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Haptotropism in a Nickel Complex with a Neutral, π -Bridging *cyclo-P*₄ Ligand Analogous to Cyclobutadiene

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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 P₄ in pentane yielded the dinuclear complex [(2)Ni]₂($\mu_2, \eta^2: \eta^2$ -P₄), **3**, formally featuring a cyclobutadiene-like, neutral, rectangular, π -bridging P₄-ring. In toluene, the butterfly-shaped complex [(1)Ni]₂($\mu_2, \eta^2: \eta^2$ -P₂), **4**, with a formally neutral P₂-unit was obtained from **2** and either P₄ or **3**. Computational studies showed that a haptotropic rearrangement involving two isomers of the $\mu_2, \eta^2: \eta^2$ -P₄ coordination mode and a low-energy $\mu_2, \eta^4: \eta^4$ -P₄ 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 P₇(SiMe₃)₃, forming complex **5** with a norbornane-like P₇ 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 P₄ ligands are of particular interest because they are hypothesized to constitute the first stage in the activation of P₄.^[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)₂(CNR)₂; M = Fe,^[11] L_n = (C₂PCH₂CH₂)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 P₄ 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 P₄^{2−} (**C** and **D**), P₄^{4−} (**E** and **F**), or P₄ (**G** and **H**), based on structural, spectroscopic, and computational data. For example, the $\mu_2: \eta^4, \eta^4$ -bridging mode has been observed in complexes of type **C** (M = Fe,^[19] L_n = β -diketiminato; M = Sm,^[20] L_n = {[DippN]₂CH)₂), **C**[−] (M = Co, L_n = β -diketiminato),^[21,22] **E** (M = Zr, L_n = PhP(CH₂SiMe₂NSiMe₂CH₂)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]

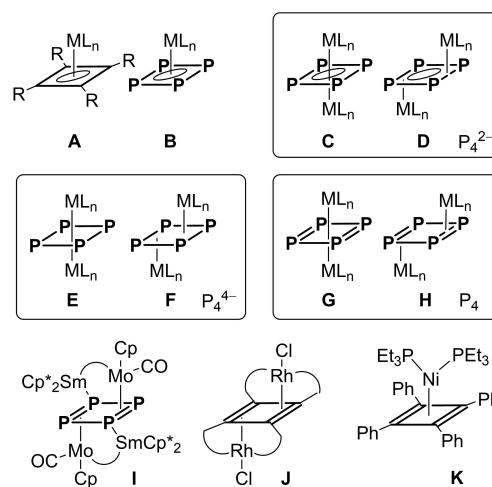


Figure 1. Reported coordination modes of the planar *cyclo-P*₄ ligand (**B–I**) and relevant cyclobutadiene analogues (**A**, **J**, and **K**).

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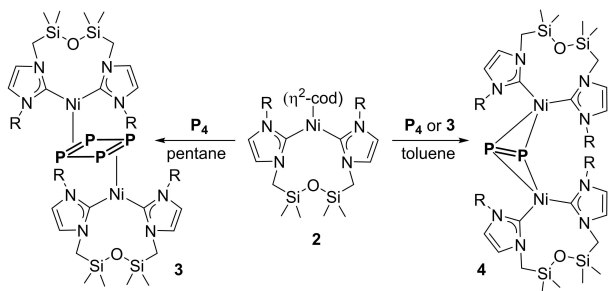
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$L_n = (\text{DippO})_3$; $M = \text{Nb}$, Ta ,^[27] $L = (\beta\text{-diketiminato})(t\text{BuN})$ display $\mu_2:\eta^2,\eta^2$ - and $\mu_2:\eta^3,\eta^3$ -bridging modes, respectively. Complex **1** is the only known example featuring a neutral $\mu_2:\eta^2,\eta^2$ - 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 $(L_n\text{Ni})_x\text{P}_x$ 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 $[(\mathbf{1})\text{Ni}(\eta^2\text{-cod})]$,^[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 $(\text{Et}_3\text{P})_2\text{Ni}$ 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) $\text{Ni}(\text{PH}_3)_2$ 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) $\text{Pt}(\text{diphosphinylethane})$ gave a slightly greater energy difference.^[35] These findings led us to investigate the reactivity of **2** with P_4 in pursuit of the



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

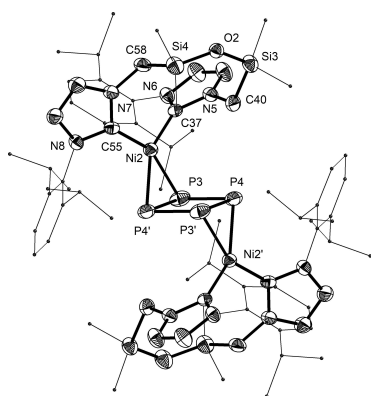


Figure 2. Solid-state structure of one of the two independent molecules of **3**, with 50% thermal ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: P3–P4' 2.145(2), 2.149(2), P3–P4 2.237(2), 2.242(2), Ni–P 2.2436(15)–2.2822(14), Ni–C 1.911(5)–1.933(5); P–P–P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

elusive $\mu_2:\eta^2,\eta^2$ - P_4 bridging mode **H**. This chemistry, as well as the reactivity of **2** with $\text{P}_7(\text{SiMe}_3)_3$, will be reported herein.

Reaction of **2** with P_4 in pentane afforded diamagnetic, crystalline complex $[(\mathbf{1})\text{Ni}]_2\text{P}_4$, **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 $\text{PhP}=\text{PPh}$ coordinated to Ni^0),^[37] suggestive of a neutral P_4 ligand bound by two $(\mathbf{1})\text{Ni}^0$ fragments, i.e., **H**. For comparison, the P_4 ligand adopts a very similar geometry in **G**, $M = \text{Co}^1$ (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**, $M = \text{Co}^1$, 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 $(\mathbf{1})\text{Ni}$ 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 $((\mathbf{1})\text{Ni})_2$ 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 $(\mathbf{1})\text{Ni}^0$ fragments to P_4 , underlining

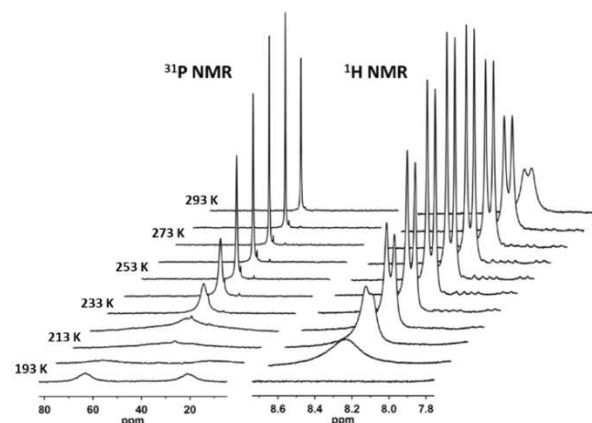


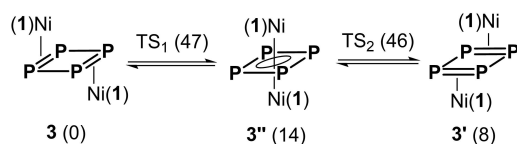
Figure 3. Stack plots of variable-temperature (193–293 K) ^{31}P (left) and ^1H (right) NMR spectra of **3** in toluene- d_8 .

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*-P₄ 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 (P₄-ring whizzing) accounting for the low temperature coalescence in the ³¹P NMR data of **3**. Fluxional P₄-ring behaviour has been proposed for *cyclo*-P₄ 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)NiGeCl₂.^[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 P₄²⁻ 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*-P₄ ring in **3''** having two almost equal bond lengths (2.163 and 2.172 Å) and bond angles (88 and 92°).

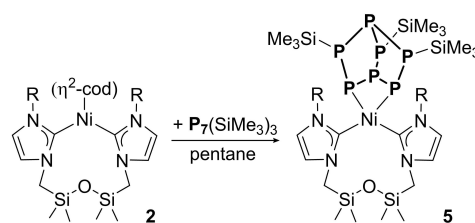
In toluene, the reaction of **2** with either a stoichiometric or an excess amount of P₄ yields exclusively **4** (Scheme 1), which can also be prepared from **3** and **2** in toluene; notably, **3** does not convert to **4** upon dissolution in toluene. Under an inert atmosphere at -40 °C, solids **3** and **4** are stable for months but at room temperature in solution decomposition of both compounds leads within hours to the disappearance of all ³¹P resonances and formation of unidentified products. The solid state structure of **4** (Figure S21) features a butterfly-shaped Ni₂P₂ 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($\mu,\eta^2:\eta^2$ -P₂), the P₂ unit (P–P 2.0906 (8) Å) was described as P₂⁴⁻ based on the visual inspection of frontier orbitals and their localization on P₂.^[39] Quantitative bonding analyses performed for **4** show that, while its frontier Kohn–Sham orbitals are similar to those of [(NHC)₂Ni]₂($\mu,\eta^2:\eta^2$ -P₂) (Figure S25), the contribution from P₂ is much less than 50 % in all cases. Thus, complex **4** can be formally described as a neutral P₂ ligand bound by



Scheme 2. Calculated haptotropic rearrangement between **3** and **3'** (which differ in the relative orientation of ligand **1** with respect to *cyclo*-P₄), via **3''** over transition states TS₁ and TS₂. Relative Gibbs free energies (in kJ mol⁻¹ at 298 K) in parenthesis.

two (1)Ni(0) fragments, akin to the reported dinuclear Ni⁰-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 P₂, 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 P₂, 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 P₄ are P₇R₃, which were used extensively as a ligands,^[41] P–P bond activation has only been reported for the parent Zintl ion P₇³⁻.^[42] Reaction of **2** with P₇(SiMe₃)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 P₃ ring of P₇(SiMe₃)₃, generating a complex with a norbornane-like P₇ ligand (Figure 4). This mirrors the transformations observed for the activation of P₇³⁻,^[44] except in the latter case η^4 -P₇³⁻ complexes were usually obtained. The insertion was accompanied by an inversion at phosphorus, leading to a change of the P₇(SiMe₃)₃ conformation from *syn*, which is typical to all P₇R₃ 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 P₇(SiMe₃)₃.^[45] The ³¹P NMR spectrum of **5** in toluene-*d*₈ features seven multiplet signals that were assigned using 2D NMR.



Scheme 3. Synthesis of **5**.

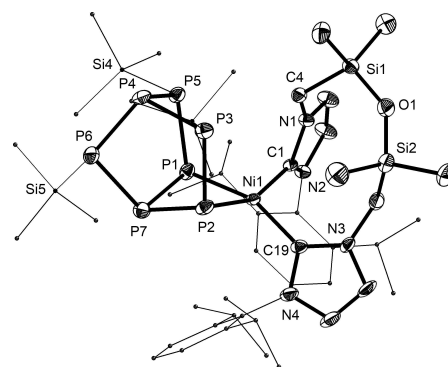


Figure 4. Solid-state structure of **5** with 50% thermal ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å]: P4–P3 2.184(2), P4–P5 2.186(2), P4–P6 2.201(2), P1–P5 2.227(2), P2–P3 2.233(2), P7–P6 2.160(2), P1–P7 2.205(2), P2–P7 2.220(2), P1...P2 3.007(2), Ni–C 1.954(5), 1.992(5), 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 $\mu_2:\eta^2,\eta^2\text{-P}_4$ 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**₇**R**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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