

Phosphaorganic Frameworks

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

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In memory of François Mathey

Abstract: The first mixed phosphatetrahedranes were reported only recently and their reactivity is virtually unexplored. Herein, we present a reactivity study on di-*tert*-butyldiphosphatetrahedrane (**1**), which is the dimer of *tert*-butylphosphaalkyne. The (*t*BuCP)₂ tetrahedron is activated selectively by *N*-heterocyclic carbene (NHC) nickel(I) and nickel(0) complexes, resulting in novel complexes featuring diverse (*t*BuCP)_{*n*}-frameworks (*n* = 2, 4). Release of the (*t*BuCP)₄ framework from one of the complexes was achieved by addition of CO gas. Furthermore, **1** can be used as a source for P₂ units by elimination of di-*tert*-butylacetylene in the coordination sphere of nickel.

Tetrahedranes have long fascinated the chemical community due their simple structure and typically high reactivity.^[1] The first tetrahedral molecule to be prepared was white phosphorus, P₄, which was discovered as early as 1669, although its tetrahedral structure was recognised only in the early 20th century.^[2] P₄ is produced on a megaton scale each year and used as the common building block for incorporation of P atoms into organophosphorus compounds.^[3] The heavier homologue As₄ and the mixed interpnictogen compound AsP₃ are likewise accessible.^[4] Purely carbon-based tetrahedranes are also well-known, in line with the diagonal relationship between carbon and phosphorus in the periodic table.^[5] Indeed, the synthesis of (*t*BuC)₄ in 1978 was a pinnacle of organic synthesis.^[5]

In contrast, the first mixed C/P tetrahedranes were only reported last year. We showed that the “hybrid” of (*t*BuC)₄ and P₄, di-*tert*-butyldiphosphatetrahedrane (*t*BuCP)₂ (**1**), can be synthesised in a simple nickel-catalysed dimerisation reaction of *tert*-butylphosphaalkyne, *t*BuCP.^[6] Shortly after our report, the synthesis of the related tri-*tert*-butylphosphatetrahedrane (*t*BuC)₃P was published by Cummins and co-workers.^[7] Given the similar molecular structures and isolobal

relationship between **1** and P₄, a comparison of the reaction properties of both molecules is a tantalising prospect.^[5] Indeed, the activation of the P₄ 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.^[8] In one of our recent contributions to this area, we demonstrated the use of mononuclear cyclopentadienyl nickel(I) complexes [CpNi(NHC)] [NHC = IMes (1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene), IPr (1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene)]. Such “nickel(I) radicals” selectively break one P–P bond of P₄ to afford μ-η¹:η¹-bridging P₄²⁻ ligands with a “butterfly”-type structure (Figure 1, centre left).^[9] Subsequent studies demonstrated that P₄ activation by Ni⁰-NHC complexes affords unusual di- and trinuclear cluster compounds, including a *closo*-[(IPr)₃Ni₃P₈] cluster shown in Figure 1 (bottom left).^[10]

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 investiga-

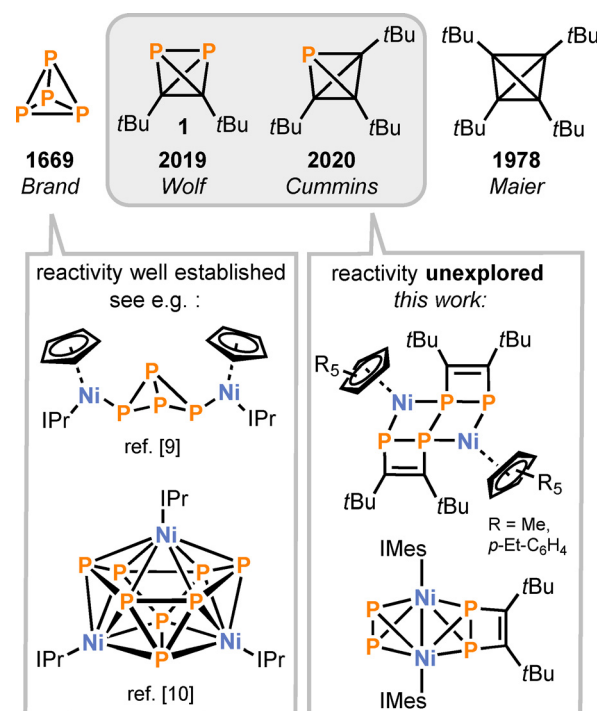


Figure 1. (Mixed) group 14/15 tetrahedranes and reactivity of P₄ with NHC-stabilised Ni^I metalloradicals and Ni⁰ complexes.^[9,10]

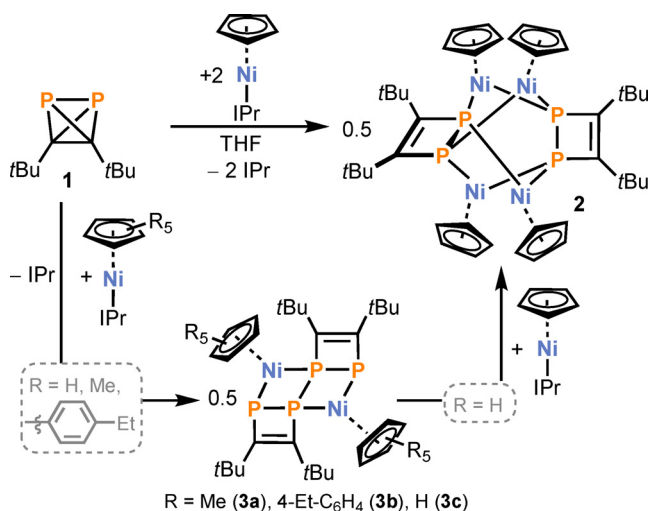
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tions have led to the preparation of polynuclear nickel complexes, which incorporate a variety of (*t*BuCP)_{*n*} (*n* = 2, 4) ligands in unusual coordination modes that are not known to be accessible using other synthetic precursors. We further discuss 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 P₄ and, indeed, also from those of *t*BuCP, the monomer of **1**.

This investigation commenced with the nickel(I) radical [CpNi(IPr)], which had previously been shown to react with white phosphorus under P–P bond scission (see Figure 1).^[9] Reaction of two equivalents of [CpNi(IPr)] with **1** in THF instantaneously afforded a deep red solution at room temperature (Scheme 1). Analysis of the crude reaction mixture by ¹H NMR spectroscopy revealed consumption of the paramagnetic starting material and release of IPr. A singlet



Scheme 1. Reactions of [Cp^RNi(IPr)] (R = H; Me, 4-Et-C₆H₄) with (*t*BuCP)₂.

resonance at 93.0 ppm was observed in the ³¹P{¹H} NMR spectrum. Crystals grown from toluene were characterised by single-crystal X-ray analysis (SCXRD) as the tetranuclear complex [(CpNi)₂(*t*Bu₂C₂P₂)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 [CpNi(IPr)] induces P–C bond cleavage to give a metalated 1,2-diphosphacyclobutene rather than forming the isomeric “butterfly” compound [(CpNi(IPr))₂(μ-κ²P-*t*Bu₂C₂P₂)] by P–P bond scission. Such a complex was observed with the valence isoelectronic P₄ molecule, see Figure 1.^[9] In agreement with this, DFT calculations of the hypothetical reaction of **1** with two equivalents of a radical (methyl radical or [CpNi(IPh)]) (Iph = 1,3-diphenylimidazolin-2-ylidene) 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 π-system in these examples.^[11] 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.^[12] The bond metric data is thus consistent with the presence of a dianionic (*t*Bu₂C₂P₂)²⁻ ligand, which coordinates in a μ⁴,η²:η²-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 ¹H NMR spectrum of **2** showed one signal for the *t*Bu groups (δ = 1.32 ppm) and one resonance for the cyclopentadienyl ligand (δ = 5.17 ppm). In the ¹³C-¹H NMR spectrum four resonances were observed, which are consistent with the presence of a Cp and a (*t*Bu₂C₂P₂)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 (Cp*) and pentaarylcyclopentadienyl (Cp^{BIG}) ligands (Scheme 1).^[13] As with the

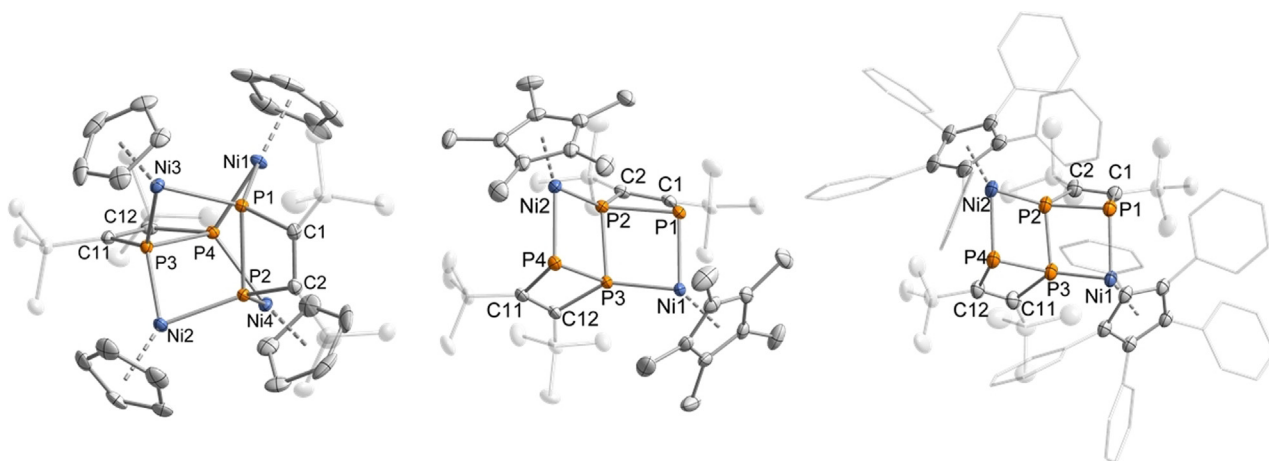


Figure 2. Molecular structures of **2** (left), **3a** (middle) and **3b** (right) in the solid state.^[19] Thermal ellipsoids are set at 50% probability level. For **2**, only one molecule of the asymmetric unit is shown. Hydrogen atoms, solvent molecules, disorder in the aryl rings, and *p*-Et groups of **3b** are omitted for clarity.

previous reaction, deep red solutions were obtained when a 1:2 stoichiometry was used. However, analysis by ^1H NMR spectroscopy revealed broad resonances corresponding to unconsumed paramagnetic starting material, which disappeared upon addition of another equivalent of **1**.

Single-crystal X-ray diffraction studies revealed the formation of dinuclear species $[(\text{Cp}^R\text{Ni})_2(\text{tBu}_4\text{C}_4\text{P}_4)]$ [$\text{Cp}^R = \text{Cp}^*$ (**3a**), Cp^{BIG} (**3b**)], where two molecules of **1** have formally undergone radical coupling to produce a $\text{tBu}_4\text{C}_4\text{P}_4$ 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**.^[6,14] 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% yield (**3b**) as dark-red, crystalline solids. Single-crystal X-ray diffraction revealed a three-rung ladder structure composed of two Ni and four P atoms, 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 reveals the expected signal sets for the cyclopentadienyl ligands and two singlets for the *t*Bu groups. The $^{31}\text{P}\{^1\text{H}\}$ 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 $^1J_{\text{PP}}$ coupling constants and small $^2J_{\text{PP}}$ 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 nm (**3b**).

Considering these first insights into the reaction of **1** with $[\text{CpNi}(\text{IPr})]$ 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 $[\text{CpNi}(\text{IPr})]$. Two pseudo-triplet resonances at –72.5 and 22.1 ppm were observed in the $^{31}\text{P}\{^1\text{H}\}$ 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 $[(\text{CpNi})_2(\text{tBu}_4\text{C}_4\text{P}_4)_2]$ (**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 $[\text{CpNi}(\text{IPr})]$ even when heated to temperatures of 70 °C. The sluggish reactivity of **3a** toward $[\text{CpNi}(\text{IPr})]$ 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 $[(\text{IMes})_2\text{Ni}]$ and $[(\text{IPr})\text{Ni}(\eta^6\text{-toluene})]$.^[15] The reactions of these complexes with P_4 afforded Wade Clusters, as reported previously.^[10] The reaction of **1** with $[(\text{IMes})_2\text{Ni}]$ at –80 °C afforded a brown reaction solution. Analysis by $^{31}\text{P}\{^1\text{H}\}$ 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 $(\text{tBu}_4\text{C}_4\text{P}_4)$ framework in compounds **3a/b**. An X-ray diffraction experiment confirmed the presence of $[(\text{IMes})\text{Ni}]_2(\text{tBu}_4\text{C}_4\text{P}_4)$ (**4**), a dinuclear complex featuring a Ni–Ni bond and a $(\text{tBu}_4\text{C}_4\text{P}_4)$ 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 **3a/b** (2.2445(7) Å). The Ni1–Ni2 bond length of 2.4293(4) Å compares well to other nickel(I) dimers (e.g. $[(\text{IPr})\text{Ni}]_2(\mu\text{-Cp})(\mu\text{-Cl})$; 2.4015(3) Å).^[16]

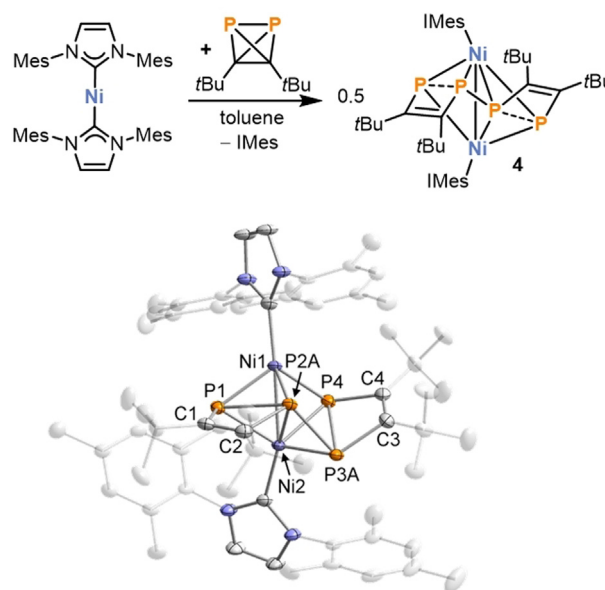
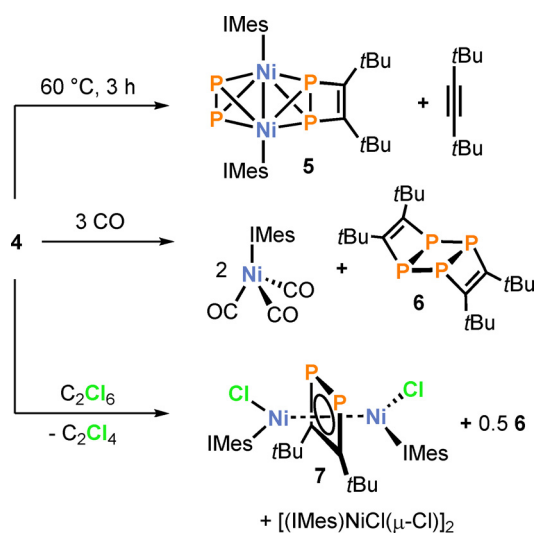


Figure 3. Dimerisation of **1** in the coordination sphere of $[(\text{IMes})_2\text{Ni}]$ (top) and molecular structure of **4** in the solid state (bottom).^[19] Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and solvent molecules and a minor disordered component (P2B and P3B) are omitted for clarity.

The bonding situation of the truncated model complex **4'** $[(\text{IPh})\text{Ni}]_2(\text{P}_4\text{C}_4\text{tBu}_4)$ 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 .^[10] 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 $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are in agreement with the structure determined by SCXRD, showing the expected signal sets for the IMes ligand and the $(\text{tBu}_4\text{C}_4\text{P}_4)$ moiety. The $^{31}\text{P}\{^1\text{H}\}$ 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).

Upon storage of solutions of **4** in C₆D₆ at room temperature overnight, **4** was partially converted into a new compound according to ¹H and ³¹P{¹H} NMR spectroscopy (Scheme 2, top). Heating a mixture of **1** and [(IMes)₂Ni] to



Scheme 2. Reactivity of **4** upon heating and addition of CO and hexachloroethane.

60 °C for three hours resulted in selective formation of this new species, which is characterised by two multiplet resonances in the ³¹P{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(P₂)-(tBu₂C₂P₂)]-IMes (**5**-IMes, Figure 4). The formation of **5** involves the elimination of di-*tert*-butylacetylene, which was identified by the ¹³C{¹H} NMR resonance of the alkyne carbon atom detected at a chemical shift of 87.5 ppm. A related example of *t*BuC≡C*t*Bu elimination from a metal complex was recently reported by our group from a ruthenium

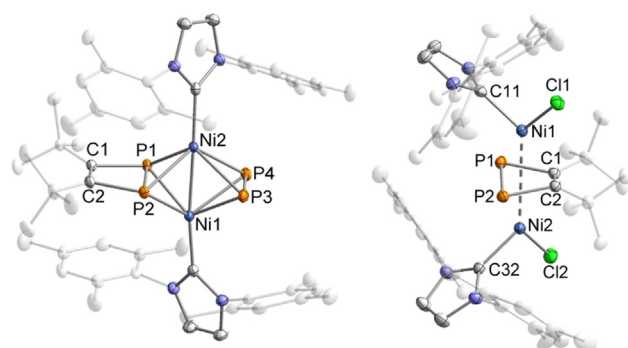


Figure 4. Molecular structures of **5** and **7** in the solid state.^[19] Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and one molecule of IMes (co-crystallising with **5**) are omitted for clarity.

complex,^[17] but in contrast to that example, where the alkyne remains as η²-bound ligand in the coordination sphere of ruthenium, di-*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 P₂ units.

Conveniently, dark brown crystals of **5** were isolated in 50% yield directly starting from [(IMes)₂Ni] 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 μ-η²:η²-P₂ dumbbell and a μ-η²:η²-(*t*Bu₂C₂P₂)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 P₂ ligand (2.0294(5) Å) is comparable to other complexes with a Ni₂P₂ core such as [(IMesNi(CO))₂(μ-η²:η²-P₂)] (2.076(2) Å).^[18] The ³¹P{¹H} NMR spectrum of isolated **5** is identical to the species obtained from **4** (see above). The ¹H NMR and ¹³C{¹H} NMR spectra are in agreement with the proposed molecular structure of **5**.

Further reactivity studies were conducted with complex **4** in order to examine the possible release and functionalisation of the *t*Bu₄C₄P₄ framework. Treatment of a solution of **4** in C₆D₆ with carbon monoxide (1 bar) results in an instantaneous colour change of the solution from brown to pale beige and formation of [(IMes)Ni(CO)₃] and the known phosphalkyne tetramer (*t*BuCP)₄ (**6**, Scheme 2) as corroborated by ¹H and ³¹P{¹H} NMR spectroscopy (see SI for spectra).^[14] Moreover, the addition of hexachloroethane affords **6** and the chlorinated inverted sandwich complex [(IMes)NiCl]₂(μ-*t*Bu₂C₂P₂) (**7**) as revealed by single-crystal X-ray crystallography (Figure 4). Complex **7** contains a 1,2-diphosphacyclobutadiene ligand in an unusual μ,η⁴:η⁴-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 [(IMes)NiCl(μ-Cl)]₂ could not be separated due to similar solubilities. However, we were able to crystallise [(IMes)NiCl(μ-Cl)]₂ from the reaction mixture as violet blocks (see SI for SCXRD data).

In an attempt to evaluate the influence of the steric bulk of the NHC ligand, the related, bulkier [(IPr)₂Ni] was reacted with one equivalent of **1** (Figure 5). However, ³¹P{¹H} NMR spectroscopy suggested the formation of a different product with multiplet resonances (see below). A similar spectrum was obtained when [(IPr)Ni(η⁶-toluene)] was reacted with **1** (see SI for spectra). Single-crystal XRD on a crystal obtained from toluene revealed the formation of [(IPr)Ni(*t*Bu₄C₄P₄)] (**8**), that is, a mononuclear complex of the phosphalkyne tetramer **6** (Figure 5).^[14] The chemistry of the phosphalkyne tetramer **6** 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 [(IPr)Ni(η⁶-toluene)] with **6** as a dark red solid and isolated in 35% yield. Considering the short time necessary (< 5 minutes) to form **8** from [(IPr)₂Ni] and **1** in solution (much quicker than the known, “background” dimerisation of **1**), we assume that coordinated **6** is formed upon dimerisation of **1** at the Ni atom.

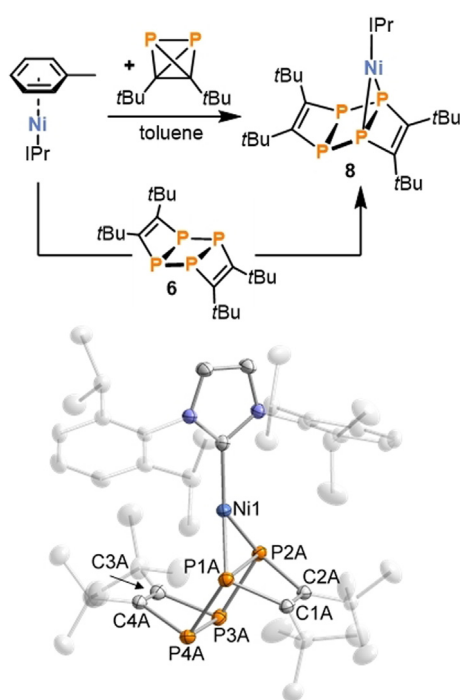


Figure 5. Formation of the ladderane complex **8** (top) and molecular structure of **8** in the solid state (bottom).^[9] Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and a minor disordered component (P1B-4B, C1B-4B) are omitted for clarity.

The molecular structure of **8** reveals that the (*t*BuCP)₄ ligand coordinates through two lone pairs of adjacent P atoms to a (IPr)Ni fragment. As a consequence, the P1A–P2A bond is elongated (2.5821(7) Å) in comparison to the P3A–P4A bond (2.2020(8) Å, free **6**: 2.219(1) and 2.236(1) Å).^[14] The ³¹P{¹H} 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 by variable-temperature NMR at –20 °C (see the SI for spectra and simulation). The ¹H and ¹³C{¹H} NMR spectra of **8** are in line with the molecular structure in the solid state.

In summary, reactions of di-*tert*-butyldiphosphatetrahydropyridane (**1**) with Ni^I–NHC and Ni⁰–NHC complexes afford coordination compounds with unusual (*t*BuCP)_{*n*} (*n* = 2, 4) frameworks. Dimerisation of **1** on the nickel atom is a notable feature observed in several of these reactions. Moreover, elimination of di-*tert*-butylacetylene was observed from complex **5**, which has stimulated further, ongoing studies on the use of **1** as a source for P₂ 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 P₄ furthermore reveals the distinct reactivity of **1**. These promising results bode well for the future development of **1** and related phosphatetrahydropyridanes as sources for a plethora of other previously inaccessible phosphoorganometallic molecules. Work in this direction is underway.

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Conflict of interest

The authors declare no conflict of interest.

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- [1] G. Maier, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 309–332; *Angew. Chem.* **1988**, *100*, 317–341.
- [2] O. Reinmuth, *J. Chem. Educ.* **1928**, *5*, 1473.
- [3] D. E. C. Corbridge, *Phosphorus 2000. Chemistry, Biochemistry and Technology*, Elsevier, Amsterdam, **2000**.
- [4] a) B. M. Cossairt, M.-C. Diawara, C. C. Cummins, *Science* **2009**, *323*, 602; b) M. Seidl, G. Balázs, M. Scheer, *Chem. Rev.* **2019**, *119*, 8406–8434.
- [5] A. R. Jupp, J. C. Slootweg, *Angew. Chem. Int. Ed.* **2020**, *59*, 10698–10700; *Angew. Chem.* **2020**, *132*, 10786–10788.
- [6] G. Hierlmeier, P. Coburger, M. Bodensteiner, R. Wolf, *Angew. Chem. Int. Ed.* **2019**, *58*, 16918–16922; *Angew. Chem.* **2019**, *131*, 17074–17078.
- [7] M.-L. Y. Riu, R. L. Jones, W. J. Transue, P. Müller, C. C. Cummins, *Sci. Adv.* **2020**, *6*, eaaz3168.
- [8] a) B. M. Cossairt, N. A. Piro, C. C. Cummins, *Chem. Rev.* **2010**, *110*, 4164–4177; b) M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, *Chem. Rev.* **2010**, *110*, 4178–4235; c) M. Scheer, G. Balázs, A. Seitz, *Chem. Rev.* **2010**, *110*, 4236–4256.
- [9] S. Pelties, D. Herrmann, B. de Bruin, F. Hartl, R. Wolf, *Chem. Commun.* **2014**, *50*, 7014–7016.
- [10] G. Hierlmeier, P. Coburger, N. P. van Leest, B. de Bruin, R. Wolf, *Angew. Chem. Int. Ed.* **2020**, *59*, 14148–14153; *Angew. Chem.* **2020**, *132*, 14252–14257.
- [11] a) A. Chirila, R. Wolf, J. Chris Slootweg, K. Lammertsma, *Coord. Chem. Rev.* **2014**, *270–271*, 57–74; b) C. Jones, J. A. Platts, A. F. Richards, *Chem. Commun.* **2001**, 663–664; c) S. Deng, C. Schwarzmaier, M. Zabel, J. F. Nixon, M. Bodensteiner, E. V. Peresypkina, G. Balázs, M. Scheer, *Eur. J. Inorg. Chem.* **2011**, 2991–3001; d) A. D. Burrows, A. Dransfeld, M. Green, J. C. Jeffery, C. Jones, J. M. Lynam, M. T. Nguyen, *Angew. Chem. Int. Ed.* **2001**, *40*, 3221–3224; *Angew. Chem.* **2001**, *113*, 3321–3324; e) F. W. Heinemann, S. Kummer, U. Seiss-Brandl, U. Zenneck, *Organometallics* **1999**, *18*, 2021–2029; f) C. Jones, C. Schulten, A. Stasch, *Dalton Trans.* **2006**, 3733–3735; g) P. Binger, G. Glaser, S. Albus, C. Krüger, *Chem. Ber.* **1995**, *128*, 1261–1265; h) E.-M. Rummel, G. Balázs, V. Heintz, M. Scheer, *Angew. Chem. Int. Ed.* **2017**, *56*, 9592–9596; *Angew. Chem.* **2017**, *129*, 9720–9725.
- [12] a) B. Cordero, V. Gómez, A. E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán, S. Alvarez, *Dalton Trans.* **2008**, 2832–2838; b) P. Pykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 186–197; c) P. Pykkö, *J. Phys. Chem. A* **2015**, *119*, 2326–2337.
- [13] U. Chakraborty, F. Urban, B. Mühlendorf, C. Rebreyend, B. de Bruin, N. van Velzen, S. Harder, R. Wolf, *Organometallics* **2016**, *35*, 1624–1631.

- [14] B. Geissler, S. Barth, U. Bergsträsser, M. Slany, J. Durkin, P. B. Hitchcock, M. Hofmann, P. Binger, J. F. Nixon, P. von Ragué Schleyer, M. Regitz, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 484–487; *Angew. Chem.* **1995**, *107*, 485–488.
- [15] a) Y. Hoshimoto, Y. Hayashi, H. Suzuki, M. Ohashi, S. Ogoshi, *Organometallics* **2014**, *33*, 1276–1282; b) A. J. Arduengo III, S. F. Gamper, J. C. Calabrese, F. Davidson, *J. Am. Chem. Soc.* **1994**, *116*, 4391–4394.
- [16] a) J. Wu, A. Nova, D. Balcells, G. W. Brudvig, W. Dai, L. M. Guard, N. Hazari, P.-H. Lin, R. Pokhrel, M. K. Takase, *Chem. Eur. J.* **2014**, *20*, 5327–5337; b) C.-Y. Lin, P. P. Power, *Chem. Soc. Rev.* **2017**, *46*, 5347–5399.
- [17] C. Rödl, R. Wolf, *Chem. Eur. J.* **2019**, *25*, 8332–8343.
- [18] G. Hierlmeier, A. Hinz, R. Wolf, J. M. Goicoechea, *Angew. Chem. Int. Ed.* **2018**, *57*, 431–436; *Angew. Chem.* **2018**, *130*, 439–444.
- [19] Deposition Numbers 2043979 (**2**), 2043974 (**3a**), 2043977 (**3b**), 2043978 (**4**), 2043975 (**5**), 2043976 (**7**), 2043980 (**8**), and 2043981 ($[(\text{IMes})\text{Ni}(\text{Cl})(\mu\text{-Cl})_2]_2$) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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