Metallate-Mediated Functionalization of P₄ by Trapping Anionic [Cp*Fe(CO)$_2$(η$^1$-P₄)]$^-$ with Lewis Acids

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Metalate-Mediated Functionalization of $P_4$ by Trapping Anionic $[\text{Cp}^*\text{Fe}(\text{CO})_2(\eta^1-P_4)]^-$ with Lewis Acids


The development of selective functionalization strategies of white phosphorus ($P_4$) 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 $P_4$ with a metal anion [$\text{Cp}^*\text{Fe}(\text{CO})_2]^-$ ($\text{Cp}^* = \text{C}_5(\text{CH}_3)_5$), which, in the presence of bulky Lewis acids (LA; $\text{Bi}(_2\text{H}_3)_3$, or $\text{BPh}_3$), leads to unique TM-substituted LA-stabilized bicyclo[1.1.0]tetraphosphido anions [$\text{Cp}^*\text{Fe}(\text{CO})_2(\eta^1-P_4\cdot\text{LA})]^-$.$^3$ Their P-nucleophilic site can be subsequently protonated to afford the transient LA-free neutral butterflies $\text{exo,endo-}$ and $\text{exo,exo-}$-$\text{Cp}^*\text{Fe}(\text{CO})_2(\eta^1-P_4\cdot\text{H})$, allowing controllable stepwise metalate-mediated functionalization of $P_4$.

Organophosphorus compounds (OPCs) play a crucial role in synthetic chemistry, but are typically produced through large-scale halogenation of white phosphorus ($P_4 \to \text{PCI}_3$) and subsequent salt elimination, generating equimolar halogenide waste. However, this is avoidable by direct functionalization of the $P_4$ tetrahedron. This desirable avenue has been scrutinized for both main-group compounds$^5$ and transition-metal (TM) complexes, ultimately in search of catalytic conversions.$^6$ The challenge is to control the unpredictable reactivity of $P_4$. To date, steps invoking reducing neutral metal complexes have been reported by, for example, the groups of Scheer (Fe),$^6$ Driess (Fe,$^5$ Co,$^5$ Nb,$^7$ and Ni,$^8$) and Cummins (Nb)$^9$ 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 $P_4$ with TM anions have hardly been considered.

In 2002, Ellis and co-workers provided the first insights by reacting $P_4$ with a naphthalene-stabilized titanate that afforded the all-inorganic metalloocene [$(\eta^1-P_4)_2\text{Ti}^2$]$^-$ (A; Scheme 1).$^{12}$ Later, Wolf and co-workers described the formation of iron polyporphidines B and C through $P_4$-aggregation induced by anionic [$(\eta^1-C_5(\text{H}_3))_2\text{Fe}^-$] and recently the preparition of dinuclear cobalt tetraphosphido complex D by reaction of $P_4$ with both [Co(BIAN)(cod)$_2$]$^-$ (BIAN = 1,2-bis(2,6-disopropylphenyl)imino)acenaphthene, cod$_2$ (1,5-cyclooctadiene)$^{14}$ The group of Ruiz reported the fragmentation of $P_4$, facilitated by the triply bonded molybdenate [Mo$_2$CP$_3$($\mu$-PC$_3$)$_2$] that can be substituted or fragmented to novel OPCs containing $P_4$, $P_3$, and $P_1$ units.$^{18}$ Herein, we show this approach to also allow the [$(\eta^1-P_4)_2\text{Fe}^-$] anion to functionalize $P_4$ in a controlled manner, providing the first examples of LA-stabilized TM($\eta^1-P_4)_2^-$ butterfly anions (1a and 1b; Scheme 1).

Scheme 1. Anionic metal-mediated $P_4$ functionalization products (counter cations omitted). $\text{Cp} = \text{C}_5(\text{H}_5)_5$, $\text{Cp}^* = \text{C}_5(\text{CH}_3)_5$, BIAN = 1,2-bis(2,6-disopropylphenyl)imino)acenaphthene.
and report on their P-nucleophilicity by protonation experiments.

To selectively generate anionic TM(η1-P4)− from P4, we reasoned that a stable, bulky metalate with well-defined nucleophilic character would be required, for which the readily available Li[CrFe(CO)3] 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 P3 in toluene to a cooled (0 °C) mixture of Li[CrFe(CO)3] and B(C6F5)3 instantaneously gave the novel LA-stabilized bicyclo[1.1.0]tetraphosphabutanide 1 a (δ13P1(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 [CrFe(CO)3(η1-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)])+ counter cation and non-coordinated Et2O molecules are omitted for clarity). Selected bond lengths (Å) and angles (°): P1–P1/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).

**Figure 1.** Molecular structure of 1a in the crystal (displacement ellipsoids are set at 30% probability; H atoms, [Li(12-crown-4)]+ counter cation and non-coordinated Et2O molecules are omitted for clarity).

**Scheme 3.** Relative ν09B7X-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] = CrFe(CO)3.

Having established the formation of the [CrFe(CO)3(η1-P4)]− butterfly anion, we wondered whether the weaker Lewis acid BPh3 would, likewise, enable its isolation.22 Indeed, addition of Li[CrFe(CO)3] to a THF solution of P3 and BPh3 at 0 °C afforded 1b (δ13P1(H): −66.6 (P4), −84.3 (P1), −337.0 (P2/P3) ppm), which was isolated as a brown powder in 86% yield (Scheme 2). Notably, the Li[CrFe(CO)3]/BPh3 combination in THF results in a higher yield than Li[CrFe(CO)3]/
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. ωB97X-D/6–311 + G(2d,p)/6-31G(d) calculations (Scheme 3) revealed the nucleophilic addi-

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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 [Me₂NH][BPH₃] in THF.[28] 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]tetraphosphabutenes, which were identified as the neutral protonated LA-free exo,endo and exo,exo isomers of Cp*Fe(CO)₂(P₃) (2: 1:1.2 ratio; Scheme 4). Simulation of (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.[28] Subsequent cleavage of the exo-cyclic P–B bonds by the liberated 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 P₁ anions 1a and 1b confirms their P-nucleophilic character and provides a simple route to hitherto scarce nonsymmetrical neutral TM-complexed P₂ 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.[32] The present report lies the foundation for the isolation of new TM-mediated P₂-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]tetraphosphabutenes anions. Their P-nucleophilic site can be protonated, affording the novel transient LA-free tetraphosphabutenes exo,endo- and exo,exo-Cp*Fe(CO)₂(P₃). 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 · $P_4$ functionalization · white phosphorus