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Synthesis of a Pentasilapropellane. Exploring the Nature of a Stretched Silicon−Silicon Bond in a Nonclassical Molecule

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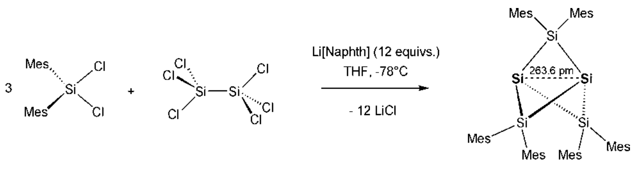
Abstract: We report on the successful synthesis of Si_5Mes_6 (Mes = 2,4,6-trimethylphenyl), which consists of an archetypal [1.1.1] cluster core featuring two ligand-free, "inverted tetrahedral" bridgehead silicon atoms. The separation between the bridgehead Si atoms is much longer, and the bond strength much weaker, than usually observed for a regular Si−Si single bond. A detailed analysis of the electronic characteristics of Si_5Mes_6 reveals a low-lying excited triplet state, indicative of some biradical(oid) character. Reactivity studies provide evidence for both closed-shell and radical-type reactivity, confirming the unusual nature of the stretched silicon−silicon bond in this "nonclassical" molecule.

Silicon-based analogues of hydrocarbons intrigue chemists for a number of reasons. They are often fundamentally different from their carbon counterparts and have remained a challenge for both experimentalists and theoreticians for a long time.[1] After the first isolation of a kinetically stabilized disilene $R_2Si{=}SiR_2$ by West *et al.* in 1981,[2] the synthesis and characterization of several silicon−silicon multiple bonds, spiro- and bicyclic structures, and clusters followed.[3] The isolation of the first spirocyclic pentasiladiene[4] fused the chemistry of unsaturated Si═Si moieties with that of annulated ring systems such as tetrasilabicyclo[1.1.0]butanes.[5] However, the parent structure of these annulated ring systems, that is, the pentasila[1.1.1]propellane Si_5R_6, remained elusive until now. This heavier homologue of the widely investigated carbon propellanes C_5R_6[6] was targeted by theory more than 2 decades ago[7] and designated a synthetic challenge.[8] Unsurprisingly, only three closely related silicon clusters consisting of "naked" Si atoms have been reported so far, by Wiberg[9] and Scheschkewitz.[10]

The intrinsic [1.1.1] scaffold of propellanes belongs to the "nonclassical" structures showing "inverted tetrahedral" bridgehead atoms. The bonding between the bridgehead atoms is far from trivial. Even the well-established all-carbon [1.1.1]propellane has attracted renewed interest from both experimentalists[11] and theoreticians.[12] The heavy [1.1.1]propellanes $[E_5R_6]$ (E = Si, Ge, Sn) have frequently been described as biradicaloids[13] due to the considerably stretched bond between their bridgeheads, E_b. Although numerous quantum chemical calculations[7] have been performed on these species, synthetically accessible and structurally characterized species are very rare.[14−17] In the present contribution, we report on the synthesis and characterization of pentasila[1.1.1]propellane Si_5Mes_6 (**1**), the last missing member within the Group 14 element series, finally closing the gap between theoretical predictions and discussions.

For the synthesis of **1** (Scheme 1), we reacted Si_2Cl_6 with 3 equiv of Mes_2SiCl_2 and 12 equiv of a freshly prepared lithium naphthalenide solution ($Li^+[Naphth]^{\bullet-}$, 0.8 M in THF).[17] ^1H NMR spectroscopic monitoring of the crude product of the reaction showed that the target compound **1** is formed in about 10% yield. After a nonoptimized workup procedure, **1** was isolated by column chromatography and recrystallization from toluene/acetonitrile in analytically pure form as bright yellow crystals. **1** is extremely sensitive to air and moisture (see below). The elemental analysis and electron impact (EI) mass spectra were consistent with the composition Si_5Mes_6. **1** is EPR-silent at room temperature and 100 K. The ^1H and ^{13}C NMR spectra of **1** (in C_6D_6) are very similar to those found for Ge_5Mes_6,[17] further supporting the formation of the pentasila analogue. Most revealingly, two resonances were observed in the ^{29}Si NMR spectrum at $\delta = 25.5$ and -273.2 ppm for the bridging (Si_{br}) and bridgehead (Si_b) atoms in **1**, respectively ($\delta_{calcd} = 34$ and -270 ppm; see Supporting Information).

Scheme 1



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Despite the sensitivity of **1**, we were able to grow single crystals suitable for X-ray structure analysis (Figure 1). As expected for [1.1.1]propellane core structures, **1** consists of two ligand-free bridgehead silicon atoms (Si1 and Si2), which are bonded to three bridging silicon atoms (Si3, Si4, and Si5) at distances between 233.2(1) and 236.0(1) pm. Of particular interest is the separation of 263.6(1) pm between the two bridgehead silicon atoms, which is *ca.* 30 pm (13%) longer than usually observed for a regular Si−Si single bond. Based on this very long separation and previous quantum chemical calculations,[17] it appears that the $Si_b\cdots Si_b$ interaction in **1** is fairly weak—in this case considerably stretched, though not fully broken. Note that a comparably elongated Si−Si bond of 269.7 pm was found by Wiberg *et al.* for the sterically encumbered disilane $t\mathrm{Bu}_3\mathrm{Si}{-}\mathrm{Si}t\mathrm{Bu}_3$.[18] The latter was shown to be a convenient source (heating to *ca.* 50 °C) for very reactive supersilyl radicals ($t\mathrm{Bu}_3\mathrm{Si}^\bullet$). The bond strength in $t\mathrm{Bu}_3\mathrm{Si}{-}\mathrm{Si}t\mathrm{Bu}_3$ was estimated to be considerably weaker than in normal disilanes.

With these observations on the related though topologically different Si_2R_6 molecule in mind, we tried to explore the weak $Si_b\cdots Si_b$ bond

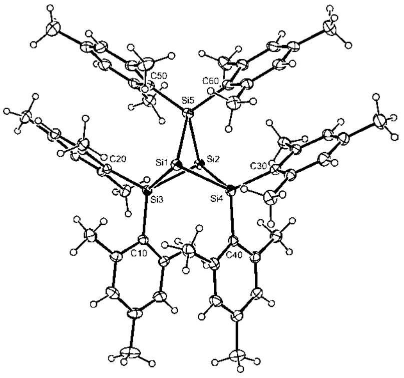

Figure 1. Molecular structure of Si_5Mes_6 (**1**).

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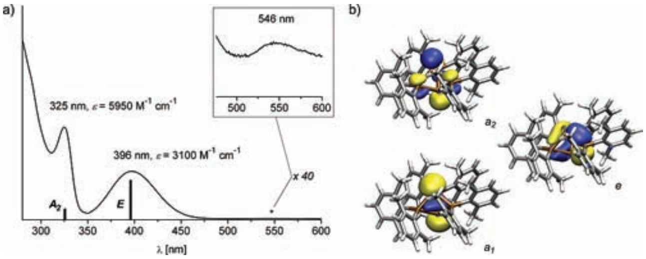

Figure 2. (a) Experimental UV−vis spectrum of **1** in THF and most relevant TD-DFT calculated UV−vis transitions of A_2 and E symmetry (b) DFT calculated frontier orbitals of Si_5Dmp_6 (**1q**): HOMO−1 (a_1, −5.86 eV); HOMO (e, −5.64 eV); and LUMO (a_2, −1.77 eV).

in **1** a little further, both experimentally by Raman spectroscopy and theoretically by time-dependent (TD)-DFT calculations on Si_5Dmp_6 (**1q**, Dmp = 2,6-$Me_2C_6H_3$, see Supporting Information). However, the aim to extract the contribution of the restoring $Si_b\cdots Si_b$ bond forces from the totally symmetric Raman bands cannot be achieved for **1** with the desired accuracy, because too many internal coordinates are involved in each of the totally symmetric normal modes observed at $\nu = 479$, 370, and 340 cm^{-1} ($\nu_{calcd} = 455$, 349, and 312 cm^{-1}). In order to obtain at least an estimation of the $Si_b\cdots Si_b$ bond strength in **1**, we calculated the reaction energy for the process **1q** + $H_2 \rightarrow H_2$**1q**. Accordingly, the addition of H_2 to the bridgehead Si atoms is exothermic by $\Delta H°(0\ K) = -90$ kJ mol^{-1}. By using $D(H_2) = 436$ kJ mol^{-1} and assuming a Si−H bond strength of ∼350 kJ mol^{-1} for silyl-substituted silanes,[19] the $Si_b\cdots Si_b$ bond strength can be estimated to amount to ∼174 kJ mol^{-1}. Based on this approximation and as expected, the $Si_b\cdots Si_b$ interaction is considerably weaker than in normal disilanes (*ca.* 306−332 kJ mol^{-1}).[19]

Alongside these remarkable bonding features, we determined some interesting electronic properties for **1**. The electronic transitions observed in the experimental UV−vis spectrum of **1** in THF fit perfectly to the TD-DFT calculated singlet excitations for the model compound **1q** (Figure 2).[17] The calculated vertical singlet excitation wavelength of 325.7 nm ($^1A_2$, HOMO−1 (a_1) → LUMO (a_2)) directly corresponds to the experimentally observed absorption at $\lambda = 325$ nm, whereas $\lambda_{max} = 396$ nm belongs to electronic transitions between the cluster-bonding HOMO (e) and the LUMO (a_2) (Figure 2). The excitation to the first excited triplet state ($^3A_2$) was calculated to correspond to a wavelength of 546.8 nm.[17] Usually, these transitions are not visible in the UV−vis spectrum. The experimental spectrum of **1**, however, shows a broad absorption of very low intensity at $\lambda = 546$ nm (Figure 2). Its wavelength corresponds to an excitation energy of 219 kJ mol^{-1}, that is, about 25 and 10 kJ mol^{-1} *below* the respective excitation energies of its Ge and Sn analogues.[17] This is remarkable, because the first singlet A_2 excitation energy of **1q** is *larger* than those of its analogues. Whereas the increase in the HOMO−1 → LUMO gaps along the series Sn → Ge → Si is consistent with the computed singlet excitation energies, the close proximity (reflected by the rather localized excited ground state difference densities of the $^1A_2$ and $^3A_2$ states, see Supporting Information) of the orbitals involved in **1q** leads to a larger exchange interaction $\langle a_1a_2|a_2a_1\rangle$ and extra stabilization of the $^3A_2$ state compared to the Ge and Sn analogues.

The relatively high LUMO energy of **1q** (−1.77 eV; cf. −2.10 eV for Ge_5Dmp_6 and −2.48 eV for Sn_5Dmp_5) was experimentally confirmed by electrochemical studies using cyclic voltammetry under strictly anaerobic and dry conditions. By analogy to the heavy Ge[17] and Sn propellanes,[14] **1** is quasi-reversibly reduced to the radical anion $[Si_5Mes_6]^{\bullet-}$ and dianion $[Si_5R_6]^{2-}$ at potentials of $E°_{1/2} = -2.88$ and −3.12 V, respectively. Compared to the heavier homologues, however, both half-wave potentials are more cathodically shifted, which is in accord with an energetically destabilized LUMO. On the basis of these findings, one would *a priori* expect a less facile addition of nucleophiles to **1** as compared to the heavier homologues. In contrast, however, we found a *higher* reactivity of the silicon propellane.

The first experimental evidence came from observations regarding the moisture sensitivity of **1**. Note that Sn_5Dep_6 (Dep = 2,6-$Et_2C_6H_3$)[14] and Ge_5Mes_6[17] are stable toward degassed water, without any sign of decomposition and/or reaction. Hydrocarbon solutions of **1**, however, rapidly decolorize when exposed to traces of water. In order to address this as well as the general reactivity of **1** a little further, we performed some preliminary NMR tube scale reactions using selected reagents. It appears that **1** shows both closed-shell *and* radical-type reactivity. Several reagents, such as H_2O, PhSH, PhOH, and Me_3SnH (not Me_3SiH), can readily be added across the bridge, furnishing the corresponding bicyclo[1.1.1]pentasilane derivatives (see Supporting Information). Evidence for biradicaloid reactivity of **1** came from studies using typical reagents for radical-type reactivity, such as Me_3SnH or 9,10-dihydroanthracene. The latter gave the dihydrogen adduct H_2**1** in low yield after prolonged reaction times.

All these promising results clearly indicate distinctive peculiarities of the stretched bond between the bridgehead atoms in heavy propellanes in general, and in particular in **1**. Once designated as synthetic challenge and targeted by theory over 2 decades ago, pentasila[1.1.1]propellane is indeed revealed to be an intriguing species from the perspectives of both bonding and reactivity.

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Supporting Information Available: Details of experimental procedures, preliminary reactivity studies, analytical data, X-ray structure determination, and quantum chemical calculations (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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