Phosphorous Compounds

[{HC(CMeNAr)$_2$}$_2$Al$_2$P$_4$] (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$): A Reduction to a Formal {P$_4$}$^{4-}$ Charged Species[**]

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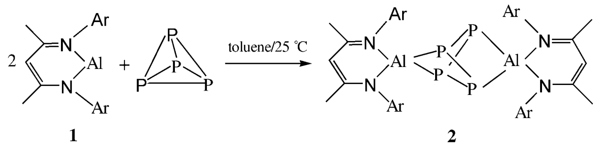
The chemistry of white phosphorus has generated much interest over the past decades owing to its unique tetrahedral structure and variable bonding situation. Organophosphorus compounds can be used as reagents[1] and as ligands for innumerable complexes in catalytic processes.[2] The reactions of transition-metal complexes with white phosphorus have been extensively studied and have resulted in a large variety of P$_x$ ligands with unpredictable structures.[3] Among them, only one compound [Cp*$_2$(CO)$_2$Co$_2$P$_4$] (Cp* = C$_5$Me$_5$)[4] with a {P$_4$}$^{4-}$ species is reported. However, the reactions of the P$_4$ molecule with main-group complexes are limited to a few examples, [(AlCp*)$_6$P$_4$],[5a] [(GaR)$_3$P$_4$] (R = (SiMe$_3$)$_3$C),[5b] and [Ga$_2$P$_4$*t*Bu$_6$].[5c]

[LAl$^{\mathrm{I}}$] (**1**) (L = HC(CMeNAr)$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$)[6] with its nonbonding lone pair of electrons at aluminum indicates a singlet carbene-like character. It could be used in carbene-type reactions, as a Lewis base and moreover as a reducing reagent, which may show unprecedented chemical reactions. To our knowledge, the study of the chemical behavior of **1** is limited so far to coupling reactions.[7,8] Compounds containing the heavy elements of Group 13 and 15 are used as models in bonding theory[9] and as precursors for semiconducting materials.[10] Herein we report the reaction of **1** with white phosphorus to yield the first main-group complex of composition [(LAl)$_2$P$_4$] (**2**) containing the {P$_4$}$^{4-}$ species.

Treatment of two equivalents of **1** with white phosphorus at room temperature leads to **2** in good yield (Scheme 1). In contrast, the reaction of the tetrahedral aluminum(I) compound [(AlCp*)$_4$] with white phosphorus gave the electron-deficient cage compound [(AlCp*)$_6$P$_4$],[5a] which consists of two face-sharing heterocubanes with two opposing corners unoccupied, and four P atoms from the complete cleavage of the P$_4$ molecule. Therefore we treated **1** with P$_4$ in a 4:1 ratio to explore the possibility of complete cleavage of all P–P bonds, however we obtained **2** and residual **1**, based on the results of ^{1}H and ^{31}P NMR spectroscopic investigations. Clearly the bulky ligand L prevents the arrangement of a larger number of LAl moieties around the P atoms. When the reaction was carried out in a ratio of 1:1 between **1** and P$_4$, **2** and residual P$_4$ together with some byproducts were obtained, again based on the results of ^{1}H and ^{31}P NMR spectroscopic investigations. Compound **2** is air sensitive and decomposes at 145 °C. **2** is sparingly soluble in pentane and hexane, however readily soluble in benzene, toluene, and diethyl ether. In CDCl$_3$ we observed the decomposition of **2**.



Scheme 1. The synthesis of **2**. Ar = 2,6-*i*Pr$_2$C$_6$H$_3$.

Compound **2** was characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy using [D$_6$]benzene as the solvent, and by EI mass spectrometry and elemental analysis. The EI mass spectrum shows the molecular ion of **2**. The ^{31}P NMR spectrum of **2** ($\delta = 78.6$ ppm) has a very different chemical shift compared to that of the free P$_4$ molecule ($\delta = -519$ ppm). No resonance signals were observed in C$_6$D$_6$ solution for the ^{27}Al NMR spectrum of **2**, thus measurement in the solid state was carried out and signals in a range of 50–120 ppm were found which are comparable to those for four-coordinate Al$^{\mathrm{III}}$ compounds, and much different from the resonance for [LAl$^{\mathrm{I}}$] (**1**) (590 ± 40 ppm, $v_{1/2} = 30000$ Hz).[7] In the ^{1}H NMR pattern of **2**, just one set of resonances for the ligands L is detected indicating that the two ligands are in the same chemical environment. The X-ray single-crystal structural analysis confirms the composition of **2** (Figure 1). Compound **2** crystallizes in the orthorhombic space group $P2_12_12_1$ with one molecule of pentane. As shown in Figure 1,[11] compound **2** contains an {Al$_2$P$_4$} core, and the four-membered P$_4$ ring is attached to two LAl moieties. The Al–P bond length (av. 2.37 Å) of **2** is in the range of those in [(AlCp*)$_6$P$_4$] (2.31–2.42 Å).[5a] The P–P bond length (av. 2.29 Å) is slightly longer than that in [Cp*$_2$(CO)$_2$Co$_2$P$_4$] (av. 2.23 Å).[4] The distances between P(1)···P(3) and P(2)···P(4) in **2** (3.049(2) and 3.063(2) Å) are distinctly longer than those in [Cp*$_2$(CO)$_2$Co$_2$P$_4$] (2.560(2), 2.597(2) Å),[4] and indicate the complete cleavage of two P–P bonds within the P$_4$ molecule. The Al–N bond length (av. 1.90 Å) is in the range of those aluminum derivatives bearing the ligand L.[12] The average P-Al-P bond angle is 80.27°.

DFT calculation with RI-BP86/TZVP within TURBOMOLE[13,14] was carried out to investigate the electronic structure of **2**. The calculated Mulliken charges on the P atom (−0.22) show a significant charge transfer from the Al atoms to P$_4$, which indicates the formation of an ionic Al–P bond. The bond order (shared electrons between two P atoms) of P–P bonds (0.01) supports the complete cleavage of the P(1)–P(3) and P(2)–P(4) bonds. The calculated binding energy $((E_{(\mathrm{LM})_2-\mathrm{P}_4} - 2*E_{\mathrm{L-M}} - E_{\mathrm{P}_4})/2.0)$ (36.4 kcal mol^{-1}) shows the strong interaction between P$_4$ and the Al atoms. (In the

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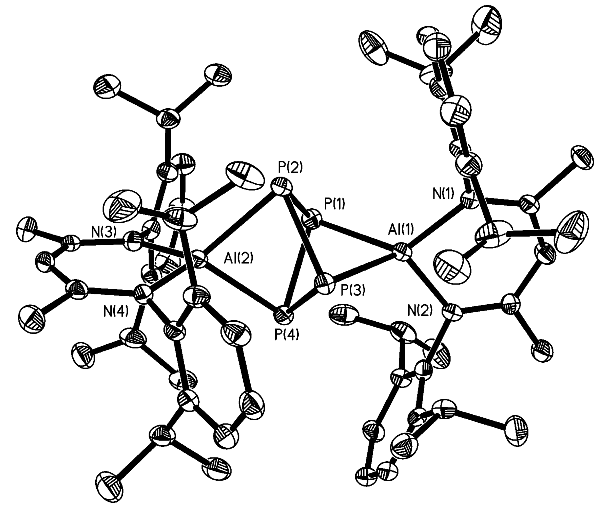

Figure 1. The crystal structure of **2**. The hydrogen atoms and cocrystallized pentane are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al(1)-P(1) 2.377(2), Al(1)-P(3) 2.359(2), Al(2)-P(2) 2.387(2), Al(2)-P(4) 2.360(2), P(1)-P(2) 2.287(2), P(1)-P(4) 2.292(2), P(2)-P(3) 2.284(2), P(3)-P(4) 2.295(2), P(1)···P(3) 3.049(2), P(2)···P(4) 3.063(2), Al(1)-N(1) 1.897(5), Al(1)-N(2) 1.912(5), Al(2)-N(3) 1.901(5), Al(2)-N(4) 1.909(5); P(3)-Al(1)-P(1) 80.16(7), P(4)-Al(2)-P(2) 80.37(7), P(2)-P(1)-P(4) 83.98(7), P(3)-P(2)-P(1) 83.69(8), P(2)-P(3)-P(4) 83.96(8), P(1)-P(4)-P(3) 83.34(8), P(2)-P(1)-Al(1) 81.64(8), P(4)-P(1)-Al(1) 77.60(7), P(2)-P(3)-Al(1) 82.07(8), P(4)-P(3)-Al(1) 77.91(7), P(3)-P(2)-Al(2) 77.84(7), P(1)-P(2)-Al(2) 81.02(7), P(1)-P(4)-Al(2) 81.50(7), P(3)-P(4)-Al(2) 78.19(7).

above calculation the P atoms are the P atoms of the coordinated P–P edge.)

In the uncoordinated P_4 molecule the P–P bonds are about 2.21 Å. Herein we use PH_2–PH_2 as an example to study how much the P–P bond loses energy during its extension.[15] The energy curve of PH_2–PH_2 for the P–P separation (1.7 to 3.6 Å) is given in the Supporting Information. It shows that near the minimum the curve is quite flat. At $r(P–P) > 3.0$ Å, most of the bond energy is lost and the bond order is about zero. Thus, both the charge calculation and the P–P bond analysis support an ionic Al–P_4 bond for **2**. Therefore, in **2**, the P_4 unit is carrying formally four negative charges.

In summary, the reaction of LAl^{I} (**1**) with white phosphorus yields the first main-group complex $[(LAl)_2P_4]$ (**2**) containing the $\{P_4\}^{4-}$ moiety, in which two P–P edges of the P_4 tetrahedron are opened and each is bridged by a LAl moiety.

Experimental Section

2: Toluene (30 mL) was added to a mixture of **1** (0.445 g, 1 mmol) and P_4 (0.062 g, 0.5 mmol). The resulting solution was stirred at room temperature for one week. After removal of the solvent, the residue was recrystallized from a mixture of hexane and pentane at room temperature to afford red crystals (0.40 g, 79 %). M.p. 145 °C dec; EI-MS: *m/z* (%) 1012 (30) [M^+], 429 (100) [LAl-Me]. ^{1}H NMR (500.13 MHz, C_6D_6): $\delta = 7.15$–7.02 (m, 12 H, Ar-H), 5.03 (s, 2 H, γ-H), 3.61 (sept, $J = 6.8$ Hz, 8 H, C*H*Me$_2$), 1.70 (s, 12 H, Me), 1.15 (d, $J = 6.8$ Hz, 24 H, CH*Me*$_2$), 1.13 ppm (d, $J = 6.8$ Hz, 24 H, CH*Me*$_2$); ^{13}C NMR (125.77 MHz, C_6D_6): $\delta = 169.97$ (*C*N), 143.94, 142.07, 124.14 (Ar), 97.79 (γ-C), 29.26 (*C*HMe$_2$), 25.43(CH*Me*$_2$), 24.57 (CH*Me*$_2$), 23.86 ppm (Me); ^{31}P NMR (121.5 MHz, C_6D_6): $\delta = 78.6$ ppm; ^{27}Al NMR (600 MHz, 26 KHz, MAS, $AlCl_3$): $\delta = 50$–120 ppm (MAS = magic-angle spinning). elemental analysis calcd (%) for $C_{63}H_{94}Al_2N_4P_4$ (1085.26): C 69.72, H 8.73, N 5.16; found C 69.88, H 8.12, N 5.76.

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[11] Crystal data for **2**·pentane: $C_{63}H_{94}Al_2N_4P_4$, $M_r = 1085.26$, orthorhombic, space group $P2_12_12_1$, $a = 13.8751(7)$, $b = 14.3627(8)$, $c = 31.8580(16)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 6348.8(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.135$ Mg m^{-3}, $F(000) = 2344$, $\lambda = 0.71073$ Å, $T = 133(2)$ K, $\mu = 0.186$ mm^{-1}; $1.28 \leq \theta \leq 22.63°$; of 25400 reflections collected, 8387 were independent ($R(int) = 0.0983$). The R values are $R1 = 0.0618$ and $wR2 = 0.1372$ ($I > 2\sigma(I)$); The Flack value is $-0.17(14)$; max./min. residual electron density: 0.491/-0.410 e Å^{-3}. All non-hydrogen atoms were refined anisotropically except for the pentane carbon atoms. All hydrogen atoms were included at geometrically calculated positions and refined using a riding model. CCDC-224941 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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