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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]

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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 = $(Cy_2PCH_2CH_2)_2PPh$; 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 = $PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$),[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]

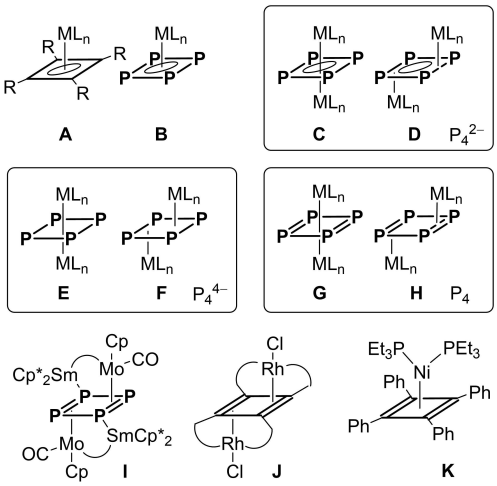
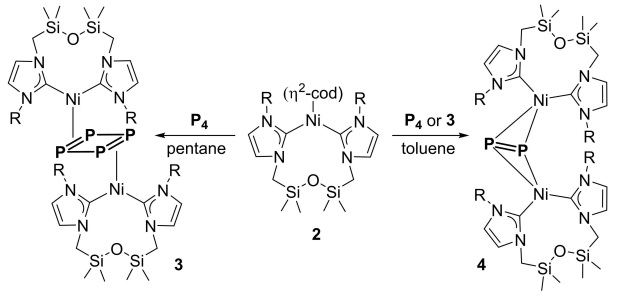


Figure 1. Reported coordination modes of the planar cyclo-P_4 ligand (**B–I**) and relevant cyclobutadiene analogues (**A**, **J**, and **K**).

L_n = (DippO)$_3$; M = Nb, Ta,[27] L = (β-diketiminato)(*t*BuN)) display μ_2:η^2,η^2- and μ_2:η^3,η^3-bridging modes, respectively. Complex **I** is the only known example featuring a neutral μ_2:η^2,η^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 μ_2:η^2,η^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 [(**1**)Ni(η^2-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 μ_2:η^2,η^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**.

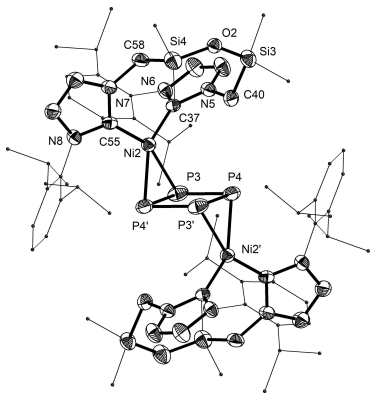


Figure 2. Solid-state structure of one of the two independent molecules of **3**, with 50% thermal ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: P3–P4′ 2.145(2), 2.149(2), P3–P4 2.237(2), 2.242(2), Ni–P 2.2436(15)–2.2822(14), Ni–C 1.911(5)–1.933(5); P-P-P 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 μ_2:η^2,η^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 (**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 (**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 (**1**)Ni^0 fragments to P_4, underlining

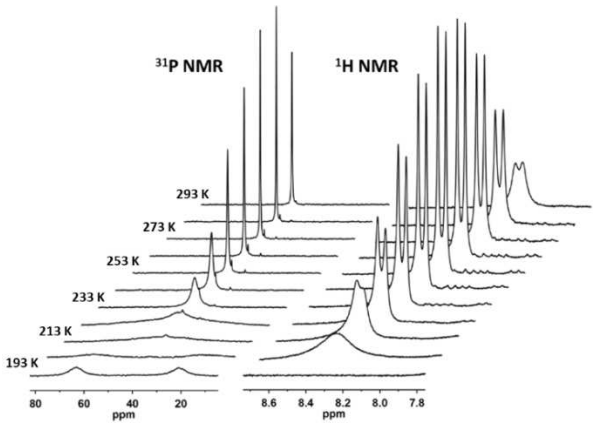


Figure 3. Stack plots of variable-temperature (193–293 K) ^{31}P (left) and ^1H (right) NMR spectra of **3** in toluene-d_8.

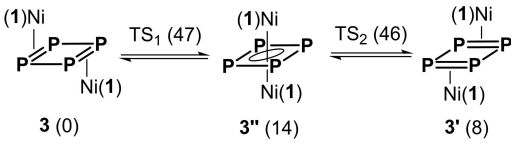
the fact that the use of integer oxidation states and charges is inevitably an oversimplification.

Further inspection of the potential energy surface of **3** with DFT revealed that a $\mu_2:\eta^4,\eta^4$-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 $\mu_2:\eta^2,\eta^2$-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.

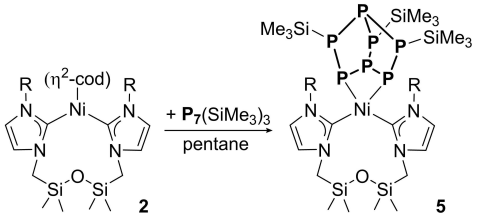
The singlet ground state of **3**″ shows an instability, leading to a broken-symmetry singlet solution in which approximately 0.6 α spin becomes localized on one Ni centre and 0.6 β spin on the other. This suggests that coordination mode **C**, involving two (**1**)Ni^{I} fragments bridged by a dianionic 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 $((\mathbf{1})Ni)_2$ 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**.

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 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.



Scheme 3. Synthesis of **5**.

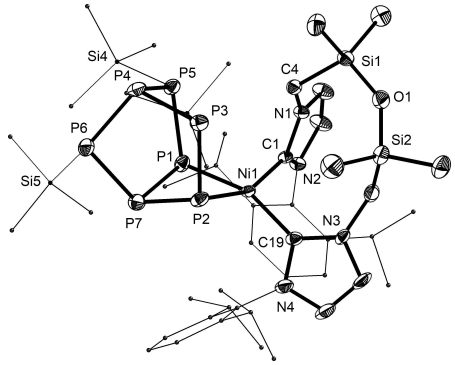


Figure 4. Solid-state structure of **5** with 50 % thermal ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å]: P4–P3 2.184(2), P4–P5 2.186(2), P4–P6 2.201(2), P1–P5 2.227(2), P2–P3 2.233(2), P7–P6 2.160(2), P1–P7 2.205(2), P2–P7 2.220(2), P1···P2 3.007(2), Ni–C 1.954(5), 1.992(5),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