

P₄ Functionalization

Functionalization of P₄ Using a Lewis Acid Stabilized Bicyclo-[1.1.0]tetraphosphabutane Anion**

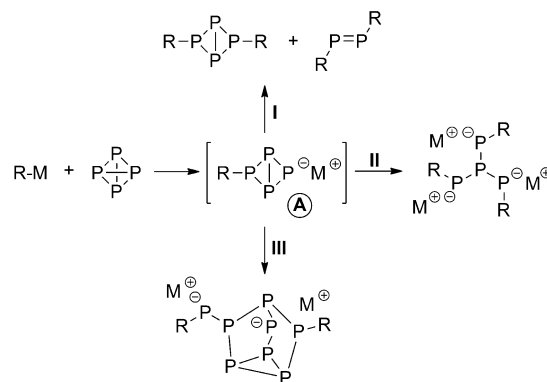
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In memory of Michael F. Lappert

Abstract: Reacting white phosphorus (P₄) with sterically encumbered aryl lithium reagents (aryl = 2,6-dimesitylphenyl or 2,4,6-tBu₃C₆H₂) and B(C₆F₅)₃ gives the unique, isolable Lewis acid stabilized bicyclo[1.1.0]tetraphosphabutane anion. Subsequent alkylation of the nucleophilic site of the RP₄ anion gives access to non-symmetrical disubstituted bicyclic tetraphosphorus compounds. This novel method enables P–C bond formation in a controlled fashion using white phosphorus as starting material.

White phosphorus (P₄) is the archetypal building block for organophosphorus compounds. Current conversions proceed through PCl₃, which is obtained by halogenation of P₄. The chlorine atoms are subsequently substituted with organic groups by salt metathesis, generating equimolar amounts of halogenide waste. Direct, selective processes are needed if chlorinated intermediates are to be circumvented.^[1] This conundrum has given rise to a plethora of P₄ chemistry, but selective, direct functionalization methods remain very scarce.^[2] Illustrative are Weigand's use of phosphonium ions that insert into P–P bonds to form P₅⁺ cage compounds,^[3] which react with ambiphilic NHCs^[4a] and chalcogens,^[4b] Bertrand's use of nucleophilic carbenes that selectively cleave P–P bonds^[5] to render P₄[–], P₂[–], and P₁[–]-fragments,^[6] and Scheer's very recent symmetrical functionalization by cyclopentadienyl radicals mediated by transition metals.^[7] In contrast, the use of anionic carbon-centered nucleophiles has barely been touched upon.

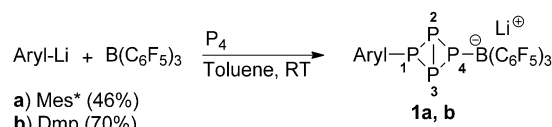
In 1963, Rauhut et al. showed that organoalkali reagents degrade P₄ to complex mixtures of polyphosphides, which on hydrolysis gave low conversions (0–40%) to primary and secondary phosphanes.^[8] Two decades later, Fluck and co-workers found P₄ to react with Mes*Li to give in low yield (<10%) a disubstituted P₄ butterfly compound and diphos-



Scheme 1. Investigations toward nucleophilic functionalization of P₄. I) R–M = Mes*Li (1.9 equiv), Et₂O, reflux, <10%;^[9] II) R–M = MesLi (3 equiv), benzene, RT, 60%;^[10] III) R–M = [K(18-crown-6)][Si(SiMe₃)₃] (1 equiv), toluene, RT, 29%.^[11]

phene Mes*–P=P–Mes* in a 3:1 ratio (Scheme 1, route I).^[9] Using instead three equiv of the less bulky MesLi, Lerner et al. obtained a trianionic tetraphosphide (Scheme 1, route II),^[10] whereas Wright et al. obtained with the bulkier hypersilyl complex [(Me₃Si)₃Si][–][K(18-crown-6)]⁺ a Zintl-type P₇-cage compound (Scheme 1, route III), supposedly from dimerization of anionic **A**.^[11] The common anion in these reactions is presumably the initial P₄ addition product.^[2b,12] We now present the isolation and characterization of a Lewis acid-stabilized version of RP₄ anion **A** as well as its selective functionalization.

To stabilize bicyclo[1.1.0]tetraphosphabutane anion **A** and avoid degradation and aggregation (Scheme 1), its reactivity must be tailored. We envisioned to accomplish this by activating and functionalizing P₄ with a bulky nucleophile in the presence of a Lewis acid, thereby mimicking an FLP approach.^[13,14] Gratifyingly, **1a** was formed on adding toluene at room temperature to a stoichiometric mixture of P₄, Mes*Li, and B(C₆F₅)₃ (Scheme 2). ³¹P{¹H} NMR spectroscopy showed a steady decrease (with 56% conversion in 4 weeks' time) of the P₄ resonance at –524 ppm with the



Scheme 2. Reaction of bulky nucleophiles and a Lewis acid with P₄.

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concurrent increase of only three new signals in a 1:1:2 ratio at, respectively, -125.7 (P1), -153.3 (P4) and -322.4 ppm (P2,3) (AMX₂ spin system). From the reaction mixture, 46 % of white solid **1a** could be isolated that is storable under inert conditions.

The molecular structure of **1a** obtained by an X-ray crystal structure determination (Figure 1)^[15] shows an RP₄ butterfly anion (fold angle = $93.61(3)^\circ$) capped with a toluene-complexed lithium cation that is coordinated to the P1

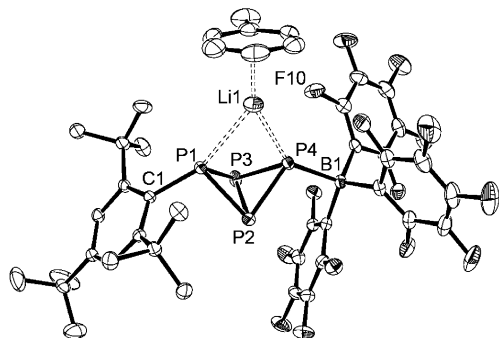


Figure 1. Molecular structure of **1a** in the crystal^[15] (ellipsoids are set at 50 % probability; hydrogen atoms are omitted for clarity). Selected bond lengths [Å], angle, and torsion angle [°]: P1–P2/P3 2.2166(6)/2.2286(6), P4–P2/P3 2.2031(6)/2.2177(7), P2–P3 2.1694(7), P1–P4 2.8183(7), C1–P1 1.8628(17), P4–B1 2.064(2), Li1–P1/P4 2.677(4)/2.504(4); P1–Li1–P4 65.81(8); P1–P2–P3–P4 93.61(3).

and P4 atoms. The P1–P2 (2.2166(6) Å), P1–P3 (2.2286(6) Å) and P4–P2 (2.2031(6) Å), P4–P3 (2.2177(7) Å) bonds are elongated compared to the bridgehead P2–P3 bond (2.1694(7) Å), which resembles those of neutral bicyclic analogues.^[16] The “Lewis” P4–B1 bond (2.064(2) Å) is of similar length to that of H₃P–B(C₆F₅)₃ (2.046(5) Å^[17]), but B3LYP/6-311 + G(d)//6-31 + G(d) calculations^[18] suggest it to be 17 kcal mol^{−1} stronger (**1a** 23.0; H₃P–B(C₆F₅)₃ 6.1 kcal mol^{−1}), which is attributable to the higher basicity of the anionic P₄ fragment.

The slow conversion of P₄ into **1a**, caused by the low solubility of Mes⁺Li in toluene, could not be improved by longer reaction times and variation in temperature.^[19] We then decided to use DmpLi (Dmp = 2,6-dimesitylphenyl), which readily dissolves in toluene. Reaction of a 1:1:1 mixture of DmpLi, B(C₆F₅)₃, and P₄ at room temperature gave only **1b** within one hour and in 70 % isolated yield (Scheme 2; $\delta^{31}\text{P}\{^1\text{H}\}$: -154.6 (P1), -172.0 (P4), and -342.9 ppm (P2,3)); $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed that full conversion of P₄ (instead of 84 %) could be achieved on using 1.5 equivalents of DmpLi and B(C₆F₅)₃.

Compound **1b** crystallizes as a centrosymmetric dimer (Figure 2) in which the Li⁺ cations are in tetrahedral environments^[20] with intramolecular Li⋯F interactions (2.149(3) Å) that are much shorter than the sum of the van der Waals radii ($\Sigma r(\text{vdW})[\text{Li}, \text{F}] = 3.28$ Å^[21]), but also much larger than the bond length computed for lithium fluoride (1.595 Å^[22,23]); the Li⋯F interactions were not observed in solution, as no Li–F coupling was detected in the ⁷Li and ¹⁹F NMR spectra. The

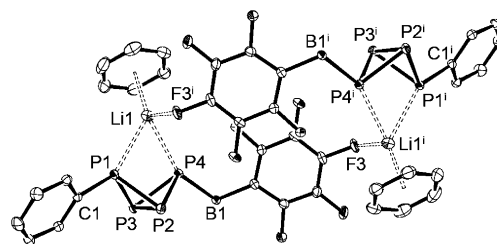


Figure 2. Molecular structure of **1b** in the crystal^[15] (ellipsoids are set at 50 % probability; hydrogen atoms, non-coordinated benzene solvent molecules, mesityl rings, and two C₆F₅ rings are omitted for clarity). Selected bond lengths [Å], angle, and torsion angle [°]: P1–P2/P3 2.2180(4)/2.2131(4), P4–P2/P3 2.2121(4)/2.2184(4), P2–P3 2.1793(4), P1–P4 2.8251(5), C1–P1 1.8413(12), P4–B1 2.0692(14), Li1–P1/P4 2.623(2)/2.661(2), Li1–F3 2.149(3), P1–Li–P4 64.64(6), P1–P2–P3–P4 94.16(2). Symmetry code (i): 1–x, 1–y, 1–z.

observed P4–B1 bond length (2.0692(14) Å) and its computed strength (23.8 kcal mol^{−1}) are similar to those of **1a**.

Bicyclo[1.1.0]tetraphosphabutanes **1a** and **1b** are to the best of our knowledge the first isolated monofunctionalized P₄ anions. B3LYP/6-311 + G(d)//6-31 + G(d) calculations reveal **1b** to result from nucleophilic attack of DmpLi onto P₄, causing a 20.6 kcal mol^{−1} exothermic scission of one P–P bond that is further enhanced (by 23.8 kcal mol^{−1}) by addition of the Lewis acid (Figure 3). No minimum could be found for end-on or side-on coordination of B(C₆F₅)₃ to P₄ and neither

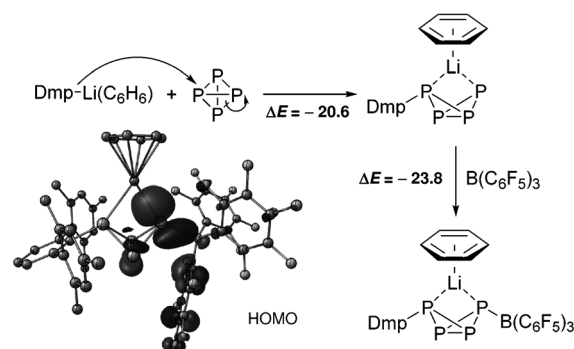
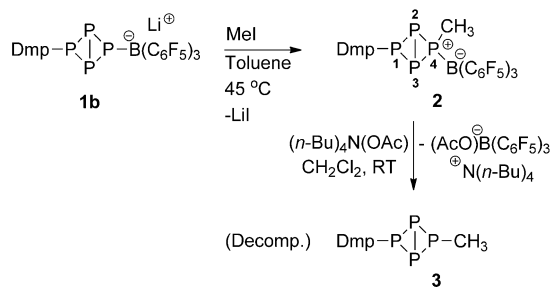


Figure 3. Calculated reaction pathway (E , kcal mol^{−1}) of the reaction of P₄ with DmpLi and B(C₆F₅)₃, and the HOMO of the calculated geometry of monomer **1b**.^[18]

could such complexes be detected by ³¹P NMR spectroscopy. This suggests a reaction sequence in which Dmp[−] attacks P₄ upon which the incipient anion is trapped by the Lewis acid. In fact, no Dmp-substituted P₄ anion could be detected without the Lewis acid, not even at -78°C , thereby further exemplifying its trapping role; only a mixture of polyphosphides resulted, in analogy to the studies by Rauhut et al.^[8]

To further functionalize P₄, we targeted the alkylation of **1b**, which would be expected to occur at the phosphorus atom bonded to the B(C₆F₅)₃ group, because it contributes most to the HOMO (Figure 3). Indeed, adding MeI to a solution of **1b** in toluene caused a downfield shift of the three $^{31}\text{P}\{^1\text{H}\}$ NMR resonances to -57.5 (P4), -154.2 (P1), and -296.4 ppm



Scheme 3. Methylation of **1b** giving the neutral P_4 butterfly **2**, and Lewis acid removal to obtain **3**.

(P2,3) (1:1:2 ratio; AMX₂ spin system ($^1J_{P(4),P(2,3)} = 286.7$ Hz, $^1J_{P(1),P(2,3)} = 199.3$ Hz)), thereby suggesting the formation of **2** (Scheme 3). Solvent evaporation and extraction into *n*-hexane allowed the isolation of the neutral methylated tetraphosphorus compound **2** in 80 % yield.

The molecular structure of **2** (Figure 4) confirms a borane-complexed P_4 butterfly frame with a methyl group at P4 positioned “*trans*” to the Dmp group at P1. Noteworthy is the larger P1–P2–P3–P4 dihedral angle (102.98(2)°) than of the

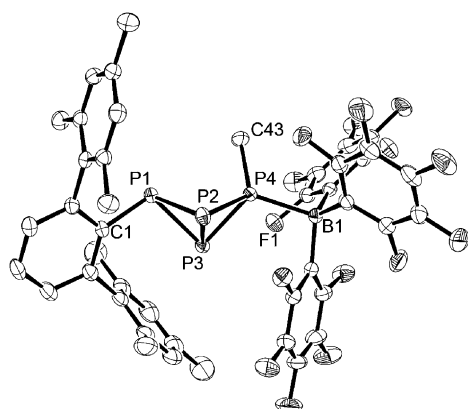


Figure 4. Molecular structure of **2** in the crystal^[15] (ellipsoids are set at 50 % probability; hydrogen atoms and *n*-hexane solvent molecule are omitted for clarity). Selected bond lengths [Å] and torsion angle [°]: P1–P2/P3 2.2113(6)/2.2353(5), P4–P2/P3 2.1686(5)/2.1802(5), P2–P3 2.2448(5), P1–P4 2.9591(6), C1–P1 1.8516(15), C43–P4 1.8262(16), P4–B1 2.0668(17); P1–P2–P3–P4 (102.98(2)).

anion **1b** (94.16(2)°), which may be attributable to steric repulsion between the CH₃ group and the lone pair at P1. The experimental length of the P4–B1 bond (2.0668(17) Å) is almost equal to that of **1b**, but its calculated value (2.1408 Å) is 0.041 Å longer than that calculated for **1b** (2.0998 Å). Furthermore, its strength is predicted to be weaker (4.1 vs 23.8 kcal mol^{−1} for **1b**) and is instead similar to that computed for H₃P–B(C₆F₅)₃ (6.1 kcal mol^{−1}). This difference between **2** and **1b** may be due to the lower Lewis basicity of the neutral fragment.

Finally, we targeted the removal of the Lewis acid from **2**. This was accomplished with tetra-*n*-butylammonium acetate^[24] in dichloromethane that gave, as monitored by $^{31}P\{^1H\}$

NMR spectroscopy, the desired **3** quantitatively and the insoluble ammonium acetate borate^[25] (Scheme 3). Unfortunately, **3** decomposed upon attempted isolation, which is likely due to its limited steric protection,^[26] but in situ characterization by 1H and $^{31}P\{^1H\}$ NMR spectroscopy confirmed its integrity; the AMX₂ spin system is akin to that of **2** and supports a neutral P_4 butterfly structure (Figure 5). Compound **3** is a rare example of a non-symmetrically substituted P_4 derivative and exemplifies a novel pathway to activate and functionalize P_4 .

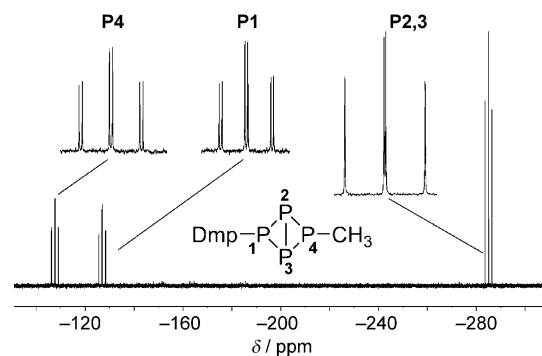


Figure 5. $^{31}P\{^1H\}$ NMR spectrum (CD₂Cl₂, RT) of **3** directly after addition of (*n*Bu)₄N(OAc). Multiplicity and integrals of the signals are P4 (td, 1P):P1 (td, 1P):P2,3 (dd, 2P). Coupling constants $^1J_{P4,P2,3} = 230.0$, $^2J_{P4,P1} = 24.3$, $^1J_{P1,P2,3} = 220.3$, $^2J_{P1,P4} = 24.3$, $^1J_{P2,3,P4} = 230.0$, $^1J_{P2,3,P1} = 220.3$ Hz.

In conclusion, the direct functionalization of white phosphorus is achieved with bulky aryl lithium reagents and B(C₆F₅)₃ via a unique bicyclo[1.1.0]tetraphosphabutane anion. The presented method allows the controlled formation of two P–C bonds using P_4 as the starting material, enabling access to non-symmetrically substituted bicyclic tetraphosphorus compounds. Currently, we are investigating the scope of this approach and the reactivity of the anionic and neutral P_4 entities.

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