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)₄]⁻ (Cp* = C₅(CH₃)₅), which, in the presence of bulky Lewis acids (LA; B(Cl)F₃ or BPh₃), leads to unique TM-substituted LA-stabilized bicyclo[1.1.0]tetraphosphabutane anions [Cp*Fe(CO)₄(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)₄(η¹-P₄-H), allowing controllable stepwise metalate-mediated functionalization of P₄.

Organophosphorus compounds (OPCs) play a crucial role in synthetic chemistry, 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 and transition-metal (TM) complexes, ultimately in search of catalytic conversions. 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), Dries (Fe, Co, Ni) and Cummins (Nb) and cations by Peruzzini and co-workers (Fe, Ru, Rh, and Ir). 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 metalallocene ([η¹-P₄]₃Ti)₂⁻ ([A]; Scheme 1).

Later, Wolf and co-workers described the formation of iron polypephosphides B and C through P₂-aggregation induced by anionic [Cp*Fe(CO)₄(η¹-C₅H₅)]⁻ (Cp* = C₅(CH₃)₅) 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), cod = 1,5-cyclooctadiene. The group of Ruiz reported the fragmentation of P₄ into P₃ (E), facilitated by the triply bonded molybdenate [Mo₃(Cp₃)₄(μ-PCy₃)(μ-η¹-CO)]⁻ (Cp = C₅H₅).[15,16]

The marked unpredictability when using metal anions is reminiscent to the often uncontrolled reactions of P₄ with carbanions. For this, we developed a selective functionalization strategy by trapping the initial P₁ aduct (using sterically encumbered AryLii) 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 P₃, P₄, and P₁ units. Herein, we show this approach to also allow the [Cp*Fe(CO)₄]⁻ 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).

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\(\{n\}^{-}\) from \(P_{n}\) we reasoned that a stable, bulky metathate 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(C\(\text{F}_{3}\))\(_{3}\), as strong LA. Indeed, addition of a solution of \(P_{3}\) in toluene to a cooled (0 °C) mixture of Li[CP\(^{*}\)Fe(CO)]\(_{2}\) and B(C\(\text{F}_{3}\))\(_{3}\), instantaneously gave the novel LA-stabilized bicyclo[1.1.0]tetraphosphabutenate 1a (\(\Delta^{3}\)P\(^{3}\)(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).

\[
\text{Li}[\text{Fe}] + \text{P}_{4} \xrightarrow{\text{BA}_{3} \text{Solvent}} \text{Fe}^{+} + \text{P}_{4} \xrightarrow{0^\circ \text{C}} \text{Fe}^{+} \text{P}_{4} \text{BA}_{3}
\]

\(\text{[Fe]} = \text{CP}^{*}\text{Fe(CO)}_{2}\)

Scheme 2. Synthesis of Lewis-acid-stabilized [CP\(^{*}\)Fe(CO)\(_{2}\)]\(\{n\}^{-}\) 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 and non-coordinated Et\(_{2}\)O molecules are omitted for clarity). Selected bond lengths (\(\AA\)) and angles (\(^{\circ}\)) are given in Table 1.

![Scheme 3](image-url)  
Figure 1. Molecular structure of 1a in the crystal (displacement ellipsoids features an on-symmetric substitution pattern butterfly-type derivatives. In toluene (86% and 55%, respectively), likely owing to better solubility of the anions in THF. Its use as solvent for compounds 1a and 1b is excluded, owing to formation of the reaction THF-B(C\(\text{F}_{3}\))\(_{3}\) adduct.\(^{20}\)

Having established the formation of the [CP\(^{*}\)Fe(CO)\(_{2}\)]\(\{n\}^{-}\) butterfly anion, we wondered whether the weaker Lewis acid BPh\(_{3}\) would, likewise, enable its isolation.\(^{22}\) Indeed, addition of Li[CP\(^{*}\)Fe(CO)]\(_{2}\) to a THF solution of \(P_{3}\) and BPh\(_{3}\) at 0 °C afforded 1b (\(\Delta^{3}\)P\(^{3}\)(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)]\(_{2}\)/BPh\(_{3}\) combination in THF results in a higher yield than Li[CP\(^{*}\)Fe(CO)]\(_{2}\)/B(C\(\text{F}_{3}\))\(_{3}\) 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\(\text{F}_{3}\))\(_{3}\) adduct.\(^{23}\)

Phosphides 1a and 1b are the first examples of isolable TM-generated \(P_{n}\) butterfly anions. \(\omega\text{B97X-D/6-311+G(2d,p)/6-31G(d)}\) calculations (Scheme 3) revealed the nucleophilic addi-
expectedly 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 phosphide 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 isolomers of Cp⁺Fe(CO)₂([η]³-P₄H) (2, 1:1.2 ratio; Scheme 4). Simulation of the ³¹P NMR resonances confirms their P-nucleophilic character and provides a simple route to hitherto scarce non-symmetrical neutral TM-complexed Pₓ 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 Pₓ-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]tetraphosphanes anions. Their P-nucleophilic site can be protonated, affording the novel transient LA-free tetraphosphanes exo,endo- and exo,exo-Cp⁺Fe(CO)₂([η]³-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.

Acknowledgements

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Scheme 5. Relative vS97X-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 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 P₄ anions 1a and 1b confirms their P-nucleophilic character and provides a simple route to hitherto scarce non-symmetrical neutral TM-complexed Pₓ 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 Pₓ-functionalized products.
Conflict of Interest

The authors declare no conflict of interest.

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

[8] The reaction of Li[Cp*Fe(CO)] with P₃ in THF in absence of Lewis acid showed no bicyclic tetraphosphorus species in the recorded 31P[H] NMR spectrum, and only several broad signals between 100 and −200 ppm indicative of a mixture of iron polyphosphides (see the Supporting Information).
[9] The same trend was observed in studies using AroyLi reagents, see Ref. [18].
[10] Theoretical calculations were performed at ZORA-BP86-D3/TZ2P usingADF2014; see the Supporting Information for details.
[11] The vanishing of ΔErsstp arises primarily from a lower electrostatic interaction energy: ΔErsstp = −234.3; 1b : −254.0 kcal mol⁻¹. This small value is a negative confirmation of the previously reported L(Mes*P₃)BP₃ reaction as described in Ref. [18].
[12] Spectral parameters were determined by iterative full line shape analysis using the gnm simulation program: P. H. M. Budzelaar, gnmVR, Version 5.06.0.0; DFT calculations were performed at the ωB97X-D/6-31G(d,p)//6-31G(d) level of theory using Gaussian09 (Revision D.01); see the Supporting Information for further details.
[13] Projection energies are overestimated in the gas phase and are modified in solution because of solvent stabilization of the charges.