Cluster Compounds

A Molecular Silicon Cluster with a "Naked" Vertex Atom**

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Silicon clusters have been the subject of intense research efforts^[1] owing to the ubiquitous role of elemental silicon in a variety of electronic and optical applications, such as integrated circuits, photovoltaic cells, and optical sensors.^[2] In fact, the optical properties of many silicon-based materials depend to a large extent on the presence of small- to medium-sized, partially hydrogenated clusters within the surrounding matrix of bulk silicon. Luminescence phenomena in porous silicon, for instance, have been attributed to the photo-excitation of such clusters.^[3,4]

The difficulties in the structural characterization of these compounds could be circumvented by the synthesis of discrete molecular derivatives. Advances in the preparation of molecular germanium and tin clusters with "naked" (unsubstituted) vertices have been recently summarized.^[5] Indeed, in the case of silicon's higher homologues a few examples have been prepared.^[6] Whereas a variety of alkyl-terminated, medium-sized silicon clusters have been characterized by electron microscopic techniques,^[7] small discrete molecular clusters are known only as either totally unsubstituted Zintl-type anions^[8] or fully substituted deltahedral derivatives of the type Si_nR_n.^[9] Theoretical studies predict interesting structural motifs for their elusive partially substituted congeners.^[10]

Reductive dehalogenation of a divalent species in the presence of GeCl₂ had proven successful for the preparation of the germanium cluster Ge₆R₂ as reported by Power and coworkers.^[6c] Unfortunately, the instability of divalent silicon compounds renders such an approach unsuitable.^[11] On the other hand, the recently reported disilenides, analogues of vinyl anions, should be good precursors for multiply unsaturated silicon π systems, which could subsequently rearrange to yield the desired partially substituted clusters owing to the low stability of Si=Si double bonds. The pentadiene **2** was chosen as the initial target compound, produced by treatment of SiCl₄ with 2 equivalents of the lithium salt of disilenide **1** (Scheme 1).^[12a] Crystallization of the complex reaction mixture yielded uniform red crystals in marginal yield (<1%).

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Scheme 1. Synthesis of the partially substituted silicon cluster **3** (R = Tip = 2,4,6-triisopropylphenyl).

However, a preliminary X-ray diffraction study on the crystals of mediocre quality revealed the connectivity of the partially substituted, five-vertex cluster **3** with one "naked" endohedral silicon atom.

Formation of **3** from **1** and SiCl₄ requires a further 2 equivalents of the disilenide **1** for reduction of the putative intermediate **2**. Indeed, the use of 4 equivalents of disilenide **1** essentially led to a 1:1 mixture of **3** and **4**, the formal oxidation product of **1** (Scheme 1). The tetrasilabutadiene **4** was identified by comparison of the ¹H and ²⁹Si NMR spectroscopic shift values with those reported in the literature.^[13] Separation of the reaction mixture proved tedious, affording yields of **3** that varied between 22 and 37 % of theoretical prediction.^[14]

The ²⁹Si NMR spectrum shows three signals in a ratio of 2:2:1 at $\delta = 7.4$, -108.4, and -124.8 ppm. In the ²⁹Si–¹H-correlated 2D NMR spectrum only the signals at $\delta = 7.4$ and -108.4 ppm show cross-peaks to two and one aryl substituents, respectively. These findings, together with an apparent C_2 symmetry deduced from ¹³C and ¹H NMR spectra, confirm the structural integrity of the cluster **3** in solution. Two distinct UV/Vis spectroscopic absorptions are observed at $\lambda = 365$ and 540 nm, the latter being significantly less intense.

An especially notable analytical feature of **3** was found in the EI MS data: a peak at m/z = 1415.9 can be assigned to Si₇Tip₆ by comparison with the calculated isotopic distribution pattern. This cluster expansion apparently takes place upon heating of the sample in the condensed phase (required for evaporation of the compound under high vacuum preceding ionization), given that no such peak was observed with milder ionization techniques. The highest mass detected by FAB MS is the molecular ion peak at m/z = 1359.9. This interpretation is supported by the detection of an exothermic process at 144°C by differential scanning calorimetry of **3**. It should be noted that the hydrogenated congeners of **3** have been implied as intermediates in the chemical vapor deposition of silanes for the preparation of thin elemental silicon films.^[10]

With a reproducible synthetic protocol in hand, good quality single crystals of **3** were finally obtained. X-ray crystallographic analysis (Figure 1) confirmed the structure of the partially substituted silicon cluster.^[15] The distance between Si2 and Si3 (2.306(1) Å) is significantly shorter than a conventional Si–Si single bond (2.34 Å).^[16] Surprisingly, the transannular distances Si2–Si5 (2.343(1) Å) and Si3–Si5 (2.337(1) Å) precisely reflect the typical Si–Si single bond length. Nevertheless, if one ignores these transannular



Figure 1. Molecular structure of **3** in the solid state (thermal ellipsoids at 50% probability). Isopropyl groups and protons are omitted for clarity. Selected bond lengths [Å]: Si1–Si2 2.3651(9), Si1–Si5 2.3456(9), Si2–Si3 2.3061(9), Si2–Si5 2.3430(9), Si3–Si5 2.3373(8), Si3–Si4 2.3596(9), Si4–Si5 2.3445(9), Si1–C1 1.929(2), Si1–C16 1.916(2), Si2–C31 1.917(2), Si3–C46 1.913(2), Si4–C61 1.915(2), Si4–C76 1.925(2); selected bond angles [°]: Si5-Si1-Si2 59.65(2), Si3-Si4 59.89(3), Si4-Si5-Si1 161.02(3).

interactions, Si2 and Si3 are only slightly pyramidal (bondangle sums: Si2, 358.9°; Si3, 359.0°). The planes defined by Si1-Si2-C31 and Si3-Si4-C46 are almost perpendicular (torsion angle = 88.7°). The corresponding angle was determined to be 54.4° for the highly twisted disilene $(tBu_2MeSi)_2Si=$ Si(SiMetBu₂)₂.^[17]

DFT calculations at the B3LYP/6-31G(d,p) level of theory on the H-substituted parent compound 3u were carried out to clarify the nature of the interactions that lead to the extreme distortions of $\mathbf{3}^{[18]}$ Interestingly, $\mathbf{3u}$ was only found to be a transition state of the ring inversion of the potential bishomoaromatic isomer in which both silicon bridges are present on the same side of the central three-membered ring moiety.^[19] The bulky substituents apparently favor **3** to an extent that the transition state becomes an energy minimum. Nonetheless, the experimental structure is reasonably wellreproduced by the calculations. Whereas the transannular distances Si5–Si2 and Si5–Si3 in **3u** are slightly longer (2.42 Å; **3**: 2.34 Å), the Si2–Si3 bond is a bit shorter (2.26 Å; **3**: 2.30 Å) than the corresponding distances in 3. The dihedral angle H-Si2-Si3-H of 138.2° is significantly wider (3: C31-Si2-Si3- $C46 = 112.8^{\circ}$) and thus is even closer to an ideal *trans* arrangement of the somewhat more pyramidal, formal sp²hybridized silicon centers (bond-angles sum: 354.3°).

To provide more insight into this curious bonding situation, the molecular orbitals of 3u were calculated (Figure 2). Whereas HOMO and HOMO-1 are only separated by 0.14 eV, the difference to the next highest orbital HOMO-2 (1.34 eV) is almost ten times as large. The Heilbronner criterion for Möbius aromaticity, namely that 4n mobile electrons must be available, is therefore formally fulfilled.^[20] Indeed, the appearance of the HOMO-1 does resemble a Möbius array, such as that calculated for *trans*-



Figure 2. Molecular orbitals of 3u as calculated at the B3LYP/6-31G-(d,p) level of theory: a) HOMO and HOMO-1, b) schematic representation of the atomic orbitals involved.

benzene.^[21] The unsuccessful search for corresponding 3c-2e bonds in **3u** by NBO analysis, however, draws a picture that seemingly contradicts this interpretation of the canonical MOs. The analysis yields two degenerate orbitals with high p-character (95.26%) which are each strictly localized between two silicon atoms: Si5 and Si2, and Si5 and Si3. Therefore, an alternative description of **3** as a classical Lewis structure exclusively with 2c-2e bonds must be considered as well.

In conclusion, the first discrete partially substituted silicon cluster has been isolated and structurally characterized. Its chemical and physical features suggest that it might serve as a model for its partially hydrogenated congeners in bulk silicon materials.

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- [15] Crystal structure determination of **3**: red blocks from hexane; $C_{90}H_{138}Si_5$, monoclinic, space group $P2_1/c$; a = 1426.8(3), b = 1361.4(3), c = 4453.1(10) pm, $a = 90^\circ$, $\beta = 95.296(4)^\circ$, $\gamma = 90^\circ$, $V = 8613(3) \times 10^{-30}$ m³; Z = 4, $\rho_{calc} = 1.049$ g cm⁻³; crystal dimensions: $0.28 \times 0.25 \times 0.12$ mm³; diffractometer: Bruker SMART APEX CCD; MO_{Ka} radiation, 173 K; $2\theta_{max} = 52.74$; 68217 reflections, 17602 independent ($R_{int} = 0.0408$), direct methods; absorption correction SADABS ($\mu = 1.24$ cm⁻¹); refinement (against F_o^2) with SHELXTL (version 5.1) and SHELXL-97, 971 parameters, 0 restraints, $R_1 = 0.0562$ ($I > 2\sigma$) and wR_2 (all data) = 0.1429, GooF = 1.038, max/min residual electron density: $0.426/-0.184 \times 10^{30}$ e m⁻³. CCDC-256745 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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