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Assembly of a Triple-Cage Species Containing B, P, and Si Atoms

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Interest in inorganic ring and cage compounds containing boron and phosphorus atoms continues to expand and diversify.[1−3] In particular, our group has been interested in developing general assembly approaches for $B_xP_yE_z$ cage compounds that would permit a wide latitude in the selection of element stoichiometries and resultant cage sizes and structures. At this point, syntheses have been developed for bicyclic cages of the type $P_2(R_2NB)_3$,[4] $P_2(R_2NB)_2SiR_2$,[5] $P_2(R_2NB)_2GeR_2$,[6] $P_2(R_2NB)_2SnR_2$,[7] and $P_2(R_2NB)_2(SiR_2)_2$.[5] We report here an extension of this chemistry that leads to isolation of an unprecedented triple-cage molecule, $P_6(^{i}Pr_2NB)_6Si_2$ (**1**), containing 14 atoms in the cage core.

Compound **1** is obtained as pale yellow crystals from the 4:1 combination of $^{i}Pr_2N\overline{BP(H)(^{i}Pr_2NB)P}Li{\cdot}DME$ with Si_2Cl_6 in hexane.[8] The compound is stable in dry air but slowly hydrolyzes in water or wet solvents. The composition of the molecule is confirmed by CHN analysis and high-resolution FAB-MS, which shows an intense envelope of ions in the region *m/e* 904−912 corresponding to the parent species. The molecular structure of **1** was deduced from single-crystal X-ray diffraction analysis,[9] and a view of the molecule is shown in Figure 1. The structure consists of a bicyclic $P_2B_2Si_2$ cage and two P_2B_2Si bicyclic cages, which share the two silicon atoms and are joined through a Si−Si bond. The P(1)B(1)P(2)B(2) four-membered ring in the $P_2B_2Si_2$ fragment is slightly folded (fold angle 17.0°) away from the Si−Si vector, and the two P_2B_2Si fragments are nearly eclipsed: the angle between the P(1)Si(1)Si(2) and P(2)Si(1)Si(2) planes is 10.9°. The metrical parameters for the bicyclic units are similar to those previously reported for the five-atom cage $P_2(^{i}Pr_2NB)_2SiPh_2$ (**2**)[5] and the six-atom cage $P_2(^{i}Pr_2NB)_2Si_2Me_4$ (**3**).[5] The Si(1)−Si(2) bond length, 2.273(2) Å, is in the single-bond range but is considerably shorter than the value in **3**, 2.352(2) Å. The average P−Si distances in the P_2B_2Si fragment, 2.262 Å, and in the $P_2B_2Si_2$ fragment, 2.267 Å, are identical to the average distance in **3** but slightly longer than that in **2**, 2.244 Å. The average P−B bond lengths in the P_2B_2Si fragment and $P_2B_2Si_2$ fragment are identical, 1.964 Å (range 1.947(6)−1.984(7) Å), and these compare with 1.973 Å in **2** and 1.978 Å in **3**. There is likely a larger strain energy involved in the P_2B_2Si cage fragments than in the $P_2B_2Si_2$ fragment, as suggested by differences in internal angles (e.g., the average sum of angles about the P atoms in the P_2B_2Si fragments is 212.9° compared to the sum in $P_2B_2Si_2$, 254.8°).

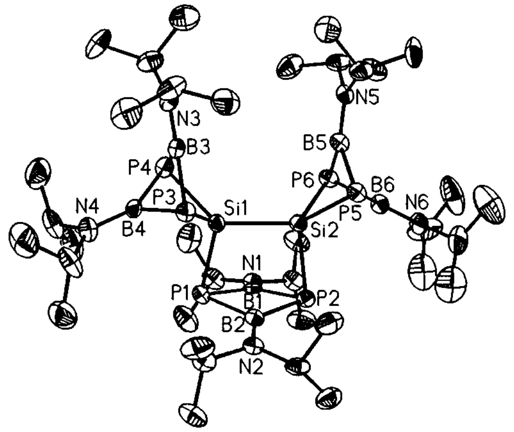

Figure 1. Molecular structure and atom-labeling scheme for $P_6(^{i}Pr_2NB)_6Si_2$, **1**, with H atoms omitted and ^{i}Pr carbon atom labels removed for clarity (30% probability ellipsoids). Selected bond lengths (Å): Si(1)−Si(2) 2.373(2), Si(1)−P(1) 2.271(2), Si(1)−P(3) 2.258(2), Si(1)−P(4) 2.271(2), Si(2)−P(2) 2.262(2), Si(2)−P(5) 2.262(2), Si(2)−P(6) 2.253(2), P(1)−B(1) 1.975(6), P(1)−B(2) 1.957(6), P(2)−B(1) 1.950(6), P(2)−B(2) 1.973(5), P(3)−B(3) 1.947(6), P(3)−B(4) 1.959(6), P(4)−B(3) 1.972(6), P(4)−B(4) 1.984(7), P(5)−B(5) 1.964(6), P(5)−B(6) 1.969(7), P(6)−B(5) 1.947(6), P(6)−B(6) 1.970(6).

The NMR spectra for **1** are consistent with this structure. The $^{31}P\{^{1}H\}$ NMR spectrum shows two resonances at δ 9 and −59 in a 2:1 area ratio that are assigned to the P atoms in the P_2B_2Si and $P_2B_2Si_2$ fragments, respectively. These shifts may be compared with values for the five-atom cage **2**,[5] δ −18.4, and the six-atom cage **3**,[5] δ −84.9. The $^{11}B\{^{1}H\}$ NMR

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(8) A sample of $^{i}Pr_2N\overline{BP(H)(^{i}Pr_2NB)P}Li{\cdot}DME$ (1.5 g, 3.9 mmol) was added to Si_2Cl_6 (0.28 g, 1.0 mmol) in hexane (60 mL) at −78 °C. The mixture was stirred (1 h), warmed to 23 °C, and stirred (5 h). The suspension was filtered, the filtrate cooled to −78 °C, $^{t}BuLi$ (1.8 mL, 1.7 M pentane solution, 3.0 mmol) added, and the mixture stirred (1 h). The mixture was warmed to 23 °C, stirred (15 h), and then evaporated to dryness. The residue was extracted with toluene, and a pale yellow powder was recovered following vacuum evaporation of the toluene. Recrystallization of the powder from cold (−10 °C) hexane/THF solution afforded pale yellow crystals: yield 0.32 g (35%); mp >250 °C. HR-FAB-MS, *m/e*: calcd for $C_{36}H_{84}N_6P_6Si_2{}^{10}B_2{}^{11}B_4$, 906.5353; found, 906.5347; deviation 0.6 ppm. $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 9.0(2), −59.0(1). $^{11}B\{^{1}H\}$ NMR (C_6D_6): δ 50.8(1), 42.8(2). ^{1}H NMR (C_6D_6): δ 4.02 (br, 4H, C*H*), 3.86 (sept, 8H, $^{3}J_{HH}$ = 6.8 Hz, C*H*), 1.25−1.24 (m, 72H, CH_3). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 52.8 (*C*H), 51.4 (*C*H), 24.7, 24.6, 23.8, 23.6, 23.4 (*C*H_3).

(9) Crystal data for **1**: $C_{36}H_{84}B_6N_6P_6Si_2$, M_r = 908.0, monoclinic space group $P2_1/c$, a = 18.341(4) Å, b = 12.167(2) Å, c = 26.584(5) Å, $\alpha = \gamma = 90°$, β = 106.49(3)°, V = 5689(2) Å^3, Z = 4, ρ_{calcd} = 1.060 g cm^{-3}, $F(000)$ = 1960, λ = 0.710 73 Å, T = 20 °C, μ(Mo Kα) = 0.260 mm^{-1}. Data were collected in the ω-scan mode on a Siemens R3m/V diffractometer for a pale yellow crystal (0.25 × 0.31 × 0.46 mm) in a glass capillary. A total of 16 609 reflections were collected, with 8307 independent for which 4669 were observed with $F > 1.42\sigma(F)$. The structure was solved by direct methods, and data were corrected for Lorentz and polarization effects. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions (riding model) with $U_{iso} = 1.25U_{eq}$ (parent atom). Refinement by full-matrix least-squares techniques converged with R = 5.71% and R_w = 3.32%.

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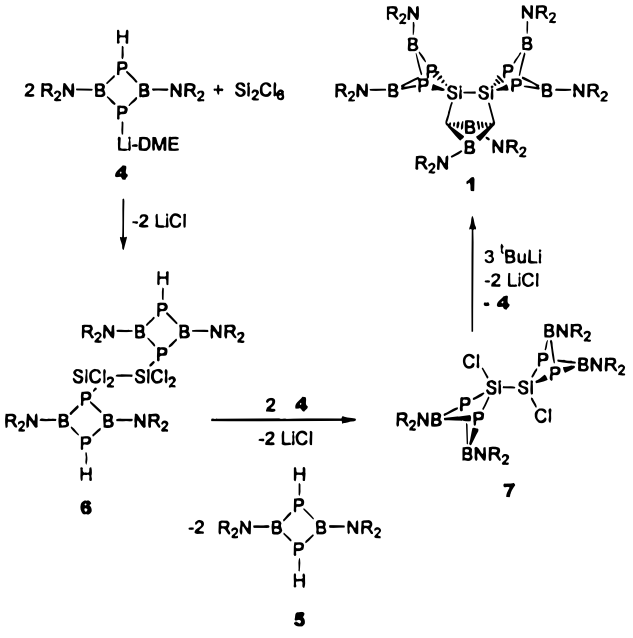
spectrum also contains two resonances centered at δ 42.8 and 50.8, with a 2:1 area ratio, that are assigned to equivalent boron environments in the two P_2B_2Si cages and equivalent boron atoms in the $P_2B_2Si_2$ fragment. The ^1H NMR spectrum contains a complex set of resonances in the range δ 1.25−1.24 (relative intensity 72), assigned to inequivalent methyls in the 12 ^{i}Pr groups, and two methine resonances, δ 3.86 and 4.02 (relative intensity 8:4). Two *C*H resonances and five *C*H_3 resonances are resolved in the $^{13}C\{^1H\}$ NMR spectrum.

In the context of developing syntheses for more complex cage structures, it is of interest to understand the pathway by which **1** is assembled. The proposed process is outlined in Scheme 1. The addition of 4 equiv of **4** to Si_2Cl_6 is believed to initially produce **6** by substitution of a diphosphadiboretanyl ring on each silicon atom. Compound **6** apparently is short-lived in the reaction medium and is not isolated. This proposal is supported by our previous report[5] of a tetramethyl analog of **6**, $\{[{}^i\mathrm{Pr_2N}\overline{\mathrm{BP(H)(}{}^i\mathrm{Pr_2NB}}\mathrm{)P]Si(Me)_2}\}_2$, formed from **4** and $[\mathrm{Me_2(Cl)Si}]_2$. Compound **6** undergoes rapid intramolecular dehydrohalogenation promoted by the remaining 2 equiv of **4**, producing **7** and 2 equiv of **5**. Compound **7** was not isolated and purified; however, the ^{31}P NMR spectrum of the system prior to the addition of ^{t}BuLi shows a resonance for the known compound **5**, δ 164,[10] and a resonance at δ −1.0, which is in the region expected for a bicyclic cage fragment.[5] Subsequent addition of ^{t}BuLi to this reaction mixture should produce **1**, and if sufficient ^{t}BuLi is present, **5** should be converted to **4**. The formation of both **1** and **4** is confirmed by ^{31}P NMR spectra. In fact, the presence of **4** instead of **5** in the final product mixture facilitates separation and purification of **1** since **1** and **4** have very different solubility properties.

Scheme 1



Formation of **1** represents the first of numerous, large-cage species that should be accessible through modifications of this reaction scheme, and extensions are in progress at this time.

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Supporting Information Available: X-ray crystallographic files, in CIF format, are available on the Internet only. Access information is given on any current masthead page.

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