The Main Group Macrocycle $[\{(PCH_2CH_2PAlMe_2)_2\}_4]\cdot 4[AlMe_3]$**

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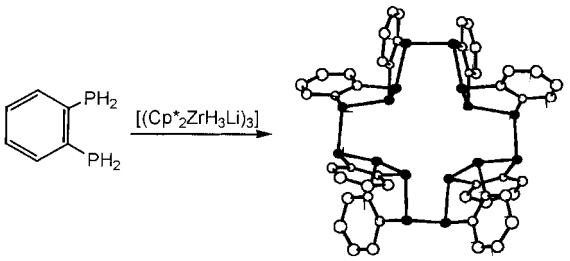
Recent reviews in the fields of main group,[1] organometallic,[2] solid-state,[3] and organo–phosphorus chemistry[4] have reflected the multidisciplinary interest in compounds containing phosphorus. While organo–phosphorus ligands are ubiquitous in transition metal chemistry, the catenation of phosphorus atoms in organophosphanes and related polyphosphorus anions has drawn attention from inorganic and solid-state chemists.[1, 3] The work of Scherer, Driess, Fenske, and others[2, 5, 6] concerning the studies of substituent-free phosphorus–metal complexes,[7] is one example where studies have crossed these disciplinary lines. These disciplinary boundaries have been further eroded with the studies of phosphanide and phosphanediyl clusters reported by the research groups of Fenske[8–11] and Driess.[12–14] While these systems employ phosphorus atoms to link metals in complex clusters, we have targeted systems in which chains of phosphorus atoms act as metal-linking units. In targeting such systems we first sought a convenient route to organopolyphosphanes as previously known syntheses were arduous.[15, 16] To this end, we developed a catalyst for the dehydrocoupling of primary phosphanes to organopolyphosphanes.[17] In a recent demonstration of such catalysis, we employed the catalyst precursor $[(Cp^*_2ZrH_3Li)_3]$ to produce the macrocyclic P_{16} ring compound $(C_6H_4P_2)_8$ [Eq. (1)].[18, 19]



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Herein we report, the catalytical synthesis of the organotetraphosphane $(PCH_2CH_2PH)_2$ (**1**) and employ it to prepare the unique P_{16}–Al_{12} compound, $[\{(PCH_2CH_2PAlMe_2)_2\}_4]\cdot 4[AlMe_3]$ **3**. This species employs four P_4 chains to link eight aluminum centers, forming Al_2P_3 rings in a unique macrocyclic structure comprised of solely main group elements (see Scheme 1).

The quantitative catalytic dehydrocoupling of the primary bidentate phosphane $PH_2CH_2CH_2PH_2$, using the catalyst precursor $[(Cp^*_2ZrH_3Li)_3]$ proceeds smoothly at room temperature over a three day period to afford the colorless product **1**. The $^{31}P\{^1H\}$ NMR spectrum of **1** consists of two resonances at $\delta = -22.5$ and -65.4, each showing second-order coupling. Simulation of the $^{31}P\{^1H\}$ NMR spectrum shows that it is consistent with an AA′BB′ pattern with one and two bond P–P coupling constants of -237 Hz, -186 Hz and 20 Hz respectively. This data is in good agreement to that reported for **1**, previously prepared by Baudler et al. in 30–55% via two different reductive coupling strategies.[15, 16] Recrystallization of **1** from hexane at $-35\,^\circ C$ afforded colorless X-ray quality crystals. An X-ray diffraction study of **1** confirmed the formulation as the product of the dehydrocoupling of two molecules of the starting diphosphane, that is $(PCH_2CH_2PH)_2$ (Figure 1).[20] This molecule

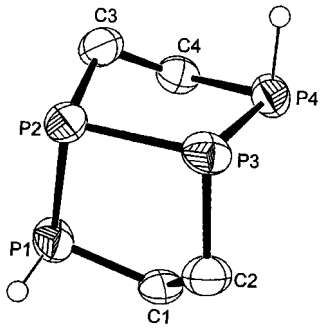

Figure 1. ORTEP drawing of **1**, thermal ellipsoids are set at the 50% level. Carbon-bound hydrogen atoms are omitted for clarity. P1-P2 2.1928(14), P2-P3 2.2217(14), P3-P4 2.2063(14); P1-P2-P3 97.22(5), P4-P3-P2 96.96(5).

comprises two interlinked five-membered rings, in which one phosphorus atom of each of two diphosphane fragments forms P–P bonds with the two phosphorus atoms of the other diphosphane moiety. This results in a chain of four phosphorus atoms where the terminal phosphorus atoms retain a single proton. The average P–P bond length in **1** is 2.2069(14) Å while the P-P-P angles average 97.09(5)°. The two five-membered rings are approximately orthogonal, the angle between the mean P_3C_2 planes is 94.9(1)°. This constrained orientation directs the terminal protons in essentially orthogonal directions, the torsion angles about the H-P-P-P-P-H chain average 88.9°. This geometry of **1** is analogous to one quarter of the previously reported macrocycle $(C_6H_4P_2)_8$.[18]

The catalytic formation of **1** provides convenient access to a corner-type molecular building block containing a P_4 chain. In attempts to employ **1** to link metal centers, reactions of **1** with $[MMe_3]$ (M = Ga, Al) were undertaken (Scheme 1). The reaction of **1** with $[GaMe_3]$ in hexane resulted in the formation of a highly unstable species **2**. This short-lived species exhibited a ^{31}P NMR spectrum showing signals at $\delta = -19.4$ and -65.1. The downfield resonance appears similar to that observed for **1** while the upfield resonance has increased multiplicity suggesting coordination to Ga and the formulation $[\{(PCH_2CH_2PH)GaMe_3\}_2]$ (**2**). The rapid degradation of this product with gas evolution (presumably methane) and the deposition of an insoluble white material, precluded further characterization of **2**. The nature of the subsequent P–Ga product(s) remains unknown, despite repeated attempts to obtain pure, crystalline material.

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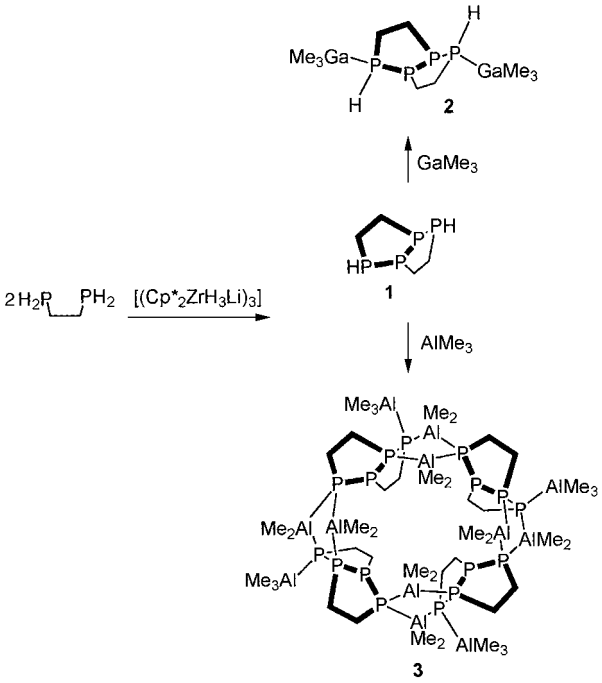

Scheme 1.

In contrast, addition of excess [$AlMe_3$] to a solution of **1** does not give a reaction at 25 °C. However, heating a solution of **1** with excess [$AlMe_3$] in hexane to 80 °C for 1 week in a sealed reaction vessel gives a white solid **3** in 64 % yield. Recrystallization of **3** from a 1:1 mixture of THF and hexane at −35 °C yielded colorless cubic crystals. The $^{31}P\{^1H\}$ NMR spectra of the crystalline **3** showed four broad resonances at $\delta = 1.9, -50.9, -67.1$, and -88.8. The ^1H NMR spectrum of **3** showed four distinct resonances attributable to aluminum bound methyl groups. While these data infer P–Al interactions, neither of the NMR spectra provided substantial structural information. This prompted an X-ray crystallographic study which confirmed the formulation of **3** as $[\{(PCH_2CH_2PAlMe_2)_2\}_4]\cdot 4\,[AlMe_3]$ (Figure 2).[20] This centrosymmetric macrocyclic compound comprises four P_4C_4 units

Figure 2. ORTEP drawing of **3**, the thermal ellipsoids are set at 20 %. Hydrogen atoms are omitted for clarity. Phosphorus atoms are depicted in orange, aluminum in blue, and carbon in gray.

that are bridged by two $AlMe_2$ units. One of the Al centers bridges the terminal P atoms of two adjacent P_4C_4 units. The second Al center is bound to the terminal phosphorous of one P_4 unit and to a central P atom of the second P_4 moiety, giving five-membered P_3Al_2 rings. The result is four such rings linked by P units (Figure 3). The bridging Al–P bonds average

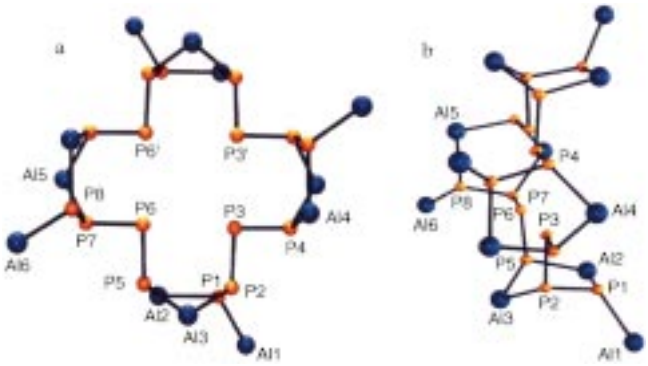

Figure 3. ORTEP drawings of the heteroatom core of **3**. Views a) and b) are approximately orthogonal. Phosphorus atoms are depicted in orange, aluminum in blue. Selected distances [Å] and angles [°] Al1-P1 2.576(4), Al2-P5 2.471(4), Al2-P1 2.484(4), Al3-P5 2.458(4), Al3-P2 2.477(4), Al4-P4 2.469(4), Al4-P8′ 2.495(4), Al5-P4′ 2.459(4), Al5-P7 2.502(4), Al6-P8 2.595(4), P1-P2 2.195(4), P2-P3 2.246(3), P3-P4 2.224(3), P5-P6 2.224(3), P6-P7 2.252(3), P7-P8 2.192(4); P5-Al2-P1 99.25(13), P5-Al3-P2 89.46(12), P4-Al4-P8′ 98.94(14), P4′-Al5-P7 87.88(12), P2-P1-Al2 105.24(14), P2-P1-Al1 117.44(15), Al2-P1-Al1 116.44(14), P1-P2-P3 98.76(13), P1-P2-Al3 110.73(13), P3-P2-Al3 116.21(13), P4-P3-P2 92.86(12), P3-P4-Al5′ 115.28(14), P3-P4-Al4 106.66(14), Al5-P4-Al4 106.49(14), P6-P5-Al3 115.44(14), P6-P5-Al2 106.37(14), Al3-P5-Al2 106.57(13), P5-P6-P7 92.69(12), P8-P7-P6 98.85(13), P8-P7-Al5 111.17(14), P6-P7-Al5 115.97(13), P7-P8-Al4′ 104.46(13), P7-P8-Al6 119.84(15), Al4′-P8-Al6 116.48(14), Al3-P8-Al2 106.49(14).

2.477(5) Å while the P–P bonds range from 2.192(4) Å to 2.252(3) Å. The angles at Al within the P_3Al_2 rings range from 89.46(12) to 99.25(13)° while the corresponding angles at phosphorous span the range from 105.24(14) to 110.73(13)°. One of the P atoms of each P_3Al_2 ring also binds an additional equivalent of [$AlMe_3$] with an average terminal Al–P bond of 2.586(4) Å. The view of **3** in Figure 3a shows the main group macrocycle within the molecule. The dimensions of the depicted central cavity of this molecule are indicated by the P3–P6, P3–P3′, and P6–P6′ distances of 3.655(5), 5.071(5), and 5.016(5) Å, respectively. The side view of **3** (Figure 3b) shows the P_3Al_2 rings are puckered (maximum deviation from the mean plane of 0.35 Å). In addition the adjacent pairs of P_3Al_2 rings are approximately perpendicular, with the angles between the mean P_3Al_2 planes being 90.6 and 91.2°.

In conclusion, we have described the catalytic synthesis of the organotetraphosphane **1**, which reacts with [$AlMe_3$] to give the main group macrocycle **3**. This species represents a rare, if not unprecedented example of a compound in which polyphosphorus chains linking metal atoms in a macrocyclic array. As this approach provides entry to compounds of cross-disciplinary interest, we are continuing to develop the chemistry of both catalytically generated organopolyphosphanes and their metal derivatives.

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Experimental Section

1: $[(Cp^*_2ZrH_3Li)_3]$[19] (0.1 g, 0.27 mmol) was dissolved in THF (3 mL), $PH_2CH_2CH_2PH_2$ (1.0 g, 10.87 mmol) was added dropwise to the stirred, colorless solution which became green, then aquamarine, and finally blue, over a period of 30 min. The reaction was stirred for 72 h, until it became colorless. Solvent was removed in vacuo, leaving a white solid which was dissolved in hexane, filtered, and placed in a freezer (−35 °C). Colorless, X-ray quality crystals (0.86 g, 87% yield) precipitated from solution, over 24 h. ^{1}H NMR (C_6D_6): $\delta = 3.65$ (dt, 2H, $^1J_{P,H} = 330$, $^3J_{H,H} = 10$ Hz), 2.43 (m, 2H), 1.87 (m, 2H), 1.14 (m, 2H), 0.74 (m, 2H); ^{13}C{^{1}H} NMR (C_6D_6): $\delta =$ 38.36, 30.66; ^{31}P NMR (C_6D_6): $\delta = -22.5$ (P_1: $^1J_{P1,P1} = -237$, $^1J_{P1,P0} = -186$, $^2J_{P1,P0} = 20$ Hz), −65.4 (P_0: $^1J_{P1,P1} = -237$, $^1J_{P1,P0} = -186$, $^2J_{P1,P0} = 20$ Hz); elemental analysis (%) calcd for $P_4C_4H_{10}$: C 26.39, H 5.54; found: C 26.18, H 5.42.

2: A 10% by weight solution of $[GaMe_3]$ in hexane (378 mg, 0.33 mmol) was added to a vial containing **1** (30 mg, 0.16 mmol), with stirring. A very fine white precipitate was evident in the clear colorless solution after 10 min. An aliquot of the reaction mixture was used immediately for ^{31}P NMR spectroscopic characterization. This compound rapidly degraded on standing. ^{31}P NMR (C_6D_6): $\delta = -19.4$ (m), −65.1 (m).

3: A 2M hexane solution of $[AlMe_3]$ (0.14 mL, 0.28 mmol) was quickly added to a stirred toluene (1 mL) solution of **1** (20 mg, 0.11 mmol). The reaction mixture was heated to 80 °C in a sealed reaction vessel for 1 week, during which time the solution turned a very pale orange. Solvent was removed in vacuo, and the resulting white solid was dissolved in a 1:1 mixture of THF and hexane, and placed in a freezer (−35 °C) until clear, colorless, cubic crystals of **3** precipitated from solution in 64% yield. ^{1}H NMR (C_7D_8): $\delta = 2.3$ (brs, 2H), 1.8 (brs, 2H), 1.2 (brs, 3H), 1.1 (brs, 2H), 0.8 (brs, 3H), 0.6 (brs, 2H), −0.2 (brs, 3H), −0.3 (9H), −0.7 (brs, 3H); ^{31}P NMR (C_6D_6): $\delta = 1.9$ (brm), −50.9 (brm), −67.1 (brm) −88.8 (brm); elemental analysis (%) calcd for $C_{11}H_{29}P_4Al_3$: C 36.08, H 7.98; found: C 35.88, H 7.78.

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[20] Diffraction experiments were performed on a Siemens SMART System CCD diffractometer and solved with the SHELX-TL software package. Crystal data for **1**: space group: $P\bar{1}$, $a = 6.6064(1)$, $b = 6.6258(2)$, $c = 10.6067(3)$ Å, $\alpha = 80.624(2)$, $\beta = 74.3540(10)$, $\gamma = 67.241(2)^\circ$, $V = 411.373(18)$ Å^3, $Z = 2$, data/parameters: 1331/81, $R = 0.0549$, $R_w = 0.1355$, GOF = 1.014. Crystal data for **3**: space group: $C2/c$, $a = 26.7605(2)$, $b = 18.0602(3)$, $c = 23.085$ (3) Å, $\beta = 98.04(1)^\circ$, $V = 11047.4(2)$ Å^3, $Z = 8$, data/parameters: 6497/326, $R = 0.0996$, $R_w = 0.2875$, GOF = 1.130. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-152132 and CCDC-152133. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Experimental and Theoretical Observations of Aromaticity in Heterocyclic XAl_3^- (X = Si, Ge, Sn, Pb) Systems**

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The concept of aromaticity may seem foreign for metallic systems. After all, aromaticity usually refers to cyclic, planar, or conjugated organic molecules which possess $(4n+2)$ π electrons and have a specific chemical and structural stability. Nevertheless, aromaticity has been extended to include

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