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P Ligands **Hot Paper**

Haptotropism in a Nickel Complex with a Neutral, π-Bridging *cyclo*-P_4 Ligand Analogous to Cyclobutadiene

Chris Gendy, Juuso Valjus, Heikki M. Tuononen, and Roland Roesler**

Abstract: Dedicated to Professor Manfred Scheer on the occasion of his 65th birthday
The reaction of (**1**)Ni(η^2-cod), **2**, incorporating a chelating bis(*N*-heterocyclic carbene) **1**, with P_4 in pentane yielded the dinuclear complex [(**2**)Ni]$_2$(μ_2,η^2:η^2-P_4), **3**, formally featuring a cyclobutadiene-like, neutral, rectangular, π-bridging P_4-ring. In toluene, the butterfly-shaped complex [(**1**)Ni]$_2$(μ_2,η^2:η^2-P_2), **4**, with a formally neutral P_2-unit was obtained from **2** and either P_4 or **3**. Computational studies showed that a haptotropic rearrangement involving two isomers of the μ_2,η^2:η^2-P_4 coordination mode and a low-energy μ_2,η^4:η^4-P_4 coordination mode, as previously predicted for related nickel cyclobutadiene complexes, could explain the coalescence observed in the low-temperature NMR spectra of **3**. The insertion of the (**1**)Ni fragment into a P–P bond of $P_7(SiMe_3)_3$, forming complex **5** with a norbornane-like P_7 ligand, was also observed.

Transition metal complexes incorporating P_x ligands have been extensively investigated due to their appealing structural variety and intriguing bonding.[1] White phosphorus is the entryway to the production of most phosphorus compounds,[2] and more recently the interest toward P_x metal complexes has expanded to include the metal-mediated activation and further transformation of this molecule.[3] Complexes incorporating P_4 ligands are of particular interest because they are hypothesized to constitute the first stage in the activation of P_4.[4] Hydrocarbon-based π-ligands such as cyclobutadiene,[5] cyclopentadienyl, and benzene have been used as a guideline for systematizing the chemistry of substituent-free, or "naked", phosphorus ligands because the CH and P fragments are isolobal.[6]

Mirroring cyclobutadiene complexes **A** (Figure 1), the planar *cyclo*-P_4 ligand forms mononuclear, 18-valence-electron sandwich and half sandwich complexes **B** (M = V,[7] Nb,[8] Ta,[9] L_n = Cp^x(CO)$_2$; M = Mo,[10] L_n = (CO)$_2$(CNR)$_2$; (CO)I$_2$(CNR)$_2$; M = Fe,[11] L_n = (Cy$_2$PCH$_2$CH$_2$)$_2$PPh; M = Co,[12] L_n = Cp^x), **B**$^-$ (M = Mo,[13] L_n = (CO)I(CNR)$_2$; M = Fe,[14] L_n = Cp^x; M = Co,[15] L = bis(2,6-Dipp)phenanthrene-9,10-diimine), and **B**$^{2-}$ (M = Mo,[13] L_n = (CO)(CNR)$_2$, (CO)$_2$-(CNR)). The phosphorus ring in **B** can σ-donate up to four lone pairs to additional metals, generating multinuclear complexes.[1] By analogy to cyclobutadiene, the P_4 ligand in **B** is considered to be dianionic, and this view is supported by Mössbauer measurements[11] and computational studies.[13,14] *cyclo*-P_4^{2-} has been described as antiaromatic as a free ligand,[16] lone pair aromatic in alkali metal salts,[17] and aromatic in transition metal complexes.[11,13]

In contrast to cyclobutadiene, which rarely π-bridges transition metals,[18] *cyclo*-P_4 forms a variety of bridged complexes where the planar ligand can be formally considered P_4^{2-} (**C** and **D**), P_4^{4-} (**E** and **F**), or P_4 (**G** and **H**), based on structural, spectroscopic, and computational data. For example, the μ_2:η^4,η^4-bridging mode has been observed in complexes of type **C** (M = Fe,[19] L_n = β-diketiminato; M = Sm,[20] L_n = {[DippN]$_2$CH}$_2$), **C**$^-$ (M = Co, L_n = β-diketiminato),[21,22] **E** (M = Zr, L_n = PhP(CH$_2$SiMe$_2$NSiMe$_2$CH$_2$)$_2$PPh),[23] **E**$^-$ (M = Co, L_n = BIAN)[24] and **G** (M = Co, L_n = β-diketiminato),[21,22] while complexes **D** (M = U, L_n = Cp*(COT))[25] and **F** (M = Nb,[26]

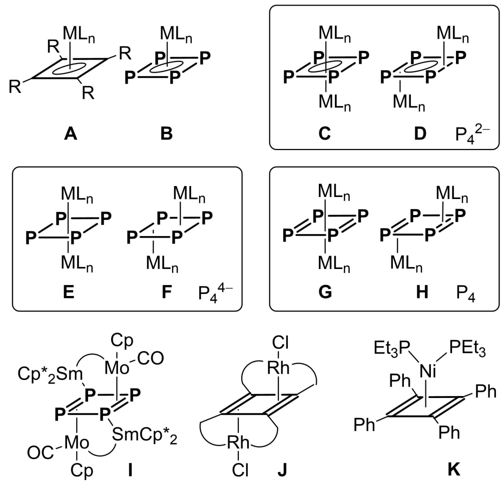

Figure 1. Reported coordination modes of the planar cyclo-P_4 ligand (**B**–**I**) and relevant cyclobutadiene analogues (**A**, **J**, and **K**).

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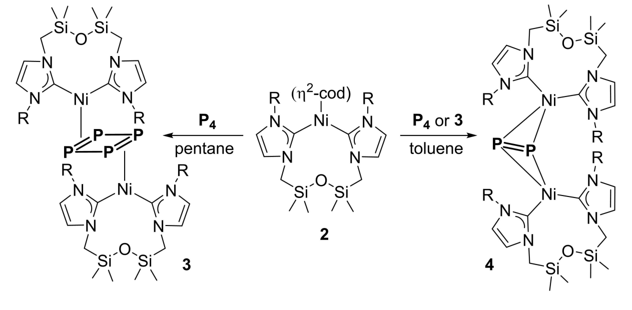
$L_n = (DippO)_3$; M = Nb, Ta,[27] L = (β-diketiminato)(*t*BuN)) display $\mu_2{:}\eta^2,\eta^2$- and $\mu_2{:}\eta^3,\eta^3$-bridging modes, respectively. Complex **I** is the only known example featuring a neutral $\mu_2{:}\eta^2,\eta^2$-P_4 ligand, presumably because the constrained geometry does not allow for η^4-coordination.[28] This mirrors the behaviour of cyclobutadiene, which is known to coordinate in $\mu_2{:}\eta^2,\eta^2$-fashion only in **J**.[29]

Although the chemistry of nickel with P_4 has been extensively investigated, leading to the isolation of a variety of $(L_nNi)_yP_x$ derivatives ($x = 2$–5, 8),[1,3,30] a planar, π-coordinating *cyclo*-P_4 nickel complex has remained elusive.[31] The excellent π-donating properties of the metal in $[(\mathbf{1})Ni(\eta^2\text{-cod})]$,[32a] **2** (Scheme 1; **1** = bis(NHC)),[32b] recommend it as a promising synthon for the stabilization of π-bonded P_x-ligands. In a similar manner, the $(Et_3P)_2Ni$ fragment has allowed the isolation of complex **K**, having structural features consistent with Ni^0 and a neutral, η^4-cyclobutadiene ligand, as opposite to Ni^{II} and cyclobutadienyl.[33] Furthermore, a computational study on the model system (cyclobutadiene) $Ni(PH_3)_2$ suggested that the η^4- and η^2-coordination modes had similar energies and a tiny interconversion barrier.[34] Higher-level calculations for the analogous (cyclobutadiene)Pt(diphosphinylethane) gave a slightly greater energy difference.[35] These findings led us to investigate the reactivity of **2** with P_4 in pursuit of the elusive $\mu_2{:}\eta^2,\eta^2$-P_4 bridging mode **H**. This chemistry, as well as the reactivity of **2** with $P_7(SiMe_3)_3$, will be reported herein.



Scheme 1. Synthesis of **3** and **4**.

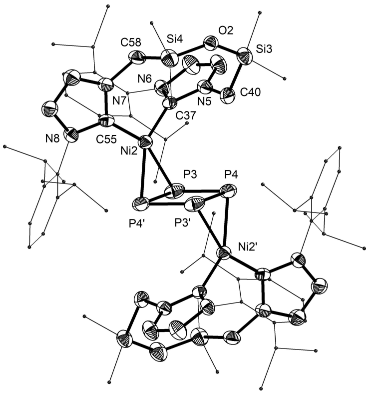


Figure 2. Solid-state structure of one of the two independent molecules of **3**, with 50% thermal ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: P3–P4′ 2.145(2), 2.149(2), P3–P4 2.237(2), 2.242(2), Ni–P 2.2436(15)–2.2822(14), Ni–C 1.911(5)–1.933(5); P-P-P 89.58(7)–90.42(7), C-Ni-C 109.9(2), 110.8-(2).[38]

Reaction of **2** with P_4 in pentane afforded diamagnetic, crystalline complex $[(\mathbf{1})Ni]_2P_4$, **3**, irrespective of stoichiometry (Scheme 1). An X-ray diffraction experiment revealed a dinuclear, C_i-symmetric structure with a planar, rectangular $\mu_2{:}\eta^2,\eta^2$-P_4 core (Figure 2). The *cyclo*-P_4 ligand features alternating long (2.242(8) Å) and short (2.149(3) Å) P–P bonds (cf. P–P 2.1994(3) Å in P_4[36] and P=P 2.140(1) in PhP=PPh coordinated to Ni^0),[37] suggestive of a neutral P_4 ligand bound by two $(\mathbf{1})Ni^0$ fragments, i.e., **H**. For comparison, the P_4 ligand adopts a very similar geometry in **G**, M = Co^I (*av.* P–P 2.29 Å and P=P 2.13 Å).[21,22]

A room-temperature ^{31}P NMR spectrum of **3** in toluene-d_8 revealed a single, broad resonance at 45 ppm (cf. 128 and 169 ppm for **G**, M = Co^I, in the solid state),[21] indicative of a dynamic process. The variable-temperature study revealed two coalescence temperatures (Figure 3). At low temperature, the presence of two ^{31}P resonances (21 and 63 ppm) is consistent with a centrosymmetric C_i-structure, as observed in the solid state. Upon heating above 210 K, all phosphorus atoms become equivalent on the NMR time scale. Resonance broadening suggestive of a second coalescence is apparent slightly above room temperature, but incipient decomposition precluded the investigation of this process. The ^1H NMR spectrum features four AB doublets for the methylene protons (3.3, 4.3, 5.0, and 8.2 ppm, Figure S1), and two resonances for the carbene carbons are observed in ^{13}C NMR (192.8 and 202.7 ppm, Figure S2). This indicates that the solid-state structure of the $(\mathbf{1})Ni$ fragment is retained in solution between 210–293 K.

DFT calculations on **3** yielded a closed-shell singlet ground state free of instabilities, supporting the proposed coordination mode **H**. An ETS-NOCV analysis of bonding in **3** using closed- shell fragments $((\mathbf{1})Ni)_2$ and P_4 showed significant interaction of nickel *d*-orbitals with the π-type orbitals of P_4, giving two strongly stabilizing contributions (Figure S24). Population analyses suggested a net flow of 0.7–0.8 e^- from the two $(\mathbf{1})Ni^0$ fragments to P_4, underlining

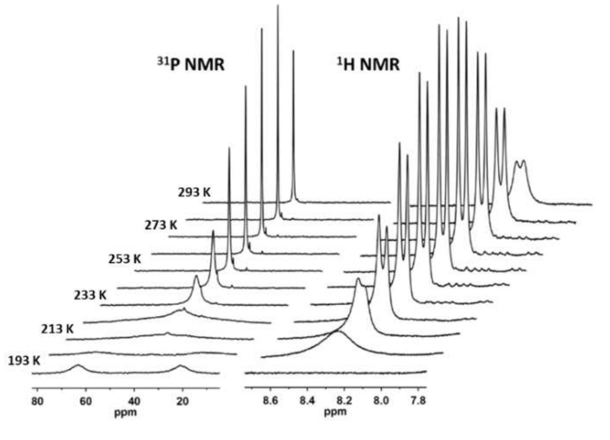


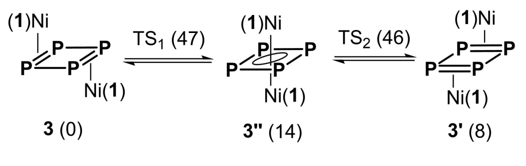
Figure 3. Stack plots of variable-temperature (193–293 K) ^{31}P (left) and ^1H (right) NMR spectra of **3** in toluene-d_8.

the fact that the use of integer oxidation states and charges is inevitably an oversimplification.

Further inspection of the potential energy surface of **3** with DFT revealed that a μ_2:η^4,η^4-bound C_i-isomer (**3**″) with a square-like *cyclo*-P_4 ring is only 14 kJ mol^{-1} higher in energy than **3**, while a second C_i-symmetric μ_2:η^2,η^2-bound isomer (**3**′) has a relative energy of only 8 kJ mol^{-1} (Scheme 2, Figure S23). Both **3** and **3**′ connect to **3**″ with barriers <50 kJ mol^{-1}, in agreement with the value of 44 kJ mol^{-1} calculated from the coalescence temperature. These results are in accordance with a haptotropic rearrangement (P_4-ring whizzing) accounting for the low temperature coalescence in the ^{31}P NMR data of **3**. Fluxional P_4-ring behaviour has been proposed for *cyclo*-P_4 complexes.[11,23,26] The high-temperature coalescence is tentatively assigned to ligand symmetrisation via dynamic motion that was shown to involve an activation energy of 53 kJ mol^{-1} in (**1**)NiGeCl$_2$;[32b] the barrier for **3** is expected to be higher due to increased steric strain.

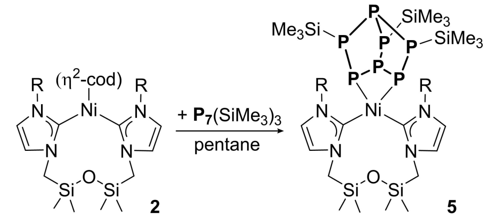
The singlet ground state of **3**″ shows an instability, leading to a broken-symmetry singlet solution in which approximately 0.6 α spin becomes localized on one Ni centre and 0.6 β spin on the other. This suggests that coordination mode **C**, involving two (**1**)Ni^{I} fragments bridged by a dianionic P_4^{2-} ring, is a reasonable first-order approximation of bonding in the intermediate **3**″. This description is well in line with the square-shaped structure calculated for the *cyclo*-P_4 ring in **3**″ having two almost equal bond lengths (2.163 and 2.172 Å) and bond angles (88 and 92°).

In toluene, the reaction of **2** with either a stoichiometric or an excess amount of P_4 yields exclusively **4** (Scheme 1), which can also be prepared from **3** and **2** in toluene; notably, **3** does not convert to **4** upon dissolution in toluene. Under an inert atmosphere at −40 °C, solids **3** and **4** are stable for months but at room temperature in solution decomposition of both compounds leads within hours to the disappearance of all ^{31}P resonances and formation of unidentified products. The solid state structure of **4** (Figure S21) features a butterfly-shaped Ni_2P_2 core with a very short (2.0784(16) Å) P–P bond and a dihedral angle of 120.87(3)°. In similar complexes $[\{(NHC)_2Ni\}_2(\mu,\eta^2{:}\eta^2\text{-}P_2)]$, the P_2 unit (P–P 2.0906 (8) Å) was described as P_2^{4-} based on the visual inspection of frontier orbitals and their localization on P_2.[39] Quantitative bonding analyses performed for **4** show that, while its frontier Kohn–Sham orbitals are similar to those of $[\{(NHC)_2Ni\}_2(\mu,\eta^2{:}\eta^2\text{-}P_2)]$ (Figure S25), the contribution from P_2 is much less than 50 % in all cases. Thus, complex **4** can be formally described as a neutral P_2 ligand bound by two (**1**)Ni(0) fragments, akin to the reported dinuclear Ni^0-alkyne complexes.[40] An ETS-NOCV analysis of **4** using this fragmentation scheme shows charge flow between the *d*-orbitals on the metals and the π-type orbitals on P_2, resulting in both metal-to-ligand and ligand-to-metal bonding contributions (Figure S26). Population analyses indicate a net flow of 0.5–0.6 e$^-$ from ((**1**)Ni)$_2$ to P_2, illustrating, again, that the discussed promolecular fragments should only be treated as good first-order approximations of bonding in **3** and **4**.



Scheme 2. Calculated haptotropic rearrangement between **3** and **3**′ (which differ in the relative orientation of ligand **1** with respect to *cyclo*-P_4), via **3**″ over transition states TS_1 and TS_2. Relative Gibbs free energies (in kJ mol^{-1} at 298 K) in parenthesis.

The most accessible phosphorus clusters other than P_4 are P_7R_3, which were used extensively as a ligands;[41] P–P bond activation has only been reported for the parent Zintl ion P_7^{3-}.[42] Reaction of **2** with $P_7(SiMe_3)_3$[43] resulted into the formation of **5** (Scheme 3). At room temperature, short reaction times were needed to limit thermal decomposition. Crystallographic analysis revealed that the (**1**)Ni fragment inserted into the P_3 ring of $P_7(SiMe_3)_3$, generating a complex with a norbornane-like P_7 ligand (Figure 4). This mirrors the transformations observed for the activation of P_7^{3-},[44] except in the latter case η^4-P_7^{3-} complexes were usually obtained. The insertion was accompanied by an inversion at phosphorus, leading to a change of the $P_7(SiMe_3)_3$ conformation from *syn*, which is typical to all P_7R_3 analogues, to *anti*. The Ni–P bonds in **5** measure 2.2253(16) and 2.2950(16) Å, while the P–P bonds change little in comparison to $P_7(SiMe_3)_3$.[45] The ^{31}P NMR spectrum of **5** in toluene-d_8 features seven multiplet signals that were assigned using 2D NMR.



Scheme 3. Synthesis of **5**.

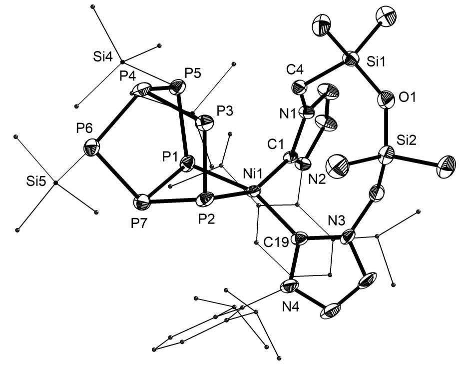


Figure 4. Solid-state structure of **5** with 50 % thermal ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å]: P4–P3 2.184(2), P4–P5 2.186(2), P4–P6 2.201(2), P1–P5 2.227(2), P2–P3 2.233(2), P7–P6 2.160(2), P1–P7 2.205(2), P2–P7 2.220(2), P1···P2 3.007(2), Ni–C 1.954(5), 1.992(5), Ni1–P1 2.2253(16), Ni1–P2 2.2950(16).[38]

In conclusion, complex **2** displays solvent-dependent reactivity with P_4, leading to **3** in pentane and **4** in toluene. Moreover, in reaction with **2**, **3** generates **4**, supporting the postulate that *cyclo*-P_4 complexes represent the first step in the activation of P_4 by transition metals. Compound **3** features the elusive $\mu_2{:}\eta^2,\eta^2$-P_4 bridging mode **H**, previously only characterized in the geometry-constrained system **I**. The low-temperature coalescence observed in the NMR spectra of **3** can be explained with a haptotropic rearrangement involving two isomers of the crystallographically characterized $\mu_2{:}\eta^2,\eta^2$ bridging mode, as well as a slightly less stable isomer with a $\mu_2{:}\eta^4,\eta^4$-bound ligand. This leads to the equivalence of all phosphorus atoms of **3** on the NMR timescale and mirrors the ring-whizzing mechanism proposed for the analogous nickel-cyclobutadiene complex **K**. Employing **2**, the first P–P bond activation in a P_7R_3 cluster was also achieved, leading to complex **5**. The low energy barrier haptotropism of **3** and the formalism that best describes the structures **3**, **3′**, and **3″** suggest that the classification of *cyclo*-P_4 complexes in categories **C**–**H** (Figure 1) is somewhat fluid.

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Conflict of Interest

The authors declare no conflicts of interest.

Keywords: Haptotropism · *N*-Heterocyclic Carbene · Nickel · Phosphorus · π-Ligands

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[1] a) L. Giusti, V. R. Landaeta, M. Vanni, J. A. Kelly, R. Wolf, M. Caporali, *Coord. Chem. Rev.* **2021**, *441*, 213927.

[2] a) M. B. Geeson, C. C. Cummins, *Science* **2018**, *359*, 1383–1385; b) D. J. Scott, J. Cammarata, M. Schimpf, R. Wolf, *Nat. Chem.* **2021**, *13*, 458–464.

[3] C. M. Hoidn, D. J. Scott, R. Wolf, *Chem. Eur. J.* **2021**, *27*, 1886–1902.

[4] G. Luo, S. Du, P. Wang, F. Liu, W.-X. Zhang, Y. Luo, *Chem. Eur. J.* **2020**, *26*, 13282–13287.

[5] Y. Shoji, Y. Ikabata, I. Ryzhii, R. Ayub, O. El Bakouri, T. Sato, Q. Wang, T. Miura, B. S. B. Karunathilaka, Y. Tsuchiya, C. Adachi, H. Ottosson, H. Nakai, T. Ikoma, T. Fukushima, *Angew. Chem. Int. Ed.* **2021**, *60*, 21817–21823; *Angew. Chem.* **2021**, *133*, 21988–21994.

[6] R. Hoffmann, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 711–724; *Angew. Chem.* **1982**, *94*, 725–739.

[7] M. Herberhold, G. Frohmader, W. Milius, *J. Organomet. Chem.* **1996**, *522*, 185–196.

[8] O. J. Scherer, J. Vondung, G. Wolmershäuser, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1355–1357; *Angew. Chem.* **1989**, *101*, 1395–1397.

[9] O. J. Scherer, G. Winter, G. Wolmershäuser, *Z. Anorg. Allg. Chem.* **1993**, *619*, 827–835.

[10] K. A. Mandla, C. E. Moore, A. L. Rheingold, J. S. Figueroa, *Angew. Chem. Int. Ed.* **2019**, *58*, 1779–1783; *Angew. Chem.* **2019**, *131*, 1793–1797.

[11] A. Cavaillé, N. Saffon-Merceron, N. Nebra, M. Fustier-Boutignon, N. Mézailles, *Angew. Chem. Int. Ed.* **2018**, *57*, 1874–1878; *Angew. Chem.* **2018**, *130*, 1892–1896.

[12] F. Dielmann, A. Timoshkin, M. Piesch, G. Balázs, M. Scheer, *Angew. Chem. Int. Ed.* **2017**, *56*, 1671–1675; *Angew. Chem.* **2017**, *129*, 1693–1698.

[13] K. A. Mandla, M. L. Neville, C. E. Moore, A. L. Rheingold, J. S. Figueroa, *Angew. Chem. Int. Ed.* **2019**, *58*, 15329–15333; *Angew. Chem.* **2019**, *131*, 15473–15477.

[14] U. Chakraborty, J. Leitl, B. Mühldorf, M. Bodensteiner, S. Pelties, R. Wolf, *Dalton Trans.* **2018**, *47*, 3693–3697.

[15] C. M. Hoidn, T. M. Maier, K. Trabitsch, J. J. Weigand, R. Wolf, *Angew. Chem. Int. Ed.* **2019**, *58*, 18931–18936; *Angew. Chem.* **2019**, *131*, 19107–19112.

[16] J. O. C. Jiménez-Halla, E. Matito, J. Robles, M. Solà, *J. Organomet. Chem.* **2006**, *691*, 4359–4366.

[17] a) F. Kraus, J. C. Aschenbrenner, N. Korber, *Angew. Chem. Int. Ed.* **2003**, *42*, 4030–4033; *Angew. Chem.* **2003**, *115*, 4162–4165; b) F. Kraus, N. Korber, *Chem. Eur. J.* **2005**, *11*, 5945–5959; c) F. Kraus, T. Hanauer, N. Korber, *Inorg. Chem.* **2006**, *45*, 1117–1123.

[18] D. Patel, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Nat. Commun.* **2013**, *4*, 2323.

[19] F. Spitzer, C. Graßl, G. Balázs, E. M. Zolnhofer, K. Meyer, M. Scheer, *Angew. Chem. Int. Ed.* **2016**, *55*, 4340–4344; *Angew. Chem.* **2016**, *128*, 4412–4416.

[20] C. Schoo, S. Bestgen, R. Köppe, S. N. Konchenko, P. W. Roesky, *Chem. Commun.* **2018**, *54*, 4770–4773.

[21] S. Yao, N. Lindenmaier, Y. Xiong, S. Inoue, T. Szilvási, M. Adelhardt, J. Sutter, K. Meyer, M. Driess, *Angew. Chem. Int. Ed.* **2015**, *54*, 1250–1254; *Angew. Chem.* **2015**, *127*, 1266–1270.

[22] F. Spitzer, C. Graßl, G. Balázs, E. Mädl, M. Keilwerth, E. M. Zolnhofer, K. Meyer, M. Scheer, *Chem. Eur. J.* **2017**, *23*, 2716–2721.

[23] W. W. Seidel, O. T. Summerscales, B. U. Patrick, M. D. Fryzuk, *Angew. Chem. Int. Ed.* **2009**, *48*, 115–117; *Angew. Chem.* **2009**, *121*, 121–123.

[24] S. Pelties, T. Maier, D. Herrmann, B. de Bruin, C. Rebreyend, S. Gärtner, I. G. Shenderovich, R. Wolf, *Chem. Eur. J.* **2017**, *23*, 6094–6102.

[25] A. S. P. Frey, F. G. N. Cloke, P. B. Hitchcock, J. C. Green, *New J. Chem.* **2011**, *35*, 2022–2026.

[26] A. Velian, C. C. Cummins, *Chem. Sci.* **2012**, *3*, 1003–1006.

[27] C. Camp, L. Maron, R. G. Bergman, J. Arnold, *J. Am. Chem. Soc.* **2014**, *136*, 17652–17661.

[28] N. Arleth, M. T. Gamer, R. Köppe, N. A. Pushkarevsky, S. N. Konchenko, M. Fleischmann, M. Bodensteiner, M. Scheer, P. W. Roesky, *Chem. Sci.* **2015**, *6*, 7179–7184.

[29] K. Okamoto, Y. Omoto, H. Sano, K. Ohe, *Dalton Trans.* **2012**, *41*, 10926–10929.

[30] S. Carenco, I. Resa, X. Le Goff, P. Le Floch, N. Mézailles, *Chem. Commun.* **2008**, 2568–2570.

[31] a) S. Yao, Y. Xiong, C. Milsmann, E. Bill, S. Pfirrmann, C. Limberg, M. Driess, *Chem. Eur. J.* **2010**, *16*, 436–439; b) S. Pelties, D. Herrmann, B. de Bruin, F. Hartl, R. Wolf, *Chem. Commun.* **2014**, *50*, 7014–7016. For a wider selection of L_nNi–P_x complexes, see Ref #2 in the Supporting Information.

[32] a) B. M. Puerta Lombardi, C. Gendy, B. S. Gelfand, G. M. Bernard, R. E. Wasylishen, H. M. Tuononen, R. Roesler, *Angew. Chem. Int. Ed.* **2021**, *60*, 7077–7081; *Angew. Chem.* **2021**, *133*, 7153–7157; b) C. Gendy, A. Mansikkamäki, J. Valjus, J. Heidebrecht, P. C.-Y. Hui, G. M. Bernard, H. M. Tuononen, R. E. Wasylishen, V. K. Michaelis, R. Roesler, *Angew. Chem. Int. Ed.* **2019**, *58*, 154–158; *Angew. Chem.* **2019**, *131*, 160–164.

[33] J. J. Eisch, A. M. Piotrowski, A. A. Aradi, C. Krüger, M. J. Romão, *Z. Naturforsch. B* **1985**, *40*, 624–635.

[34] J. Silvestre, T. A. Albright, *Nouv. J. Chim.* **1985**, *9*, 659–668.

[35] O. A. Oloba-Whenu, T. A. Albright, C. Soubra-Ghaoui, *Beilstein J. Org. Chem.* **2016**, *12*, 1410–1420.

[36] B. M. Cossairt, C. C. Cummins, A. R. Head, D. L. Lichtenberger, R. J. F. Berger, S. A. Hayes, N. W. Mitzel, G. Wu, *J. Am. Chem. Soc.* **2010**, *132*, 8459–8465.

[37] D. Fenske, K. Merzweiler, *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 635–637; *Angew. Chem.* **1984**, *96*, 600–602.

[38] Deposition Numbers 2115737, 2115738, and 2115739 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.

[39] B. Zarzycki, T. Zell, D. Schmidt, U. Radius, *Eur. J. Inorg. Chem.* **2013**, 2051–2058.

[40] R. Barrios-Francisco, T. Benítez-Páez, M. Flores-Alamo, A. Arévalo, J. J. García, *Chem. Asian J.* **2011**, *6*, 842–849.

[41] a) M. Baudler, K. Glinka, *Chem. Rev.* **1993**, *93*, 1623–1667; b) G. Fritz, P. Scheer, *Chem. Rev.* **2000**, *100*, 3341–3401.

[42] R. S. P. Turbervill, J. M. Goicoechea, *Chem. Rev.* **2014**, *114*, 10807–10828.

[43] a) G. Fritz, W. Holderich, *Naturwissenschaften* **1975**, *62*, 573–575.

[44] a) S. Charles, S. G. Bott, A. L. Reinghold, B. W. Eichhorn, *J. Am. Chem. Soc.* **1994**, *116*, 8077–8086; b) S. Charles, J. C. Fettinger, S. G. Bott, B. W. Eichhorn, *J. Am. Chem. Soc.* **1996**, *118*, 4713–4714; c) B. Kesanli, S. Charles, Y.-F. Lam, S. G. Bott, J. Fettinger, B. Eichhorn, *J. Am. Chem. Soc.* **2000**, *122*, 11101–11107; d) C. M. Knapp, J. S. Large, N. H. Rees, J. M. Goicoechea, *Chem. Commun.* **2011**, *47*, 4111–4113.

[45] W. Hönle, H. G. von Schnering, *Z. Anorg. Allg. Chem.* **1978**, *440*, 171–182.

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