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)₅]⁻ (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)₅(C₄H₆–P₄LA)]⁻. Their P-nucleophilic site can be subsequently protonated to afford the transient LA-free neutral butterflies exo,endo- and exo,exo-Cp*Fe(CO)₅(C₄H₆–P₄), 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 metal complexes have been reported, by for example, the groups of Scheer (Fe),[4] Dries (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 metalloocene [(η⁵–P₄)₂Ti]⁻ (A; Scheme 1).[12]

Later, Wolf and co-workers described the formation of iron polyphosphabiphosphido complexes B and C through P₄-aggregation induced by anionic [Cp*Fe(CO)₅(C₆H₅–PCy)]⁻ (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 [(AryP₄–LA)]⁻ (LA = B(C₆F₅)₃ or BPh₃) that can be substituted or fragmented to novel OPCs containing P₄, P₃, and P₂ units.[16] Herein, we show this approach to also allow the [Cp*Fe(CO)₅]⁻ anion to functionalize P₄ in a controlled manner, providing the first examples of LA-stabilized TM(η⁵–P₄)⁻ butterfly anions (1a and 1b; Scheme 1),

Scheme 1. Anionic metal-mediated P₄ functionalization products (counter cations omitted). Cp = C₅H₅, Cp* = C₅(CH₃)₅, BIAN = 1,2-bis(2,6-disopropylphenylimino)acenaphthene.
and report on their P-nucleophilicity by protonation experiments. To selectively generate anionic TM[\(\eta^1\)-P\(_4\)]\(^-\) from P\(_4\), we reasoned that a stable, bulky metatate with well-defined nucleophilic character would be required, for which the readily available Li[Cp*Fe(CO)]\(_3\) was considered a good candidate.\(^{19}\) To capture the incipient phosphido, we opted for B(C\(_6\)F\(_5\))\(_3\) as strong LA. Indeed, addition of a solution of P\(_4\) in toluene to a cooled (0 °C) mixture of Li[Cp*Fe(CO)]\(_3\) and B(C\(_6\)F\(_5\))\(_3\), instantaneously gave the novel LA-stabilized bicyclo[1.1.0]tetraphosphaphubute 1a (\(\delta^{13}\)P(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).

\[
\text{Li}[\text{Fe}] + \text{P}_4 \xrightarrow{\text{BA}_3 \text{Solvent}} 0^\circ C \quad 1a: \text{Ar} = \text{C}_6\text{F}_5 (55\% \text{ yield}) \\
1b: \text{Ar} = \text{Ph} (86\% \text{ yield})
\]

Scheme 2. Synthesis of Lewis-acid-stabilized [Cp*Fe(CO)]\(_2\)(\(\eta^1\)-P\(_4\))\(^-\) butterfly anions. Solvent: toluene for 1a and THF for 1b.

Crystals of 1a, suitable for single-crystal X-ray diffraction, were grown from Et\(_2\)O 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 P\(_4\) core (P1–P2–P3–P4 98.21(6)°) showing a slightly shorter transannular P2–P3 bond (2.1768(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 P\(_4\) 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)\(_3\) moiety (Fe1–P1 2.3192(11) Å) and the B(C\(_6\)F\(_5\))\(_3\) (P4–B1 2.080(4) Å) Lewis acid. The “Lewis” bond is marginally longer than that found in the related substituted anion Li[Mes\(_2\)]\(_2\)B(C\(_6\)F\(_5\))\(_3\) (P–B 2.0642(2) Å),\(^{19d}\) whereas the coordination bond connecting the iron complex is shorter than that observed in the neutral symmetric [(Cp*[t]Fe)\(_2\)](\(\mu_2\)(\(\eta^1\)-P\(_4\))\(^-\)) (Fe–P 2.3552(19) Å).\(^{20a}\)

Having established the formation of the [Cp*Fe(CO)]\(_2\)(\(\eta^1\)-P\(_4\))\(^-\) butterfly anion, we wondered whether the weaker Lewis acid BPH\(_3\) would, likewise, enable its isolation.\(^{22}\) Indeed, addition of Li[Cp*Fe(CO)]\(_3\) to a THF solution of P\(_4\) and BPH\(_3\) at 0 °C afforded 1b (\(\delta^{13}\)P(H): −466.4 (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)]\(_3\)/BPH\(_3\) combination in THF results in a higher yield than Li[Cp*Fe(CO)]\(_2\)/B(C\(_6\)F\(_5\))\(_3\) 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(C\(_6\)F\(_5\))\(_3\) adduct.\(^{23}\)

Phosphides 1a and 1b are the first examples of isolable TM-generated P\(_4\) butterfly anions. \(\delta^{19}\)F(0)/D=6–311+G(2d,p)/6-31G(d) calculations (Scheme 3) revealed the nucleophilic addition of [Cp*Fe(CO)]\(_3\) to P\(_4\) to cause exothermic cleavage (\(\Delta\varepsilon = −15.6\) kcal mol\(^{-1}\)) of one P–P bond. The resulting [Cp*Fe(CO)]\(_2\)(\(\eta^1\)-P\(_4\))\(^-\) “butterfly” anion is stabilized by a significant −59.5 kcal mol\(^{-1}\) as the B(C\(_6\)F\(_5\))\(_3\) adduct (1a) and by −35.1 kcal mol\(^{-1}\) (\(\Delta\varepsilon\)) with the weaker bonding BPH\(_3\) (1b). The stronger bond with B(C\(_6\)F\(_5\))\(_3\) as compared to BPH\(_3\), is reflected in the observed 19.3 ppm downfield shift of the \(\delta^{13}\)P(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(C\(_6\)F\(_5\))\(_3\) adduct. ETS–NOCV analysis revealed a smaller total bonding energy to that in the BPH\(_3\) adduct (\(\Delta\varepsilon = 13.7\) kcal mol\(^{-1}\)) and showed a lower contribution for \(\pi\) donation in the orbital interaction terms (1a: −101.6; 1b: −107.0 kcal mol\(^{-1}\); \(\pi\) backdonation 1a: −10.6; 1b: −10.9 kcal mol\(^{-1}\)).\(^{23}\) 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 [Me\(_{3}\)NH][BPh\(_{4}\)] in THF.\[26\] Addition of the acid to the most reactive phosphide 1b (1:1 stoichiometry) showed, in the \(^{31}\)P[H] NMR spectrum, the instantaneous formation of two new bicyclo[1.1.0]tetraphosphabutanes, which were identified as the neutral protonated LA-free \(\text{exo,endo}\) and \(\text{exo,exo}\) isomers of Cp\(^*\)Fe(CO)\(_{3}\)(\(\eta^{1}\)-P,H) (2; 1:1.2 ratio; Scheme 4). Simulation of (Scheme 5).\[28\] Protonation of the anions by Me\(_{3}\)NH\(^{+}\) to give 1aH or 1bH was calculated to be quite exothermic (\(\Delta E = -76.8\) and \(-89.0\) kcal mol\(^{-1}\), respectively), as expected.\[28\] Subsequent cleavage of the \(\text{exo-cyclic P}\_B\) bonds by the liberated NMe\(_{3}\) is driven by the formation of the amine–borane adduct and gives \(\text{exo,endo}\)-2. This reaction is more exothermic for BPh\(_{3}\) (b, \(\Delta E = -7.3\) kcal mol\(^{-1}\)) than B(C\(_6\)F\(_5\))\(_3\) (a, \(\Delta E = -0.2\) kcal mol\(^{-1}\)). The \(\text{exo,exo}\)-2 isomer was computed to be almost equally stable (\(\Delta E = -0.2\) kcal mol\(^{-1}\)) and is likely formed experimentally through Lewis or Bransted 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 P\(_{4}\) anions 1a and 1b confirms their P-nucleophilic character and provides a simple route to hitherto scarce non-symmetrical neutral TM-complexed \(\text{P}_4\) 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 \(\text{P}_4\)-functionalized products.

In conclusion, reacting anionic Li(Cp\(^*\)Fe(CO))\(_{2}\) with P\(_{4}\) in the presence of either the B(C\(_6\)F\(_5\))\(_3\) or BPh\(_{3}\) 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 tetraphosphabutanes \(\text{exo,endo}\)- and \(\text{exo,exo}\)-Cp\(^*\)Fe(CO)\(_{3}\)(\(\eta^{1}\)-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.

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Conflict of Interest

The authors declare no conflict of interest.

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


[15] The reaction of Li[Cp*Fe(CO)2Cl] with P4 in THF in absence of Lewis acid showed no bicyclic tetraphosphorus species in the recorded [1R]H NMR spectrum, and only several broad signals between 100 and −200 ppm indicative of a mixture of iron polyphosphides (see the Supporting Information).

[16] The same trend was observed in studies using ArYlLi reagents, see Ref. [18].

[17] ETS-NOCV analyses were performed at ZORA-BP86-D3/TZ2P using ADF2014; see the Supporting Information for details.

[18] The remainder of ΔEtotal, arises primarily from a lower electrostatic interaction energy: ΔEint, 1a* = −234.3; 1b* = −254.0 kcal mol−1 (ΔEint, 1a* = 156.4; 1b* = 169.4 kcal mol−1). This method was found to selectively protonate the previously reported Li[Mes*P2]Cl, see Ref. [18].

[19] Spectral parameters were determined by iterative full line shape analysis using the gNMR simulation program: P.H. M. Budzelaar, gNMR, Version 5.0.6.0.2006.

[20] DFT calculations were performed at the mB97X-D/6-31 +[G(d,p)/6-31G(d)] level of theory using Gaussian09 (Revision D.01); see the Supporting Information for further details.


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