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 (P\textsubscript{4}) is important to avoid the current chlorinated intermediates. The use of transition metals (TM)s 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\textsubscript{4} with a metal anion [Cp\textsuperscript{*}Fe(CO)\textsubscript{2}(η\textsuperscript{1}-P\textsubscript{4})\textsuperscript{-}] with Lewis Acids (LA) and recently the group of Ruiz reported the fragmentation of P\textsubscript{4} and Ni,\textsuperscript{(Cp*)} (Cp* = C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5}), which is, in the presence of bulky Lewis acids (LA; B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} or BPh\textsubscript{3}), leads to unique TM-substituted LA-stabilized bicyclo[1.1.0]tetraphosphabutane anions [Cp\textsuperscript{*}Fe(CO)\textsubscript{2}(η\textsuperscript{1}-P\textsubscript{4}LA)]. Their P-nucleophilic site can be subsequently protonated to afford the transient LA-free neutral butterflies \textit{exo},\textit{endo}- and \textit{exo,exo}-Cp\textsuperscript{*}Fe(CO)\textsubscript{2}(η\textsuperscript{1}-P\textsubscript{4}H), allowing controllable stepwise metalate-mediated functionalization of P\textsubscript{4}.

Organophosphorus compounds (OPCs) play a crucial role in synthetic chemistry,\textsuperscript{[1]} but are typically produced through large-scale halogenation of white phosphorus (P\textsubscript{4} → PCl\textsubscript{3}) and subsequent salt elimination, generating equimolar halogenide waste. However, this is avoidable by direct functionalization of the P\textsubscript{4} tetrahedron. This desirable avenue has been scrutinized for both main-group compounds\textsuperscript{[2]} and transition-metal (TM) complexes, ultimately in search of catalytic conversions.\textsuperscript{[3]} The challenge is to control the unpredictable reactivity of P\textsubscript{4}. To date, steps invoking reducing neutral metal complexes have been reported by, for example, the groups of Scheer (Fe),\textsuperscript{[4]} Driess (Fe,\textsuperscript{[5]} Co,\textsuperscript{[6]} and Ni),\textsuperscript{[7]} and Cummins (Nb)\textsuperscript{[8]} and cations by Peruzzini and co-workers (Fe,\textsuperscript{[9]} Ru,\textsuperscript{[10]} Rh, and Ir).\textsuperscript{[11]} However, in spite of its inherent electrophilic character, reactions of P\textsubscript{4} with TM anions have hardly been considered.

In 2002, Ellis and co-workers provided the first insights by reacting P\textsubscript{4} with a naphthalene-stabilized titanate that afforded the all-inorganic metalloocene [(η\textsuperscript{1}-P\textsubscript{4})\textsubscript{2}Ti\textsuperscript{2-}] (A; Scheme 1),\textsuperscript{[12]}

Later, Wolf and co-workers described the formation of iron polyphosphides B and C through P\textsubscript{4}-aggregation induced by anionic [Cp\textsuperscript{*}Fe(η\textsuperscript{1}-C\textsubscript{5}H\textsubscript{5})\textsubscript{2}] (C\textsubscript{5}H\textsubscript{5} = C\textsubscript{5}(CH\textsubscript{3})\textsubscript{5}) and recently the preparation of dinuclear cobalt tetraphosphido complex D by reaction of P\textsubscript{4} with [Co(BIAN)(cod)]\textsuperscript{1-} (BIAN = 1,2-bis(2,6-disopropylphenylimino)acenaphthene).

The marked unpredictability when using metal anions is reminiscent to the often uncontrolled reactions of P\textsubscript{4} with carbanions.\textsuperscript{[13]} For this, we developed a selective functionalization strategy by trapping the initial P\textsubscript{4} adduct (using sterically encumbered AryLLi) with Lewis acids to give stabilized bicyclo[1.1.0]tetraphosphabutane anions [[(AryLLi)\textsubscript{2}LA]\textsuperscript{-}; LA = B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} or BPh\textsubscript{3}]) that can be substituted or fragmented to novel OPCs containing P\textsubscript{4}, P\textsubscript{3}, and P\textsubscript{2} units.\textsuperscript{[14]} Herein, we show this approach to also allow the [Cp\textsuperscript{*}Fe(CO)\textsubscript{2}]\textsuperscript{-} anion to functionalize P\textsubscript{4} in a controlled manner, providing the first examples of LA-stabilized TM(η\textsuperscript{1}-P\textsubscript{4})\textsuperscript{-} butterfly anions (1a and 1b; Scheme 1),
and report on their P-nucleophilicity by protonation experiments.

To selectively generate anionic TM[η^1-Pd] from Pd, we reasoned that a stable, bulky metalate with well-defined nucleophilic character would be required, for which the readily available Li[Cp*Fe(CO)] was considered a good candidate. To capture the incipient phosphide, we opted for B(C6F5) as strong LA. Indeed, addition of a solution of Pd in toluene to a cooled (0 °C) mixture of Li[Cp*Fe(CO)] and B(C6F5) instantaneously gave the novel LA-stabilized bicyclo[1.1.0]tetraphosphaphubutane 1a (δ^3P(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).

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 (°) are 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).

Having established the formation of the [Cp*Fe(CO)]− “butterfly” anion, we wondered whether the butterfly anion is stabilized by a significant inductive effect also leads to a weaker Fe1−P bond in the B(C6F5)3 adduct (1a) and by −35.1 kcal mol−1 (∆E) with the weaker bonding BPh3 (1b). The stronger bond with B(C6F5)3 compared to BPh3, reflected in the observed 19.3 ppm downfield shift of the 31P{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 leads to a weaker Fe1−P bond in the B(C6F5)3 adduct. ETS-NOCV analysis revealed a smaller total bonding energy to that in the BPh3 adduct (∆E = 13.7 kcal mol−1) and showed a lower contribution for σ donation in the orbital interaction terms (1a: −106; 1b: −107.0 kcal mol−1; π backdonation 1a: −106; 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-

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

![Scheme 3](image-url)  
**Scheme 3.** Relative ω0897X-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)3.
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\(_2\)NH][BPh\(_4\)] in THF.\(^{[26]}\) Addition of the acid to the most reactive phosphide 1b (1:1 stoichiometry) showed, in the \(^{31}\)P{\(^1\)H} 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)\(_3\)(\(\eta^1\)-P\(_3\)) (2, 1:1.2 ratio; Scheme 4). Simulation of (Scheme 5).\(^{[26]}\) Protonation of the anions by Me,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.\(^{[26]}\) Subsequent cleavage of the exo-cyclic P–B bonds by the liberated NMe\(_3\) is driven by the formation of the amine–borane adduct and gives 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 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 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 P\(_3\) anions 1a and 1b confirms their P-nucleophilic character and provides a simple route to hitherto scarce nonsymmetrical neutral TM-complexed P\(_3\) 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 P\(_3\)-functionalized products.

In conclusion, reacting anionic Li[Cp*Fe(CO)\(_3\)] with P\(_3\) 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 tetraphosphohanes \textit{exo,endo-} and \textit{exo,exo-Cp*Fe(CO)\(_3\)(\(\eta^1\)-P\(_3\))}. 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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