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Borger, J.E.; Jongkind, M.K.; Ehlers, A.W.; Lutz, M.; Slootweg, J.C.; Lammertsma, K.

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Metallate-Mediated Functionalization of P₄ by Trapping Anionic [Cp*Fe(CO)₂(η¹-P₄)]⁻ with Lewis Acids


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]⁻ (Cp* = C₅(CH₃)₅), which, in the presence of bulky Lewis acids (LA; Bi(C₆F₅)₃ or BPh₃), leads to unique TM-substituted LA-stabilized bicyclo[1.1.0]tetraphosphabutane anions [Cp*Fe(CO)₂(η¹-P₄)L₂]. Their P₄-nucleophilic site can be subsequently protonated to afford the transient LA-free neutral butterflies exo,endo- and exo,exo-Cp*Fe(CO)(CO)(η¹-P₄H), allowing controllable stepwise metallate-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 neutral 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 metalloccene [(η¹-P₄)₂Ti]⁺ (A; Scheme 1).[12]

Later, Wolf and co-workers described the formation of iron polyporphospholes B and C through P₄-aggregation induced by anionic [Cp*Fe(CO)₂(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 AryLII) with Lewis acids to give stabilized bicyclo[1.1.0]tetraphosphabutane anions ([ArYp₂-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)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).

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.

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[a] J. E. Borger, M. K. Jongkind, Dr. A. W. Ehlers, Dr. J. C. Slootweg
Department of Chemistry and Pharmaceutical Sciences
Vrije Universiteit Amsterdam
De Boelelaan 1083, 1081 HV Amsterdam (The Netherlands)
E-mail: K.Lammertsma@vu.nl
[b] Dr. A. W. Ehlers, Prof. Dr. K. Lammertsma
Department of Chemistry, University of Johannesburg
Auckland Park, Johannesburg, 2006 (South Africa)
[c] Dr. M. Lutz
Crystal and Structural Chemistry
Bijvoet Center for Biomolecular Research, Utrecht University
Padualaan 8, 3584 CH Utrecht (The Netherlands)
[d] Dr. A. W. Ehlers, Dr. J. C. Slootweg
Van ’t Hoff Institute for Molecular Sciences, University of Amsterdam
Science Park 904, 1098 XH Amsterdam (The Netherlands)

Supporting Information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/open.201700027.

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and report on their P-nucleophilicity by protonation experiments.

To selectively generate anionic TM(η²-P₄)⁻ from P₄, we reasoned that a stable, bulky metatell ate 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]tetraphosphaphubutanide 1a (δ³P(H): 650.0 (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 [CP*Fe(CO)]₂(η²-P₄)]⁻ butterfly anions. Solvent: toluene for 1a and THF for 1b.](image)

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-borate (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 (2.1676(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 P₄ butterfly-type derivatives.18-21 Compounds 1a and 1b features a non-symmetric substitution pattern with the tetraphosphide unit being flanked by the Cp*Fe(CO)₂ moiety (Fe1–P1 2.3192(11) Å and the B(C₆F₅)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}⁺P₄B(C₆F₅)₃ (P-B 2.064(2) Å),22 whereas the coordination bond connecting the iron complex is shorter than that observed in the neutral symmetric [[CP*(CO)₂]Fe{μ₁-1-P₄}] (Fe-P 2.3552(19) Å).22

Having established the formation of the [CP*Fe(CO)]₂(η²-P₄)]⁻ butterfly anion, we wondered whether the weaker Lewis acid BPh₃ would, likewise, enable its isolation.22 Indeed, addition of Li(Cp*Fe(CO))₂ to a THF solution of P₄ and BPh₃ at 0 °C afforded 1b (δ³P(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))₂/BPh₃ combination in THF results in a higher yield than Li(Cp*Fe(CO))₂/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. ω97X-D/6-311 + G(2d,p)//6-31G(d) calculations (Scheme 3) revealed the nucleophilic addition of [CP*Fe(CO)]₂⁻ to P₄ to cause exothermic cleavage (∆E = −15.6 kcal mol⁻¹) of one P–P bond. The resulting [CP*Fe(CO)]₂(η²-P₄)]⁻ “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 (∆E) 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(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–NOCV analysis revealed a smaller total bonding energy to that in the BPh₃ adduct (∆ΔE = 13.7 kcal mol⁻¹) and showed a lower contribution for σ 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).24

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\(_2\)NH][PPh\(_3\)] in THF.\(^{[26]}\) Addition of the acid to the most reactive phosphide 1b (1:1 stoichiometry) showed, in the \(^{31}\)P[\(\text{H}\)] 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)\(_3\)\(\eta^2\)-PMe\(_3\)) (2, 1:1.2 ratio; Scheme 4). Simulation of (Scheme 5).\(^{[28]}\) Protonation of the anions by Me\(_2\)NH\(^+\) to give 1aH or 1bH was calculated to be quite exothermic (\(\Delta\text{E} = -76.8\) and −89.0 kcal mol\(^{-1}\)) respectively, as expected.\(^{[28]}\) 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, \(\Delta\text{E} = -7.3\) kcal mol\(^{-1}\)) than B(C\(_6\)F\(_5\))\(_3\) (a, \(\Delta\text{E} = -0.2\) kcal mol\(^{-1}\)). The exo,exo-2 isomer was computed to be almost equally stable (\(\Delta\text{E} = -0.2\) 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\(_2\) anions 1a and 1b confirms their P-nucleophilic character and provides a simple route to hitherto scarce non-symmetrical neutral TM-complexed P\(_2\) 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.\(^{[34]}\) The present report lies the foundation for the isolation of new TM-mediated P\(_2\)-functionalized products.

In conclusion, reacting anionic Li[Cp\(^*\)Fe(CO)\(_3\)] with P\(_2\) 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]tetraphosphanes anions. Their P-nucleophilic site can be protonated, affording the novel transient LA-free tetraphosphanes exo,endo- and exo,exo-Cp\(^*\)Fe(CO)\(_3\)\(\eta^2\)-PMe\(_3\)). 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

[6] The reaction of LiCp³Fe(CO)₃ with P in THF in absence of Lewis acid showed no bicyclic tetraphosphorus species in the recorded ²²P NMR spectrum, and only several broad signals between 100 and −200 ppm indicative of a mixture of iron polyphosphides (see the Supporting Information).
[7] The same trend was observed in studies using AryLi reagents, see Ref. [18].
[8] ETS-NOCV analyses were performed at ZORA-BP86-D3/TZ2P using ADF2014; see the Supporting Information for details.
[9] The remainder of ΔE₂₉₅°ₐ₅ arises primarily from a lower electrostatic interaction energy: ΔE₂₉₅°ₐ₅ = ΔE₂₉₅°ₐ₅ − ΔE₂₉₅°ₐ₅. This was found to selectively protonate the previously reported Li(MesP)₂(BPh₄)²⁺, see Ref. [18c].
[10] Spectral parameters were determined by iterative full line shape analysis using the gnmr simulation program: P. H. M. Budzelaar, gNMR, Version 5.0.6.0.0.
[11] DFT calculations were performed at the B3LYP-D3/B97XD level using Gaussian09 Revision D.01; see the Supporting Information for further details.
[12] Protonation energies are underestimated in the gas phase and are modified in solution because of solvent stabilization of the charges.
[13] Schulz et al. reported on the GaCl₂-N,N-dimethylformamide (DMF) and GaCl₂-N,N-dimethylacetamide (DMA) complexes; see Ref. [20].
[14] The GaCl₂-N,N-dimethylacetamide (DMA) complex was found to selectively protonate the previously reported Li(MesP)₂(BPh₄)²⁺, see Ref. [18c].
[15] Spectral parameters were determined by iterative full line shape analysis using the gnmr simulation program: P. H. M. Budzelaar, gNMR, Version 5.0.6.0.0.
[16] DFT calculations were performed at the B3LYP-D3/B97XD level using Gaussian09 Revision D.01; see the Supporting Information for further details.
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