



A Journal of the Gesellschaft Deutscher Chemiker

# Angewandte Chemie

GDCh

International Edition

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## Accepted Article

**Title:** Activation of Di-tert-butylidiphosphatetrahedrane: Access to (tBuCP)<sub>n</sub> (n = 2, 4) Ligand Frameworks by P–C Bond Cleavage

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**To be cited as:** *Angew. Chem. Int. Ed.* 10.1002/anie.202015680

**Link to VoR:** <https://doi.org/10.1002/anie.202015680>

## COMMUNICATION

# Activation of Di-*tert*-butyldiphosphatetrahedrane: Access to $(t\text{BuCP})_n$ ( $n = 2, 4$ ) Ligand Frameworks by P–C Bond Cleavage

Gabriele Hierlmeier<sup>[a]</sup> and Robert Wolf<sup>\*[a]</sup>

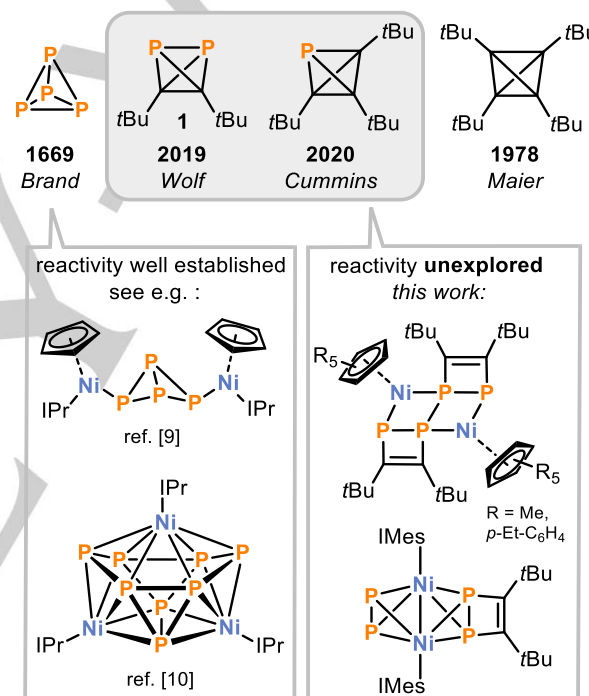
In memory of François Mathey

**Abstract:** The first mixed phosphatetrahedranes were reported only recently and their reactivity is virtually unexplored. Here we present a reactivity study on di-*tert*-butyldiphosphatetrahedrane (**1**), which is the dimer of *tert*-butylphosphaalkyne. The  $(t\text{BuCP})_2$  tetrahedron is activated selectively by N-heterocyclic carbene (NHC) nickel(I) and nickel(0) complexes, resulting in novel complexes featuring diverse  $(t\text{BuCP})_n$ -frameworks ( $n = 2, 4$ ). Release of the  $(t\text{BuCP})_4$  framework from one of the complexes was achieved by addition of CO gas. Furthermore, **1** can be used as a source for  $\text{P}_2$  units by elimination of bis-*tert*-butylacetylene in the coordination sphere of nickel.

Tetrahedranes have long fascinated the chemical community due their simple structure and typically high reactivity.<sup>[1]</sup> The first tetrahedral molecule to be prepared was white phosphorus,  $\text{P}_4$ , which was discovered as early as 1669, although its tetrahedral structure was recognised only in the early 19<sup>th</sup> century.<sup>[2]</sup>  $\text{P}_4$  is produced on a megaton scale each year and used as the common building block for incorporation of P atoms into organophosphorus compounds.<sup>[3]</sup> The heavier homologue  $\text{As}_4$  and the mixed interpnictogen compound  $\text{AsP}_3$  are likewise accessible.<sup>[4]</sup> Purely carbon-based tetrahedranes are also well-known, in line with the diagonal relationship between carbon and phosphorus in the periodic table.<sup>[5]</sup> Indeed, the synthesis of  $(t\text{BuC})_4$  in 1978 was a pinnacle of organic synthesis.<sup>[5]</sup>

In contrast, the first mixed C/P tetrahedranes were only reported last year. We showed that the ‘hybrid’ of  $(t\text{BuC})_4$  and  $\text{P}_4$ , di-*tert*-butyldiphosphatetrahedrane  $(t\text{BuCP})_2$  (**1**), can be synthesised in a simple nickel-catalysed dimerisation reaction of *tert*-butylphosphaalkyne,  $t\text{BuCP}$ .<sup>[6]</sup> Shortly after our report, the synthesis of the related tri-*tert*-butylphosphatetrahedrane  $(t\text{BuC})_3\text{P}$  was published by Cummins and co-workers.<sup>[7]</sup> Given the similar molecular structures and isolobal relationship between **1** and  $\text{P}_4$ , a comparison of the reaction properties of both molecules is a tantalising prospect.<sup>[5]</sup> Indeed, the activation of the  $\text{P}_4$  tetrahedron by main group and transition metal complexes has attracted significant interest as a means of gaining control over its transformations, and of accessing fascinating new polyphosphorus compounds.<sup>[8]</sup> In one of our recent contributions to this area, we demonstrated the use of mononuclear cyclopentadienyl nickel(I) complexes  $[\text{CpNi}(\text{NHC})]$  [NHC = IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), IPr (1,3-bis(2,6-di-*iso*-propylphenyl)imidazol-2-ylidene)]. Such ‘nickel(I)

radicals’ selectively break one P–P bond of  $\text{P}_4$  to afford  $\mu\text{-}\eta^1\text{:}\eta^1$ -bridging  $\text{P}_4^{2-}$ -ligands with a ‘butterfly’ type structure (Figure 1, centre left).<sup>[9]</sup> Subsequent studies demonstrated that  $\text{P}_4$  activation by Ni(0)-NHC complexes affords unusual di- and trinuclear cluster compounds, including a *closo*  $[(\text{IPr})_3\text{Ni}_3\text{P}_8]$  cluster shown in Figure 1 (bottom left).<sup>[10]</sup>



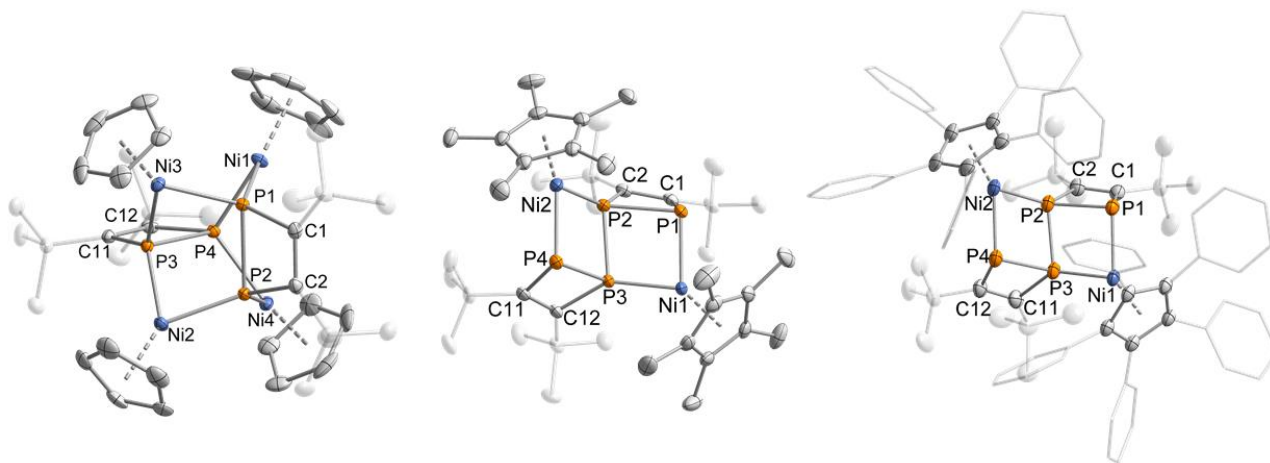
**Figure 1.** (Mixed) group 14/15 tetrahedranes and reactivity of  $\text{P}_4$  with NHC-stabilised Ni(I) metalloradicals and Ni(0) complexes.<sup>[9][10]</sup>

Here, we describe a study into the reactivity of diphosphatetrahedrane **1** with the same N-heterocyclic carbene (NHC) nickel(I) and nickel(0) complexes. These investigations have led to the preparation of polynuclear nickel complexes, which incorporate a variety of  $(t\text{BuCP})_n$  ( $n = 2, 4$ ) ligands in unusual coordination modes that are not known to be accessible using other synthetic precursors. We furthermore discuss the follow-up chemistry and remarkable thermal transformation of one of these compounds. The results of this work provide a valuable first insight into the reaction behaviour of **1** toward transition metal centres and reveal that its reaction patterns are clearly distinct from those of  $\text{P}_4$  and, indeed, also from those of  $t\text{BuCP}$ , the monomer of **1**.

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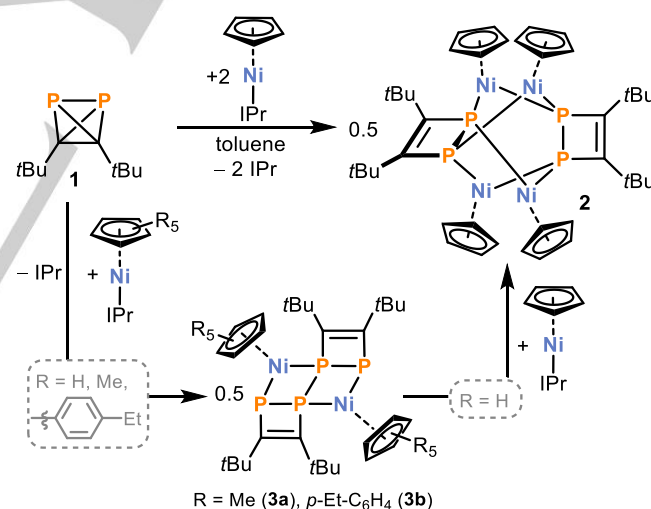


**Figure 2.** Molecular structures of **2** (left), **3a** (middle) and **3b** (right) in the solid state. Thermal ellipsoids are set at 50% probability level. For **2**, only one molecule of the asymmetric unit is shown. Hydrogen atoms, solvent molecules, disorder in the aryl rings and *p*-Et groups of **3b** are omitted for clarity.

This investigation commenced with the nickel(I) radical  $[(\text{Cp})\text{Ni}(\text{IPr})]$ , which had previously been shown to react with white phosphorus under P–P bond scission (see Figure 1).<sup>[9]</sup> Reaction of two equivalents of  $[\text{CpNi}(\text{IPr})]$  with **1** in THF instantaneously afforded a deep red solution at room temperature (Scheme 1). Analysis of the crude reaction mixture by  $^1\text{H}$  NMR spectroscopy revealed consumption of the paramagnetic starting material and release of IPr. A singlet resonance at 93.0 ppm was observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. Crystals grown from toluene were characterised by single crystal X-ray analysis (SCXRD) as the tetranuclear complex  $[(\text{CpNi})_2(\text{tBu}_2\text{C}_2\text{P}_2)]_2$  (**2**, Figure 2 left) containing two 1,2-diphosphacyclobutene-1,2-diide ligands coordinated by four (CpNi) units in a realgar-type fashion. Notably, the reaction with  $[\text{CpNi}(\text{IPr})]$  induces P–C bond cleavage to give a metalated 1,2-diphosphacyclobutene rather than forming the isomeric ‘butterfly’ compound  $[(\text{CpNi}(\text{IPr}))_2(\mu-\kappa^2\text{P}-\text{tBu}_2\text{C}_2\text{P}_2)]$  by P–P bond scission. Such a complex was observed with the valence isoelectronic  $\text{P}_4$  molecule, see Figure 1.<sup>[9]</sup> In agreement with this, DFT calculations of the hypothetical reaction of **1** with two equivalents of a radical (methyl radical or  $[\text{CpNi}(\text{IPh})]$ ) suggest that the cyclobutene compound is thermodynamically preferred over the butterfly compound (see Figure S50 and S51 in the SI).

Structurally characterised 1,2-diphosphacyclobutadiene transition metal complexes are scarce, and the ligand commonly coordinates via the  $\pi$ -system in these examples.<sup>[11]</sup> The P1–P2 bond length in **2** (2.2244(7) Å) suggests the presence of a P–P single bond, whereas the C–C bond length of 1.360(3) Å is indicative of a C=C double bond.<sup>[12]</sup> The bond metric data is thus consistent with the presence of a dianionic  $(\text{tBu}_2\text{C}_2\text{P}_2)^{2-}$  ligand, which coordinates in a  $\mu^4, \eta^2, \eta^2$ -mode through the lone-pairs of the P atoms, which was previously unknown for this type of ligand. Dark red, crystalline **2** was isolated in 56% yield and further analysed by NMR spectroscopy. The  $^1\text{H}$  NMR spectrum of **2** showed one signal for the *t*Bu groups ( $\delta = 1.32$  ppm) and one resonance for the cyclopentadienyl ligand ( $\delta = 5.17$  ppm). In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum four resonances were observed, which are consistent with the presence of a Cp and a  $(\text{tBu}_2\text{C}_2\text{P}_2)^{2-}$  ligand. The UV/Vis absorption spectrum of **2** reveals two bands at 400 and 520 nm, the latter accounting for its red colour.

Next, we assessed the reactivity of nickel radicals bearing bulkier pentamethylcyclopentadienyl ( $\text{Cp}^*$ ) and pentaarylcyclopentadienyl ( $\text{Cp}^{\text{BIG}}$ ) ligands (Scheme 1).<sup>[13]</sup> As with the previous reaction, deep red solutions were obtained when a 1:2 stoichiometry was used. However, analysis by  $^1\text{H}$  NMR spectroscopy revealed broad resonances corresponding to unconsumed paramagnetic starting material, which disappeared upon addition of another equivalent of **1**.



**Scheme 1.** Reactions of  $[\text{Cp}^{\text{R}}\text{Ni}(\text{IPr})]$  ( $\text{R} = \text{H}; \text{Me}, \text{C}_6\text{H}_4\text{-Et}$ ) with  $(\text{tBuCP})_2$ .

Single crystal X-ray diffraction studies revealed the formation of dinuclear species  $[(\text{Cp}^{\text{R}}\text{Ni})_2(\text{tBu}_4\text{C}_4\text{P}_4)]$  [ $\text{Cp}^{\text{R}} = \text{Cp}^*$  (**3a**),  $\text{Cp}^{\text{BIG}}$  (**3b**)], where two molecules of **1** have formally undergone radical coupling to produce a  $(\text{tBuCP})_4$  moiety (Scheme 1 bottom). Notably, however, compounds **2** and **3** were not formed upon reaction of the nickel complexes with the known ladderane-type phosphalkyne tetramer  $(\text{tBuCP})_4$  (**6**), which is the known dimerisation product of **1**.<sup>[6][14]</sup> This illustrates the value of **1** as a synthetic precursor to novel P/C ligand frameworks. Compounds **3a** and **3b** were isolated in 33% (**3a**) and 44% (**3b**) yields as dark-red, crystalline solids. Single-crystal X-ray diffraction revealed a three-rung ladder structure composed of two Ni and four P atoms,

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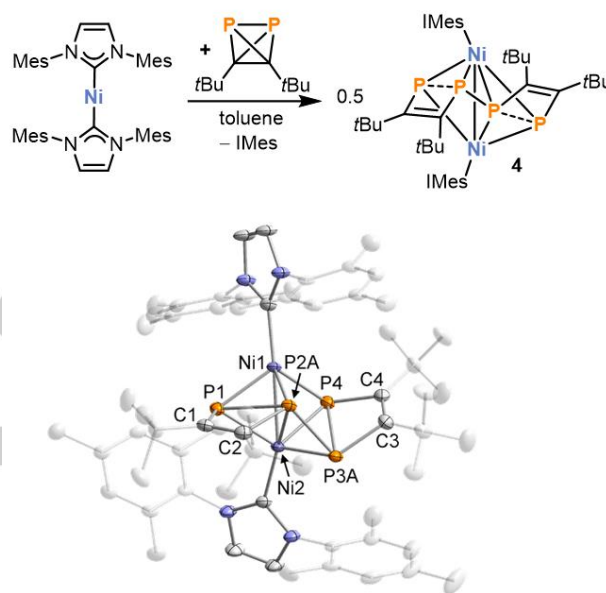
which is fused with two four-membered  $P_2C_2$  heterocycles. The P–P bond lengths range from 2.1717(9) to 2.2252(5) Å, with the shortest bond length for the P2–P3 bond, which connects the two  $P_2C_2$  rings. Analysis of **3a** and **3b** by  $^1H$  NMR spectroscopy reveal the expected signal sets for the cyclopentadienyl ligands and two singlets for the *t*Bu groups. The  $^{31}P\{^1H\}$  NMR spectra of both compounds show two pseudo triplet resonances. For **3a** these signals arise at –61.4 and 31.3 ppm with a coupling constant of 44.2 Hz (similar values were obtained for **3b**, see the Supporting Information for details). The signal shape likely arises from an AA'BB' spin system with two similar  $^1J_{PP}$  coupling constants and small  $^2J_{PP}$  couplings. Indeed, DFT calculations at the TPSS pcSseg-2 level of theory for **3a** reproduce the two small coupling constants of 28 and 47 Hz. The absorption spectra of **3a** and **3b** show bands at 420 (**3a**) and 520 (**3b**) nm.

Considering these first insights into the reaction of **1** with [CpNi(IPr)] and bulkier metalloradicals, we reasoned that **3a** and **3b** might be intermediates in the formation of realgar-type compounds such as **2**. In order to evaluate this hypothesis, **1** was reacted with just 1.5 equivalents of [CpNi(IPr)]. Two pseudo-triplet resonances at –72.5 and 22.1 ppm were observed in the  $^{31}P\{^1H\}$  NMR spectrum with a coupling constant of 45.5 Hz (see Figure S25 in the SI). In addition, formation of **2** was observed. These data are in good agreement with the spectroscopic data obtained for **3a** and **3b** and point towards formation of  $[(CpNi)_2(tBu_4C_4P_4)_2]$  (**3c**). Nevertheless, all attempts to crystallise this compound failed (instead, crystals of **2** were obtained). Furthermore, no reaction occurred between **3a** and one equivalent of the smallest nickel radical [CpNi(IPr)] even when heated to temperatures of 70 °C. The sluggish reactivity of **3a** toward [CpNi(IPr)] is presumably due to the central P–P bond being shielded by the Cp\* ligand.

Aiming at the synthesis of further oligonuclear nickel complexes, we next investigated the reactions of **1** towards the Ni(0) complexes  $[(IMes)_2Ni]$  and  $[(IPr)Ni(\eta^6\text{-toluene})]$ .<sup>[15]</sup> The reactions of these complexes with **1** afforded Wade-Clusters, as reported previously.<sup>[10]</sup> The reaction of **1** with  $[(IMes)_2Ni]$  at –80 °C afforded a brown reaction solution. Analysis by  $^{31}P\{^1H\}$  NMR spectroscopy revealed a selective reaction and two pseudo-triplet resonances at –9.9 ppm and 299.1 ppm ( $J = 40.3$  Hz), which is reminiscent of the  $(tBu_4C_4P_4)$ -framework in compounds **3a/b**. An X-ray diffraction experiment confirmed the presence of  $[(IMesNi)_2(P_4C_4tBu_4)]$  (**4**), a dinuclear complex featuring a Ni–Ni bond and a  $(tBu_4C_4P_4)$ -moiety (Figure 3). The P–P bond lengths for the bonds within the diphosphacyclobutene ring are significantly longer compared to **3a/b**, with 2.6304(7) (P1–P2A) and 2.6702(7) Å (P3A–P4), whereas the exocyclic P2A–P3A bond is similar to that in **3** (2.2445(7) Å). The Ni1–Ni2 bond distance of 2.4293(4) Å compares well to other nickel(I) dimers (e.g.  $[(IPr)Ni]_2(\mu\text{-Cp})(\mu\text{-Cl})$ : 2.4015(3) Å).<sup>[16]</sup>

The bonding situation of the truncated model complex **4'**  $[(IPh)Ni]_2(P_4C_4tBu_4)$  (IPh = 1,3-diphenylimidazolin-2-ylidene) was analysed by means of intrinsic bond orbitals (IBO) on the BP86/def2-TZVP level of theory. Two of these orbitals show multicentre bonds between Ni1/P1/P2a and Ni2/P3A/P4 (see Figure S52 in the SI for a depiction of the IBOs), which is reminiscent of the trinuclear Wade-clusters we obtained from a similar reaction with  $P_4$ .<sup>[10]</sup> Moreover, the Mayer bond indices for the P–P bonds are small with values of <0.1 and 0.11 for the P1–P2a and P3a–P4 bonds, suggesting only a weak interaction. The low Mayer bond index of 0.31 for the Ni1–Ni2 bond

contradicts a strong covalent interaction. Compound **4** can be isolated in 28% yield by crystallisation. The  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra are in agreement with the structure determined by SCXRD, showing the expected signal sets for the IMes ligand and the  $(tBu_4C_4P_4)$  moiety. The  $^{31}P\{^1H\}$  NMR spectrum is inconsistent with the asymmetrical structure of **4**. However, we propose that the higher symmetry in the NMR spectrum results from a process which leads to an averaging of the signals for P1/P4 and P2/P3. Decoalescence was not observed upon cooling to 193 K. This suggests that the proposed fluxional process has a low activation barrier (see the SI for variable temperature NMR spectra).

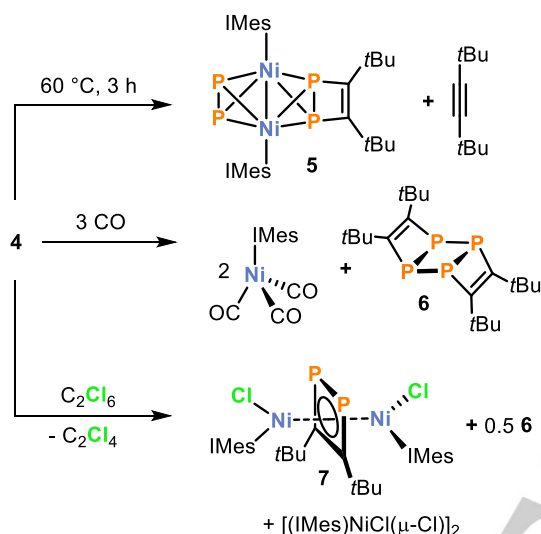


**Figure 3.** Dimerisation of **1** in the coordination sphere of  $[(IMes)_2Ni]$  (top) and molecular structure of **4** in the solid state (bottom). Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and solvent molecules and a minor disordered component (P2B and P3B) are omitted for clarity.

Upon storage of solutions of **4** in  $C_6D_6$  at room temperature overnight, **4** was partially converted into a new compound according to  $^1H$  and  $^{31}P\{^1H\}$  NMR spectroscopy. Heating a mixture of **1** and  $[(IMes)_2Ni]$  to 60 °C for three hours resulted in selective formation of this new species, which is characterised by two multiplet resonances in the  $^{31}P\{^1H\}$  NMR spectrum at chemical shifts of 115.8 and 209.8 ppm (see the SI for a simulation). X-ray diffraction analysis of a single crystal grown from saturated *n*-hexane solutions revealed the formation of  $[(IMesNi)_2(P_2)(tBu_2C_2P_2)] \cdot IMes$  (**5-IMes**), Scheme 3, top). The formation of **5** involves the elimination of bis-*tert*-butylacetylene, which was identified by the  $^{13}C\{^1H\}$  NMR resonance of the alkyne carbon atom detected at a chemical shift of 87.5 ppm. A related example of  $tBuC\equiv CtBu$  elimination from a metal complex was recently reported by our group from a ruthenium complex,<sup>[17]</sup> but in contrast to that example, where the alkyne remains as  $\eta^2$ -bound ligand in the coordination sphere of ruthenium, bis-*tert*-butylacetylene was completely liberated in the reaction reported herein, which illustrates an exciting potential for **1** and its coordination compounds to act as a source of  $P_2$  units.

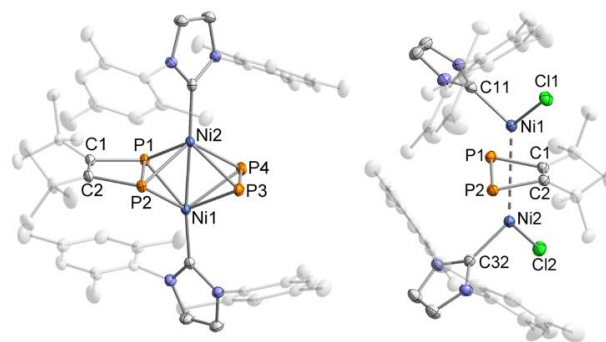
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Conveniently, dark crystals of **5** were isolated in 50% yield directly starting from  $[(\text{IMes})_2\text{Ni}]$  and **1**. The compound initially co-crystallises with one equivalent of IMes (as compound **5**·IMes). IMes can be subsequently removed by recrystallisation from toluene/*n*-hexane. The molecular structure of **5** in the solid state confirms the presence of a  $\mu\text{-}\eta^2\text{:}\eta^2\text{-P}_2$  dumbbell and a  $\mu\text{-}\eta^2\text{:}\eta^2\text{-}(\text{tBu}_2\text{C}_2\text{P}_2)^{2-}$  ligand. The P1–P2 bond of the latter ligand (2.4514(4) Å) is significantly elongated in comparison to **2** (2.2244(7) Å) and the P3–P4 bond length of the  $\text{P}_2$  ligand (2.0294(5) Å) is comparable to other complexes with a  $\text{Ni}_2\text{P}_2$  core such as  $\{(\text{IMes})\text{Ni}(\text{CO})\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-P}_2)\}$  (2.076(2) Å).<sup>[18]</sup> The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of isolated **5** is identical to the species obtained from **4** (*vide supra*). The  $^1\text{H}$  NMR and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra are in agreement with the proposed molecular structure of **5**.



**Scheme 3.** Reactivity of **4** upon heating and addition of CO and hexachloroethane.

Further reactivity studies were conducted with complex **4** in order to examine the possible release and functionalisation of the  $(\text{tBuCP})_4$  framework. Treatment of a solution of **4** in  $\text{C}_6\text{D}_6$  with carbon monoxide (1 bar) results in an instantaneous colour change of the solution from brown to pale beige and formation of  $[(\text{IMes})\text{Ni}(\text{CO})_3]$  and the known phosphacyclobutadiene  $(\text{tBuCP})_4$  (**6**, Scheme 3) as corroborated by  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy (see SI for spectra).<sup>[14]</sup> Moreover, the addition of hexachloroethane affords **6** and the chlorinated inverted sandwich complex  $\{[(\text{IMes})\text{NiCl}]_2(\mu\text{-tBu}_2\text{C}_2\text{P}_2)\}$  (**7**) as revealed by single crystal X-ray crystallography (Figure 4). Complex **7** contains a 1,2-diphosphacyclobutadiene ligand in an unusual  $\mu, \eta^4\text{:}\eta^4$ -coordination mode with a P1–P2 bond length of 2.2768(6) Å and a C1–C2 bond length of 1.437(3) Å. Unfortunately, **7** and its by-product, the dinuclear Ni(II) complex  $[(\text{IMes})\text{NiCl}(\mu\text{-Cl})_2]$  could not be separated due to similar solubilities. However, we were able to crystallise  $[(\text{IMes})\text{NiCl}(\mu\text{-Cl})_2]$  from the reaction mixture as violet blocks (see SI for SCXRD data).

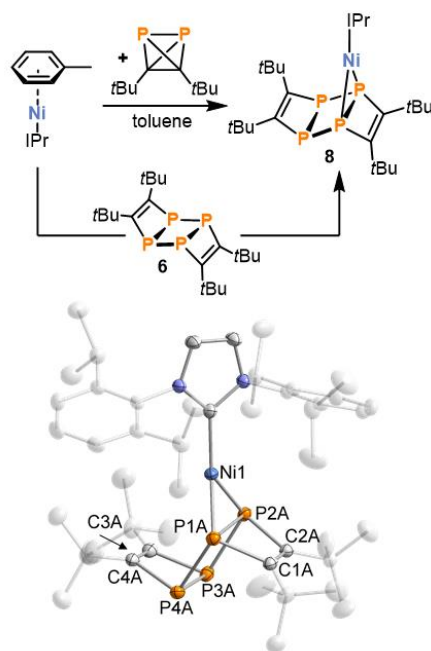


**Figure 4.** Molecular structures of **5** and **7** in the solid state. Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and one molecule of IMes (co-crystallising with **5**) are omitted for clarity.

In an attempt to evaluate the influence of the steric bulk of the NHC ligand, the related, bulkier  $[(\text{IPr})_2\text{Ni}]$  was reacted with one equivalent of **1** (Figure 5). However,  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy suggested the formation of a different product with multiplet resonances (*vide infra*). A similar spectrum was obtained when  $[(\text{IPr})\text{Ni}(\eta^6\text{-toluene})]$  was reacted with **1** (see SI for spectra). Single crystal XRD on a crystal obtained from toluene revealed the formation of  $[(\text{IPr})\text{Ni}(\text{tBu}_4\text{C}_4\text{P}_4)]$  (**8**), i.e. a mononuclear complex of the phosphacyclobutadiene **6** (Figure 5).<sup>[14]</sup> The chemistry of the phosphacyclobutadiene  $(\text{tBuCP})_4$  is barely explored and, to the best of our knowledge, this is the first example of a coordination compound of **6**. **8** was also obtained by reaction of  $[(\text{IPr})\text{Ni}(\eta^6\text{-toluene})]$  with  $(\text{tBuCP})_4$  as a dark red solid and isolated in 35% yield. Considering the short time necessary (<5 minutes) to form **8** from  $[(\text{IPr})_2\text{Ni}]$  and **1** in solution (much quicker than the known, ‘background’ dimerisation of **1**), we assume that coordinated  $(\text{tBuCP})_4$  is formed upon dimerisation of **1** at the Ni atom.

The molecular structure of **8** reveals that the  $(\text{tBuCP})_4$  ligand coordinates through two lone pairs of adjacent P atoms to a  $(\text{IPr})\text{Ni}$  fragment. As a consequence, the P1A–P2A bond is elongated (2.5821(7) Å) in comparison to the P2A–P3A bond (2.2506(8) Å, free  $(\text{tBuCP})_4$ : 2.219(1) and 2.236(1) Å).<sup>[14]</sup> The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **8**, showed an AA'XX' spin system at chemical shifts of –42.4 ppm and 102.1 ppm. The signal at high field is broad at room temperature and was resolved via variable temperature NMR at –20 °C (see the SI for spectra and simulation). The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of **8** are in line with the molecular structure in the solid state.

## COMMUNICATION



**Figure 5.** Formation of the ladderane complex **8** (top) and molecular structure of **8** in the solid state (bottom). Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and a minor disordered component (P1B-4B, C1B-4B) are omitted for clarity.

In summary, reactions of di-*tert*-butyldiphosphatetrahedrane (**1**) with Ni(I)- and Ni(0)-NHC complexes afford coordination compounds with unusual (*t*BuCP)<sub>*n*</sub> (*n* = 2, 4) frameworks. Dimerisation of **1** on the nickel atom is a notable feature observed in several of these reactions. Moreover, elimination of bis-*tert*-butylacetylene was observed from complex **5**, which has stimulated further, ongoing studies on the use of **1** as a source for P<sub>2</sub> fragments. It is noteworthy that complexes **2**–**4** and **8** cannot be obtained from reactions of the nickel precursors with *t*BuCP. Moreover, a comparison with the previously described reactivity of the same complexes with P<sub>4</sub> furthermore reveals the distinct reactivity of **1**. These promising results bode well for the future development of **1** and related phosphatetrahedranes as sources for a plethora of other previously inaccessible phosphoorganometallic molecules. Work in this direction is underway.

## Acknowledgements

Financial support by the Fonds der Chemischen Industrie (Kekulé Fellowship for G.H.) and the European Research Council (CoG 772299) is gratefully acknowledged. We thank Daniel Scott and Sebastian Bestgen for helpful comments on the manuscript.

**Keywords:** Phosphorus • nickel • phosphatetrahedranes • phosphoalkyne oligomers • bond activation

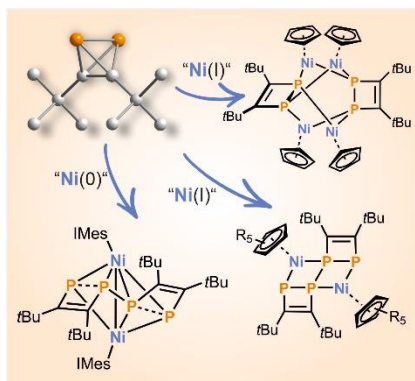
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## COMMUNICATION

## Entry for the Table of Contents



**Dimers of the dimer:** Reaction of  $(t\text{BuCP})_2$  with N-heterocyclic carbene nickel(I) and nickel(0) complexes result in P–C bond scission and the coupling of  $(t\text{BuCP})_2$  units. The resulting metal complexes feature uncommon phosphoorganic frameworks and an intriguing subsequent reactivity. These results illustrate that  $(t\text{BuCP})_2$  can be used as a building block for unusual phosphoorganometallic compounds.