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P_4 Functionalization

Functionalization of P_4 Using a Lewis Acid Stabilized Bicyclo[1.1.0]tetraphosphabutane Anion**

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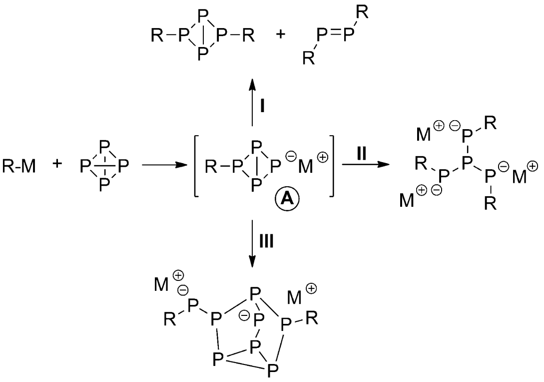
In memory of Michael F. Lappert

***Abstract:** Reacting white phosphorus (P_4) with sterically encumbered aryl lithium reagents (aryl = 2,6-dimesitylphenyl or 2,4,6-$tBu_3C_6H_2$) and $B(C_6F_5)_3$ gives the unique, isolable Lewis acid stabilized bicyclo[1.1.0]tetraphosphabutane anion. Subsequent alkylation of the nucleophilic site of the RP_4 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.*

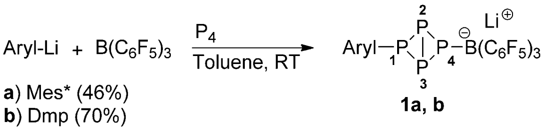
White phosphorus (P_4) is the archetypal building block for organophosphorus compounds. Current conversions proceed through PCl_3, which is obtained by halogenation of P_4. The chlorine atoms are subsequently substituted with organic groups by salt metathesis, generating equimolar amounts of halogenide waste. Direct, selective processes are needed if chlorinated intermediates are to be circumvented.[1] This conundrum has given rise to a plethora of P_4 chemistry, but selective, direct functionalization methods remain very scarce.[2] Illustrative are Weigand's use of phosphenium ions that insert into P–P bonds to form P_5^+ 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 P_4-, P_2-, and P_1-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 P_4 to complex mixtures of polyphosphides, which on hydrolysis gave low conversions (0–40%) to primary and secondary phosphanes.[8] Two decades later, Fluck and coworkers found P_4 to react with Mes*Li to give in low yield (< 10%) a disubstituted P_4 butterfly compound and diphosphene 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 $[(Me_3Si)_3Si]^-[K(18\text{-crown-}6)]^+$ a Zintl-type P_7-cage compound (Scheme 1, route III), supposedly from dimerization of anionic **A**.[11] The common anion in these reactions is presumably the initial P_4 addition product.[2b,12] We now present the isolation and characterization of a Lewis acid-stabilized version of RP_4 anion **A** as well as its selective functionalization.



Scheme 1. Investigations toward nucleophilic functionalization of P_4. I) R–M = Mes*Li (1.9 equiv), Et_2O, reflux, < 10%;[9] II) R–M = MesLi (3 equiv), benzene, RT, 60%;[10] III) R–M = $[K(18\text{-crown-}6)][Si(SiMe_3)_3]$ (1 equiv), toluene, RT, 29%.[11]

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 P_4 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 P_4, Mes*Li, and $B(C_6F_5)_3$ (Scheme 2). $^{31}P\{^1H\}$ NMR spectroscopy showed a steady decrease (with 56% conversion in 4 weeks' time) of the P_4 resonance at −524 ppm with the



Scheme 2. Reaction of bulky nucleophiles and a Lewis acid with P_4.

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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) (AMX$_2$ 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 RP$_4$ butterfly anion (fold angle = 93.61(3)°) capped with a toluene-complexed lithium cation that is coordinated to the P1 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 H$_3$P·B(C$_6$F$_5$)$_3$ (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; H$_3$P·B(C$_6$F$_5$)$_3$ 6.1 kcal mol^{-1}), which is attributable to the higher basicity of the anionic P$_4$ fragment.

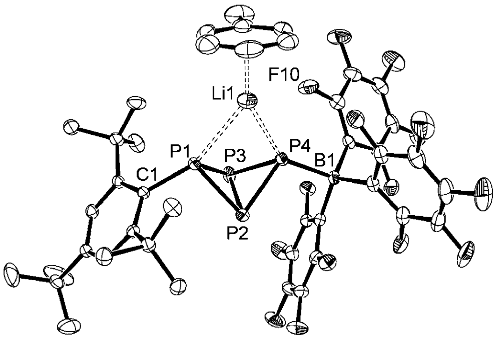


Figure 1. Molecular structure of **1a** in the crystal[15] (ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity). Selected bond lengths [Å], angle, and torsion angle [°]: P1–P2/P3 2.2166(6)/2.2286(6), P4–P2/P3 2.2031(6)/2.2177(7), P2–P3 2.1694(7), P1–P4 2.8183(7), C1–P1 1.8628(17),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

The slow conversion of P$_4$ 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(C$_6$F$_5$)$_3$, and P$_4$ at room temperature gave only **1b** within one hour and in 70% isolated yield (Scheme 2; δ ^{31}P{^{1}H}: −154.6 (P1), −172.0 (P4), and −342.9 ppm (P2,3)); ^{31}P{^{1}H} NMR spectroscopy showed that full conversion of P$_4$ (instead of 84%) could be achieved on using 1.5 equivalents of DmpLi and B(C$_6$F$_5$)$_3$.

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 (Σr(vdW)[Li, 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 ^{7}Li and ^{19}F NMR spectra. The observed P4−B1 bond length (2.0692(14) Å) and its computed strength (23.8 kcal mol^{-1}) are similar to those of **1a**.

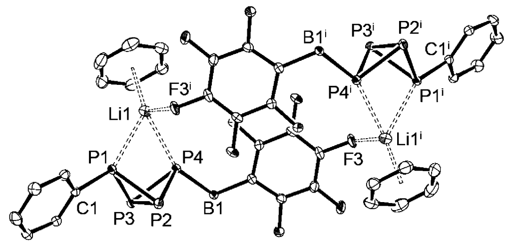


Figure 2. Molecular structure of **1b** in the crystal[15] (ellipsoids are set at 50% probability; hydrogen atoms, non-coordinated benzene solvent molecules, mesityl rings, and two C$_6$F$_5$ rings are omitted for clarity). Selected bond lengths [Å], angle, and torsion angle [°]: P1–P2/P3 2.2180(4)/2.2131(4), 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^i 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*.

Bicyclo[1.1.0]tetraphosphabutanes **1a** and **1b** are to the best of our knowledge the first isolated monofunctionalized P$_4$ anions. B3LYP/6-311+G(d)//6-31+G(d) calculations reveal **1b** to result from nucleophilic attack of DmpLi onto P$_4$, 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(C$_6$F$_5$)$_3$ to P$_4$ and neither could such complexes be detected by ^{31}P NMR spectroscopy. This suggests a reaction sequence in which Dmp$^-$ attacks P$_4$ upon which the incipient anion is trapped by the Lewis acid. In fact, no Dmp-substituted P$_4$ 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]

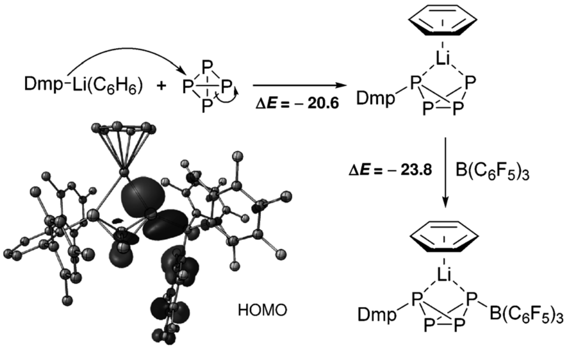
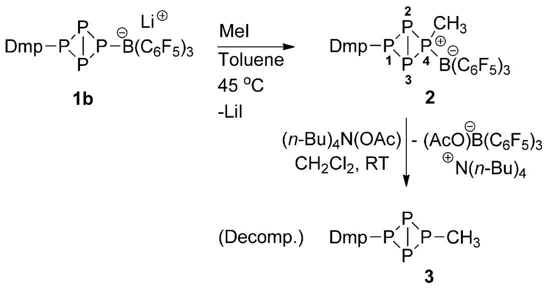


Figure 3. Calculated reaction pathway (*E*, kcal mol^{-1}) of the reaction of P$_4$ with DmpLi and B(C$_6$F$_5$)$_3$, and the HOMO of the calculated geometry of monomer **1b**.[18]

To further functionalize P$_4$, we targeted the alkylation of **1b**, which would be expected to occur at the phosphorus atom bonded to the B(C$_6$F$_5$)$_3$ 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}P{^{1}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; AMX_2 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 anion **1b** (94.16(2)°), which may be attributable to steric repulsion between the CH_3 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 $H_3P{\cdot}B(C_6F_5)_3$ (6.1 kcal mol^{-1}). This difference between **2** and **1b** may be due to the lower Lewis basicity of the neutral fragment.

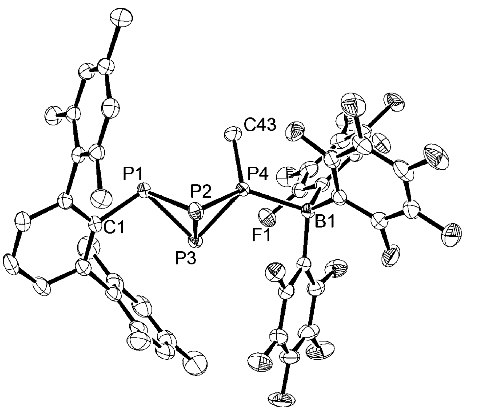


Figure 4. Molecular structure of **2** in the crystal[15] (ellipsoids are set at 50% probability; hydrogen atoms and *n*-hexane solvent molecule are omitted for clarity). Selected bond lengths [Å] and torsion angle [°]: P1–P2/P3 2.2113(6)/2.2353(5), P4–P2/P3 2.1686(5)/2.1802(5), P2–P3 2.2448(5), P1–P4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

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 AMX_2 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.

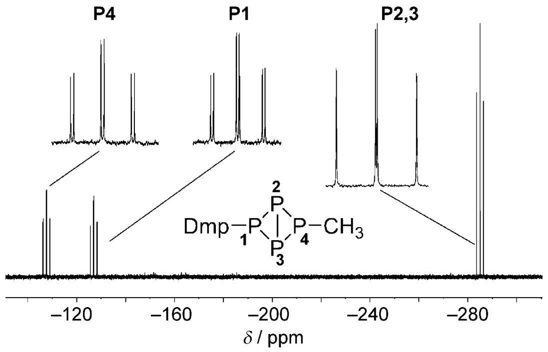


Figure 5. $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, RT) of **3** directly after addition of $(nBu)_4N(OAc)$. Multiplicity and integrals of the signals are P4 (td, 1P):P1 (td, 1P):P2,3 (dd, 2P). Coupling constants $^1J_{P4\text{-}P2,3} = 230.0$, $^2J_{P4\text{-}P1} = 24.3$, $^1J_{P1\text{-}P2,3} = 220.3$, $^2J_{P1\text{-}P4} = 24.3$, $^1J_{P2,3\text{-}P4} = 230.0$, $^1J_{P2,3\text{-}P1} = 220.3$ Hz.

In conclusion, the direct functionalization of white phosphorus is achieved with bulky aryl lithium reagents and $B(C_6F_5)_3$ 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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