P_4 activation

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An Unexpected Pathway in the Cage Opening and Aggregation of P_4**

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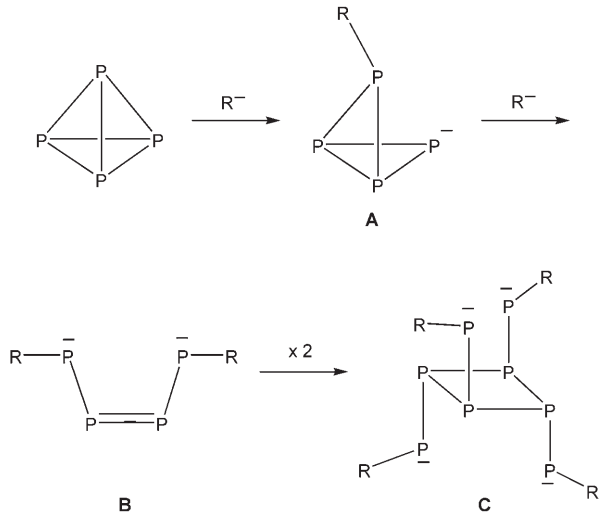
The reactions of white phosphorus with transition-metal organometallic compounds have been investigated extensively in the past few decades, producing a variety of P_x^{n-} ligands which result from reduction and (commonly) rearrangement and aggregation of the P_4 units.[1] In comparison, only a few reactions of white phosphorus with main-group complexes have been reported. Whereas the reactions of low-oxidation-state Group 13 species to some extent parallel those of transition-metal organometallic compounds,[2–4] the reactions of P_4 with more nucleophilic main-group complexes follow a distinctly different pathway, involving nucleophilic addition to the P_4 framework.[5–8] In the case of the 1:1 reaction of tBu_3Ga with P_4, attack of the tBu^- ion across one of the P–P bonds gives a butterfly-shaped $[tBuP_4]^-$ ion (**A**, Scheme 1).[5,6] In contrast, the 2:1 reaction of tBu_3SiNa with P_4 in the presence of the Lewis base donors THF or DME (1,2-dimethoxyethane) gives adducts containing the $[(tBu_3Si)P{-}P{=}P{-}P(SitBu_3)]^{2-}$ ion (**B**, Scheme 1), whereas the reaction in the presence of *tert*-butyl methyl ether results in [2+2] cycloaddition to give the $[P_4(PSitBu_3)_4]^{4-}$ ion (**C**, Scheme 1).[7] Notably, however, little or no mechanistic details of these nucleophilic reactions are known. We present herein a study of the reaction of the potassium hypersilyl complex $[(Me_3Si)_3SiK([18]crown-6)]$ (**1**) with P_4, which provides a significant new insight into the electronic factors influencing the nature of the products of reactions involving nucleophilic main-group reagents.

The 1:1 reaction of the hypersilyl complex **1** with P_4 in toluene and subsequent crystallization from a toluene/THF/hexane mixed solvent gave a few crystals of $[K([18]crown-6)(thf)_2]^+$ $[P_8\{Si(SiMe_3)_3\}_2{\cdot}K([18]crown-6)]^-$ (**2**) [Eq. (1)].

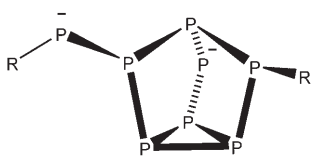
$$2[(Me_3Si)_3SiK([18]crown\text{-}6)] + 2\,P_4 \xrightarrow[RT]{toluene} [K([18]crown\text{-}6)(thf)_2]^+[P_8\{Si(SiMe_3)_3\}_2 \cdot K([18]crown\text{-}6)]^- \quad (\mathbf{2}) \qquad (1)$$

Owing to the low yield obtained, the complex was characterized initially by X-ray crystallography alone. However, the complex can be isolated in moderate yield (29%) as a powder by removal of the solvent under vacuum. ^1H, ^{29}Si, and ^{31}P NMR spectroscopy and elemental analysis confirm that this material is identical to the structurally characterized material. The surprising result of this reaction is the formation of a $[R_2P_8]^{2-}$ ($R = Si(SiMe_3)_3$) cage dianion, which consists of a nortricyclic P_7 arrangement with a single branched phosphorus atom positioned *exo* to the cage (Scheme 2). The room-temperature ^{31}P NMR spectrum of **2** was highly complicated. Unfortunately, lowering of the temperature (down to about −90 °C in toluene) only led to broadening of the spectrum, and any fluxional processes occurring in the core could not be resolved.



Scheme 1. Fragmentation aggregation of the P_4 unit of white phosphorus with nucleophiles.

Although a number of Zintl-type compounds containing similar P_7 cage arrangements have been reported previously,[9,10] to our knowledge the $[P_8R_2]^{2-}$ dianion of **2** is unprecedented in this area. Perhaps more significant, however, are the implications of this result on the limited



dianion of **2**

Scheme 2. Connectivity of the $[R_2P_8]^{2-}$ ion.

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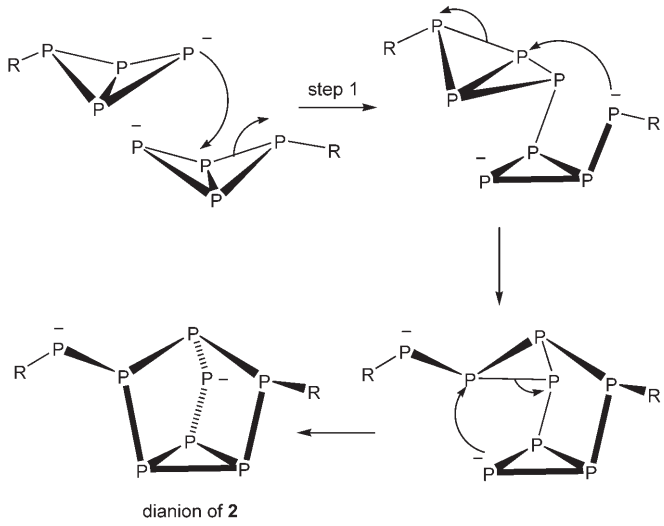
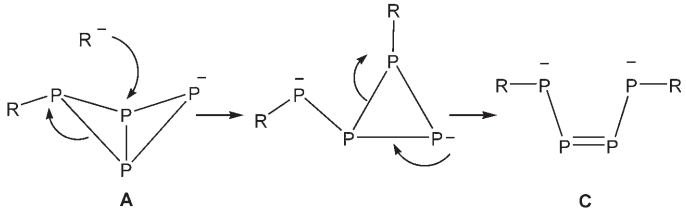
mechanistic knowledge of this kind of reaction. Referring back to Scheme 1, it can be seen that the $[R_2P_8]^{2-}$ dianion of **2** is in fact a dimer of the previously reported $[RP_4]^-$ ion **A** and, indeed, results from the same 1:1 reaction stoichiometry. A plausible mechanism for the dimerization into the $[R_2P_8]^{2-}$ ion of **2** is outlined in Scheme 3. The key point is that



Scheme 3. Plausible mechanism of formation of the dianion of **2**.

nucleophilic attack onto the $[RP_4]^-$ ion **A** by another dianion in step 1 is most likely to occur at a P center that is α to the anionic P atom, with retention of the hinge P–P bond. This mode of attack not only avoids the formation of an intermediate in which two negatively charged P centers are bonded to each other, but also results in stabilization of the resulting negatively charged P center by an adjacent Si(SiMe$_3$)$_3$ group. The fact that such stabilization is not possible where an aliphatic R group is present explains why the previously reported 1:1 reaction of *t*Bu$_3$Ga with P_4 does not proceed beyond the $[RP_4]^-$ ion.[5] Furthermore, this mode of attack also provides an obvious reason for the formation of the $[R{-}P{-}P{=}P{-}P{-}R]^{2-}$ ion **B** in Scheme 1 from the 2:1 reaction of *t*Bu$_3$SiNa with P_4 (Scheme 4).[5]

Model DFT calculations[11] were undertaken to explore the attack of the $[H_3Si]^-$ ion onto P_4 and the thermodynamics of dimerization of the resulting $[\{H_3Si\}P_4]^-$ ion (see the Supporting Information). As expected, reaction of the $[H_3Si]^-$ ion with P_4 leads to cleavage of one of the P–P bonds. Examination of the frontier orbitals of the resulting



Scheme 4. Formation of the $[R{-}P{-}P{=}P{-}P{-}R]^{2-}$ ion.

$[\{H_3Si\}P_4]^-$ ion shows that the HOMO has a strong contribution from a p orbital on the wing-tip P atom, which also bears the greatest negative charge (based on either Mulliken or electrostatic potential charges of about 0.4 e$^-$), while the LUMO has large coefficients on the hinge P atoms. Thus, the dimerization of two $[\{H_3Si\}P_4]^-$ ions is expected to involve attack of the negatively charged "wing-tip" P atom of one anion onto the electrophilic P_2 "hinge" of another $[\{H_3Si\}P_4]^-$ ion (as anticipated in step 1 of Scheme 3). Significantly, dimerization of the $[\{H_3Si\}P_4]^-$ ion into a $[\{H_3SiP_4\}_2]^{2-}$ ion akin to that of **2** and the overall reaction of P_4 with two $[H_3Si]^-$ ions to give the $[\{H_3SiP_4\}_2]^{2-}$ ion are highly favorable.

A low-temperature X-ray study of **2** shows that it has an ion-separated structure, composed of $[K([18]crown\text{-}6)(thf)_2]^+$ and $[P_8\{Si(SiMe_3)_3\}_2{\cdot}K([18]crown\text{-}6)]^-$ ion pairs (Figure 1).[12]

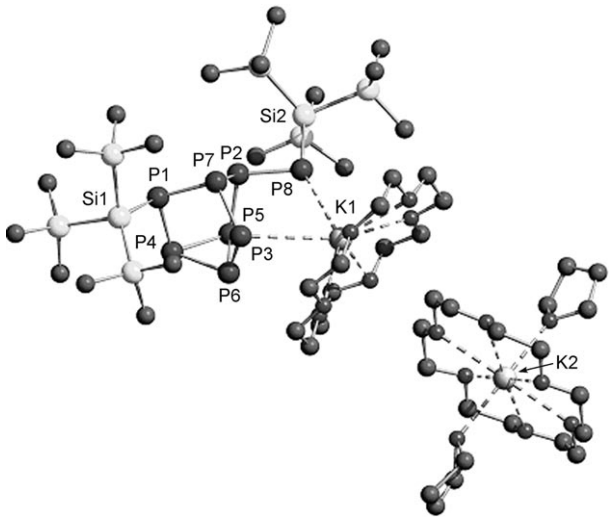


Figure 1. Structure of **2**. For clarity, H atoms are omitted and the O atoms of the thf and [18]crown-6 ligands are not labeled (their coordination to the K atoms is indicated by dashed lines). Key bond lengths [Å] and angles [°]: P1-P7 2.203(3), P2-P7 2.216(3), P3-P7 2.135(3), P5-P2 2.204(4), P6-P3 2.152(3), P4-P1 2.205(4), P4-P5 2.239(3), P5-P6 2.229(3), P4-P6 2.235(3), P2-P8 2.167(3), P1-Si1 2.266(3), P8-Si2 2.238(3), P3-K1 3.435(3), P8-K1 3.378(3); P1-P7-P2 88.4(1), P3-P7-P1 105.3(1), P3-P7-P2 105.8(1), P-P(1,2,3)-P range 99.5(1)–101.5(1), P(1,2,3)-P(4,5,6)-P range 98.9(1)–107.4(1), basal P-P(4,5,6)-P range 59.8(1)–60.2(1), P2-P5-P8 102.4(2), Si2-P8-P2 93.29(1).

The $[P_8\{Si(SiMe_3)_3\}_2{\cdot}K([18]crown\text{-}6)]^-$ ion is based on a nortricyclic P_7 core, with a single branched phosphorus atom bonded *exo* to the ring (P8). The three basal phosphorus atoms (P4, P5, and P6) are coordinated to three other phosphorus atoms in the structure, as is the apical phosphorus atom (P7). One of the equatorial phosphorus atoms (P2) is bonded to the branched *exo* phosphorus atom (P8), while the other is covalently bonded to one of two hypersilyl groups in the structure. The third equatorial phosphorus atom (P3) formally carries a negative charge, as does the *exo* phosphorus atom, thus rendering the P_8 unit of **2** dianionic. A single K^+ ion, coordinated by [18]crown-6, is chelated by the two charge-carrying phosphorus atoms of the dianion, while the second K^+ ion is located within a $[K([18]crown\text{-}6)(thf)_2]^+$

counterion. Although the P–P (range 2.135(3)–2.239(3) Å), P–K (range 3.378(3)–3.435(3) Å), and Si–P (range 2.238(3)–2.266(3) Å) bond lengths within the $[P_8\{Si(SiMe_3)_3\}_2{\cdot}K([18]crown\text{-}6)]^-$ ion of **2** are typical of those reported in the literature,[13] there is a noticeable distortion in the P_8 fragment resulting, at least in part, from its coordination to the K^+ ion (K1). The shortest P–P bond lengths within the core occur to the coordinating P centers P3 and P8 (range 2.135(3)–2.167(3) Å), with the remaining P–P bonds (2.203(3)–2.239(5) Å) being significantly longer. The nortricyclic P_7 core arrangement found in **2** has been observed in a number of anionic and neutral P_x^{n-} cage structures.[9] However, the Cr^0 complex $[\{P_7(PtBu_2)_3\}\{Cr(CO)_4\}_2]$,[14] which contains a neutral, nortricyclic $P_7(PtBu_2)_3$ ligand, is the closest analogue to **2**.

In summary, the unexpected formation of the $[P_8\{Si(SiMe_3)_3\}_2]^{2-}$ ion sheds new light on the mechanism of reactions of P_4 with nucleophilic main-group species, suggesting that rearrangement of the phosphorus frameworks can be directed by stabilization of the negative charge by R_3Si units. The resulting arrangement of the $[P_8\{Si(SiMe_3)_3\}_2]^{2-}$ ion is unprecedented in this area. Further experimental and theoretical studies are underway to explore the implications of this preliminary study.

Experimental Section

2: White phosphorus (0.11 g, 0.89 mmol of P_4) was added to a solution of **1** (0.50 g, 0.91 mmol) in dry toluene (10 mL) at room temperature under dry, oxygen-free N_2. The solution immediately turned dark brown with the formation of a solid. The slurry was allowed to stir (45 min) and was then filtered through celite. The blood-red filtrate was concentrated under vacuum. Dry THF (5 mL) and hexane (1 mL) were added, and the solution was stored at −20 °C (3 days), giving a few crystals of **2**. In a separate experiment, the solvent was removed from the blood-red solution prior to crystallization, and the resulting light-yellow powder of **2** was washed with dry hexane (20 mL). Yield: 0.20 g (29 % based on **1**); ^{1}H NMR (25 °C, 500.20 MHz, C_6D_6): $\delta =$ 0.72 (9H, m, $P_7Si(CH_3)_3$), 0.80 (9H, m, $PSi(CH_3)_3$), 3.52 ppm (48H, s, [18]crown-6); ^{29}Si NMR (25 °C, 99.38 MHz, C_6D_6): $\delta = -115.9$ ($P_7Si(CH_3)_3$), −135.7 ($PSi(CH_3)_3$); ^{31}P NMR (25 °C, 202.48 MHz, C_6D_6): $\delta = 72.9$ (m, P_{exo}), −30.5 (m, P_e), −43.2 (m, P_e), −82.0 (t, P_a), −121.4 (m, P_b), −191.6 (m, P_b). Elemental analysis (%) calcd for **2**: C 37.4, H 7.6, P 18.4; found: C 36.7, H 6.5, P 19.3.

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[11] DFT calculations (LSDA/pBP86/DN*) were carried out with Spartan Pro (Wavefunction Inc., 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612, USA. http://wavefunction.com/). This DFT approach utilizes a perturbative Becke–Perdew (pBP86) procedure (A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3089; J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822) within the local spin density approximation LSDA. Instead of Gaussian basis sets, Spartan Pro utilizes atomic solutions supplemented with d-type functions for heavy atoms, including numerical polarization (DN*).
[12] Crystal data for **2**: $C_{50}H_{118}K_2O_{14}P_8Si_8$, $M_r = 1494.12$, monoclinic, space group $C2/c$, $Z = 2$, $a = 24.633(5)$, $b = 27.543(6)$, $c = 31.052(6)$ Å, $\beta = 111.49(3)°$, $V = 19603(7)$ Å^3, $\mu(Mo_{K\alpha}) = 0.366$ mm^{-1}, $\rho_{calcd} = 1.013$ Mg m^{-3}, $Z = 8$, $T = 180(2)$ K. Data were collected on a Nonius KappaCCD diffractometer. Of a total of 26212 reflections collected, 8661 were unique ($R_{int} = 0.107$). The structure was solved by direct methods and refined by full-matrix least squares on F^2 (G. M. Sheldrick, SHELX-97, Göttingen, Germany, **1997**). Relatively high displacement parameters indicated considerable rotational disorder of the silyl groups and conformational disorder of the counterion. The two Si atoms and eleven C atoms of the silyl groups were resolved (50:50) as were all the C atoms of the thf ligands (60:40), and two C atoms of the [18]crown-6 ligands of the counterion (60:40). The disorder resulted in poor diffraction at high angle and the relatively high final R values: $R1 = 0.089$ [$I > 2\sigma(I)$] and $wR2 = 0.254$ (all data). Nevertheless, the principal features of the unexpected P_8 dianion are well-established. CCDC-623921 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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