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Metalate-Mediated Functionalization of P₄ by Trapping Anionic [Cp*Fe(CO)₂(η¹-P₄)]⁻ with Lewis Acids

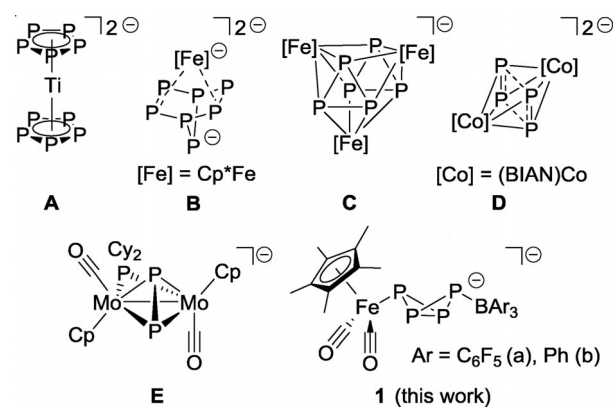
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The development of selective functionalization strategies of white phosphorus (P₄) is important to avoid the current chlorinated intermediates. The use of transition metals (TMs) could lead to catalytic procedures, but these are severely hampered by the high reactivity and unpredictable nature of the tetrahedron. Herein, we report selective first steps by reacting P₄ with a metal anion [Cp*Fe(CO)₂]⁻ (Cp* = C₅(CH₃)₅), which, in the presence of bulky Lewis acids (LA; B(C₆F₅)₃ or BPh₃), leads to unique TM-substituted LA-stabilized bicyclo[1.1.0]tetraphosphabutane anions [Cp*Fe(CO)₂(η¹-P₄·LA)]⁻. Their P-nucleophilic site can be subsequently protonated to afford the transient LA-free neutral butterflies *exo,endo*- and *exo,exo*-Cp*Fe(CO)₂(η¹-P₄H), allowing controllable stepwise metalate-mediated functionalization of P₄.

Organophosphorus compounds (OPCs) play a crucial role in synthetic chemistry,^[1] but are typically produced through large-scale halogenation of white phosphorus (P₄ → PCl₃) and subsequent salt elimination, generating equimolar halogenide waste. However, this is avoidable by direct functionalization of the P₄ tetrahedron. This desirable avenue has been scrutinized for both main-group compounds^[2] and transition-metal (TM) complexes, ultimately in search of catalytic conversions.^[3] The challenge is to control the unpredictable reactivity of P₄. To date, steps invoking reducing neutral metal complexes have

been reported by, for example, the groups of Scheer (Fe),^[4] Driess (Fe,^[5] Co,^[6] and Ni),^[7] and Cummins (Nb)^[8] and cations by Peruzzini and co-workers (Fe,^[9] Ru,^[10] Rh, and Ir).^[11] However, in spite of its inherent electrophilic character, reactions of P₄ with TM anions have hardly been considered.

In 2002, Ellis and co-workers provided the first insights by reacting P₄ with a naphthalene-stabilized titanate that afforded the all-inorganic metallocene [(η⁵-P₅)₂Ti]²⁻ (**A**; Scheme 1).^[12]



Scheme 1. Anionic metal-mediated P₄ functionalization products (counter cations omitted). Cp = C₅H₅, Cp* = C₅(CH₃)₅, BIAN = 1,2-bis(2,6-diisopropylphenylimino)acenaphthene.

Later, Wolf and co-workers described the formation of iron polyphosphides **B** and **C** through P₄-aggregation induced by anionic [Cp*Fe(η⁴-C₁₀H₈)]⁻ (Cp* = C₅(CH₃)₅),^[13] and recently the preparation of dinuclear cobalt tetraphosphido complex **D** by reaction of P₄ with [Co(BIAN)(cod)]⁻ (BIAN = 1,2-bis(2,6-diisopropylphenylimino)acenaphthene, cod = 1,5-cyclooctadiene).^[14] The group of Ruiz reported the fragmentation of P₄ into P₂ (**E**), facilitated by the triply bonded molybdenate [Mo₂Cp₂(μ-PCy₂)(μ-CO)₂]⁻ (Cp = C₅H₅).^[15,16]

The marked unpredictability when using metal anions is reminiscent to the often uncontrolled reactions of P₄ with carbanions.^[17] For this, we developed a selective functionalization strategy by trapping the initial P₄ adduct (using sterically encumbered ArylLi) with Lewis acids to give stabilized bicyclo[1.1.0]tetraphosphabutane anions ([ArylP₄·LA]⁻; LA = B(C₆F₅)₃ or BPh₃) that can be substituted or fragmented to novel OPCs containing P₄, P₃, and P₁ units.^[18] Herein, we show this approach to also allow the [Cp*Fe(CO)₂]⁻ anion to functionalize P₄ in a controlled manner, providing the first examples of LA-stabilized TM(η¹-P₄)⁻ butterfly anions (**1 a** and **1 b**; Scheme 1),

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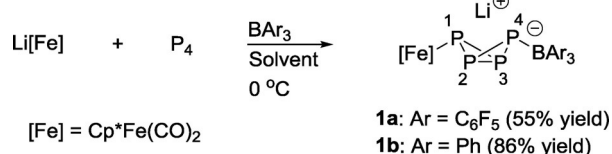
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and report on their P-nucleophilicity by protonation experiments.

To selectively generate anionic TM(η^1 -P₄)⁻ from P₄, we reasoned that a stable, bulky metalate with well-defined nucleophilic character would be required, for which the readily available Li[Cp*Fe(CO)₂] was considered a good candidate.^[19] To capture the incipient phosphide, we opted for B(C₆F₅)₃ as strong LA. Indeed, addition of a solution of P₄ in toluene to a cooled (0 °C) mixture of Li[Cp*Fe(CO)₂] and B(C₆F₅)₃ instantaneously gave the novel LA-stabilized bicyclo[1.1.0]tetraphosphabutane **1a** ($\delta^{31}\text{P}\{^1\text{H}\}$: -65.0 (P1), -107.1 (P4), -340.7 (P2/P3) ppm), which could be isolated in 55% yield as a dark yellow powder (Scheme 2).



Scheme 2. Synthesis of Lewis-acid-stabilized [Cp*Fe(CO)₂(η^1 -P₄)⁻] butterfly anions. Solvent: toluene for **1a** and THF for **1b**.

Crystals of **1a**, suitable for single-crystal X-ray diffraction, were grown from Et₂O after slow (1 min) addition of 12-crown-4. The molecular structure revealed the unprecedented metal-phosphido-borane (Figure 1; [Li(12-crown-4)₂]⁺ counter cation omitted) with a bicyclic P₄ core (P1–P2–P3–P4 98.21(6)°) showing a slightly shorter transannular P2–P3 bond (2.1676(13) Å) compared to the peripheral P1–P2/P1–P3 (2.2324(13)/2.2100(12) Å) and P4–P2/P4–P3 (2.2091(13)/2.2252(13) Å) bonds, as is common for P₄ butterfly-type derivatives.^[18,20,21] Compound **1a** features a non-symmetric substitution pattern with the tetraphosphide unit being flanked by the Cp*Fe(CO)₂ moiety (Fe1–P1 2.3192(11) Å) and the B(C₆F₅)₃ (P4–B1 2.080(4) Å) Lewis acid. The “Lewis” bond is marginally longer than that found in the related organyl-substituted anion Li[Mes*P₄-B(C₆F₅)₃] (P–B 2.064(2) Å),^[18a] whereas the coordination bond connecting the iron complex is shorter than that observed in the neutral symmetric [(Cp*Fe(CO)₂Fe)(μ , η^1 -P₄)] (Fe–P 2.3552(19) Å).^[20a]

Having established the formation of the [Cp*Fe(CO)₂(η^1 -P₄)⁻] butterfly anion, we wondered whether the weaker Lewis acid BPh₃ would, likewise, enable its isolation.^[22] Indeed, addition of Li[Cp*Fe(CO)₂] to a THF solution of P₄ and BPh₃ at 0 °C afforded **1b** ($\delta^{31}\text{P}\{^1\text{H}\}$: -46.6 (P4), -84.3 (P1), -337.0 (P2/P3) ppm), which was isolated as a brown powder in 86% yield (Scheme 2). Notably, the Li[Cp*Fe(CO)₂]/BPh₃ combination in THF results in a higher yield than Li[Cp*Fe(CO)₂]/B(C₆F₅)₃ in toluene (86% and 55%, respectively), likely owing to better solubility of the anions in THF. Its use as a solvent for the synthesis of **1a**, however, is precluded, owing to formation of the reactive THF·B(C₆F₅)₃ adduct.^[23]

Phosphides **1a** and **1b** are the first examples of isolable TM-generated P₄ butterfly anions. ω B97X-D/6-311+G(2d,p)//6-31G(d) calculations (Scheme 3) revealed the nucleophilic addi-

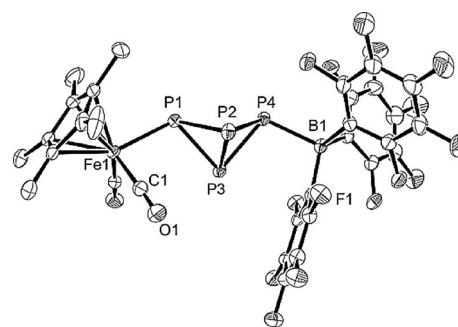
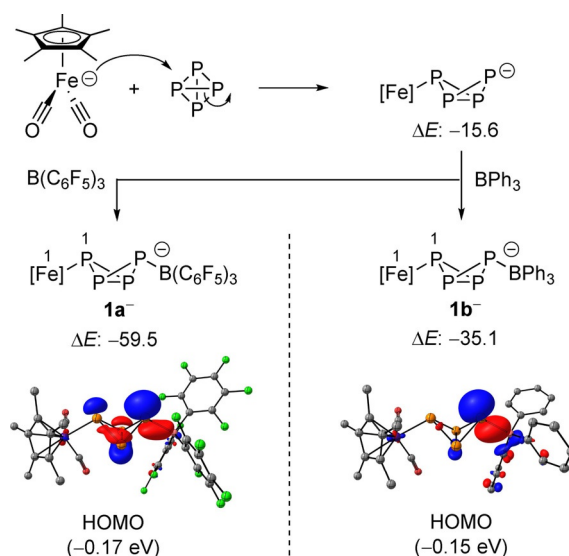


Figure 1. Molecular structure of **1a⁻** in the crystal (displacement ellipsoids are set at 30% probability; H atoms, [Li(12-crown-4)₂]⁺ counter cation and non-coordinated Et₂O molecules are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–P2/P3 2.2324(13)/2.2100(12), P4–P2/P3 2.2091(13)/2.2252(13), P2–P3 2.1676(13), Fe1–P1 2.3192(11), P4–B1 2.080(4), C1–O1 1.151(5); P1–P2–P3–P4 98.21(6).

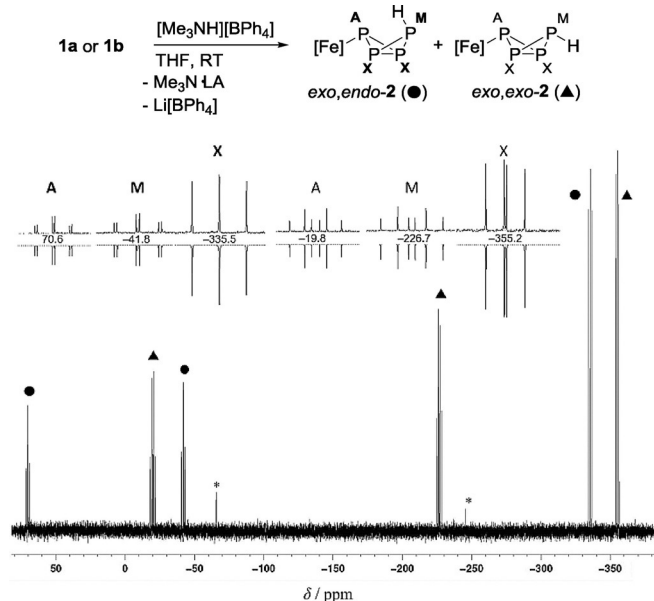


Scheme 3. Relative ω B97X-D/6-311+G(2d,p)//6-31G(d) energies (in kcal mol⁻¹) for the formation of anionic **1a⁻** and **1b⁻** and computed HOMOs (contour value = 0.05). [Fe] = Cp*Fe(CO)₂.

tion of [Cp*Fe(CO)₂]⁻ to P₄ to cause exothermic cleavage ($\Delta E = -15.6$ kcal mol⁻¹) of one P–P bond. The resulting [Cp*Fe(CO)₂(η^1 -P₄)⁻] “butterfly” anion is stabilized by a significant -59.5 kcal mol⁻¹ as the B(C₆F₅)₃ adduct (**1a⁻**) and by -35.1 kcal mol⁻¹ (ΔE) with the weaker bonding BPh₃ (**1b⁻**). The stronger bond with B(C₆F₅)₃, as compared to BPh₃, is reflected in the observed 19.3 ppm downfield shift of the ³¹P{¹H} NMR resonance for the P1 atom (**1a** vs. **1b**), owing to the larger electron-withdrawing effect of the fluorinated triarylborane. This difference in inductive effect also leads to a weaker Fe1–P1 bond in the B(C₆F₅)₃ adduct. ETS–NOCV analysis revealed a smaller total bonding energy to that in the BPh₃ adduct ($\Delta\Delta E = 13.7$ kcal mol⁻¹)^[24] and showed a lower contribution for σ donation in the orbital interaction terms (**1a⁻**: -101.6 ; **1b⁻**: -107.0 kcal mol⁻¹; π backdonation **1a⁻**: -10.6 ; **1b⁻**: -10.9 kcal mol⁻¹).^[25] The highest occupied molecular orbital (HOMO) reflects the lone pair on the boron-coordinated wing-tip P atom and is ex-

pectedly lower in energy for **1a**[−] (−0.17 eV) compared to **1b**[−] (−0.15 eV), suggesting P-nucleophilic character for both.

To probe the utility of anions **1a** and **1b** as nucleophilic reagents, protonation experiments were performed by using the mild acid [Me₃NH][BPh₄] in THF.^[26] Addition of the acid to the most reactive phosphide **1b** (1:1 stoichiometry) showed, in the ³¹P{¹H} NMR spectrum, the instantaneous formation of two new bicyclo[1.1.0]tetraphosphabutanes, which were identified as the neutral protonated LA-free *exo,endo* and *exo,exo* isomers of Cp*Fe(CO)₂(η¹-P₄H) (**2**, 1:1.2 ratio; Scheme 4). Simulation of

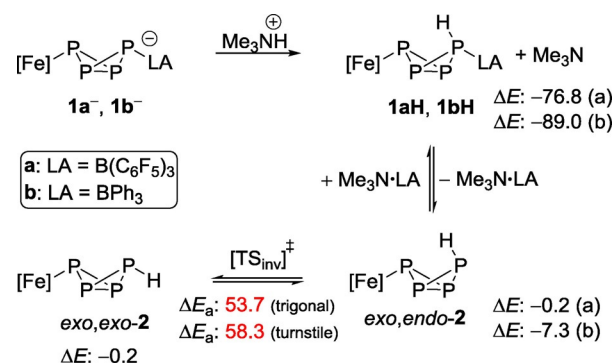


Scheme 4. Top: Protonation of **1a** and **1b**. [Fe] = Cp*Fe(CO)₂, LA = B(C₆F₅)₃ (**1a**) or BPh₃ (**1b**). Bottom: ³¹P{¹H} NMR spectrum (162.0 MHz, [D₈]THF, 297 K) recorded directly after mixing **1b** and [Me₃NH][BPh₄]. Insets show expanded experimental and simulated^[27] (inverted) regions. The resonance signals marked with an asterisk (*) correspond to unidentified side products.

the ³¹P NMR resonances^[27] confirms the expected AMX₂ spin systems for *exo,endo*-**2** (δ_{PA} 70.6, δ_{PM} −41.8, δ_{PX} −335.5 ppm; ¹J_{PA,PX} = −194.5, ¹J_{PM,PX} = −198.4, ²J_{PA,PM} = 27.6 Hz) and *exo,exo*-**2** (δ_{PA} −19.8, δ_{PM} −226.7, δ_{PX} −355.2 ppm; ¹J_{PA,PX} = −166.4, ¹J_{PM,PX} = −149.9, ²J_{PA,PM} = 243.3 Hz). The isomers could be distinguished through the difference in the ²J_{PA,PM} (ΔJ = 215.7 Hz) and ¹J_{PH} (145.9 Hz *endo*-PH; 109.3 Hz *exo*-PH) coupling constants. The ¹H NMR spectrum showed a resonance for only the *endo*-PH isomer (−1.14 ppm; ¹J_{H,P} = 152.9 Hz). The ¹¹B{¹H} NMR spectrum revealed two signals at 27.3 and −8.4 ppm, attributed to the amine–borane adduct Me₃N·BPh₃ in equilibrium with its constituents and Li[BPh₄]. The phosphanes decompose within 24 h, owing to a lack of steric protection, which is common for neutral bicyclic tetraphosphanes bearing “small” substituents.^[18a,c]

Protonation of the less reactive **1a**, likewise, gave a mixture of *exo,endo*-**2** and *exo,exo*-**2** (1:1.2 ratio) with Me₃N·B(C₆F₅)₃ (δ¹¹B{¹H} = −3.0 ppm) as the sole byproduct. We resorted to DFT calculations to obtain more insight into the product formation from the different precursors **1a**[−] and **1b**[−]

(Scheme 5).^[28] Protonation of the anions by Me₃NH⁺ to give **1aH** or **1bH** was calculated to be quite exothermic (ΔE = −76.8 and −89.0 kcal mol^{−1}, respectively), as expected.^[29] Subsequent cleavage of the *exo*-cyclic P–B bonds by the liberated



Scheme 5. Relative ωB97X-D/6-311+G(2d,p)//6-31G(d) energies (in kcal mol^{−1}) for the formation of **2**. [Fe] = Cp*Fe(CO)₂.

NMe₃ is driven by the formation of the amine–borane adduct and gives *exo,endo*-**2**. This reaction is more exothermic for BPh₃ (**b**, ΔE = −7.3 kcal mol^{−1}) than B(C₆F₅)₃ (**a**, ΔE = −0.2 kcal mol^{−1}). The *exo,exo*-**2** isomer was computed to be almost equally stable (ΔE = −0.2 kcal mol^{−1}) and is likely formed experimentally through Lewis or Brønsted acid enhanced isomerization^[30] in light of the high trigonal and turnstile inversion barriers of 53.7 and 58.3 kcal mol^{−1}, respectively.^[31]

The selective protonation at the wing-tip P atoms of the complexed P₄ anions **1a** and **1b** confirms their P-nucleophilic character and provides a simple route to hitherto scarce non-symmetrical neutral TM-complexed P₄ derivatives. The reactivity is analogous to the organyl-substituted congeners and should, therefore, be extendable to alkylations and possibly [3+1] fragmentations, on which we reported recently.^[18c] The present report lies the foundation for the isolation of new TM-mediated P₄-functionalized products.

In conclusion, reacting anionic Li[Cp*Fe(CO)₂] with P₄ in the presence of either the B(C₆F₅)₃ or BPh₃ Lewis acid provides facile access to unique metal-substituted bicyclo[1.1.0]tetraphosphabutane anions. Their P-nucleophilic site can be protonated, affording the novel transient LA-free tetraphosphanes *exo,endo*- and *exo,exo*-Cp*Fe(CO)₂(η¹-P₄H). The controlled and selective formation of these intriguing new anionic and neutral derivatives enables the selective functionalization of white phosphorus by anionic metalates to be explored.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: anions · iron · Lewis acids · P₄ functionalization · white phosphorus

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- [25] The remainder of ΔΔE_{total} arises primarily from a lower electrostatic interaction energy: ΔE_{elstat} **1a**[−]: −234.3; **1b**[−]: −254.0 kcal mol^{−1} (ΔE_{Pauli} **1a**[−]: 156.4; **1b**[−]: 169.4 kcal mol^{−1}).
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