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The "Missing" Hexasilaprismane: Synthesis, X-ray Analysis, and Photochemical Reactions[1]

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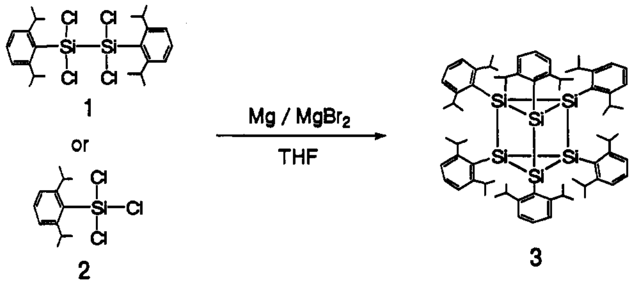
The chemistry of polyhedranes comprised of group 14 elements heavier than carbon is growing rapidly.[2,3] Very recently, we reported the synthesis of hexagermaprismane,[3a] octasilacubane,[3c] and octagermacubane[3c] by reductive coupling of chlorogermanes and chlorosilanes. The missing hexasilaprismane is of special interest in relation to the hitherto unknown hexasilabenzene,[4] and we report herein the first successful preparation and characterization of hexasilaprismane together with its crystal structure.

For the synthesis of strained polyhedranes, proper choice of both starting compounds with a suitable substituent and metals as reducing reagent is of crucial importance. Alkali metals are powerful reducing agents but sometimes cause cleavage of the Si–Si bond. We used the $Mg/MgBr_2$ reagent that was hoped not to cleave the resulting Si–Si bonds.[5,6]

The hexasilaprismane, hexakis(2,6-diisopropylphenyl)tetracyclo[2.2.0.$0^{2,6}$.$0^{3,5}$]hexasilane (**3**), was thus prepared by the dechlorinative coupling reaction of 1,2-bis(2,6-diisopropylphenyl)-1,1,2,2-tetrachlorodisilane (**1**, 10.0 g, 19.2 mmol) with Mg (80 mmol)/$MgBr_2$ (80 mmol) in THF (Scheme I). Purification by chromatography on silica gel with hexane/toluene afforded **3** (514 mg, 7.1%) as orange crystals: mp > 220 °C, MS (FAB) 1134–1140 (M^+ cluster), consistent with $Si_6C_{72}H_{102}$. The previous study demonstrated that the reaction of **1** with lithium naphthalenide did not give the hexasilaprismane **3**.[7] The reaction of (2,6-diisopropylphenyl)trichlorosilane (**2**) with $Mg/MgBr_2$ also gave **3** but in very low yield (1%).

Contrary to other polyhedranes, the hexasilaprismane **3** is thermally and oxidatively fairly stable in the solid state, no change being observed even after a couple of months in air. The structure of **3** was elucidated unequivocally by the X-ray diffraction method (Figure 1).[8] The crystal structure of **3** occluding toluene possesses a crystallographic 2-fold axis. The skeleton is slightly distorted from the regular prismane structure made up from two triangular units (Si–Si: 2.374–2.387 Å, av 2.380 Å, and Si–Si–Si: 59.8–60.3°, av 60.0°) and three rectangular units (Si–Si′: 2.365–2.389 Å, av 2.373 Å and Si–Si–Si′: 89.6–90.5°, av 90.0°). The lengths of exocyclic Si–C bonds are 1.901–1.920 Å (av 1.908 Å). Because of the geometry, the exocyclic bond angles are significantly expanded to 133.5° (av) for Si–Si–C and 126.9° (av) for Si′–Si–C.

Scheme I



All the Si–Si bonds in **3** are elongated from the normal Si–Si bond length (2.34 Å) and are somewhat longer than those calculated for Si_6H_6 (2.359 Å for triangular units and 2.375 Å for rectangular units).[4c] The aryl planes are so arranged in a screw-shaped manner around the three-membered ring that the skeleton of the prismane is effectively covered with the six 2,6-diisopropylphenyl groups.

Owing to the large steric congestion, the ^1H NMR spectrum of **3** at 25 °C shows that the two isopropyl and aryl protons are nonequivalent, indicating significantly hindered rotation of the substituents. However, the six 2,6-diisopropylphenyl groups attached to each silicon are equivalent on the NMR time scale.[9] The ^{29}Si NMR spectroscopy demonstrated that the six silicons of the skeleton are equivalent, with the single resonance appearing at −22.3 ppm.[10] ^1H NMR spectrum is temperature-dependent, and the coalescence temperatures (T_c) were 328 K for the meta protons and 363 K for the isopropyl methine protons ($\Delta G^{\ddagger}_{rot}$ = 16.5 kcal/mol).

In the UV–visible spectrum, **3** exhibits an absorption maximum at 241 nm (ε 78 000, hexane) tailing into the visible region (ca. 500 nm). Upon irradiation of **3** with a light of 340–380-nm wavelength in solution (3-MP or 2-MeTHF) at ca. 223 K or in a glass matrix at 77 K, new absorption bands appeared at 456 and 502 nm, the intensity ratio being approximately 3:1. Excitation of these bands with a light of wavelength longer than 460 or 500 nm resulted in the immediate regeneration of the original absorption due to **3**. Thermally these bands also reverted to **3** above −10 °C.

A single chemical species is produced during the reaction since the two bands appeared and disappeared simultaneously. There are several possible candidates for the species. If the divalent silylene is involved, significant blue shift in the UV spectrum

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(1) Chemistry of Organosilicon Compounds. 303.

(2) For reviews on group 14 polyhedranes: (a) Nagase, S. *Polyhedron* **1991**, *10*, 1299. (b) Sekiguchi, A.; Sakurai, H. In *The Chemistry of Inorganic Ring Systems*; Steudel, R., Ed.; Elsevier: New York, 1992; Chapter 7. (c) Sakurai, H.; Sekiguchi, A. In *Frontiers of Organogermanium, -Tin and -Lead Chemistry*; Lukevics, E., Ignatovich, L., Eds.; Latvian Institute of Organic Synthesis: Riga, 1993; pp 97–108.

(3) Hexagermaprismane: (a) Sekiguchi, A.; Kabuto, C.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 55. Octasilacubane and octagermacubane: (b) Matsumoto, H.; Higuchi, K.; Hoshino, Y.; Koike, H.; Naoi, Y.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1083. (c) Sekiguchi, A.; Yatabe, T.; Kamatani, H.; Sakurai, H. *J. Am. Chem. Soc.* **1992**, *114*, 6260. (d) Furukawa, K.; Fujino, M.; Matsumoto, N. *Appl. Phys. Lett.* **1992**, *60*, 2744. (e) Matsumoto, H.; Higuchi, K.; Kyushin, S.; Goto, M. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1354. Octastannacubane: (f) Sita, L. R.; Kinoshita, I. *Organometallics* **1990**, *9*, 2865. Decastannaprismane: (g) Sita, L. R.; Kinoshita, I. *J. Am. Chem. Soc.* **1991**, *113*, 1856.

(4) For theoretical calculations on Si_6H_6: (a) Nagase, S.; Kudo, T.; Aoki, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1121. (b) Sax, A.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 651. (c) Nagase, S.; Nakano, M.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1987**, 60. (d) Nagase, S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 329.

(5) For the use of $Mg/MgBr_2$ for the coupling reactions of chlorosilanes and chlorogermanes, see: (a) Smith, C. L.; Gooden, R. *J. Organomet. Chem.* **1974**, *81*, 33. (b) Smith, C. L.; Pounds, J. *J. Chem. Soc., Chem. Commun.* **1975**, 910. (c) Ando, W.; Tsumuraya, T. *Ibid.* **1987**, 1514. (d) Sekiguchi, A.; Yatabe, T.; Naito, H.; Kabuto, C.; Sakurai, H. *Chem. Lett.* **1992**, 1697.

(6) The reactive species in the Mg/MgX_2 system may be MgX(I). (a) Gomberg, M. *Recl. Trav. Chim.* 1929, *48*, 847. (b) Gomberg, M.; Bachmann, W. E. *J. Am. Chem. Soc.* **1927**, *49*, 236.

(7) Tsumuraya, T.; Batcheller, S. A.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 902.

(8) Crystal data of **3** at 150 K: $Si_6C_{72}H_{102}\cdot C_7H_8$; monoclinic; a = 13.898(2), b = 23.995(3), and c = 21.964(2) Å, β = 95.63(1)°, V = 7289.4(15) $Å^3$, space group $C2/c$; Z = 4; D_c = 1.119 g/cm^3. The final R factor was 0.0815 (R_w = 0.0899).

(9) ^1H NMR (300 MHz, C_6D_6): δ 0.63 (d, 18 H, J = 6.6 Hz), 1.01 (d, 18 H, J = 6.6 Hz), 1.10 (d, 18 H, J = 6.6 Hz), 1.62 (d, 18 H, J = 6.6 Hz), 3.45 (sept, 6 H, J = 6.6 Hz), 4.82 (sept, 6 H, J = 6.6 Hz), 6.98 (d, 6 H, J = 7.6 Hz), 7.09 (d, 6 H, J = 7.6 Hz), 7.17 (t, 6 H, J = 7.6 Hz). ^{13}C NMR (75.5 MHz, C_6D_6): δ 25.4, 25.5, 26.8, 26.9, 36.7, 37.1, 123.3 (meta), 123.6 (meta), 130.2 (para), 135.4 (ipso), 153.6 (ortho), 156.7 (ortho).

(10) A solid-state ^{29}Si NMR spectrum of **3** showed signals at δ −22.2 and −30.8 (intensity ratio = 2:1), in agreement with the distorted prismane structure.

(11) (a) Gillette, G. R.; Noren, G. H.; West, R. *Organometallics* **1987**, *6*, 2617. (b) Ando, W.; Sekiguchi, A.; Hagiwara, K.; Sakakibara, A.; Yoshida, H. *Ibid.* **1988**, *7*, 558. (c) Gillette, G. R.; Noren, G. H.; West, R. *Ibid.* **1989**, *8*, 487. (d) Kira, M.; Maruyama, T.; Sakurai, H. *Tetrahedron Lett.* **1992**, *33*, 243.

0002-7863/93/1515-5853$04.00/0

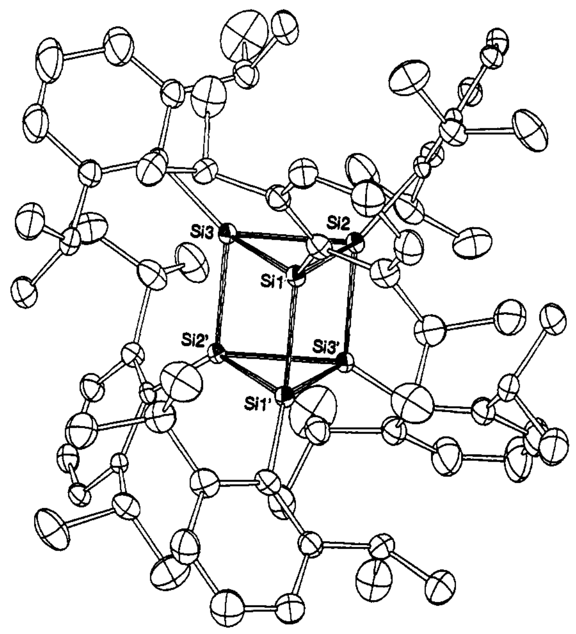

Figure 1. ORTEP drawing of 3. Selected bond lengths (Å): Si1–Si2 2.374, Si1–Si3 2.379, Si1–Si1′ 2.389, Si2–Si3 2.387, Si2–Si3′ 2.365, Si3–Si2′ 2.365 (esd = 0.002 Å). Selected bond angles (deg): Si2–Si1–Si3 60.3, Si1–Si2–Si3 60.0, Si1–Si3–Si2 59.8, Si2–Si1–Si1′ 89.6, Si3–Si1–Si1′ 89.9, Si1–Si2–Si3′ 90.5, Si3–Si2–Si3′ 90.4, Si1–Si3–Si2′ 90.0, Si2–Si3–Si2′ 89.6 (esd = 0.0°).

resulting from the formation of a silylene–ether complex should be observed, but no such blue shift was observed in 2-MeTHF.[11] It may be premature to draw a conclusion at this moment, but a likely reaction is the photochemical generation of the haxasila-Dewar benzene **4** and regeneration of **3**. The bands in the visible region may be assigned to the Si═Si double bonds of **4**.[12] However, all the attempts to trap **4** with methanol or sulfur failed, probably due to the rapid intramolecular reaction to regenerate **3**.

Hexagermaprismane **5**, with 2,6-diisopropylphenyl groups, was also prepared in 10% yield by the reaction of (2,6-diisopropylphenyl)trichlorogermane with Mg. The structure was determined by X-ray diffraction.[13] The Ge–Ge bond lengths are 2.503 Å (av) for the triangular units and 2.468 Å (av) for the rectangular units.[14]

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Supplementary Material Available: Tables of X-ray experimental data, atomic parameters, anisotropic temperature factors, bond distances, and bond angles for **3** and **5** (20 pages); tables of observed and calculated structure factors (53 pages). Ordering information is given on any current masthead page.

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(12) For the electronic spectra of disilenes, see: (a) West, R. *Pure Appl. Chem.* **1984**, *56*, 163. (b) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419. (c) West, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1201. (d) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S.; Rappoport, Z., Eds.; John Wiley & Sons; New York, 1989; Part 2.

(13) Crystal data of **5** at 200 K: $Ge_6C_{72}H_{102}\cdot C_7H_8$; monoclinic; $a = 14.040(4)$, $b = 24.204(6)$, and $c = 22.264(3)$ Å, $\beta = 95.97(2)°$, $V = 7524.6(30)$ Å^3, space group $C2/c$; $Z = 4$; $D_c = 1.320$ g/cm^3. The final R factor was 0.0602 ($R_w = 0.0667$).

(14) Like **3**, hexagermaprismane **5** resulted in the formation of an isomer with absorption bands at 450 and 562 nm upon irradiation.