Metalate-Mediated Functionalization of $P_4$ by Trapping Anionic $[\text{Cp}^*\text{Fe}(\text{CO})_2(\eta^1-P_4)]^-$ 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(η¹-P₄)]⁻ with Lewis acids.

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 Nb,[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 [(η¹-P₄)₂Ti]⁺ (A; Scheme 1).[12]

Later, Wolf and co-workers described the formation of iron polyphosphides B and C through P₄-aggregation induced by anionic [Cp*Fe(η¹-C₅H₅)]⁻ (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-disopropylphenylimino)acenaphthene).

The marked unpredictability when using metal anions is reminiscent to the often uncontrolled reactions of P₄ with carbanions.[15] For this, we developed a selective functionalization strategy by trapping the initial P₄ adduct (using sterically encumbered ArYLi with Lewis acids to give stabilized bicyclo[1.1.0]tetraphosphabutane anions [(ArY)₂LA]⁻; LA = (C₅F₁₀), or BPh₃) that can be substituted or fragmented to novel OPCs containing P₄, P₃, and P₄ 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 (1a and 1b; Scheme 1)
and report on their P-nucleophilicity by protonation experiments.

To selectively generate anionic TM(I)-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. 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]tetraphosphabutanide 1a (0.53P(1)(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).

\[
\text{Li[Fe] + P₄ \rightarrow \text{BA₃}}_{\text{Solvent \ 0 °C}} \rightarrow \{[\text{Fe}]^+ \text{P₂/P₃} \text{BA₃}\}
\]


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 omitted) with a bicyclic P₄ core (P1−P2−P3−P₄ 98.21(6)°) showing a slightly shorter transannular P2−P₃ bond (2.2167(13) Å) compared to the peripheral P1−P2/P1−P₃ (2.2324(13)/2.2100(12) Å) and P₄−P₃ (2.2091(13)/2.2252(13) Å) bonds, as is common for P₄⁻ butterfly-type derivatives. Indeed, addition of Li(Cp*Fe(CO)₂)₂ to a THF solution of P₄ afforded 1b (δ³P(1)(H): −46.6 (P1), −84.3 (P1), −337.0 (P2/P3) ppm), which was isolated as a brown powder in 86% yield (Scheme 2).

Having established the formation of the [Cp*Fe(CO)₂]⁻ P₄⁻ butterfly anion, we wondered whether the weaker Lewis acid BPh₃ would, likewise, enable its isolation. Indeed, addition of Li(Cp*Fe(CO)₂)₂ to a THF solution of P₄ and BPh₃ at 0 °C afforded 1b (δ³P(1)(H): −46.6 (P4), −84.3 (P1), −337.0 (P2/P3) ppm), which was isolated as a brown powder in 86% yield (Scheme 2).

Phosphides 1a and 1b are the first examples of isolable TM-generated P₄⁻ butterfly anions. ω97X-D/6–311 + G(2d,p)/6–31G(d) calculations (Scheme 3) revealed the nucleophilic addi-

tion of [Cp*Fe(CO)₂]⁻ to P₄ to cause exothermic cleavage (ΔE = −15.6 kcal mol⁻¹) of one P−P bond. The resulting [Cp*Fe(CO)₂]⁻ “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 (ΔΔE = 13.7 kcal mol⁻¹) 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(1)(H) 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–NOCCV analysis revealed a smaller total bonding energy to that in the BPh₃ adduct (ΔΔE = 13.7 kcal mol⁻¹) and showed a lower contribution for α 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). 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 [Me6NH][BPh4] in THF. Addition of the acid to the most reactive phosphate 1b (1:1 stoichiometry) showed, in the 31P{1H} NMR spectrum, the instantaneous formation of two new bicyclo[1.1.0]tetraphosphanes, which were identified as the neutral protonated LA-free exo,endo and exo,exo isomers of Cp*Fe(CO)2(η1-P,H) (2:1.12 ratio; Scheme 4). Simulation of (Scheme 5). Protonation of the anions by Me6NH+ to give 1aH or 1bH was calculated to be quite exothermic (ΔE = −76.8 and −89.0 kcal mol−1, respectively), as expected. 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 Bronsted acid enhanced isomerization in light of the high trigonal and turnstile inversion barriers of 53.7 and 58.3 kcal mol−1, respectively.

The selective protonation at the wing-tip P atoms of the complexed P 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. 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 of the B(C6F5)3 or BPh3 Lewis acid provides facile access to unique metal-substituted bicyclo[1.1.0]tetraphosphaned 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-P,H). 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.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

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

[14] The reaction of LiCp²Fe(CO)₃ with P in THF in absence of Lewis acid showed no bicyclic tetraphosphorus species in the reported [P₄H] NMR spectrum, and only several broad signals between 100 and −200 ppm indicative of a mixture of iron polyphosphides (see the Supporting Information).
[15] The same trend was observed in studies using AryLı reagents, see Ref. [18].
[16] ETS-NOCL analyses were performed at ZORA-PPP6-D3/TZ2P usingADF2014; see the Supporting Information for details.
[17] The remainder of ΔE(π) arises primarily from a lower electrostatic interaction energy: ΔE(π) = −234.3; b) = −254.0 kcal mol⁻¹ (ΔE(π) = 156.4; b) = 169.4 kcal mol⁻¹).
[18] This acid was found to selectively protonate the previously reported Li[Si₄P₆]⁺, see Ref. [18].
[19] Spectral parameters were determined by iterative full line shape analysis using the gnm simulation program: P. H. M. Budzelaar, gNMR, Version 5.06.0.0. 2006.
[20] DFT calculations were performed at the cc-pVQZ-D/6–311 + (G(d,p)/6-31G(d)) level of theory using Gaussian09 (Revision D.01); see the Supporting Information for further details.
[21] Protonation energies are overestimated in the gas phase and are moderated in solution because of solvent stabilization of the charges.

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