11.40960975510725
H	-2.43601102280463	0.00801059943012	8.01143523680600
H	-0.89010485702079	5.88772039018098	8.99616131396995
H	-2.87921917029051	4.20512793162607	5.59537745208089
H	-0.23034312258940	7.55926382442538	5.08139031724970
H	-0.37021984487243	0.81580606716427	4.72545762038701
H	-0.09786763903975	2.43535355268509	4.03861733396105
H	-1.66765172242874	1.99564848566545	4.76076115821951
C	2.39549316422576	4.73642017559263	8.57239740438238
H	2.09756396795740	5.67890362077760	8.09444952606528
H	3.34882011691036	4.43361298796060	8.12095092962714
H	2.55637870064427	4.91539375612043	9.64013016157393
P	0.60649455691331	2.86924851401866	9.64477106022620

TS2 (R = Me, R' = Ph)

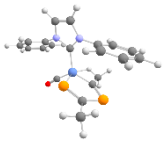
TPSS D3BJ/def2-TZVP
E = −3149.44694600 Eh
G = −3149.17517501 Eh
im. freq. = −196.93 cm^{-1}

0 1

C	0.72569521442240	-1.47107106172247	3.60078383503379
C	3.35981503364876	-2.33555682414426	3.98638514976151
Ni	1.81226320731550	-0.00385718889795	3.06403073951303
C	2.24705603844115	1.24967336788280	4.24767160405739
N	2.08287736453293	-0.86005364164614	0.21789407057911
N	2.54560685516325	1.22748310943928	0.44009831520858
C	2.21196056846758	0.11240742426606	1.17439079034286
C	2.31101277398009	-0.36775072898492	-1.06070620239598
H	2.25056496386144	-0.99913630790592	-1.93212974972665
C	2.59442025863877	0.95229003720032	-0.92237619308965
H	2.84202934305658	1.71016663031678	-1.64766658663191
O	2.41840351495526	2.07727838235157	5.04068600926725
P	3.84450105979192	-0.83686188706325	3.37293541968277
P	1.62982248956296	-2.81842813166784	4.16512369254519
C	4.39704776121225	-3.36272676170346	4.40398309275563
C	-0.77553538064621	-1.59767686307142	3.68451174950550
C	2.83197198094007	2.51843004267386	0.99469644066511
C	3.87371001584734	2.65181992424325	1.91109415111766
C	2.07566457971431	3.61832250119819	0.59531912514237
C	4.15013263126304	3.90892217162721	2.44359177180373
H	4.44655413002778	1.77771347061757	2.20157173465905
C	2.36743067788948	4.87493044530407	1.12682474965123
H	1.25858282576514	3.48548087792222	-0.10765011463159
C	3.39968664060657	5.01963754247827	2.05342244230067
H	4.95207940910719	4.01809577352419	3.16685565426363
H	1.77855892167460	5.73578523759434	0.82501117382839
H	3.61811669028092	5.99668652443778	2.47376692867118
C	1.73664751564891	-2.23017116553938	0.49336378993535
C	2.74927403037466	-3.15601961355479	0.72296955319590
C	0.39547273492841	-2.60291230822060	0.50639192858861

C	2.40500979499393	-4.48100064241340	0.98592916833109
H	3.78376596894402	-2.83090613376285	0.72617909032798
C	0.06115717545943	-3.93057711416892	0.76192080766699
H	-0.37018137040983	-1.85349303456798	0.33500629899323
C	1.06490489603311	-4.86721000915361	1.00708504200629
H	3.18521693571667	-5.20897005911960	1.18554582229473
H	-0.98268114016970	-4.22735884983559	0.78931746377011
H	0.80251801800001	-5.89769865438559	1.22605231571334
H	-1.24422346189581	-1.34490142474441	2.72387947997585
H	-1.16278860562439	-0.86760649598906	4.40853517744145
H	-1.12773964150924	-2.59508449682187	3.98815728533903
H	5.41985043613639	-3.00561491603963	4.24051141909425
H	4.25833057972630	-4.29157532824862	3.83625443584385
H	4.28352656412603	-3.60941381970422	5.46617112760206

Int3 (R = Me, R' = Ph)

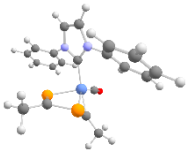


TPSS D3BJ/def2-TZVP
E = −3149.46401579 Eh
G = −3149.19196505 Eh

0 1

C	-0.03770074921312	0.82605152613694	7.54597660613099
C	-1.13750747152661	1.07636080567524	5.28516262841111
Ni	-0.04557316218485	2.64261158250919	7.89726123312813
C	1.30860180896432	3.79671403869591	7.59243873591515
N	-1.81414401200586	4.75050371820091	9.14618546735021
N	-2.85161546610069	2.89150028523996	8.87918832159798
C	-1.59423534521294	3.43344647581858	8.81782549448455
C	-0.78719598015914	5.74068497791858	9.24835855634755
C	0.29252588627809	5.51799930739907	10.10210977496525
C	-0.88102696188462	6.91221461501293	8.49963744882470
C	-3.14873390619081	1.51242080288101	8.61078994229634
C	-3.16262496026040	5.01570149294126	9.36242769972541
H	-3.51423567451934	5.99426989727883	9.64615261360659
C	-3.81691358278171	3.83857582872668	9.19675358236602
H	-4.85835698462826	3.57945204251589	9.29700972723171
C	0.12391746316368	7.87304715217850	8.60858976602947
H	0.06198899949542	8.78256018559448	8.01887483904855
C	1.29491273857880	6.47965863034290	10.19816610889372
H	2.14229032847562	6.30825376921810	10.85487608730645
C	0.63695778411841	0.59429882193874	8.86148406722503
C	-3.85707191802224	1.17624020329701	7.46016630570709
C	-2.74396112269830	0.53893235151297	9.52123381141726
C	1.21235359577963	7.65726538479986	9.45338833134672
O	2.18519049732008	4.47139103638249	7.26326598691116
C	-3.74977698292398	-1.14835434167357	8.11827576226341
C	-3.04847523606995	-0.79693198220658	9.27174142897581
H	-2.73008463961369	-1.56287621368507	9.97227765608668
C	-4.15448635182359	-0.16353612217812	7.21730860413248
H	-4.68783553957506	-0.43893641523888	6.31274902011171
H	-2.19713192927902	0.83671599789984	10.41016556107415
H	-3.97234527985468	-2.19148152337183	7.91618308229964
H	-4.13410848757832	1.95159975863604	6.75432292241854
H	0.33842461727422	4.59591072416960	10.67108233414796
H	-1.71664000684803	7.05168063425417	7.82063805672481
H	1.99813482369460	8.40284017142686	9.52715838160341
H	0.75449896061341	1.56275422330784	9.42825116825569
H	1.65142626361002	0.19539939843719	8.74764049733208
H	0.05218483437567	-0.05486177966981	9.52511878248611
C	-1.79956318668648	0.83536618838839	3.95239048815913
H	-1.12746853795625	0.30613775027345	3.26459623200092
H	-2.09895398402420	1.77787609241351	3.47887323061517
H	-2.69553216681259	0.20960299454845	4.06676642989108
P	-0.95167355237573	2.65881985583252	5.90023571800517
P	-0.52345442273150	-0.25206534418006	6.32560650684882

TS3 (R = Me, R' = Ph)

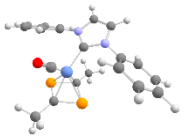


TPSS D3BJ/def2-TZVP
E = −3149.44896734 Eh
G = −3149.17671048 Eh
im. freq. = −85.85 cm^{-1}

0 1

C	0.98672267213895	-2.27922172715090	-0.65525487887015
C	0.08054110736748	-1.83558797414740	1.85412036396303
Ni	0.03057599167892	-0.76046197840060	-0.75659191668701
N	-1.32943853655879	1.77751543731020	0.24662399777174
N	0.81626325580690	1.90625625109217	0.29192949689076
C	-0.20325494656067	1.07391850593597	-0.10462187863547
C	-2.67106990924144	1.32056647954498	0.05990390437009
C	-3.06414825837943	0.81261227922039	-1.17642096527407
C	-3.57031147121891	1.39324689081840	1.12380739616709
C	2.20564087386656	1.60697022514865	0.14238701015104
C	-1.01478439487041	2.98550104770494	0.86646812524614
H	-1.77707667185525	3.67912681923878	1.18108713419258
C	0.33619231822554	3.06556558645618	0.89727159193101
H	0.99652400569887	3.84229632252254	1.24633756499233
C	-4.87668740275845	0.94384575039955	0.94622175834653
H	-5.57553277949974	0.98652091713288	1.77607661150603
C	-4.36756237875971	0.34825383742961	-1.33859933668528
H	-4.67296405191002	-0.05936179736369	-2.29743705597944
C	1.49450005519974	-3.28471512685016	-1.61699796977248
C	3.06569793003221	1.78137814270584	1.22516469266106
C	2.67809834699979	1.13429656758586	-1.08116341324095
C	-5.27533078992394	0.41325675776262	-0.28117236923379
O	-0.66895426605867	-0.82119686785031	-3.62345730946960
C	-0.33311538605055	-0.75561559303172	-2.51629429104303
C	4.89878704590991	0.98534336512523	-0.13361527562542
C	4.02716932384907	0.81640125920900	-1.21114420842327
H	4.39803733408958	0.43856706334205	-2.15914988658516
C	4.41791171087299	1.47463875522279	1.08001154601479
H	5.08912341527988	1.59775938191672	1.92446099740402
H	1.98648827111346	1.00580551103053	-1.90619045924149
H	5.94966349326702	0.73350406571874	-0.23960064468902
H	2.67248881726880	2.12051549712475	2.17872705748347
H	-2.35393842806465	0.78377543824293	-1.99284964159039
H	-3.23545210855295	1.76122601766839	2.08865835209210
H	-6.28991166213601	0.04926721305180	-0.41204215015775
H	1.18857132020698	-3.08200991108692	-2.64797425524237
H	1.12387067250876	-4.28342560847861	-1.34212865085439
H	2.59351052034654	-3.33775453032492	-1.56780903718315
C	0.10216601687237	-2.12496629480898	3.32949325333715
H	0.61664354084950	-1.32670141128391	3.88255503284921
H	0.64321197167779	-3.05686629551372	3.54567875581441
H	-0.91700312802475	-2.21246905530666	3.72398420420244
P	-1.31133830339090	-1.58894267641188	0.90841517783582
P	1.63036386268767	-1.74854953765210	0.88715556926082

C (R = Me, R' = Ph)

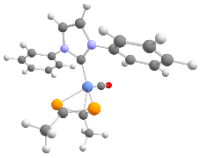


TPSS D3BJ/def2-TZVP
E = −3149.52253693 Eh
G = −3149.24640076 Eh

0 1

C	0.00035630057191	2.79533090393195	-0.58058722561002
C	0.00196505106382	0.85597334988777	-1.79784640072713
Ni	-0.00029779944040	0.92237417385364	0.25715257856241
N	-1.07619815818400	-1.83883823141960	0.34882751271608
N	1.07563439741250	-1.83884347930010	0.34872966110883
C	-0.00028049766418	-0.98809909246526	0.37721510672828
C	-2.44624366950376	-1.42436865368697	0.30746450236297
C	-2.92201367517366	-0.50057215945405	1.23581066633428
C	-3.28403725910417	-1.95421373206085	-0.67256753349710
C	2.44567644646451	-1.42440500404998	0.30687529636169
C	-0.67737271858274	-3.17204153128374	0.28090015421382
H	-1.39089803106399	-3.97952104982580	0.28273286276498
C	0.67678124171004	-3.17204240989699	0.28077552675619
H	1.39030103236022	-3.97952689882672	0.28246312329413
C	-4.61820516839994	-1.55133827151637	-0.72310895675659
H	-5.27126975626500	-1.95402751247036	-1.49133608831880
C	-4.25475036950593	-0.10210287651146	1.17459614140014
H	-4.62789321215487	0.62212663362994	1.89200025953591
C	-0.00065085229267	4.08810789163011	0.17704472521229
C	3.28297267260174	-1.95401017739708	-0.67371005233758
C	2.92193176914112	-0.50085890611185	1.23522267249392
C	-5.10350577618109	-0.62305770534995	0.19725304628882
O	-0.00348266476593	1.77014756087413	3.04814374181580
C	-0.00221460759439	1.43778717568352	1.93681202844078
C	5.10289255600015	-0.62308389650588	0.19551522228926
C	4.25463954702297	-0.10237829446446	1.17342699364409
H	4.62816157204727	0.62164025357084	1.89084813902567
C	4.61711521836011	-1.55112907054697	-0.72483166162008
H	5.26977930865207	-1.95361331517683	-1.49350642838095
H	2.25313986179312	-0.10251440905516	1.98752189336154
H	6.13956150436554	-0.30354293153645	0.14875833155602
H	2.88689510512001	-2.65382558466436	-1.40370182900822
H	-2.25280454164002	-0.10197936706580	1.98762160925543
H	-2.88834769612812	-2.65425958026805	-1.40254760770120
H	-6.14019493206172	-0.30351911677050	0.15094170355924
H	-0.89108378764820	4.19016266197453	0.80735020112431
H	0.00002217986699	4.92447664737745	-0.53424795827598
H	0.88836297684777	4.19039866153257	0.80931212920958
C	0.00308790169346	-0.38772743474475	-2.63317911552453
H	0.89453359166790	-0.99893422334010	-2.45326127521945
H	0.00427789763714	-0.10876220957002	-3.69477851347901
H	-0.88859989819516	-0.99916575775228	-2.45534372813727
P	-1.40396248910084	1.88706313353190	-1.29247640027231
P	1.40649242825041	1.88744383561039	-1.28939505455026

TS4 (R = Me, R' = Ph)



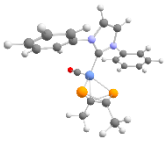
TPSS D3BJ/def2-TZVP
E = −3149.47153533 Eh
G = −3149.19931130 Eh
im. freq. = −125.20 cm^{-1}

0 1

Ni	-0.00123519093267	0.57029364161360	0.89475450203034
N	1.07337717383092	-1.86796317051976	-0.43439970495602
N	-1.07886134185160	-1.86857461945652	-0.43229697941358
C	-0.00238875009076	-1.13012848751065	0.00982881226482
C	2.44343550179477	-1.51055780827208	-0.24617656032871
C	3.31850800644208	-1.57166561783718	-1.32992491659290
C	2.88972245447814	-1.10471210547946	1.01131851088892
C	-2.44877307026859	-1.51150059942972	-0.24286708967054
C	0.67342998759483	-2.99919032773285	-1.14393549438253
H	1.38470595889777	-3.70799561991389	-1.53480493861757
C	-0.67949615495832	-2.99957369878000	-1.14255151569923
H	-1.39100214006910	-3.70879114391873	-1.53222405361526
C	4.22472357346471	-0.74501864726771	1.17565299027251
H	4.57305515215374	-0.42140121046996	2.15182779309568
C	4.65647345498934	-1.21903551586446	-1.15249889191531
H	5.33737487206225	-1.25683580988378	-1.99756199131167
P	1.46837120182191	1.85140791574708	-0.43618488104011
C	-2.89153355791974	-1.09469006513145	1.01230245063159
C	-3.32772346375211	-1.58418436845692	-1.32285672454045
C	5.11024786670516	-0.80015662549688	0.09730185652803
O	-0.00335263972659	0.27031644511129	3.80154388449443
C	-0.00055269265996	0.39730188621909	2.64428284501325
C	-5.11586518085495	-0.80252033702038	0.10340552831150
C	-4.66571129082432	-1.23237253187964	-1.14394987905787
H	-5.34957622242522	-1.27953567548738	-1.98616685240706
C	-4.22652298109197	-0.73567278765062	1.17794122886468
H	-4.57183652858357	-0.40364259950752	2.15233796355800
H	-2.95996656115973	-1.88489394722741	-2.29940459241806

H	-6.15505137397471	-0.51781390579021	0.23809304347067
H	-2.18751423399734	-1.04209552697329	1.83375725116337
H	2.94736998609322	-1.86393562759720	-2.30777284942671
H	2.18844552584169	-1.06061698422090	1.83563412458303
H	6.14937428605318	-0.51473331771666	0.23098118192102
C	0.02099689398348	3.02693583067747	-2.68218522654855
C	0.01573160506368	2.18733691159487	-1.43229846174293
H	0.97577627151384	2.95511589445259	-3.21151621847178
H	-0.14163285557837	4.07998154338621	-2.41936243327273
H	-0.79974567993255	2.73232697701897	-3.34553164403509
P	-1.45435280842000	1.85424805617391	-0.45175240826724
C	-0.00129195912395	2.44068078942940	0.56947460521315
C	0.00053397633877	3.72245985030967	1.35835288507067
H	0.88367937904841	3.76845368982525	2.00278411886117
H	-0.89834273769488	3.78417992157700	1.97933772237132
H	0.01697528771915	4.59403134735679	0.69383400912377

Int4 (R = Me, R' = Ph)

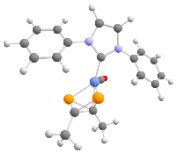


TPSS D3BJ/def2-TZVP
E = −3149.47577383 Eh
G = −3149.20238964 Eh

0 1

Ni	0.00004823666158	0.67164765245413	0.70966037343198
N	1.07673756431715	-1.91392009274989	-0.24066244133169
N	-1.07805157349606	-1.91342764947532	-0.24047848530551
C	-0.00044414803099	-1.11623916633756	0.08209332327627
C	2.44728338665132	-1.53194420617947	-0.11637389511815
C	3.30838759831723	-1.72796075784828	-1.19552008817821
C	2.90902454761476	-0.97091132327428	1.07446315037331
C	-2.44839798586938	-1.53082912394482	-0.11594355063966
C	0.67529614608906	-3.14074701012370	-0.76726502449618
H	1.38678081377593	-3.90128706775117	-1.04373760775071
C	-0.67725954130252	-3.14042272667361	-0.76718722123724
H	-1.38913267709933	-3.90063328164666	-1.04356492060802
C	4.24516875479992	-0.59221474561964	1.17443196348274
H	4.60566300916674	-0.14845111474698	2.09745691451621
C	4.64800899743559	-1.35525935858618	-1.08124360254363
H	5.31786188981156	-1.49813162599691	-1.92384264382054
P	1.48926910294761	1.71247955743869	-0.70715158663606
C	-2.90959909352631	-0.96931133341924	1.07487629897223
C	-3.30986129070421	-1.72672604004996	-1.19482613870155
C	5.11681388974840	-0.78276779253849	0.10001415864330
O	0.00147542475841	0.60342058034655	3.64839620260842
C	0.00058421403525	0.64928974788744	2.48538060613505
C	-5.11755239258886	-0.78043835291493	0.10093780754826
C	-4.64929113509823	-1.35341315481935	-1.08030132832743
H	-5.31941596150666	-1.49619387101756	-1.92269946401415
C	-4.24555335461895	-0.59000995381819	1.17508992003069
H	-4.60562536321910	-0.14587394620972	2.09810080263070
H	-2.92682151445049	-2.13987663840027	-2.12315075611654
H	-6.15745801578116	-0.47924141671798	0.18426867647946
H	-2.21890793247011	-0.82247532330930	1.89607182401316
H	2.92492562855885	-2.14072386365429	-2.12384291640339
H	2.21862563819452	-0.82400179152188	1.89588911432325
H	6.15687074095373	-0.48204128525872	0.18315561685361
C	0.00080384437914	3.22383185378836	-2.72096786117693
C	0.00053793571710	2.20277207904408	-1.60520086172078
H	0.00077580227353	2.68683189261070	-3.67668049657148
H	0.89489146665788	3.85438640411876	-2.69120329534323
H	-0.89305583869291	3.85471338657871	-2.69133324435547
P	-1.48854219504269	1.71309364844375	-0.70736583618156
C	0.00045992801660	2.53686994901885	0.05979739437183
C	0.00070626346629	3.88873281436333	0.73810379486884
H	0.88860527397995	4.00067289487354	1.36590113588795
H	-0.88717643370132	4.00100439573463	1.36586617559270
H	0.00087034887118	4.69560495790283	-0.00380516746188

TS5 (R = Me, R' = Ph)

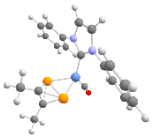


TPSS D3BJ/def2-TZVP
E = −3149.46837859 Eh
G = −3149.19373718 Eh
im. freq. = −115.75 cm^{-1}

0 1

Ni	0.04537336990149	0.62142195894466	0.48295690353368
N	1.38321843408941	-1.78038546041558	-0.53898124812051
N	-0.75726035921503	-2.05710022098570	-0.47071132002045
C	0.21751753089712	-1.11203854833605	-0.25232337423444
C	2.69063926638666	-1.21217109102738	-0.42460461680909
C	2.95862161946997	0.03078108289767	-0.99880712707814
C	3.68060566778754	-1.91282671506431	0.26258990052418
C	-2.15852939011903	-1.89510663936732	-0.22312222099698
C	1.14101138571986	-3.10448246441355	-0.89957392585661
H	1.93623944559070	-3.77038827385231	-1.19138799788038
C	-0.20059276326028	-3.27661585979637	-0.85751334612908
H	-0.81637164541910	-4.12606244511444	-1.10244350839661
C	4.95710553049381	-1.35983567045466	0.37647689688945
H	5.72771363165543	-1.89890347668298	0.91907043016689
C	4.23296229353224	0.57758171850427	-0.87175558609678
H	4.44454446920210	1.54523566463882	-1.31655058834224
P	-0.25080214752748	1.65984187102516	-1.46081874363178
C	-2.82926235589719	-2.89049079814626	0.48936148252106
C	-2.83425674008748	-0.76355379360326	-0.67842262596988
C	5.23326031313468	-0.11414841974555	-0.18438900900292
O	1.68106652702114	0.16005729670220	2.88141598997336
C	1.03214816911939	0.34976455599661	1.94185029694672
C	-4.88244358256874	-1.63428883503070	0.27755976327985
C	-4.20068778944138	-0.64309175117459	-0.42643528911244
H	-4.72849726669671	0.23693595653334	-0.78095109154291
C	-4.19466416654124	-2.75964486980016	0.73549830878978
H	-4.71532237377041	-3.53051498039972	1.29558554310281
H	-5.94541982039469	-1.52979935388680	0.47378301775491
H	6.22471152396526	0.31786886478250	-0.08695705323856
C	-2.11999368594100	3.93683905351082	-1.12655572640342
C	-1.52287993111235	2.66310841027152	-0.59655951390976
P	-1.69474549665239	1.95041328067413	1.07373995593094
C	-0.10263639437695	2.62723329614335	0.08048053174165
C	0.77130860028920	3.79940582818167	0.44782913119479
H	-2.30232235854154	-0.00080314038520	-1.23183647730793
H	-2.27870214694800	-3.74607498406654	0.86919137177458
H	3.44483824913247	-2.86472140230494	0.72877752855011
H	2.17883526306141	0.55044282664307	-1.54482838099525
H	-1.47199331768705	4.41218081615881	-1.87400024544745
H	-3.08860265521134	3.73553531380177	-1.59597959939239
H	-2.28637714455004	4.64210539839982	-0.30230191871675
H	0.48890618060541	4.19355689761825	1.42732900552194
H	0.67554690279371	4.60516049742730	-0.29044122228650
H	1.82038315811044	3.49445760519861	0.48879069872252

D (R = Me, R' = Ph)

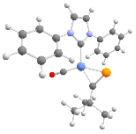


TPSS D3BJ/def2-TZVP
E = −3149.50569778 Eh
G = −3149.23335113 Eh

0 1

Ni	-0.00031043056122	0.47221910646628	0.97212457984136
N	1.07667022374674	-2.05165970785564	-0.26951570616250
N	-1.07779381037483	-2.05147992843112	-0.26946253530086
C	-0.00049049558510	-1.30762418190435	0.16698356463733
C	2.43354153733288	-1.65929328131681	-0.08761364343605
C	3.37136174700459	-1.91187064187212	-1.09055799628276
C	2.80932732439845	-1.00447717034151	1.08653795734302
C	-2.43459089894357	-1.65892296073186	-0.08743695075411
C	0.67548678552579	-3.19690849551791	-0.95831444149502
H	1.38167247920391	-3.91897322383104	-1.33368787618691
C	-0.67683787067720	-3.19679367966764	-0.95828472935304
H	-1.38316319410729	-3.91874033335038	-1.33361790946248
C	4.12902261932483	-0.59177250536204	1.24815488726406
H	4.41691478480226	-0.07636947074163	2.15949164764265
C	4.69270228957321	-1.50463441362099	-0.91302242864951
H	5.41953714851804	-1.69366992756576	-1.69747329881513
P	1.15907982504325	1.87060790055896	-0.37358342624417
C	-2.81021055199336	-1.00421900524643	1.08682923301817
C	-3.37250329960379	-1.91121395976483	-1.09036677558684
C	5.07483661318031	-0.84007501383196	0.25249760369751
O	-0.00160795214734	1.53541981051983	3.70910327169889
C	-0.00094969978542	1.03722007857887	2.66023289686083
C	-5.07573083248474	-0.83932097757491	0.25292169991958
C	-4.69376475305584	-1.50377955783194	-0.91271148834360
H	-5.42066966494482	-1.69258317634603	-1.69715268712316
C	-4.12982975491741	-0.59132214454835	1.24857100085812
H	-4.41759170254198	-0.07600101991062	2.15999571128473
H	-3.06588968928984	-2.39283344924599	-2.01385757858437
H	-6.10366984952243	-0.51461957932594	0.38282173193914
H	-2.06329350745134	-0.82114508606320	1.85420404436392
H	3.06462386828951	-2.39356728077308	-2.01396832247672
H	2.06247314768327	-0.82116253801323	1.85391838752882
H	6.10283548083284	-0.51552433774455	0.38230029199881
C	0.00076877039296	2.19229260564995	-3.26252421438986
C	0.00065420512611	2.22333539040529	-1.77125545763068
H	0.00037087699047	1.16164994695202	-3.63184575270187
H	0.88890081486187	2.69758205412917	-3.66164840157872
H	-0.88688121868744	2.69831277368048	-3.66179703749062
P	-1.15820396045377	1.87159256219115	-0.37371565958059
C	0.00105579605635	3.26679392463296	-0.72677010466821
C	0.00165552649452	4.75821768271869	-0.69070811163260
H	0.88975289242637	5.15732135089973	-1.19577231369442
H	0.00172371209998	5.12358342330239	0.34075207991528
H	-0.88604333177980	5.15803343764610	-1.19590974218741

B (R = *t*Bu, R' = Ph)



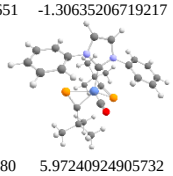
TPSS D3BJ/def2-TZVP
E = −2848.07141193 Eh
G = −2847.75975250 Eh

0 1

Ni	0.02777204254174	0.57803235288691	0.18686813214003
P	1.17496473375433	1.07210317783319	-1.67889630866288
N	0.75021880278485	-2.33272940171710	-0.02011922150305
N	-1.37489226031529	-2.03164809692031	-0.19396145006233
C	-0.20112211018468	-1.34019426737430	-0.00993750075310
C	2.14786055586897	-2.09466067751132	0.13408531045752
C	3.06351838668279	-2.84604901714917	-0.60356678100306
C	2.58470250157665	-1.09870430736191	1.00900138583285
C	-2.66102229535368	-1.41501090998371	-0.23760626235982
C	0.18125266545916	-3.59240719158695	-0.20905945889066
H	0.77223810692246	-4.49313174914094	-0.22438308147957
C	-1.15479014644099	-3.40376376552458	-0.31387261943781
H	-1.95764497624117	-4.10158918399577	-0.48532947889568
C	3.94890026527109	-0.84899348158427	1.13313876481979
H	4.28751497102462	-0.06837045773378	1.80760017758996
C	4.42755297483754	-2.59685155001494	-0.46110021907556
H	5.13985687599328	-3.17543261188086	-1.04163166701651
C	0.71691509360775	3.63441185694307	-0.18411390062237
C	0.72277240457510	2.19216199999636	-0.57610508143982
C	-3.74364732409538	-2.03572163474576	0.38745943616443
C	-2.81926182666593	-0.19067020049063	-0.88986019222491
C	4.87355701038447	-1.59640857616520	0.40285719242427
O	-1.41276959995283	1.31254856381217	2.61281877413915
C	-0.81912255839074	1.03404726363480	1.65703988291972
C	-5.16126894935266	-0.19236557412219	-0.27712584505508
C	-4.07150823181164	0.41982263727878	-0.89759884698072
H	-4.19313821995235	1.37543958080039	-1.39862750343658

C	-4.99520012155582	-1.42266033997953	0.35948161672082
H	-5.83600680678833	-1.90065366447053	0.85317844623564
H	-6.13516188521453	0.28769805349840	-0.28740319538809
H	5.93643436703911	-1.39859224673075	0.50375712118433
C	-0.74372467159726	4.13337999551533	-0.12689454747344
C	1.50529530489139	4.46430776043578	-1.21912893186665
C	1.36624603541225	3.79471943561570	1.20720974932626
H	-0.76431649441249	5.19164923331593	0.15916087041405
H	-1.31909733049414	3.56021302855021	0.60526334593401
H	-1.22485085088078	4.02650123644323	-1.10446928619912
H	1.50145517421933	5.52606639173584	-0.94432308843903
H	1.05907750936291	4.35762225310026	-2.21276970944262
H	2.54296000490376	4.12030073800818	-1.27231727075812
H	1.37211500437231	4.85239178299309	1.49615016951654
H	2.39862119670241	3.43083715854246	1.19300647086815
H	0.81083333252501	3.22848972422312	1.95972867441789
H	-1.96537978115371	0.26935397369496	-1.37917780245118
H	-3.60110259945079	-2.97313005752053	0.91662415505684
H	1.85426981324267	-0.52728668296659	1.57478164197569
H	2.71235290634921	-3.59554155218651	-1.30635206719217

Int1 (R = *t*Bu, R' = Ph)

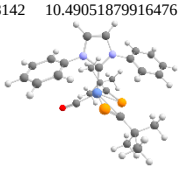


TPSS D3BJ/def2-TZVP
E = −3385.50123589 Eh
G = −3385.07018264 Eh

0 1

C	0.84401494732186	2.49847260389480	5.97240924905732
C	0.46854727405948	1.91619859301875	8.96549277324613
Ni	-0.72902782101076	2.19242453051671	7.29263596231378
N	-2.64856681743558	4.35879046691246	8.28557057565474
N	-2.79305257482366	2.59176820919157	9.49099038285072
C	-2.16440125717593	3.07344982775996	8.36408428180183
C	-2.36787168337663	5.28608422108186	7.23520235028255
C	-1.85229357791881	6.54136734202455	7.54998472226265
C	-2.62237416291023	4.92265670280012	5.91343660150557
C	-2.72421968924480	1.24978577775139	9.98154064805609
C	-3.48875524975547	4.67504629361891	9.35045604263219
H	-3.96421552722276	5.63863100835018	9.43301268897754
C	-3.58029304468648	3.56008088366062	10.11089323620335
H	-4.15593666785557	3.34254837250124	10.99574126330603
C	-2.33717073378744	5.82697433166174	4.89368761522573
H	-2.51839901796162	5.54390606076047	3.86151382985510
C	-1.57625544458284	7.44253329457904	6.52212508932378
H	-1.15946540884744	8.41659355612130	6.75963332534403
C	1.70903213304458	1.52918951876815	5.23925862867975
C	-3.06269865321495	0.19134420047685	9.14126472417723
C	-2.35506235672886	1.02491439535191	11.30600340837888
C	-1.81323362487648	7.08539611239220	5.19519821201730
O	-2.54549409456046	0.82781546116009	5.41711668562201
C	-1.78719400596605	1.34003516275075	6.12692005352620
C	-2.60937362279621	-1.35090661120657	10.94891114848067
C	-2.30028413842597	-0.28117140857041	11.78885872856088
H	-1.99813809809117	-0.46186342237749	12.81598370615505
C	-2.99342362230232	-1.11197365500290	9.62869804432212
H	-3.23977711418965	-1.94112652684275	8.97267567748672
H	-2.08932921892929	1.86469280163717	11.94051622458094
C	-2.55265786592240	-2.36886760235309	11.32238353317309
H	-3.36169097915288	0.39289340217560	8.11983783047428
H	-1.63931804985421	6.79201451087808	8.58464283281993
H	-3.01782495712809	3.93667870680722	5.69786900743337
H	-1.58505353360399	7.78412546449930	4.39608809887213
C	2.90385428749954	1.14776841487882	6.14597099728365
C	2.24672074583479	2.22504937136194	3.96731103917838
C	0.95316711634512	0.24862282132722	4.83956306621531
C	1.15156717960800	2.88686582479692	9.86872468799023
C	0.35523569428997	4.19387555186430	10.04036196024047
C	2.54120961113875	3.22206542982066	9.27431515232537
C	1.34913424403927	2.21915559139754	11.24871505922577
P	0.15580300408877	0.40172216724439	8.53622345061228
P	0.44442888798986	4.01316730400069	6.32203189483382
H	1.92825312669276	1.29699921725550	11.14413504266370
H	0.38359098535283	1.96497900895571	11.69502506452934
H	1.88284463205655	2.89928717227849	11.92408548049790
H	2.43738572363692	3.68348881166317	8.28935765476354
H	3.13978323425160	2.31278437975751	9.16922260017103
H	3.06415569050155	3.91741358815516	9.94231395176921
H	3.56763180174126	0.46352096959923	5.60358593802973
H	2.55513210002804	0.65525196113768	7.05713019916277
H	3.47011187436584	2.03955696697116	6.42917564928921
H	2.91390064300468	1.54601129822539	3.42247622504403
H	2.80356377023388	3.12836912920426	4.23444108828241
H	1.42144618778849	2.51211448914901	3.30861868486238
H	1.63210400152894	-0.43141822068895	4.31211400525196
H	0.11271007422816	0.47966684964004	4.17821545252623
H	0.56595702703072	-0.25879565052327	5.72770994813024
H	0.20457686675571	4.67586940818930	9.07021724638173
H	0.90645955598888	4.87886743020657	10.69532247891381
H	-0.62388980610775	4.00311812738142	10.49051879916476

TS1 (R = *t*Bu, R' = Ph)

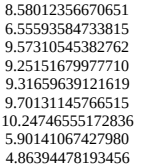


TPSS D3BJ/def2-TZVP
E = −3385.47845219 Eh
G = −3385.04759701 Eh
im. freq. = −141.52 cm^{-1}

0 1

P	2.36167377844222	0.82734688468023	-1.52163137409133
C	1.25004379670771	-0.35066519415212	-1.74494327854408
C	2.71922808556578	1.14023959390354	0.91232819097711
Ni	1.00648205157705	-0.49585638750473	0.16635417028352
N	-1.56709750661892	1.04704460577458	-0.40349075446163
N	-1.84414721531905	-0.74790476990683	0.74204593587924
C	-0.84820572613192	0.05828170416043	0.23195447591162
C	-1.00483520308158	2.15873216992557	-1.09883478098289
C	-0.00942074337281	2.92495227930391	-0.49711310101795
C	-1.47977256913700	2.47196168780857	-2.37294568609269
C	-1.61553960869202	-1.95228214901101	1.48141535552778
C	-2.94345132969192	0.83153551286634	-0.32467761003020
H	-3.65358641234581	1.52494698990930	-0.74447121272711
C	-3.11566364614261	-0.30114990460036	0.39536437611539
H	-4.00706182264829	-0.80843598564157	0.72656734506423
C	-0.95352517648232	3.56973331140824	-3.05135951668129
H	-1.31462339039196	3.80887600328035	-4.04719552376411
C	0.50892628163224	4.02016442027280	-1.18450172005280
H	1.28644621084383	4.61886721203408	-0.72267036420132
C	0.65783391730310	-1.15084257499460	-2.86961124828560
C	-2.08985021179316	-3.16187954577599	0.97711682487663
C	-0.93820380366884	-1.89807482428087	2.69851454725842
C	0.04051788637622	4.34683802849306	-2.45752628226215
O	1.68297280944612	-3.29062590270674	0.75185517021488
C	1.49540056377855	-2.17111062843033	0.51493798736322
C	-1.18598836854820	-4.29427513172772	2.91116866496072
C	-0.72086218695533	-3.07565269607956	3.40867297445220
H	-0.18402780886095	-3.04046921616701	4.35171973726048
C	-1.87366581366702	-4.33546064867412	1.69907460466724
H	-2.23070542808966	-5.28212685610609	1.30491961358162
H	-0.58040993140014	-0.94423581319318	3.06846479993299
H	-1.00799039018231	-5.21061241895968	3.46579642232837
H	-2.60100674133859	-3.18145858012140	0.01936280594797
H	0.36064573840142	2.64875084239255	0.48440508047241
H	-2.23720545468352	1.84577164597919	-2.83502873260783
H	0.45196824221164	5.20108704575929	-2.98672719307078
C	1.53708913798062	-2.41251582657678	-3.04686692912987
C	0.67661731518297	-0.33029721447205	-4.17679333266024
C	-0.78298150077781	-1.59622054706926	-2.55768998597105
C	4.00992563203507	1.92835236507421	0.86507030832550
C	3.85331748777780	3.26989641290454	0.12050707400914
C	5.13322709145260	1.09148432667383	0.21532083094098
C	4.41854305595494	2.23872970092039	2.32443126508130
P	1.75232169794924	0.49785776137611	2.05085529813080
H	4.91508671930010	0.88248527224692	-0.83583881749667
H	5.24915743610436	0.13801937198910	0.73907809758574
H	6.07829415263243	1.64463585336331	0.27244086597557
H	5.34783239250402	2.82150560421012	2.33128975922749
H	4.57758025201549	1.31234121667327	2.88386047731551
H	3.63744495393923	2.81625698632028	2.82812348587311
H	3.53738303107883	3.12369526154190	-0.91532871294154
H	4.81339530311418	3.79881849863367	0.11960466522747
H	3.11411361936591	3.89787057080611	0.62792452387216
H	0.25944540147537	-0.91850907817116	-5.00337040115153
H	1.70251247651563	-0.04599850776139	-4.43134302168355
H	0.08749717205633	0.58454800090597	-4.06325543954745
H	1.13471857453803	-3.02503345814383	-3.86276608257221
H	1.54700615484475	-3.01140843515063	-2.13253945571214
H	2.56585907726192	-2.13084504978551	-3.28828720077926
H	-1.16864242127613	-2.21267335901529	-3.37839133080691
H	-1.44344329989586	-0.73254410917930	-2.43718686538679
H	-0.80632378617228	-2.17921232823275	-1.63287977992760

Int2 (R = *t*Bu, R' = Ph)



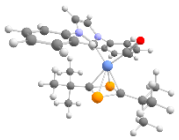
TPSS D3BJ/def2-TZVP
E = −3385.48846820 Eh
G = −3385.05746350 Eh

0 1

P	1.12699300975413	3.25363743036457	6.37193425810596
C	-0.11742333120992	2.10370571344274	6.28788472335433
C	1.40938330783985	3.84741644819197	8.13579232799238
Ni	-0.57685958869204	2.07629498930881	8.11782532121922
N	-2.67731747306196	4.23313682673260	8.54663497255904
N	-3.19841290618467	2.26927863213772	9.26065621244305
C	-2.22083470663016	2.93682877233263	8.54967050902770
C	-2.04556348681257	5.33477438202590	7.89133397791821
C	-1.87597568601152	6.53717173247901	8.58012356670651
C	-1.66948933410440	5.21618618007015	6.55593584733815
C	-3.14261000802852	0.87783938192917	9.57310545382762
C	-3.87561822803360	4.36396326122100	9.25151679977710
H	-4.39374875382076	5.30645868665175	9.31659639121619
C	-4.20043995439071	3.13006332405431	9.70131145766515
H	-5.05789578762100	2.77237196595305	10.24746555172836
C	-1.12232275997842	6.31748189862189	5.90141067427980
H	-0.81726894653386	6.22233421878160	4.86394478193456
C	-1.34113521870085	7.63664144109500	7.91277326284985
H	-1.20319858537892	8.57248536314706	8.44604290819120
C	-0.53347481665500	1.36633491781845	5.04243280312673
C	-2.90650608624487	-0.04428533127812	8.55311713568654
C	-3.31790491475268	0.45802753469104	10.89088283177780
C	-0.96700925482891	7.53028602051407	6.57164024484870
O	0.66928383889262	-0.36548753830730	9.10065193611453
C	0.23254984143431	0.63243980162935	8.70968538665595
C	-3.00417478517682	-1.83197386836307	10.17786048131889
C	-3.25237026567826	-0.90318716897344	11.18839552328294
H	-3.37767905398840	-1.23382118475485	12.21501737132180
C	-2.83191493678020	-1.40009865336425	8.86178220644030
H	-2.63833613321981	-2.11901085735336	8.07152156193033
H	-3.47420358023166	1.19248585634066	11.67513226795644
H	-2.94129534258505	-2.88951573679982	10.41544162127425
H	-2.77960652679765	0.31130146067727	7.53688768029096
H	-2.14566690755854	6.60147331549696	9.62991840288229
H	-1.80578424882198	4.27022115670553	6.04841510947438
H	-0.54283999880486	8.38679657250197	6.05646736728492
C	-0.38886079624058	-0.14739180345630	5.31609890911386
C	0.29958666845841	1.73551584481504	3.79847562628644
C	-2.02021788347287	1.68121708687897	4.75948541300911

C	2.58562013145888	4.85893858510695	8.17494925828044
C	2.32034788542842	6.03905133784767	7.22147773391549
C	3.87427710184230	4.12751905906091	7.74073737037871
C	2.78855261663481	5.41837763998525	9.59205463524521
P	0.59635043664902	3.35677387264718	9.53474167825490
H	-2.38677723183491	1.06108718291972	3.93278368308072
H	-2.14844515021302	2.73196728080747	4.47845882926949
H	-2.63220750392906	1.49025103399787	5.64645512995610
H	-0.05094256023752	1.17688097692232	2.92213727960436
H	1.35705382714888	1.50332567801501	3.96025173036449
H	0.21719812899556	2.80620640672051	3.58289589071638
H	-0.71909012915080	-0.71972484317042	4.44071611726438
H	-0.99113521156546	-0.43890841943746	6.18144430766314
H	0.65383822354078	-0.40160474151965	5.52938347284228
H	3.77830642545299	3.73159436885772	6.72416280488605
H	4.08574697820103	3.29298854585525	8.41669110225827
H	4.72158991956049	4.82388456060700	7.76143657415766
H	2.15929354603116	5.69315380778458	6.19520401820759
H	3.18338652755930	6.71617951693378	7.22449667391917
H	1.43454405193762	6.59586698149467	7.53768515710960
H	3.62056909824079	6.13317424987561	9.58907333560846
H	3.02064881059253	4.61994356466976	10.30485923733996
H	1.88810769830902	5.93502528005812	9.94102510146436

C (R = *t*Bu, R' = Ph)

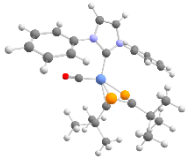


TPSS D3BJ/def2-TZVP
E = −3385.55397917 Eh
G = −3385.11942203 Eh

0 1

Ni	-0.23872247552406	-0.48088687535489	-0.44861995263059
N	2.04184991187315	1.46571746045525	-0.84658687756919
N	0.12031630087985	2.41708677624757	-0.63102169754720
C	0.71284795994567	1.17842681378811	-0.62648747627689
C	3.11798398029955	0.52263506095755	-0.86640919522909
C	4.33953836135553	0.88927429152968	-0.29473874389328
C	2.94928926668844	-0.74156990612360	-1.42936926122776
C	-1.27440737731014	2.66943255342289	-0.40533086591162
C	2.25538408475597	2.84050809479730	-0.95307085453889
H	3.22864066863763	3.25200730498115	-1.16087979897472
C	1.04870009930690	3.43621860555091	-0.81380989968061
H	0.75295300011812	4.47127467607558	-0.86272833876334
C	4.01006957853424	-1.64481129689084	-1.40337876728562
H	3.87118937213428	-2.63362827249212	-1.82926136997906
C	5.39783411724321	-0.01609603735528	-0.28975044281826
H	6.34255928129750	0.26842651629072	0.16346530026454
P	0.14477362853625	-2.40552280110421	0.76104625749921
C	-2.22730518403137	2.14584896455366	-1.27615827545378
C	-1.64671443905414	3.44458311759237	0.68964702203863
C	5.23453615585909	-1.28791628065380	-0.83965592545531
O	-0.60343753757055	-0.80798342371723	-3.31925855267241
C	-0.48514188670197	-0.73346078157864	-2.16612565262590
C	-3.96415875303110	3.14926955270227	0.07409076074200
C	-3.00006703906639	3.68271575966151	0.92818458548139
H	-3.29814082854584	4.27215580453314	1.78988586726327
C	-3.57595095509896	2.38801385763539	-1.02975444839579
H	-4.32416051907615	1.97313124244288	-1.69800483128595
H	-5.01790307355679	3.32593617398789	0.26794459305291
H	6.05601784005418	-1.99777476093387	-0.82375378581843
C	0.93143499426448	-0.24151764379505	2.63984402645242
C	0.00763822362961	-0.83282466565629	1.60206565412790
C	2.37457460480089	-0.72456146890601	2.43529791636700
C	0.41809414673503	-0.76658611954817	4.00574858783304
C	0.86877403040137	1.29502400507158	2.66258759108970
P	-1.75379635147273	-0.41442964261205	1.29023313069960
C	-1.55657452910725	-1.88944630891850	0.29090208802763
C	-2.61990823687394	-2.67591203448111	-0.43781247441102
C	-2.00409619813641	-3.65661171215462	-1.44972153357004
C	-3.62286816737661	-1.73750153565398	-1.13081677675216
C	-3.36657202283407	-3.49400066898078	0.64720781314948
H	-0.17139581649729	1.63558043110197	2.71369734447352
H	1.32784476662065	1.72269879023352	1.76751457908990
H	1.40123784936544	1.68273052767851	3.53896808095803
H	0.43026266534529	-1.86064740402975	4.02217024188422
H	-0.60783325157384	-0.43063323498148	4.18665111834204
H	1.05889294833224	-0.39388970463237	4.81398937587045
H	2.42124939229779	-1.81913479534479	2.46334040953624
H	3.02561057742686	-0.33482744408488	3.22676005190429
H	2.76691178927325	-0.39674920129336	1.47072771150798
H	-2.78418966839050	-4.29322739990890	-1.88276081043249
H	-1.26895720530820	-4.30381222224387	-0.95820292499381
H	-1.50279518161794	-3.12891723781125	-2.26497284842800
H	-4.46180451243325	-2.31028994236069	-1.54313348493358
H	-3.14217276092328	-1.18856655689038	-1.94592086377117
H	-4.02234897960464	-1.00563209547560	-0.41921687588504
H	-4.14379894466453	-4.11214381406914	0.18233155493631
H	-3.83432043475678	-2.82467771133800	1.37573382458437
H	-2.67058369015682	-4.15006343025857	1.17993415258883
H	4.44807569784817	1.85988200608240	0.17870897561260
H	1.99414448498325	-1.02044269407945	-1.85366154368775
H	-0.88478405293759	3.82591564270507	1.36215132898813
H	-1.91180170561077	1.55315209563461	-2.12561979346687

TS4 (R = *t*Bu, R' = Ph)

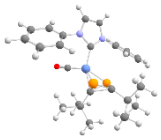


TPSS D3BJ/def2-TZVP
E = −3385.50290096 Eh
G = −3385.06963734 Eh
im. freq. = −36.56 cm^{-1}

0 1

Ni	-0.52164734091875	-0.61513994409543	-0.33292972872559
N	-1.76344730577399	1.88551836774159	0.79139859586166
N	-2.38023220813868	0.09269671119434	1.80847401958486
C	-1.50313276315707	0.53162838445251	0.83338985941477
C	-1.10897213115023	2.83193557223978	-0.05414610359629
C	0.26192271578652	3.04029162492039	0.08574173182976
C	-1.85194032604114	3.54925166851590	-0.98914854508723
C	-2.53195974021941	-1.26852251541025	2.21809768559154
C	-2.77777446174887	2.25434036586013	1.67439917931312
H	-3.08746424394473	3.28067181386128	1.78443465171532
C	-3.16447731318725	1.12636717385275	2.31323062147590
H	-3.88240703221241	0.96379322215881	3.10021871515671
C	-1.21079985236642	4.48810545963310	-1.79766948776090
H	-1.78313073716819	5.04097806514631	-2.53647897265915
C	0.89422816301690	3.98130563835602	-0.72503584572930
H	1.96148481196065	4.15208837048285	-0.62189587224384
P	0.89531725694858	0.57182011678682	-1.74309256733920
C	-3.80873380338341	-1.82670213933631	2.27066850746858
C	-1.40816260571093	-2.01984146360560	2.56072548644021
C	0.16080876356196	4.70400298756813	-1.66729643256876
O	-2.71198568937709	-2.39878512856588	-1.12466847262847
C	-1.81462632966915	-1.72804200808034	-0.81460094686500
C	-2.84204315700125	-3.91861753315100	3.00116518695120
C	-1.56854150820326	-3.34779651014812	2.94762616882490
H	-0.69401731999021	-3.93613200791600	3.20871272818619
C	-3.96001319289794	-3.15517965729312	2.66814299556959
H	-4.95199375588157	-3.59582042887696	2.69800177840568
H	-0.42810088382676	-1.56144897090377	2.50793373677216
H	-2.96159143481305	-4.95609862064508	3.29891493177449
H	-4.66904506607057	-1.23636007329327	1.97023118683889
H	0.80729837481938	2.46460086685417	0.82479868971315
H	-2.91461478654969	3.35348352864462	-1.09483037401347
H	0.65886593781542	5.43211653491068	-2.30043857060167
C	3.64348763927131	0.62703256458988	-0.61829037224532
C	2.18946712155201	0.14589656644070	-0.56726785436275
C	3.72947452563192	1.61556558578101	0.57396626299382
C	3.95971674951687	1.37809449616659	-1.91984238179580
C	4.68069350778168	-0.48396673133561	-0.38108484142319
P	1.57929369581036	-1.13460931236660	0.54548000808744
C	1.07941083656335	-1.22408950711233	-1.24375542219914
C	1.33461093247774	-2.38975160495691	-2.20010647871036
C	0.44268532204705	-2.21559006912160	-3.44226246788779
C	0.98751981610184	-3.70542486892898	-1.47899387203164
C	2.80751407985273	-2.43207911045406	-2.63408131283573
H	4.76768591535075	-1.13303212285176	-1.25411395529446
H	4.40757955038119	-1.09872851362459	0.48217176450135
H	5.66120652764390	-0.03060937003230	-0.19497887773322
H	4.73903262826093	2.03923715213705	0.61718637361749
H	3.52453233921784	1.10275639577828	1.51912952464055
H	3.01725215830678	2.43654503130637	0.46084576612360
H	3.88470696051884	0.71262287711843	-2.78497637189330
H	4.97758919092602	1.78349598086691	-1.87950707905896
H	3.25927864628435	2.20447844373280	-2.07574834700960
H	1.14986765629497	-4.55542505888914	-2.15135502769640
H	-0.05698347622305	-3.71014589346153	-1.15676124045778
H	1.62257728149611	-3.82996385236825	-0.59508025648341
H	0.59112124973810	-3.05566654805942	-4.13003941277015
H	0.69242934663674	-1.28581947083236	-3.96504547025877
H	-0.61268954499360	-2.17873397858250	-3.15984924469418
H	2.95655693795308	-3.23477389247147	-3.36458995008408
H	3.44965264049859	-2.62563559744445	-1.77139411886291
H	3.10368873059413	-1.48437906288325	-3.09557988124513

Int4 (R = *t*Bu, R' = Ph)



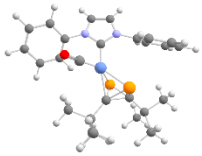
TPSS D3BJ/DEF2-TZVP
E = −3385.50290352 Eh
G = −3385.07075990 Eh

0 1

Ni	-0.50029639271722	-0.62904104321655	-0.35306786091127
N	-1.72949463656212	1.87705310814270	0.76890901789552
N	-2.34949171921150	0.08853492379543	1.79201327406590
C	-1.47445135624426	0.52202089195294	0.81263415517447
C	-1.07599320131751	2.81937066133738	-0.08186475347704
C	0.29673766042948	3.02209331014587	0.04887068014058
C	-1.82181465200036	3.53849772173110	-1.01323459670945
C	-2.50543758208170	-1.27114911947588	2.20538861113515
C	-2.73893113854153	2.25151784239328	1.65517906367332
H	-3.04407359602830	3.27929366671117	1.76443158899473
C	-3.12758348297280	1.12639485629125	2.29779604226334
H	-3.84299817674833	0.96819513266395	3.08800072917082
C	-1.18198950897329	4.47328484249426	-1.82744692954806
H	-1.75668208036602	5.02745680630236	-2.56337586612036
C	0.92777629178926	3.95888524001990	-0.76788208359193
H	1.99643954486862	4.12500529204977	-0.67217341074036
P	0.91005454891296	0.55074414472592	-1.76863341046437
C	-3.78414486300920	-1.82463936999163	2.26065962900156
C	-1.38409547934754	-2.02529267027538	2.54976213943935
C	0.19141720168159	4.68324723363546	-1.70654692416350
O	-2.70595713907868	-2.39982192105465	-1.13523893318435
C	-1.80150899553875	-1.73723244636974	-0.82823247538662
C	-2.82430125714146	-3.91753804030055	2.99737398647866
C	-1.54881582649306	-3.35137905100260	2.94116436387502
H	-0.67621408958274	-3.94192662419132	3.20368668765909
C	-3.93981246130954	-3.15128492862915	2.66255651283063
H	-4.93331599197781	-3.58834276414120	2.69456753425012
H	-0.40251160658083	-1.57043450536866	2.49506897842368
H	-2.94730513823291	-4.95360075182114	3.29863717959919
H	-4.64253974666506	-1.23212806994346	1.95899353377454
H	0.84456240097529	2.44574200643761	0.78563874344663
H	-2.88598687894464	3.34706852258954	-1.11182785190747
H	0.68852632201270	5.40798522329653	-2.34423621007858
C	3.66732874472210	0.58290927017132	-0.66522428690601
C	2.20914152710015	0.11343850745867	-0.60204054461887
C	3.76541740916932	1.58316914940727	0.51595483357928

C	3.98278527150518	1.31958562956696	-1.97526682491545
C	4.69895763737243	-0.53157232822883	-0.42079518610168
P	1.59606690593616	-1.15317336704757	0.52522283888709
C	1.10494420136295	-1.24214443946784	-1.26558502429182
C	1.34710501246546	-2.41340558331742	-2.21981669397932
C	0.44931761369878	-2.23703773106144	-3.45729098761544
C	0.99418308940771	-3.72415689111644	-1.49277622593386
C	2.81662026873920	-2.46890203451175	-2.66279114125193
H	4.78226388369802	-1.18767929655640	-1.28881554355999
H	4.42369794668047	-1.13843483904775	0.44744810125294
H	5.68196312036542	-0.08197744201626	-0.23884403922901
H	4.77760781307923	2.00124739554534	0.55020123745310
H	3.56174134203493	1.08151260584541	1.46740651725226
H	3.05736424550748	2.40703323455270	0.39763397599073
H	3.89950409841540	0.64722050538533	-2.83427002439534
H	5.00364495030974	1.71816773235395	-1.94296930064216
H	3.28740284412623	2.14943214774264	-2.13523428952972
H	1.14652519785260	-4.57734425613634	-2.16340063749933
H	-0.04852398905852	-3.71999089069931	-1.16476148164432
H	1.63303800473682	-3.85063513627596	-0.61192195711715
H	0.58654407823049	-3.08098650493780	-4.14267235754180
H	0.70324559473316	-1.31138502558387	-3.98541748165011
H	-0.60392070595177	-2.19026340718934	-3.16851992562008
H	2.95343563650789	-3.27365084096337	-3.39347292919776
H	3.46315860664953	-2.66783188512682	-1.80470406776792
H	3.11863510918774	-1.52471532100687	-3.12761746763505

TS5 (R = *t*Bu, R' = Ph)

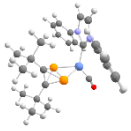


TPSS D3BJ/def2-TZVP
E = −3385.49854208 Eh
G = −3385.06503932 Eh
im. freq. = −107.36 cm^{-1}

0 1

Ni	0.42052689055212	0.18132125075921	0.58293084582875
N	2.47530128523911	-1.66238023775079	-0.41948429725506
N	0.56875722015998	-2.64902274124651	-0.22915977956961
C	1.16960217546194	-1.42514254073244	-0.05524056008530
C	3.50357094914801	-0.66993437515328	-0.45490771623961
C	3.25835977070306	0.54893613501754	-1.08816286423275
C	4.73425512543606	-0.93582914096194	0.14163799009803
C	-0.81399398095802	-2.94144197638856	0.01244176755018
C	2.67653682271344	-2.99392785713520	-0.78042741192966
H	3.63880361154396	-3.35701020079727	-1.10152290639860
C	1.47672690636696	-3.61071054599643	-0.66719906671304
H	1.17979181594716	-4.63270651366246	-0.83621432872064
C	5.73572529245359	0.03601900413893	0.10440896001728
H	6.69287659563499	-0.16223171567258	0.57697661413341
C	4.26116682694287	1.51497548245988	-1.11229684896665
H	4.07358824552729	2.46750444687296	-1.59811374377259
P	-0.73567296295461	0.48301803780832	-1.29360789904056
C	-1.35064733319517	-2.74477906014940	1.28461541362262
C	-1.58492453322610	-3.46088387032815	-1.02515539883731
C	5.49867769654563	1.26161003154632	-0.51575179020602
O	2.46406830565398	0.93918980614390	2.56527855765749
C	1.68405045604683	0.67561098226351	1.74821193098605
C	-3.46242289555074	-3.61998640271336	0.48669782853933
C	-2.91500703806525	-3.80733979156083	-0.78249706404852
H	-3.52158557434613	-4.21160317882462	-1.58711157310007
C	-2.68277313498934	-3.08764983390794	1.51450478388864
H	-3.10897322257922	-2.93933051067728	2.50197528663348
H	-4.49937570243813	-3.88306488631606	0.67359501186630
H	6.27559879620158	2.02005667892409	-0.53366927697873
C	-3.58748144085314	1.16093727001764	-0.65961534173057
C	-2.16285513778639	0.84958954430000	-0.20668566637521
C	-4.34327652656668	-0.17805854143621	-0.51322609063077
C	-3.66241604741083	1.59228565346645	-2.13338829537072
C	-4.25996425974066	2.19880589554106	0.25554078390648
P	-1.58923480633985	0.63664994671385	1.50600807882859
C	-0.85099695781363	1.73974246757255	0.02064321673958
C	-0.51066139084246	3.23421374469306	0.01097565053421
C	0.98854381004913	3.38808673238793	-0.30266599215031
C	-0.81048776153041	3.85637723722722	1.38458216479749
C	-1.28524678388494	3.98683330741207	-1.08684062020203
H	-3.80901537541705	3.18861316647251	0.14730128593562
H	-4.16629115987532	1.89968765768799	1.30436299298056
H	-5.32368838192342	2.27966244465363	0.00376902662251
H	-5.38711916797422	-0.05940284448116	-0.82688714259943
H	-4.32493451263612	-0.51594556561366	0.52749050041750
H	-3.87859587427731	-0.95378317491542	-1.12954064803521
H	-3.18175679828866	2.55716234804371	-2.30749936971534
H	-4.71119989127062	1.67409638851044	-2.44152399417398
H	-3.17737457868945	0.84952394567255	-2.77661924496164
H	-0.55112020581588	4.92192179632010	1.37515703578592
H	-0.22491028318313	3.35965816712821	2.16418249448516
H	-1.86800595089332	3.75062572232851	1.64205917863938
H	1.26057445448690	4.45019709126171	-0.31241373399730
H	1.21337523896892	2.96290218091239	-1.28712761598765
H	1.60158255789028	2.87117184779598	0.43922698209269
H	-0.94551681560857	5.02807282098980	-1.12406827255736
H	-2.35988356059684	3.99180552700452	-0.89584374865155
H	-1.10451847482021	3.52931799424521	-2.06521973401604
H	2.29242775635282	0.72402416891761	-1.54787603498528
H	4.89423247446199	-1.87922211726213	0.65500824131926
H	-1.14719626601777	-3.58280653341177	-2.01152519175037
H	-0.72695037112898	-2.33668714311592	2.06957556607896

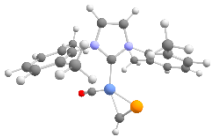
D (R = *t*Bu, R' = Ph)



TPSS D3BJ/def2-TZVP
E = −3385.54238868 Eh
G = −3385.11099189 Eh
0 1

Ni	0.44795407449200	-0.01222438519170	-1.39176602121643
N	2.58564400973411	-1.04485661017581	0.46525158021831
N	2.57010793310988	1.10852149861569	0.42244625283403
C	1.97998856561112	0.01531356208012	-0.17882414279914
C	2.24404316313762	-2.40677571007815	0.23064346926888
C	2.21616695184616	-3.30843202206228	1.29641528724903
C	1.91033239227022	-2.82206677175595	-1.05983370251517
C	2.20915628262941	2.45500463236025	0.13077116571107
C	3.49845883300949	-0.61788398456226	1.43050571757261
H	4.09499019046161	-1.30840634017894	2.00347496679612
C	3.48839159442528	0.73409164064843	1.40399169011554
H	4.07419423905332	1.45588416372422	1.94901036243658
C	1.53794132239794	-4.14577577259760	-1.27749089719896
H	1.27161926646050	-4.46477101644603	-2.28068044618205
C	1.85215559061326	-4.63408289336477	1.06481990542626
H	1.82187694649367	-5.33253969284267	1.89585890852619
P	-1.18905960893701	-1.16768119761846	-0.35388655747052
C	1.91139026174987	2.81945701115474	-1.18344051419781
C	2.12443715902151	3.38932171843381	1.16448090312514
C	1.50759284622979	-5.05567191705254	-0.21955190557293
O	-0.01108690538333	-0.01659987670500	-4.29186356363859
C	0.25560240203157	-0.01858833014360	-3.16118812177481
C	1.42907769038896	5.06872934516649	-0.43189758466513
C	1.73852578233765	4.69775781422579	0.87679494135229
H	1.66286937530217	5.42194596816047	1.68252738839821
C	1.51658889747630	4.12603330002314	-1.45760589091735
H	1.27754028621622	4.40596902892968	-2.47914653051162
H	1.11831293366540	6.08591718360164	-0.65040365446468
H	1.21461180242586	-6.08650969937706	-0.39415238416840
C	-1.65475069978374	-0.08922817320332	2.52995957958813
C	-1.70144594450681	-0.04431220038805	1.02599380261028
C	-0.17562301950528	-0.22543004904736	2.93815081706725
C	-2.44767847858947	-1.30236451987860	3.04795820852106
C	-2.22870068519434	1.21192606946015	3.11983302127157
P	-1.14528294552486	1.14031433842989	-0.28331945200248
C	-2.60419731560316	0.00873563231361	-0.13940968323390
C	-4.05779871129944	0.04851013958525	-0.53177610261406
C	-4.75278824478752	-1.25995566640170	-0.11179906406435
C	-4.12973477306456	0.19957393522650	-2.06240542715839
C	-4.74741781727377	1.25032176829359	0.13935841921022
H	-5.78625435628452	1.32932899707496	-0.20102653904953
H	-4.22819767969802	2.18113781133157	-0.11224955125996
H	-4.75253452354733	1.14239318911463	1.22848865748969
H	-5.79989373740401	-1.25096259552016	-0.43561313340377
H	-4.73189215675720	-1.38798214423815	0.97477956545744
H	-4.25445114659269	-2.12120542476921	-0.56871062125056
H	-3.51114705175444	-1.20608989249149	2.80843610953267
H	-2.34865289543640	-1.38474082038073	4.13661415278861
H	-2.07478908128540	-2.22656418479198	2.59381405379663
H	-3.28353261715287	1.33432275535025	2.85680952757827
H	-1.67794816050852	2.07846292813063	2.73880334652183
H	-2.14773248478957	1.19981717399343	4.21304325491145
H	0.25020546634992	-1.14498382374803	2.52362169747106
H	-0.07801401385467	-0.25214124209092	4.02960771238519
H	0.40400665723821	0.62123246564176	2.55570487767078
H	-5.17368990750254	0.22391732998372	-2.39488532241764
H	-3.62561719971460	-0.63808507242967	-2.55510586806470
H	-3.63949694343798	1.12562865129703	-2.37908577687676
H	2.44600149785326	-2.96941247131270	2.30187590788755
H	1.93764077104988	-2.10212402518561	-1.87307309329711
H	2.32507853375473	3.08701082576665	2.18787298608329
H	1.98096238633719	2.07325564791241	-1.96952568488646

B (R = H, R' = Xy)



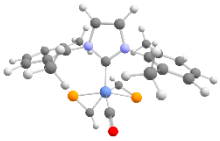
TPSS D3BJ/def2-TZVP
E = −2848.07627137 Eh
G = −2847.76749110 Eh

0 1

Ni	-0.06136124530986	1.44045177523783	0.06974404792995
P	1.39915953719411	2.03675660642703	-1.52152628778764
N	1.07577060990926	-1.33242751323230	0.13579599753205
N	-1.06090021357550	-1.34843369123947	-0.08155178542122
C	-0.00050864302149	-0.48842719533878	0.03526560995950
C	2.43600065635664	-0.87575039731117	0.23973527220745
C	3.25157840148490	-0.95341833589074	-0.89759970043781
C	2.87832113393845	-0.34981644882371	1.46044937143852
C	-2.42062827203597	-0.89573214519285	-0.20837655679498
C	0.69143741329644	-2.67032324860850	0.08721972630992
H	1.40810243835130	-3.47232748681524	0.15853680724628
C	-0.65776725899200	-2.68078797994833	-0.05289442784716
H	-1.36152144107978	-3.49315815570260	-0.13508038158240
C	4.20002286280418	0.10060235308774	1.52854413304707
H	4.56701799436294	0.51798878290114	2.46238753069107
C	4.56683576658097	-0.49415414108687	-0.78396864781416
H	5.21563727759285	-0.53025381620740	-1.65494436166771
C	0.55435760995236	3.08871371306562	-0.60886320185568
C	-3.23673058408058	-0.91102516191483	0.93038237969883
C	-2.85880548547883	-0.43392103182353	-1.45689274368754
C	5.03813373028426	0.02726726339639	0.41850447241380
O	-2.04507668194755	2.27350629285542	2.03869556113634
C	-1.25388085050590	1.92507474080932	1.26828106253229
C	-5.01618780445607	0.01074852592441	-0.43635498052132
C	-4.17813248847754	0.01955146456490	-1.54925525904144
H	-4.54322018184340	0.38810643766704	-2.50416124112943
C	-4.54887765413299	-0.44939386933687	0.79249056296758
H	-5.19907369163312	-0.43701266601271	1.66305873643366
C	-1.93247309013602	-0.40577855641753	-2.64394112806593
H	-6.03670888602573	0.37228564793823	-0.52522379528482
C	-2.70072715593910	-1.36691917703813	2.26296614131711
C	2.71065846033489	-1.46256263765925	-2.20848589817911
C	1.95278636931900	-0.24250481709015	2.64335462904457
H	6.06079099980206	0.38696434376299	0.48801513062186

H	3.43529967366169	-1.29612886359149	-3.00898548685991
H	1.78145379597928	-0.94271774670618	-2.46662522196360
H	2.48481697341590	-2.53445859569324	-2.16943427439772
H	2.50355242044273	0.06866500257000	3.53439180310112
H	1.45655589300037	-1.19659409278435	2.85303719408561
H	1.16496807286378	0.49430255185832	2.44216716869111
H	-1.77493138861649	-0.83660264097385	2.51045144899858
H	-2.46888174173232	-2.43835082606797	2.26128870701131
H	-3.43101488437226	-1.17640959310218	3.05274131941159
H	-1.48513591597639	-1.38974094264301	-2.82536218039992
H	-1.10858494069644	0.29742953382257	-2.47040423344496
H	-2.47158140898059	-0.09764904593455	-3.54303277597570
H	0.35270881811760	4.12951278429884	-0.38951524366695

Int1 (R = H, R' = Xy)

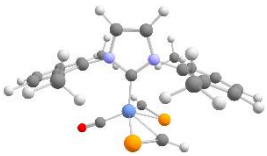


TPSS D3BJ/def2-TZVP
E = −3228.14097019 Eh
G = −3227.82154282 Eh

0 1

C	-0.99817676057537	-3.01624793957128	-0.72682431800150
C	0.72824846546012	-1.22291769759576	-2.10191470383411
Ni	0.03024803701582	-1.34635837683013	-0.19843352757732
N	-1.12390475622913	1.44587329766345	0.31777248318557
N	1.01764047581050	1.46338773157057	0.30447178946264
C	-0.04888667451427	0.61058111419642	0.13841158797939
C	-0.73822094711501	2.75832622599225	0.57975579191141
H	-1.46209259563911	3.53924473611187	0.74777183029913
C	0.61563511164082	2.76810578063788	0.57196007670415
H	1.32928332520064	3.55930922741636	0.73618243459503
O	0.85934546829564	-2.63840942091356	2.32558239528837
C	0.53471611653710	-2.07100663036980	1.37241919616466
P	2.03773919385696	-1.79478206872227	-1.38915635887801
P	-2.22024576889119	-1.98923453817292	-0.70226996518571
H	0.14892763811329	-0.92473852783890	-2.96274619680038
H	-0.54461079568716	-3.98393215239431	-0.88173964849903
C	2.40485731214692	1.08370563837893	0.23188469373527
C	3.02608107036918	0.57024961168009	1.37701823824478
C	3.08625173475916	1.29236002155528	-0.97711111963565
C	4.36997818861762	0.19569360266478	1.26914159938004
C	4.43220446733283	0.92031274503822	-1.03431977807496
C	5.06495164382359	0.36293283480030	0.07459807220561
H	4.87003215795280	-0.22860484904543	2.13569264816976
H	4.97747689851359	1.05411597235473	-1.96454419487369
H	6.10619526943230	0.06081212393963	0.00795978269585
C	-2.50804952969265	1.06444960669486	0.23029194324430
C	-3.13875629635033	0.54596327952589	1.36716755547254
C	-3.16377138732920	1.23931181194655	-0.99479774784843
C	-4.49031363897650	0.20393311181390	1.25508683702383
C	-4.51465997308983	0.88803316069462	-1.06265930119355
C	-5.17315446532272	0.37714572362459	0.05359480095493
H	-5.00302200370227	-0.21120242619320	2.11855265902869
H	-5.04474585579670	1.00108604573738	-2.00451235934820
H	-6.22133048933129	0.10117253200088	-0.01670214797855
C	2.29717608985455	0.46747789189483	2.69150299817116
H	1.24177225775758	0.22667643467031	2.55202802827238
H	2.74809758965934	-0.30147582142123	3.32305735329702
H	2.35055992004035	1.42224381821251	3.23049559523287
C	2.38210495929974	1.87512365877419	-2.17141370843066
H	1.55671380169019	1.22208629067217	-2.47837622706998
H	1.95799699370031	2.86038539558786	-1.94809465483295
H	3.07349862389617	1.97706602892657	-3.01123584570967
C	-2.36963908592314	0.30708102403226	2.63835380661000
H	-1.65174900818087	-0.50870611679403	2.49188848848254
H	-1.79961332296908	1.19194748762178	2.94094836860249
H	-3.04579183581048	0.03193174582744	3.45140910881419
C	-2.40968058634486	1.71726242534131	-2.20751269114846
H	-1.92850555021658	2.68587822743332	-2.03324920685254
H	-1.61596441635130	1.00384468411900	-2.45850721597837
H	-3.07947506673806	1.81085551670981	-3.06552524547683

TS1 (R = H, R' = Xy)

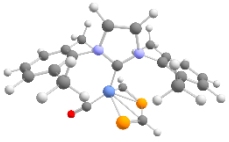


TPSS D3BJ/def2-TZVP
E = −3228.12823303 Eh
G = −3227.80826434 Eh
im. freq. = −129.91 cm^{-1}

0 1

P	1.55207018795813	-0.68375098844364	-3.25989858311874
C	0.13826740129709	0.09094175110052	-3.33064359858219
C	1.49420741942203	-1.88980252314925	-1.04164515347681
Ni	-0.29306463047136	-0.58563762395261	-1.55631448890665
N	0.98873141915876	1.61023058134065	0.18746507032301
N	-1.15097534389974	1.62769849079783	0.27328325697080
C	-0.10909293615921	0.97912098950707	-0.34095566069276
C	2.33922990918515	1.29495056433740	-0.19584506218081
C	3.10446223237754	0.46816504053764	0.63757028732722
C	2.83339833704932	1.84502256084376	-1.38651966918128
C	-2.53625075367288	1.31986131138256	0.03384009486360
C	0.64038053056053	2.61149204118681	1.09075730550113
H	1.38117874717589	3.21494932281499	1.59056767117360
C	-0.71465355245921	2.62224071343663	1.14447163771789
H	-1.40354320819850	3.23365710638735	1.70478208318709
C	4.13114438734968	1.49429518492185	-1.77190566499587
H	4.53143985319517	1.89240055902082	-2.70016354751324
C	4.39838315176903	0.14575995506898	0.21514481163885
H	5.00763339585632	-0.50660531640810	0.83520301055433
C	-3.16285682855286	1.89538396850191	-1.07864068611738
C	-3.19576236378116	0.45952646084130	0.91999956917651
C	4.90357748598888	0.64419105841665	-0.98364566948893
O	-2.96643450068985	-1.57670835220181	-2.19392870801108
C	-1.88623416306820	-1.23209348016290	-1.95476756130424
C	-5.19396291615634	0.74088189529694	-0.42779837080773
C	-4.54277942476171	0.18131559556901	0.66873934897707
H	-5.07610828950703	-0.49179799231653	1.33465490232052
C	-4.50893899859057	1.58902076742619	-1.29479919697667
H	-5.01613560217686	2.01231360412056	-2.15765691246339
H	-6.23795078029325	0.50596169747220	-0.61399171541387
H	5.90691838572330	0.37498557055371	-1.30141700362042
P	0.28838579864616	-2.16108230774056	-0.01271118688517
H	-0.49134365530983	0.68865353627857	-3.97666228275515
H	2.51631486523677	-2.14016978883414	-1.27508484503393
C	-2.46541230382440	-0.16859152944341	2.07801075995997
H	-3.13804445480232	-0.81013858551016	2.65234845302979
H	-1.62775224502523	-0.77657716498411	1.71854467726780
H	-2.04849824086667	0.58754924481651	2.75274233548517
C	-2.39165723807488	2.78410303129276	-2.01833356424396
H	-3.01882659103189	3.09563824657887	-2.85718973823113
H	-2.02257158036478	3.68251114965778	-1.50980664717565
H	-1.51757990826860	2.25013303711602	-2.40566869489018
C	1.99737285609692	2.79518896046626	-2.20043310071341
H	1.76700933017670	3.70266295848262	-1.62944904742860
H	2.52317194797940	3.08305992739759	-3.11369909385145
H	1.04826110683238	2.32626000859883	-2.47713710193465
C	2.55655690421412	-0.04433144883499	1.94188271697344
H	1.59310377046982	-0.54332505361788	1.78956202972029
H	3.24733841213019	-0.76116819493895	2.39221910641747
H	2.39513623415800	0.77258889896979	2.65498628740978

Int2 (R = H, R' = Xy)

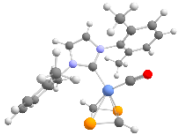


TPSS D3BJ/def2-TZVP
E = −3228.14589488 Eh
G = −3227.82410614 Eh

0 1

P	-1.95051457955435	2.49646779101084	-0.72383959804721
C	-0.61167087967435	1.86724544581403	-1.53451001896990
C	-1.69634707560041	2.18789253866017	1.09560231187586
Ni	0.37515595690597	1.15318377050259	-0.09126479558964
N	-0.98567846080422	-1.57861517982648	-0.06390412754220
N	1.16618914517323	-1.57316799009818	-0.08221450481339
C	0.08653168432284	-0.72911442159676	-0.07127254417768
C	-0.57906674234541	-2.91266161710671	-0.07717885252531
H	-1.29328562192471	-3.72000670961000	-0.08398479518770
C	0.77703356667582	-2.90903891981037	-0.08928179709046
H	1.49560295346359	-3.71237634828833	-0.10711187535776
O	2.62444854075377	2.96749834718870	0.17205479931649
C	1.67868182135523	2.30742801582105	0.09862755770760
P	-0.41439659048138	1.52298032370752	1.97159978113358
H	-0.51727565608400	2.00624795861056	-2.61079781022933
H	-2.56983016667749	2.54800189016397	1.64347145485850
C	-2.36248103201808	-1.15338136192520	-0.08547101860769
C	-2.93485792150840	-0.83377029702090	-1.32289857822706
C	-3.06730004592226	-1.08971363752250	1.12337426269045
C	-4.26108006812359	-0.39311425751863	-1.32645684297031
C	-4.39261922653653	-0.64688163896601	1.07278783935022
C	-4.98147579858169	-0.29320556838640	-0.13887447278965
H	-4.72348277921598	-0.11917402656487	-2.27051566517483
H	-4.95974493355266	-0.57577727647931	1.99704098018362
H	-6.00857549629509	0.05990214908327	-0.15791568293116
C	2.52089296041051	-1.08464071918436	-0.09412452141549
C	3.18216467212838	-0.91994757404393	1.13024986654473
C	3.10053275339900	-0.75972171269475	-1.32790804624543
C	4.48643480176488	-0.41849829488881	1.09586854761281
C	4.40610315393234	-0.26076809336029	-1.31531486397207
C	5.09309753246431	-0.09262814646537	-0.11511737428943
H	5.02015518178438	-0.27018828323677	2.03069229030501
H	4.87835132554943	0.00777381736401	-2.25640331440343
H	6.10420563600109	0.30413310949488	-0.12278495554766
C	-2.14508904339482	-0.96803330431739	-2.59640487370956
H	-1.21625524811116	-0.39138992119306	-2.53247491892815
H	-1.87315473430238	-2.01379938712615	-2.78437986236668
H	-2.72492165878344	-0.60341268769755	-3.44735644381585
C	-2.41834883823642	-1.46556593175955	2.42758857861102
H	-3.14606961973140	-1.42796019051373	3.24183855334589
H	-1.98735574036589	-2.47197004271480	2.39226047272013
H	-1.60310078799298	-0.76851210124477	2.66458928956868
C	2.32251362484884	-0.90543759623061	-2.60943681154711
H	1.96252704319289	-1.93091244816862	-2.74934421751634
H	1.44362005598322	-0.24979508524511	-2.59302976935142
H	2.94349820814744	-0.63649788930790	-3.46726075659141
C	2.48755179977302	-1.22662734663684	2.43097981763324
H	1.59783189539043	-0.59653002094255	2.54285706828091
H	2.15619840717282	-2.27003025754428	2.47820801321521
H	3.15470302522565	-1.03785887218371	3.27528322497736

C (R = H, R' = Xy)



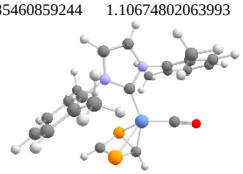
TPSS D3BJ/def2-TZVP
E = −3228.20673452 Eh
G = −3227.87935302 Eh

0 1

Ni	-0.08895912928168	1.20348588072342	0.28912609611311
N	0.97949663687754	-1.54155502350921	-0.19400309699518
N	-1.16747872963030	-1.45991602144814	-0.31651247496068
C	-0.07206834514032	-0.66304057289987	-0.09495746497603
C	2.36965745956805	-1.21624338529615	-0.00914317499240
C	3.20028723207169	-1.17917054621760	-1.13802755816068
C	2.84280279388564	-1.00147991393668	1.29330436507543
C	-2.53575289455853	-1.01043122046034	-0.28912222313608
C	0.54421997092146	-2.83568030336968	-0.46824404697218
H	1.23755743558616	-3.65374962227170	-0.57519257537176
C	-0.80703641523905	-2.78460645029265	-0.54301957442527
H	-1.54362040246430	-3.54668963045567	-0.73875310890737

C	4.20198625020920	-0.71145918884880	1.44406352638464
H	4.59174972847649	-0.52652695591584	2.44107161224098
C	4.55236966597715	-0.88362602029180	-0.93920499867583
H	5.21373883645689	-0.83020723341864	-1.79991063309475
P	1.91598663587685	2.28432413006878	0.61578636970592
C	-3.29070748230352	-1.27173860303628	0.86275183582671
C	-3.05919916757633	-0.36584997657389	-1.41811272028448
C	5.04866654150911	-0.64871327531163	0.34040478853430
O	-2.20947414366934	1.48968492159777	2.27030682554191
C	-1.39111870601053	1.33629735403846	1.46761602851849
C	-5.16908591205376	-0.19313211646246	-0.22737773293979
C	-4.39504081278992	0.04373966010427	-1.36101734359255
H	-4.82525197722770	0.55488236945686	-2.21798872558766
C	-4.62199664691718	-0.84728507654807	0.87396864229193
H	-5.22410742396901	-1.01992971024999	1.76183757636737
C	-2.20805986209328	-0.09693888760279	-2.62754258464489
H	-6.20367761849565	0.13696046186008	-0.20075941786074
C	-2.67708470831949	-1.95486393205249	2.05851085513669
C	2.66122811454410	-1.44340322153025	-2.52203851722533
C	1.92141947236695	-1.06769312942250	2.48005368321509
H	6.09989471446648	-0.41250782442571	0.47776930502854
C	1.36375105837359	1.74728196266649	-1.02741423967501
P	-0.03370578567473	2.84056788956498	-1.33342535818764
C	0.36938659124208	3.18927764374717	0.40452167976863
H	3.33765109708721	-1.03631120077190	-3.27789076533681
H	1.67143461994227	-0.99777354811411	-2.66169388854930
H	2.55843422775095	-2.51917537536348	-2.71097310553186
H	-1.47361884545747	0.68492767488421	-2.39179268990933
H	-2.82421068551318	0.24535895384800	-3.46247870405477
H	-1.65693374067887	-0.99057648582101	-2.94026308294520
H	2.49149588926474	-1.00244862933930	3.40988846333705
H	1.34425890530829	-1.99951905292673	2.48734680896479
H	1.20988994327404	-0.23363267211197	2.44226052405700
H	-2.47403936847562	-3.01356253735010	1.85777762247095
H	-3.34979381048057	-1.89415588080033	2.91704872360094
H	-1.72446608487282	-1.48972627465953	2.33130105651459
H	1.82104036882315	1.02618498795438	-1.69535860234143
H	-0.14682949096689	3.83885460859244	1.10674802063993

TS4 (R = H, R' = Xy)

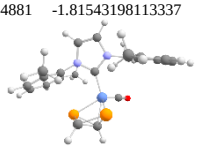


TPSS D3BJ/def2-TZVP
E = −3228.15463449 Eh
G = −3227.83094698 Eh
im. freq. = −284.49 cm^{-1}

0 1

Ni	-0.45140521570778	-0.67270664785235	-0.19521788075505
N	-1.60148722899370	1.84819384871138	0.97542996723371
N	-2.31313108062055	0.07678499338044	1.95755607148569
C	-1.48950082050954	0.47758925105197	0.93028479041648
C	-0.90784543077971	2.74131342722246	0.09177650763716
C	0.30301743086120	3.29661785769732	0.52106370762742
C	-1.46360513692149	2.99596101783056	-1.16810241959929
C	-2.55389380397838	-1.29217894838518	2.32790253638453
C	-2.45742645679646	2.27335664952535	1.98704478261210
H	-2.65584179763260	3.31842618071033	2.16153064989762
C	-2.90702906315076	1.15502038025243	2.60590289574248
H	-3.57979521000143	1.01761339422000	3.43681010284148
C	-0.74980059098224	3.83377146767499	-2.03208045615953
H	-1.14983018303876	4.03711775736823	-3.02144129946745
C	0.98420384540826	4.13014859100922	-0.37345039883109
H	1.93300040488339	4.56625980081163	-0.07203159291716
P	0.26887983239862	0.47165603043533	-2.18556264328928
C	-3.71522204517595	-1.91391419778358	1.85184301230924
C	-1.62336970296315	-1.93830406065535	3.15226746240870
C	0.46539506861773	4.39143873404893	-1.64027078228979
O	-1.55289599405091	-3.37277178974646	-0.30419073056156
C	-1.15035510860323	-2.28866997762692	-0.21636573929967
C	-3.04514434117109	-3.90346112493094	3.06558894931645
C	-1.89172304964608	-3.26209054336707	3.51204455813339
H	-1.18265963680113	-3.79170392586654	4.14267329158590
C	-3.94783542003035	-3.23571282599641	2.24153671246290
H	-4.83404726430749	-3.74695754756812	1.87556257905236
C	-0.36768232681981	-1.23635989243855	3.59411698678306
H	-3.23553075554387	-4.93386103624239	3.35194351256405
C	-4.63865269446078	-1.19838126428133	0.90042324373710
C	0.85962564723981	2.98406166898909	1.88512149173469
C	-2.76636124579749	2.36280972114029	-1.57877245172180
H	1.01188984415858	5.03232565129157	-2.32631969146644
C	1.62291128466735	1.00866143367398	-1.16119547359952
P	1.84116040353679	-0.13511791502978	0.19948482021246
C	1.04802420451898	-0.96540173083586	-1.26912620644502
H	-3.06106991489175	2.70082378491141	-2.57497629528429
H	-3.56858987271506	2.60893614443667	-0.87388795988004
H	-2.66347120538671	1.27173639834440	-1.59395015521445
H	1.87109536191794	3.38454201893432	1.98814934502326
H	0.89409542760126	1.90141440438059	2.04869687623089
H	0.23876983549697	3.41487906085482	2.67967143661403
H	-5.45687281159949	-1.85473882215437	0.59460214259172
H	-4.09113093763807	-0.88350875457491	0.00440935757954
H	-5.07008672941334	-0.29582151842808	1.34824195833234
H	0.23709486043626	-0.96506037933444	2.71990403903594
H	0.22455397622038	-1.88166917146728	4.24743852788853
H	-0.59378707705954	-0.30899707051466	4.13329483344272
H	2.40158581487310	1.70805867302164	-1.49623774100318
H	1.58152844035207	-1.74025028684881	-1.81543198113337

Int4 (R = H, R' = Xy)

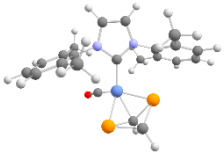


TPSS D3BJ/def2-TZVP
E = −3228.16388860 Eh
G = −3227.83873857 Eh

0 1

Ni	0.13591762883271	0.96929935723423	0.82235343501751
N	1.16696892664762	-1.28525934342311	-0.72478218365731
N	-0.98087403905671	-1.37348536903481	-0.63394520284210
C	0.08344194783298	-0.60685983525970	-0.21684734857203
C	2.52993041254260	-0.85887644623602	-0.54749075313733
C	3.09273251838159	-0.00835316993865	-1.50824471307008
C	3.23667531500997	-1.32661086536257	0.56746850377347
C	-2.36536804597908	-1.11593741826730	-0.34587145746749
C	0.78852718800547	-2.42415750101917	-1.42708570661622
H	1.51373857381266	-3.07382562255961	-1.88953486638403
C	-0.56388621067395	-2.48097516036815	-1.37090974009665
H	-1.26836183540997	-3.19239484072637	-1.76999026031816
C	4.54852047869401	-0.87366344973435	0.73644103412289
H	5.11253734675409	-1.20242778005775	1.60505452129224
C	4.40664406749864	0.42044305117323	-1.30056618524882
H	4.86274099289422	1.09481251647294	-2.02044178633115
P	0.38517973129508	2.67765098582904	-0.74304101547457
C	-2.87538414985520	-1.51536347213224	0.89743650280464
C	-3.15031333118246	-0.49844148500812	-1.33044241460420
C	5.12516925262321	-0.00093496642900	-0.18340753734544
O	1.90958956720871	0.59199471678991	3.14214521695314
C	1.22028092052015	0.70956296521640	2.21544540983916
C	-5.04308581218295	-0.69540691762785	0.17654030579824
C	-4.50403181790600	-0.29520035672592	-1.04464765277952
H	-5.13212445616284	0.19372476118317	-1.78448965183427
C	-4.23383273060938	-1.29171783135161	1.14091506730028
H	-4.65231690378303	-1.58052235551859	2.10122963141313
C	-2.53145819028062	-0.01698741474457	-2.61612253492713
H	-6.09550553866665	-0.52503664622241	0.38411296091724
C	-1.96355258486717	-2.09170412494418	1.94512124598121
C	2.31048852970782	0.40576460783382	-2.72595360048108
C	2.60632264098034	-2.29068670112017	1.53873545168807
H	6.14133305855070	0.35125021476742	-0.03010466605834
C	-1.40548143614848	2.81338960301162	-0.51712959022352
P	-2.02781270535481	1.75062792424020	0.79357593047762
C	-0.51421670051913	2.83359835560880	0.86417906009520
H	3.17879143123067	-2.32769107613145	2.46817722094317
H	2.57228936535104	-3.30299611000612	1.11638580948873
H	1.57935822687291	-1.99990099486992	1.77475373979734
H	2.81980134859677	1.21381287764912	-3.25634257944143
H	1.30840339061838	0.74695817977067	-2.44541968078243
H	2.18743983346638	-0.43594568758679	-3.41879387188393
H	-2.52927039992010	-2.38963131247333	2.83101416841141
H	-1.21802718313473	-1.33839976927759	2.23396835221503
H	-1.41522873455696	-2.96225865720727	1.56843901956643
H	-1.71604734900215	0.68185416369414	-2.39924898958418
H	-3.27579742847900	0.49367477198305	-3.23169394261036
H	-2.10800499709715	-0.84252415895509	-3.19927745869546
H	-1.95982845302725	3.69268272332561	-0.85885225106165
H	-0.41251266007294	3.68122806453645	1.53376707163276

TS5 (R = H, R' = Xy)



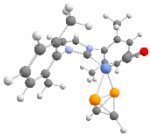
TPSS D3BJ/def2-TZVP
E = −3228.15300002 Eh
G = −3227.82772099 Eh
im. freq. = −193.24 cm^{-1}

0 1

Ni	-0.56409527879524	-0.50760472713125	-0.042035529560704
N	-1.35508206706955	2.23119631148202	0.896723676296344
N	-1.73980482076693	0.67367268993401	2.33398692507513
C	-1.23922026712270	0.87118896165877	1.06741801227235
C	-0.96858003399852	2.94815130777374	-0.28528351804664
C	0.20282378674445	3.71854770072785	-0.23702272596123
C	-1.76395013339130	2.84154509534733	-1.43451748434353
C	-1.85314513239087	-0.60620310480116	2.98400848717084
C	-1.90635744335744	2.84782384603778	2.01798668912530
H	-2.07481895902541	3.91184333269543	2.05261966121476
C	-2.14937574996899	1.86744305293285	2.91981938661845
H	-2.56768195720697	1.89569636039000	3.91271158449237
C	-1.35189553735679	3.54610543424023	-2.56983361185088
H	-1.94571122961592	3.47497489701575	-3.47714081965791
C	0.56850189418053	4.41698166558839	-1.39096463739885
H	1.47826601356389	5.01116297941651	-1.38292992263585
P	0.94779247022484	0.64677123426656	-1.20296981004313
C	-3.10900656285507	-1.22741267372810	3.00926588024480
C	-0.71554804880305	-1.15348588471847	3.59381971004439
C	-0.20124517141621	4.33131833419452	-2.54810295556628
O	-2.84154821492304	-2.36807965882557	-0.12478352404275
C	-1.96947354271954	-1.61161889704452	-0.04238983798217
C	-2.08725328671484	-3.05004282023311	4.24061463363710
C	-0.85712669107066	-2.39555979767479	4.21830972579918
H	0.01107843286632	-2.85103312163876	4.68695138548626
C	-3.20431843486693	-2.46806484360059	3.64652720224234
H	-4.16171346819394	-2.98184343809502	3.66133849350584
C	0.60543332804202	-0.43702321053530	3.55307112017462
H	-2.17523738353816	-4.01902142468664	4.72378281225553
C	-4.31140523214871	-0.58767024314920	2.36250765361493
H	1.06918444251030	3.73549197308353	0.99615540917716
C	-2.99771753288309	1.97984532522231	-1.45198702225263
H	0.10227182802715	4.87041596374856	-3.44089784787815
C	2.04984176316699	-0.77442866929981	-0.96072654216653
P	1.17769426697105	-1.99474323738768	0.07588704303720
C	0.63497802268682	-1.12046611822056	-1.56793910182955
H	-3.55913220460789	2.13259564445241	-2.37694975487898
H	-3.65247787983554	2.20320390146022	-0.60242563494532
H	-2.71864001328391	0.92157490627141	-1.37418609150668
H	2.01645404727515	4.23803877284481	0.78695959295368
H	1.28187447828182	2.71359592665988	1.32992447618679
H	0.58583161346396	4.25420923941188	1.83211309073143
H	-5.11656689505859	-1.31763997991937	2.25085904103512
H	-4.06752457026098	-0.18811149355313	1.37376325649832

H	-4.69024769300825	0.24696874099592	2.96524066106670
H	0.96553513966147	-0.39331089345579	2.51613569527213
H	1.34569182894051	-0.96269191882537	4.16125421388190
H	0.51524762024361	0.59112982360063	3.92223713225375
H	2.94087130245789	-0.95227695998336	-1.56326212934301
H	0.45383445694631	-1.59796327494582	-2.52209431342763

D (R = H, R' = Xy)

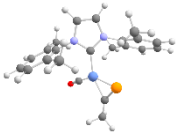


TPSS D3BJ/def2-TZVP
E = −3228.18533899 Eh
G = −3227.86259141 Eh

0 1

Ni	0.00797859912428	0.79906191449361	0.88658535275340
N	0.98326019247937	-1.62640847251187	-0.58155664453164
N	-1.16130476496666	-1.52217821180163	-0.61547880394104
C	-0.06124047908512	-0.85054199398101	-0.14335656547471
C	2.35601944654425	-1.25950017329882	-0.36342342152960
C	3.02830093172809	-0.57081555274346	-1.38211064566954
C	2.94626354575232	-1.56281790091573	0.87027412173362
C	-2.49995882879251	-1.03252570162662	-0.42722586220343
C	0.54470177331770	-2.73742539331345	-1.29984851169790
H	1.23086716578933	-3.46063197609485	-1.71030563591401
C	-0.80997153313242	-2.67146625794951	-1.32150354774389
H	-1.55013216019940	-3.32545334047805	-1.75364387574238
C	4.27064570484044	-1.16046910609189	1.06938925758953
H	4.75140279803250	-1.37842025803891	2.01933348694350
C	4.35192763309074	-0.19073844653295	-1.14316433449052
H	4.89302340024453	0.35315174403193	-1.91281987598347
P	1.36915423926665	2.35333617145147	0.01292503684141
C	-3.14185773985187	-1.28556675232361	0.79232511932280
C	-3.08852261015195	-0.28974881172043	-1.45952666331571
C	4.96798834578772	-0.48250277707646	0.07191842439298
O	-0.18292053070746	1.16707452129589	3.79488759263554
C	-0.10400997240585	0.96052265700413	2.65557467783398
C	-5.04311344870731	-0.03108737503743	-0.04617500262673
C	-4.37857272079526	0.20517615935776	-1.24760275733987
H	-4.85472616773483	0.79143972434370	-2.02900524426509
C	-4.42951307026644	-0.76831565996647	0.96418865202371
H	-4.94864986993015	-0.94426741212548	1.90264319484716
C	-2.33438711083553	0.00219003860542	-2.73057752162324
H	-6.04278118352016	0.36613840295617	0.10567947801299
C	-2.45246855140679	-2.06712380017473	1.87984357252980
C	2.32657768779926	-0.21324987979278	-2.66644511043952
C	2.16746633542386	-2.27566759324829	1.94434664692597
H	5.99486633597994	-0.17327440806625	0.24528838735079
C	0.39290636271046	3.08010893328423	-1.37074182009344
P	-0.92826906836566	2.51166487228872	-0.21610212024494
C	0.31854694421148	3.85749360150419	-0.11271972267176
H	-1.43313617306901	0.58748978975701	-2.51350960729726
H	-2.95762173934402	0.57491091078117	-3.42171666777941
H	-2.01173620091502	-0.91606194673224	-3.23323190516308
H	2.99191843120299	0.35657815034631	-3.31956973051786
H	1.43972073012202	0.39581866556207	-2.45880782382371
H	1.98951792150320	-1.10432157999417	-3.20767288172086
H	-3.11554863051457	-2.19748006458366	2.73844034953122
H	-1.54846919565713	-1.54133184811665	2.20752650735741
H	-2.14224962558498	-3.05656106431633	1.52507862586675
H	2.79667033485817	-2.45539966486494	2.81940633982251
H	1.78408449050350	-3.23825056891769	1.58719009074576
H	1.30275562887675	-1.67498956978572	2.24943001051287
H	0.51231046762063	3.33571183378566	-2.41410900042916
H	0.36677192912992	4.90516047137264	0.14637937868412

B (R = Me, R' = Xy)

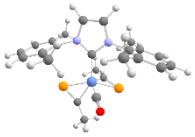


TPSS D3BJ/def2-TZVP
E = −2887.42225990 Eh
G = −2887.08775940 Eh

0 1

Ni	-0.05925576983858	1.44709356448220	0.07270788428434
P	1.37092816815870	2.03338795966048	-1.54216810936460
N	1.07403207966202	-1.33655243055916	0.13047771168152
N	-1.06185870378762	-1.34533303552561	-0.09215868935082
C	0.00039845078926	-0.48867504036053	0.03363097644168
C	2.43489003414464	-0.88339162185848	0.24073151806205
C	3.25403559505821	-0.95735687389288	-0.89418212612671
C	2.87432827835679	-0.36382400121553	1.46517619627803
C	-2.41940413538017	-0.88671756780962	-0.22013359808375
C	0.68645190541908	-2.67321056049960	0.07064042358258
H	1.40080375510154	-3.47767741945159	0.13765559014541
C	-0.66247169193482	-2.67917553132628	-0.07254165777872
H	-1.36817178971379	-3.48911710407311	-0.16202843185957
C	4.19664286329149	0.08381655063506	1.53977181105690
H	4.56146302804514	0.49583770680244	2.47690905023047
C	4.56980146242876	-0.50128389899555	-0.77407167442217
H	5.22136056826232	-0.53460084660562	-1.64312032837824
C	0.54565228642752	3.10899890070123	-0.62694770208887
C	-3.23651121001710	-0.89793499515845	0.91796305164919
C	-2.85427911553961	-0.42267301457752	-1.46899724398476
C	5.03826849996402	0.01390953948603	0.43217151187121
O	-2.01502317011236	2.28341512539900	2.06464748930788
C	-1.23413975221906	1.92846266412442	1.28442256255140
C	-5.01043359418392	0.03241949003605	-0.45014804185184
C	-4.17144763721870	0.03706862201069	-1.56241758453689
H	-4.53411080401141	0.40709186141987	-2.51773058822038
C	-4.54628141621150	-0.42981928634041	0.77919001865001
H	-5.19721834836736	-0.41441949363996	1.64918705241847
C	-1.92587933342066	-0.39740446281233	-2.65435289489473
H	-6.02929624470549	0.39849870435318	-0.53992715330749
C	-2.70325781330140	-1.35690315632608	2.25055217320220
C	2.71678385417598	-1.45950023987327	-2.20926770140875
C	1.94539157090400	-0.26072496461089	2.64582823568653
H	6.06149576935326	0.37108215372956	0.50666700975126
H	3.44561646808708	-1.29270208442819	-3.00590879853852
H	1.79092383941486	-0.93487545014267	-2.46955062243413
H	2.48691965160487	-2.53072473639351	-2.17511368079543
H	2.49397507884528	0.04591451949344	3.53987330253457
H	1.44772835432332	-1.21528779546529	2.84995788168098
H	1.15853559787559	0.47732435758623	2.44527052792077
H	-1.77726021176221	-0.82799063571572	2.50012648318361
H	-2.47241590810371	-2.42855549047251	2.24674886848536
H	-3.43450681251704	-1.16714052617761	3.03964891525266
H	-1.48252615543818	-1.38309193094800	-2.83614769524929
H	-1.09914494910164	0.30207457788082	-2.47805245467077
H	-2.46205325266101	-0.08593296880962	-3.55412150934091
C	0.24876590237187	4.52742718615265	-0.30781313951703
H	0.82113659429259	5.22368696503971	-0.93148718686508
H	-0.82025095633930	4.72980877282244	-0.44931390723756
H	0.46953401952846	4.73734205225009	0.74580616439794

Int1 (R = Me, R' = Xy)

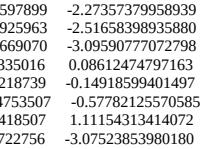


TPSS D3BJ/def2-TZVP
E = −3306.84019528 Eh
G = −3306.46648046 Eh

0 1

C	0.98373738063690	2.94103104991915	-0.05830704172036
C	-0.67359404446549	1.38679283889998	-1.89405962065138
Ni	-0.06417729444426	1.17234986692612	0.06977519014032
N	1.10736988209991	-1.66897069573773	0.06845615363770
N	-1.03649550407711	-1.67480233260346	0.03431405622589
C	0.03347319189401	-0.80833568398547	0.04587538670281
C	0.71399907067076	-3.00549467987126	0.06804232958998
H	1.43255413776548	-3.80853850702228	0.09354296867565
C	-0.63951461253364	-3.00815703144941	0.04752122279770
H	-1.35522840476139	-3.81437711150633	0.05209571639556
O	-1.10369153487510	2.04606322077022	2.68546041930587
C	-0.69026648669803	1.62706657025554	1.68824675050079
P	-1.99023149536470	1.86764387449039	-1.12099681636437
P	2.17353808041911	1.89206773501393	-0.28640568202496
C	-2.41868191727008	-1.27932166554852	0.12546458174843
C	-2.94955555725896	-1.00953248792528	1.39373265966727
C	-3.18660547062716	-1.22907618243616	-1.04648366145589
C	-4.28813675458253	-0.61007383677616	1.46314812834573
C	-4.52511468332351	-0.84377451987963	-0.92884893379600
C	-5.06761259061550	-0.52138312052487	0.31267088078664
H	-4.71680792262031	-0.37129848594665	2.43275611766892
H	-5.13607062015096	-0.77944142709277	-1.82507863981616
H	-6.10407603840695	-0.20414883899582	0.38420999143003
C	2.49058553980535	-1.28479992999569	0.16633913851948
C	2.97705560704318	-0.84979925656569	1.40708563588108
C	3.30113345573669	-1.38909747938043	-0.97138273736245
C	4.32512851483556	-0.48800878018666	1.48379968589230
C	4.64262065470849	-1.01413118962863	-0.85060174739374
C	5.15092950285663	-0.56445671776693	0.36516576379104
H	4.72110988754419	-0.13316171711124	2.43136904055273
H	5.28590407267941	-1.06707072516471	-1.72490991775762
H	6.19326460576288	-0.26826789122114	0.43993153593725
C	-2.13083782452797	-1.19164737130385	2.64523278149306
H	-1.09833006000125	-0.86613637053846	2.50453551078266
H	-2.56301527120489	-0.62492955385675	3.47310040814296
H	-2.10662502788376	-2.25041528728164	2.93423970369951
C	-2.58574248292549	-1.57551493893254	-2.38191397624703
H	-1.68136957493139	-0.98674517214104	-2.55688253992989
H	-2.30840580816091	-2.63526411710190	-2.43319384845631
H	-3.29543967155076	-1.36745416608657	-3.18611289889512
C	2.07077348760039	-0.73307044639220	2.60143415333158
H	1.37148660374678	0.09944984676832	2.45761557943464
H	1.47272660444612	-1.63972874544571	2.74236266098528
H	2.65185823220110	-0.55076368862846	3.50873313862960
C	2.74446602968715	-1.86532060413846	-2.28749366073247
H	2.54273129187986	-2.94310466597899	-2.27357379958939
H	1.79996646268609	-1.36421023925963	-2.51658398935880
H	3.45168892820400	-1.66445796669070	-3.09590777072798
C	0.36894391858216	4.27018308335016	0.08612474797163
H	1.07857270054647	5.07223841218739	-0.14918599401497
H	-0.50109068477941	4.35827564753507	-0.57782125570585
H	0.00385627933731	4.41547663418507	1.11154313414072
C	0.15928930309670	1.11133789722756	-3.07523853980180
H	0.32500901545926	0.03166880705200	-3.18845136623653
H	-0.30561249756317	1.48418237579682	-3.99600338629992
H	1.14753725567274	1.57473054872215	-2.96046821546585

TS1 (R = Me, R' = Xy)



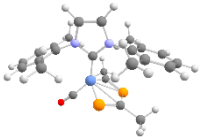
TPSS D3BJ/def2-TZVP
E = −3306.81766683 Eh
G = −3306.44538219 Eh
im. freq. = −178.82 cm^{-1}

0 1

P	1.69801940166663	-2.65862613415458	-0.63871938004647
C	0.27379873008815	-2.26569015012668	-1.32919301344960
C	1.76115878764832	-1.75328024418506	1.61174081282237
Ni	-0.19202938584541	-1.26829804698646	0.27220829728862
N	0.99798242237549	1.51266571996852	-0.27959544759455
N	-1.14555586873610	1.47948366982413	-0.31369489008182
C	-0.06175177461568	0.64269856570037	-0.17894909754024
C	2.38116430414264	1.11753834772933	-0.25575964996759
C	3.13728303707004	1.37059268272330	0.89723697725678
C	2.92710331592309	0.54503948813799	-1.41282122827070
C	-2.51161413319411	1.02643585252314	-0.32608418661540
C	0.58488120549269	2.83002023181279	-0.46826411784488
H	1.28993694820251	3.63846035912683	-0.57662303741306

C	-0.76980130301361	2.80789114018867	-0.49147461601664
H	-1.49620402943704	3.59439268639031	-0.61782128306965
C	4.27551444186194	0.17465158251901	-1.37872578080518
H	4.71756369221585	-0.28576999287005	-2.25793775287829
C	4.48583751350576	1.00056566596499	0.88141962994049
H	5.09079714185773	1.17625854392210	1.76706956752132
C	-3.09168350519100	0.70267303147720	-1.55932610748548
C	-3.20614319236636	0.93800332973554	0.88737195386278
C	5.04915776562712	0.40040705490759	-0.24250526281101
O	-2.73786163931409	-2.59349252488146	0.79261830472972
C	-1.69776514007296	-2.10715850813403	0.62701955896698
C	-5.12432637408214	0.13482207037751	-0.36370595384606
C	-4.52754578165901	0.48516890417013	0.84501968822709
H	-5.08310591811128	0.39315925343910	1.77428261185842
C	-4.41297659165089	0.24546506295752	-1.55575365766014
H	-4.88095857543424	-0.02821971870401	-2.49782757633629
H	-6.14746456592412	-0.22975673685727	-0.37602493785073
H	6.09547356149138	0.10812147678895	-0.23319824249324
P	0.54703344806133	-1.03226877510713	2.40893940934366
C	-2.53847654503362	1.29080894929566	2.18928160825152
H	-3.24568477026676	1.20743155602301	3.01803210781862
H	-1.69645413762243	0.61648206340324	2.37849082023629
H	-2.13938769547580	2.31126903892773	2.17359075003162
C	-2.32200020880751	0.85838646716395	-2.84507039495575
H	-2.79361729818649	0.28534862656288	-3.64752767248989
H	-2.28692450189029	1.90947462658901	-3.15825043960736
H	-1.28786247260282	0.52259253468337	-2.73056456112759
C	2.10075456937283	0.38234639543088	-2.65952310516229
H	1.78015056216574	1.35850289708869	-3.04391612538022
H	2.67732034181689	-0.12411378339642	-3.43708273604078
H	1.20428679589118	-0.20754472849156	-2.45127632393201
C	2.52236309529080	2.02284939723424	2.10673651630019
H	1.58580352628626	1.52577792222742	2.38062680487210
H	3.20463267671688	1.96727848457873	2.95841924012090
H	2.29379640577424	3.07899631300223	1.92014194970204
C	3.15604074519341	-2.23023789825913	1.83398171131577
H	3.47463304000711	-1.99443795372115	2.85545315096866
H	3.23139596813197	-3.31399016831492	1.68090598323268
H	3.84728484528970	-1.75540087829799	1.12873374425281
C	-0.54438980905005	-2.51536572473232	-2.54362291617574
H	-0.75224615724332	-1.57532647927889	-3.06783841735965
H	-0.05793610049228	-3.20323003351296	-3.24457799041359
H	-1.51933744384835	-2.92937110258397	-2.25888894619955

Int2 (R = Me, R' = Xy)

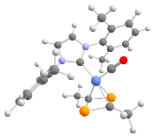


TPSS D3BJ/def2-TZVP
E = −3306.83038955 Eh
G = −3306.45620718 Eh

0 1

P	1.84538660565778	2.39601461333688	0.48745579061623
C	0.40444865660595	1.98328998498904	1.28359177847807
C	1.80911630221788	1.78415937306334	-1.28072945695317
Ni	-0.41123861977490	1.03087388173534	-0.12658112582663
N	0.77751663109448	-1.74860981894395	0.34562115373028
N	-1.36875785305060	-1.62054329466755	0.27282583240554
C	-0.23983122527309	-0.84532939223645	0.18355255926338
C	0.28957590565830	-3.04135795918775	0.53805617033391
H	0.95177155803570	-3.87715086467144	0.69598455098512
C	-1.06289157773247	-2.96029590465963	0.49169058708488
H	-1.82963083199921	-3.71087000674247	0.59536772808172
O	-2.56003132615414	2.81926595175158	-0.89764271970362
C	-1.65017318820550	2.15608795607942	-0.62989168530556
P	0.57072428726465	1.02084909761815	-2.14587152417128
C	2.17978644412715	-1.41920943905902	0.32838134716902
C	2.75481106724160	-0.89543749766805	1.49258926531179
C	2.91213023518460	-1.66265175641767	-0.84185684828237
C	4.11478018394645	-0.57266052508261	1.45490033318644
C	4.27260105214044	-1.34037523779180	-0.83000639850446
C	4.86733405864913	-0.79227744349797	0.30436295727791
H	4.57942977822289	-0.14434979892944	2.33853754932487
H	4.86178302748824	-1.51121577529414	-1.72709584859625
H	5.92264159993556	-0.53468086025349	0.29084865765647
C	-2.69172411132897	-1.07348948765165	0.12272616886447
C	-3.26173459453880	-1.05285187638511	-1.15687640998164
C	-3.33383738531368	-0.55731246243374	1.25545091278099
C	-4.53888755992294	-0.49880093636680	-1.28442872552535
C	-4.60826003908008	-0.00956122517976	1.08232847980946
C	-5.20580994782888	0.01817130289084	-0.17592833971354
H	-5.00205756639169	-0.45972028762251	-2.26661164305042
H	-5.12603832030024	0.40774915216606	1.94182912330896
H	-6.19310200027869	0.45502812201832	-0.29513242074224
C	1.93777823274053	-0.71141081417473	2.74228454559663
H	1.01039782526621	-0.17749424122476	2.51911855733531
H	1.66828785169165	-1.68120465725853	3.17920527083278
H	2.49885593562534	-0.14194416931785	3.48670990476957
C	2.25672278365892	-2.22940236580019	-2.07236368116481
H	2.99917158108465	-2.40304872087265	-2.85508922167025
H	1.74500568098193	-3.17486535673058	-1.86265843458679
H	1.50528190203808	-1.52923385061692	-2.46011692903258
C	-2.65217203662269	-0.57321527501869	2.59803011768944
H	-2.49310758539775	-1.59746525631177	2.95536719080409
H	-1.66881082723146	-0.09586200265629	2.52765033631342
H	-3.25055469310942	-0.03895845773390	3.33985577273754
C	-2.50068964957065	-1.56880649288759	-2.34957401783219
H	-1.56853867257029	-1.00638527588056	-2.47585713288599
H	-2.23126592190764	-2.62462668305642	-2.23206469759304
H	-3.09651439832504	-1.46359577888698	-3.25929930900989
C	3.14394000294049	2.11566663098506	-1.93565342005887
H	3.12668913845538	1.89158962758851	-3.00672735834950
H	3.38125378821452	3.17865124127032	-1.79993279682365
H	3.94871515928166	1.53544437739250	-1.46916755102186
C	0.03867734686809	2.45230047042299	2.65457812993395
H	0.82955766841174	3.03121706248492	3.14827942057880
H	-0.86061944258424	3.07963157825659	2.59360808343032
H	-0.22591391623692	1.60633282512157	3.30240942069458

C (R = Me, R' = Xy)

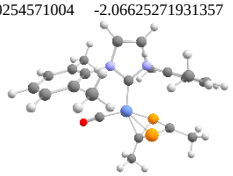


TPSS D3BJ/def2-TZVP
E = −3306.88955632 Eh
G = −3306.51004258 Eh

0 1

Ni	0.20128550544564	1.06625739675250	-0.16346811816514
N	-1.08285661234931	-1.67219665931236	-0.10331589437339
N	1.05842561552296	-1.72153381945920	0.10643328218552
C	0.01039024428320	-0.84027106462817	-0.00942440652518
C	-2.45213008669779	-1.26472857982354	-0.28505694522813
C	-3.37383061470593	-1.54196735496667	0.73788137247744
C	-2.82917737137022	-0.67463666957998	-1.50184488085865
C	2.44787236867226	-1.34603189052239	0.17913092038771
C	-0.71350031686569	-3.01503658000181	-0.04647986585280
H	-1.44395325003486	-3.80454665818816	-0.11008742920928
C	0.63328971922677	-3.04526508717490	0.08463035760536
H	1.32698815648665	-3.86593790680874	0.16725784148264
C	-4.16446435261611	-0.28646374634426	-1.64485112039033
H	-4.47407692622786	0.18827883632761	-2.57166708221921
C	-4.69924374893125	-1.13782467706881	0.54657046010390
H	-5.42417247567844	-1.32230404179889	1.33512387970781
P	-1.66237083361529	2.41655386566553	-0.02833443963347
C	3.23251353663812	-1.49391237696920	-0.97345907859217
C	2.96540328176969	-0.89378159558353	1.40055504178130
C	-5.09000488853707	-0.50224523281020	-0.62815542420591
O	2.06342053468027	1.27326720867830	-2.39915529997107
C	1.33550712132192	1.15647292235091	-1.50597728759955
C	5.11762849508211	-0.65549558668615	0.30315299791172
C	4.31778184110503	-0.54388024378942	1.43816069878374
H	4.74017033342162	-0.17756199006517	2.36980817103216
C	4.58025035814776	-1.13200780052979	-0.88976380627775
H	5.20457782483300	-1.21677303717193	-1.77511403248678
C	2.09322337927610	-0.76409171105266	2.61699291049051
H	6.16520613913022	-0.37175523973700	0.34922805112147
C	2.65017226243081	-2.01583622556317	-2.26264538040804
C	-2.98452899766965	-2.27081082028253	2.00159705174536
C	-1.85101333835583	-0.47086613943207	-2.62468063270573
H	-6.12084721524625	-0.18478468074621	-0.75604570161300
C	-0.91189190474334	1.69263652394216	1.46516959147726
P	0.66288714181399	2.56613123428999	1.52514627591501
C	0.00183460004935	3.11470810457408	-0.08623541116720
H	-3.64686063865739	-1.98276785310909	2.82251841036723
H	-1.95454152534079	-2.06069058802718	2.29762702451149
H	-3.07561603737695	-3.35670614238826	1.87202590402703
H	1.43798152421533	0.10805745182304	2.50149899254110
H	2.70112903667434	-0.62391927738079	3.51411121587662
H	1.45753181675183	-1.64511117879131	2.75428013470240
H	-2.38329683364702	-0.27958713371806	-3.56007803140080
H	-1.20735083581993	-1.34683629427437	-2.75811168613378
H	-1.20176138466007	0.38467584974715	-2.40177177255644
H	2.53226593002653	-3.10617607533373	-2.23349671398268
H	3.30641759306047	-1.77010029165858	-3.10079690782103
H	1.66385572811264	-1.58738544020023	-2.46055294664379
C	-1.55579976929945	0.84803260665762	2.51696373036398
H	-2.41698631573453	0.30573843882000	2.11980586841407
H	-0.85648543179779	0.13138943672015	2.96181731160860
H	-1.91965254598401	1.49616147023795	3.32515825437474
C	0.58682828068543	4.09598683286892	-1.05631800368159
H	0.33764463812101	5.11426901954088	-0.73047273252572
H	1.67882188284731	4.02329494627170	-1.10497299945397
H	0.18367736213048	3.96140254571004	-2.06625271931357

TS4 (R = Me, R' = Xy)



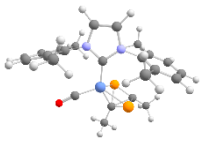
TPSS D3BJ/def2-TZVP
E = −3306.84607287 Eh
G = −3306.46916340 Eh
im. freq. = −109.80 cm^{-1}

0 1

Ni	-0.45635645686696	-0.77665581520070	-0.15382735889352
N	-1.51465646484629	1.78557360320728	1.00939415128510
N	-2.31056253650492	0.04010541333131	1.97365732560100
C	-1.46013955797114	0.41124533646598	0.95497646902762
C	-0.79680034991175	2.67080914175682	0.13743496837799
C	0.40165745759098	3.23132050563584	0.59530178333725
C	-1.34020496918825	2.95211233238103	-1.12272608112767
C	-2.63078131144212	-1.31739115962673	2.32341738505035
C	-2.35984030663810	2.24017072149984	2.01856727079471
H	-2.51514106288853	3.29169852594650	2.19797223968689
C	-2.86264485501831	1.13861179436131	2.62521804712965
H	-3.54830073446074	1.02481151039446	3.44916493251777
C	-0.63082469373543	3.82689726192146	-1.95229021305255
H	-1.02259625478607	4.05220640768288	-2.94033922554108
C	1.07172923015625	4.11211193952775	-0.26032896976969
H	2.00701164914844	4.55873432356645	0.06711056126696
P	0.33555639671216	0.31924415286456	-2.09204421864219
C	-3.81897652833175	-1.86597247749350	1.82406005760693
C	-1.75369572323567	-2.02488189660197	3.15558442930518
C	0.56290489690843	4.40438158979029	-1.52356125337323
O	-1.67603983051249	-3.43077331700935	-0.28618702513280
C	-1.23470053966410	-2.36169348968655	-0.18157356798001
C	-3.28586408840548	-3.90305380897775	3.02652871310999
C	-2.10440334104433	-3.33422723120285	3.49734786590596
H	-1.43766681509651	-3.90995569825519	4.13387458055837
C	-4.13481625133406	-3.17545036733956	2.19612661081586
H	-5.04406198119279	-3.63013105851914	1.81223973856460
C	-0.46803200406512	-1.40015672409062	3.62556899174387

H	-3.54051194188677	-4.92324936533639	3.29932550933461
C	-4.68624739395145	-1.08741150598098	0.86917418656794
C	0.94948002968163	2.88487031937159	1.95536462125361
C	-2.63020879167538	2.31428778928085	-1.56353900038194
H	1.10071417838251	5.08364683825390	-2.17913426266137
C	1.76107835696863	0.75561023730636	-1.10006674741254
P	1.81390745807679	-0.36490741791818	0.30779628031600
C	1.06512505405756	-1.16684913046608	-1.20551320040180
H	-2.91019083194234	2.66120128956952	-2.56095474701965
H	-3.44593497754287	2.54731520996419	-0.86946330536878
H	-2.51831768432439	1.22393247031141	-1.58591217416339
H	1.96589069204773	3.27034097893079	2.06913601613440
H	0.96764920006434	1.79938567869014	2.09928368894456
H	0.33311896316670	3.31014915856752	2.75664406225553
H	-5.53831689693079	-1.69091089950051	0.54707582938894
H	-4.10995469711656	-0.79662555446531	-0.01678769820852
H	-5.06783711396563	-0.16524741339599	1.32221541418521
H	0.16037237489384	-1.14505787643617	2.76319745505444
H	0.08019482467735	-2.08841463324490	4.27353766518460
H	-0.65167212543252	-0.47210993227118	4.17960080648010
C	2.93992910947418	1.54880989361345	-1.59046712733266
H	3.44463830752866	2.05015220634795	-0.75776517593144
H	3.66889551137115	0.86403677698730	-2.04400117553973
H	2.64422923486701	2.28193951548828	-2.34528509058401
C	1.67326449258151	-2.34560257403592	-1.91517449387888
H	2.61203322531995	-2.06614038686643	-2.40739165110040
H	1.88778092582624	-3.14734548570384	-1.20184802327884
H	0.98742032407053	-2.72362062339123	-2.67942298000935

Int4 (R = Me, R' = Xy)

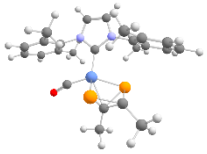


TPSS D3BJ/def2-TZVP
E = −3306.85077494 Eh
G = −3306.47447032 Eh

0 1

Ni	-0.12681960737193	0.98184285043035	-0.29895888718121
N	-1.65567877260118	-1.46111258749156	0.27594006786858
N	0.45233853188060	-1.88186462732778	0.19285621995209
C	-0.44367414808406	-0.84408414903513	0.05678320679643
C	-2.93067565846693	-0.79765749643354	0.25971011807390
C	-3.34702142891060	-0.12008178624347	1.41317290753488
C	-3.70362323918001	-0.86691197852536	-0.90628319262357
C	1.87426706272642	-1.74086435534666	0.06387902839341
C	-1.50955059159734	-2.82163870740850	0.53391082628042
H	-2.35918543278922	-3.45521550779627	0.73013336472350
C	-0.18203946660815	-3.08619538064253	0.48260043645381
H	0.37194663391160	-4.00001793441314	0.62363147485787
C	-4.95273189309906	-0.24040069815647	-0.89307929543264
H	-5.56767918632349	-0.26781833054147	-1.78855345330362
C	-4.59939293075435	0.49896711324583	1.38105729379146
H	-4.94348708498905	1.04046245359883	2.25819199352427
P	1.14365047586450	1.77449085410795	1.44306002734936
C	2.43874850085133	-1.84156858130093	-1.21676245752545
C	2.63561859800598	-1.51830000005075	1.21676419546046
C	-5.39733705796992	0.43568189079051	0.24052365761590
O	-2.57788025518041	2.30234088300730	-1.25441524743958
C	-1.66421575885368	1.70661204345206	-0.85736586392772
C	4.60742848747013	-1.45435385985884	-0.19934527277061
C	4.01952701310646	-1.37818536441639	1.05998386870814
H	4.63393966513836	-1.19555167344549	1.93800143409731
C	3.82409384606927	-1.68707022382292	-1.32909677788605
H	4.28493941110688	-1.74449575609893	-2.31123638038580
C	1.99319729084577	-1.45138597563265	2.57790826768841
H	5.68174345831868	-1.33062639862252	-0.30335724456393
C	1.57207565492890	-2.10194141118171	-2.42041045400084
C	-2.45362251852648	-0.03966461983433	2.62162595606829
C	-3.16958536872138	-1.53742843457304	-2.14557372315086
H	-6.36650890415906	0.92622541188300	0.23116193051964
C	2.50173532076764	1.70526313192107	0.24594428589532
P	1.87801373801237	1.20972938869082	-1.36491892095703
C	1.10779357372604	2.52121611074563	-0.25893992264816
H	-3.88718666551474	-1.45429870806020	-2.96531469076534
H	-2.95854189301599	-2.59965870134104	-1.97770174884489
H	-2.22971486110585	-1.06567190897752	-2.45486416581974
H	-2.93993232118842	0.52012326060009	3.42420126769153
H	-1.51333471020457	0.46027015817880	2.35857332721559
H	-2.19811575106119	-1.03705435342867	2.99833045260898
H	2.16403010034250	-2.05180455089814	-3.33715537763853
H	0.76723397703270	-1.36070904175001	-2.47827284395821
H	1.10398411761949	-3.09198664248262	-2.36383817201664
H	1.04283817926081	-0.91204465608867	2.53817320168046
H	2.65239968672407	-0.94574797182147	3.28808468722159
H	1.78726713456263	-2.45712273680992	2.96637573614885
C	3.84670474299886	2.35235055313394	0.47665005650775
H	3.78462141715272	3.15342705878457	1.22064057697512
H	4.53418323277181	1.58948914443983	0.85687061254882
H	4.26502737150050	2.74930772101464	-0.45378573603847
C	0.96146390955960	3.98748343713659	-0.59477851899530
H	0.17927798572079	4.44316506468936	0.01821625937353
H	1.89952726880589	4.52297333489642	-0.40810226881320
H	0.69700411949377	4.11634524511106	-1.64769712293830

TS5 (R = Me, R' = Xy)

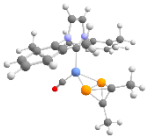


TPSS D3BJ/def2-TZVP
E = −3306.84200743 Eh
G = −3306.46550734 Eh
im. freq. = −119.81 cm^{-1}

0 1

Ni	-0.21122899987610	1.21308166961200	0.16966786552443
N	1.05120351214628	-1.45337309247730	-0.27927528414495
N	-1.10310960716135	-1.52970469490834	-0.32196713688324
C	-0.06117188951412	-0.65172302053770	-0.08769444100381
C	2.42610622701081	-1.04359633060311	-0.19898428662430
C	2.99504935553357	-0.38314892766471	-1.30035944123582
C	3.15095678171834	-1.35949068378466	0.96054928379820
C	-2.50028757354049	-1.19602647785866	-0.30307277302236
C	0.70037830750697	-2.75898027822282	-0.61290530065904
H	1.44693232715713	-3.51113378117336	-0.80978481552242
C	-0.65187197633606	-2.80520409172184	-0.64124278802280
H	-1.33683245367190	-3.60643750092319	-0.86685963003921
C	4.49437934646728	-0.98138963815330	1.00867615473245
H	5.07320612116619	-1.19611564668296	1.90292389764403
C	4.33894637868522	-0.00731270274669	-1.19993359387026
H	4.79943254945832	0.52453997212390	-2.02821502924914
P	1.80639007857089	1.66154463323792	0.88731460999775
C	-3.23390971025830	-1.45630513723053	0.86151099431722
C	-3.07068564367830	-0.65148679922754	-1.46286977699181
C	5.08151174191296	-0.30434647810820	-0.05966130706141
O	-2.97772125594314	1.92171407162162	0.85524639196206
C	-1.94880404985813	1.50567890134247	0.52633979808812
C	-5.19626627448415	-0.62075942066988	-0.29265337629804
C	-4.43861840305085	-0.36720938012629	-1.43419286127792
H	-4.90618536255217	0.06762615695611	-2.31349919657645
C	-4.59936523223767	-1.15938317938546	0.84513407211099
H	-5.19101905059050	-1.33883563854319	1.73885672696671
C	-2.21843510832221	-0.34206007202510	-2.66420553010305
H	-6.25722095853095	-0.38777167258982	-0.28642732438573
C	-2.55504286928594	-1.98752711846304	2.09690941617009
C	2.16442962786855	-0.05079667723750	-2.50575245093204
C	2.47186528951547	-2.00816869242495	2.13760568617949
H	6.12389616803576	-0.00423337435606	-0.00073368248611
C	1.83515515945095	3.07656022378872	-0.23337428889297
P	0.25116501372860	3.01973118435090	-1.16467360673062
C	0.57115584515882	3.04172895413336	0.72947225596499
H	3.17598322884114	-2.13777804404052	2.96285304551763
H	2.05454595042865	-2.98825923983050	1.88106686021500
H	1.63886773510785	-1.38483355464313	2.48362236697819
H	2.78181656638732	0.39381553364286	-3.29000866240821
H	1.37417839830553	0.66292522437097	-2.22444095959142
H	1.66892371236689	-0.94146044343358	-2.90784036121793
H	-2.07574484335771	-2.95545211243664	1.91144010752877
H	-3.27653691522162	-2.10961595956324	2.90840079848225
H	-1.77013145220050	-1.29744068825203	2.42772901137440
H	-1.45178686326670	0.39641513818834	-2.39453653702385
H	-2.82897320041187	0.06140402010235	-3.47551960643921
H	-1.69808178394016	-1.23505947384267	-3.02931190480676
C	2.81793602958692	4.21199552853086	-0.21595558833496
H	3.57852405402801	4.06178898786164	-0.98964068366606
H	2.30363518125781	5.15727281214022	-0.43387937737934
H	3.32670070157442	4.29923388448073	0.75190364505555
C	0.14392445470729	4.09730471758113	1.71697741845251
H	0.60154343029364	3.93914544722635	2.69880390486756
H	0.42739039807308	5.09153765951401	1.35113827832435
H	-0.94182194475981	4.08684191308202	1.84163796262847

D (R = Me, R' = Xy)



TPSS D3BJ/def2-TZVP
E = −3306.87489300 Eh
G = −3306.49987088 Eh

0 1

Ni	0.03479689210796	0.35897382062552	1.06453728418869
N	1.27527369870197	-1.69967755471095	-0.73000026907703
N	-0.86809293705301	-1.79986518119287	-0.80853702401470
C	0.15293047853512	-1.11254453746063	-0.19950973263116
C	2.60266850014681	-1.27841785701711	-0.37465892858914
C	3.27576710977223	-0.39495004777981	-1.22887784136070
C	3.14866583894180	-1.73895823686324	0.83080243286931
C	-2.25159421176813	-1.50391846682612	-0.55554770460754
C	0.95968786426417	-2.71267381379502	-1.63387677816089
H	1.71998442337228	-3.28763590726033	-2.13751119791137
C	-0.39433414208342	-2.77599933832579	-1.68332738760618
H	-1.05951294865064	-3.41735244538965	-2.23877201420312
C	4.42817459098501	-1.29097412948096	1.17347224084644
H	4.87367798227204	-1.62815343986090	2.10559001026272
C	4.55385326912268	0.02580192017966	-0.84944201872921
H	5.09348547929395	0.71945874490915	-1.48877560116876
P	1.15663565492993	2.16796513738859	0.35268463290141
C	-2.84401453530514	-2.01834986055202	0.60563399754851
C	-2.93557679398240	-0.68302572423761	-1.46166809741709
C	5.12534633728591	-0.41810167508499	0.34109435058242
O	-0.10200317185201	0.33330242574066	3.99819337447288
C	-0.04633074202341	0.27890501059685	2.83958306104228
C	-4.88972578507866	-0.88142407491532	-0.03773381376450
C	-4.27232469337801	-0.38323411763870	-1.18300813361223
H	-4.82347537990598	0.25889795330960	-1.86489405881466
C	-4.18125835302126	-1.68988196692572	0.84844695095759
H	-4.66389936156306	-2.06994531895939	1.74491866776571
C	-2.23449508520010	-0.10830142216743	-2.66506864982722
H	-5.92701813874527	-0.63300870644641	0.16851028395972
C	-2.05516760160253	-2.87460914543244	1.56129780777769
C	2.62186929402590	0.11244359717681	-2.48795272895305
C	2.36935860792723	-2.66247567451956	1.72994756439765
H	6.11669613275451	-0.07621387156261	0.62491680189021
C	0.03387566035152	2.94551287563793	-0.89826556241460
P	-1.14992553743680	2.07533224239018	0.23118100719201
C	-0.06291618619657	3.55439159037092	0.44350037281328
H	-1.38296005097613	0.50613649600002	-2.35112018266164
H	-2.91813445388881	0.51943794430592	-3.24187761377673
H	-1.84536079941189	-0.89305734449172	-3.32321040769007
H	3.25199054096984	0.86480135534355	-2.96835868575830
H	1.65194683942901	0.56660182352183	-2.25843614021936
H	2.44165411426136	-0.69584150530777	-3.20609428091901
H	-2.68729368196740	-3.21337068899767	2.38576213960176

H	-1.21297121261152	-2.30579889160323	1.97166830291547
H	-1.63847817837840	-3.75427639271099	1.05741159864852
H	2.97805840524508	-2.97299804272292	2.58270147210052
H	2.03754363999985	-3.55772399163578	1.19212719874630
H	1.47074140606045	-2.15701572521672	2.10252165354437
C	-0.14887517017083	4.93855224715364	0.99347048143406
H	0.73595017204848	5.52281977724552	0.71254710927908
H	-1.03523469877962	5.45511320513411	0.60513711242502
H	-0.21482078339751	4.92110585514704	2.08560649942953
C	0.08308393614808	3.45414271408810	-2.30004438479874
H	-0.81693268881308	4.03643968516797	-2.53379959926872
H	0.95512470548810	4.10319187420843	-2.44856946677790
H	0.14929128880031	2.63067188145035	-3.01912299485951

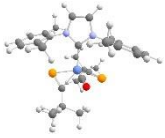
B (R = *t*Bu, R' = Xy)

TPSS D3BJ/def2-TZVP
E = −3005.43964642 Eh
G = −3005.02537803 Eh

0 1

Ni	-0.00367076295086	0.79953942933357	0.16038289792784
P	1.50258231017484	1.26247437982159	-1.42540163412531
N	0.78911220488333	-2.09695669350681	0.02193324370121
N	-1.33412076591035	-1.84287720518741	-0.17819826636099
C	-0.17890449136750	-1.12553845795262	-0.00941662006498
C	2.19421557306729	-1.81744353631616	0.15295555186216
C	3.00719189619229	-1.94619725277496	-0.98176057392637
C	2.68538137780901	-1.40569966914339	1.39869980988511
C	-2.63023537380623	-1.22505400591080	-0.26718161894445
C	0.24751746556797	-3.37273665797263	-0.11871374243214
H	0.86291480469030	-4.25764256803597	-0.10836316901234
C	-1.09311344308606	-3.21245742052098	-0.24776162986430
H	-1.88891374781904	-3.92694036290035	-0.38247191597964
C	4.05179079095067	-1.12593586332886	1.49449256671681
H	4.45677857701591	-0.79950999529299	2.44866063200996
C	4.36790757128662	-1.66005518018152	-0.83959399759005
H	5.01667379648261	-1.73792898550130	-1.70786685418924
C	0.79735741143157	3.83849142524099	-0.05495768136684
C	0.84457081555002	2.39557025852680	-0.44240814412891
C	-3.45392074026252	-1.23861834926884	0.86632555264555
C	-3.00017983701351	-0.61577784527729	-1.47383911035282
C	4.88695103175809	-1.25389478123959	0.38736229090107
O	-1.89389310807881	1.60544118078892	2.22767749400580
C	-1.13218425618009	1.28962434268022	1.41134672907729
C	-5.10115752852796	-0.00748694249251	-0.41995151080676
C	-4.25729537874460	-0.00577820238500	-1.52833499294009
H	-4.56890908588300	0.47785029607109	-2.45029165095713
C	-4.70219359534707	-0.61780056178764	0.76688945446429
H	-5.35485349690585	-0.60052664381592	1.63555430020111
C	-2.06751165295931	-0.59805158567732	-2.65570855133805
H	-6.07213482924128	0.47608955606862	-0.47886408146594
C	-2.98668439760768	-1.86020176733702	2.15739397434168
C	2.42543854979905	-2.32464049766631	-2.31921859081923
C	1.76849034324009	-1.23354386856165	2.58032323734855
H	5.94550695501371	-1.02765779578899	0.47870822577455
C	-0.63834840712102	4.37130725581351	-0.25452200512682
C	1.77511796540133	4.65183356144265	-0.92885100133374
C	1.19357127941693	3.98180221788589	1.43080900167386
H	-0.68218458390332	5.43175007140351	0.02106003026156
H	-1.34663314510633	3.81774312603175	0.36766371590803
H	-0.94480707377798	4.26866458060864	-1.30025405639759
H	1.75101629851337	5.71197417933976	-0.64878701480023
H	1.50596213569303	4.56267275145852	-1.98597728285939
H	2.79679883975856	4.27960647551206	-0.80422615175675
H	1.16568977042282	5.03827077914148	1.72328802413977
H	2.20551925573991	3.59901690893348	1.59720642719739
H	0.50455328794657	3.42235213226637	2.06935117994342
H	3.17649270875812	-2.21188168431446	-3.10469936165227
H	1.57079735863981	-1.68341444456511	-2.56131920401698
H	2.07032842175995	-3.36151186323013	-2.33364683563296
H	2.34570523150966	-1.06789160769039	3.49341476232243
H	1.12674653540745	-2.10973077099973	2.72289627213999
H	1.10697876934883	-0.37227954097945	2.42045007952967
H	-2.00424608767254	-1.46906885549330	2.44188284141185
H	-2.88997871363930	-2.94885647799713	2.07153256587373
H	-3.69267614098184	-1.64252080731179	2.96211479945494
H	-1.69125187922918	-1.60138352849198	-2.88411433619794
H	-1.19502069588934	0.03385631869920	-2.44643656496292
H	-2.57780811421713	-0.20720395017028	-3.53954950931446

Int1 (R = *t*Bu, R' = Xy)

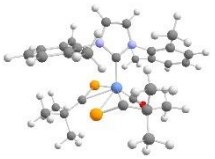


TPSS D3BJ/def2-TZVP
E = −3542.86574385 Eh
G = −3542.33230591 Eh

0 1

C	-1.53848430739506	2.07400255682762	-0.50730343523814
C	0.67729331834323	1.38212838880554	1.52951605951556
Ni	-0.03864184244167	0.66457394859310	-0.34719222358163
N	-0.56299722488512	-2.37870153365067	-0.09673328039813
N	1.53126032544094	-1.92972936169930	-0.16161679926332
C	0.30189644430607	-1.30581027683832	-0.15025283013344
C	0.10593511883307	-3.59994225222372	-0.06872474877160
H	-0.42658503850189	-4.53617167034808	-0.02989207767173
C	1.42773580291641	-3.31597557727110	-0.11032108422693
H	2.29949992671111	-3.95012896853175	-0.11783348450581
O	0.92106801353638	1.24649195105603	-3.07210952316843
C	0.52358661057084	0.96523678964989	-2.02021365713886
P	1.84483043456891	1.80062608595518	0.51866015741227
P	-2.33863429748882	0.82661942448513	0.11560236444163
C	2.80366468719333	-1.27297075794028	-0.31688239973113
C	3.27610492365996	-1.02856611489544	-1.61269808242141
C	3.54610085041215	-0.96788271001233	0.83278037216069
C	4.50691445860153	-0.37472090403984	-1.73831549047631
C	4.77961181743834	-0.33447200566335	0.66118405310926
C	5.24790912167122	-0.02320436646504	-0.61340241722462
H	4.88287624270376	-0.14621563710297	-2.73200725639284
H	5.36302569927350	-0.06888781526018	1.53840634812176
H	6.19823258799579	0.48977280986897	-0.73045241796313
C	-2.00034620501317	-2.32122670744122	-0.12817919298070
C	-2.63160582281321	-2.01146478699281	-1.34386879070517
C	-2.71541578493083	-2.62728686647732	1.03780116815494
C	-4.02795464130628	-1.96642761741422	-1.35698885135990
C	-4.11207216876775	-2.55925709736739	0.97969590124136
C	-4.76376268218072	-2.22633236504602	-0.20334009904214
H	-4.53610063813268	-1.71204950488639	-2.28304977957895
H	-4.68708290434104	-2.76712862103904	1.87837591865025
H	-5.84826389288473	-2.17110232951697	-0.22783361691701
C	2.52537076821107	-1.50199982196896	-2.83045075074727
H	1.44579460577250	-1.49517310831130	-2.67098452658913
H	2.75063808577456	-0.87048437358689	-3.69257160677662
H	2.81806664638339	-2.53090310879645	-3.07704781517490
C	3.02286781836930	-1.31536357550345	2.19800080314902
H	2.01505616555944	-0.91114695237634	2.33003819008045
H	2.96534304288993	-2.40145795323346	2.33884732311677
H	3.67048668735138	-0.90188329059105	2.97458054156656
C	-1.83942724946869	-1.69652372891586	-2.58182246394479
H	-1.38930642918893	-0.70069754213915	-2.49034701659654
H	-1.02264195770403	-2.41035197347978	-2.73077299708960
H	-2.48533131386270	-1.71073477349539	-3.46323601732659
C	-2.02892344037038	-3.03498885891225	2.31697710839691
H	-1.96926820699378	-4.12834383788611	2.39333490196264
H	-1.01292856662719	-2.64335666662264	2.37680514629320
H	-2.59110249375548	-2.67493923938638	3.18297031788737
C	-1.57385667892556	3.45495124074843	-1.07283850653227
C	0.08352048935424	1.40945275499835	2.89708217605113
C	-2.66702345347144	4.25671842184609	-0.32809958029076
H	-2.42014347530337	4.34922716847172	0.73344526609547
H	-2.75052527920995	5.26322130877691	-0.75610874679842
H	-3.63455598879483	3.75340474593227	-0.41550772979492
C	-1.96086453258681	3.35615808998376	-2.56906120500046
H	-2.01837679233679	4.36362420786302	-2.99871415889794
H	-1.21970725599079	2.78358662197968	-3.13134270721498
H	-2.93416498388786	2.86869769124557	-2.67782629167381
C	-0.22908217672523	4.19044868578306	-0.93943205813506
H	0.55917947947515	3.66577377087015	-1.48575941588325
H	-0.32050645370570	5.20431584839267	-1.34668918434448
H	0.07488954851838	4.25914528099642	0.10849261016526
C	-0.91178381648582	2.59035640430588	2.99828913554312
H	-1.74592974087881	2.45268536673315	2.30797264662313
H	-1.30033632423782	2.64903458862263	4.02240405528397
H	-0.41010180516153	3.53260282238844	2.75760409335771
C	-0.65209532167768	0.09821452868859	3.22526992338756
H	0.04375662915129	-0.74647193227595	3.21540281704857
H	-1.10460775875481	0.15817368743454	4.22211587478221
H	-1.43622747258420	-0.09206024919698	2.48781571505971
C	1.21593156699603	1.63455911721454	3.92641002239307
H	1.94088199476120	0.81672743899242	3.89082998583933
H	1.74240975080562	2.56988566219300	3.71378144988216
H	0.79632675622315	1.68693642509937	4.93866187093005

TS1 (R = *t*Bu, R' = Xy)



TPSS D3BJ/def2-TZVP
E = −3542.84093035 Eh
G = −3542.30772008 Eh
im. freq. = −80.94 cm^{-1}

0 1

P	1.37485435704613	2.20373825646629	0.73322505509538
C	-0.23631355626916	2.02723383606267	0.89614632452843
C	2.21217410561371	0.89989898378492	-1.37298604461327
Ni	-0.18786450577513	0.70022721676774	-0.54828281483790
N	0.33678306924267	-2.07042342007673	0.69521626516277
N	-1.72374805980315	-1.76531615592587	0.17986445342445
C	-0.51579246703765	-1.09371605528646	0.22275268294889
C	1.74702686645870	-1.92754798186225	0.95097545379653
C	2.65282152458238	-2.54919474894668	0.08016481938548
C	2.15097942276675	-1.27295140384606	2.12273304375325
C	-2.98307741103136	-1.20927808209359	-0.24288780865115
C	-0.31516849632033	-3.27829238635454	0.93171796674931
H	0.20914171395425	-4.13992906162814	1.31224332703912
C	-1.61386921870957	-3.08563015798827	0.60673740865234
H	-2.46602675016277	-3.74496857263158	0.63864145409710
C	3.52014998131676	-1.21445453068353	2.39652494489063
H	3.85623021855399	-0.70587689271141	3.29598628747132
C	4.01383520748207	-2.46921424366420	0.39410364712360
H	4.73625421255686	-2.93178095097764	-0.27335061343346
C	-3.93572747814450	-0.88040308819152	0.73126774838682
C	-3.24080398961441	-1.09137251308868	-1.61824097014619
C	4.44523359929099	-1.80758671625559	1.54048146239726
O	-1.95510312227999	1.96932367504102	-2.51163216794745
C	-1.24705549395013	1.50147478093628	-1.72107194438727
C	-5.40736886167092	-0.15166640100347	-1.05653034572331
C	-4.46348227837245	-0.53939177474941	-2.00568066494880
H	-4.67084291562963	-0.41342754904979	-3.06460303774947
C	-5.15169951164931	-0.33790754293825	0.29741746932667
H	-5.89522138877466	-0.05295333898345	1.03742350914408
H	-6.34902591216236	0.28568733878681	-1.37590246304268
H	5.50630043332635	-1.75231486579091	1.76702930914063
P	1.21526536952664	-0.08738385598453	-2.16387940725295
C	-2.24993234427381	-1.57952097832004	-2.63938774730665
H	-2.11601332632185	-2.66561751384057	-2.56127776954435
H	-2.59428514133777	-1.34566737259514	-3.64932598496214
H	-1.27097161316620	-1.11772246765110	-2.48401920275638
C	-3.70375100842495	-1.12898253602558	2.20039627357843

H	-4.17711601259818	-2.07029737331911	2.50759949402855
H	-2.64245976359612	-1.20149255246030	2.44323004475775
H	-4.14475555464517	-0.32827008894342	2.80040646727554
C	1.13618731943558	-0.69422502227410	3.06778476677322
H	0.42235067478324	-1.46006074424453	3.39400093233000
H	1.62649914340201	-0.27557801401331	3.95002955130668
H	0.56897221643104	0.09797084519251	2.57391647088846
C	2.19001447842262	-3.31180802921654	-1.13387583761166
H	3.00349279495211	-3.40236626213288	-1.85805722666081
H	1.86489530022815	-4.32457864363245	-0.86355145047719
H	1.34686464978126	-2.81604298635161	-1.62302663100550
C	3.56146470681072	1.55146520734009	-1.47858990648623
C	-1.37147849369457	2.59780264789178	1.70249732940494
C	-1.02433754788525	4.03810813949140	2.13819516769801
H	-0.87942727086259	4.67656047590262	1.26164491364694
H	-1.83637612889525	4.45635871088521	2.74571406464265
H	-0.10190059683772	4.04792296054853	2.72755608710094
C	-1.55336484667465	1.72374778384748	2.96170523303252
H	-2.43593908174736	2.05891773954744	3.51950915945163
H	-1.69238800934476	0.67731266833538	2.68418767636891
H	-0.67811646546193	1.79821540309512	3.61379818533939
C	-2.68540139997226	2.61300183836566	0.90152629895605
H	-2.59337584896483	3.25141070754147	0.01860181600097
H	-2.94720199081905	1.60646694454674	0.56891582527361
H	-3.49723523783957	3.00467573133787	1.52659435124750
C	4.42455752502484	1.40398819909706	-0.21072235643183
H	4.54893033191786	0.35005048527281	0.04527712317430
H	5.41157625988125	1.84213190053762	-0.39973605325125
H	3.97879397202426	1.91567761321488	0.64480866071593
C	3.39378587370161	3.04573040629940	-1.83695062480593
H	2.87185766614740	3.58373253209975	-1.04039664992026
H	4.38206348878720	3.49928834443779	-1.97790042722821
H	2.81786725592562	3.15359557928667	-2.76080206551676
C	4.30188929786309	0.84426832016318	-2.64250336547674
H	3.73250000584556	0.93601783817833	-3.57186953726850
H	5.28854305585120	1.30238696141434	-2.78282242645280
H	4.43513600178638	-0.21844719598367	-2.41887997960992

Int2 (R = *t*Bu, R' = Xy)

TPSS D3BJ/def2-TZVP
E = −3542.85728037 Eh
G = −3542.32227566 Eh

0 1

P	1.00361093321876	0.19309477947875	1.78784102783964
C	-0.48557661752971	0.92894969320477	1.44951166038786
C	1.57906955342273	-0.90684497270438	0.37758302660866
Ni	-0.84573613480848	0.08005017680140	-0.20186327605103
N	-2.46202826608104	-2.44336227145066	0.31027471591424
N	-3.55207756054798	-0.82362376727354	-0.59860728011649
C	-2.29973205555997	-1.14825148520183	-0.11794248152854
C	-3.76564417873065	-2.89702802154768	0.11060139214209
H	-4.06653542065706	-3.89260939620359	0.39407948499301
C	-4.45021710770855	-1.87896763434697	-0.46259486105105
H	-5.47576070185469	-1.79702731785445	-0.78407997475879
O	-0.17101993133338	2.24324346518919	-2.02425970999052
C	-0.36758114154596	1.37319612999406	-1.28594067576718
P	0.78859899626490	-1.19462813905901	-1.08829443901078
C	-1.40419738562995	-3.30986906705269	0.76331514938899
C	-1.04634263988007	-3.30337060178082	2.11597137555001
C	-0.80755119775883	-4.15832330894065	-0.18014833533553
C	-0.04692787400352	-4.19203575025226	2.52406898680706
C	0.19300878744262	-5.02498981769152	0.26957007125263
C	0.56742624388349	-5.04512365041014	1.61049088756644
H	0.25260215556004	-4.20368966856701	3.56849834275554
H	0.68067019450369	-5.68393163640246	-0.44370282783036
H	1.34766116126875	-5.72345671563378	1.94405448167121
C	-3.85561552781880	0.42077154843604	-1.25392493127808
C	-3.36738954754744	0.61131157906537	-2.55891159951672
C	-4.63356763462930	1.37945678082083	-0.59223885559933
C	-3.62400138789664	1.83692654342179	-3.17555691399029
C	-4.86660924473668	2.59396356014743	-1.25071236697626
C	-4.35588994755666	2.82732054996240	-2.52240588763448
H	-3.24026375244395	2.01328103716834	-4.17653197775771
H	-5.44878796485896	3.36171975311135	-0.74756904955572
H	-4.53532945246232	3.78009403068524	-3.01220019782192
C	-1.70178563546595	-2.35998707418491	3.08579658999115
H	-1.42151496864546	-1.32980253979651	2.84736553422864
H	-2.79419951107269	-2.42468299073783	3.03571183217649
H	-1.38389038343953	-2.57748953608511	4.10843441773929
C	-1.22890191730284	-4.13449476165668	-1.62606553827060
H	-0.56826931083305	-4.76493504867077	-2.22559645448609
H	-2.25664822306241	-4.49608066545999	-1.75005249803507
H	-1.18971644013079	-3.11565616946865	-2.02453290049223
C	-5.23351121652572	1.13395527038533	0.76899779072953
H	-6.30365653518810	0.90817547300365	0.68017516473495
H	-4.75905287931392	0.29573260486086	1.28108477263069
H	-5.13640521585621	2.02334943992800	1.39805553964933
C	-2.60747727568255	-0.47308721266307	-3.27637005959425
H	-1.64247840415380	-0.65719754197583	-2.78999273023119
H	-3.16262553062005	-1.41792648411066	-3.26428593701022
H	-2.42782524734869	-0.18737884586292	-4.31549180343625
C	2.99341148499042	-1.46683673090583	0.68811242731461
C	-1.14722038824920	1.98225510538166	2.30075908126015
C	-2.31767847130296	1.31927284165488	3.06062475266288
H	-1.94153929423365	0.63312733816572	3.82539782099164
H	-2.92741387018857	2.08651711503236	3.55296428863721
H	-2.94768385329206	0.75516838166550	2.36921892186107
C	-0.18998045327221	2.62868060145597	3.32252871585384
H	0.64509178505255	3.11729851037967	2.81061391363578
H	-0.72093571339778	3.37967048336438	3.92037936034090
H	0.22119000909301	1.87305159565905	4.00015738152970
C	-1.71101578468865	3.07842633243206	1.37071854193261
H	-2.22465679927759	3.84639286598748	1.96267181638452
H	-0.90382206218558	3.55685017856284	0.80763789029390
H	-2.41329727838551	2.64610868517604	0.65261380376912
C	3.42417934432508	-2.49464267749468	-0.37020931773662
H	2.73580088933328	-3.34564541164260	-0.39099742855912
H	3.44241338516129	-2.04636453442427	-1.36922781917261
H	4.43065382582618	-2.86359640563432	-0.13733945490579
C	3.98459413382350	-0.28164553962456	0.66750399861662
H	3.70761439692143	0.46956085144199	1.41500593223334
H	4.99752292663656	-0.63755147826420	0.89294347732777
H	3.98725242121079	0.19680717545023	-0.31693144840309
C	3.04354287438478	-2.14022893022382	2.07270722491139
H	4.06183996856930	-2.49933395064106	2.26614409077268
H	2.77328980407686	-1.43904791440544	2.86888270915848
H	2.35643715472610	-2.98894433716746	2.11335750125824

TS2 (R = *t*Bu, R' = Xy)

TPSS D3BJ/def2-TZVP
E = −3542.85220431 Eh
G = −3542.31804679 Eh
im. freq. = −142.63 cm^{-1}

0 1

P	2.23688975381622	0.98904865082096	1.55814684907231
C	0.67993075595494	1.58135827572911	1.15961967148884
C	2.69144051572099	-0.17004434006565	0.23968468005770
Ni	-0.00076862628224	0.82414413546003	-0.46013770666953
N	-1.41107731072189	-1.89318054211301	-0.41596992942830
N	-2.53056503581637	-0.27729487922042	-1.29058941991300
C	-1.31982180781572	-0.55352152159161	-0.70215170219090
C	-2.64158254272182	-2.41900409309152	-0.80894314344716
H	-2.89110461921622	-3.45475602672237	-0.64555766483072
C	-3.34762956099246	-1.40036367244134	-1.35772018201117
H	-4.33900841768431	-1.36169374789687	-1.77949850461519
O	0.85945519515125	2.62355194282915	-2.59992223235620
C	0.59622580315058	1.82621570930056	-1.80029652864982
P	1.70425273397548	-0.44085628017217	-1.10344847372972
C	-0.39086870140629	-2.68777476985481	0.21864773724524
C	-0.18974815302518	-2.54417364223801	1.59723620168917
C	0.33068347942898	-3.59809444730595	-0.56746762009475
C	0.78338382406763	-3.35053418602407	2.19481151655462
C	1.28750463945506	-4.38976039602584	0.07322658798387
C	1.51231710456675	-4.26820026448393	1.44290682002717
H	0.96713889995453	-3.24897175952959	3.26080271468566
H	1.86833748502283	-5.09537113310269	-0.51482912607185
H	2.26502049344021	-4.88632321042799	1.92399432944041
C	-2.86213024476372	1.03182081179911	-1.78614572791590
C	-2.45093275194895	1.37725556472998	-3.08186069364317
C	-3.56764730810933	1.90593965215392	-0.94851261234506
C	-2.75790079421065	2.66347582650730	-3.53347812721368
C	-3.85525013774813	3.18236630463624	-1.44171778050769
C	-3.45168712098885	3.55816714773221	-2.72091488003835
H	-2.43728832705161	2.96485681546097	-4.52680926921780
H	-4.38925982986667	3.88605355510238	-0.80897653563883
H	-3.67442100006725	4.55673878706331	-3.08606972380602
C	-0.97847072500621	-1.54406055687029	2.39409934488903
H	-0.72588865586545	-0.52998717890562	2.06627107786962
H	-2.05683461025369	-1.68035530106054	2.25109915791236
H	-0.75227460898339	-1.63547176168135	3.45903495678993
C	0.11547193175005	-3.68491258449751	-2.05569236393066
H	0.86348501627946	-4.33899795722759	-2.51013151276554
H	-0.87741146707850	-4.07691331305710	-2.30459629278900
H	0.19912304602897	-2.69184919375480	-2.51148042906009
C	-3.99363053971699	1.47869572875957	0.43208417313933
H	-4.81303374959788	0.75111498126143	0.38647407676002
H	-3.16653571604290	1.00209059065107	0.96661726922866
H	-4.33407875017827	2.33917335089856	1.01260876195086
C	-1.69649334106573	0.39525743225385	-3.93963108757759
H	-0.79967068531172	0.04241706840190	-3.41909643439718
H	-2.30963097863294	-0.48432396789155	-4.16907613305879
H	-1.39430572108532	0.86125894927148	-4.88007235753132
C	4.07439341596160	-0.83829355981611	0.36350710490270
C	0.08558843077598	2.71777307994382	1.98508799204116
C	-0.91098615126601	2.11185866906876	2.99880736468033
H	-0.39109164052394	1.45668222044011	3.70489141638026
H	-1.40583398480755	2.91283453400596	3.56244596821483
H	-1.67651038093295	1.52364637030016	2.48467465438390
C	1.12808882383729	3.54568539831865	2.76135359870507
H	1.85525585528353	3.99095764477690	2.07449897898920
H	0.63884559777117	4.35210695477665	3.32266629346742
H	1.67678522459686	2.91768065360426	3.47201559102509
C	-0.68842006633740	3.65134194218119	1.03283077311951
H	-1.18831617682866	4.45322808805749	1.59198810122428
H	-0.01157753669405	4.10623552610086	0.30280865550038
H	-1.44518637229101	3.08271763673258	0.47996744791394
C	4.27936404492808	-1.89948461476632	-0.73101572520982
H	3.52239977009547	-2.68702941313335	-0.65447954441496
H	4.21402051699150	-1.45159522261903	-1.73011405587545
H	5.27002313668113	-2.35881849882420	-0.62891725504502
C	5.15605129697547	0.25430096769945	0.21427778979434
H	5.04366881128576	1.01832620210171	0.98988348286877
H	6.15303462442653	-0.19492697549407	0.30530451511140
H	5.07648135241399	0.74163027653138	-0.76268065090764
C	4.21759847585648	-1.50938405033231	1.74339028879671
H	5.21314784891284	-1.96213983001067	1.83083490037827
H	4.09602212209153	-0.77851186406856	2.54907390409062
H	3.46344412228907	-2.29103268914420	1.87032674152489

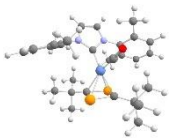
Int3 (R = *t*Bu, R' = Xy)

TPSS D3BJ/def2-TZVP
E = −3542.86337653 Eh
G = −3542.32897673 Eh

0 1

C	-0.54673267071442	-1.93868211234715	0.49488977013412
C	-2.81875073340299	-1.16085264841680	-0.57740117781171
Ni	0.34705014879413	-0.60652951260821	-0.51135169959090
C	0.99180652697552	-0.97023382003926	-2.17232145599541
N	2.37056071365070	1.40743189929717	0.46742760950851
N	0.37910761323673	2.11777857105608	0.84819388889504
C	1.05020258007761	1.05324966896726	0.29820294019231
C	2.50706852700961	2.63472210862687	1.10607569291939
H	3.47309803245527	3.06000119689915	1.32517528180710
C	1.25028108557287	3.08460494899892	1.34042657219828
H	0.88701827766060	3.98743409799231	1.80415689606391
O	1.34659910330532	-1.36003215213395	-3.19992009524222
P	-1.62352066945857	-0.18312980466853	-1.26959430254762
P	-2.20233005015287	-2.37822810423005	0.58935444733029
C	3.48240672297752	0.66076175003674	-0.06301738705708
C	4.25374529553295	-0.12400958546285	0.80443916290691
C	3.76261846983292	0.78064804359327	-1.43350215113081
C	5.31385058240089	-0.85078604612971	0.25206855873747
C	4.82510425355221	0.02954660051017	-1.94331624369972
C	5.58969972119518	-0.78519164146851	-1.11067391702431
H	5.91540521529470	-1.48141712358560	0.90123185482001
H	5.05024742074283	0.08939405124918	-3.00449581326371
H	6.40697361233105	-1.36769292635309	-1.52613919219231
C	-1.04708111164525	2.33928224425362	0.81579502455818
C	-1.55897254928600	3.10612698096428	-0.24136264602078
C	-1.84777722247543	1.82915286072127	1.84283102851762
C	-2.92911794028406	3.37828515079959	-0.24132163049566
C	-3.21350014167920	2.12828351193712	1.80443957356767
C	-3.74968608393240	2.89880122785777	0.77724467656314
H	-3.35095663127846	3.96365506092293	-1.05383039034907
H	-3.85664174821812	1.74160524184012	2.59005026990000
H	-4.81359968518036	3.11779839752381	0.76357630709214
C	-1.28186974414624	0.93536520765226	2.90859060390034
H	-0.31293926405711	1.29075964628655	3.27292798679170
H	-1.97003518192750	0.85895961995166	3.75435126701203
H	-1.13511563965577	-0.06647941057400	2.49137394553511
C	-0.67212242292579	3.56804874148971	-1.36675310852941
H	0.20988357007611	4.10402230369436	-1.00036379981241
H	-0.31663384117126	2.70315153295949	-1.93952740229616
H	-1.22307807558673	4.22557944132459	-2.04335068524274
C	3.95790351630501	-0.18427210907691	2.28022677205537
H	2.88260663371559	-0.20895620830144	2.46996088536883
H	4.40996130417014	-1.07389348747075	2.72547989087815
H	4.36207066522190	0.69363960169447	2.79952494841779
C	2.97219224655918	1.71127225944077	-2.31505207792958
H	1.89962231218010	1.51173411656101	-2.23699265875252
H	3.13437908993880	2.75537624651753	-2.02046069130024
H	3.27499873045919	1.59718003117915	-3.35825563465833
C	5.02365658622804	-2.74775157078381	1.27490429841178
C	-4.29421128630542	-1.08511542627744	-0.95310125495666
C	-5.14169413163844	-0.89485421757798	0.32270629072339
H	-4.96792816174782	-1.71363092223491	1.02867533304707
H	-4.88203767562443	0.04546099957051	0.81737890346412
H	-6.20815498955891	-0.87498300191462	0.06619437554812
C	-4.56776417350404	0.07690694959915	-1.92259980616754
H	-3.98666248000854	-0.03952990787665	-2.84522426526603
H	-5.63070038556982	0.10615420510516	-2.19039143574131
H	-4.29828589064633	1.03550936233021	-1.46680919227658
C	-4.69738175052623	-2.41483386607393	-1.62988636560447
H	-5.76190063011954	-2.39432191325909	-1.89483406315692
H	-4.11111996635249	-2.57396804695208	-2.54049945540709
H	-4.52021251390168	-3.26001553978257	-0.95694283265856
C	0.68024003584773	-2.12001580895076	2.67454654234744
H	0.94480921261154	-1.06203935305995	2.59063367378291
H	-0.25143844895108	-2.19369686159124	3.24367325454095
H	1.47259479510427	-2.63997252469923	3.22861750297631
C	0.08045679160569	-4.21900370636819	1.45216767492979
H	-0.05396701022511	-4.70383421456053	0.48065406624232
H	0.85149511398665	-4.76172272750637	2.01548409106785
H	-0.86347662426426	-4.29288008394600	2.00220025804851
C	1.85467806078578	-2.70760785503782	0.53545819223298
H	2.64258253213184	-3.17858482596099	1.13813797836246
H	1.79453510058173	-3.22508492963349	-0.42554650341497
H	2.18026432601477	-1.67143088248977	0.34654104419543

C (R = *t*Bu, R' = Xy)

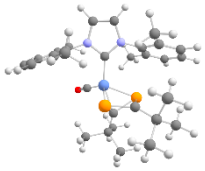


TPSS D3BJ/def2-TZVP
E = −3542.91395948 Eh
G = −3542.37512936 Eh

0 1

Ni	0.38189714181214	0.48516743420079	-0.41959720101670
N	-1.77234870331100	-1.72583767132481	-0.30841623106441
N	0.22236095665827	-2.34049675273827	0.21546862454595
C	-0.51029220851448	-1.21361278251837	-0.08677103033863
C	-2.98023513131731	-0.99681020071881	-0.60456093344203
C	-4.02932849689232	-1.05475038937767	0.33243235357687
C	-3.11248810635926	-0.33264089766537	-1.83525999369953
C	1.63101063943347	-2.34657818482919	0.52470642070218
C	-1.80025900633210	-3.11194263918165	-0.15552537046929
H	-2.70550523069036	-3.67667962220800	-0.30462183173039
C	-0.54651127462551	-3.49617298933920	0.17592852764579
H	-0.12455128225685	-4.46644130334826	0.38103223256441
C	-4.31647262849546	0.33437780770577	-2.08714107799597
H	-4.43116382946667	0.86175220104296	-3.03019045532901
C	-5.21206368519432	-0.37235225914411	0.03261524854719
H	-6.02373680155766	-0.38883166940160	0.75517645111332
P	0.01957762624009	2.75401483275922	-0.66271227149684
C	2.54160426322552	-2.73965099217135	-0.46424279066791
C	2.02218958910831	-2.01230588561527	1.82987860702298
C	-5.35504600773261	0.32493216848212	-1.16248676794495
O	1.48723004346043	-0.36794167166459	-2.97436830395818
C	1.08603830241402	-0.02145375426027	-1.94192417484632
C	4.32458345719300	-2.31821125278463	1.12962923037180
C	3.38932740859113	-1.99118195482477	2.11029519560758
H	3.71786691308237	-1.71091053551093	3.10725939147905
C	3.90292405058271	-2.70489573585948	-0.13806552063790
H	4.63280538422927	-2.98092351433382	-0.89469808481989
C	0.99949150144838	-1.72935855740084	2.89502471477610
H	5.38567433383987	-2.28135823782449	1.35929356250441
C	2.09720178034044	-3.23359682082499	-1.81816084106001
C	-3.94053616559494	-1.83494189369199	1.62259520710303
C	-2.02408163423720	-0.31230989394096	-2.86988991642731
H	-6.27836834221977	0.85577192884274	-1.37549343353443
C	-1.67838350692272	2.10791636273911	1.67219349477779
C	-0.40685707133702	1.97818315072591	0.87388945266351
C	-2.87702036739191	2.37210712788342	0.75007440783664
C	-1.49196019198220	3.32686136403239	2.61003870561927
C	-1.90800848783712	0.85919840069744	2.53317579684015
P	1.25984189915565	1.47601318793798	1.47537885133162
C	1.66685387913377	2.10163191716791	-0.14122121340367
C	0.03756490031120	2.35629555905618	-0.72606655412987
C	2.96193919437093	2.73634374801030	-2.21473992800148
C	3.95851791173922	1.14220827525682	-0.51623056518513
C	3.61799955050547	3.56597063392198	0.05151155760973
H	-1.07453685134685	0.71407040634561	3.22962953273883
H	-1.98019300285515	-0.02508707199671	1.89775202948948
H	-2.83042574068325	0.95288537185713	3.11799063324908
H	-1.33805182955853	4.23798229412479	2.02361709775441
H	-0.62261133762246	3.18430028465706	3.26025395967806
H	-2.38233932212385	3.45726719850894	3.23728347386655
H	-2.70704452179897	3.27891697874801	0.15809166889005
H	-3.79162122957229	2.51369693821481	1.33719099291288
H	-3.03254426539358	1.54086575057744	0.06050010698759
H	-4.53873929006913	-1.34571794606863	2.39602206309089
H	-2.91645379934428	-1.92927437559778	1.98798058776603
H	-4.33844613684921	-2.84936122341620	1.49242984588916
H	0.28024310696414	-0.98106967197416	2.55421506405197
H	1.48294109692194	-1.35558868450977	3.80025847389258
H	0.44324124275523	-2.64086347862399	3.15035466910539
H	-2.45361074945559	-0.16361035413990	-3.86459640751520
H	-1.44378498845783	-1.23893371726117	-2.87138328760489
H	-1.32763503991931	0.50792153867388	-2.66077006346829
H	2.07644079314780	-4.33099853827447	-1.83146003996193
H	2.79112650506555	-2.90477545380211	-2.59569853716939
H	1.09937226411482	-2.88004666040163	-2.07977558226406
H	3.95839758992209	3.00271568717812	-2.58580951249015
H	2.30370248197967	3.60086139978122	-2.35675191127110
H	2.58173397507349	1.91498349622012	-2.82545136908035
H	4.98530761162355	1.38145600367574	-0.81828544363351
H	3.61088836455330	0.28526717821369	-1.09883169124122
H	3.96903435545519	0.84199605536374	0.53734749651176
H	4.60016122367744	3.83604407722934	-0.35470457046946
H	3.72780772823766	3.32136763286663	1.11247011134669
H	2.95520819895153	4.43334284587094	-0.03446693409143

TS4 (R = *t*Bu, R' = Xy)



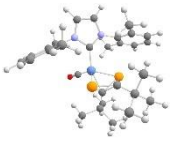
TPSS D3BJ/def2-TZVP
E = −3542.87775564 Eh
G = −3542.34136108 Eh
im. freq. = −54.15 cm^{-1}
im. freq. = −7.77 cm^{-1}

0 1

Ni	-0.61960114511008	-0.69915494487241	-0.35152717975333
N	-1.55556760503620	1.85750200595795	0.93875625520987
N	-2.23042942605319	0.09320581583253	1.96326364931877
C	-1.45426917180055	0.48361869013472	0.89414465879623
C	-0.91356029668054	2.77429107593781	0.03919298224525
C	0.19020543425341	3.49864409145407	0.51040199447830
C	-1.43893593375913	2.93983404053301	-1.25046887706663
C	-2.46416672148020	-1.27825694362568	2.33078063251885
C	-2.36373830318893	2.28830905029321	1.98993849649753
H	-2.55709653452458	3.33422683201573	2.16416530729865
C	-2.78914809281003	1.17561998760588	2.63353646707329
H	-3.42891580685880	1.04555955341761	3.49132324873576
C	-0.79994837510991	3.85216663065686	-2.09559751534666
H	-1.17595041165435	3.98567235589712	-3.10619511697115
C	0.79689594064491	4.40238841750321	-0.36761316488929
H	1.66309415195390	4.96625894157275	-0.03085988019804
P	0.75402261036776	0.56316116508128	-1.72813503843161
C	-3.62988982007553	-1.90329883749532	1.87086528255782
C	-1.52823858513038	-1.91772171684331	3.15476172150027
C	0.30862394455443	4.57547348223513	-1.66129578599454
O	-2.68190996992482	-2.58801140439473	-1.23099525353503
C	-1.86733832011160	-1.84596880778154	-0.85509305350533
C	-2.90369974179963	-3.91198833555783	3.02203306584632
C	-1.76602271971960	-3.25402030775781	3.48649397179091
H	-1.04833977368537	-3.77923703513035	4.11114353951611
C	-3.82987880541226	-3.24027592759745	2.22831720564619
H	-4.71367741715692	-3.75712266231726	1.86429533347147
C	-0.31862412001610	-1.17904847661928	3.65921453079241
H	-3.06903411300391	-4.95407044616304	3.28088915612037
C	-4.62625421054229	-1.16387520948000	1.01571429584598
C	0.71104331718577	3.29005406049061	1.90977991507949
C	-2.61945081610399	2.13090442472296	-1.71021600225545
H	0.79589616044136	5.27526534038018	-2.33420813058939
C	3.50763521959193	0.64493382719825	-0.65432853630559
C	2.07332726986143	0.11859505618223	-0.59129482356828

C	3.55232284747602	1.66983943093670	0.50831628904731
C	3.80340511827113	1.38197811926646	-1.96958922600732
C	4.57380829824204	-0.43098047050514	-0.39118310809333
P	1.50818822376428	-1.24589818489862	0.44789419135876
C	0.95740871548212	-1.24927928202707	-1.33037442386848
C	1.22823321576773	-2.35216803104891	-2.35274877249888
C	0.33591820725426	-2.11813522049046	-3.58503018905405
C	0.90464939209843	-3.71438375410010	-1.71127130906097
C	2.70302770553979	-2.34528942810379	-2.78416889352452
H	4.65609517573775	-1.11778181548691	-1.23585874500043
H	4.33286644801778	-1.01403808987243	0.50300276556692
H	5.54798918460467	0.05033632584425	-0.24639660437047
H	4.55096854009304	2.11957649287318	0.54928990128784
H	3.34936649843381	1.18280758573163	1.46727878616933
H	2.81776433941462	2.46339081765104	0.35272713994947
H	3.75681367748181	0.70015892615632	-2.82373339439850
H	4.80742834236132	1.82078835414502	-1.93119289746400
H	3.07804905007970	2.18366385800125	-2.14021151648592
H	1.10585356667706	-4.52033665397841	-2.42617884302690
H	-0.14471689127062	-3.76887726729988	-1.41253594947292
H	1.52665101535156	-3.87021570361291	-0.82313328733807
H	0.48906953788506	-2.91963235970938	-4.31645109433498
H	0.58216255046506	-1.16066903604297	-4.05692069201841
H	-0.72014344224393	-2.10252584869795	-3.30285979386277
H	2.86683746381355	-3.10384084675832	-3.55754539923974
H	3.34750522598048	-2.57512766872427	-1.93183298892963
H	2.98343775229714	-1.36916351285180	-3.19229914849425
H	-2.93547087506491	2.44081533119149	-2.70925130993025
H	-3.46727829695541	2.23857757598613	-1.02407415875102
H	-2.35336170141916	1.06519983293662	-1.73144994600071
H	1.67067861683768	3.79561077779665	2.04131789407723
H	0.84392236149741	2.22430528790728	2.12098706371557
H	0.01652495834439	3.68466225577364	2.66049616383240
H	-5.29180508869202	-1.86791013880632	0.51109113469524
H	-4.12427431569908	-0.55766484811931	0.25676974914344
H	-5.24129349698107	-0.48714474109113	1.62236281232296
H	0.24450053740119	-0.75729437830907	2.81888119873704
H	0.33697659272984	-1.84914683946157	4.22050265135559
H	-0.60715686318062	-0.34783064166805	4.31418059803792

Int4 (R = *t*Bu, R' = Xy)

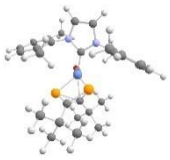


TPSS D3BJ/def2-TZVP
E = −3542.87798665 Eh
G = −3542.34153088 Eh

0 1

Ni	-0.37099580832222	-0.89401234824180	-0.73863390627512
N	-0.63747289494651	1.72276919053434	0.70010996043836
N	-1.27794490873596	0.04366614807251	1.88081054012402
C	-0.72825105950688	0.34778100855216	0.65559358047592
C	-0.08319850981976	2.55886856455815	-0.32794887973652
C	1.18861329436984	3.11045995659555	-0.11425532919154
C	-0.84026988126680	2.81771110892113	-1.47977035997332
C	-1.54691285124715	-1.29941334190740	2.32011599445098
C	-1.11755357970258	2.23722307410001	1.90388420952823
H	-1.13132495895840	3.29666062352752	2.10135147476601
C	-1.52119629759567	1.17883803156731	2.64618285033545
H	-1.95695207035452	1.11967511382358	3.63038000924622
C	-0.27426896178744	3.64897055229577	-2.45119537051064
H	-0.83425256812318	3.85190560028671	-3.36000989882556
C	1.71587567687382	3.93554629158124	-1.11245016516405
H	2.70653993761783	4.36195322095483	-0.97699537617800
P	1.06730300279788	0.18491249651220	-2.18519937484616
C	-2.83252052294544	-1.82394057378120	2.14029560844082
C	-0.50913617776353	-2.01466927572918	2.93416386209094
C	0.99086149138037	4.20332873354048	-2.27176667067737
O	-2.89488497889833	-2.30528187146283	-1.25632973859043
C	-1.89858275913152	-1.73634866966121	-1.05657591397176
C	-2.03386213637524	-3.89079087319283	3.13110771700518
C	-0.77388618470991	-3.32779498141628	3.32934936161950
H	0.01796221401593	-3.91074113263137	3.79221529519135
C	-3.05489361689849	-3.14241385983373	2.55140117558184
H	-4.03693361258445	-3.58286722203527	2.40149097734199
C	0.83323959193434	-1.37533551817069	3.16813621566479
H	-2.22074915490144	-4.91744059742066	3.43328582740416
C	-3.94039647787660	-0.99493787147836	1.54324998046825
C	1.96627503339936	2.80207331371148	1.13936363006781
C	-2.18469106401929	2.17638170870760	-1.67605365529896
H	1.41670354844221	4.84058084107808	-3.04145281513608
C	3.86306157774020	-0.54823743790545	-1.53332069247153
C	2.35717951534841	-0.70891540991313	-1.29690775812956
C	4.24404403693909	0.57857709112683	-0.54035073447519
C	4.21648031337401	-0.07172431837240	-2.95112837534711
C	4.66500086598774	-1.80839004673778	-1.17386995981476
P	1.60516797996996	-1.96817465428466	-0.24299187524531
C	0.97231954765619	-1.65805027119919	-1.96586253882535
C	0.82542496997236	-2.70013002050021	-3.08025108762379
C	-0.23649886983544	-2.20244968165686	-4.07835049270879
C	0.37804693523244	-4.03493313448633	-2.45882649043691
C	2.14891058970713	-2.90563559293318	-3.83109545007272
H	4.43286486482050	-2.63729113273644	-1.84791152547203
H	4.44483948287840	-2.13639195304657	-0.15350760285220
H	5.73776011976042	-1.59534731190403	-1.24950940941590
H	5.32302809871128	0.76149734281357	-0.59664344219344
H	3.99113232311022	0.29946971941990	0.48731423187867
H	3.71788126335403	1.50366915489582	-0.79251747509265
H	4.02665925616200	-0.85168957031756	-3.69113287961597
H	5.28057983970171	0.18878214130828	-2.99434319713832
H	3.62847778453667	0.80938239310150	-3.22551920550822
H	0.19925266903885	-4.77595136751602	-3.24610814161941
H	-0.54534560508546	-3.90363857113111	-1.88831711086723
H	1.14886592016013	-4.41908403338603	-1.78220226636442
H	-0.34745805790399	-2.92283921650893	-4.89675678591176
H	0.06402843556805	-1.23657694650594	-4.49931850054514
H	-1.20538699292221	-2.07842274201507	-3.58862827717710
H	2.02834736244993	-3.69206271096689	-4.58441432063336
H	2.94456937205932	-3.20747961521862	-3.14432567081655
H	2.44742243143426	-1.98500151589286	-4.33979044465894
H	-2.67043964720765	2.56315145191767	-2.57520131674866
H	-2.84123745911992	2.35155266614231	-0.81650485628815
H	-2.06275956831900	1.08790000100666	-1.77149257453669
H	3.00150551172176	3.13680046759640	1.03959592625244
H	1.96304035856162	1.72753611020634	1.34590865212674
H	1.53389079641032	3.30130362973761	2.01446634995021
H	-4.72372347132931	-1.63856827071010	1.13674971986643
H	-3.57231421651829	-0.35092131533907	0.74105805934088
H	-4.39356525302333	-0.34741403047478	2.30510491745758
H	1.22421249378003	-0.95452227441603	2.23504169950857
H	1.54813420741354	-2.10873095697972	3.54856939282894
H	0.75934997334369	-0.55541062117565	3.89320611753287

TS5 (R = *t*Bu, R' = Xy)



TPSS D3BJ/def2-TZVP
E = −3542.86850879 Eh
G = −3542.33207610 Eh
im. freq. = −131.15 cm^{-1}

0 1

Ni	-0.77713548495108	-0.47991481678254	-0.16736969337740
N	-1.43759926942618	2.24461519856822	0.84196799461571
N	-1.77445081707167	0.68733873671486	2.29227858564009
C	-1.32871122589164	0.88640490765667	1.00938292509039
C	-1.03004320545521	2.95246477198611	-0.34226604063841
C	0.18017951288859	3.66231074450431	-0.30054622131159
C	-1.85145745460788	2.91706892507221	-1.47796926111308
C	-1.78282104401867	-0.59497176336004	2.94736793861229
C	-1.93603814758205	2.86421038038526	1.98688244752744
H	-2.09583987372877	3.92923676599746	2.03041192606270
C	-2.14933899335500	1.88368320238708	2.89780815530861
H	-2.53080162990751	1.91360991426592	3.90539456627841
C	-1.41537809671972	3.61023791538703	-2.61138015330598
H	-2.03097096299931	3.59230720267954	-3.50677371370022
C	0.57151147666756	4.34815435156588	-1.45397571492758
H	1.51256702921593	4.89145089829148	-1.45061421885789
P	1.14087247943296	0.51880771368318	-0.71863012704903
C	-2.98693361984860	-1.30208339500299	3.03821639551477
C	-0.57247559740415	-1.07184212162709	3.47106252221765
C	-0.21609509527702	4.31935029413957	-2.60162245964330
O	-3.35719988949666	-1.79627492925004	-0.68563728944158
C	-2.35038298897173	-1.23430242119054	-0.53827913299621
C	-1.76526870350316	-3.06133707314946	4.18040494896573
C	-0.58653668530653	-2.32207194252906	4.09199437578951
H	0.33984549995840	-2.72085728020977	4.49652597968887
C	-2.95331966022529	-2.55425816304396	3.66273938507851
H	-3.86963073834938	-3.13469978203124	3.73107897657946
C	0.69587661719869	-0.27402460781769	3.33743884243697
H	-1.75631552503195	-4.03861173643611	4.65479850753207
C	-4.27616685317526	-0.74082488510341	2.49435010107254
C	1.04342607685258	3.66362461229432	0.93497737977577
C	-3.14741188510027	2.15455201908834	-1.48526053609895
H	0.10636098423663	4.84994525892099	-3.49296292830049
C	3.41098262480851	-1.41422591104341	-0.40346729454893
C	1.91759511782761	-1.09572656793843	-0.35095640910171
C	3.86447485927751	-1.42168481294720	1.07362911367117
C	4.21643525814061	-0.33767957888016	-1.14949743764833
C	3.67238304877469	-2.80917732626696	-0.99717406244345
P	0.59374204647863	-2.23563223446829	0.17397276623562
C	0.74596171503797	-1.10371250448231	-1.44477856458841
C	0.60709858199891	-1.49519151516723	-2.92016993326191
C	-0.62012457422426	-0.76427980781200	-3.49686130099012
C	0.40907929490564	-3.01337857696995	-3.05839254911429
C	1.83605835236022	-1.04729610143096	-3.73404514025500
H	3.45959500021838	-2.83741028505553	-2.06909583438607
H	3.03809246990916	-3.55498596816592	-0.50688962629904
H	4.72281894081483	-3.08617797998991	-0.85106629556686
H	4.94053726882918	-1.62031968454205	1.13924122994555
H	3.33043669294209	-2.19721932033127	1.63276570530377
H	3.66081675232389	-0.45467376681610	1.54652878133666
H	3.93850564061276	-0.27572231311264	-2.20401699719875
H	5.28690322355152	-0.56678796882144	-1.09105353104354
H	4.05303408558010	0.64738641602189	-0.69850639311372
H	0.29370725699745	-3.28003968889761	-4.11596578643015
H	-0.48553166526086	-3.33292214337929	-2.51569348006485
H	1.26192155596953	-3.55987062692610	-2.64689811394538
H	-0.72045535429278	-0.99275252614339	-4.56471621417549
H	-0.51369422698041	0.31953464173481	-3.37728852197875
H	-1.53348500191911	-1.07315181064723	-2.98259300435033
H	1.66739993967895	-1.25341608788912	-4.79711070268035
H	2.74014528651746	-1.57822002323049	-3.42892497535922
H	2.00420658427725	0.02799121780536	-3.61092468741935
H	-3.73294807753601	2.40203828025594	-2.37421627706999
H	-3.74779324782985	2.37584257788639	-0.59628369071835
H	-2.94881449207611	1.07624953434733	-1.48047833141408
H	2.03325414670392	4.06461673994999	0.70460428514759
H	1.16282557684337	2.64975936278510	1.33204704771790
H	0.60639728096839	4.27404306004045	1.73437557880546
H	-4.97844994199083	-1.54712165557467	2.26908871586418
H	-4.11237624445156	-0.16286276689784	1.58205311987996
H	-4.75274082401944	-0.07478003077732	3.22528538256584
H	0.97190351007710	-0.20015766762639	2.27839518850648
H	1.51298957399124	-0.75816510861640	3.87783611710805
H	0.57479575511771	0.74398161396586	3.72544772005243

D (R = *t*Bu, R' = Xy)

TPSS D3BJ/def2-TZVP
E = −3542.90794427 Eh
G = −3542.37507155 Eh

0 1

Ni	-2.25083340173116	1.86665856536673	6.56725241245995
N	-2.76199116989299	4.29309236332479	8.22935342186577
N	-3.10142188448234	2.51419626418071	9.38325227763955
C	-2.71164235670932	2.92516076683468	8.13169999848208
C	-2.45785166223705	5.14591079553000	7.11190061930429
C	-1.14576461299052	5.61173231305316	6.96043096724903
C	-3.48005665864731	5.43273581957230	6.19724260644820
C	-3.19391435266927	1.12571563085505	9.74388465801260
C	-3.16411613755689	4.71509178704768	9.49526721668708
H	-3.26275883813725	5.75891001024483	9.74640045176795
C	-3.37956222863424	3.59059864687580	10.22394538177883
H	-3.70647633244709	3.45216723490894	11.24187246827444
C	-3.15751057777509	6.23426349041759	5.09786606094050
H	-3.92924027878358	6.46788608627701	4.36916371017039
C	-0.86591950045264	6.41060336254611	5.84772278453477
H	0.14626909046420	6.77840999180748	5.70166522354299
P	-0.20200769885935	1.85872392521814	5.62466234497523
C	-4.32462206399146	0.40301311308017	9.34037572445523
C	-2.12800011458147	0.54316776011470	10.44146687747557
C	-1.86313019195139	6.72001792263433	4.92523143468814
O	-4.02899009772954	1.08987577663468	4.36585361192720
C	-3.36804075783048	1.44319950255831	5.25338930002492
C	-3.32953483935727	-1.56213229847552	10.36128144278419
C	-2.21724406587184	-0.81774153624218	10.74778669582384
H	-1.39692457152115	-1.29601401168188	11.27645523627647
C	-4.37259622754475	-0.95661580032058	9.66380353555172
H	-5.23521139895527	-1.54168907658039	9.35614735913882
C	-0.91310960696073	1.35466920989541	10.80449728229603
H	-3.38056444572748	-2.62106560473305	10.59837121183387
C	-5.43169970870790	1.06920228888007	8.56661156058510
C	-0.07540028637889	5.22429149566997	7.94557054755928
C	-4.86208328007039	4.86434590951833	6.38436187246280
H	-1.62825580511307	7.33701939722637	4.06244026944130
C	2.20089349471915	0.82399853767488	7.39007999485469
C	0.87288370348274	0.76707223208886	6.67534718526346
C	2.24060266933627	2.08465510426300	8.26989827799125
C	3.34931535654995	0.88577723928676	6.36663202022396
C	2.35776176324188	-0.42532218714334	8.27830493687435
P	-0.84810876961541	0.18122629265729	7.06770803087349
C	0.21667568273471	0.05592586718103	5.56070922231285
C	0.45462089958345	-0.96155190131955	4.47471474830822
C	1.40573690204151	-0.38851102693949	3.40754844949034
C	-0.90258997360397	-1.28198955233584	3.82165207867389
C	1.05289743489010	-2.24251519885616	5.08397911835030
H	1.15918847179907	-3.01618529380330	4.31486104697283
H	0.40407416820513	-2.62927836876481	5.87716991115308
H	2.04201246194816	-2.04812946613225	5.51107375858831
H	1.55630136641107	-1.12063069277528	2.60567264263155
C	2.38197236831882	-0.14227898998543	3.83436916727117
H	0.98263146904785	0.52243459395683	2.97160391344386
H	3.40237125223729	-0.03744242176246	5.78193962662850
H	4.30796836631904	1.01830500035463	6.88173908574317
H	3.20977467910531	1.72488853432209	5.67672142243481
H	2.30340938333531	-1.34049459919364	7.68133154021123
H	1.55959317642968	-0.45966170777920	9.02689781891920
H	3.32464137387700	-0.40691757512229	8.79487977250551
H	2.16311526194435	2.98401630851550	7.65164165266426
H	3.17846094097486	2.12872119097635	8.83579826245234
H	1.41009240025696	2.08357039082657	8.98185049661432
H	-0.52799045321384	1.87413741742999	9.92114016772383
H	-0.12531784195602	0.71134833476504	11.20370489815627
H	-1.14544817297654	2.11955837216953	11.55464567914227
H	0.89138862728020	5.63484729270071	7.64415876779149
H	0.01084816522535	4.13439934710099	8.00188334967990
H	-0.30439294241753	5.58533163459588	8.95483198699744
H	-0.77215917776329	-2.00043323104040	3.00411610821274
H	-1.35834058463966	-0.37298354764926	3.41710003918546
H	-1.59208769175005	-1.70903334100267	4.55669248019197
H	-6.25235262427385	0.36962525994841	8.39047960626124
H	-5.05657974278829	1.42476060998206	7.59987447017837
H	-5.82316142950070	1.94141729067464	9.10225957599525
H	-5.52615986874379	5.19508915188790	5.58223318988515
H	-5.29538503304271	5.16957045443739	7.34363798888645
H	-4.82081146917455	3.76914032356923	6.37934976200296

B (R = H, R' = Dipp)

TPSS D3BJ/def2-TZVP
E = −3162.77650843 Eh
G = −3162.25352312 Eh

0 1

Ni	0.06462001729273	0.13605838669117	1.71754888900429
P	-1.86304586822776	-0.76393508959100	2.42742348344236
N	-1.04822377153446	0.20959439463276	-1.08163865273204
N	1.06018468095357	-0.20625705980461	-1.06729633810566
C	0.00515626619489	0.02471448230280	-0.21899892712964
C	-2.41617394324138	0.40219043871844	-0.67655464987880
C	-3.32505561399389	-0.64074816636773	-0.90673099044619
C	-2.77866048743160	1.61171629213381	-0.05368990289343
C	2.41294720491025	-0.42010827689097	-0.62581191288570
C	-0.65344249324384	0.10589998704397	-2.41292950782741
H	-1.35303057049127	0.22650493809341	-3.22376811014091
C	0.67523464464148	-0.16019887613149	-2.40414105774930
H	1.37693389696202	-0.32251772607965	-3.20558752475179
C	-4.11678000926756	1.76345472960852	0.31462282339209
H	-4.43350606057324	2.67580453274313	0.80835585999499
C	-4.65719765483028	-0.43157111719315	-0.52950414121480
H	-5.38445857054713	-1.22266866155688	-0.68962010006472
C	-0.72479669400617	-0.14156107080739	3.41122052170055
C	3.35353155204288	0.59499779353803	-0.85396321268855
C	2.72905213941780	-1.62940731891623	0.02377550944154
C	-5.05070249919718	0.75727068509808	0.07083170043580
O	2.61198181492887	1.25704983195961	2.59204662202713
C	1.61186210478234	0.83086374014356	2.19409305325184
C	5.01702551781960	-0.82675241350793	0.19364576530490
C	4.05350062426555	-1.80671694154329	0.42899940911880
H	4.33661620021025	-2.71984867033310	0.94154248852739
C	4.66977923025547	0.36024177416350	-0.43867027522645
H	5.42230247841275	1.12770043461284	-0.59622386852170
C	1.66739989464154	-2.69374047952571	0.25820742737748
H	6.04077695616025	-0.98777256909131	0.51962985172555
C	2.98147990810918	1.92102077418315	-1.49894662379349
C	-2.90506824664962	-1.98211984262060	-1.48754406227101
C	-1.74364003125581	2.69130776894147	0.21804294007777
H	-6.08609886245646	0.89841469166466	0.36798991622806
H	-1.82776155030648	-1.95515245670774	-1.67235095318285
H	-0.83272067236856	2.17316487288079	0.55020579812722
H	1.89790136471347	1.93556101434758	-1.64778695873777
H	0.74854706075642	-2.16907194650772	0.54851812587365
H	-0.42833978682216	0.07386425579113	4.42993266133888
C	-3.16619242922527	-3.12165027909330	-0.48591806439362
H	-4.23582237422978	-3.22381628614376	-0.27255097362981
H	-2.81069704923080	-4.07266566650968	-0.89820774473199
C	-2.64896676514326	-2.93379808934226	0.45915546863192
C	-3.60389113183475	-2.25507124435092	-2.83099986710662
H	-3.38973417709780	-1.46423041834606	-3.55784531893011
C	-3.26547585946086	-3.20904174681719	-3.24992629576348
H	-4.69089125769207	-2.30751964928407	-2.70503920869825
C	-1.40087518397897	3.47334479541885	-1.06434589784233
H	-1.04551342304362	2.80875405565200	-1.85763336780689
H	-2.28182908083616	4.00895833883584	-1.43631378285475
H	-0.61413416695122	4.20766087469361	-0.85809427482621
C	-2.14470545942896	3.64345913982629	1.34927748747210
H	-1.30601437489313	4.30808276530573	1.58099552492114
C	-2.99748829628407	4.27461727634204	1.07286033186176
H	-2.39973929841491	3.08761865038539	2.25682104460399
C	2.01009145043165	-3.65336325091848	1.40303781653724
H	1.15375386672267	-4.30657929655808	1.59900839065955
H	2.86471314204023	-4.29472436067284	1.15788599843542
H	2.23662368111288	-3.10653747200934	2.32345146430226
C	1.37729116213852	-3.47567883885926	-1.03799737645231
H	1.07346060403810	-2.80801412006772	-1.84955720831321
H	2.26794393068031	-4.02525344645500	-1.36362170405230
H	0.56967085379458	-4.19704310556090	-0.87078943600943
C	3.33379411756035	3.11064906997203	-0.58880920274887
H	4.41417402549242	3.17592783552369	-0.42043429422170
H	3.00964477222209	4.04687345565133	-1.05682168871297
H	2.84532549568933	3.02031143025088	0.38455412263239
C	3.65008810727192	2.07126135708148	-2.87764869890157
H	4.74134191479843	2.08445082396436	-2.78113168312920
H	3.38438240866380	1.24284514274870	-3.54270579587751
H	3.33931062406192	3.00839212322073	-3.35217707120272

C (R = H, R' = Dipp)

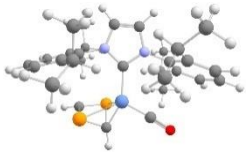
TPSS D3BJ/def2-TZVP
E = −3542.90648026 Eh
G = −3542.36417863 Eh

0 1

Ni	-0.12366834230466	0.51608219410329	1.46904267987965
N	1.02526626481877	-0.43056255352073	-1.11936083026263
N	-1.11271050389583	-0.17139917600141	-1.21050547418409
C	-0.05065775107551	-0.05710801170301	-0.34688870458962
C	2.38865043534559	-0.59597085913439	-0.67456620773749
C	3.36240899751509	0.30829760180781	-1.12883294942563
C	2.69381001673615	-1.70486083219722	0.13862153445056
C	-2.49718792270881	-0.01267065959197	-0.84283711653100
C	0.63187906372035	-0.76583213458596	-2.41338361823610
H	1.34409083194473	-1.09578132921353	-3.15039863870467
C	-0.70995185036931	-0.60250980545750	-2.47066038120521
H	-1.41591665254148	-0.75113982535588	-3.27063309612490
C	4.03290480108357	-1.89234990647338	0.48858205008690
H	4.30287999465965	-2.72860745587406	1.12442878407899
C	4.68914450101100	0.07184419294332	-0.74948576164036
H	5.46653170459551	0.75415986996287	-1.07999167263857
P	1.92574346708119	0.57490617908098	2.51175894074151
C	-3.26379803339964	-1.17528284156894	-0.66437950361900
C	-3.01923482110653	1.28524669009299	-0.69507777095116
C	5.02182281471907	-1.01702348336809	0.04764450933452
O	-2.56569113589167	-0.60894148578084	2.59997783126878
C	-1.61121502655683	-0.19188609017197	2.09785329398629
C	-5.15632685736158	0.25770125446359	-0.16464624756583
C	-4.36668963870735	1.39252784299527	-0.34402077888050
H	-4.80353917980537	2.37546199694732	-0.20455371747699
C	-4.61190350650262	-1.01032444889648	-0.32661604132025
H	-5.23339105094415	-1.88784687699442	-0.17295841398178
C	-2.14731001771544	2.50681898257838	-0.93189788304833
H	-6.20167414758308	0.36632289904173	0.11065776785592
C	-2.67906678431621	-2.57067424737268	-0.82338845415018
C	3.02222883490572	1.49430329875932	-2.01951323707608
C	1.61517962380178	-2.67702946657433	0.58869706070401
H	6.05642903221634	-1.18049790835687	0.33590468384477
C	1.39423421196428	1.84553406804403	1.31085667895852
P	0.09350551868099	2.68011564453867	2.21406778180040
C	0.46370954123408	1.25410326482849	3.29182775157238
H	1.93726068559090	1.64376477219215	-1.98224022357556
H	-1.16215573367416	2.27375210023821	-0.51063062390517
H	0.69333932971501	-2.09226255894519	0.72158996228810
H	-1.60019781152291	-2.47362079000509	-0.97281099150553

H	1.81048224447533	2.09039033007498	0.34121311094018
H	-0.03205590186016	0.94568559183141	4.20838823657277
C	-2.89129429833930	-3.43640982275803	0.43049389846509
H	-3.95625165259183	-3.60138850373602	0.62587054819600
H	-2.42187992499062	-4.41605742884589	0.28799025558386
H	-2.45457035509505	-2.96712799131890	1.31495834989294
C	-3.26294787467773	-3.26511370274116	-2.06804725120937
H	-2.80258142221586	-4.24931280203297	-2.20813676813238
H	-4.34425004206021	-3.40671852465734	-1.96276806357609
H	-3.09061646956036	-2.67261671129565	-2.97263095920730
C	1.36263575839506	-3.74938635062547	-0.48974045929538
H	2.26210317579037	-4.35507903354701	-0.64817997387830
H	0.55164137921894	-4.41665051114872	-0.17653982159928
H	1.08252729952449	-3.30005522744864	-1.44770461272633
C	1.92126504839668	-3.32793719503938	1.94235266419600
H	2.76211630085646	-4.02866464468082	1.88125471313334
H	2.15123649717332	-2.56537309059010	2.69221027443990
H	1.04695811929208	-3.89387038550916	2.28081772399902
C	2.65548101358735	3.76127526210929	-0.21425770420916
H	-1.92282154294893	4.56695100497313	-0.32458955215878
H	-3.60374360496610	4.11650809264737	-0.63484529310728
H	-2.78818402367872	3.57424252861499	0.85489926733771
C	-1.98181812406031	2.77582985131553	-2.44096562910151
H	-1.55516216495967	1.91302010742533	-2.96111516744079
H	-2.94987615183183	3.00704433101955	-2.89981833493950
H	-1.31558944141944	3.63125696705843	-2.59949241407435
C	3.41604823374023	1.21148982057019	-3.48314428672684
H	3.15043838343065	2.06151554306205	-4.12116507528625
H	4.49685278594645	1.04965021315710	-3.55999009058200
H	2.91580480752198	0.32118402449391	-3.87470207499994
C	3.69887740383208	2.79460893608350	-1.54857987505699
H	4.78446171625157	2.74613828002466	-1.68421359671546
H	3.32950262154058	3.64038221326547	-2.13803014586399
H	3.50143833010057	2.99675872277386	-0.49239386538418

TS4 (R = H, R' = Dipp)

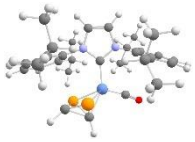


TPSS D3BJ/def2-TZVP
E = −3542.85590759 Eh
G = −3542.31690254 Eh
im. freq. = −298.93 cm^{-1}

0 1

Ni	0.13549720853187	-0.32942182807414	1.49263880113225
N	-0.87845615705401	0.39288838941836	-1.25254327593522
N	1.25172473968095	0.11152135337515	-1.18653588871802
C	0.14268994338581	0.11103940344551	-0.37179014689097
C	-2.25967104896258	0.52957166317971	-0.87745470024315
C	-3.13360916722029	-0.54100245574800	-1.11920846175998
C	-2.66301248304261	1.72798148213285	-0.26040479246965
C	2.60587842058221	-0.06698051397086	-0.73244428263060
C	-0.41359155305640	0.55475171832944	-2.55466715108384
H	-1.07705534399140	0.78802401173942	-3.37005384673851
C	0.92798623408751	0.37564665752095	-2.51333395742754
H	1.68004081519018	0.41265699620661	-3.28439210987947
C	-4.00324902512314	1.83065828654612	0.12563265170285
H	-4.34925953970945	2.73316131431688	0.61774898033588
C	-4.46647428478520	-0.38609080823075	-0.71522174401897
H	-5.17106615608852	-1.19523208986388	-0.88077987662604
P	-1.92710779297408	0.32295087742166	2.53286634514105
C	3.40602368714369	1.07796716221477	-0.58377159716608
C	3.06591963327292	-1.36733315272831	-0.46946623554516
C	-4.89489712222105	0.78338086614333	-0.09623447319813
O	2.73285532633275	0.08431355635417	2.75889697405781
C	1.72401161691138	-0.06906951895946	2.20763717898761
C	5.21731907337780	-0.39130006182749	0.08868213308649
C	4.39455355793546	-1.50460809128908	-0.05742509517947
H	4.78539962897940	-2.49317310549753	0.16191182686650
C	4.72736735648348	0.88574582906904	-0.16771533855289
H	5.37572848064064	1.74562429291783	-0.03228841184336
C	2.15580472334593	-2.57164721176267	-0.63657203718552
H	6.24534144651201	-0.51891302216369	0.41613845836423
C	2.83890331773977	2.47509749536394	-0.78864318685213
C	-2.67414595561994	-1.80787589809511	-1.82298647763694
C	-1.67745425305758	2.86554506620697	-0.03886627929312
H	-5.92991241925311	0.87985854703186	0.21982304806938
C	-2.51965237647792	-1.22867553150532	1.89295326766220
P	-1.13691132810162	-2.33273612098283	1.61662072720660
C	-0.76141770746674	-1.08373266233380	2.94796706542818
H	-0.71853347166808	2.40392623933582	0.21753954962277
H	-1.58622971335407	-1.87157175611587	-1.71288277472905
H	1.98030555551296	2.39542751043146	-1.46365014314478
H	1.12687004546122	-2.21680361245793	-0.52262268714083
H	-3.56130844919523	-1.56797477194020	1.98173198933175
H	-0.62543078130656	-1.40066286249835	3.97972761017572
C	-3.28004893110341	-3.08747105517973	-1.22629347534685
H	-4.36292335532971	-3.13314636497080	-1.38550522505144
H	-2.83925795867840	-3.96391906023501	-1.71252300849288
H	-3.08649679807302	-3.16577553945380	-0.15290390236528
C	-3.00746972551961	-1.73482103917194	-3.32770793343704
H	-4.09249359873235	-1.68756545041926	-3.47296884075159
H	-2.56804183447977	-0.85104492181491	-3.79816857414263
H	-2.62956800382302	-2.62293856351755	-3.84587353123905
C	-2.06480095627783	3.78485520958033	1.12555983616097
H	-1.24825806340708	4.48711155437012	1.32292848804263
H	-2.95858173553864	4.37730466930822	0.89697871243823
H	-2.25034016676427	3.20960310013793	2.03726147723731
C	-1.48865253085182	3.68886189715004	-1.32853115514449
H	-1.12933522800039	3.06909507175513	-2.15466198081490
H	-2.43482783433421	4.15118177215855	-1.63185645655784
H	-0.75667526039239	4.48692863913826	-1.16063035130952
C	2.37729601630523	-3.63234928082099	0.44992765250351
H	1.61235828788776	-4.41097021844975	0.36575247430329
H	3.35633865044552	-4.11625028607789	0.35858554261287
H	2.30157967022227	-3.18571565419344	1.44589143075124
C	2.30413309659749	-3.17595682355449	-2.04586865759177
H	1.61635316763882	-4.01984291780253	-2.17144535137394
H	2.08040362423923	-2.43444021744793	-2.81985664356546
H	3.32556824859152	-3.53861725718598	-2.20832617396400
C	3.84354703046756	3.44039237809641	-1.43476197800974
H	4.24854600134975	3.03253667794517	-2.36690439793064
H	3.35099891629924	4.39234239450179	-1.65970364772811
H	4.68281953623121	3.65652708230705	-0.76521807187103
C	2.31877581793530	3.03738259226375	0.54951665441300
H	3.13568525026739	3.12048551424652	1.27439565459456
H	1.88520542307073	4.03276612135904	0.39864866617985
H	1.55357056237855	2.38321933332111	0.97813013216891

Int4 (R = H, R' = Dipp)



TPSS D3BJ/def2-TZVP
E = −3542.86682611 Eh
G = −3542.32665437 Eh

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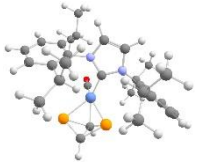
Ni	-0.09459583367570	-0.38169826625941	1.47294994172916
N	-1.24591226962693	0.11151691429967	-1.17002300507530
N	0.89308640583847	0.35783186550450	-1.23090141590963
C	-0.13557105724856	0.07277909627659	-0.35733095065026
C	-2.60449147321208	-0.03050730715161	-0.71943789244189
C	-3.11356899880580	-1.31961025358451	-0.49845553349512
C	-3.36116141761402	1.13882474980686	-0.53488555854379
C	2.27449193337816	0.49821471253699	-0.85547091165418
C	-0.91575815181010	0.39984790739981	-2.49074305534899
H	-1.66726312807329	0.46654001423773	-3.26027966840214
C	0.42821496647087	0.55823036301422	-2.52815725835995
H	1.09511242052403	0.79953257039406	-3.33834376516482
C	-4.68757725027183	0.98304369839856	-0.12005147913659
H	-5.30329630815772	1.86191638389555	0.04391015704352
C	-4.44584927567269	-1.42061958259929	-0.08802618652852
H	-4.87377965312953	-2.40064165030689	0.09850625912444
P	1.06882001239865	-2.37776053498612	1.52381402016248
C	2.68089330751350	1.71710625602484	-0.27601068282002
C	3.15215530927947	-0.57171766134534	-1.08196884117800
C	-5.22489484399650	-0.28215598070650	0.09798408750514
O	-2.72894618152923	-0.00183241988643	2.74042234995198
C	-1.73085072574793	-0.13377798031302	2.16503357414397
C	4.92148154818160	0.79134739515763	-0.12611047237574
C	4.49025785936722	-0.39544993518190	-0.70737841857169
H	5.19725654068986	-1.20444907244611	-0.86157968920843
C	4.02583230007675	1.83708801685614	0.08875174953753
H	4.37296053284767	2.75394012894502	0.55294824082894
C	2.68681693473613	-1.86514603974036	-1.73139452568127
H	5.96121243900837	0.90257429878551	0.16875448664710
C	1.69466881660484	2.85833290431501	-0.07512571209200
C	-2.25369078422812	-2.55306903282407	-0.71177021572726
C	-2.74642747512780	2.52044309934993	-0.70617232216204
H	-6.25620548765625	-0.38093648571545	0.42502348616887
C	2.40653331458166	-1.31914339221204	2.12774980802043
P	1.87511777845106	0.37366654920890	2.37489314430121
C	0.97380862231211	-1.17491534621940	2.92323695097830
H	-1.87257762997345	2.42194343627602	-1.35843209075397
H	-1.20886640005891	-2.23449749216552	-0.65249447654091
H	0.73182453995324	2.40158397736352	0.17555207866411
H	1.60859342077405	-1.94971226380148	-1.55527597241257
H	3.29480138336328	-1.73281362591834	2.61336522513201
H	0.79627339710476	-1.44302464643628	3.95925822526314
C	-2.45990430290133	-3.60610190610876	0.38582905464279
H	-3.46524454256271	-4.04056228124583	0.35174899994989
H	-1.74078816391878	-4.42170237922833	0.25723080123491
H	-2.30521763550591	-3.16576476640439	1.37522217808095
C	-2.49565704704120	-3.14656773905723	-2.11257652223242
H	-3.53644635554135	-3.47155559024332	-2.22317214875194
H	-2.28566774009024	-2.40897202027658	-2.89438141893857
H	-1.84577300162080	-4.01365610777612	-2.27548598025939
C	-3.70441129393563	3.51916418509886	-1.37278239840098
H	-4.08641047218479	3.13261983974333	-2.32349944206943
H	-4.56143489907232	3.74779968103450	-0.73034085889502
H	-3.18134684583679	4.46134528426653	-1.56846160464700
C	3.36109509240993	-3.11130555816157	-1.13672912998916
H	2.89154265669987	-4.01350781674495	-1.54203441975511
H	4.42562233612086	-3.15192849572454	-1.39282956664709
H	3.26812077746359	-3.13767387145141	-0.04782798617442
C	2.92494382446993	-1.82814656482694	-3.25509756375946
H	2.56273302183589	-2.75224508695978	-3.71906115590464
H	2.40957974364222	-0.98701269218852	-3.72589843763501
H	3.99505232513279	-1.73251528272102	-3.47074172842677
C	1.52052972172426	3.67311765449684	-1.37230925437616
H	2.47177334121038	4.12782057681807	-1.67098995131210
H	1.16374875338103	3.05011831609041	-2.19678332188212
H	0.79177869063599	4.47640766417620	-1.21551663364609
C	2.07272818319211	3.78999243069856	1.08384180240764
H	2.96633922326393	4.38192533522732	0.85402664829157
H	1.25333267687325	4.49217086268412	1.26904094054948
H	2.25665229366576	3.22802961300912	2.00445967415553
C	-2.24831014889666	3.05576242969289	0.65089294565804
H	-1.78142344676372	4.03892302057401	0.52043655993862
H	-3.08256112492416	3.15888542034713	1.35316871896234
H	-1.51518643876473	2.37547747691440	1.09495651425537

TS5 (R = H, R' = Dipp)



TPSS D3BJ/def2-TZVP
E = −3542.85280435 Eh
G = −3542.31265554 Eh
im. freq. = −192.40 cm^{-1}

0 1

Ni	0.10557074585377	0.18019806993108	1.50125475467410
N	-1.06518583845160	0.38282230632848	-1.23411382319943
N	1.07380396903600	0.10246962333059	-1.23502329270020
C	-0.00224546092653	0.19931987222030	-0.38596377209693
C	-2.44523497967542	0.39297911591269	-0.82660950730302
C	-3.20710951211401	-0.76508072372650	-1.07000652567223
C	-2.97193988409803	1.53797014573365	-0.20928950438339
C	2.42255919221051	-0.21134519361779	-0.82541178148964
C	-0.65787472364701	0.41587994641766	-2.56564231420804
H	-1.36076674059992	0.56352009036782	-3.36850633967750
C	0.68421600451865	0.23698654187749	-2.56609313945304
H	1.39582458021238	0.18285908150178	-3.37224957938272
C	-4.32031364321694	1.50309035651314	0.16163073238182
H	-4.75948597236860	2.37085100514514	0.64466817547587
C	-4.55494876636864	-0.73899551243167	-0.69889773690115
H	-5.17207448515520	-1.61553062096605	-0.87372377035997
P	-1.64248666558477	-1.12854153229294	1.91141791949753
C	3.39758585405902	0.79650684112210	-0.87205502208631
C	2.70358680587075	-1.53556656925626	-0.43554762277255
C	-5.10656647591850	0.38158749024846	-0.08684858723617
O	1.35324073301633	2.80888588453367	1.89751936321208
C	0.89515268472445	1.75980869363522	1.71646882093204
C	5.01273922473840	-0.85109783085267	-0.11741417650857
H	4.02083394756596	-1.82912716571544	-0.07866324458619
H	4.27378688236343	-2.83428963254515	0.24122628803845
C	4.70451567848869	0.44476862869477	-0.51193755594290
H	5.48374082688464	1.20049688823440	-0.53200989352271
C	1.62399804176036	-2.60704681155693	-0.43431759978460
H	6.03060809091566	-1.10249554018094	0.16769498395957
C	3.07961574522284	2.21483492147282	-1.31855235806064
C	-2.61203558545965	-2.01121132602765	-1.70919518860279
C	-2.14228518021558	2.78920543745079	0.01581120396241
H	-6.15286449499998	0.37887341999398	0.20566115543126
C	-0.58902734788935	-1.94289526551062	3.14841961474805
P	1.06066666965646	-1.16702479914361	3.08410267765318
C	-0.70237884858639	-0.37616608463621	3.28767790202553
H	-1.09300874502136	2.52527453335813	-0.13891347384307
H	-1.52598129804847	-1.88703284230914	-1.74910718633445
H	1.99569157007356	2.35524262793486	-1.24604485969608
H	0.70152014925312	-2.12491084080970	-0.09462784922720
H	-0.98234699829381	-2.57305413759692	3.94662164227893
H	-1.07378385828822	0.16048312861689	4.15124570629098
C	-2.89782355115314	-3.27841416292072	-0.88560780042314
H	-3.96934020260600	-3.50282057839843	-0.85518417041859
C	-2.38848473951080	-4.13711776648766	-1.33646944899219
H	-2.54577101246370	-3.16749795886698	0.14398273004990
C	-3.12370190114985	-2.18424256535934	-3.15163467459069
H	-2.89649369387130	-1.30768725011221	-3.76651386288815
H	-2.66148233904380	-3.06090254132556	-3.61847969422986
H	-4.21019203897738	-2.32564746573200	-3.15978788078770
C	-2.51937794687752	3.87496848604673	-1.01039769895099
H	-2.37959136323225	3.51651185517158	-2.03581432033048
H	-3.56810109150931	4.17174880189484	-0.89591783777564
H	-1.89517823770507	4.76396434319682	-0.86786416987348
C	-2.27272578873021	3.31440561925310	1.45350548922010
H	-1.58982830075538	4.15632931944619	1.60618397263172
H	-3.28940478699182	3.66396814175919	1.66467941036559
H	-2.01671112025741	2.53031981247812	2.17188015886671
C	3.49353941814517	2.42726462898502	-2.78914640678635
H	3.24047070810754	3.44224741375246	-3.11504394438755
H	4.57498411058246	2.29110295464652	-2.90050143340379
H	2.99709657838227	1.71965816555414	-3.45942970994574
C	3.75445165293981	3.27781891950619	-0.43520059912245
H	4.84083184811543	3.27685050055245	-0.57531031932655
H	3.38878421077957	4.27278817529218	-0.71042645838717
H	3.54181504933389	3.11478438860362	0.62297025741977
C	1.39713697439856	-3.16190158221550	-1.85479282879388
H	1.12068299547665	-2.37167304050305	-2.55921168346779
H	2.30538426629256	-3.64867146796127	-2.22791713400139
H	0.59161071988738	-3.90515499978346	-1.84445279789194
C	1.90791819743785	-3.75061699723288	0.54518472606852
H	1.03242830644125	-4.40532809152697	0.60390283221731
H	2.75899108346552	-4.36426932876471	0.22709553237204
H	2.10947110805199	-3.36280695034812	1.54806153003355

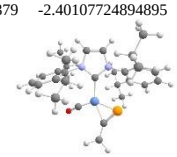
D (R = H, R' = Dipp)

TPSS D3BJ/def2-TZVP
E = −3542.88572799 Eh
G = −3542.34818686 Eh

0 1

Ni	0.00000099876292	0.54603969786464	1.37036436576746
N	-1.07465942890996	0.05657865442462	-1.39026282429671
N	1.07419844853149	0.05698151940533	-1.39053099674742
C	-0.00014610103451	0.17806093604286	-0.54336901523888
C	-2.43260224420950	0.02881865908291	-0.91511161619091
C	-3.05612814453548	-1.21928543239356	-0.76289232884728
C	-3.05950573503812	1.24491661251140	-0.59001254664962
C	2.43227492356681	0.02975744606301	-0.91572308432201
C	-0.67827341200606	-0.13949259976546	-2.71177146685658
H	-1.39107553404749	-0.25527662480938	-3.51158382198957
C	0.67755412553171	-0.13922569997841	-2.71194353924552
H	1.39019619954661	-0.25472793297106	-3.51193805997320
C	-4.36970440558199	1.17961010289943	-0.10843363613605
H	-4.88530203434576	2.09495720067065	0.16294156168954
C	-4.37262650796969	-1.22919243431720	-0.28858176803325
H	-4.88528135214998	-2.17795362938042	-0.15898684195667
P	-1.15600710944614	-0.89791404198650	2.63513456075617
C	3.05872051362174	1.24609303131264	-0.59062230970543
C	3.05639508913799	-1.21808942385179	-0.76383328689116
C	-5.02209130166395	-0.04341902163712	0.03596099365235
O	-0.00033884809774	3.17705096953978	2.67348676628674
C	-0.00026897987144	2.16601558139563	2.10284521606737
C	5.02202170844887	-0.04145036346838	0.03471424884117
C	4.37301234662313	-1.22746815881154	-0.28984188626092
H	4.88613432936984	-2.17601140613375	-0.16050238079000
C	4.36905841404790	1.18130841140662	-0.10935981666657
H	4.88431355686039	2.09684390699115	0.16202906019105
C	2.34685323681874	-2.51939626041933	-1.10250123491621
H	6.04059190846812	-0.06766846943555	0.41210501465568
C	2.34076942274747	2.57181743532785	-0.78901136113639
C	-2.34605647909439	-2.52031763174248	-1.10150220721666
C	-2.34221166214225	2.57094312066619	-0.78877470216727
H	-6.04056190097437	-0.07003727000994	0.41359173319257
C	0.00094497582461	-2.30493835897416	2.91299877471902
P	1.15712647638244	-0.89735463759203	2.63476692523289
C	0.00087772961848	-1.30696877651937	4.00557472699260
H	1.28633092575435	-2.29306027243969	-1.24947468558716
H	-1.28567448999878	-2.29350000413070	-1.24874275690170
H	1.28113569948414	2.39818868196808	-0.57097703355250
H	-1.28243111631362	2.39782770877058	-0.57103790600016
H	0.00120711363194	-3.38482981969351	2.86616159033653
H	0.00105685349061	-1.34745782807390	5.08507212978368
C	-2.44366647054369	-3.54727754540678	0.03811863014060
H	-3.47855493264332	-3.86782037999792	0.20015899449940
H	-1.85490091071453	-4.43735949551857	-0.21074629234127
H	-2.06293477065858	-3.12821800164182	0.97336561042297
C	-2.89211984025132	-3.11177654362553	-2.41507055962123
H	-3.95456650860867	-3.36022535678605	-2.31347942518387
H	-2.79200318656860	-2.40436432886037	-3.24452332970105
C	-2.35093706759568	-4.02790885847460	-2.67674837029942
C	-2.45757893523065	3.03358926316524	-2.25495455901587
H	-2.04836212579522	2.28687791845251	-2.94196180590240
H	-3.50597103313150	3.20777025748365	-2.52253358910097
H	-1.90514030596138	3.96858841410121	-2.40113582695448
C	-2.82783563605796	3.66955830969251	0.16460860041857
C	-2.18398236003920	4.54962805817772	0.06806178970482
H	-3.85214123588118	3.98497239913577	-0.06541857729379
H	-2.79234719553162	3.33651250904030	1.20583478249542
C	2.89290753375032	-3.11036902276510	-2.41629280296419
H	3.95548347695721	-3.35837277712825	-2.31497148678292
H	2.35207024292957	-4.02668977419366	-2.67802472609658
H	2.79230794586268	-2.40284750499967	-3.24559420402662
C	2.44521116426130	-3.54651264100447	0.03691160473248
H	1.85691238364713	-4.43688149171136	-0.21203365558927
H	3.48030668877634	-3.86649524919632	0.19873113769785
H	2.06438568215580	-3.12785061834090	0.97229701804515
C	2.82618102281486	3.67054677290720	0.16434654775075
H	3.85028301722457	3.98643268491782	-0.06593624623782
H	2.18191577303814	4.55034444766353	0.06806526591027
H	2.79112619665572	3.33738511078712	1.20554926068487
C	2.45547857419698	3.03468993804797	-2.25517352850367
H	3.50370479361215	3.20940946213986	-2.52304989500908
H	2.04641227387376	2.28786059968696	-2.94214066681871
H	1.90254253661746	3.96943786644379	-2.40107724894895

B (R = Me, R' = Dipp)



TPSS D3BJ/def2-TZVP
E = −3202.12258283 Eh
G = −3201.57354689 Eh

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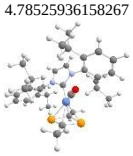
Ni	0.06541313752780	0.15330787696492	1.57918477770650
P	-1.83893732701522	-0.78356589396357	2.28491710291275
N	-1.03561568450198	0.17395235497932	-1.23373353840545
N	1.07155110661453	-0.24646575235388	-1.19846542852738
C	0.01254087342583	0.00630768291863	-0.36131636052371
C	-2.40457093853666	0.38398655528872	-0.84053729157657
C	-3.32040962549228	-0.65621874500713	-1.05549896063952
C	-2.76216668642331	1.60931935531107	-0.24697495492282
C	2.42175121400637	-0.44729666852243	-0.74366084452530
C	-0.63381605030368	0.03859207176776	-2.56030231309609
H	-1.32867715796380	0.14117989934303	-3.37761798824545
C	0.69409146864503	-0.23041363317180	-2.53841294523513
H	1.39946929325498	-0.41336527281487	-3.33220271645248
C	-4.10168703494586	1.78033758809749	0.10706529726047
H	-4.41460034801004	2.70606576751439	0.57796867481580
C	-4.65362777993854	-0.42800269978841	-0.69371292361341
H	-5.38646778157506	-1.21616760097219	-0.84254958760870
C	-0.72892590904287	-0.12742968082888	3.29003227282697
C	3.36194327294985	0.56375375002903	-0.99071099594791
C	2.73591642282786	-1.63871893617439	-0.06071435905304
C	-5.04199839194022	0.77683827952024	-0.12240797234642
O	2.59001633458425	1.32060972016201	2.44869196011634
C	1.59678202341510	0.87820865409643	2.04679754776198
C	5.02151018707953	-0.82726478447698	0.10323097979949
C	4.05815648761228	-1.80276654481508	0.35726442603929
H	4.33983049320933	-2.70181404981996	0.89490568242005
C	4.67596781732272	0.34262210269217	-0.56099554650391
H	5.42768842855171	1.10781224357756	-0.73285025818972
C	1.67391658567744	-2.69717372477498	0.19784611910016
H	6.04346201257254	-0.97795684267243	0.43972131163394
C	2.99158085819882	1.87281704822614	-1.67049546399577
C	-2.90695728325469	-2.01182489732956	-1.60704648493388
C	-1.72103255733549	2.68755633128241	0.00560782430165
H	-0.67863260969150	0.93285894782547	0.16288889816781
H	-1.82563247201807	-2.00137255712089	-1.76871076309052
H	-0.81132853674989	2.17092035222888	0.34216071084569
H	1.90903103631443	1.88150813093648	-1.82680839393329
H	0.75530783669422	-2.16543311997399	0.47678008645913
C	-3.20484309616538	-3.13365374692246	-0.59597201873859
H	-4.28053623599005	-3.22215769799754	-0.40838476647594
H	-2.84928404569531	-4.09410089617645	-0.98579106944039
H	-2.70917863147581	-2.93681542628548	0.35875205616480
C	-3.58123159691121	-2.29441791468648	-2.96123676990320
H	-3.34169292001921	-1.51696569321134	-3.69461656184899

H	-3.24773392205907	-3.25873436896227	-3.36010526415502
H	-4.67119465274536	-2.33012491991339	-2.85658605588778
C	-1.38026051408186	3.44818707512623	-1.29014297248859
H	-1.03623520966556	2.76814251808442	-2.07539309196193
H	-2.25942302275870	3.98507779212833	-1.66461832831632
H	-0.58599539824656	4.17907269561301	-1.10090167364015
C	-2.11366397950461	3.65783748499112	1.12448431943771
H	-1.27052308672870	4.32071060353005	1.34526228782301
H	-2.96356645728835	4.29033006798258	0.84235038490071
H	-2.37017542641106	3.11512942691454	2.03965876093762
C	2.01675324082853	-3.62963683181250	1.36483678738377
H	1.16079597293598	-4.27868914255337	1.57561354959024
H	2.87246824154353	-4.27538050564559	1.13542292506793
H	2.24211461846277	-3.06096421628236	2.27231729645542
C	1.38177479539392	-3.50971973081751	-1.07876184786590
H	1.07175789769163	-2.86239722890120	-1.90434621817170
H	2.27261006184795	-4.06431683614985	-1.39537180677563
H	0.57706606215668	-4.22919295306686	-0.89069910920886
C	3.33570024478543	3.08491422829661	-0.78726954857269
H	4.41488190109135	3.15700312732252	-0.61390585808428
H	3.01222254015679	4.00884887599081	-1.27960980589014
H	2.84137094435967	3.01680685192317	0.18496767389646
C	3.66889085791688	1.99057441200051	-3.04803306815340
H	4.75953955551289	2.00629535398575	-2.94502226688473
H	3.40747310048973	1.14642656575157	-3.69478595015947
H	3.36108135430370	2.91598588581574	-3.54694660929646
C	-0.31341790459726	0.20026406068892	4.67659116846220
H	-1.05229227691561	-0.12299530444778	5.41868430499906
H	0.64636896961896	-0.27819319348929	4.90792220441699
H	-0.15732969758220	1.28055127299510	4.78525936158267

C (R = Me, R' = Dipp)

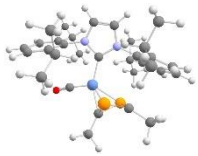


TPSS D3BJ/def2-TZVP
E = −3621.58898442 Eh
G = −3620.99400419 Eh

0 1

Ni	0.13522683711303	-0.83533331138670	1.13452353495529
N	-1.01615863728078	0.75491492933069	-1.12729419203059
N	1.11503716308657	0.46546351975104	-1.31817532832306
C	0.05529274298450	0.15984058885986	-0.49575250714802
C	-2.32674515023221	0.96114440765485	-0.55478304347809
C	-3.44473226703830	0.36740316829264	-1.16219478286111
C	-2.43816910467444	1.82271711851877	0.55407168012917
C	2.50560771883866	0.28860878442293	-0.96777459809360
C	-0.62363291541363	1.39132453500835	-2.30467497002714
H	-1.32911793472206	1.91872853641294	-2.92431038182710
C	0.71109835757903	1.20597894154888	-2.42560040388898
H	1.41184901150672	1.52571865225015	-3.17865375819945
C	-3.71584589728225	2.04511417065580	1.07152365920011
H	-3.83102779737911	2.69785888494295	1.93157081812882
C	-4.70231620213944	0.62777185864592	-0.60540512338625
H	-5.58246503220638	0.17191349941912	-1.04902854008487
P	-1.98589753406246	-1.55822168657526	1.66092058483629
C	3.21367112164482	1.41898770110172	-0.52571389186921
C	3.09512758437431	-0.98066448304854	-1.09444463823367
C	-4.83914387303440	1.45033755014263	0.50519129805213
O	2.27450512075395	0.38933048339477	2.68829407709265
C	1.43354090372121	-0.06543820818386	2.03409949375563
C	5.17613692605566	0.00540200819404	-0.32288928937063
C	4.44419910215208	-1.09904797212512	-0.75482863173233
H	4.92882282501267	-2.06709854224810	-0.82400386128243
C	4.56747151363313	1.24946617503799	-0.21337168197597
H	5.14280732926249	2.10263527502953	0.13403003333772
C	2.28438325348909	-2.15633906627370	-1.60476798131727
H	6.22481621645780	-0.10963171358597	-0.06326730021152
C	2.56902558226174	2.79093717657036	-0.38956321396548
C	-3.34056445482862	-0.51592354054110	-2.39324041624189
C	-1.24805728393023	2.55049283514949	1.15572170090860
H	-5.82274820680642	1.63304707285084	0.92859627079361
C	-0.89283469526988	-2.56457472382530	0.56029582409967
P	0.35093537667100	-3.04659688180737	1.72746780757206
C	-0.63344534813541	-1.88709154298373	2.76465200267780
H	-2.28465873074128	-0.76485195338115	-2.54130982880378
H	1.28546574800046	-2.04867787247727	-1.16908957897243
H	-0.33819815577912	2.06560409439508	0.79669649825191
H	1.48850491069857	2.67309314770606	-0.51223424270184
C	2.81136120019901	3.41911491218781	0.99325772700082
H	3.87689612139391	3.60512854267298	1.16478423223784
H	2.29216188249101	4.38164721879234	1.05603886100799
H	2.44755083650710	2.77300849262849	1.79459690286313
C	3.06957609457559	3.73644212920796	-1.49843057678778
H	2.56714320367833	4.70741712082365	-1.42826928340683
H	4.14847511478798	3.90212645774478	-1.40371332414134
H	2.88195649307960	3.32282845166738	-2.49421010210306
C	-1.22899757280554	4.01758976488490	0.68616861034188
H	-2.12960261986088	4.54473634221079	1.02036564942272
H	-0.35658371877954	4.53639411048288	1.09843482693425
H	-1.18485619464561	4.08281021176722	-0.40637033641664
C	-1.21789684893016	2.45022739514938	2.68765876929014
H	-2.06149661997133	2.97573671579812	3.14823644852451
H	-1.24696154316717	1.40090072540062	2.99339582983650
H	-0.29556527856021	2.89825148828949	3.07231351416141
C	2.83611535221378	-3.51410803068435	-1.15966718925899
H	2.14515896730299	-4.30835489490757	-1.46151375536243
H	3.80493655256984	-3.73167680588430	-1.62439400706165
H	2.94617455246382	-3.55699020853828	-0.07229801328318
C	2.15060802367384	-2.09988499309027	-3.13946302862328
H	1.68836866806434	-1.16402440386313	-3.46732168219135
H	3.13461018531147	-2.18003008853804	-3.61528129764403
H	1.52888936151316	-2.92862331171150	-3.49641281180612
C	-3.83095294060678	0.23182630383103	-3.64854803125466
H	-3.72066132935790	-0.39906454692311	-4.53746724799238
H	-4.88928400537286	0.49597121713021	-3.54591868937105
H	-3.27218465967551	1.15824656168148	-3.81401037019442
C	-4.12447637357894	-1.82957054191681	-2.22627532126731
H	-5.20427052939954	-1.64649836677236	-2.23098237770937
H	-3.89960282878062	-2.50937040986324	-3.05500420396063
H	-3.87036080661921	-2.32799839132459	-1.28802529591675
C	-0.45277190342609	-1.53143482531191	4.20843712316535
H	-0.84865067185383	-2.33784346874290	4.84028172145762
H	0.60376284792556	-1.40249204610532	4.46859576248954
H	-0.98560236699480	-0.61040665668210	4.47056427637730
C	-1.11220813250901	-3.09121430145614	-0.82398897143530
H	-1.34088608748053	-2.29996852072632	-1.54404729570010
H	-0.23249546224836	-3.63448705845529	-1.18533421485075
H	-1.95617508746795	-3.79337288769823	-0.83021092513634

TS4 (R = Me, R' = Dipp)



TPSS D3BJ/def2-TZVP
E = −3621.54782237 Eh
G = −3620.95563317 Eh
im. freq. = −106.59 cm^{-1}

0 1

Ni	-0.16320490074675	-0.62189710304725	-1.21398593587556
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N	-1.44819692161130	0.51403297657451	1.16679213217536
C	-0.29590015886305	0.34681770700182	0.42886679963922
C	2.05727295321218	1.03384075701503	0.90915890439010
C	2.94444513822381	0.16788092959454	1.56622151718977
C	2.47710620892495	2.00167562631758	-0.02330079330165
C	-2.76233957892158	0.09998575429945	0.75141224630130
C	0.11326650586532	1.45028938653309	2.40232443755865
H	0.72014780010111	1.95113902920673	3.13763754948329
C	-1.21188035015208	1.17684808251904	2.36702917860263
H	-2.00533536665220	1.38759496667549	3.06530970734742
C	3.84581330482786	2.07502052486936	-0.29756325377718
H	4.20688699158417	2.79842527933743	-1.02057642674416
C	4.30749476873359	0.29429959534958	1.26770986300182
H	5.02381761877925	-0.35648554773792	1.76072224158464
P	1.85516857819812	-0.15911796765813	-2.33950633847057
C	-3.64005439569754	1.08141883717414	0.26047813953385
C	-3.11310751466104	-1.25436802436985	0.87023443620187
C	4.75257199202325	1.23205557624447	0.34357907406341
O	-2.72191589315790	-0.74586066404560	-2.62454129877541
C	-1.73842487462025	-0.67479077083866	-2.01115334196716
C	-5.30233299530320	-0.66848125007947	0.00060920541043
C	-4.40673264453256	-1.61748959731421	0.48415881715934
H	-4.71219406014289	-2.65660173022712	0.55554372807746
C	-4.92247611917168	0.66585713111454	-0.11129594094019
H	-5.62784951700449	1.39208593645493	-0.50204557675168
C	-2.13299029438728	-2.27832452923304	1.41606180061058
H	-6.30153518844546	-0.97170046249182	-0.29960286805484
C	-3.18896869432193	2.52256498469822	0.07198154274732
C	2.47104820653982	-0.83538363635331	2.60710601558106
C	1.47722871884411	2.94629854427718	-0.67262967997989
H	5.81282156240766	1.30842979736129	0.11790771004057
C	2.55794289128904	-1.47712777926795	-1.35365897930619
P	1.19419106898227	-2.47952630729490	-0.73914007439179
C	0.81322105970784	-1.71899405356124	-2.40363860616147
H	0.57774693011085	2.35632173089763	-0.87772038396401
H	1.38599326172845	-0.93641952671824	2.50708541184458
H	-2.41840347817098	2.73485043173152	0.82138673277861
H	-1.12627146144155	-1.88123770674612	1.25685870469755
C	3.08385968860564	-2.23143015259651	2.41640963636574
H	4.17309414936719	-2.21293923297321	2.52990905316666
H	2.68346223644664	-2.91777392413763	3.17017253464240
H	2.84272003294379	-2.63902644176637	1.43081585782523
C	2.78041109023242	-0.31755722709725	4.02618620345281
H	3.86256640473552	-0.22045587488026	4.16919795672122
H	2.33118231852260	0.66375387663300	4.20582287372844
H	2.39623365679382	-1.01437225191125	4.77917491310290
C	1.96313014066789	3.52401268962236	-2.00705157167783
H	1.14842213202906	4.08230218216793	-2.47961008393176
H	2.79931901654798	4.21938349495185	-1.86704369833404
H	2.27793377192177	2.73190477862906	-2.69286366472276
C	1.09657716687067	4.08922740758152	0.29043612249426
H	0.65850452490343	3.70749620110234	1.21651498695808
H	1.97837308156896	4.68745709582411	0.54647259541451
H	0.36161432722343	4.74802711280112	-0.18524088394246
C	-2.20241961546382	-3.61505635382696	0.66598984435722
H	-1.39712379907440	-4.27360568075259	1.00703087536815
H	-3.15250203296644	-4.13385288622942	0.83705885572557
H	-2.08144578781270	-3.45800370306227	-0.41013059800769
C	-2.34133542759742	-2.47381662124504	2.92978374527376
H	-1.60148937467800	-3.17750674068789	3.32787695372648
H	-2.23736321186038	-1.52591070649573	3.46815282778655
H	-3.34106843190302	-2.87275672685110	3.13686733705833
C	-4.31950782858460	3.54062852218647	0.27776241849998
H	-4.82276943524714	3.39438967218738	1.23939072794344
H	-3.91018484339810	4.55608658816987	0.25338662589100
H	-5.07255175462503	3.47405765562745	-0.51498333897197
C	-2.54098435502454	2.69990783867350	-1.31615559114639
H	-3.26450097121008	2.47332765420155	-2.10659958446057
H	-2.19752557224635	3.73301248693184	-1.44382149144565
H	-1.68660757319361	2.02762336577225	-1.44147556414643
C	0.57522652035359	-2.51335784770367	-3.65813612617373
H	0.22499843929928	-1.85723574759340	-4.46092518095852
H	1.49785002292295	-3.00048455303706	-3.99464678933761
H	-0.17475903613119	-3.29057064406427	-3.48110587320220
C	3.98698933768291	-1.93445766129540	-1.43156989512219
H	4.08660585212697	-2.65231141827275	-2.25664870254659
H	4.66115348197232	-1.09655723517911	-1.62734927160288
H	4.28772656581795	-2.45019823242256	-0.51420574898889

Int4 (R = Me, R' = Dipp)

TPSS D3BJ/def2-TZVP
E = −3621.55283909 Eh
G = −3620.96099526 Eh

0 1

Ni	-0.09369475928162	-0.63117099872096	1.17426745258973
N	-1.48073193966284	0.51234546309670	-1.14041954485957
N	0.62675133558584	0.94864758494644	-1.23720148696771
C	-0.31191823675105	0.33470714639807	-0.43325564288958
C	-2.78493630115668	0.09338582318360	-0.70121117134835
C	-3.14240490302956	-1.25676072839229	-0.84175411723877
C	-3.64684733072571	1.06581528172425	-0.16646843362675
C	2.02676303918287	1.05689508417527	-0.92646544737162
C	-1.26986444864498	1.19931352656907	-2.33271980676056
H	-2.07887324109800	1.42168191073383	-3.00911497319540
C	0.05394467464825	1.47499959685537	-2.39239889058176
H	0.64094014596039	1.99562718451151	-3.12981877814807
C	-4.92024365124095	0.64455283582051	0.22929900598998
H	-5.61333529591929	1.36352109339637	0.65417178075925
C	-4.42667944613943	-1.62591837489778	-0.43130572331719
H	-4.73727405505874	-2.66223532620689	-0.51948143749900
P	1.18263619447919	-2.43526130857686	0.57865840118818
C	2.43280304900151	2.06986484808109	-0.03521653213714
C	2.92436242803494	0.16006356354730	-1.52487035488254
C	-5.30652833675816	-0.68609962857738	0.09725903634959
O	-2.63985082824776	-0.84721560478677	2.63852959554110
C	-1.67928920119497	-0.72801426313030	1.99775825103527
C	4.71233862538744	1.28178107895889	-0.32144190761950
C	4.28138719821351	0.29977396304739	-1.20590490038110
H	5.00493229598697	-0.37832783332684	-1.64813048469595
C	3.79706615175710	2.15806550022956	0.25920281884372
H	4.14486072079407	2.91470859122307	0.95430534622023
C	2.45985871238775	-0.89770779518830	-2.51356822632986
H	5.76789173134785	1.36465989571343	-0.07754218610359
C	1.42103030500696	3.03757288233343	0.55940157011039
C	-2.18097237474613	-2.26938925058436	-1.43927930065587
H	-6.29846857602087	-0.99385001047113	0.41625927343548
C	2.51691176694874	-1.53233380757456	1.41078399957986
P	1.87067653588617	-0.03191028020721	2.15462181900528
C	1.09444693184455	-1.74032706553704	2.29819361901766
H	-1.17001117594433	-1.86942160768681	-1.31790045581565
H	0.50036426646386	2.46714560774172	0.72021617521072
H	1.39703049453030	-1.08204072799011	-2.32206696447405
C	-2.21675363154062	-3.61560629367689	-0.70355864378714
H	-3.17518448028318	-4.12990951496645	-0.83672106965997
H	-1.43058306514242	-4.27169812538776	-1.09105330482190
H	-2.04530274015168	-3.47268064367358	0.36757778754218
C	-2.45086002483510	-2.44532676036338	-2.94573245889227
H	-3.45813964044956	-2.84200343059548	-3.11724512824319
H	-2.36903816648021	-1.48984698874736	-3.47448870225452
H	-1.72784014414571	-3.14294483003546	-3.38343959067551
C	-2.53895484132945	2.65996852412634	1.42888639244229
H	-3.26289816421291	2.42959727893126	2.21792218713111
H	-1.68900935175745	1.98042344362172	1.54551912239568
H	-2.18897244732833	3.68946399945370	1.56814844557397
C	3.20588025218916	-2.23199233540960	-2.35926629837574
H	2.74597821298674	-2.98936428344407	-3.00245002643819
H	4.25601168706748	-2.14111614981446	-2.65834833951297
H	3.17116997044811	-2.59477446903830	-1.32858369347821
C	2.60947268223962	-0.38812760185056	-3.96184839405343
H	2.24596417963539	-1.14099981460933	-4.66991390709460
H	2.04642529917442	0.53435831822338	-4.12629859683487
H	3.66288895559092	-0.18568170060272	-4.18531261041442
C	1.11560253973468	4.18484911130522	-0.42481841056794
H	0.02075510550741	4.76940223578293	-0.62445557343246
H	0.73278501964431	3.80856613753850	-1.37714311255276
H	0.36166661496151	4.85533676789761	0.00259485409701
C	1.85143027752267	3.61033917619554	1.91584323092087
H	2.69758786808822	4.29983608136899	1.81335806475278
H	1.02085337194016	4.17373559420065	2.35337994441156
H	2.13343288844270	2.81661779212705	2.61422162646028
C	0.90457176141795	-2.52183023337187	3.57731018207356
H	0.11849767396679	-3.27180915650327	3.45441589390382
H	1.83037866324259	-3.03885923798546	3.85502853517862
H	0.62417374894035	-1.85586131939715	4.39765664082101
C	3.85296368436854	-2.14893175736797	1.74983444063919
H	4.56604425699018	-1.87881607596542	0.96356031634025
H	4.24095718875635	-1.76906992600393	2.70037374265251
H	3.79133225093254	-3.24150204560709	1.79144165491467
H	-2.41952012415710	2.72105496545996	-0.70811728262591
C	-4.31702947772865	3.52664404750317	-0.15333642235805
H	-4.81954511708730	3.39398456750734	-1.11727498719865
H	-3.90486703084666	4.54059352627588	-0.11565815794591
H	-5.07134218869627	3.45217518957808	0.63744354163994
C	-3.18956101944334	2.50244108688900	0.03983472935048

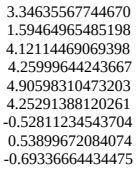
TS5 (R = Me, R' = Dipp)

TPSS D3BJ/def2-TZVP
E = −3620.83812246 Eh
G = −3620.94871914 Eh
im. freq. = −154.71 cm^{-1}

0 1

Ni	0.09016933614170	0.32607697103298	-1.26412251008008
N	-0.88815528878229	-1.13639030658115	1.14064925047157
N	1.23882977195801	-0.77892202491141	1.16447914171061
C	0.11145769425827	-0.53423197321166	0.41847367337779
C	-2.29142955452137	-0.99869596339537	0.85423804324689
C	-3.02790561407382	-0.08703584477260	1.63334556321725
C	-2.86241748269816	-1.75300251144157	-0.18166568658843
C	2.54317366883609	-0.22883246105289	0.88013700541082
C	-0.39190792710799	-1.75197923052903	2.28740672148765
H	-1.03581479890648	-2.28232232347673	2.96900750411201
C	0.94332989790133	-1.52614520622348	2.30298192413186
H	1.70559566523398	-1.81018485353473	3.00857430937860
C	-4.22976516503602	-1.58050664181459	-0.42167123463231
H	-4.70377242226923	-2.14637916461265	-1.21813608074714
C	-4.39556583546618	0.03054119969126	1.36713050213495
H	-4.99403704808022	0.72356244247172	1.95126055313200
P	-1.69075603595005	1.60099494741066	-0.95480033854323
C	3.54472771827758	-1.07806783432025	0.38796775893680
C	2.75465797185633	1.13851555502372	1.14317626041954
C	-4.99108320875488	-0.70545126474491	0.34842180253151
O	1.26951423252179	-1.79806913579546	-2.91168215966072
C	0.84218635540093	-0.95804732220594	-2.23427378815416
C	5.05066593531075	0.82539085622862	0.41331374454428
C	4.03208108318596	1.64475764166187	0.89603770309906
H	4.23121355060233	2.69599709419774	1.07442402410827
C	4.80945732472501	-0.51978874300832	0.16369700822148
H	5.60783187194284	-1.14663078412798	-0.22165811496961
C	1.64811366499349	2.02144368766989	1.70134244465731
H	6.03595037976165	1.24280279025059	0.22481879403542
C	3.29544623175183	-2.55366743225123	0.12203520502985
C	-2.38471926603545	0.75089355711654	2.72865803766123
C	-2.05484286535191	-2.75266212214200	-0.98997071523858
H	-6.05260807952768	-0.59131553544277	0.14715983472630
C	-0.72152698680189	2.95523985558836	-1.68030098843482
P	0.94842934899376	2.29872417652072	-2.03185944408366
C	-0.79614303371284	1.62763304419545	-2.56519485968033
H	-0.99665207170658	-2.55528131092770	-0.80070849461780
H	-1.29937225037577	0.63972002033076	2.64955970548783
H	2.21232833661501	-2.70263483480885	0.05458000268078
H	0.71614414918287	1.70303971600567	1.22233316877860
C	-2.70298435066478	2.24795554030024	2.57675737068318
H	-3.77447662009830	2.44298741923483	2.69229364844343
H	-2.17404212927470	2.82063502841938	3.34635567744670
H	-2.39578618337259	2.61932241107236	1.59464965485198
C	-2.81407013471992	0.25062941432788	4.12114469069398
H	-2.56866511675179	-0.80690258073657	4.25999644243667
H	-2.31172929174109	0.82656370650578	4.90598310473203
H	-3.89591716124927	0.36323778258329	4.25291388120261
C	-2.36488278437185	-4.18922590938783	-0.52811234543704
H	-2.15236022929600	-4.31471170134428	0.53899672084074
H	-3.42054898945916	-4.43319224534752	-0.69336664434475
H	-1.75605883420008	-4.90804910731934	-1.08751601106080
C	-2.28256812924679	-2.58937828752744	-2.50005641081386
H	-1.61740347085615	-3.26053593934264	-3.05279092657449
H	-3.31346083646438	-2.82959666668905	-2.78293031839785
H	-2.06584725975873	-1.56240309341797	-2.80764551476631
C	3.82666024374919	-3.41332461183415	1.28664472089594
H	3.61977824972988	-4.47372990002766	1.10450797092936
H	4.91053344397562	-3.28742870709637	1.38647044394537
H	3.36869828604687	-3.13421299411450	2.24004522956162
C	3.92068152091607	-3.02839101784395	-1.20040660609669
H	5.01465452196517	-3.02862054154549	-1.14334905976993
H	3.60205686852413	-4.05458391662990	-1.41180737529249
H	3.61713080619532	-2.39573189409874	-2.03660984264856
C	1.51096399865380	1.83651431700651	3.22616623908592
H	1.29066487106887	0.79812472386538	3.49034996394738
H	2.43706833003387	2.12966703497954	3.73336084792993
H	0.69865965050315	2.46402254233388	3.61031944365004
C	1.83168634433254	3.50543289134478	1.36312901491386
H	0.93536676431472	4.06019155466623	1.65969093576816
H	2.68344468889252	3.94475125721091	1.89548211298405
H	1.97893936289239	3.64522857402292	0.28821674430440
C	-1.31689721560565	1.49021041881913	-3.97456782279192
H	-1.30095747963486	2.46292739379401	-4.48076924682954
H	-0.68641608504232	0.80683399210450	-4.54858842286906
H	-2.34073751278829	1.10413110901380	-3.98720701465836
C	-1.28383780684744	4.26434136160767	-2.16148188322455
H	-1.08122415745574	5.04960370219090	-1.42525831238095
H	-0.79794484733657	4.55813222509730	-3.10097222467631
H	-2.36803957985035	4.21430298373896	-2.32089210291330

D (R = Me, R' = Dipp)



TPSS D3BJ/def2-TZVP
E = −3621.57573933 Eh
G = −3620.98672458 Eh

0 1

Ni	0.00001296036870	-0.06407181873426	1.32239741680436
N	-1.07490015141322	0.85515967074507	-1.32426018958963
N	1.07501289662463	0.85510461783085	-1.32426163073217
C	0.00004527186640	0.55534380749600	-0.52262813944087
C	-2.43722026638325	0.70171041269863	-0.88542779541878
C	-3.15132887619776	-0.43624965610081	-1.29236770648524
C	-2.98294530222604	1.68787795055177	-0.04368747065042
C	2.43732626244111	0.70164436271927	-0.88540968492080
C	-0.67774550912125	1.32418011081994	-2.57530369500020
H	-1.38947511448697	1.61605392716265	-3.32953232081353
C	0.67787683125146	1.32417247719261	-2.57529292654160
H	1.38961681691010	1.61605637840630	-3.32950814118309
C	-4.30450507577194	1.51313902675432	0.37597820592619
H	-4.75736020758303	2.24865463975154	1.03290151578714
C	-4.47452666483504	-0.55800298625322	-0.85410201198788
H	-5.05726011322913	-1.42554691776189	-1.14876582397678
P	-1.15560759409761	-1.95609113237819	1.66116824360709
C	2.98308128649038	1.68789031712812	-0.04378465353742
C	3.15142542702916	-0.43634957496741	-1.29228320455385
C	-5.04552536743251	0.40582274297880	-0.02994329959232
O	0.00026615103655	1.51708574059111	3.79519192266719
C	0.00016927302723	0.94707521429758	2.78309965159664
C	5.04565217937265	0.40582652591918	-0.02997018258997
C	4.47463115167699	-0.55806728922219	-0.85403734647400

H	5.05736494990025	-1.42562696705964	-1.14865232146847
C	4.30465191594656	1.51318544469791	0.37586585013602
H	4.75752885456550	2.24876146502694	1.03270655144787
C	2.52416708564169	-1.49697476936889	-2.18225187051764
H	6.07145890583531	0.28887856764338	0.30864282916269
C	2.17289451165015	2.90807546963553	0.36443117014973
C	-2.52406550160006	-1.49687009975873	-2.18233478701988
C	-2.17273540863048	2.90801083695323	0.36463527628238
H	-6.07132239162832	0.28884856482860	0.30869004532050
C	-0.00039213229191	-3.32088747259695	1.17570004177304
P	1.15518634118844	-1.95637214144072	1.66109305640380
C	-0.00031047040951	-3.03193200427846	2.62331754787372
H	1.43770665916690	-1.37190359074099	-2.12714614831688
H	-1.43761333662062	-1.37164301279948	-2.12742481596556
H	1.12640410253954	2.59195893487862	0.42796419042559
H	-1.12625380021271	2.59185949901620	0.42813696057965
C	-2.85008056833666	-2.92325544089811	-1.71338659923926
H	-3.91561661486620	-3.15065308015758	-1.82714874305364
H	-2.29298681979579	-3.64875641071444	-2.31616478123909
H	-2.57674693338437	-3.06046766687182	-0.66360543055110
C	-2.95527786775852	-1.30210619793839	-3.64899841178215
H	-4.04116257631478	-1.41319697185837	-3.74570545695063
H	-2.68455894968056	-0.30827801289618	-4.01788129627950
H	-2.47571830421624	-2.04881858707909	-4.29175922354290
C	-2.27739282301394	4.01242715943712	-0.70589628699398
H	-1.93683329929921	3.65728225897761	-1.68312414216283
H	-3.31461882361820	4.35155880306556	-0.80738665562337
H	-1.66071533438434	4.87318890851888	-0.42364485479398
C	-2.56348153739607	3.45596091470638	1.74315986589331
H	-1.85320344514196	4.23287929966427	2.04413711814885
H	-3.56153741650431	3.90898564341591	1.73263686180841
H	-2.54700891238985	2.66905797417697	2.50223447582591
C	2.95511214358982	-1.30199875421866	-3.64896682305073
H	4.04099981850749	-1.41290284682426	-3.74585022097066
H	2.47557313046351	-2.04872976942542	-4.29172113677230
H	2.68417147342418	-0.30818198278269	-4.01771636883247
C	2.85046731208800	-2.92337040266083	-1.71353317123428
H	2.29334220626077	-3.64887272663098	-2.31628051431420
H	3.91600715260290	-3.15062308398858	-1.82754659900022
H	2.57736474104060	-3.06073582084301	-0.66371094511107
C	2.56367723794410	3.45616150686682	1.74289333046384
H	3.56172801397487	3.90919509890007	1.73229358372697
H	1.85340577031342	4.23310594199157	2.04381881253142
H	2.54724489560430	2.66933129621247	2.50204079345481
C	2.27758164566388	4.01238274262705	-0.70621080008638
H	3.31481404895751	4.35148872486366	-0.80772068613202
H	1.93704020391783	3.65713987005640	-1.68340721075976
H	1.66091118589839	4.87318482809292	-0.42406519393730
C	-0.00037026999710	-3.83480927387313	3.88070795282410
H	-0.88825848518333	-4.47699565112420	3.93036582603048
H	0.88736149835963	-4.47721594551741	3.93031007752271
H	-0.00026195732055	-3.18322798949766	4.75987088039494
C	-0.00057213019060	-4.55698056660826	0.34025528783053
H	0.88701799249749	-5.16664038915139	0.55033871793709
H	-0.88823669599337	-5.16648166727257	0.55048227677638
H	-0.00063525668109	-4.31501100500295	-0.72681161792251

B (R = *t*Bu, NHC = *i*Pr$_2$Im^{Me})

TPSS D3BJ/def2-TZVP
E = −2700.40298464 Eh
G = −2700.02899215 Eh

0 1

Ni	0.05343667973151	0.72603589716477	0.18453049453422
P	0.90354276388996	1.31145065140401	-1.81633050851460
N	0.74616994454348	-2.21010049647172	0.16717880866222
N	-1.31641912272851	-1.90281471778695	-0.35499070781552
C	-0.18162504925254	-1.22125080145783	-0.01062857829247
C	2.18118829164413	-2.00898732029988	0.47619119868011
C	2.96718134461612	-1.71212926005488	-0.80444097151362
C	2.39800351985052	-0.94704805336327	1.55143228035238
C	-2.65773814023766	-1.30308809129440	-0.54388308352367
C	0.20653586824565	-3.48030647871277	-0.07008109849747
C	0.99055479366549	-4.74374128267408	0.04197275758688
C	-1.10333722862140	-3.28593549191462	-0.39209880000704
C	-2.16670447671325	-4.27591474188558	-0.72938625106700
C	0.68302485895459	3.79701378311882	-0.15234717308041
C	0.61798406965504	2.37321888655782	-0.60439061676148
C	-3.30996026399433	-1.02745820585103	0.81415853164487
C	-2.62113756135911	-0.06461472428355	-1.43460355139765
O	-0.83951601650397	1.35826201325828	2.88487711404977
C	-0.48477477960269	1.11820628072432	1.80547901411823
C	-0.73308564640954	4.28104924577754	0.22842426311028
C	1.24373582333985	4.68471953893861	-1.28299337427444
C	1.60383114964551	3.89462477350558	1.08374576446943
H	-0.69199931530444	5.32499155863761	0.56140492209140
H	-1.14521188984473	3.67142034728661	1.03696927710997
H	-1.40712979832009	4.21578002561886	-0.63176006395751
H	1.29566750801240	5.73188286863086	-0.96089938447533
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H	2.24860562929061	4.35409399979897	-1.56388232516046
H	1.66334740763480	4.93572545163030	1.42279710642029
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H	1.21746432234847	3.28088679640575	1.90197524853664
H	0.35529221290765	-5.59366127562055	-0.21878740026399
H	1.36208189834777	-4.90757843805704	1.06114479407784
H	1.85471432642652	-4.75436233828986	-0.63284848522320
H	-2.55723811277296	-4.12904481730150	-1.74384311915538
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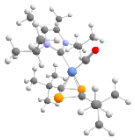
H	3.45600543766021	-0.94078895570491	1.83461188202676
H	1.79526955032118	-1.15458976258554	2.43989606211875
H	2.64397876142644	-0.75726542643695	-1.22873684404402
H	2.81119706558880	-2.49624698515244	-1.55234633937375
H	4.03702624950539	-1.65348657064266	-0.57882051242663

C (R = *t*Bu, NHC = *i*Pr$_2$Im^{Me})



TPSS D3BJ/def2-TZVP
E = −3237.89155936 Eh
G = −3237.39401173 Eh

0 1

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N	-1.64474143637115	-1.34928702545188	-0.55276760132322
N	-0.04371597764335	-2.15604122763269	0.66091809177563
C	-0.43918895930638	-1.02714221460298	0.00216342303597
C	-2.34188125005148	-0.40144413540751	-1.45795098360145
C	-3.82890145500527	-0.23123048939419	-1.13716788439583
C	-2.10241028221609	-0.77908314364030	-2.92143712824176
C	1.29777305795738	-2.23779474939396	1.29181033098317
C	-1.99715897793541	-2.66964806967971	-0.25503629044338
C	-3.25911654151083	-3.33675247477125	-0.68990025812176
C	-0.98464049662056	-3.17961813951705	0.51207880911855
C	-0.87031205208957	-4.53929784517109	1.11650220462981
P	-0.20332516231278	2.70288377950222	-0.30548258221006
C	2.27427890334345	-2.98308922799756	0.37903227399122
C	1.27238689214007	-2.80929538790558	2.71104939158338
O	1.76060884471876	-0.71338136787061	-2.71788356748831
C	1.33802489866378	-0.16114037697232	-1.78784585060314
C	-0.91224693225038	1.56341657039126	2.36398072928510
C	0.05888851277771	1.77083576658700	1.22621271247388
C	-2.33739107387672	1.33000757475803	1.84408694618813
C	-0.88470399799264	2.86870676705196	3.19774710728782
C	-0.48435940861642	0.38989003409041	3.25623370411851
P	1.86753324933425	1.63842305120278	1.26155079343529
C	1.58225020429542	2.36430699600914	-0.38002840232297
C	2.59987642278358	2.90562021521941	-1.35572821822958
C	2.01318853158018	3.01488131963554	-2.77300222114565
C	3.87844309946196	2.05116034934300	-1.36082942794434
C	2.95557510392632	4.32838531655475	-0.85356547525031
H	0.55664894484649	0.50384453268291	3.57954816821900
H	-0.57638172155175	-0.55008495299137	2.70745660955177
H	-1.11713471622957	0.33403978073213	4.14983439528100
H	-1.19164978317582	3.72173171567673	2.58469487559386
H	0.12434694850321	3.06123423405038	3.57534234023382
H	-1.56964580681782	2.78136628933944	4.04971466156709
H	-2.62958559252065	2.11604545254620	1.13834675987522
H	-3.05574812163698	1.32691576735636	2.67232716835259
H	-2.39381938998931	0.36659211459705	1.33261818387821
H	2.71755954011379	3.52771370165889	-3.43813072721567
H	1.07727897967090	3.58533519614844	-2.76066560898568
H	1.80268141746432	2.02678146655640	-3.19075916568729
H	4.64861634129242	2.52104170845673	-1.98340180891996
H	3.68134120168917	1.05003399456370	-1.75303233030909
H	4.27626911337684	1.94719246431921	-0.34482526512508
H	3.69304615456859	4.78806131849673	-1.52209550568943
H	3.37550142114023	4.28381467276186	0.15633811545271
H	2.06260306542800	4.96103561348859	-0.82707286335542
H	-3.42462589360280	-3.23895529888270	-1.76733964036540
H	-4.13799896955306	-2.93000604318954	-0.17801635987230
H	-3.20327248474231	-4.40305503159064	-0.45865714516724
H	-1.65443212645321	-5.18346956421929	0.71172307699947
H	-0.98633455072589	-4.51721156483932	2.20552609189193
H	0.09309052938961	-5.00720790388809	0.89201680992294
H	-1.82282958254342	0.54357966068538	-1.25689643615258
H	-4.43235391700896	-1.06848631563323	-1.49798710317707
H	-4.18476976183450	0.67368994830095	-1.63911676350116
H	-3.99769205369417	-0.10912583653206	-0.06468006367226
H	-2.56654617772119	-1.73906699952090	-3.17122158813472
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H	-2.54095846205485	-0.01271098456352	-3.56840703192170
H	2.30741732927727	-2.51894463996166	-0.60906135161033
H	1.99775384064822	-4.03665355080661	0.26389746980279
H	3.27853396809995	-2.94208877378099	0.81272716227958
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H	1.16899712990348	-3.89770411081129	2.72075749789368
H	0.46741288670675	-2.37193130127857	3.30637910608587
H	2.22176142255187	-2.56260309965953	3.19614923926283

5.5 Notes and references

‡ Ongoing calculations for **Int1**, **Int2**, and **TS1** (R = Mes, R' = Xy) have not been completed due to the computational cost associated with these large molecules.

§ A hypothetical 1,2-mechanism is conceivable. However, attempts to localise the corresponding **Int1'** have been unsuccessful in the timeframe of this thesis.

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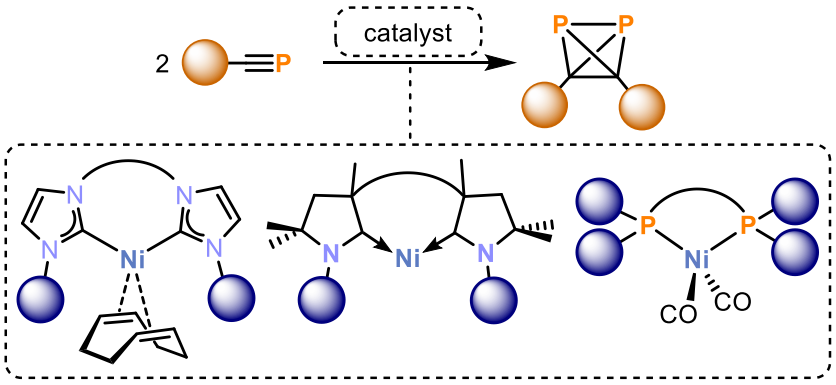
6 Nickel-Catalysed Phosphaalkyne Dimerisation: Impact of Ligands on Reactivity[a]

Abstract: Diphosphatetrahedranes are molecules with two phosphorus and two carbon atoms in a tetrahedral structure, promising versatile reactivity due to their unusual bonding. Unfortunately, only one diphosphatetrahedrane (*t*BuCP)$_2$ (**1**) has been isolated by the nickel-catalysed dimerisation of *t*BuCP with NHC-stabilised Ni catalysts (NHC = N-heterocyclic carbene). Here, we show that Ni complexes containing bidentate NHCs, CAACs, and diphosphines also catalyse the dimerisation of phosphaalkynes (CAAC = cyclic alkylaminocarbene). These promising preliminary results will stimulate further studies towards the synthesis of a wider variety of diphosphatetrahedranes.



[a] Maria K. Uttendorfer conducted all synthetic experiments, the characterisation of all compounds, the single-crystal X-ray diffraction analyses of **11**, **12**, **18**, and **20**, and wrote the manuscript. Wen Zhou performed single-crystal X-ray diffraction analyses of **9** and **14**. Alexander Harrison, Devon S. Louwe, and Morgan R. Faas synthesised **7**, **8**, and **16**. Roland Roesler and Robert Wolf conceptualised, supervised, and directed the project.

6.1 Introduction

Phosphatetrahedranes are molecules with a tetrahedral core composed of phosphorus and carbon atoms. Although their existence was predicted several decades ago, their synthesis has only been achieved within the last six years.[1] The first example, (*t*BuCP)$_2$ (**1**), Figure 1a), was reported in 2019 by Wolf and co-workers,[2] followed shortly thereafter by tri-*tert*-butylphosphatetrahedrane ((*t*BuC)$_3$P) (**2**) and triphosphatetrahedrane (HCP$_3$) (**3**), both synthesised by Cummins and co-workers.[3,4] Due to their unusual bonding pattern, these molecules exhibit intriguing reactivity. While coordination of the intact tetrahedrane to transition atoms has been reported,[1,4,5] their reactivity is generally dominated by bond cleavage and isomerisation processes, providing access to a wide variety of organophosphorus compounds.[6-13]

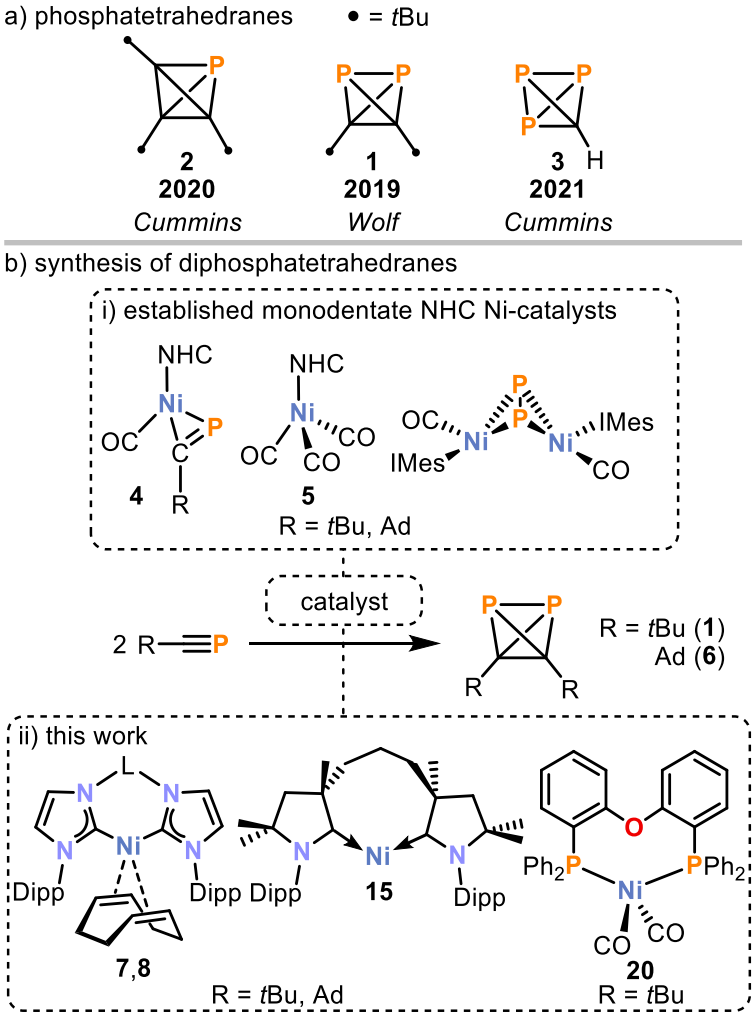


Figure 1. a) Phosphatetrahedranes isolated up to date.[2-4] b) Catalytic dimerisation of *t*BuCP and AdCP to form the diphosphatetrahedranes **1** and **6**. i) Established monodentate NHC Ni-catalysts (NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (IMes), 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (IPr)).[2] ii) This work: nickel complexes bearing bidentate bis(NHC) (**7** (L =–CH_2–$SiMe_2$–CH_2–), **8** (L = –CH_2–$SiMe_2$–O–$SiMe_2$–CH_2–)), a bidentate bis(CAAC) (**15**), or a bis(phosphine) ligand (**20**). Dipp = 2,6-diisopropylphenyl.

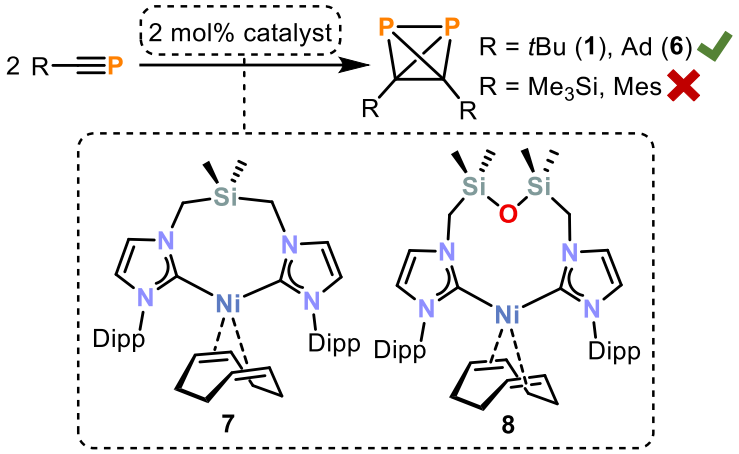
With only three examples **1**–**3** isolated to date,[2-4] the synthesis of new phosphatetrahedranes promises to provide further insights into this compound class and enable broader reactivity studies.

In contrast to **2** and **3**, which require multi-step syntheses,[3,4] **1** can be prepared by nickel-catalysed dimerisation of *tert*-butylphosphaalkyne, (*t*BuCP).[2] So far, Ni-complexes with monodentate NHC ligands were identified as catalysts with [(NHC)Ni(CO)(*t*BuCP)] (**4**) being the most effective catalyst reported to date [Figure 1b.i, NHC = N-heterocyclic carbenes: 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (IMes) and 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene (IPr)]. Complex **4** is generated in the catalytic reaction mixture from [(NHC)Ni(CO)$_3$] (**5**) with *t*BuCP. The use of other phosphaalkynes (RCP) has been unsuccessful, with the exception of AdCP. However, the yield of (AdCP)$_2$ (**6**) was low (10%) and isolation not possible.[2] Based on our experimental and computational findings, the dimerisation of the phosphaalkyne on the metal centre requires a very subtle balance between the steric properties of the phosphaalkyne and the ancillary ligand on nickel (see Chapter 5).[2] Therefore, further studies on ligands that could enable this transformation are necessary.

In this work, we studied the influence of bidentate NHCs, CAACs, and diphosphines on the catalytic dimerisation of phosphaalkynes to diphosphatetrahedranes (Figure 1b.ii). This approach expands the scope of catalysts capable of dimerizing phosphaalkynes to diphosphatetrahedranes and can serve as a starting point for testing a broader range of catalysts in the future.

6.2 Results and Discussion

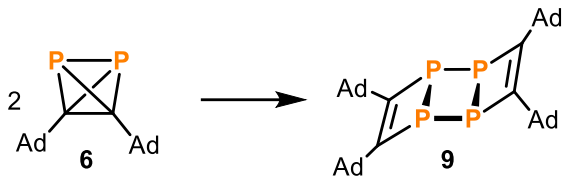
Complexes bearing bidentate NHCs have demonstrated their utility in a variety of catalytic transformations.[14,15] Their particular appeal in the synthesis of diphosphatetrahedranes lies in the enhanced steric and electronic tunability afforded by variation of the tethering linker.[14,16] Such tunability is crucial, as the optimal ligand choice depends on the specific phosphaalkyne undergoing dimerisation (see Chapter 5).[15] To assess whether bidentate NHCs are suitable for the catalytic formation of diphosphatetrahedranes, we decided to investigate the complexes **7** and **8** reported by Roesler and co-workers (Scheme 1).[16,17]



Scheme 1. Dimerisation of phosphaalkynes catalysed by **7** or **8**. Reactions of *t*BuCP and AdCP formed **1** and **6**, respectively, while reactions of Me_3SiCP or MesCP (Mes = 2,4,6-trimethylphenyl) did not yield the corresponding diphosphatetrahedranes. Reaction conditions: C_6D_6, 18 h, r.t. or 60 °C.

The complexes have a similar molecular structure but differ in that they contain a silane and a siloxane-based linker. Reactions of four different phosphaalkynes (RCP, R = *t*Bu, Ad, Mes, Me_3Si; Mes = 2,4,6-trimethylphenyl) were performed in the presence of catalytic amounts of these complexes. The reaction mixtures were analysed by ^{31}P NMR spectroscopy. The reactions of MesCP and Me_3SiCP did not afford the corresponding diphosphatetrahedranes (see Figures S23-S26 and S29-S32). In contrast, complexes **7** and **8** successfully catalyse the dimerisation of *t*BuCP and AdCP to the corresponding diphosphatetrahedranes **1** and **6**, respectively (Scheme 1 and Tables S1 and S2).

Notably, the yield of **6** increased significantly from 10% when using [(IMes)Ni(CO)$_3$] to 44% and 53%, respectively, when using **7** and **8** (see Table S1).[2] Unfortunately, the isolation of **6** remains challenging, which is part due to its tendency to dimerise to the ladderane $(AdCP)_4$ (**9**, Scheme 2), which is characterised by a singlet at −27.2 ppm in the ^{31}P NMR spectrum. Colourless crystals of **9** suitable for single-crystal X-ray diffraction analysis (SCXRD, Figure 2) were obtained from the crude reaction mixture of AdCP and 6 mol% **7** in toluene after crystallisation for 7 days at room temperature. The resulting solid-state structure closely resembles that of $(t\text{BuCP})_4$ (**10**),[18] which is formed upon irradiation of **1**.[2,12]



Scheme 2. Dimerisation of **6** to form the ladderane **9**. Observed in solutions containing **6**.

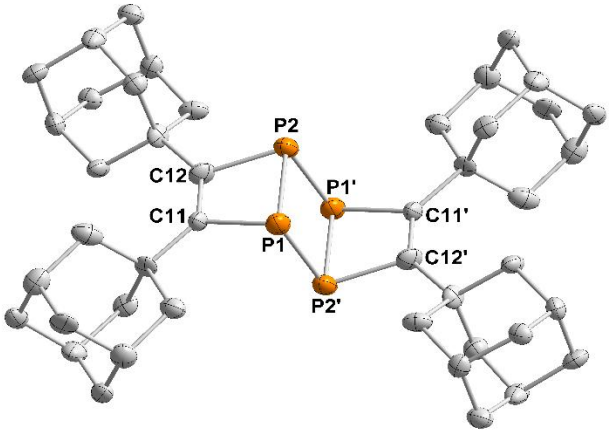
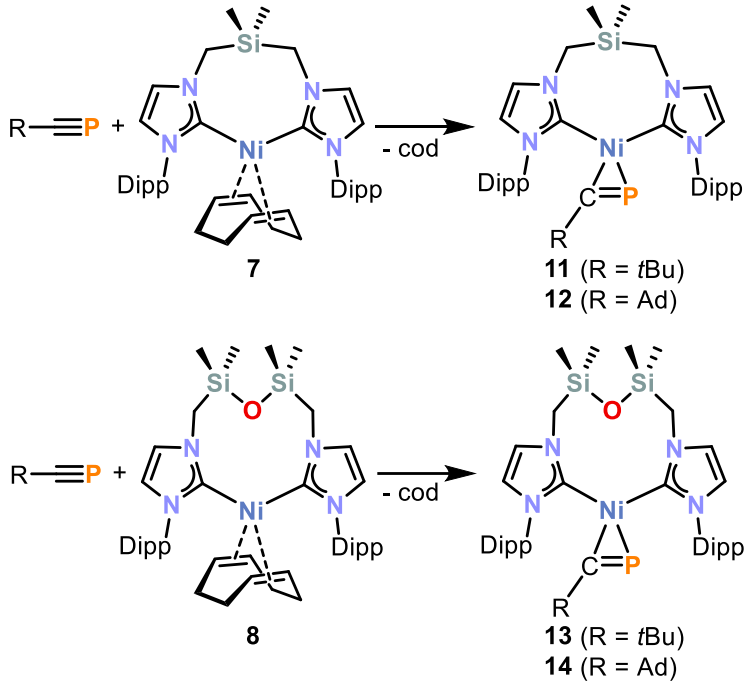


Figure 2. Molecular structure of **9** in the solid state. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–P2: 2.221(3), P1–C11: 1.863(8), P2–C12: 1.882(9), P1–P2': 2.251(4), P1–C11–C12: 104.4(6), C11–C12–P2: 101.5(6), C12–P2–P1: 77.5(3), P2–P1–C11: 76.6(3), C12–P2–P1': 96.9(3), C11–P1–P2': 96.9(3), P1–P2–P1': 89.27(13), P2–P1–P2': 90.73(13).

To identify possible intermediates, one equivalent of RCP (R = *t*Bu, Ad) was treated with one equivalent of **7** or **8** in toluene at −30 °C. This reaction resulted in η^2-phosphaalkyne complexes **11**-**14** (Scheme 3). Analogous complexes are formed in reactions of monodentate NHC-Ni-complexes with one equivalent of phosphaalkyne.[2] The formation of **11**-**14** hints that the mechanism of diphosphatetrahedrane formation is analogous for nickel complexes bearing either monodentate NHC or bidentate bis(NHC) ligands.

The complexes are characterised by their characteristic singlet resonance in the $^{31}P\{^1H\}$ NMR spectra (**11**: 146.2 ppm, **12**: 144.8 ppm, **13**: 151.0 ppm, **14**: 147.0 ppm). In addition, the solid-state structures of **11**, **12** and **14** were determined by SCXRD analysis (Figure 3 for **11** and **12**, for **14** see Figure S44). The structural data show close similarity to the related isoelectronic complexes [(NHC)Ni(CO)(R)] (NHC = IMes, IPr; R = *t*Bu, Ad) and [(*i*Pr$_2$Im)$_2$Ni(*t*BuCP)] (*i*Pr$_2$Im = 1,3-di(*iso*-propyl)imidazolin-2-ylidene),[2,19] particularly with respect to the elongation of the P–C bond of the coordinated phosphaalkine relative to uncoordinated *t*BuCP (1.548(1) Å)[20] Due to time constraints, isolation and complete characterisation of these complexes have so far not been achieved.



Scheme 3. Reaction of RCP (R = *t*Bu, Ad) with **7** (top) and **8** (bottom) yielding Ni-phosphaalkyne complexes (**11-14**; cod = 1,5-cyclooctadiene). Conditions: Tol., r.t., 2 d.

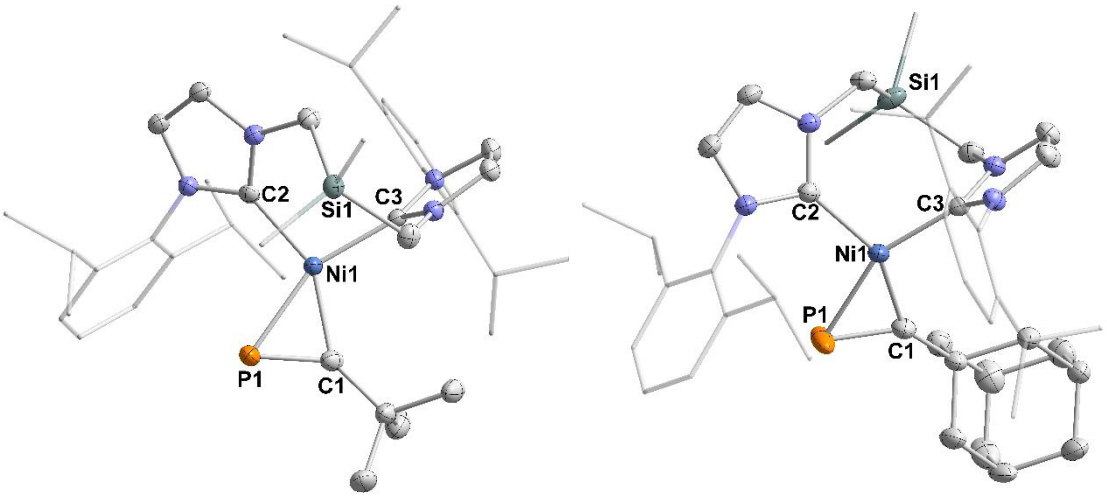
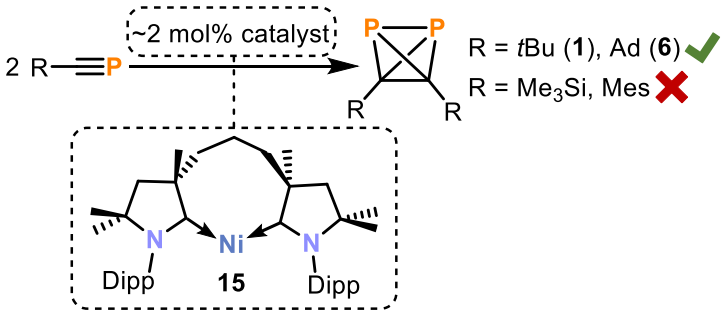


Figure 3. Molecular structure of **11** (left) and **12** (right) in the solid state. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **11:** Ni1–C1: 1.908(2), Ni1–C2: 1.905(2), Ni1–C3: 1.919(2), Ni1–P1: 2.1981(6), P1–C1: 1.642(2), C1–Ni1–P1: 46.49(7), C2–Ni1–P1: 102.39(6), C3–Ni1–P1: 154.04(6), C2–Ni1–C1: 148.86(9), C3–Ni1–C1: 108.62(9), C1–P1–Ni1: 57.40(7), C2–Ni1–C3: 101.94(8).

In comparison with NHC ligands, CAACs exhibit stronger σ-donating and π-accepting properties.[21] To investigate the effect of the different ligand properties on the Ni-catalysed phosphaalkyne dimerisation, we used the bidentate bis(CAAC) Ni-complex **15** recently reported by Roesler and co-workers (Scheme 4).[22] To avoid decomposition prior to catalysis, **15** was generated in situ by reacting the corresponding nickel dibromide complex (**16**) with an excess of KC_8 in THF, followed by filtration to remove excess KC_8 and the formed KBr as well as graphite.

The filtered solution was added to the RCP solution (R = *t*Bu, Ad, Me_3Si, Mes, Scheme 4), and the mixture was stirred for 18 h at room temperature or 60 °C.



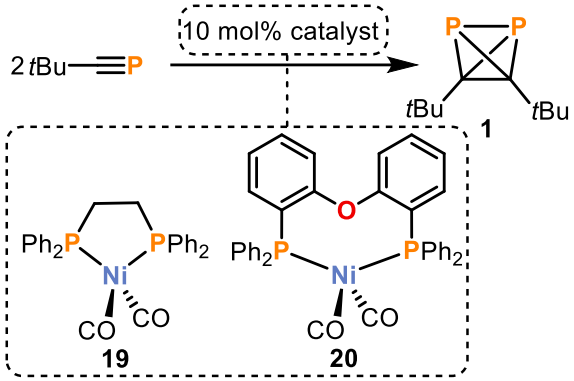
Scheme 4. Dimerisation of phosphaalkynes catalysed by **15**. Reactions of *t*BuCP and AdCP formed **1** and **6**, respectively, while reactions of Me_3SiCP or MesCP (Mes = 2,4,6-trimethylphenyl) did not yield the corresponding diphosphatetrahedranes. Reaction conditions: THF, 18 h, r.t. or 60 °C.

Similar to the bidentate NHC Ni-complexes **7** and **8**, complex **15** dimerises *t*BuCP and AdCP to form the corresponding diphosphatetrahedranes (although in lower yields, 25% of **1** and 29% of **6**, see Tables S1 and S2) but fails with Me_3SiCP and MesCP. Interestingly, the temperature dependence of catalytic performance differed between the systems. While catalytic reactions with **7** and **8** gave higher yields at 60 °C than at room temperature, the opposite trend was observed for **15**. These results suggest that the catalyst decomposes at elevated temperatures.

Overall, earlier results in combination with our study demonstrate that several complexes containing monodentate NHCs,[2] bidentate NHCs, and bidentate CAACs are capable of catalysing the formation of diphosphatetrahedranes. A key limitation of all these systems, however, is the time-consuming and multi-step nature of their synthesis.[16,17,23] Owing to the mechanistic insight that each phosphaalkyne may require a tailored catalyst, this poses a significant synthetic challenge (see Chapter 5).[12]

To overcome this issue, we explored the use of phosphines, which are versatile ligands in a wide array of catalytic reactions, as a more synthetically and commercially accessible alternative.[23-26] Several Ni-phosphine complexes were screened for their ability to catalyse the dimerisation of *t*BuCP. Reactions of 10 mol% of monodentate phosphine Ni-complexes (tBu_3P)Ni(CO)$_3$] (**17**), or [(Cy_3P)Ni(CO)$_3$] (**18**) did not afford **1** according to ^{31}P NMR spectroscopy. Encouraged by the success of Ni-complexes bearing bidentate NHCs and CAACs (*vide supra*), we turned to diphosphine Ni-complexes [(L)Ni(CO)$_2$]. Gratifyingly, diphosphatetrahedrane **1** was detected upon treatment of *t*BuCP at 60 °C in C_6D_6 for 18 h with catalytic amounts (10 mol%) of complexes **19** with L = 1,2-bis(diphenylphosphino)ethane) and **20** L = bis[(2-diphenylphosphino)phenyl]ether) (Scheme 5). Using **20**, the reaction appears to be very selective according to ^{31}P NMR spectra. Nevertheless, these reactions are very low-yielding (0.8% for **19** and 2.6% for **20**) in comparison with the reactions using NHC-Ni catalysts. Significant amounts

of unreacted *t*BuCP were observed even when the reactions were performed for 50 hours at 60 °C. indicating a significantly slower conversion than with NHC-based systems. The low yields are also attributed to the temperature sensitivity of **1**, which decomposes over prolonged reaction times, as indicated by the decreasing signal intensity in the ^{31}P NMR spectrum (see Figure S43).[2] Although further reaction optimisation and testing of other diphosphine ligands is required, these results clearly indicate that diphosphine Ni-complexes can catalyse diphosphatetrahedrane formation.



Scheme 5. Dimerisation of *tert*-butylphosphaalkyne catalysed by **19** or **20**, forming **1**. Reaction conditions: C_6D_6, 18 h, r.t. or 60 °C.

6.3 Conclusion

The results of this work demonstrate that the dimerisation of phosphaalkynes to diphosphatetrahedranes can be catalysed not only by monodentate Ni-NHC complexes, but also by Ni-complexes bearing bidentate NHCs (**7** and **8**), CAACs (**15**), and diphosphines (**20**). All of these systems are suitable for the synthesis of (*t*BuCP)$_2$ (**1**), currently the only isolable diphosphatetrahedrane.[2] Moreover, **7**, **8**, and **15** enabled the synthesis of (AdCP)$_2$ (**6**), with **7** and **8** providing significantly improved yields over previous methods.[2] Further optimisations might not only allow for higher yields, but also for systems tailored to specific phosphaalkynes, enabling their selective dimerisation and expanding the scope of accessible diphosphatetrahedranes.

6.4 Supporting Information

General: All reactions and manipulations were carried out in flame-dried glassware under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques (maintained at <0.1 ppm H_2O and <0.1 ppm O_2). [(NHC)Ni(η^2-cod)] (NHC = dimethylsilylbis(methylimidazolylidene) (**7**),[17a] tetramethyl-disiloxanebis(methylimidazolylidene) (**8**)),[17b] [($C_{41}H_{62}N_2$)$NiBr_2$] (**16**),[22] [(*t*Bu_3P)$Ni(CO)_3$] (**17**),[27] [(($Ph_2P)_2C_2H_4$)$Ni(CO)_2$] (**19**),[28] *t*BuCP,[29] MesCP,[30] AdCP,[31] and Me_3SiCP,[32] were prepared according to procedures previously reported in the chemical literature. All other chemicals were purchased from commercial suppliers and used without further purification. All catalytic reactions were performed in the dark, as much as possible, e.g. by wrapping flasks in aluminium foil.

Solvents were dried and degassed with a MBraun SPS800solvent purification system. All dry solvents except *n*-hexane were stored under argon over activated 3 Å molecular sieves in gas-tight ampules. *n*-Hexane was stored over a potassium mirror.

NMR spectroscopy: NMR spectra were recorded on Bruker Avance III HD 400 and Bruker Advance *Neo* 500 spectrometers. All spectra were recorded at 300 K and internally referenced to residual solvent resonances (^{1}H NMR: C_6D_6: 7.16 ppm, $^{13}C\{^1H\}$ NMR: C_6D_6: 128.06 ppm). Chemical shifts (δ) are given in ppm referring to external standards of tetramethylsilane (^{1}H, $^{13}C\{^1H\}$) and 85% phosphorus acid ($^{31}P\{^1H\}$). ^{13}C NMR signals were assigned based on 2D NMR spectra (^{1}H,^{13}C-HSQC, ^{1}H,^{13}C-HMBC). Spectroscopic yields of products obtained in the catalytic reactions (Section 6.4.2) were determined using quantitative $^{31}P\{^1H\}$ NMR (zgig30, D1 = 30 s, inverse gated decoupled) with PPh_3 as an internal standard.

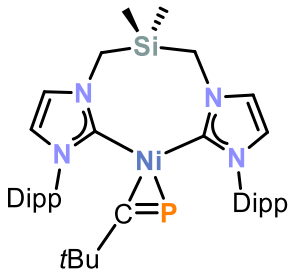
Elemental analysis: The elemental analysis was determined by the analytical department of the University of Regensburg with a Micro Vario Cube (Elementar).

6.4.1 Synthesis of Compounds

Reaction of 7 with *t*BuCP, formation of 11:

*t*BuCP (35 µL, 2.76 mol/L in $(Me_3Si)_2O$, 0.096 mmol, 1.05 eq.) was added to the dark orange solution of **7** (65 mg, 0.092 mmol, 1.0 eq.) in toluene (4 mL) at −30 °C, and the brown reaction mixture stirred for 19 h at room temperature and subsequently investigated by NMR spectroscopy (Figure S1). The isolation and complete characterisation of **11** have not been achieved to date.

Single crystals suitable for X-ray analysis were obtained as orange blocks from slow diffusion of *n*-hexane (3 mL) into a concentrated solution in toluene (1 mL) at ambient temperature after 13 days.



$C_{39}H_{59}N_4NiPSi$, MW = 701.68 g/mol

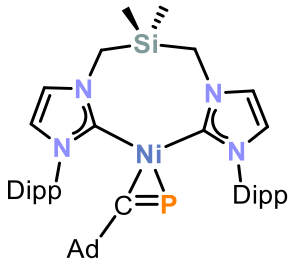
$^{31}P\{^1H\}$ NMR (202 MHz, 300 K, C_6D_6): δ = 146.7 ppm.

Reaction of 7 with AdCP, formation of 12:

AdCP (18.3mg, 0.096 mmol, 1.05 eq.)[a] was added to the brownish solution of **7** (65 mg, 0.092 mmol, 1.0 eq.) in toluene (4 mL) at −30 °C, and the reaction mixture was stirred for 19 h at room temperature and subsequently investigated by NMR spectroscopy (Figure S2). The isolation and complete characterisation of **12** have not been achieved to date.

[a]Contains 13 mol% DME.

Single crystals suitable for X-ray analysis were obtained as orange plates through the slow diffusion of *n*-hexane (3 mL) into a concentrated THF solution (1 mL) at ambient temperature after 13 days.

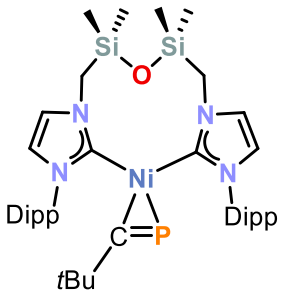


$C_{45}H_{65}N_4NiPSi$, MW = 779.80 g/mol

$^{31}P\{^1H\}$ NMR (202 MHz, 300 K, C_6D_6): δ = 145.1 ppm.

Reaction of 8 with *t*BuCP, formation of 13:

*t*BuCP (3.9 µL, 2.76 mol/L in $(Me_3Si)_2O$, 0.011 mmol, 1.05 eq.) was added to the orange solution of **8** (8.0 mg, 0.010 mmol, 1.0 eq.) in toluene (0.5 mL) at −30 °C and the reaction mixture stirred for 22 h at room temperature. The solvent was removed *in vacuo* and the resulting brown solid dissolved in C_6D_6 and investigated by NMR spectroscopy (Figure S3). The isolation and complete characterisation of **13** have not been achieved to date.



$C_{39}H_{59}N_4NiPSi$, MW = 701.68 g/mol

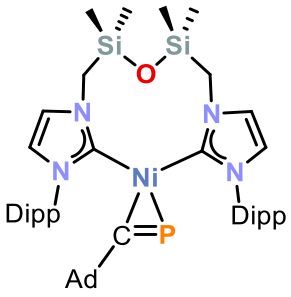
$^{31}P\{^1H\}$ NMR (202 MHz, 300 K, C_6D_6): δ = 151.0 ppm.

Reaction of 8 with AdCP, formation of 14:

AdCP (2.0 mg, 0.011 mmol, 1.05 eq.)[a] was added to the orange solution of **8** (8.0 mg, 0.010 mmol, 1.0 eq.) in toluene (0.5 mL) at −30 °C , and the reaction mixture was stirred for 22 h whilst letting it warm to room temperature. The solvent was removed *in vacuo*, and the resulting brown solid dissolved in C_6D_6 and investigated by NMR spectroscopy (Figure S4). The isolation and complete characterisation of **14** have not been achieved to date.

[a]Contains 13 mol% DME.

Single crystals suitable for X-ray analysis were obtained as orange plates from slow diffusion of *n*-pentane (a mL) into a concentrated solution in toluene (0.3 mL) at −30 °C after eleven days.



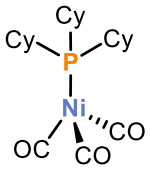
$C_{45}H_{65}N_4NiPSi$, MW = 779.80 g/mol

$^{31}P\{^1H\}$ NMR (202 MHz, 300 K, C_6D_6): δ = 147.0 ppm.

[(Cy_3P)$Ni(CO)_3$] (18):

To Cy_3P (140 mg, 0.5 mmol, 1.0 eq.) in toluene (5 mL) $Ni(CO)_4$ (0.5 mL, 1.21 mol/L in toluene, 0.6 mmol, 1.2 eq.) in toluene (5 mL) at −40 °C was added, and the reaction mixture was stirred for 16 h at room temperature. The solvent was removed *in vacuo*, and the remaining residue was taken up in *n*-pentane (1.5 mL). The mixture was then filtered and left to crystallise at −30 °C. After six days, the clean compound was isolated as colourless crystals.

Single crystals suitable for X-ray analysis were obtained as colourless blocks from a concentrated solution in *n*-hexane (1 mL) at −30 °C after seven days.



$C_{21}H_{33}NiO_3P$, MW = 423.16 g/mol

Yield: 91 mg (0.22 mmol, 44%).

NMR signals are in agreement with literature reports.[33]

^{1}H NMR (500 MHz, 300 K, C_6D_6): δ = 0.89–1.30 (m, 15H, Cy-*H*), 1.41–1.94 (m, 18H, Cy-*H*) ppm.

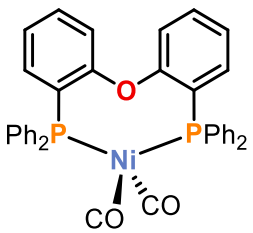
^{13}C{^{1}H} NMR (151 MHz, 300 K, C_6D_6): δ = 26.2 (s, Cy), 27.3 (d, J_{PC} = 10.6 Hz, Cy), 29.9 (d, J_{PC} = 2.0 Hz, Cy), 34.6 (d, J_{PC} = 14.7 Hz, Cy), 198.3 (s, 3C, *C*O) ppm.

^{31}P{^{1}H} NMR (202 MHz, 300 K, C_6D_6): δ = 45.1 ppm.

[(DPEphos)$Ni(CO)_2$] (20):

To $Ni(CO)_4$ (1.6 mL, 1.21 mol/L in toluene, 1.95 mmol, 1.3 eq.) in toluene (20 mL) at −40 °C bis[(2-diphenylphosphino)phenyl]ether (DPEphos, 820 mg, 1.5 mmol, 1.0 eq.) in toluene (40 mL) was added, and the reaction mixture was stirred for 16.5 h at room temperature. The yellowish white precipitate formed during the reaction was filtered off and dried *in vacuo*.

Single crystals suitable for X-ray analysis were obtained as colourless blocks from slow diffusion of *n*-hexane (3 mL) into a concentrated solution in toluene (1 mL) at ambient temperature after seven days.



$C_{38}H_{28}NiO_3P_2$, MW = 653.28 g/mol

Yield: 410 mg (containing 0.8 eq. toluene, 0.564mmol, 38%).

^{1}H NMR (500 MHz, 300 K, C_6D_6): δ = 6.45 (t, *J* = 7.5 Hz, 2 H), 6.60-6.63 (m, 2H), 6.67-6.73 (m, 4H), 6.98-7.03 (m, 12H), 7.58-7.62 (m, 8H) ppm.

^{13}C{^{1}H} NMR (151 MHz, 300 K, C_6D_6): δ = 132.2 (d, *J* = 3.8 Hz, Ar), 123.7 (d, *J* = 4.4 Hz, Ar), 128.1 (s, Ar), 128.2 (s, Ar), 128.0 (s, Ar), 130.3 (s, Ar), 133.4 (s, Ar), 133.5 (s, Ar), 133.7 (s, Ar), 136.4 (dd, *J* = 4.0 Hz, 31.0 Hz, Ar), 159.1 (d, *J* = 5.0 Hz, 11.0 Hz, Ar), 200.0 (t, *J* = 5.0 Hz Hz, *C*O) ppm.

^{31}P{^{1}H} NMR (202 MHz, 300 K, C_6D_6): δ = 22.2 ppm.

Elemental Analysis calcd. (for **20** + 0.8 toluene) C 72.03, H 4.77; found C 72.92, H 4.74.

6.4.2 Additional Experiments

General Procedure 1 (GP1):

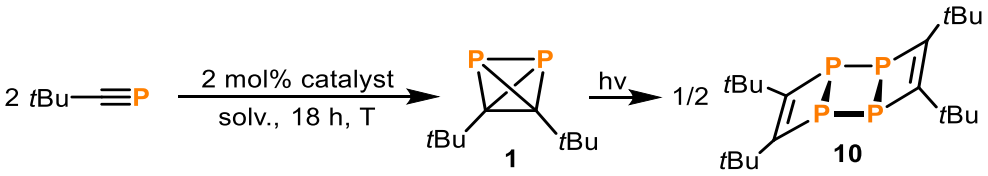
Phosphaalkyne was added to a solution of the Ni complex in C_6D_6 (0.5 mL), and the reaction was stirred at a defined temperature (T) for 18 h. Subsequently, internal standard PPh_3 was added and the reaction investigated by quantitative $^{31}P\{^1H\}$ NMR spectroscopy to determine the yield of diphosphatetrahedrane formed in the reaction.

General Procedure 2 (GP2):

To **16** in THF (1 mL) KC_8 was added and the reaction mixture stirred at room temperature for 5 min, forming **15**. The magenta solution was filtered, added to phosphaalkyne and the reaction stirred at a defined temperature (T) for 18 h. Subsequently, internal standard PPh_3 was added and the reaction investigated by NMR spectroscopy to determine the yield of diphosphatetrahedrane formed in the reaction.

Reactions of *t*BuCP with NHC catalysts

Table S1. Catalytic dimerisation of *t*BuCP (0.065 mL, 1.94 mol/L, 0.13 mmol, 1.0 eq.) with 2 mol% (0.025 mmol) of **7**, **8**, and **15** to form **1**.

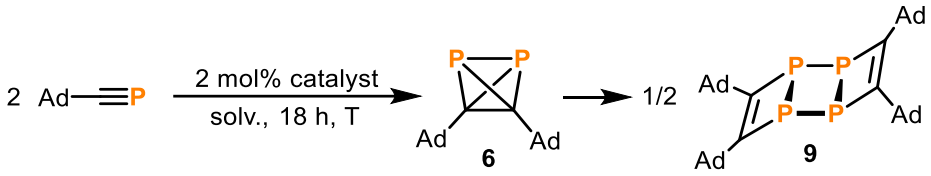


Entry	Catalyst	Temperature (T)	Yield (**1**)	Yield (**10**)
1[a]	**7**	r.t.	18%	not detected
2[a]	**7**	60 °C	68%	9%
3[a]	**8**	r.t.	28%	2%
4[a]	**8**	60 °C	35%	4%
5[b]	**15**	r.t.	25%	9%
6[b]	**15**	60 °C	1%	39%

[a] Following GP1. Solv. = C_6D_6. [b] Following GP2. KC_8 (2.0 mg, 0.015 mmol, 12 mol%). Solv. = THF.
For ^{31}P NMR spectra of entries 1-6 see Figures S11-S16.

Reactions of AdCP with NHC catalysts

Table S2. Catalytic dimerisation of AdCP (23 mg, 0.13 mmol, 1.0 eq.)[a] with 2 mol% (0.025 mmol) of **7**, **8**, and **15** to form **8**.

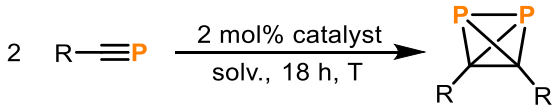


Entry	Catalyst	Temperature (T)	Yield (**6**)	Yield (**9**)
1[b]	**7**	r.t.	25%	1%
2[b]	**7**	60 °C	44%	2%
3[b]	**8**	r.t.	31%	1%
4[b]	**8**	60 °C	53%	2%
5[c]	**15**	r.t.	29%	2%
6[c]	**15**	60 °C	15%	3%

[a] Contains 13 mol% DME.
[b] Following GP1. Solv. = C_6D_6. [c] Following GP2. KC_8 (2.0 mg, 0.015 mmol, 12 mol%). Solv. = THF.
For ^{31}P NMR spectra of entries 1-6 see Figures S17-S22.

Reactions of MesCP and Me_3SiCP with NHC catalysts

Table S3. Catalytic reactions of RCP (R = Mes, Me_3SiCP) with 2 mol% (0.025 mmol) of **7**, **8**, and **15**.

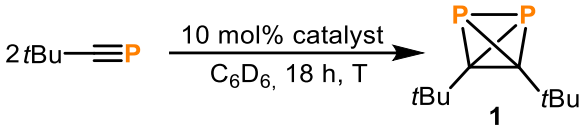


Entry	RCP	Catalyst	Temperature (T)	$(RCP)_2$
1[a]	MesCP[b]	**7**	r.t.	not detected
2[a]	MesCP[b]	**7**	60 °C	not detected
3[a]	MesCP[b]	**8**	r.t.	not detected
4[a]	MesCP[b]	**8**	60 °C	not detected
5[c]	MesCP[b]	**15**	r.t.	not detected
6[c]	MesCP[b]	**15**	60 °C	not detected
7[a]	Me_3SiCP[d]	**7**	r.t.	not detected
8[a]	Me_3SiCP[d]	**7**	60 °C	not detected
9[a]	Me_3SiCP[d]	**8**	r.t.	not detected
10[a]	Me_3SiCP[d]	**8**	60 °C	not detected
11[e]	Me_3SiCP[d]	**15**	r.t.	not detected
12[e]	Me_3SiCP[d]	**15**	60 °C	not detected

[a] Following GP1. Solv. = C_6D_6. [b] MesCP (1.1 mL, 0.028 mol/L in *n*-pentane, 0.031 mmol, 1.0 eq.). [c] Following GP2. KC_8 (2.0 mg, 0.015 mmol, 12 mol%). Solv. = THF. [d] Me_3SiCP (1.6 mL, 0.022 mol/L in toluene, 0.035 mmol, 1.0 eq.).
[e] Following GP2. KC_8 (0.5 mg, 0.004 mmol, 8 mol%). Solv. = THF.
For ^{31}P NMR spectra of entries 1-12 see Figures S23-S34.

Reactions of *t*BuCP with phosphine Ni catalysts

Table S4. Catalytic dimerisation of *t*BuCP (0.091 mL, 2.76 mol/L, 0.25 mmol, 1.0 eq.) with 10 mol% (0.025 mmol) of **17**-**20,** forming **1**.



1

Entry[a]	Catalyst	Temperature (T)	Yield (**1**)
1	**17**	r.t.	not detected
2	**17**	60 °C	not detected
3	**18**	r.t.	not detected
4	**18**	60 °C	not detected
5	**19**	r.t.	not detected
6	**19**	60 °C	0.8%
7	**20**	r.t.	not detected
8	**20**	60 °C	2.6%
9[b]	**20**	60 °C	0.7%

[a] Following GP1. [b] Reaction time 50 h.
For ^{31}P NMR spectra of entries 1-9 see Figures S35-S43.

6.4.3 NMR Spectra

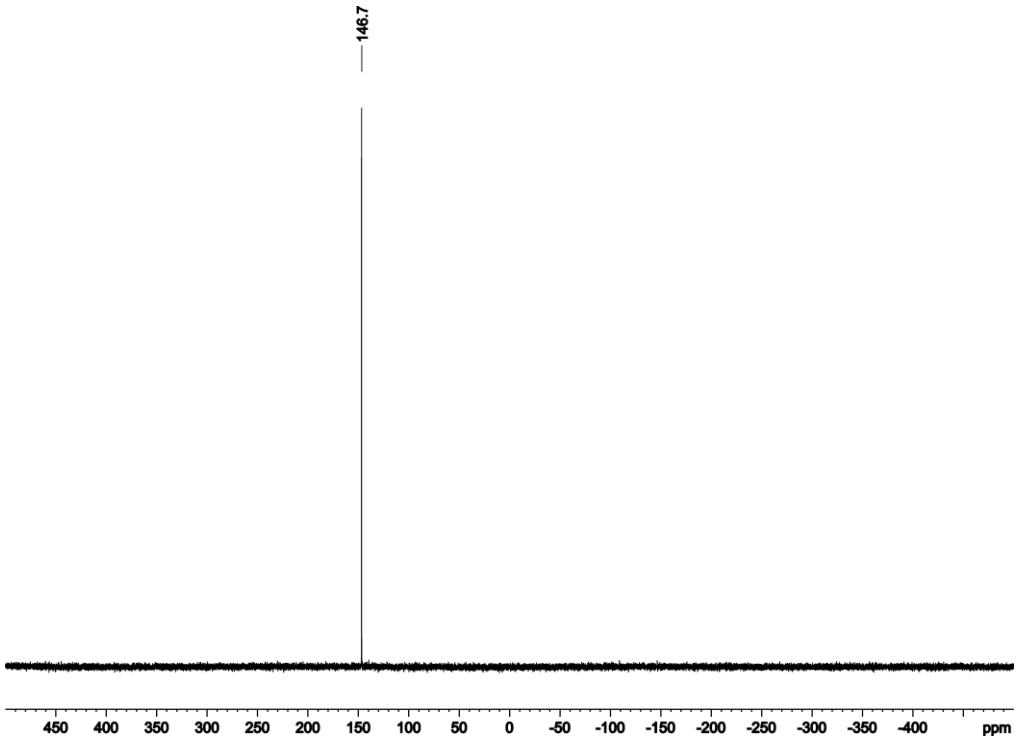


Figure S1. $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of 1 eq. of **7** with 1.05 eq. of *t*BuCP, yielding **11**.

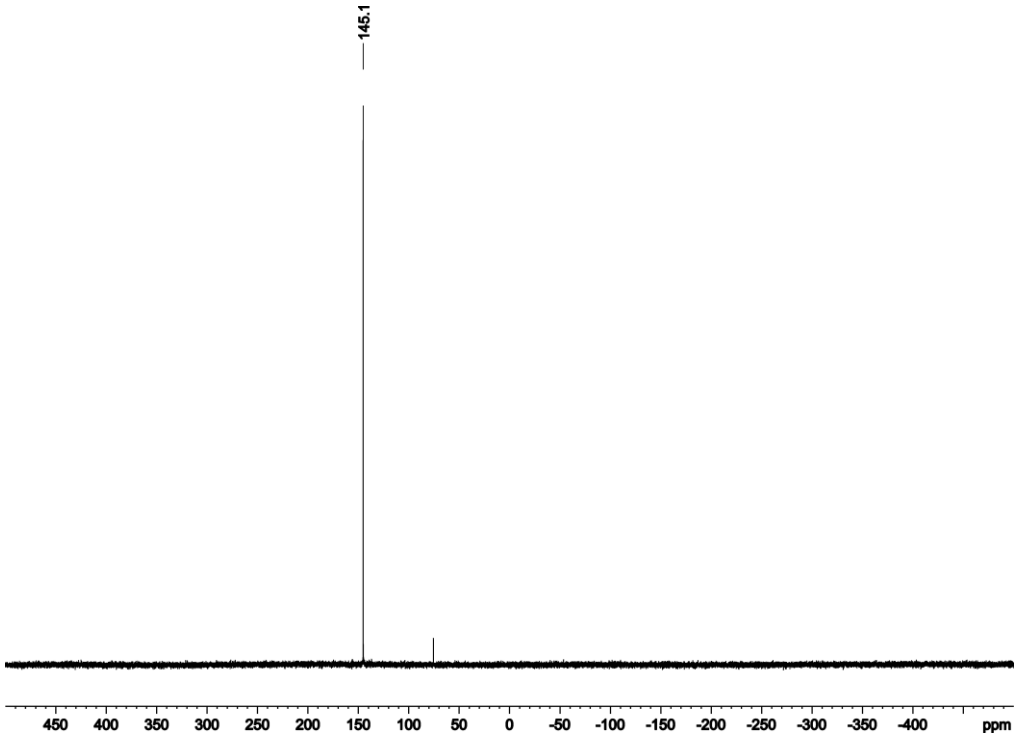


Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of 1 eq. **7** with 1.05 eq. AdCP, yielding **12**.

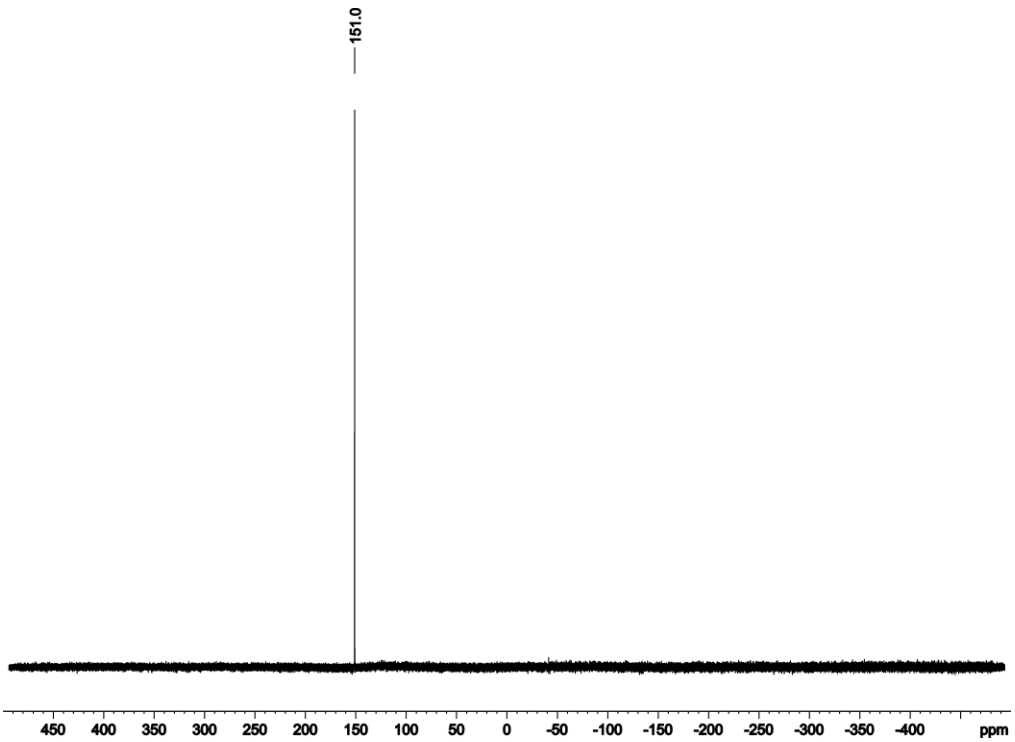


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of 1 eq. **8** with 1 eq. *t*BuCP, yielding **13**.

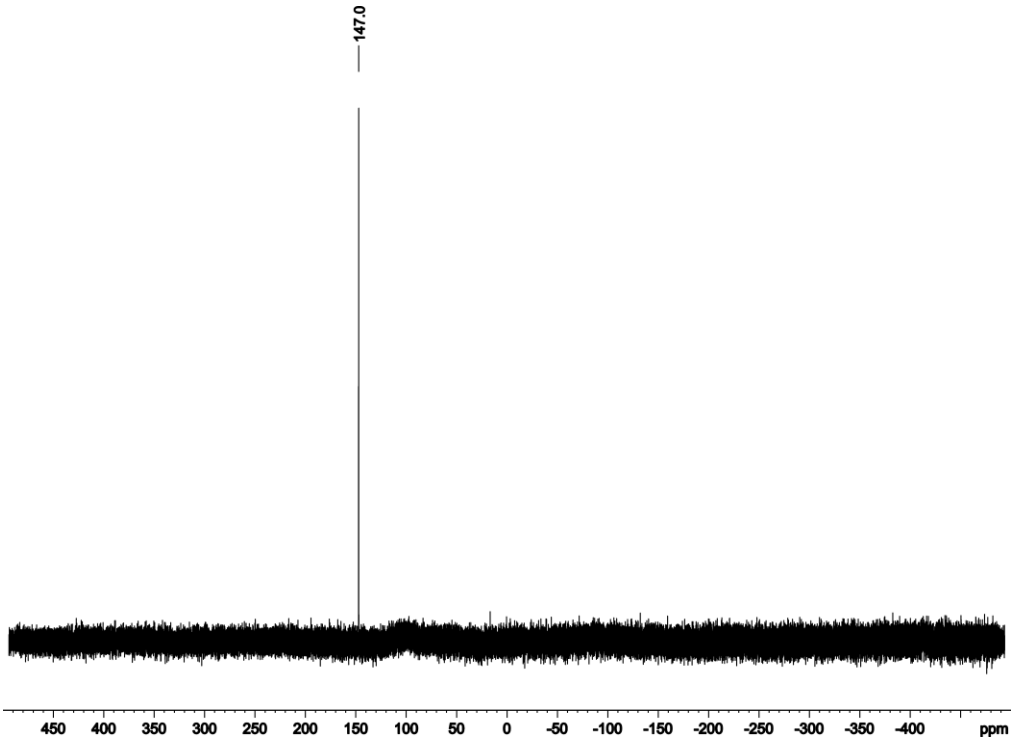


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of 1 eq. **8** with 1 eq. AdCP, yielding **14**.

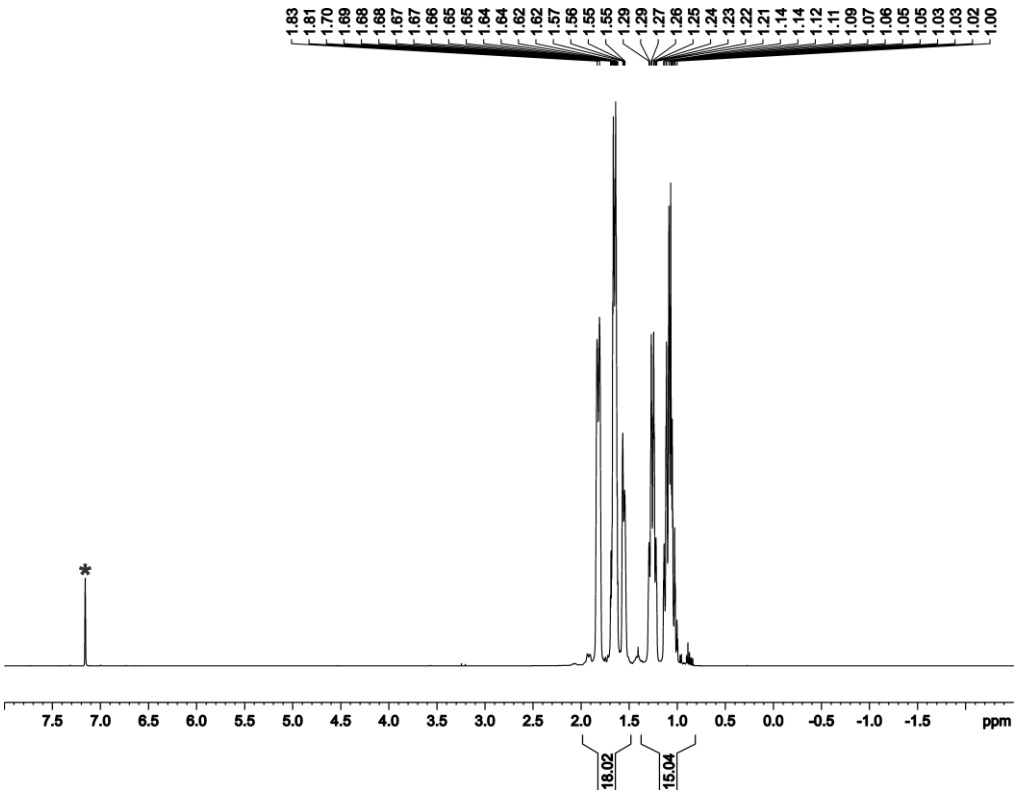


Figure S5. ^{1}H NMR spectrum (500 MHz, 300 K, C_6D_6) of **18**. *C_6D_5H.

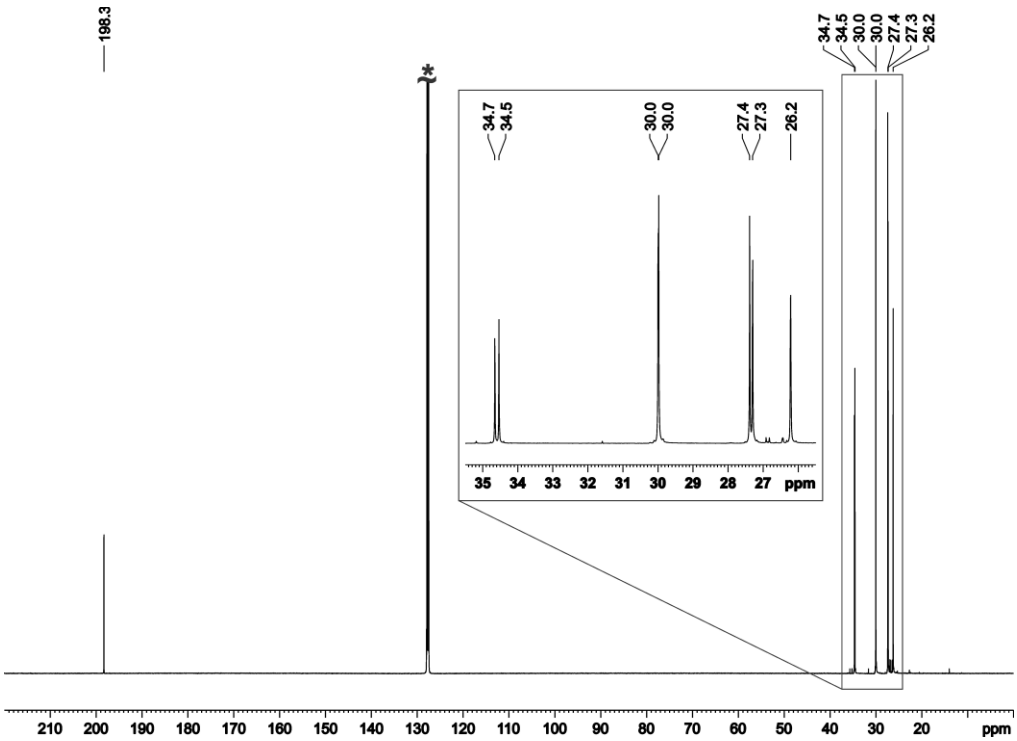


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, 300 K, C_6D_6) of **18**. *C_6D_6.

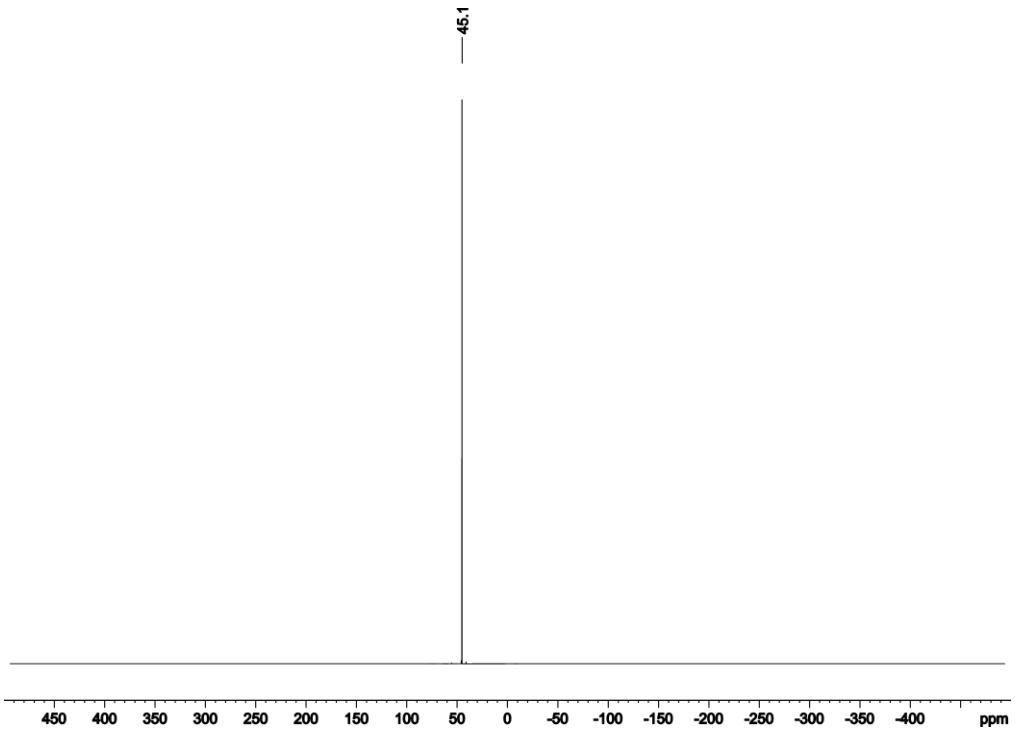


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of **18**.

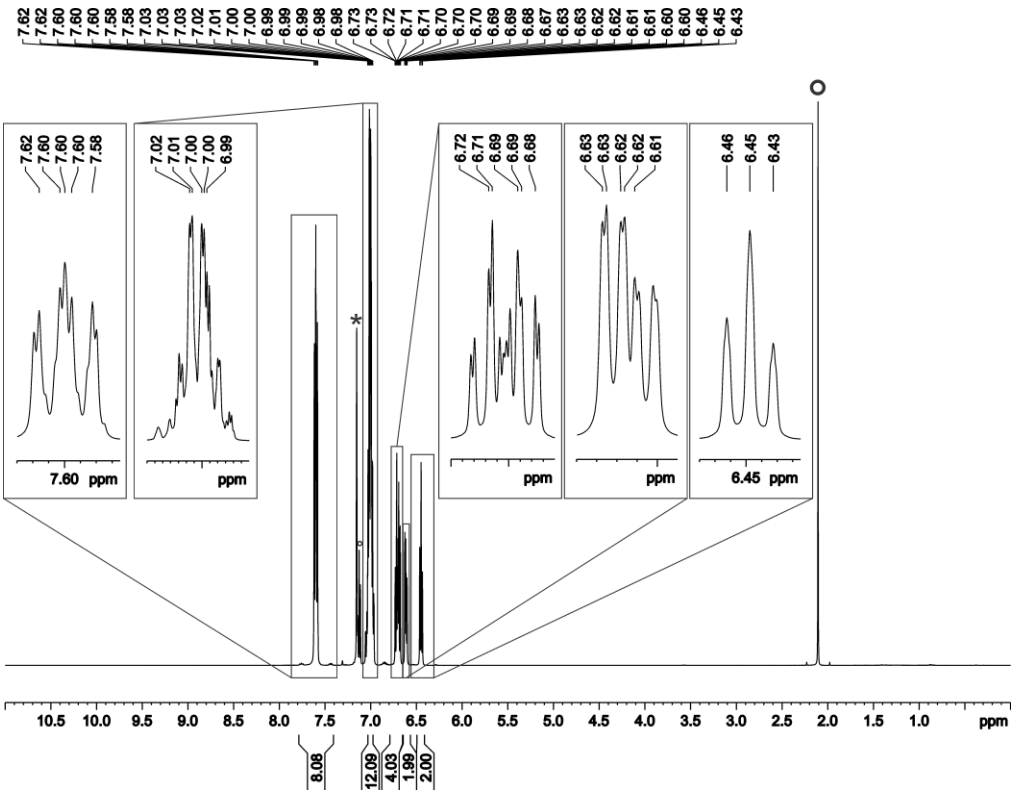


Figure S8. ^{1}H NMR spectrum (500 MHz, 300 K, C_6D_6) of **20**. *C_6D_5H. O Toluene.

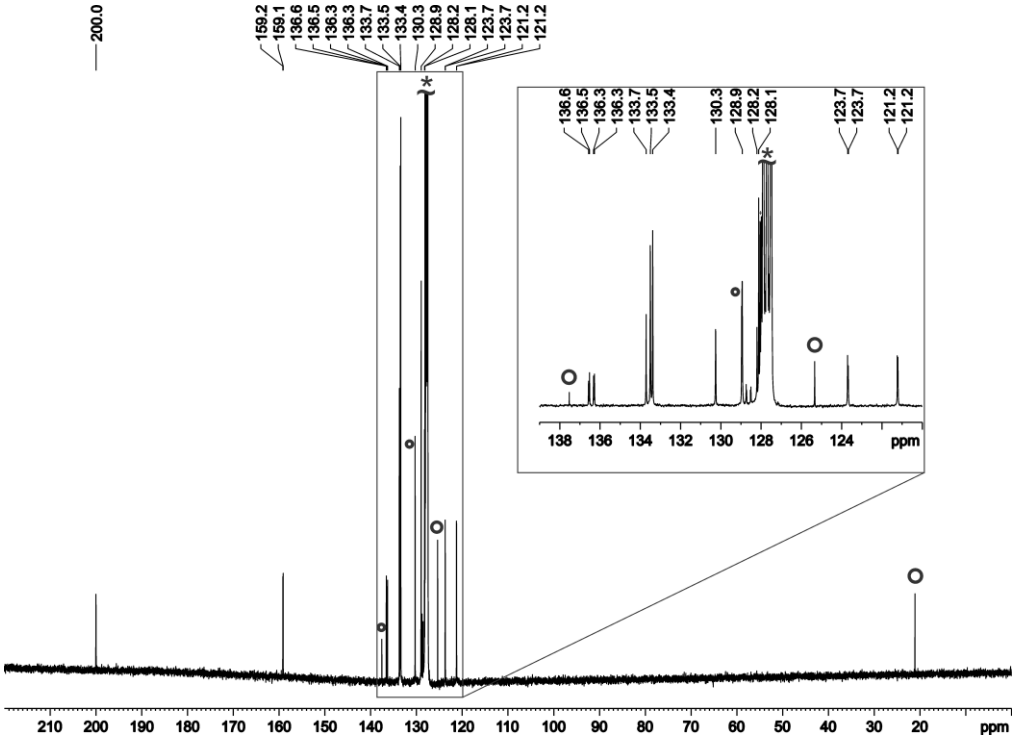


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, 300 K, C_6D_6) of **20**. *C_6D_6. O Toluene. + C_6D_5H.

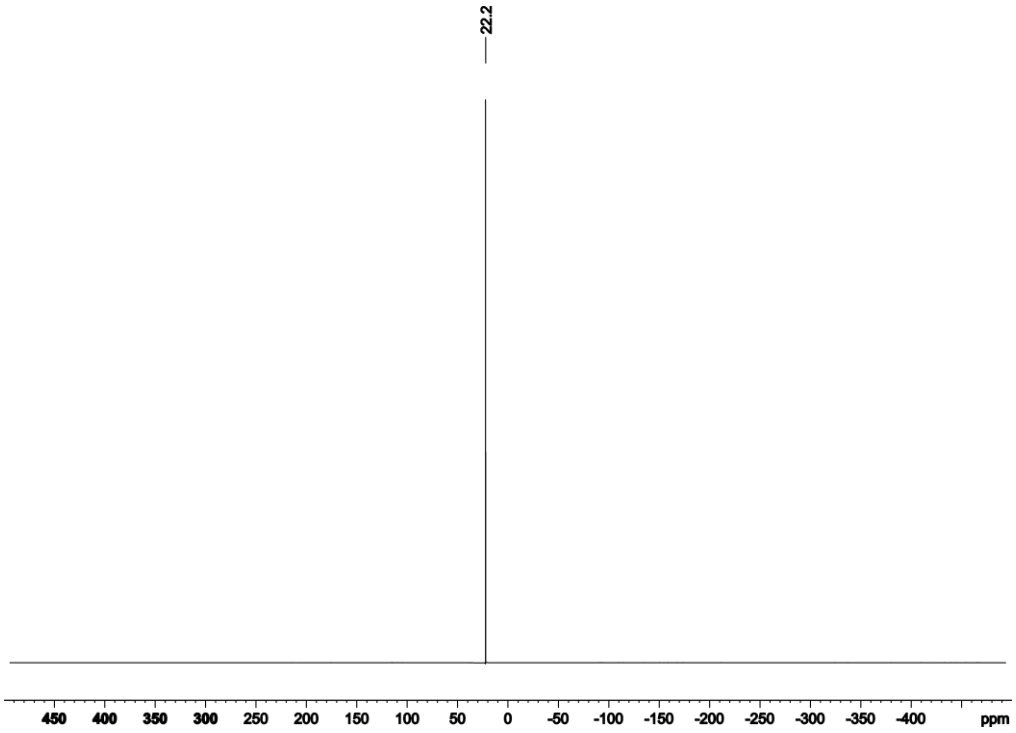


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of **20**.

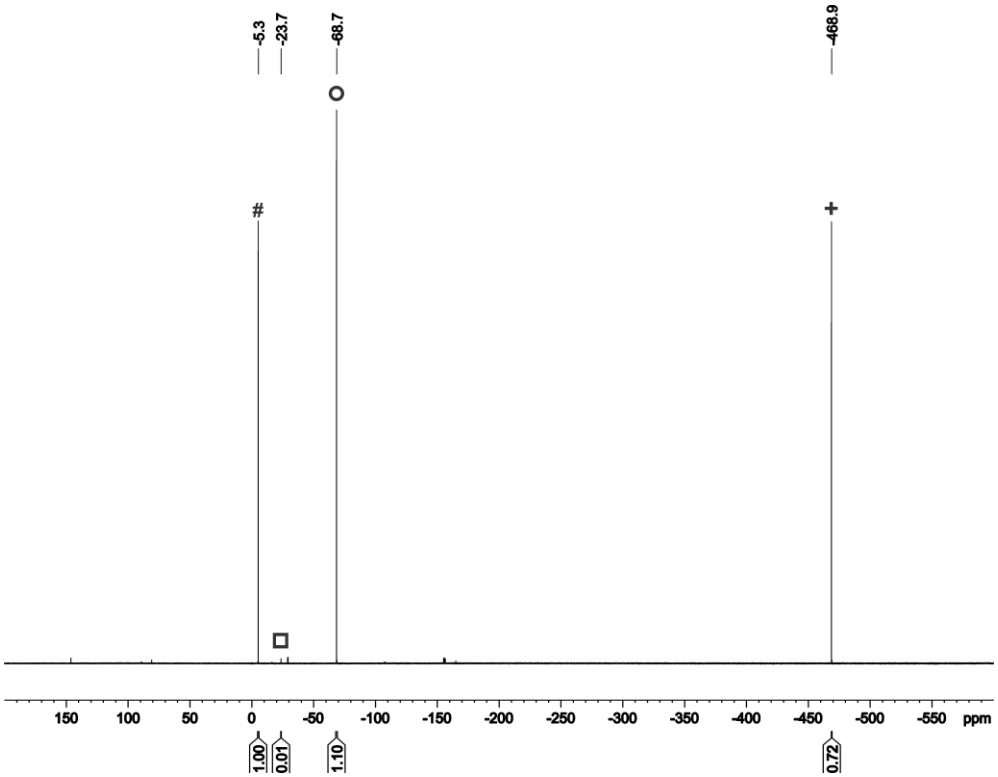


Figure S11. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of *t*BuCP (○) with catalytic amounts of **7** after 18 h at room temperature. Internal standard PPh_3 (#). $(t\text{BuCP})_4$ (**10**, □). $(t\text{BuCP})_2$ (**1**, +).

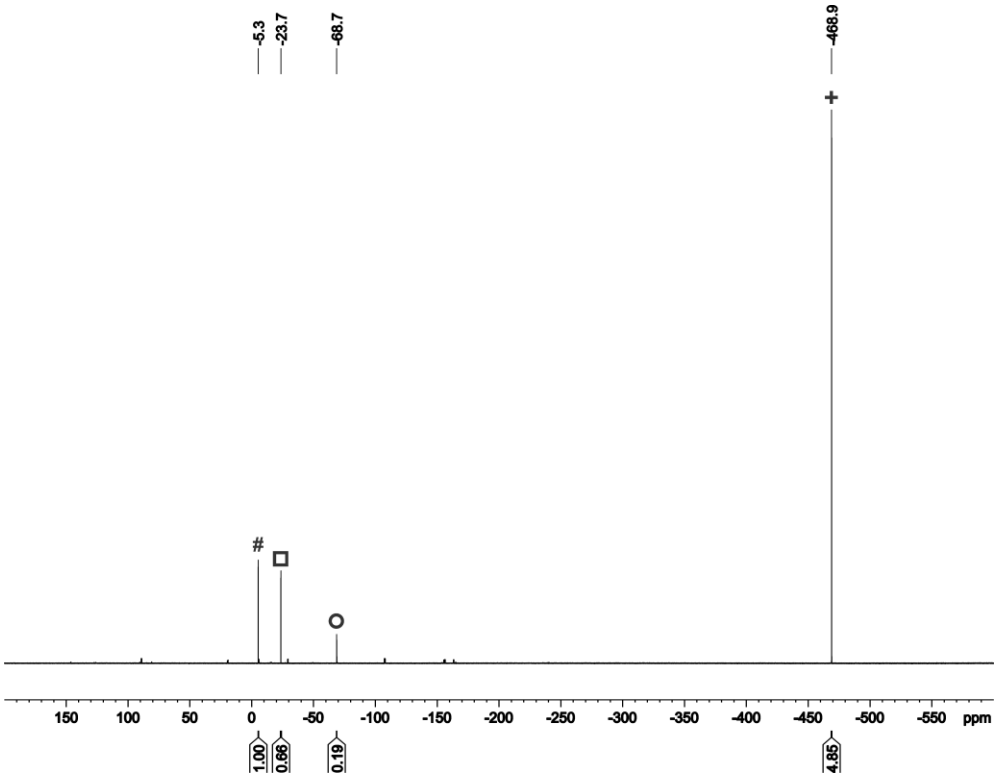


Figure S12. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of *t*BuCP (○) with catalytic amounts of **7** after 18 h at 60 °C. Internal standard PPh_3 (#). $(t\text{BuCP})_4$ (**10**, □). $(t\text{BuCP})_2$ (**1**, +).

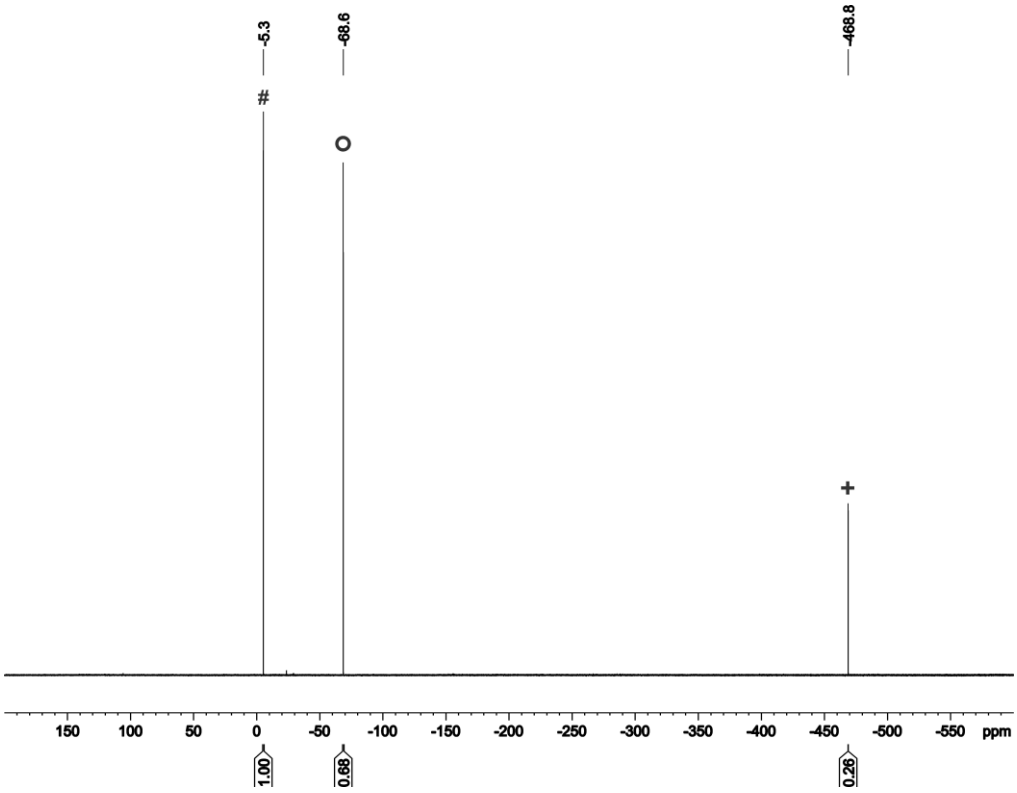


Figure S13. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of *t*BuCP (O) with catalytic amounts of **8** after 18 h at room temperature. Internal standard PPh_3 (#). $(t\text{BuCP})_2$ (**1**, +).

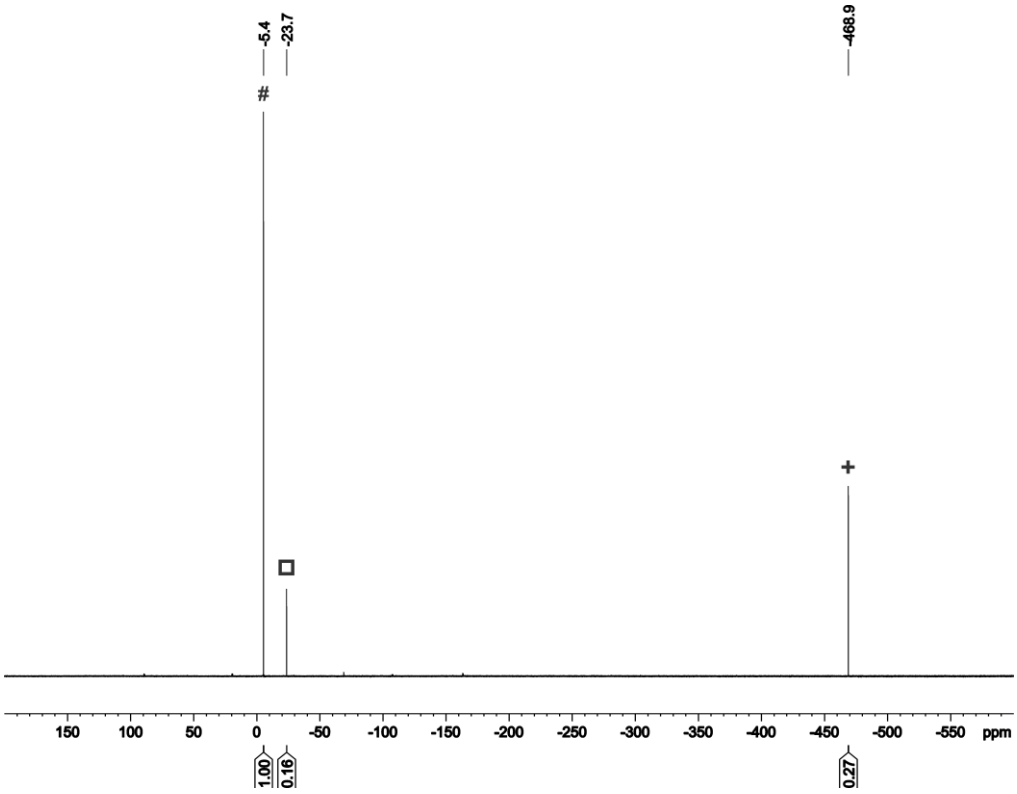


Figure S14. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of *t*BuCP with catalytic amounts of **8** after 18 h at 60 °C. Internal standard PPh_3 (#). $(t\text{BuCP})_4$ (**10**, □). $(t\text{BuCP})_2$ (**1**, +).

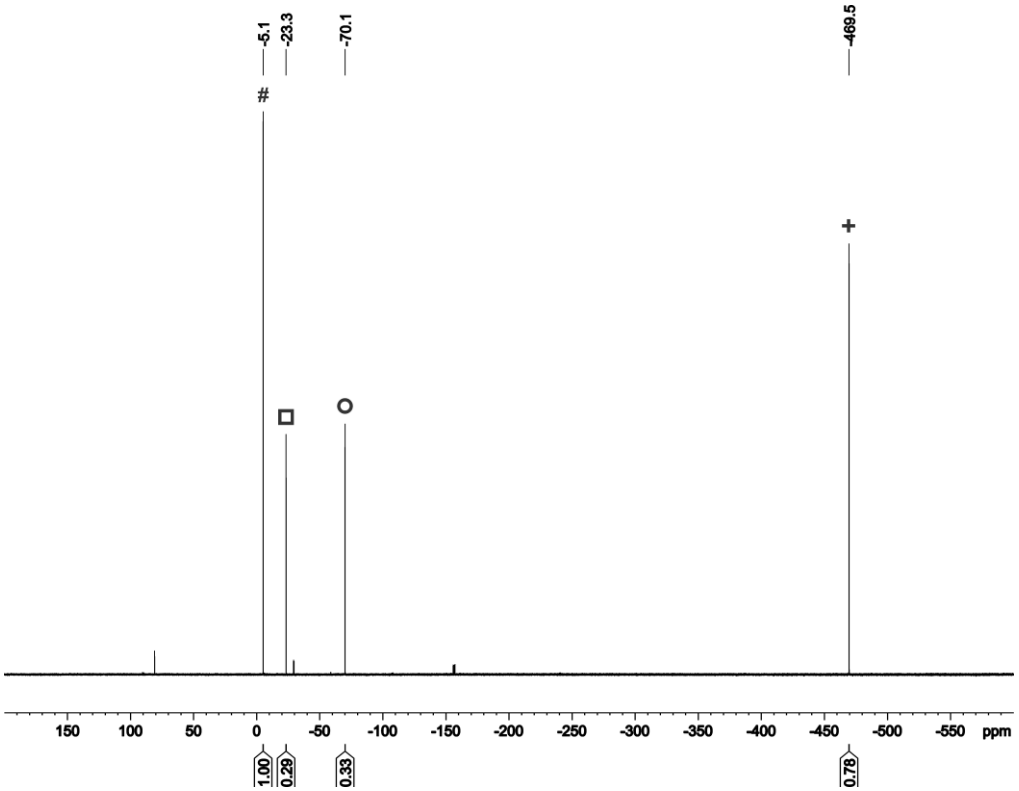


Figure S15. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, THF with C_6D_6-capillary) of the reaction of *t*BuCP (○) with catalytic amounts of **15** after 18 h at room temperature. Internal standard PPh_3 (#). $(t\text{BuCP})_4$ (**10**, □). $(t\text{BuCP})_2$ (**1**, +).

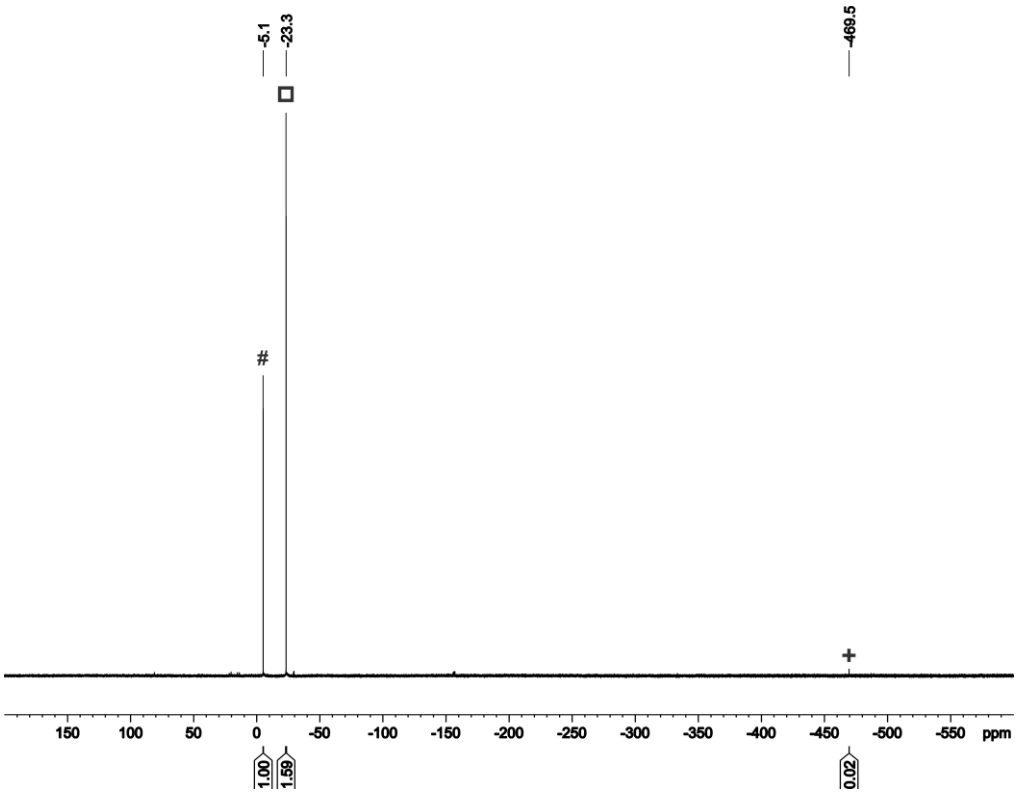


Figure S16. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, THF with C_6D_6-capillary) of the reaction of *t*BuCP with catalytic amounts of **15** after 18 h at 60 °C. Internal standard PPh_3 (#). $(t\text{BuCP})_4$ (**10**, □). $(t\text{BuCP})_2$ (**1**, +).

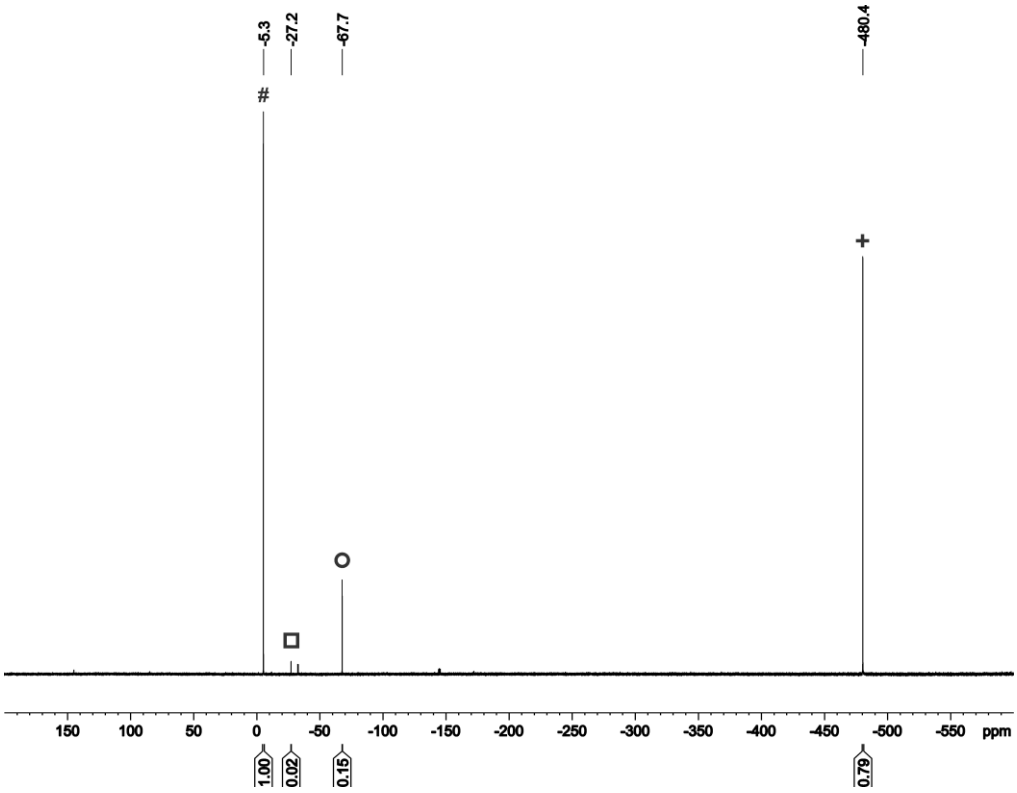


Figure S17. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of AdCP (O) with catalytic amounts of **7** after 18 h at room temperature. Internal standard PPh_3 (#). $(AdCP)_4$ (**9**, □). $(AdCP)_2$ (**6,** +).

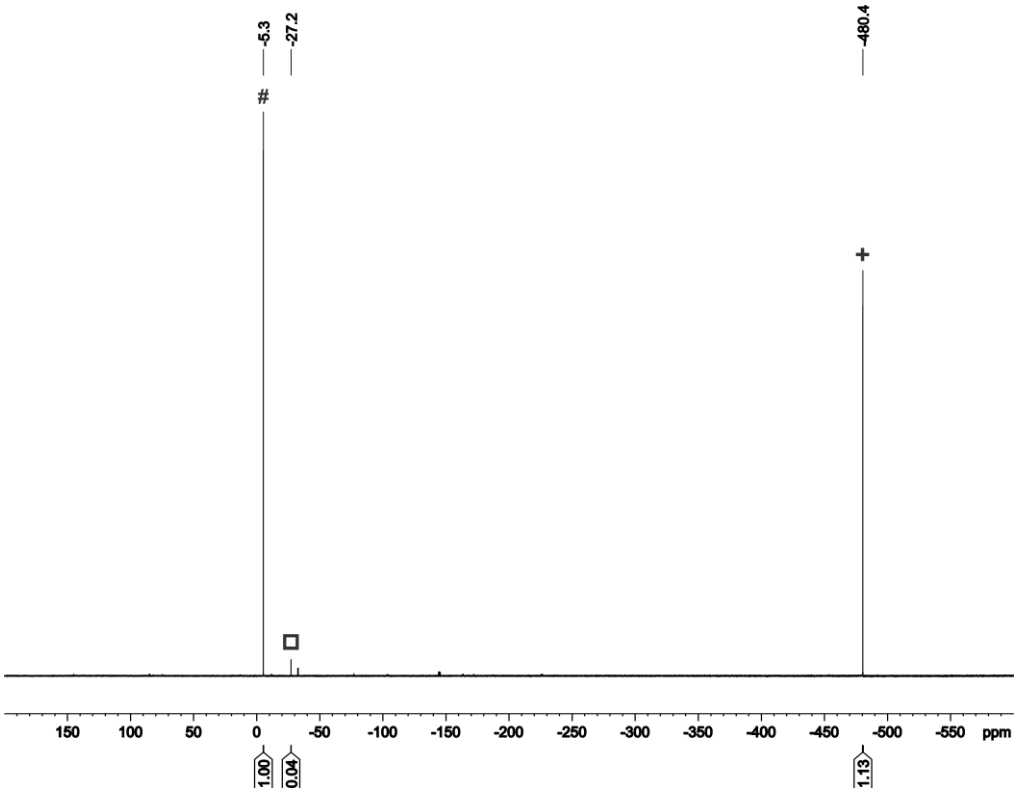


Figure S18. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of AdCP with catalytic amounts of **7** after 18 h at 60 °C. Internal standard PPh_3 (#). $(AdCP)_4$ (**9**, □). $(AdCP)_2$ (**6,** +).

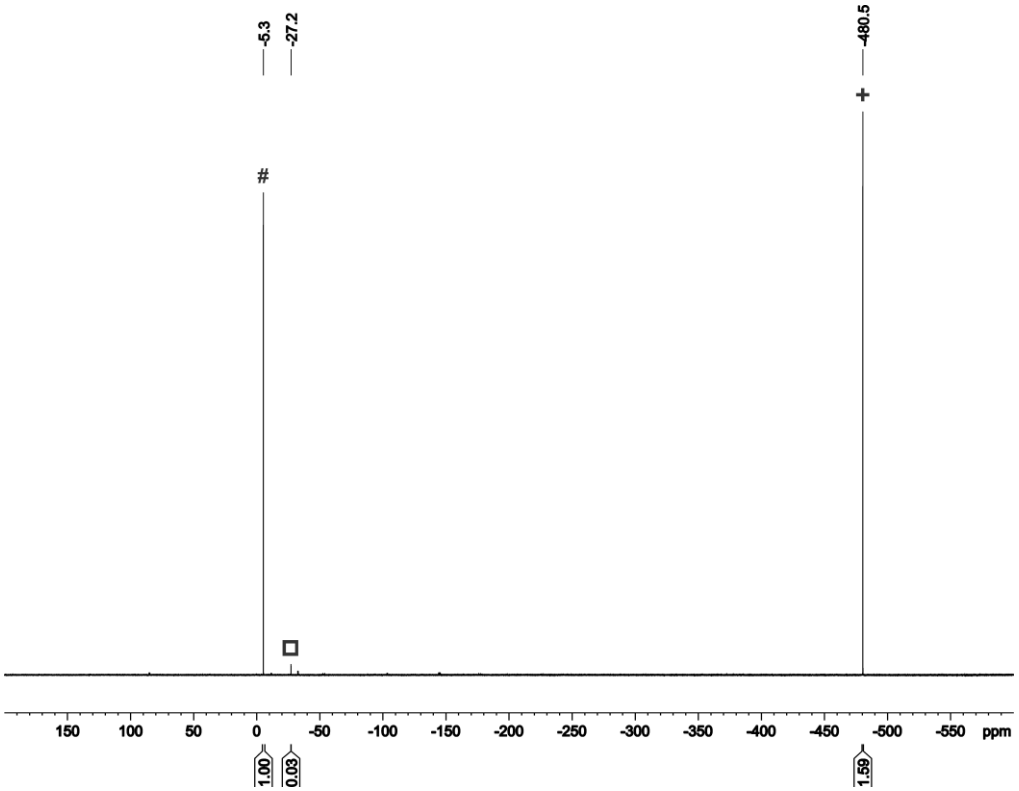


Figure S19. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of AdCP with catalytic amounts of **8** after 18 h at room temperature. Internal standard PPh_3 (#). $(AdCP)_4$ (**9**, □). $(AdCP)_2$ (**6,** +).

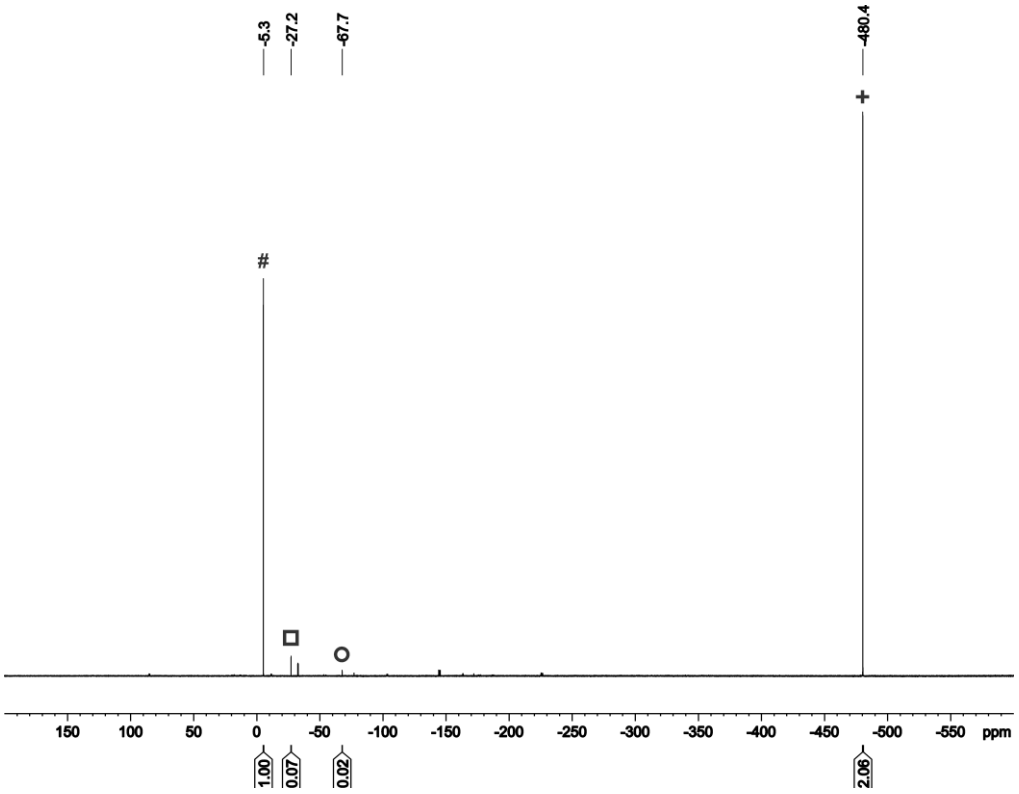


Figure S20. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of AdCP (○) with catalytic amounts of **8** after 18 h at 60 °C. Internal standard PPh_3 (#). $(AdCP)_4$ (**9**, □). $(AdCP)_2$ (**6,** +).

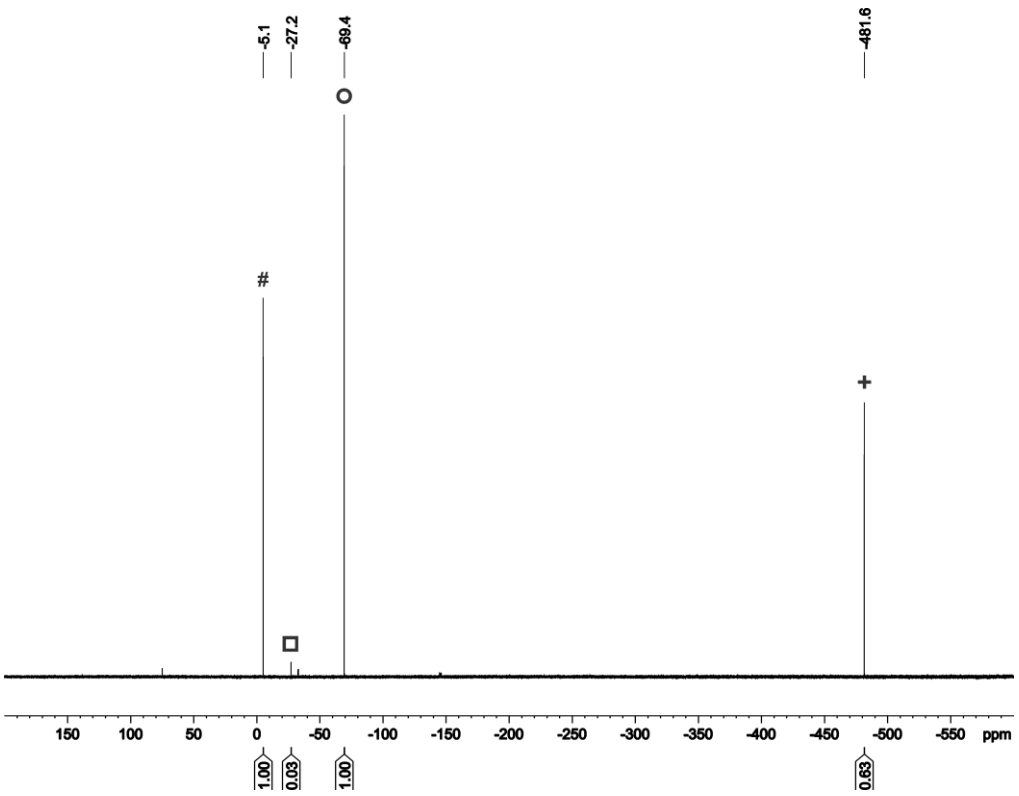


Figure S21. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, THF with C_6D_6-capillary) of the reaction of AdCP (○) with catalytic amounts of **15** after 18 h at room temperature. Internal standard PPh_3 (#). $(AdCP)_4$ (**9**, □). $(AdCP)_2$ (**6,** +).

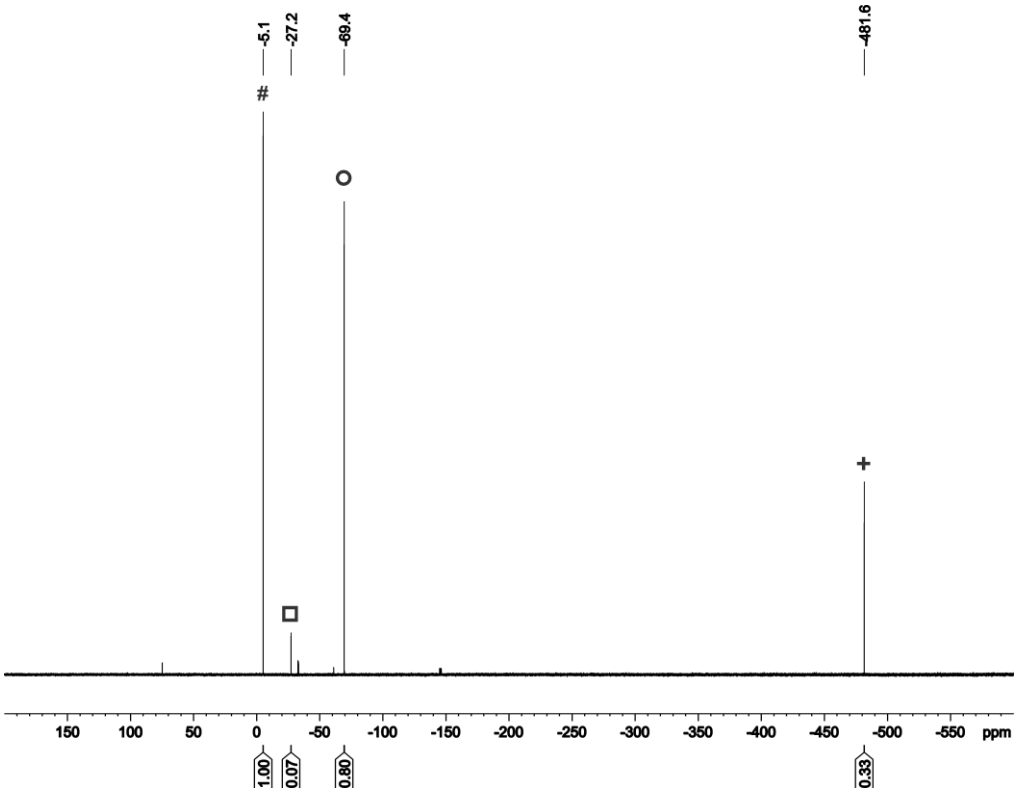


Figure S22. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, THF with C_6D_6-capillary) of the reaction of AdCP (○) with catalytic amounts of **15** after 18 h at 60 °C. Internal standard PPh_3 (#). $(AdCP)_4$ (**9**, □). $(AdCP)_2$ (**6,** +).

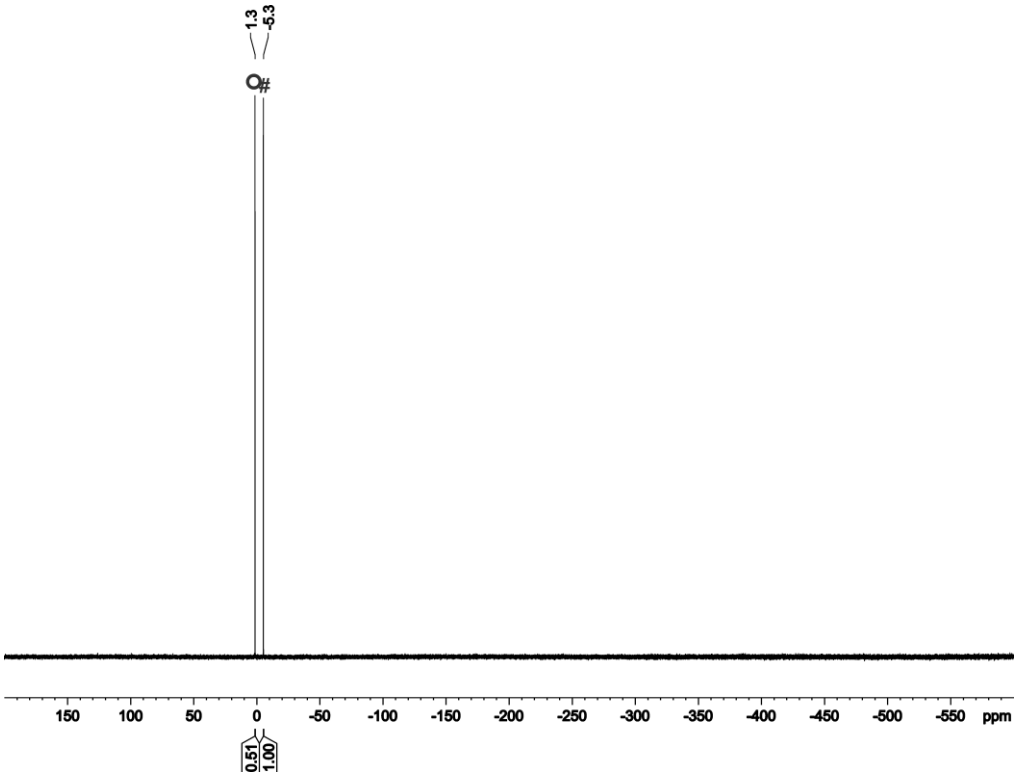


Figure S23. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of MesCP (O) with catalytic amounts of **7** after 18 h at room temperature. Internal standard PPh_3 (#).

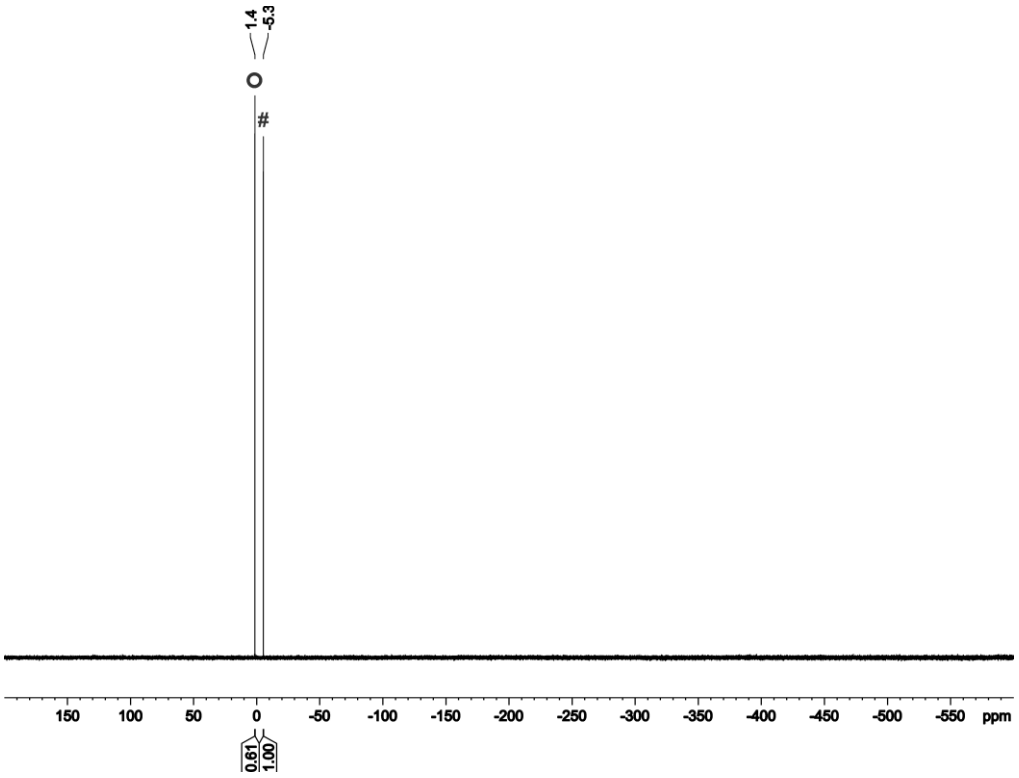


Figure S24. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of MesCP (O) with catalytic amounts of **7** after 18 h at 60 °C. Internal standard PPh_3 (#).

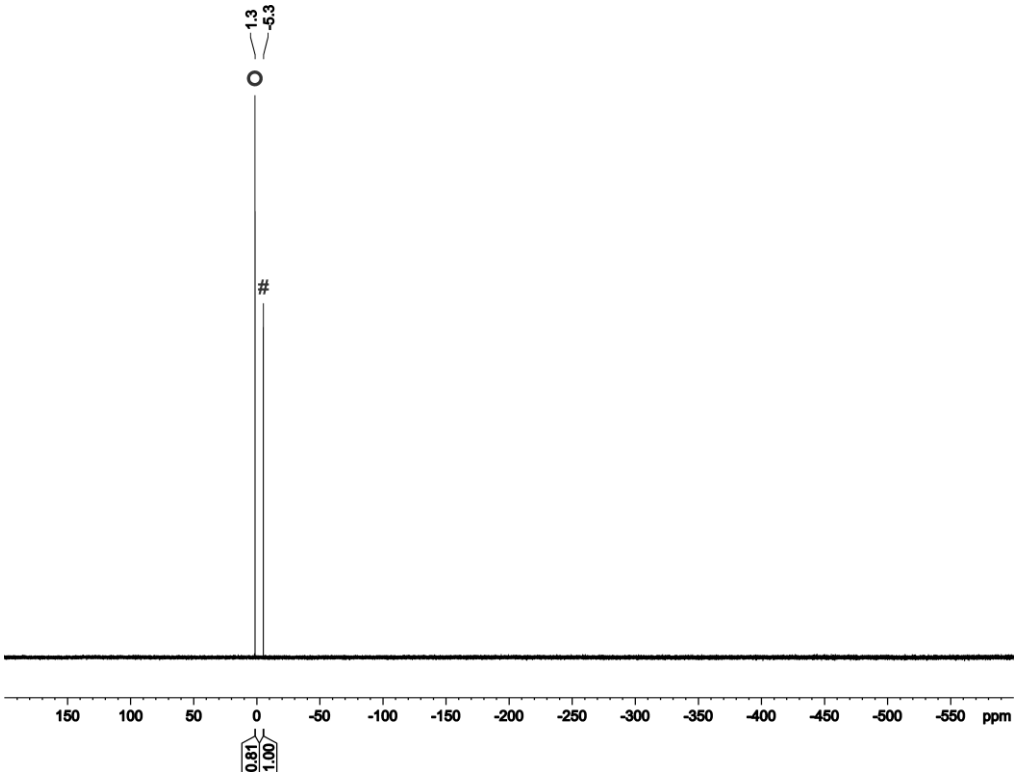


Figure S25. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of MesCP (O) with catalytic amounts of **8** after 18 h at room temperature. Internal standard PPh_3 (#).

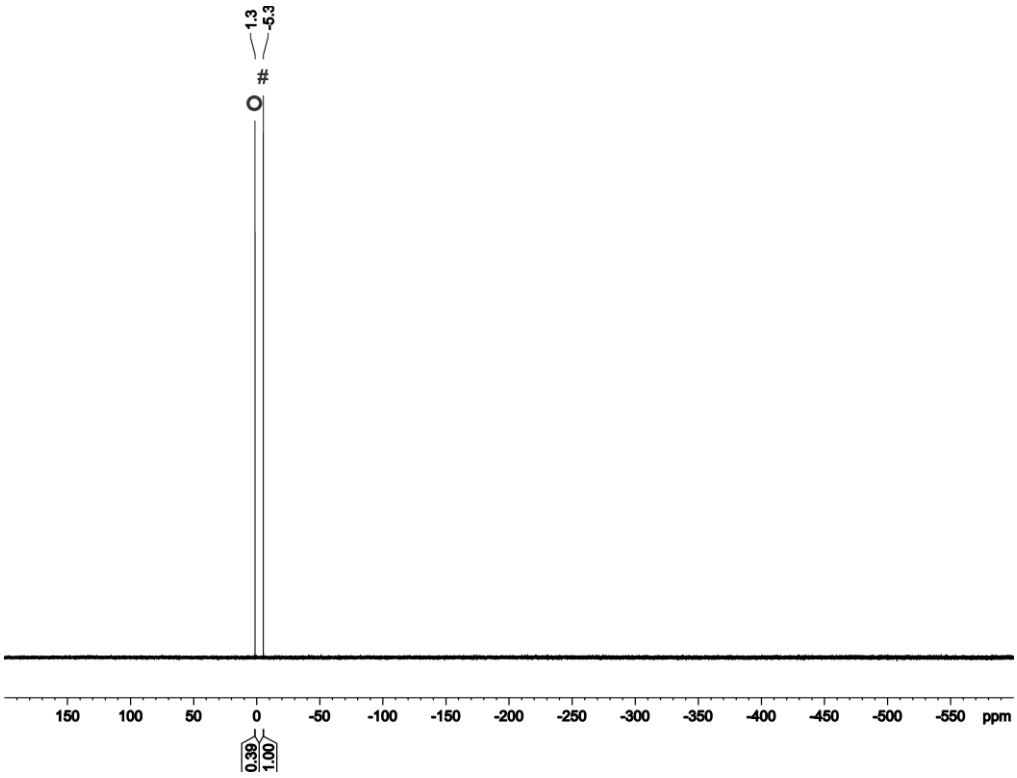


Figure S26. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of MesCP (O) with catalytic amounts of **8** after 18 h at 60 °C. Internal standard PPh_3 (#).

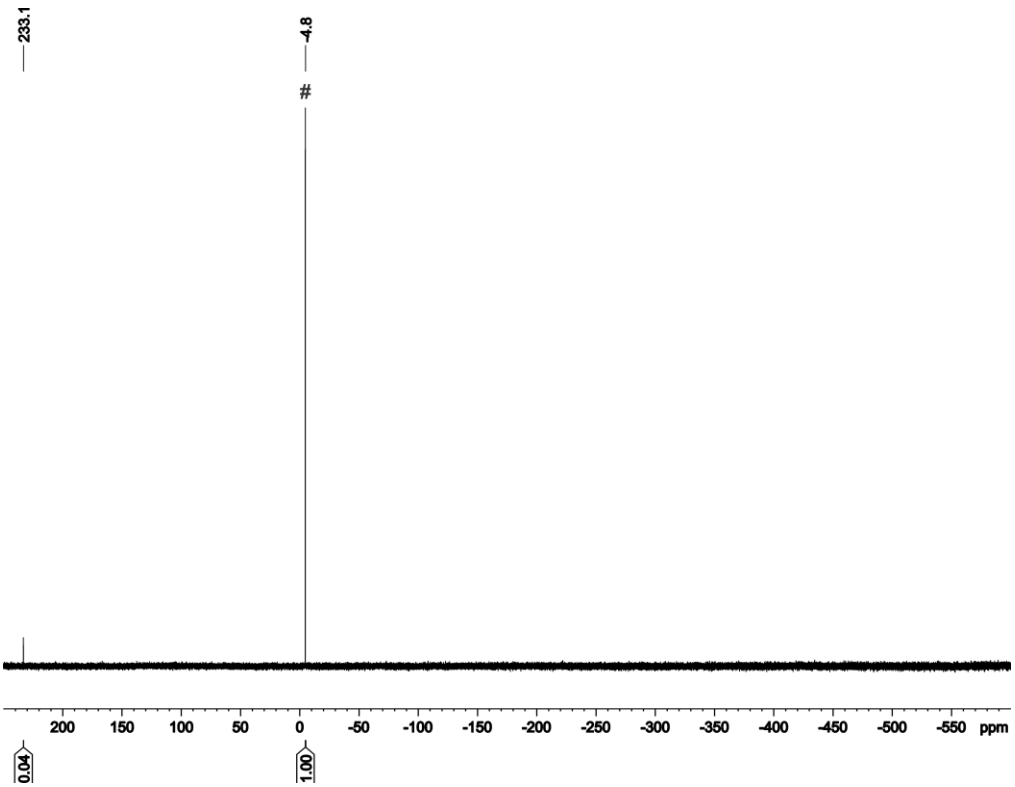


Figure S27. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, THF with C_6D_6-capillary) of the reaction of MesCP with catalytic amounts of **15** after 18 h at room temperature. Internal standard PPh_3 (#).

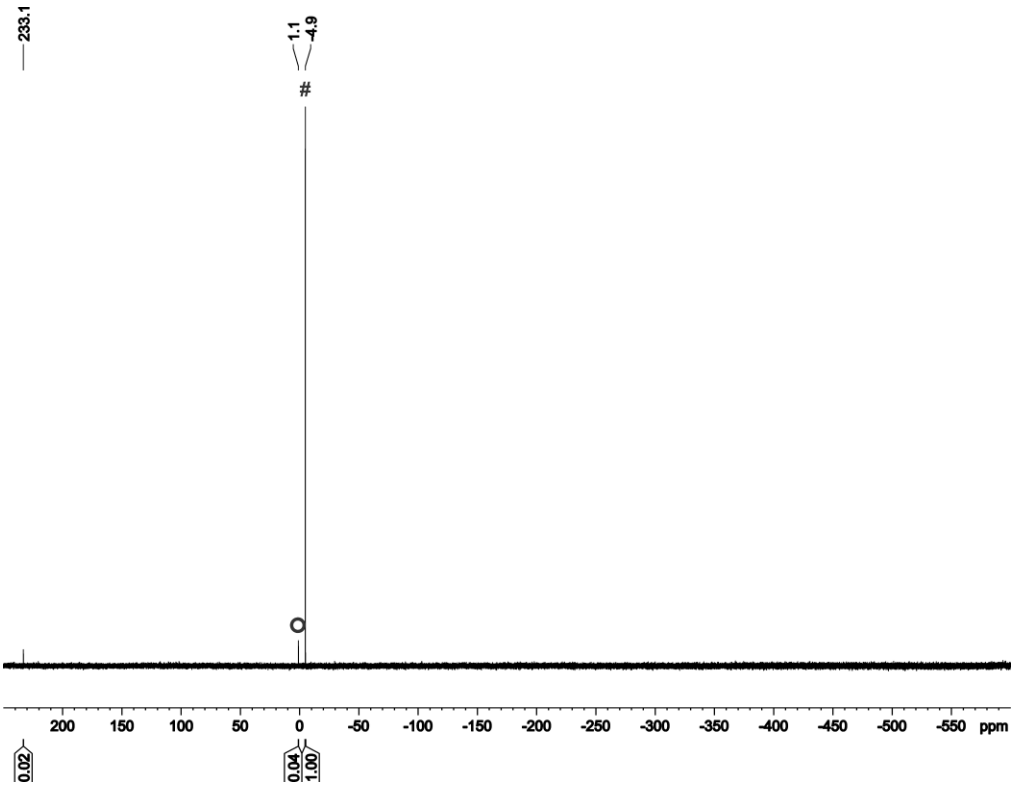


Figure S28. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, THF with C_6D_6-capillary) of the reaction of MesCP (O) with catalytic amounts of **15** after 18 h at 60 °C. Internal standard PPh_3 (#).

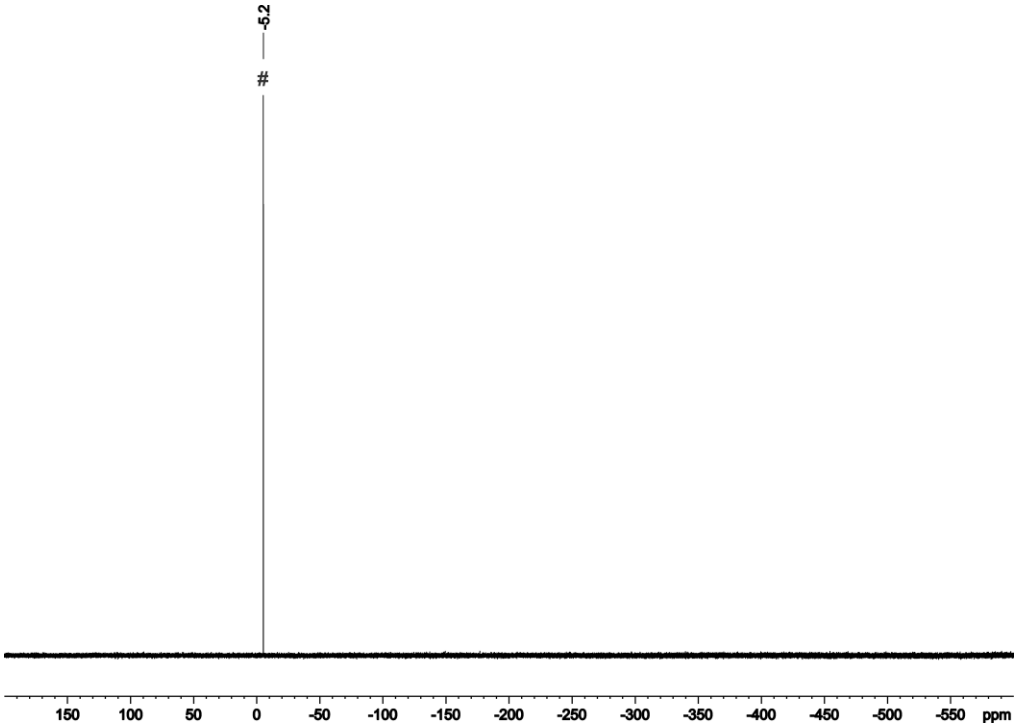


Figure S29. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of Me_3SiCP with catalytic amounts of **7** after 18 h at room temperature. Internal standard PPh_3 (#).

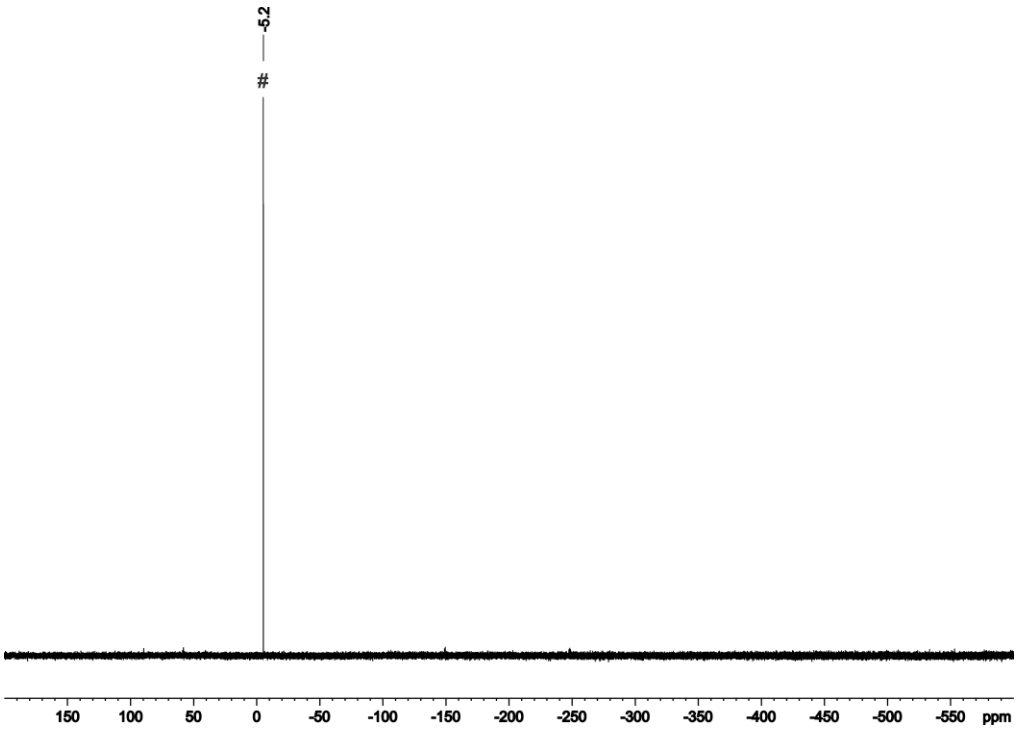


Figure S30. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of Me_3SiCP with catalytic amounts of **7** after 18 h at 60 °C. Internal standard PPh_3 (#).

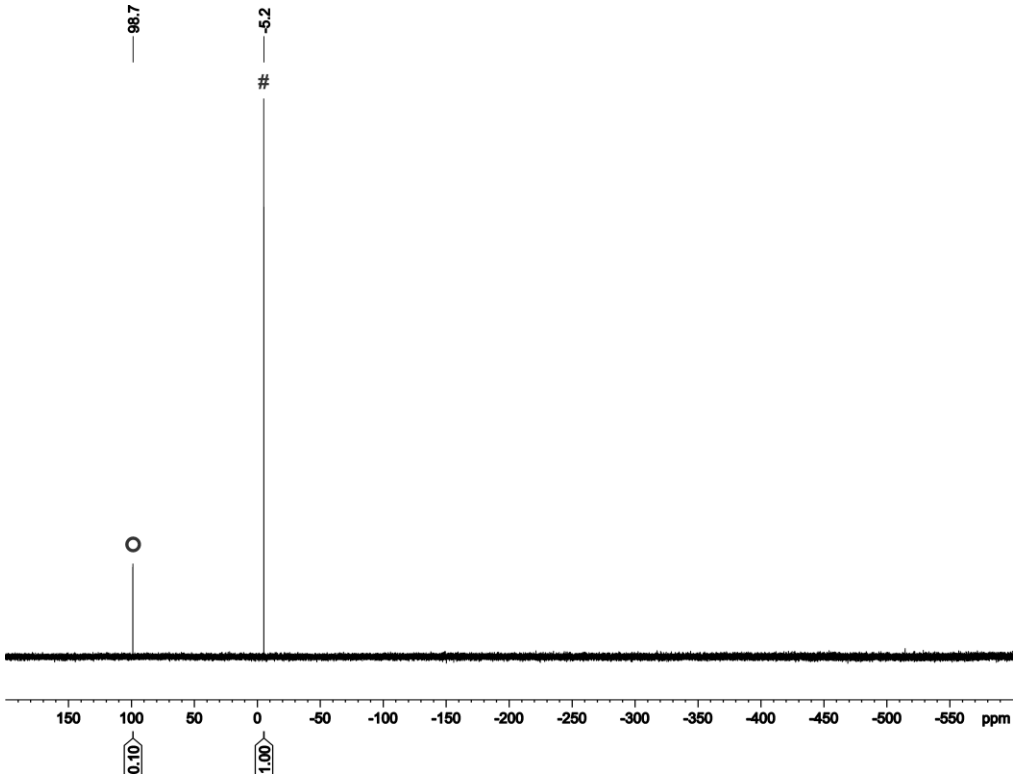


Figure S31. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of Me_3SiCP (O) with catalytic amounts of **8** after 18 h at room temperature. Internal standard PPh_3 (#).

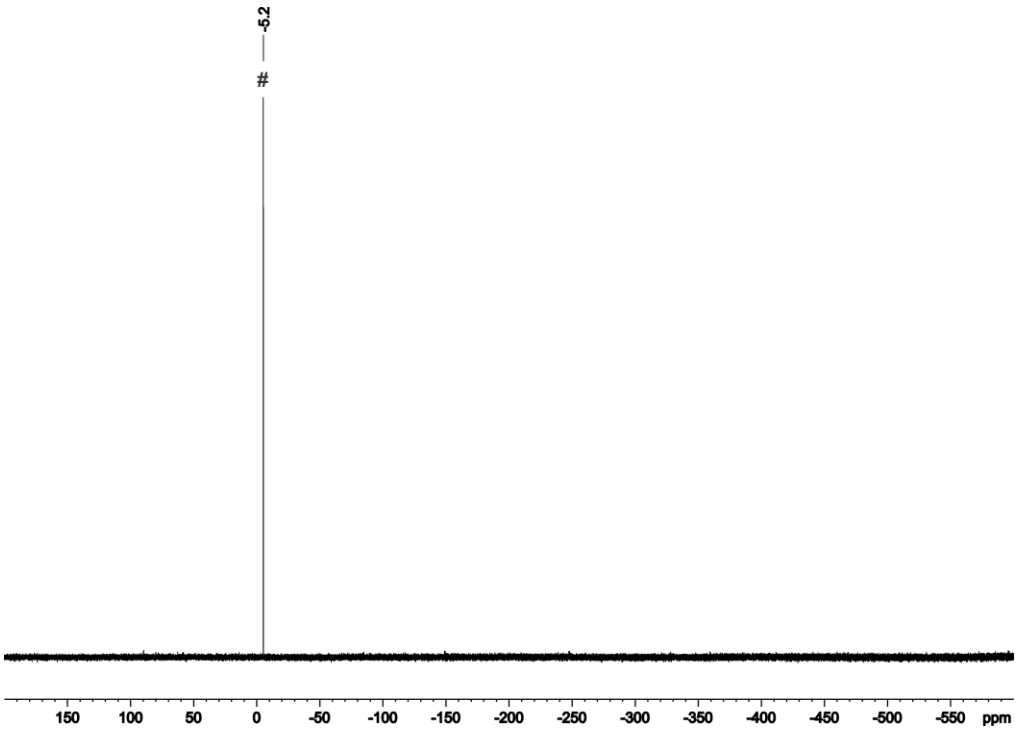


Figure S32. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of Me_3SiCP with catalytic amounts of **8** after 18 h at 60 °C. Internal standard PPh_3 (#).

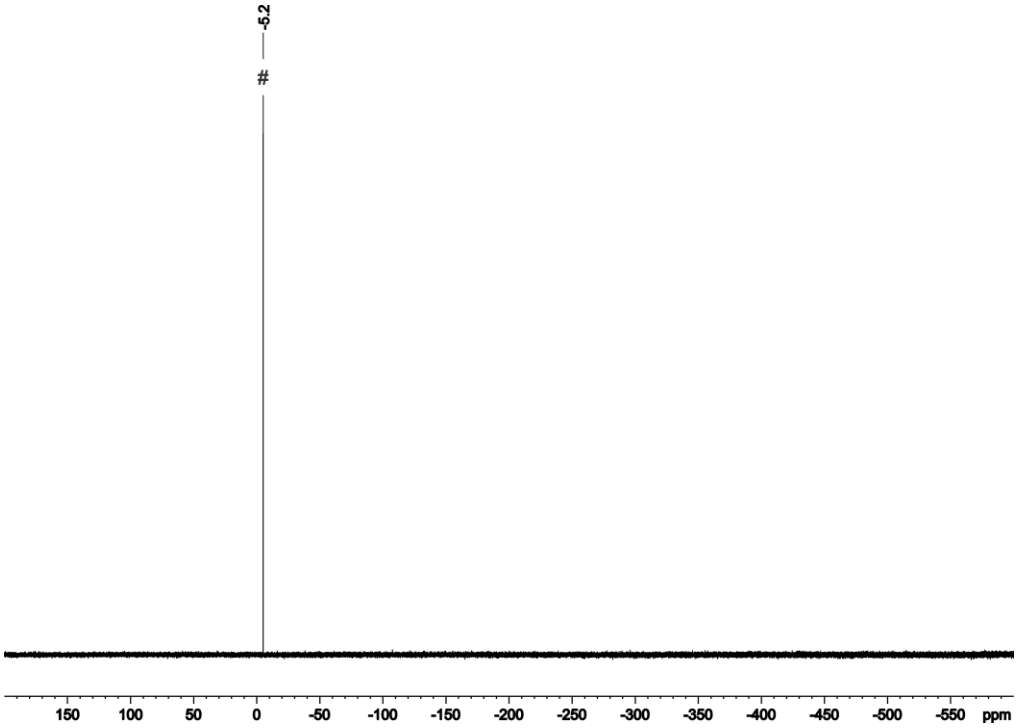


Figure S33. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, THF with C_6D_6-capillary) of the reaction of Me_3SiCP with catalytic amounts of **15** after 18 h at room temperature. Internal standard PPh_3 (#).

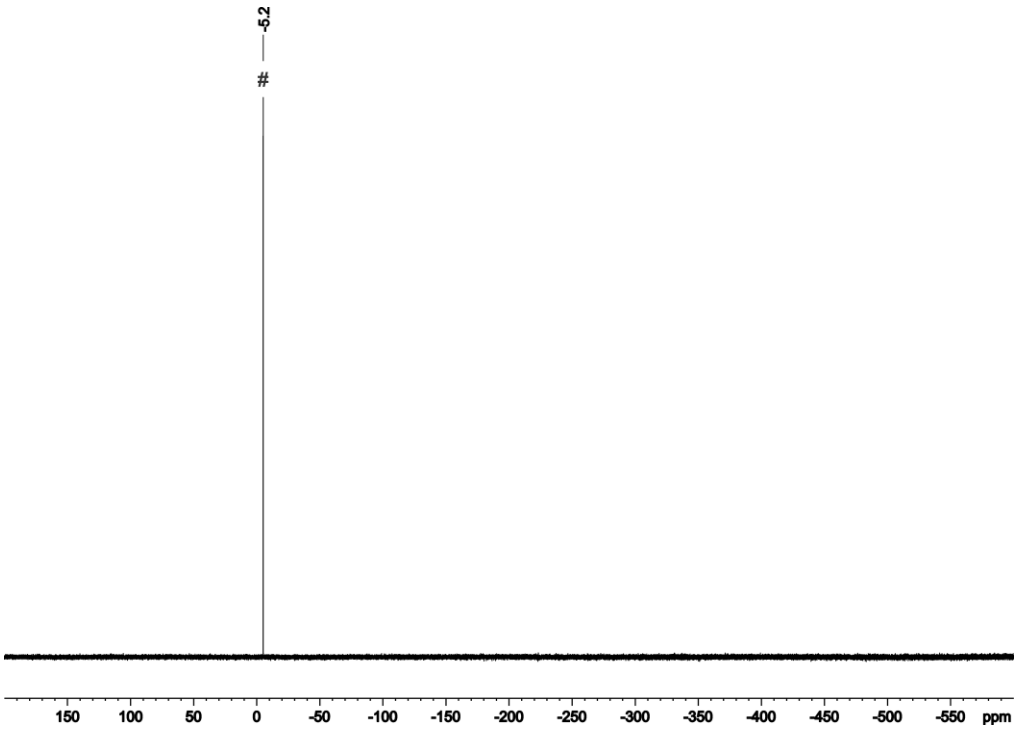


Figure S34. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, THF with C_6D_6-capillary) of the reaction of Me_3SiCP with catalytic amounts of **15** after 18 h at 60 °C. Internal standard PPh_3 (#).

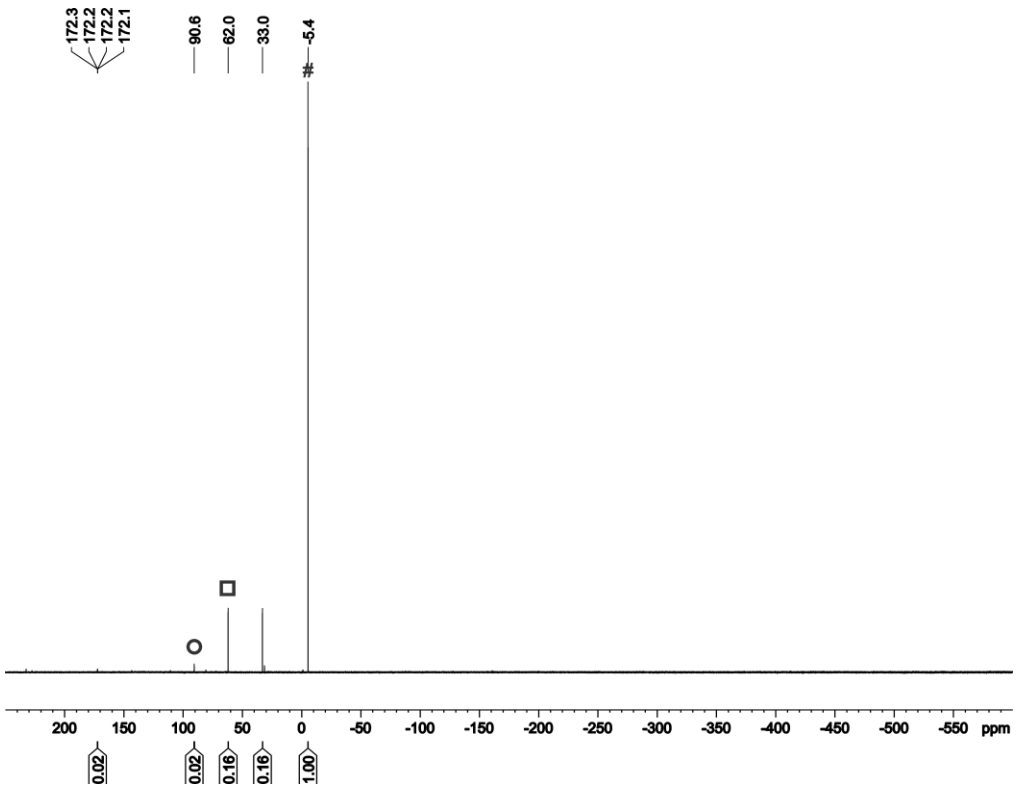


Figure S35. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of *t*BuCP with catalytic amounts of **17** (○) after 18 h at room temperature. Internal standard PPh_3 (#). *t*Bu_3P (□).

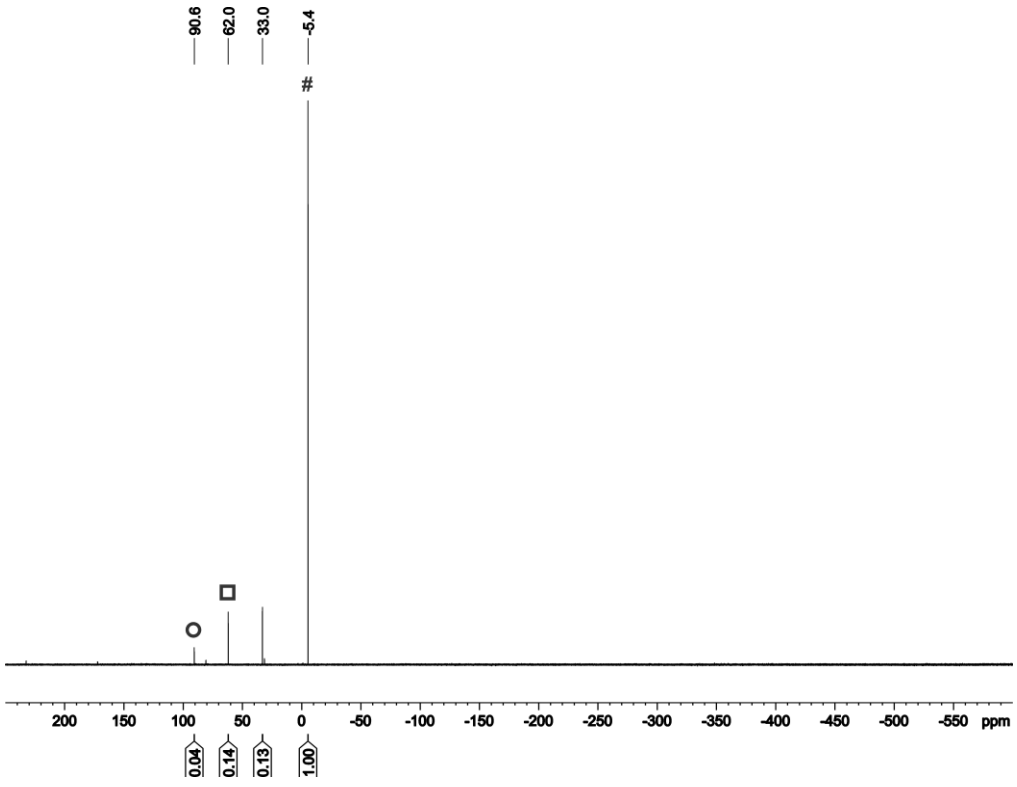


Figure S36. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of *t*BuCP with catalytic amounts of **17** (○) after 18 h at 60 °C. Internal standard PPh_3 (#). *t*Bu_3P (□).

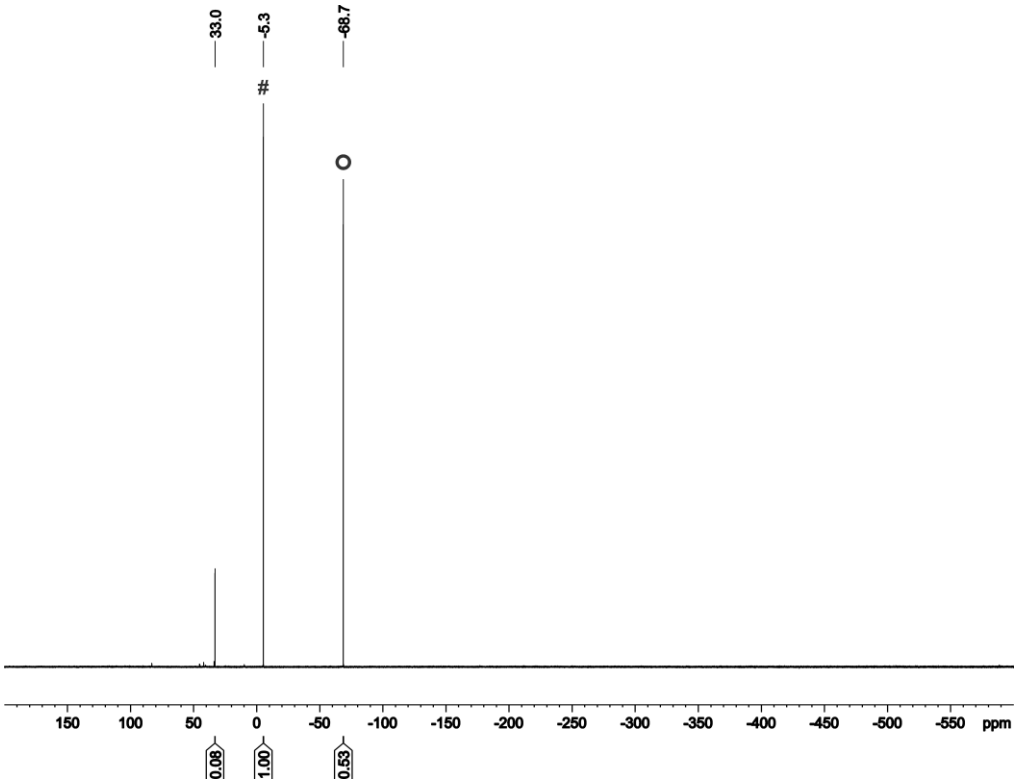


Figure S37. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of *t*BuCP (O) with catalytic amounts of **18** after 18 h at room temperature. Internal standard PPh_3 (#).

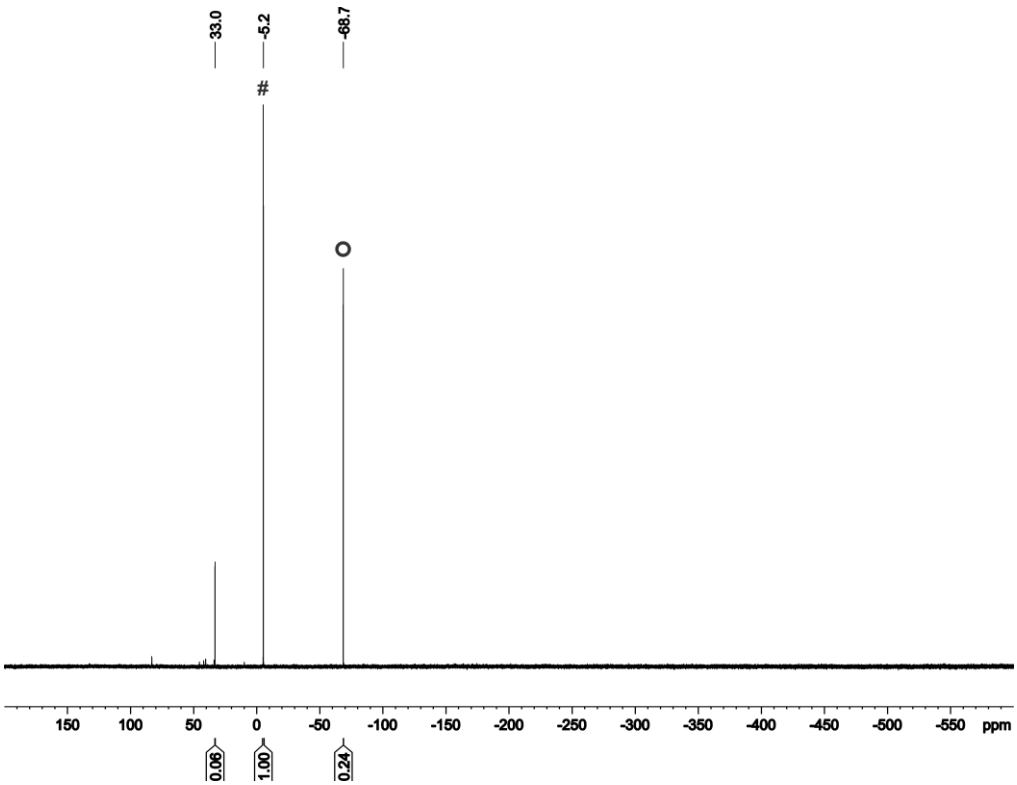


Figure S38. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of *t*BuCP (O) with catalytic amounts of **18** after 18 h at 60 °C. Internal standard PPh_3 (#).

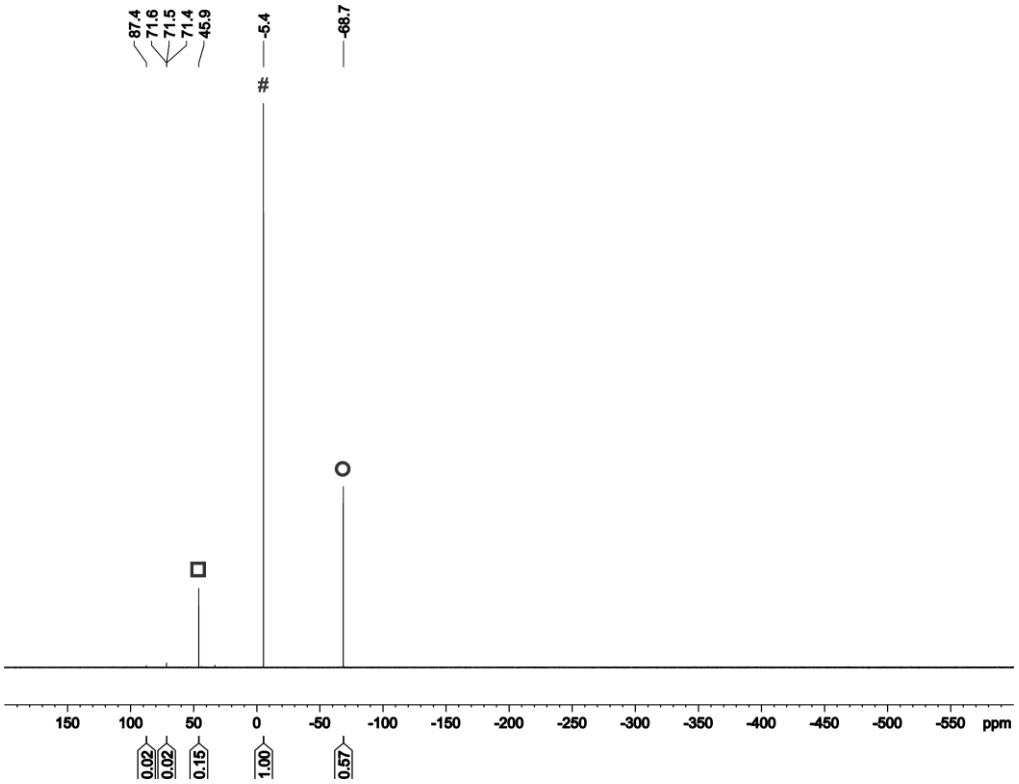


Figure S39. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of *t*BuCP (○) with catalytic amounts of **19** (□) after 18 h at 60 °C. Internal standard PPh_3 (#).

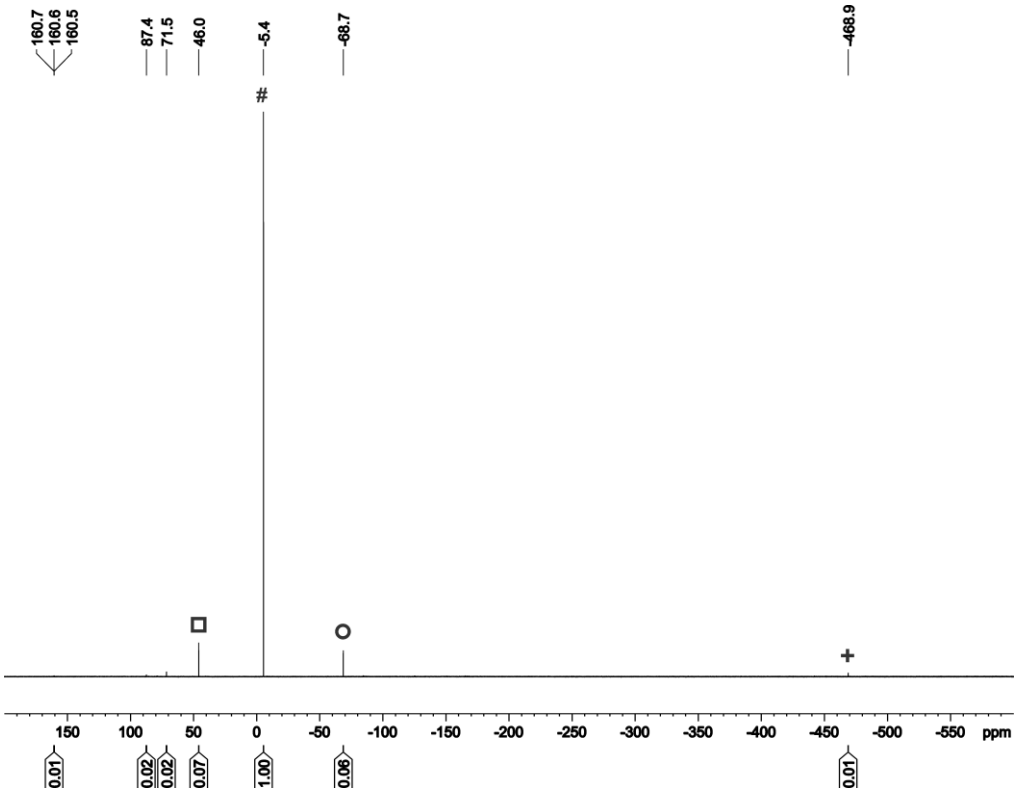


Figure S40. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of *t*BuCP (○) with catalytic amounts of **19** (□) after 18 h at 60 °C. Internal standard PPh_3 (#). $(t\text{BuCP})_2$ (**1**, +).

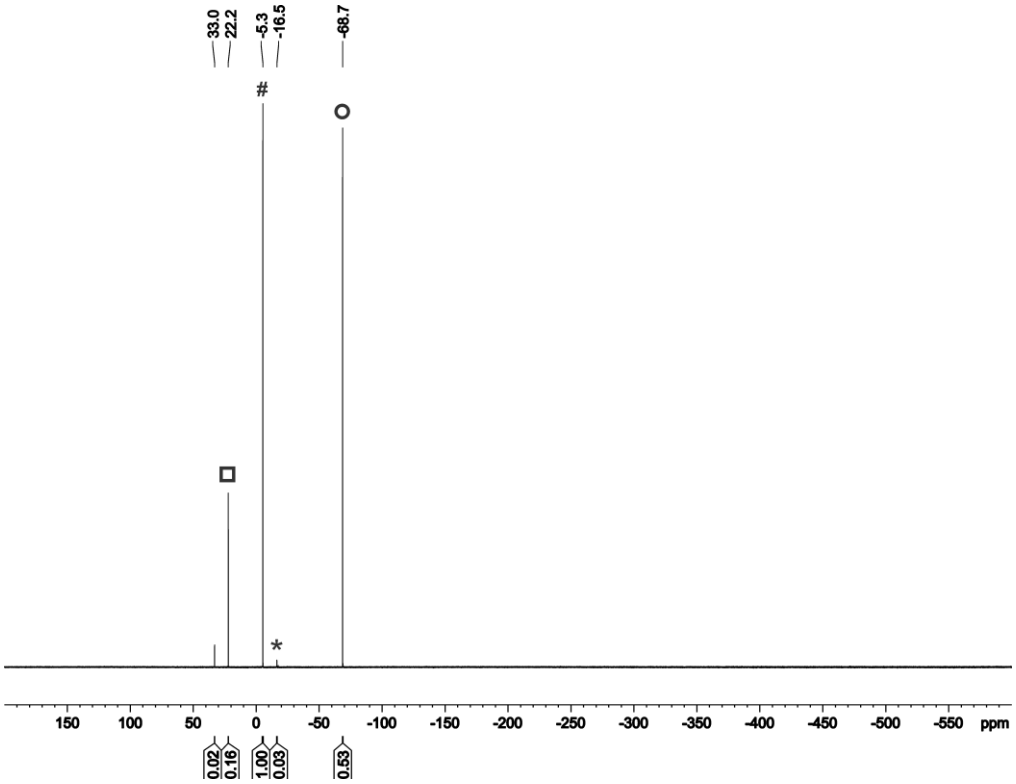


Figure S41. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of *t*BuCP (○) with catalytic amounts of **20** (□) after 18 h at r.t.. Internal standard PPh_3 (#). Free ligand DPEPhos (*).

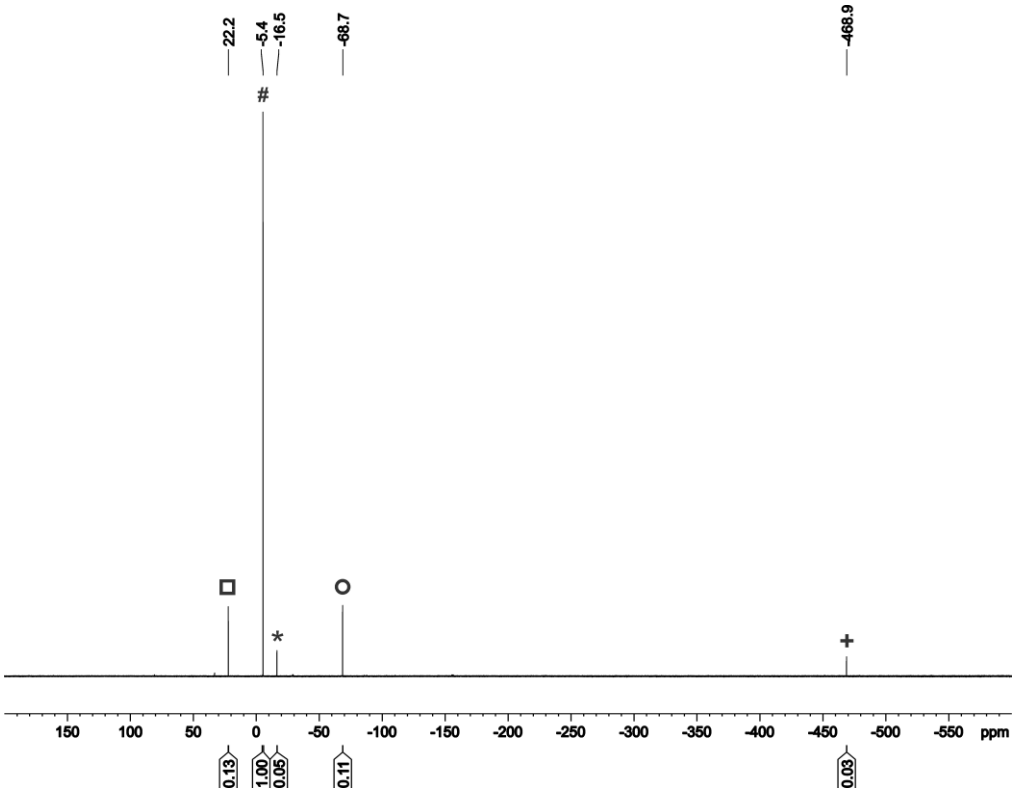


Figure S42. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of *t*BuCP (○) with catalytic amounts of **20** (□) after 18 h at 60 °C. Internal standard PPh_3 (#). $(t\text{BuCP})_2$ (**1**, +). Free ligand DPEPhos (*).

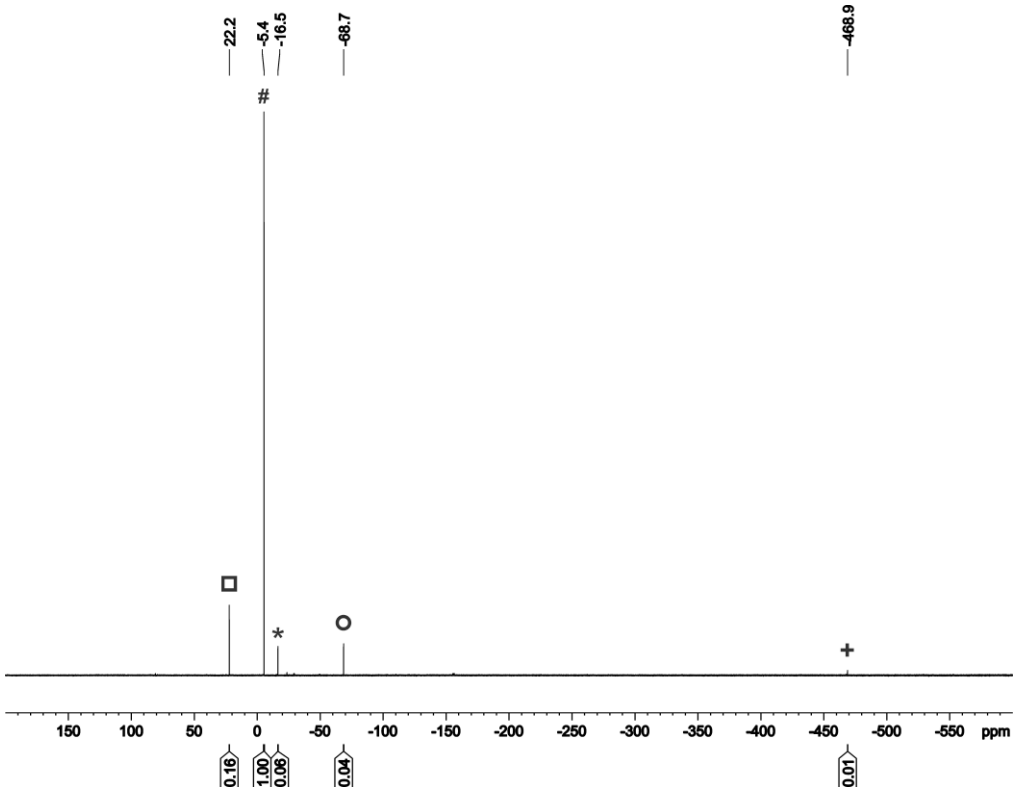


Figure S43. Quantitative $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, 300 K, C_6D_6) of the reaction of *t*BuCP (○) with catalytic amounts of **20** (□) after 50 h at 60 °C. Internal standard PPh_3 (#). $(t\text{BuCP})_2$ (**1**, +). Free ligand DPEPhos (*).

6.4.5 Single-Crystal X-ray Diffraction Data

The single-crystal X-ray diffraction data were recorded on Rigaku XtaLAB Synergy DW R (DW system, HyPix-Arc 150) or Bruker SMART APEX II CCD diffractometers with microfocus Cu-Kα radiation (λ = 1.54184 Å). Crystals were selected under mineral oil, mounted on micromount or glass-fibre loops and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device. Either semi-empirical multi-scan absorption corrections[34] or analytical ones[35] were applied to the data. Using Olex2,[36] the structure was solved with the SHELXT[37] structure solution programme using Intrinsic Phasing and refined with the SHELXL[38] refinement package using Least Squares refinements on F^2. The hydrogen atoms were located in idealised positions and refined isotropically with a riding model.

9 crystallises in the triclinic space group $\bar{1}$ with half a formula unit and one benzene molecule in the asymmetric unit. The solvent molecule is disordered over a symmetry element, which was treated with a restraint (SIMU). **11** crystallises in the monoclinic space group C_C with one formula unit in the asymmetric unit. **12** crystallises in the monoclinic space group $P2_1/c$ with one formula unit in the asymmetric unit. **14** crystalises in the triclinic space group $\bar{1}$ with four formula units and five toluene molecules in the asymmetric unit. The disorder of the solvent molecules was treated with restraints (SIMU, DFIX, and ISOR).

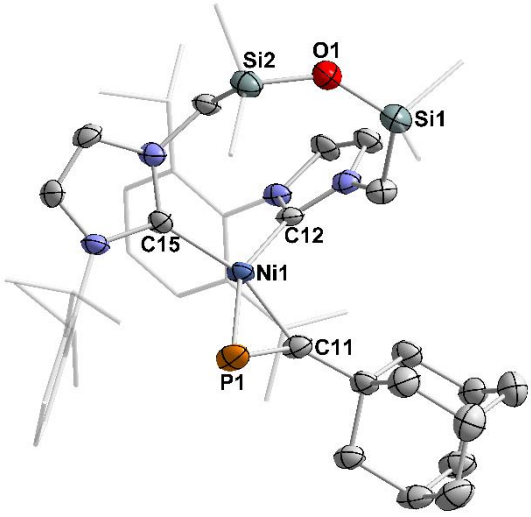


Figure S44. Molecular structure of **14** in the solid state. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1–C11: 1.901(7), Ni1–C12: 1.930(7), Ni1–C15: 1.934(7), Ni1–P1: 2.186(2) , P1–C11: 1.640(7), C11–Ni1–P1: 46.7(2), C12–Ni1–P1: 152.2(2), C15–Ni1–P1: 102.5(2), C12–Ni1–C11: 105.9(3), C15–Ni1–C11: 149.0(3), C11–P1–Ni1: 57.5(3), C12–Ni1–C15: 104.5(3).

18 crystalises in the triclinic space group $\bar{1}$ with one formula unit in the asymmetric unit.

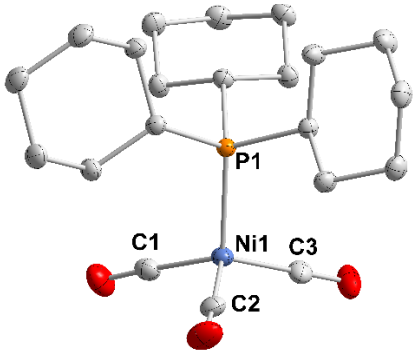


Figure S45. Molecular structure of **18** in the solid state. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1–C1: 1.8033(14), Ni1–C2: 1.8014(14), Ni1–C3: 1.7921(13), Ni1–P1: 2.2407(3), C1–Ni1–P1: 110.45(4), C2–Ni1–P1: 103.08(4), C3–Ni1–P1: 107.41(4), C2–Ni1–C1: 109.28(6), C3–Ni1–C1: 110.98(6), C3–Ni1–C2: 115.31(6).

20 crystalises in the triclinic space group $\bar{1}$ with one formula unit and one toluene molecule in the asymmetric unit.

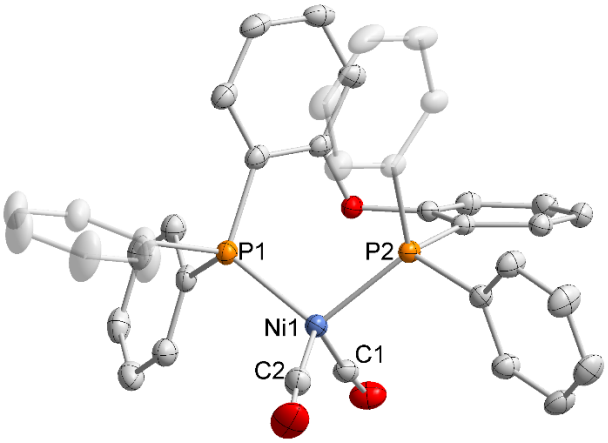


Figure S46. Molecular structure of **20** in the solid state. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ni1–C1: 1.768(2), Ni1–C2: 1.772(2), Ni1–P1: 2.2125(6), Ni1–P2: 2.2054(6), C1–Ni1–P1: 103.51(7), C2–Ni1–P1: 117.37(8), P2–Ni1–P1: 105.25(2), C2–Ni1–C1: 117.31(11), C1–Ni1–P2: 102.62(8), C2–Ni1–P2: 109.20(8).

Table S5. Crystal data and structure refinement for **9** and **11**.

Compound	**9**[a]	**11**
Empirical formula	$C_{51}H_{64}P_4$	$C_{39}H_{57}N_4SiPNi$
Formula Weight	800.90	699.65
Temperature [K]	296	123(1)
Crystal System	triclinic	monoclinic
Space Group	P-1	Cc
a [Å]	6.4777(6)	19.7030(2)
b [Å]	12.6677(10)	11.28720(10)
c [Å]	13.3777(13)	17.5495(2)
α [°]	72.069(6)	90
β [°]	86.951(7)	94.8920(10)
γ [°]	82.344(7)	90
Volume [Å^3]	1035.03(17)	3888.65(7)
Z	1	4
ρ_{calc} [g/cm^3]	1.285	1.195
μ [mm^{-1}]	1.947	1.630
F(000)	430.0	1504.0
Crystal Size [mm^3]	0.106 × 0.054 × 0.029	0.175 × 0.146 × 0.072
Radiation	CuKα (λ = 1.54178)	Cu Kα (λ = 1.54184)
2Θ range for data collection [°]	6.946 to 144.904	9.01 to 150.256
Index ranges	? ≤ h ≤ ?, ? ≤ k ≤ ?, ? ≤ l ≤ ?	-24 ≤ h ≤ 23, -14 ≤ k ≤ 14, -21 ≤ l ≤ 21
Reflections collected	3961	46704
Independent reflections	3961 [R_{int} = ?, R_{sigma} = 0.3804]	7482 [R_{int} = 0.0329, R_{sigma} = 0.0174]
Data / restraints / parameters	3961/42/262	7482/2/428
Goodness-of-fit on F^2	0.995	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.1329, wR_2 = 0.3015	R_1 = 0.0262, wR_2 = 0.0735
Final R indexes [all data]	R_1 = 0.2482, wR_2 = 0.3460	R_1 = 0.0265, wR_2 = 0.0737
Largest diff. peak/hole [e Å^{-3}]	1.02/-0.57	0.39/-0.33
Flack parameter		0.001(8)

[a]A B-level alert referring to low bond precision on C–C bonds is due to the crystal being a small twinning crystal with poor diffraction pattern.

Table S6. Crystal data and structure refinement for **12** and **14**.

Compound	**12**	**14**
Empirical formula	$C_{48}H_{70}N_4NiPSi$	$C_{223}H_{315.01}N_{16}Ni_4O_4P_4Si_8$
Formula Weight	820.85	3867.33
Temperature [K]	123(1)	173(1)
Crystal System	monoclinic	triclinic
Space Group	$P2_1/c$	P-1
a [Å]	11.28090(10)	12.0935(5)
b [Å]	23.9827(2)	19.6286(8)
c [Å]	17.38530(10)	24.9270(12)
α [°]	90	76.136(4)
β [°]	100.8760(10)	78.996(4)
γ [°]	90	89.874(3)
Volume [Å^3]	4619.04(6)	5633.2(4)
Z	4	1
ρ_{calc} [g/cm^3]	1.180	1.140
μ [mm^{-1}]	1.443	1.466
F(000)	1772.0	2081.0
Crystal Size [mm^3]	0.229 × 0.115 × 0.045	0.212 × 0.161 × 0.054
Radiation	Cu Kα (λ = 1.54184)	CuKα (λ = 1.54178)
2Θ range for data collection [°]	6.354 to 150.4	4.642 to 133.19
Index ranges	$-14 \le h \le 13$, $-28 \le k \le 30$, $-21 \le l \le 20$	$-14 \le h \le 14$, $-23 \le k \le 23$, $-29 \le l \le 29$
Reflections collected	116002	68413
Independent reflections	9455 [R_{int} = 0.0263, R_{sigma} = 0.0121]	19140 [R_{int} = 0.1182, R_{sigma} = 0.1015]
Data / restraints / parameters	9455/0/479	19140/705/1317
Goodness-of-fit on F^2	1.042	1.097
Final R indexes [I>=2σ (I)]	R_1 = 0.0353, wR_2 = 0.0929	R_1 = 0.1207, wR_2 = 0.3085
Final R indexes [all data]	R_1 = 0.0379, wR_2 = 0.0946	R_1 = 0.1553, wR_2 = 0.3350
Largest diff. peak/hole [e Å^{-3}]	1.08/-0.84	2.16/-0.70

Table S7. Crystal data and structure refinement for **18** and **20**.

Compound	**18**	**20**
Empirical formula	$C_{21}H_{33}NiO_3P$	$C_{45}H_{36}O_3P_2Ni$
Formula Weight	423.15	745.39
Temperature [K]	123(1)	100(1)
Crystal System	triclinic	triclinic
Space Group	P-1	P-1
a [Å]	9.43510(10)	9.8863(2)
b [Å]	9.67820(10)	11.1178(2)
c [Å]	13.49010(10)	17.7757(4)
α [°]	96.3100(10)	80.391(2)
β [°]	99.7560(10)	80.233(2)
γ [°]	115.7660(10)	77.7190(10)
Volume [Å^3]	1069.69(2)	1863.97(7)
Z	2	2
ρ_{calc} [g/cm^3]	1.314	1.328
μ [mm^{-1}]	2.143	1.878
F(000)	452.0	776.0
Crystal Size [mm^3]	0.26 × 0.195 × 0.133	0.157 × 0.11 × 0.079
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection [°]	6.796 to 150.922	8.216 to 150.412
Index ranges	$-11 \le h \le 11$, $-11 \le k \le 12$, $-11 \le l \le 16$	$-11 \le h \le 12$, $-13 \le k \le 13$, $-21 \le l \le 22$
Reflections collected	17255	45873
Independent reflections	4305 [R_{int} = 0.0170, R_{sigma} = 0.0137]	7552 [R_{int} = 0.0180, R_{sigma} = 0.0127]
Data / restraints / parameters	4305/0/236	7552/0/461
Goodness-of-fit on F^2	1.048	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0232, wR_2 = 0.0611	R_1 = 0.0484, wR_2 = 0.1408
Final R indexes [all data]	R_1 = 0.0241, wR_2 = 0.0616	R_1 = 0.0498, wR_2 = 0.1420
Largest diff. peak/hole [e Å^{-3}]	0.34/-0.19	0.73/-0.72

6.5 References

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7 Summary and Conclusion

Chapter 1. *Phosphatetrahedranes*

Molecules with atoms arranged in a tetrahedral geometry continue to fascinate due to their unique bonding and distinct reactivity. Among the plethora of tetrahedranes reported, the introductory chapter of this thesis focuses on neutral group 14 and group 15 tetrahedranes, with an emphasis on molecules that incorporate elements of both groups in their tetrahedral core. The first section introduces group 14 tetrahedranes, including the first organic example, tetra-*tert*-butyltetrahedrane ((*t*BuC)$_4$, **1-1**, Figure 1), alongside tetrahedral molecules of group 15, such as white phosphorus (P_4, **1-2**), first isolated in 1669, which remains an important industrial feedstock.

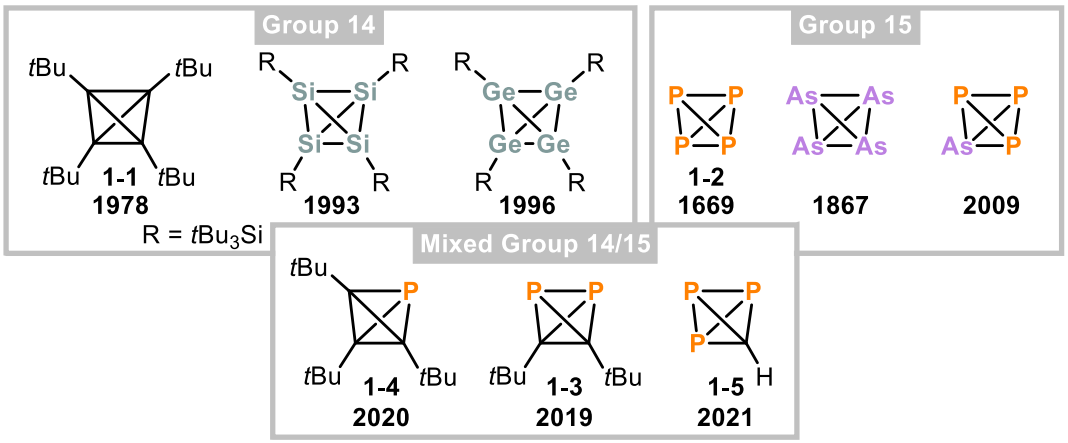


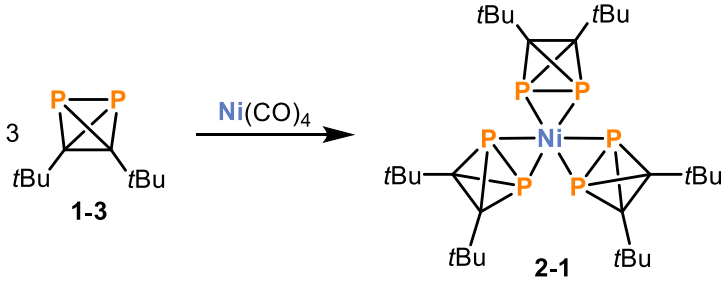
Figure 1. Selected group 14 and group 15 tetrahedranes.

Building on these established systems, the second section of this chapter explores the synthesis, stability, and reactivity of tetrahedranes containing both group 14 and group 15 elements. To date, such compounds are limited to tetrahedranes comprised of phosphorus and carbon. The first phosphatetrahedranes were reported in 2019, and isolated examples remain limited to three: di-*tert*-butyldiphosphatetrahedrane (*t*BuCP)$_2$ (**1-3**), tri-*tert*-butylphosphatetrahedrane (*t*BuC)$_3$P (**1-4**) and triphosphatetrahedrane (HCP_3, **1-5**). Reactivity studies on these three compounds demonstrate that their unique bonding situation enables access to a variety of organophosphorus compounds otherwise difficult to obtain. Nevertheless, the broader reactivity of this novel compound class remains largely unexplored. This omission, along with the still limited number of phosphatetrahedranes, provided the central motivation for the investigations in this thesis, which focused on reactivity studies of phosphatetrahedrane **1-3** and a deeper understanding of the synthesis of diphosphatetrahedranes.

Chapter 2. *A Homoleptic Diphosphatetrahedrane Nickel(0) Complex*

Inspired by previous studies on the coordination chemistry of phosphatetrahedranes, Chapter 2 explores the reactivity of (*t*BuCP)$_2$ (**1-3**) towards Ni(CO)$_4$. Upon CO substitution with **1-3**, the

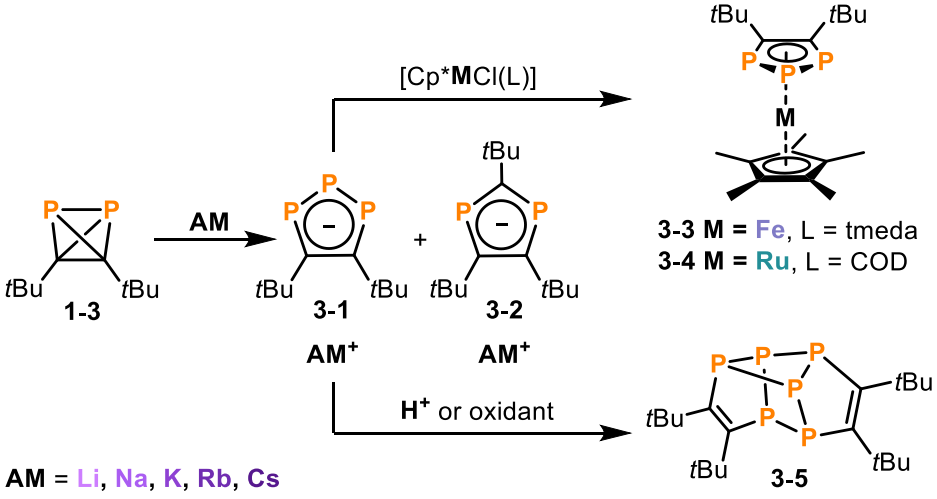
formation of a new phosphatetrahedrane Ni-complex, [Ni{η^2-(*t*BuCP)$_2$}$_3$] (**2-1**, Scheme 1), was observed. It features three intact diphosphatetrahedrane ligands coordinated to the Ni(0) atom in an η^2-fashion *via* their P–P bonds. Quantum chemical calculations imply that this coordination is facilitated by 3-centre-2-electron bonds, indicating similarities to tris(ethylene)nickel(0) and the few reported complexes featuring intact P_4 tetrahedra. To date, **2-1** is one of three reported complexes featuring intact phosphatetrahedrane ligands other than P_4 and is particularly remarkable due to its homoleptic nature.



Scheme 1. Synthesis of [Ni{η^2-(*t*BuCP)$_2$}$_3$] (**2-1**) by substitution of CO-ligands by (*t*BuCP)$_2$ (**1-3**).

Chapter 3. *Access to 1,2,3-Triphospholide Ligands by Reduction of Di-tert-butyldiphosphatetrahedrane*

To gain an understanding of the so far unexplored redox enfa of phosphatetrahedranes, Chapter 3 describes investigations regarding the reactivity of (*t*BuCP)$_2$ (**1-3**) towards reducing agents. No reaction occurred in initial attempts with magnesium and zinc powder. However, reactions of **1-3** with strongly reducing alkali metals (Li-Cs) led to the formation of 1,2,3-triphospholide anion **3-1**, along with the 1,3-diphospholide anion **3-2** as a minor by-product (Scheme 2). In contrast, the reduction of *tert*-butylphosphaalkyne with alkali metals yields the related 1,2,4-triphospholide isomer, with **3-2** as a side product, highlighting the distinct reactivity of **1-3** compared to its monomer.

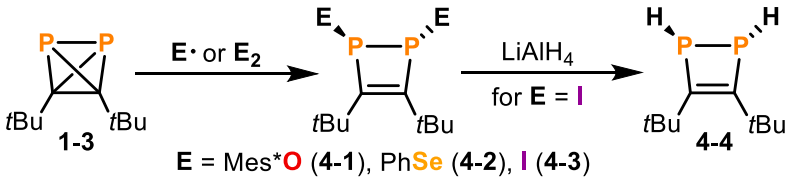


Scheme 2. 1,2,3-Triphospholide anion (**3-1**) and 1,3-diphospholide anion (**3-2**) formed upon reduction of (*t*BuCP)$_2$ (**1-3**) with alkali metals and follow-up reactivity of **3-1**.

Reactivity studies of the isolated potassium salt of **3-1** with iron(II) and ruthenium(II) chlorides enabled the synthesis of the sandwich complexes [Cp*M(η^5-1,2,3-P_3C_2tBu$_2$)] (**3-3,** M = Fe; **3-4**, M = Ru) upon transmetallation, featuring the triphospholide ligand in an η^5-coordination. Upon reaction of **3-1** with [Cp_2Fe][BAr_4^F] or [H(Et_2O)$_2$$BAr_4^F$] ($BAr_4^F$ = B{$C_6H_3(CF_3)_2$}$_4$), the tetracyclic compound tBu$_4C_4P_6$ (**3-5**) is obtained. Quantum chemical investigations into its unexpected formation indicate that oxidation of **3-1** yields a radical species which rapidly undergoes dimerisation and cycloaddition, forming **3-5**. Overall, these results illustrate the variety of organophosphorus compounds accessible through phosphatetrahedranes.

Chapter 4. *A Radical Path to 1,2-Diphosphacyclobutenes*

Following the reduction behaviour of tetrahedrane **1-3** (Chapter 3), Chapter 4 describes the reactivity of (tBuCP)$_2$ (**1-3**) towards oxidants. Reactions of **1-3** with the bulky aryloxy radical Mes*****O**·** and the formal radical sources Ph_2Se_2 and I_2 lead to the formation of 1,2-diphosphacyclobutadiene derivatives (**4-1**, **4-2**, and **4-3**, Scheme 3). This outcome contrasts with the reactivity of P_4 towards radicals, where P–P bond cleavage affords the [1.1.0]bicyclobutane product ("P_4-butterfly"). Quantum chemical calculations revealed that P–P bond cleavage in **1-3** is energetically more favourable for the small aryloxy radical PhO**·**, while cleavage of the P–C bond followed by formation of the 1,2-diphosphacyclobutadiene **4-1** is thermodynamically preferred for the bulky Mes*****O**·**. The reduction of 1,2-diiodo-1,2-diphosphacyclobutene **4-3** unexpectedly led to formation of the ladderane (tBuCP)$_4$, a compound typically obtained via isomerisation and dimerisation of **1-3**. In contrast, nucleophilic substitution of iodine with hydride furnished the 1,2-dihydro-1,2-diphosphacyclobutene **4-4**.



Scheme 3. 1,2-diphosphacyclobutene derivatives obtained upon oxidation of **1-3**.

Overall, the reactivity studies of **1-3** described in Chapters 2-4 demonstrate its manifold reactivity, which allows access to a broad variety of organophosphorus compounds.

Chapter 5: *Synthesis of Diphosphatetrahedranes: Quantum Chemical and Experimental Investigations on the Mechanism*

To date, (tBuCP)$_2$ (**1-3**) is the only isolated diphosphatetrahedrane, which limits the exploration of the reactivity of this class of compounds. Compound **1-3** is generated by nickel-catalysed dimerisation of *tert*-butylphosphaalkyne. It would be highly desirable if this method could be applied to other phosphaalkynes to access a larger variety of diphosphatetrahedranes. As a first

step towards this goal, Chapter 5 describes a quantum chemical and experimental investigation on the reaction mechanism, evaluating diverse phosphaalkyne substrates and Ni-catalysts with different N-heterocyclic carbene ligands (NHC). This analysis identified two competing effects:

1) Bulky phosphaalkynes and sterically demanding NHCs lead to a high activation barrier for the formation of the diphosphete derivatives **5-1** (Figure 2), which typically represents the rate-determining step of the catalytic cycle.
2) Steric repulsion between the phosphaalkyne and NHC is a prerequisite for the formation of the diphosphatetrahedrane because it destabilises the key intermediate (**5-1**, Figure 2). For sterically less bulky NHCs and phosphaalkynes, **5-1** is energetically lower than the corresponding tetrahedrane, which therefore does not form.

These results indicate that a delicate balance in the steric demand of phosphaalkyne and NHC must be achieved for diphosphatetrahedrane synthesis. Nevertheless, with the crucial mechanistic steps identified, computational probing of the rate-determining step and the key intermediate can guide the future identification of suitable phosphaalkyne/NHC combinations.

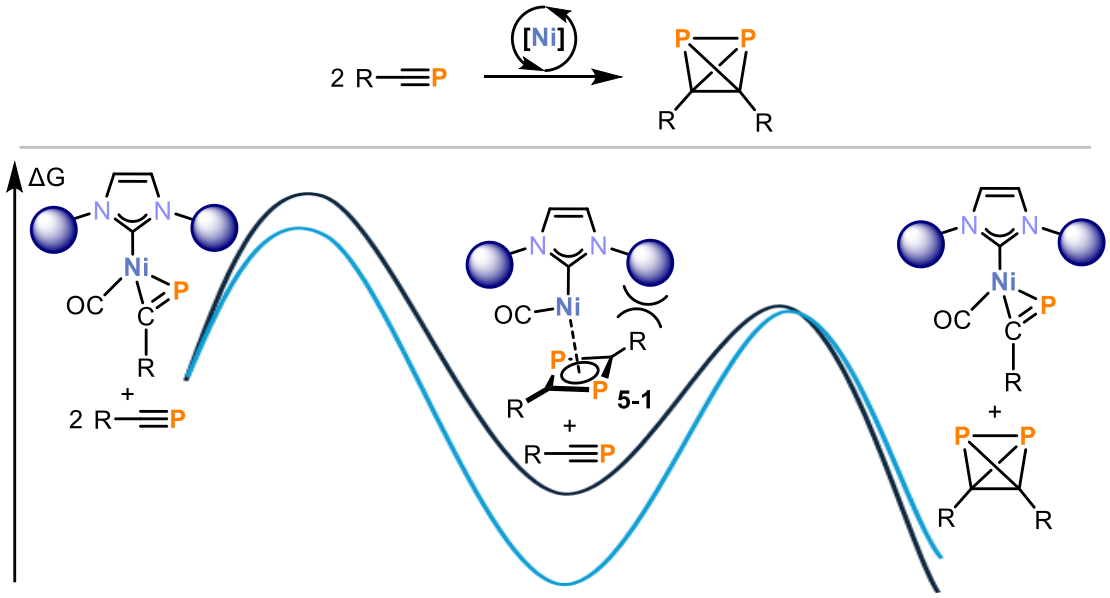
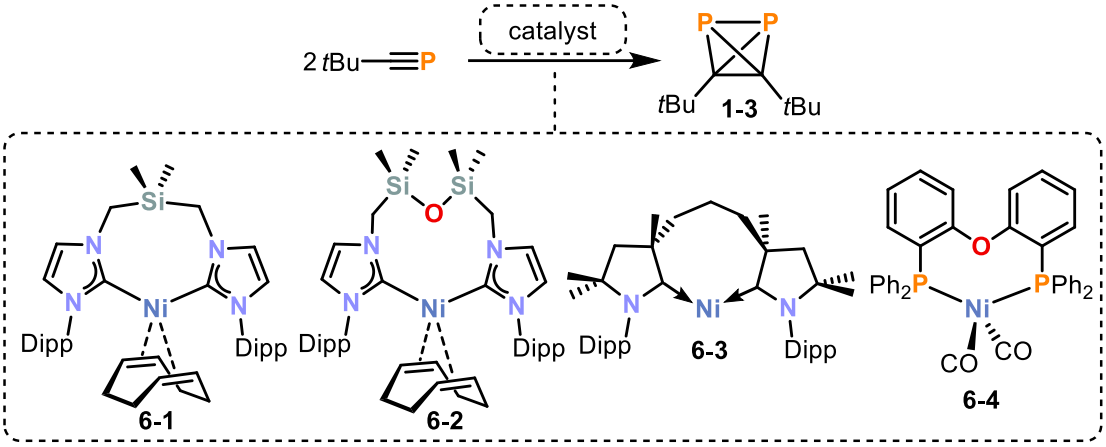


Figure 2. Synthesis of diphosphatetrahedranes by the nickel-catalysed dimerisation of phosphaalkynes (top). Schematic, simplified Gibbs free energy diagram (bottom) for bulky phosphaalkynes and NHCs (dark blue) and small phosphaalkynes and NHCs (light blue).

Chapter 6: *Nickel-Catalysed Phosphaalkyne Dimerisation: Impact of Ligands on Reactivity*

The results described in Chapter 5 indicate that each product needs a tailored catalyst. To address this, the preliminary studies described in Chapter 6 evaluate nickel complexes with different ligand classes on their ability to catalytically promote diphosphatetrahedrane formation. Gratifyingly, reactions of *t*BuCP and AdCP with catalytic amounts of Ni complexes supported by (N-heterocyclic) dicarbenes (**6-1** to **6-3**, Scheme 4) afforded the desired diphosphatetrahedranes. Unfortunately, $(AdCP)_2$ could not be isolated due to its decomposition to $(AdCP)_4$. In contrast,

the respective diphosphatetrahedranes could not be synthesised from mesitylphosphaalkyne and trimethylsilylphosphaalkyne using these catalysts. Unlike the tested monodentate phosphine complexes, di(phosphine) Ni complexes **6-4** enabled the formation of (*t*BuCP)$_2$ (**1-3**), albeit in very low yields.



Scheme 4. Bidentate bis(NHC) (**6-1**, **6-2**) bis(CAAC) (**6-3**) and did(phosphine) (**6-4**) ligands capable of dimerizing *tert*-butylphosphaalkyne to **1-3**.

Future research should screen further bidentate di(phosphine) complexes towards an array of phosphaalkynes and optimise reaction conditions. Nevertheless, these exploratory findings clearly demonstrate that nickel complexes bearing a variety of ligands can enable the catalytic synthesis of diphosphatetrahedranes. In combination with the mechanistic insights from computational studies (see Chapter 5), this work lays the foundation for future synthesis of a variety of diphosphatetrahedranes.

Conclusion

In summary, this doctoral thesis highlights the unique reactivity of phosphatetrahedranes, which serve as precursors for a wide range of organophosphorus compounds. This was emphasised by investigations focussed on the reactivity of (tBuCP)$_2$ (**1-3**) towards Ni(CO)$_4$, as well as its behaviour under reductive and oxidative conditions. These studies demonstrated the broad synthetic potential of **1-3**, affording a variety of new compounds, including a coordination complex with the intact phosphatetrahedrane, 1,2,3-triphospholide and 1,3-diphospholide anions and 1,2-diphosphacyclobutene derivatives. Nevertheless, the number of reported isolated phosphatetrahedranes remains limited, which has restricted comprehensive reactivity studies of this compound class. Detailed DFT studies were performed to gain a deeper understanding of the nickel-catalysed synthesis of diphosphatetrahedranes from phosphaalkynes, alongside the evaluation of alternative Ni catalysts supported by bidentate N-heterocyclic carbenes and diphosphines. It is hoped that these results lay the foundation for the future synthesis of new diphosphatetrahedranes which will expand our knowledge of phosphatetrahedrane chemistry and will serve as useful synthons for a wide variety of organophosphorus compounds.

8 Acknowledgements

9 Curriculum Vitae

10 List of Publications

7) Maria K. Uttendorfer, Lisa M. Schneider, Lukas S. Diener, Gabriele Hierlmeier, Gábor Balázs, Robert Wolf,* „A Radical Path to 1,2-Diphosphacyclobutenes“ *Chem. Commun.* **2025**, *61*, 17464–17467.

6) J. Cammarata,‡ F. F. Westermair,‡ P. Coburger, D. Duvinage, M. Janssen, M. K. Uttendorfer, J. Beckmann,* R. M. Gschwind,* R. Wolf,* D. J. Scott,* „Unravelling White Phosphorus: Experimental and Computational Studies Reveal the Mechanisms of P_4 Hydrostannylation”, *Angew. Chem. Int. Ed.* **2024**, e202408423.

5) M. K. Uttendorfer, G. Hierlmeier, G. Balázs, R. Wolf,* “Access to 1,2,3-Triphosphospholide Ligands by Reduction of Di-*tert*-butyldiphosphatetrahedrane”, *Dalton Trans.* **2024**, *53*, 10113–10119**.**

4) W. Sun,‡ M. Uttendorfer,‡ F. I. M. Idiris, A. Y. R. Werling, K. Siddiq, C. R. Jones,* “Selective access to dihydrophenanthridines and phenanthridinones via cyclisation of aryl amines onto N-tethered arynes“, *Chem. Commun.* **2023**, *59*, 11823–11826.

3) M. K. Uttendorfer, G. Hierlmeier, R. Wolf,* “A Homoleptic Diphosphatetrahedrane Nickel(0) Complex“, *Z. Anorg. Allg. Chem.* **2022**, e202200124.

2) G. Hierlmeier, M. K. Uttendorfer, R. Wolf,* “Di-*tert*-butyldiphosphatetrahedrane as a building block for phosphaalkenes and phosphirenes”, *Chem. Commun*. **2021**, *57*, 2356–2359.

1) C. G. P. Ziegler, C. Taube, J. A. Kelly, G. Hierlmeier, M. Uttendorfer, J. J. Weigand,* R. Wolf,* “An unusual $Ni_2Si_2P_8$ cluster formed by complexation and thermolysis“, *Chem. Commun.* **2020**, *56*, 14071–14074.

Eidesstattliche Erklärung

Ich erkläre hiermit an Eides statt, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe; die aus anderen Quellen direkt oder indirekt übernommenen Daten und Konzepte sind unter Angabe des Literaturzitats gekennzeichnet. Die Arbeit wurde bisher weder im In- noch im Ausland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde vorgelegt.

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