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A Homoleptic Diphosphatetrahedrane Nickel(0) Complex

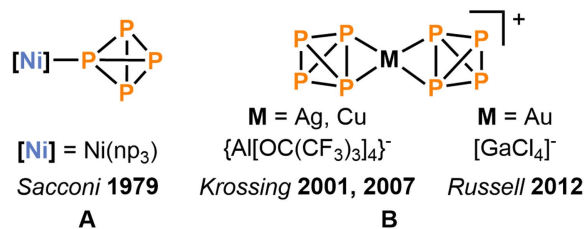
Maria K. Uttendorfer,^[a] Gabriele Hierlmeier,^[a, b] and Robert Wolf^{*[a]}Dedicated to Professor Cameron Jones on the occasion of his 60th birthday

The stable diphosphatetrahedrane, (tBuCP)₂, was isolated only recently, and its coordination chemistry has been little explored so far. Herein we report the synthesis of [Ni{η²-(tBuCP)₂}₃] (1) by CO substitution of Ni(CO)₄ with (tBuCP)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 behavior of (tBuCP)₂ is compared to the isoelectronic P₄ molecule, which scarcely forms complexes of intact P₄ tetrahedra.

In 1970 *Ginsberg* and *Lindsell* reported the first transition metal complexes of white phosphorus (P₄) [RhCl₂(η²-P₄)] (L=PPh₃, P(*p*-Tol)₃, P(*m*-Tol)₃, AsPh₃; Tol=C₇H₈).^[1] Since then, a wide variety of coordination compounds have resulted from coordination studies of P₄.^[2] These complexes often contain reduced polyphosphide units resulting from a formal electron transfer from the metal atom to P₄. 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 to this, the number of transition metal complexes featuring an intact, neutral P₄ tetrahedron has remained limited.

Figure 1a shows the structure of [(np₃)Ni(η¹-P₄)] (A, np₃ = tris(2-diphenylphosphinoethyl)amine) reported by *Sacconi* and co-workers in 1979, the first structurally characterized transition metal complex in which the P₄ moiety coordinates end-on via a single phosphorus atom.^[4] Further examples for this end-on coordination mode have been reported for a variety of transition metals such as Fe, Ru, Os, Mn, and W.^[5] In addition, several complexes with intact, side-on coordinated P₄ molecules have been reported.^[3c,6] Such complexes are typically stabilized

a) Coordination of P₄ tetrahedra

b) Coordination of intact phosphatetrahedrane moieties

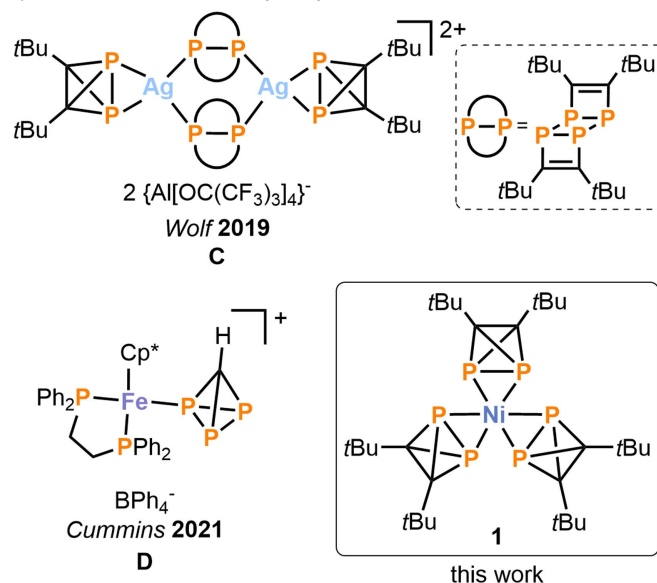


Figure 1. a) Selected examples of complexes featuring P₄ tetrahedra,^[3c,4,6a,b] b) coordination of intact phosphatetrahedranes.^[7,9]

by different ancillary ligands, while the coinage metal complexes [M(P₄)₂]X (B; M=Cu, Ag, X = Al{OC(CF₃)₃}₄⁻; M=Au, X = GaCl₄⁻) displayed in Figure 1a are the only isolated homoleptic P₄ complexes to the best of our knowledge.^[3c,6a,b,d] These rare homoleptic complexes are stabilized by weakly coordinating anions. The coordinated P–P bonds are only slightly elongated

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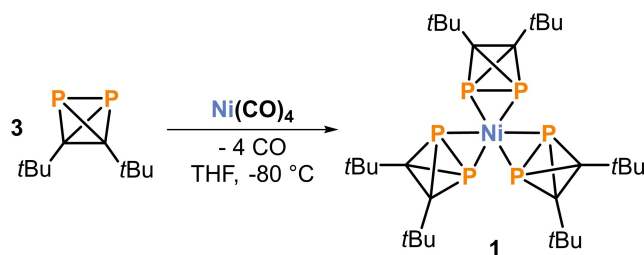
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by 0.10 to 0.20 Å with respect to those in the free P_4 molecule, indicating the presence of intact P_4 tetrahedra.

Phosphatetrahedranes comprised of phosphorus and carbon atoms were isolated only recently. We synthesized di-*tert*-butyldiphosphatetrahedrane ($tBuCP)_2$,^[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 behavior of $(tBuCP)_2$ have revealed that this species easily undergoes P–C bond cleavage upon coordination to transition metal centers. Thus, reactions with anionic metalates of Fe and Co afforded η^4 -coordinated diphosphacyclobutadiene complexes.^[10a] Similar diphosphacyclobutenediide ligands were formed when reacting $(tBuCP)_2$ with Ni(0) and Ni(II) 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 characterized so far. The silver complex $[Ag(\eta^2-tBuCP)_2(\eta^2-tBuCP)_4]_2[Al\{OC(CF_3)_3\}_4]_2$ (C, Figure 1b) was obtained by reacting $(tBuCP)_2$ with $[Ag(CH_2Cl)_2\{Al\{OC(CF_3)_3\}_4\}]$.^[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 $[Cp^*Fe(dppe)(\eta^1-HCP_3)][BPh_4]$ (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.

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 behavior of related low-coordinate organophosphorus compounds such as phosphalkynes 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-stabilized Ni(0) complexes, we studied its reaction towards the highly reactive tetracarbonyl nickel(0) complex $Ni(CO)_4$. Herein we report the isolation and characterization of $[Ni\{\eta^2-(tBuCP)_2\}_3]$ (**1**), which features three intact di-*tert*-butyldiphosphatetrahedrane moieties that coordinate to the Ni(0) core.

The reaction of three equivalents of di-*tert*-butyldiphosphatetrahedrane with $Ni(CO)_4$ (Scheme 1) was performed in toluene at $-80^\circ C$ under exclusion of light to prevent the light-mediated dimerization of $(tBuCP)_2$. After warming to $0^\circ C$ 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 $\delta = -337.7$ ppm (see Figures S4 and S5, SI). In addition, signals for $(tBuCP)_2$ ($\delta = -469.0$ ppm) and the ladder-type compound $(tBuCP)_4$ ($\delta = -23.4$ ppm) were observed. After work-up and crystallization 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-



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

centrosymmetric molecular structure with the presence of two formula units of **1** per unit cell.

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 crystallizes 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

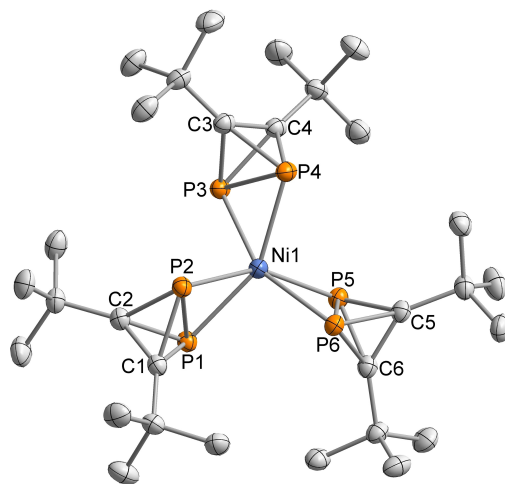


Figure 2. Solid-state molecular structure of $[Ni\{\eta^2-(tBuCP)_2\}_3]$ (**1**). Displacement ellipsoids are drawn at the 50% probability level; H-atoms have been omitted for clarity; selected bond lengths [Å] and angles [°]: Ni1–P1 2.3082(4), Ni1–P2 2.3005(4), Ni1–P3 2.2962(4), Ni1–P4 2.3035(4), Ni1–P5 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).

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-characterized diphosphatetrahdane complex [(Ag(η²-tBuCP)₂(η²-tBuCP)₄][Al{OC(CF₃)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 μ₂η²-P₂ moiety or a side-on coordinated μ₂η²-P₄ unit, e.g. 2.2354(7) to 2.2648(8) Å in [Ni₂(tPr₂Im)₄(μ₂η²-P₂)],^[14] 2.241(1) to 2.250(1) Å in ((μ²:η²,η²-P₂)[Ni(IMes)(CO)]₂),^[15] 2.255(4) to 2.277(2) Å in [(Dippnacnac)Si(μ₂η²-P₄)Ni(nacnac)],^[16] and 2.2657(6) to 2.2923(8) Å in [(IPr)Ni{(μ₂η²-P₄)Si(Dippnacnac)}₂] (tPr₂Im = 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, Dippnacnac = CH[C(Me)N(Dipp)][C(CH₃)N(Dipp)], Dipp = 2,6-di-*iso*-propylphenyl, IPr = 1,3-bis(2,6-di-*iso*-propylphenyl)imidazolin-2-ylidene).^[17]

The Ni complex **1** was isolated in 23% yield as an indigo-colored solid. The relatively low yield can likely be attributed to the thermal instability of **1** at room temperature. **1** is characterized by a ³¹P{¹H} NMR singlet at –338.4 ppm, which is significantly shifted to low field in comparison to the resonance of free diphosphatetrahdane (tBuCP)₂ (δ(³¹P) = –468.2 ppm). The low-field shift is far less pronounced for the Ag complex **C** (δ(³¹P) = –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 ¹³C{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 ³¹P 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 color 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 (tBuCP)₂ and its dimerization product, the ladderane (tBuCP)₄, according to ³¹P{¹H} NMR monitoring.^[7] The reaction proceeds without formation of side products as NMR spectra of the crude reaction

mixture illustrate (see Figures S4 and S5 in the SI), yet 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 analyzed by calculating intrinsic bond orbitals (IBOs) on the BP86/def2-TZVP level of theory.^[18] Three filled orbitals forming 3-center-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 NiP₂ moieties; these orbitals and further relevant IBOs are displayed in Figure S7, SI). Such 3-center-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-center-2-electron bonds between Ni1/C1/C2, Ni1/C3/C4 and Ni1/C5/C6 (see Figure S8 in the SI for a graphical representation of these orbitals). Similarly, the binding mode of η²-coordinated intact P₄ tetrahedra is analogous to the Dewar-Chatt-Duncanson model.^[69] Moreover, a 3d¹⁰ configuration for the nickel could be derived from the IBO analysis of **1**, confirming the oxidation state Ni(0) (see Figure S7 in the SI for a depiction of the orbitals).

In summary, complex **1** is only the third reported example of coordination of an intact phosphatetrahdane other than P₄ and the first homoleptic complex among these compounds. In the structure of **1**, diphosphatetrahdane acts as a bidentate ligand coordinating in an η²-fashion *via* the P–P bond to nickel. So far, mainly coinage metal cations stabilized by weakly coordinating anions have been reported to side-on coordinate intact tetrahedra of phosphatetrahdanes and the isoelectronic P₄ molecule. Prior to this work, only one example of the side-on coordination of an intact P₄ tetrahedron to a Ni core was proposed, however, this compound was neither isolated nor

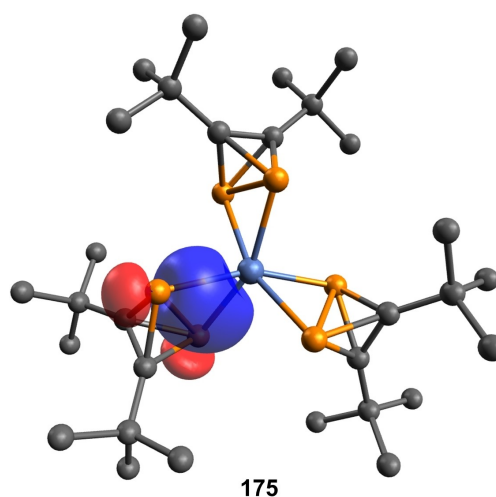


Figure 3. Intrinsic Bond Orbital of **1** showing a 3-center-2-electron bond between the nickel core and the phosphorus atoms. Surface isovalue = 0.06. Hydrogen atoms have been omitted for clarity.

confirmed by an X-ray structure.^[6c] Quantum chemical calculations support the oxidation state Ni(0) in **1** and indicate the formation of 3-center-2-electron bonds between the P atoms of (tBuCP)₂ and the Ni center. 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 P₄ tetrahedron.^[6g,19] Further studies exploring the coordination chemistry of (tBuCP)₂ and related molecules are currently underway in our laboratory.

Experimental Section

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: ¹H NMR: 2.08 ppm, ¹³C{¹H} NMR: 20.43 ppm). Chemical shifts (δ) are given in ppm referring to external standards of tetramethyl silane (¹H and ¹³C{¹H}) and 85% phosphorus acid (³¹P{¹H}). ¹³C NMR signals were assigned based on 2D NMR spectra (¹H, ¹³C-HMBC, ¹H, ¹³C-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).

X-ray diffraction: 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 N₂ 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 program using Intrinsic Phasing and refined with the SHELXL^[24] refinement package using Least Squares refinements on *F*². The hydrogen atoms were located in idealized 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).

[Ni(η²-(tBuCP)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 (tBuCP)₂. A colorless 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 colorless solution of (tBuCP)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-colored residue. This was extracted in *n*-hexane (6 mL). Storage of the extract in the freezer (-35 °C) for 21 days afforded indigo-colored 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. Yield: 13.1 mg (23 %). UV-Vis: (*n*-hexane, λ_{max}/nm, ε_{max}/L mol⁻¹ cm⁻¹): 225 (36000), 280 (23000), 315 (16000), 415 (9000), 680 (2000). ¹H NMR (400.13 MHz, 243 K, toluene-*d*₈): δ/ppm = 1.33 (s, 54 H). ¹³C{¹H} NMR (100.61 MHz, 243 K, toluene-*d*₈): δ/ppm = 29.7 (s, C(CH₃)₃), 32.0 (s, CH₃), 45.5 (m, P₂C₂). ³¹P{¹H} NMR (161.98 MHz, 243 K, toluene-*d*₈): δ/ppm = -338.4 (s). Elemental analysis (calculated values for C₃₀H₅₄NiP₆, MW = 659.30 g·mol⁻¹, in parentheses): C 54.83 (54.65), H 8.16 (8.26)%.

Crystallographic details for 1: C₃₀H₅₄NiP₆ (MW = 659.26 g·mol⁻¹): triclinic, space group P $\bar{1}$ (no. 2), *a* = 11.85730(10) Å, *b* = 13.1518(2) Å, *c* = 13.2185(2) Å, α = 117.796(2)°, β = 96.9280(10)°, γ = 97.4380(10)°, *V* = 1769.25(5) Å³, *Z* = 2, *T* = 123(1) K, μ(Cu Kα) = 3.479 mm⁻¹, ρ_{calc} = 1.238 g/cm³, 31861 reflections collected (7.684° ≤ 2θ ≤ 147.012°), 6870 independent reflections (*R*_{int} = 0.0252, *R*_{sigma} = 0.0236) which were used in all calculations. The final *R*₁ was 0.0265 [*I* > 2σ(*I*)] and *wR*₂ was 0.0707 (all data).

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: phosphorus · nickel · coordination chemistry · tetrahedrane · organophosphorus compounds

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