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 (tBuCP)₂ tetrahedron is activated selectively by N-heterocyclic carbene (NHC) nickel(I) and nickel(0) complexes, resulting in novel complexes featuring diverse (tBuCP)$_n$-frameworks (n = 2, 4). Release of the (tBuCP)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, P_4, which was discovered as early as 1669, although its tetrahedral structure was recognised only in the early 20th century.[2] 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.[3] The heavier homologue As_4 and the mixed interpnictogen compound AsP_3 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 P_4, 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)$_3$P was published by Cummins and co-workers.[7] Given the similar molecular structures and isolobal

relationship between **1** and P_4, a comparison of the reaction properties of both molecules is a tantalising prospect.[5] Indeed, the activation of the 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.[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 P_4 to afford μ-η^1:η^1-bridging P_4^{2-} ligands with a "butterfly"-type structure (Figure 1, centre left).[9] Subsequent studies demonstrated that P_4 activation by Ni^0–NHC complexes affords unusual di- and trinuclear cluster compounds, including a *closo*-[(IPr)$_3$Ni$_3$P$_8$] 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-
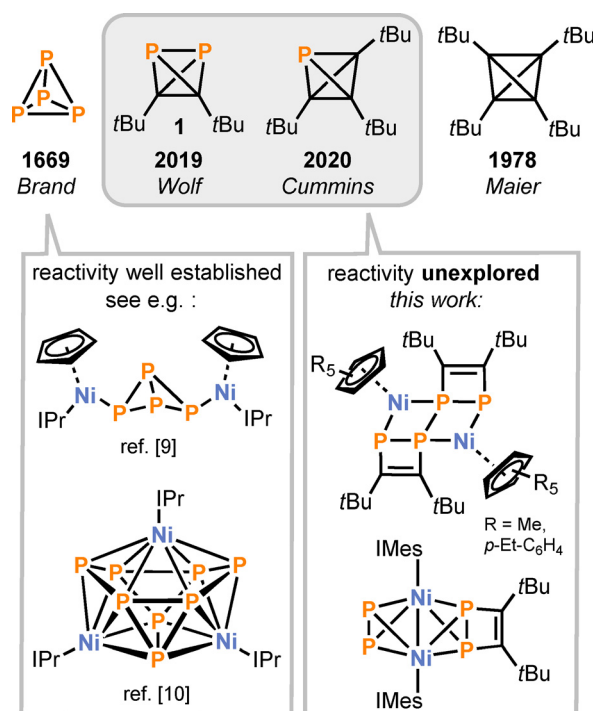
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Figure 1. (Mixed) group 14/15 tetrahedranes and reactivity of P_4 with NHC-stabilised Ni^I metalloradicals and Ni^0 complexes.[9, 10]

tions have led to the preparation of polynuclear nickel complexes, which incorporate a variety of $(tBuCP)_n$ $(n = 2, 4)$ 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 P_4 and, indeed, also from those of $tBuCP$, 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
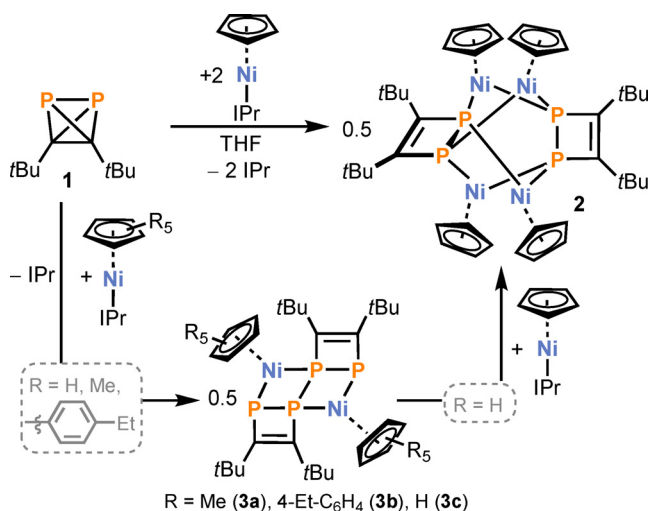
resonance at 93.0 ppm was observed in the $^{31}P\{^1H\}$ NMR spectrum. Crystals grown from toluene were characterised by single-crystal X-ray analysis (SCXRD) as the tetranuclear complex $[(CpNi)_2(tBu_2C_2P_2)]_2$ (**2**, Figure 2, left) containing two 1,2-diphosphacyclobutene-1,2-diide ligands coordinated by four (CpNi) units in a realgar-type fashion. Notably, the reaction with [CpNi(IPr)] induces P−C bond cleavage to give a metalated 1,2-diphosphacyclobutene rather than forming the isomeric "butterfly" compound $[\{CpNi(IPr)\}_2(\mu\text{-}\kappa^2P\text{-}tBu_2C_2P_2)]$ by P−P bond scission. Such a complex was observed with the valence isoelectronic P_4 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 $(tBu_2C_2P_2)^{2-}$ 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 ^1H NMR spectrum of **2** showed one signal for the tBu groups ($\delta = 1.32$ ppm) and one resonance for the cyclopentadienyl ligand ($\delta = 5.17$ ppm). In the $^{13}C\{^1H\}$ NMR spectrum four resonances were observed, which are consistent with the presence of a Cp and a $(tBu_2C_2P_2)^{2-}$ 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 (Cp*) and pentaarylcyclopentadienyl (Cp^{BIG}) ligands (Scheme 1).[13] As with the

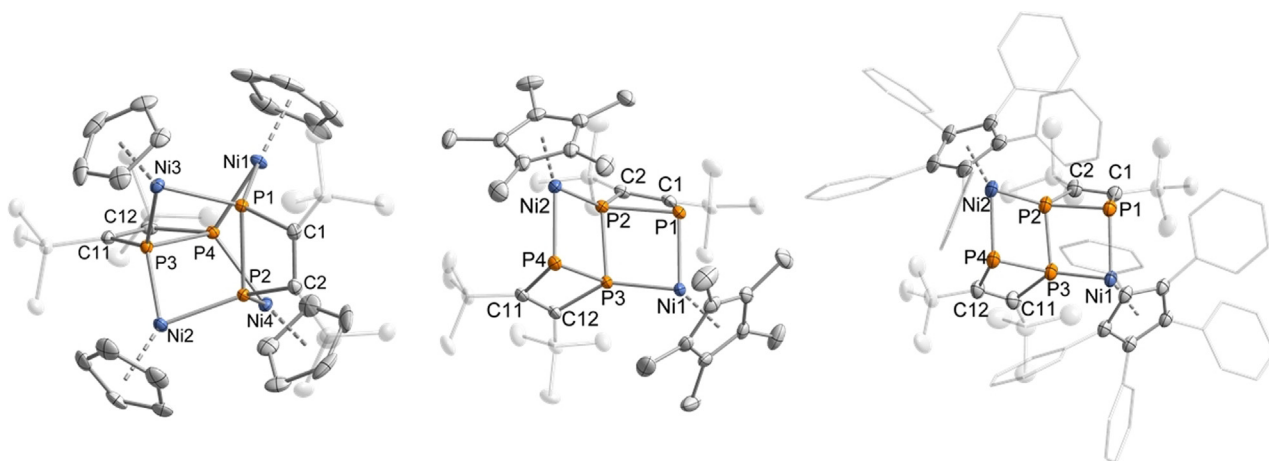**Scheme 1.** Reactions of [Cp^{R}Ni(IPr)] (R = H; Me, 4-Et-C$_6$H$_4$) with $(tBuCP)_2$.

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 ^{1}H 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 $[(Cp^RNi)_2(tBu_4C_4P_4)]$ $[Cp^R = Cp^*$ (**3a**), Cp^{BIG} (**3b**)], where two molecules of **1** have formally undergone radical coupling to produce a $tBu_4C_4P_4$ moiety (Scheme 1, bottom). Notably, however, compounds **2** and **3** were not formed upon reaction of the nickel complexes with the known ladderane-type phosphaalkyne tetramer $(tBuCP)_4$ (**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 ^{1}H NMR spectroscopy reveals the expected signal sets for the cyclopentadienyl ligands and two singlets for the tBu groups. The ^{31}P{^{1}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 $^1J_{PP}$ 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 nm (**3b**).

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 realgartype 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{^{1}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 $[(CpNi)_2(tBu_4C_4P_4)_2]$ (**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 $[(IPr)Ni(\eta^6\text{-toluene})]$.[15] The reactions of these complexes with P_4 afforded Wade Clusters, as reported previously.[10] The reaction of **1** with $[(IMes)_2Ni]$ at −80°C afforded a brown reaction solution. Analysis by ^{31}P{^{1}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 $(tBu_4C_4P_4)$ framework in compounds **3a/b**. An X-ray diffraction experiment confirmed the presence of $[\{(IMes)Ni\}_2(tBu_4C_4P_4)]$ (**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 **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. $[\{(IPr)Ni\}_2(\mu\text{-Cp})(\mu\text{-Cl})]$: 2.4015(3) Å).[16]

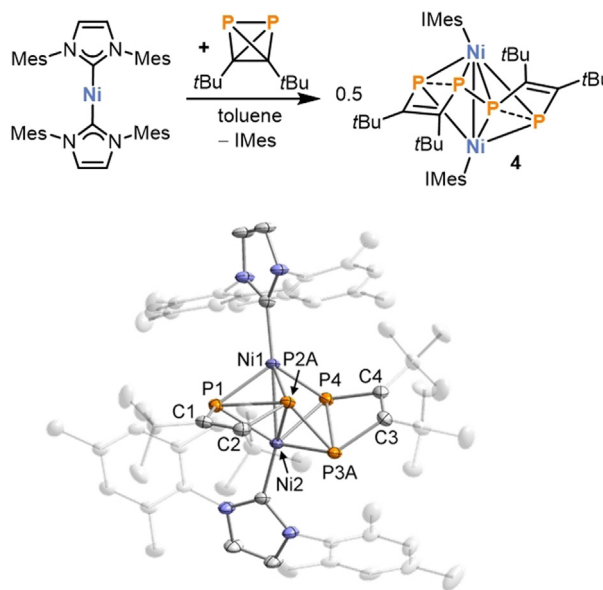***Figure 3.*** Dimerisation of **1** in the coordination sphere of $[(IMes)_2Ni]$ (top) and molecular structure of **4** in the solid state (bottom).[19] Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and solvent molecules and a minor disordered component (P2B and P3B) are omitted for clarity.

The bonding situation of the truncated model complex **4′** $[\{(IPh)Ni\}_2(P_4C_4tBu_4)]$ 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 ^{1}H and ^{13}C{^{1}H} 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{^{1}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 C_6D_6 at room temperature overnight, **4** was partially converted into a new compound according to ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 2, top). Heating a mixture of **1** and [(IMes)$_2$Ni] to
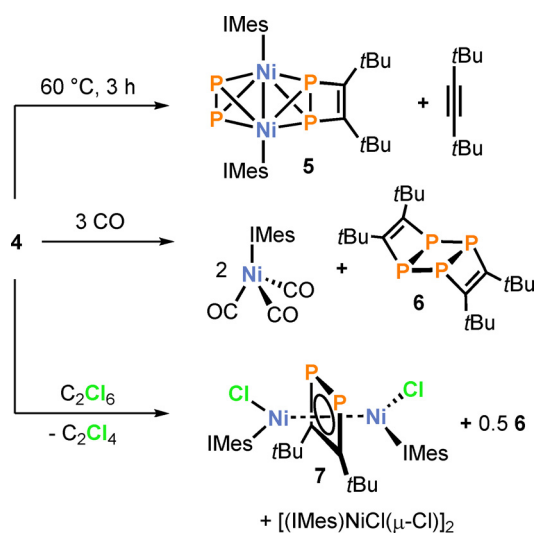
Scheme 2. Reactivity of **4** upon heating and addition of CO and hexachloroethane.

60 °C for three hours resulted in selective formation of this new species, which is characterised by two multiplet resonances in the $^{31}P\{^1H\}$ 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$_2$)-($tBu_2C_2P_2$)]·IMes (**5**·IMes, Figure 4). The formation of **5** involves the elimination of di-*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
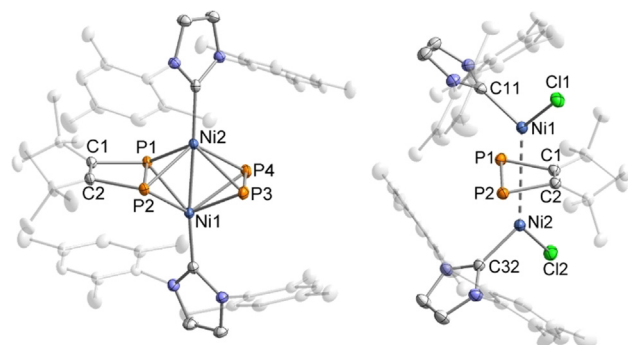
Figure 4. Molecular structures of **5** and **7** in the solid state.[19] Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and one molecule of IMes (co-crystallising with **5**) are omitted for clarity.

complex,[17] but in contrast to that example, where the alkyne remains as η^2-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 P_2 units.

Conveniently, dark brown crystals of **5** were isolated in 50% yield directly starting from [(IMes)$_2$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 μ-η^2:η^2-P_2 dumbbell and a μ-η^2:η^2-($tBu_2C_2P_2$)$^{2-}$ 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 P_2 ligand (2.0294(5) Å) is comparable to other complexes with a Ni_2P_2 core such as [{(IMes)Ni(CO)}$_2$(μ-η^2:η^2-P_2)] (2.076(2) Å).[18] The $^{31}P\{^1H\}$ NMR spectrum of isolated **5** is identical to the species obtained from **4** (see above). The ^1H NMR and $^{13}C\{^1H\}$ 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 $tBu_4C_4P_4$ framework. Treatment of a solution of **4** in C_6D_6 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 phosphaalkyne tetramer ($tBuCP$)$_4$ (**6**, Scheme 2) as corroborated by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy (see SI for spectra).[14] Moreover, the addition of hexachloroethane affords **6** and the chlorinated inverted sandwich complex [{(IMes)NiCl}$_2$(μ-$tBu_2C_2P_2$)] (**7**) as revealed by single-crystal X-ray crystallography (Figure 4). Complex **7** contains a 1,2-diphosphacyclobutadiene ligand in an unusual μ,η^4:η^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 [(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)$_2$Ni] was reacted with one equivalent of **1** (Figure 5). However, $^{31}P\{^1H\}$ NMR spectroscopy suggested the formation of a different product with multiplet resonances (see below). A similar spectrum was obtained when [(IPr)Ni(η^6-toluene)] was reacted with **1** (see SI for spectra). Single-crystal XRD on a crystal obtained from toluene revealed the formation of [(IPr)Ni-($tBu_4C_4P_4$)] (**8**), that is, a mononuclear complex of the phosphaalkyne tetramer **6** (Figure 5).[14] The chemistry of the phosphaalkyne 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(η^6-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)$_2$Ni] 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.
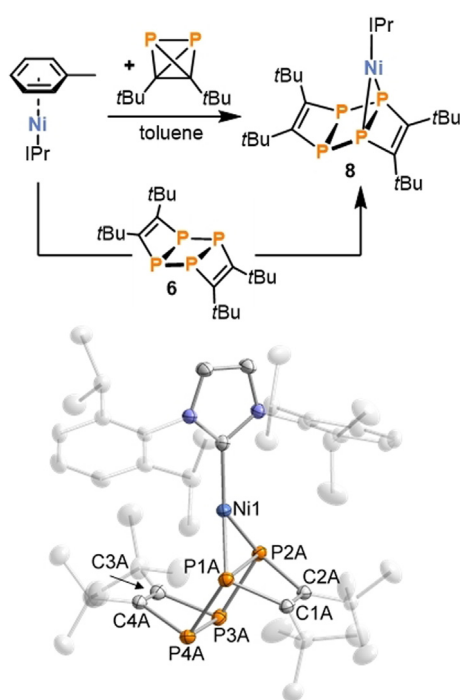
Figure 5. Formation of the ladderane complex **8** (top) and molecular structure of **8** in the solid state (bottom).[19] Thermal ellipsoids are set at 50% probability level. Hydrogen atoms and a minor disordered component (P1B-4B, C1B-4B) are omitted for clarity.

The molecular structure of **8** reveals that the $(tBuCP)_4$ 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 ^{31}P{^{1}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 by variable-temperature NMR at −20 °C (see the SI for spectra and simulation). The ^{1}H and ^{13}C{^{1}H} NMR spectra of **8** are in line with the molecular structure in the solid state.

In summary, reactions of di-*tert*-butyldiphosphatetrahedrane (**1**) with Ni^I–NHC and Ni^0–NHC complexes afford coordination compounds with unusual $(tBuCP)_n$ ($n = 2, 4$) 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 P$_2$ 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$_4$ 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 phosphaorganometallic molecules. Work in this direction is underway.

Conflict of interest

The authors declare no conflict of interest.

Keywords: bond activation · nickel · phosphaalkyne oligomers · phosphatetrahedranes · phosphorus

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