P_4 Activation

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A P_4 Chain and Cage from Silylene-Activated White Phosphorus**

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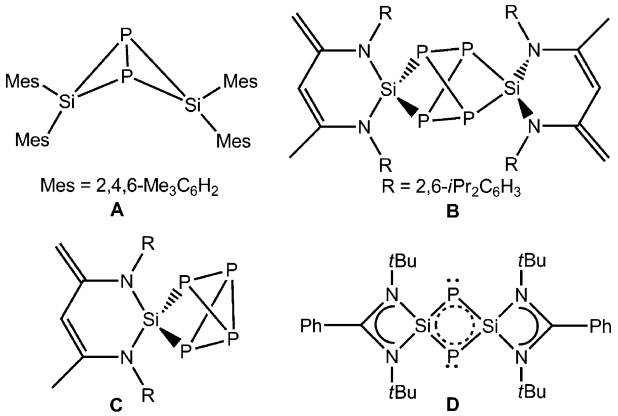
Dedicated to Professor Philip P. Power

Transition-metal-mediated degradation of white phosphorus has been extensively studied,[1] and it has attracted considerable interest owing to its demand in industrial applications for a more facile production of organophosphorus derivatives. Recently in a seminal review,[2] Power pointed out that main-group elements in lower oxidation states exhibit an amazing resemblance to transition metals in many ways, for example their ability to activate small molecules, such as dihydrogen.[3–6] In fact, Bertrand et al. mentioned that cyclic alkyl amino carbene (CAAC) can activate NH_3,[7] which is a much more difficult task for transition metals.[8] The carbene footsteps were immediately followed by its heavier congeners: silylene, germylene, and stannylene, which all display the activation of NH_3 under ambient condition.[9–11] Another remarkable breakthrough in this field is the fragmentation of P_4 by a N-heterocyclic carbene (NHC) and related carbene ligands.[12–14] Among these, the most intriguing example was the activation of P_4 by a bulky rigid CAAC and the isolation of the resulting acyclic P_4 chain.[13]

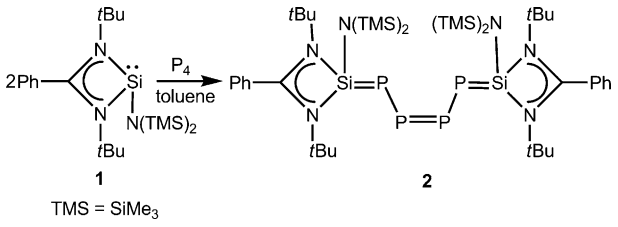
Owing to the similar properties between N-heterocyclic carbene and silylene (both having a singlet ground state[15,16] and a lone pair of electrons on the low-valent carbon and silicon atom), it is expected that subvalent silicon compounds can also activate P_4; however, only four examples of P_4 activation by compounds with low-valent silicon have been reported to date (Scheme 1). West et al. described the isolation of 1,3-diphospha-2,4-disilabicyclo[1.1.0]butane (**A**),[17] which was later structurally characterized.[18] Driess et al. described the activation of P_4 by a N-heterocyclic silylene [{RNC(=CH_2)−CH=C(Me)NR}Si] (R = 2,6-*i*$Pr_2C_6H_3$) to afford bicyclotetraphosphine derivatives **B** and **C**.[19] Very recently, we isolated a novel four-membered zwitterionic Si_2P_2 ring (**D**) by P_4 activation with silicon(II) chloride [PhC(N*t*Bu)$_2$SiCl] and bis(silylene) [(PhC(N*t*Bu)$_2$Si)$_2$].[20] The latter, compound **D**, was also isolated by Driess et al. by treating [PhC(N*t*Bu)$_2$SiP(SiMe$_3$)$_2$] with Ph_3PCl_2.[21]



Scheme 1. Examples of P_4 activation by compounds with low-valent silicon.

In a surprisingly short period of time, the activation of phosphorus by subvalent Group 14 elements has flowered into an engaging, intriguing, and emerging area of chemistry.[22,23] Nevertheless, a neutral acyclic P_4 chain stabilized by an N-heterocyclic silylene is still elusive. Herein, we present the synthesis of a neutral acyclic P_4 chain stabilized by the recently isolated silicon(II) bis(trimethylsilyl)amide [PhC(N*t*Bu)$_2$SiN(SiMe$_3$)$_2$] (**1**).[24]

Addition of toluene to the mixture of **1** and P_4 at −10 °C in a 2:1 molar ratio immediately gave rise to a dark bluish-green solution that turned purple after stirring for 30 minutes at room temperature. The solution was concentrated and kept at −30 °C to afford **2** in a 50% yield as purple-colored, extremely air- and moisture-sensitive crystals (Scheme 2). Compound **2** is stable in solution at −30 °C for a long time, but decomposes rapidly (within a few minutes) after separation of crystallized material from the supernatant mother liquor and subsequent drying. The constitution of **2** was unequivocally



Scheme 2. Synthesis of **2**.

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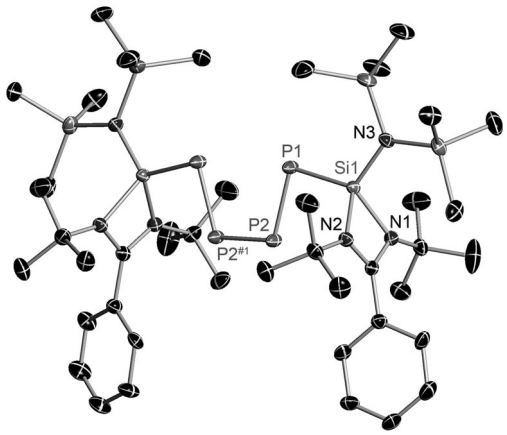
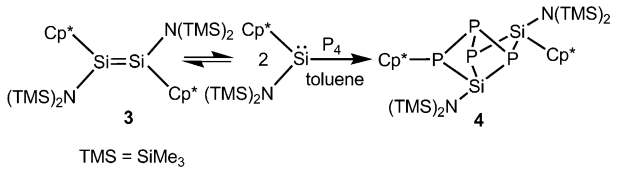


Figure 1. Molecular structure of **2**·2 C_7H_8. Ellipsoids are set at 50% probability; hydrogen atoms and the two toluene molecules are omitted for clarity. Atom P1 is part of a disordered moiety with the highest site occupation factor. Atom P2#1 (and those shown to the left of P2#1; #1 = *x*, $-y+0.5$, *z*) are symmetry-generated by a mirror plane lying between and perpendicular to P2–P2#1. Selected bond distances [Å] and angles [°]: P2–P2#1 2.0559(7), P1–P2 2.1317(14), Si1–P1 2.1602(12), N1–Si1 1.8316(12), N2–Si1 1.8339(13), Si1–N3 1.7264(12); N1-Si1-P1 116.57(9), N2-Si1-P1 117.82(10), N3-Si1-P1 116.56(6), P2-P1-Si1 94.22(5), P2#1-P2-P1 106.93(3).

characterized by cryogenic single-crystal X-ray diffraction studies.[25–27] Figure 1 depicts the molecular view of **2**, which crystallizes in the orthorhombic space group *Pnma*. The molecular structure shows the presence of the *Z*-diphosphene isomer (with a dihedral angle of 0°) and benzamidinato-stabilized phosphasilene substituents, whereas the reported CAAC-supported acyclic P_4 is an *E* isomer (major product).[13] A C_2 axis passes through the middle of the central P=P double bond of **2**. The main structure consists of two Si atoms and four P atoms, which together form a neutral acyclic Si_2P_4 (Si=P–P=P–P=Si) chain with 6π electrons contained in a diphosphene and two phosphasilene units. The two Si atoms are four-coordinate each and display a distorted tetrahedral geometry by coordination with two N atoms from the amidinato ligand. The remaining two sites of the tetrahedron are occupied by the $N(SiMe_3)_2$ moiety and P atom each. The central P2–P2#1 bond length is 2.0559(7) Å, which falls in the range of a typical double bond, while the P1–P2 distance (2.1317(14) Å) is halfway between a P–P single (2.21 Å)[28–30] and double bond[31,32] (1.954 to 2.044 Å) and corresponds well with the reported value (2.083(4) Å) for a CAAC-stabilized acyclic P_4 unit.[13] Moreover, the Si1–P1 bond in **2** (2.1602(12) Å) is longer than the Si=P double bond (2.09 Å),[33,34] but significantly shorter than the reported Si–P single bond (2.25 Å)[35] and is in good accordance with the bond lengths of the recently reported $CPSi_2$ and P_2Si_2 cycles.[20] From the X-ray structural data it is clear that each SiP_2 (Si=P–P) moiety shows a delocalized electron density.

Compound **2** was also characterized by multinuclear NMR spectroscopy, EI-MS spectrometry, and elemental analysis. In the ^{1}H NMR spectrum, *t*Bu protons give rise to a singlet at $\delta = 1.29$ ppm, which confirms the presence of only one isomer. Two resonances appear at $\delta = 0.46$ and 0.77 ppm that are assigned to $SiMe_3$ protons. The ^{31}P NMR spectrum of **2** shows an AA′XX′ system with two multiplets at $\delta = -77.19$ ppm and $+381.72$ ppm ($J_{A,A'} = 346.14$, $J_{A,X} = 295.77$, $J_{X,X'} = 184.18$, and $J_{A,X'} = 50.36$ Hz), which can be assigned to P of Si=P and P=P, respectively. In the EI-MS spectrum, the most abundant peak with the highest relative intensity at *m*/*z* 900.5 was observed for the fragment after the probable elimination of a P_2 unit.

The $N(SiMe_3)_2$-substituted disilene $[(Me_3Si)_2N(\eta^1\text{-}Me_5C_5)Si{=}Si(\eta^1\text{-}Me_5C_5)N(SiMe_3)_2]$ (**3**) was first reported by Jutzi et al. in 2004,[36] which was later shown to exist in equilibrium with the corresponding silylene in solution.[37] Very recently, we have successfully synthesized **3** in 68% yield by treating $[(\eta^1\text{-}Me_5C_5)SiHCl_2]$ with $KN(SiMe_3)_2$.[38] This high-yield access of **3** and its ability to exist in equilibrium with the corresponding silylene prompted us to investigate its reactivity with P_4. It can be used as a source for two-coordinate silylene $[(Me_5C_5)SiN(SiMe_3)_2]$ and can be compared with the reactivity of three-coordinate silylene **1**. Unlike **1**, the reaction of **3** with P_4 in a 1:1 molar ratio in toluene at ambient temperature under stirring for 12 h yields an extraordinary Si–P cage (**4**; Scheme 3). The ^{1}H NMR



Scheme 3. Synthesis of **4**.

spectrum exhibits a broad resonance for thirty protons of the methyl groups attached to the two five-membered rings ($\delta =$ 1.73–1.86 ppm). Two resonances at $\delta = 0.41$ and 0.49 ppm correspond to protons of two different $SiMe_3$ groups. The ^{29}Si NMR spectrum of **4** in C_6D_6 shows four resonances ($\delta =$ -78.9, 0.2, 5.8, and 8.1 ppm) for four different silicon atoms. A quartet at $\delta = -78.9$ ppm ($^1J(^{29}\text{Si-}^{31}\text{P}) = 48.20$ Hz) appears for silicon attached to three phosphorus atoms, while the silicon attached to two phosphorus atoms has a broad triplet at $\delta = 0.2$ ppm ($^1J(^{29}\text{Si-}^{31}\text{P}) = 42.86$ Hz).[19] The remaining two resonances result from the silicon atoms of the $SiMe_3$ groups. As shown by ^{31}P NMR spectroscopy, **4** exhibits four chemically different phosphorus atoms (A, B, X, Y) giving rise of the resonance signals as a doublet of doublets of doublets at $\delta = 257.6$, 128.4, 114.2, and -141.8 ppm ($J_{A,B} = 30.9$, $J_{A,X} =$ 10.2, $J_{A,Y} = 78.6$, $J_{B,X} = 126.6$, $J_{B,Y} = 110.2$, and $J_{X,Y} =$ 156.5 Hz), respectively. The composition of **4** is further supported by EI mass spectrometry (molecular ion *m*/*z* 770), which clearly indicates the formation of a 1:1 complex of **3** with P_4.

Figure 2 shows a molecule of **4**. Compound **4** crystallizes in the triclinic space group $P\bar{1}$.[25–27] The X-ray crystal structure confirms the triply opened P_4 tetrahedron, in which one P_3 face is capped, and one opened edge is bridged by a silicon atom each, and a Cp* group has migrated from Si4 to one of the adjacent phosphorus atoms (P4) under simultaneous formation of a new Si–P bond. Both silicon atoms (Si4 and Si7) are four-coordinate and have a distorted tetrahedral

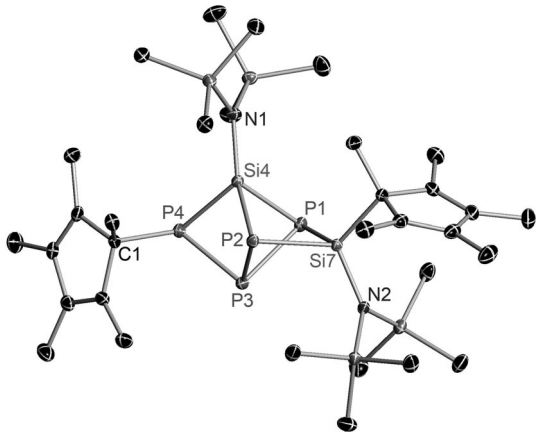


Figure 2. Molecular structure of **4**. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: P1–P3 2.2747(7), P2–P3 2.2831(8), P3–P4 2.2457(7), P1–Si4 2.2829(8), P1–Si7 2.2979(6), P2–Si4 2.2868(6), P2–Si7 2.2922(8), P4–Si4 2.2600(7), P4–C1 1.9133(15), Si7–N2 1.7450(13), Si4–N1 1.7300(13); P3-P1-Si4 69.98(2), P3-P1-Si7 77.09(3), Si4-P1-Si7 85.78(3), P3-P2-Si4 69.76(2), P3-P2-Si7 77.09(3), Si4-P2-Si7 85.82(3), P4-P3-P1 86.44(3), P4-P3-P2 97.19(3), P1-P3-P2 86.98(3), P3-P4-Si4 70.91(2), C1-P4-P3 110.69(5), C1-P4-Si4 113.30(5), P4-Si4-P1 85.89(3), P4-Si4-P2 96.65(2), P1-Si4-P2 86.69(3), P1-Si7-P2 86.22(3).

geometry. The bridging atom Si4 is furthermore attached to one nitrogen atom of the $N(SiMe_3)_2$ substituent. All Si–P bonds are comparable and consistent with previously reported Si–P single bonds.[35] Atom Si7 is attached to two phosphorus atoms (P1 and P2), one $N(SiMe_3)_2$ group, and one Cp* group. The central four-membered Si4-P2-Si7-P1 ring is nonplanar, with a dihedral angle between two Si-P-P planes of 138.2°. A trigonal bipyramidal structure is shown by P1, P2, P3, P4, and Si4 atoms of the central core if we assume that three phosphorus atoms (P1, P2, P4) occupy equatorial positions while axial positions are attributed to Si4 and P3 with distances of 1.315 and 1.299 Å, respectively, from the center. All of the phosphorus atoms are three-coordinate with distorted tetrahedral geometry (considering the lone pair of electrons on phosphorus atoms). P3 is attached to P1, P2, and P4 with bonds P1–P3, P2–P3, and P3–P4 of 2.2747(5), 2.2831(8), and 2.2457(7) Å, respectively, which are very similar to those of **B** and slightly longer than the mean P–P single-bond length found in **C** (2.23 Å)[19] and the P_4 tetrahedron (2.21(2) Å). The two Cp* rings attached to P4 and Si7 are nearly perpendicular to each other with an angle of 82.55° between the planes of two Cp* rings, while $N(SiMe_3)_2$ groups attached to Si4 and Si7 face in the opposite direction to each other.

In summary, we have demonstrated the reactions of $[PhC(NtBu)_2SiN(SiMe_3)_2]$ and *E*-$[(Me_3Si)_2N(\eta^1\text{-}Me_5C_5)Si{=}Si(\eta^1\text{-}Me_5C_5)N(SiMe_3)_2]$ with P_4, which yielded an unusual acyclic P_4 chain **2** and silicon–phosphorus cage **4** by P_4 and Si–C activation through insertion of two molecules of the corresponding silylene into the P_4 tetrahedron. We chose *E*-$[(Me_3Si)_2N(\eta^1\text{-}Me_5C_5)Si{=}Si(\eta^1\text{-}Me_5C_5)N(SiMe_3)_2]$ as a source for $\{Cp^*SiN(SiMe_3)_2\}$ and compared the reactivity pattern of both the $N(SiMe_3)_2$-substituted silylenes for the activation of P_4. The formation of two different kinds of products from the reaction of the abovementioned silylenes with P_4 confirms the significant role of the substituents to yield the final products. Such Si–P compounds can be used as electron-rich chelating ligands for transition metals and may find application in metal-mediated catalytic process.[39–41] Furthermore, **2** and **4** may have commercial application as precursors for semiconducting materials.[42,43]

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