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[$Sn_4Si\{Si(SiMe_3)_3\}_4\{SiMe_3\}_2$]: A Model Compound for the Unexpected First-Order Transition from a Singlet Biradicaloid to a Classical Bonded Molecule**

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Metalloid cluster compounds of the general formula M_nR_m ($n > m$; M = metal or semi-metal, R = ligand) are ideal model compounds for the system size range encompassed by molecules and the solid state, paving the way for further understanding of element formation from oxidized species on an atomic scale.[1] In the case of tin, metalloid cluster compounds were first synthesized by reductive coupling of Sn^{II} compounds, such as $SnCl_2$.[2] Recently it was shown that metalloid cluster compounds of tin can also be synthesized by the disproportionation reaction of tin monohalides.[3] The monohalides are thereby obtained by employing a preparative co-condensation technique.[4] Hence, the reaction of SnBr with $LiSi(SiMe_3)_3$ leads to the metalloid cluster compound [$Sn_{10}\{Si(SiMe_3)_3\}_6$] (**1**) in moderate yield of approximately 17%.[5] Because only six of the ten tin atoms in **1** bear a $Si(SiMe_3)_3$ ligand, the average oxidation state of the tin atoms is 0.6. Thus, the metalloid cluster **1** is a reduction product of the disproportionation reaction on the way to elemental tin.[6] Because the reaction starts with the monohalide SnBr, oxidized species with an average tin atom oxidation state of greater than 1 must also be present in the reaction solution. Early examples of such compounds were anionic stannylene [$Sn\{Si(SiMe_3)_3\}_3$]$^-$ and cyclotristannene [$Sn_3\{Si(SiMe_3)_3\}_4$] (**2**), in which the average oxidation states of the tin atoms is +2 and +1.3, respectively.[7] The shortest tin–tin double bond of 258 pm was observed in **2**, caused by the steric bulk of the ligands forcing the double bond into a planar arrangement. As **2** is only obtained together with the metalloid cluster compound [$Sn_{10}\{Si(SiMe_3)_3\}_6$] (**1**), subsequent investigations on **2** are always hindered by the presence of **1**. Crystallization of **2** from the reaction mixture was attempted to circumvent this problem. During these attempts, another type of black diamond shaped crystals were obtained, and single crystal X-ray diffraction analysis of these crystals revealed a yet unknown crystal system. However, solution of the crystal structure showed that the metalloid cluster compound **1** is present in the crystal lattice,[8] this time crystallizing together with the novel polyhedral cluster compound [$Sn_4Si\{Si(SiMe_3)_3\}_4(SiMe_3)_2$] (**3**). The molecular structure of **3** is best described as a butterfly arrangement of four tin atoms bridged by a $Si(SiMe_3)_2$ group (Figure 1). Every tin atom is additionally bound to a $Si(SiMe_3)_3$ ligand, with slightly different Sn–Si distances of 261 pm (Sn11–Si7A, Sn13–Si7) and 265 pm (Sn14–Si8, Sn12–Si8A). The capping $Si(SiMe_3)_2$ group most likely comes from the degradation of the $Si(SiMe_3)_3$ ligand, and a plausible mechanism is given in the supporting information.

The tin–tin distances (284 pm) inside the Sn_4 butterfly unit in **3** are within the range of a normal single bond (283–285 pm). The capping silicon atom is bound to two tin atoms, with a Si–Sn distance of 263 pm also within the range of a single bond, leading to a nearly tetrahedral arrangement for these two tin atoms (Sn11, Sn13). In spite of this arrangement,

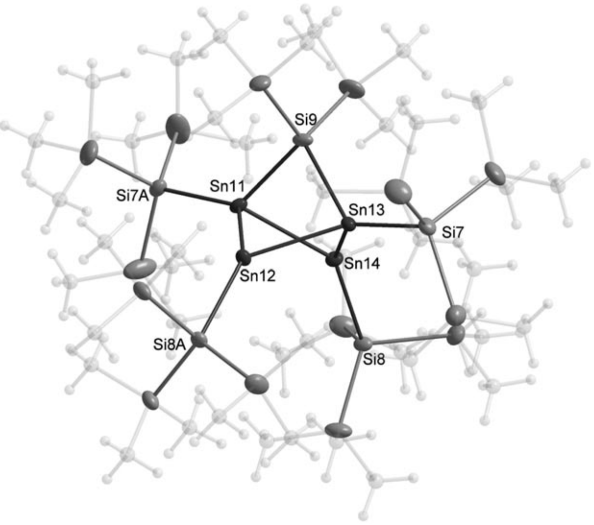

Figure 1. Molecular structure of [$Sn_4Si\{Si(SiMe_3)_3\}_4(SiMe_3)_2$] (**3**). The methyl groups are depicted with 50% transparency (thermal ellipsoids are only shown for tin and silicon atoms, the probability is set at 25%). Selected distances [pm] and angles [°]: Sn11–Sn12 284.22(8), Sn12–Sn13 283.16(8), Sn13–Sn14 284.85(8), Sn14–Sn11 284.47(8), Sn12–Sn14 381.8(1), Sn11–Sn13 356.3(1), Sn11–Si7A 261.2(2), Sn13–Si7 260.6(2), Sn12–Si8A 264.4(2), Sn14–Si8 264.8(2), Si9–Sn11 263.2(2), Si9–Sn13 262.4(2); Sn14-Sn12-Si8A 127.00(1), Sn12-Sn14-Si8 125.39(1), Sn13-Sn12-Sn11 77.82(3), Si8A-Sn12-Sn11 137.66(5), Sn11-Si9-Sn13 85.37(7).

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however, the coordination number of the other two tin atoms of the butterfly arrangement (Sn12, Sn14) is three instead of four, since the tin–tin distance between these atoms (382 pm) is significantly larger than the sum of the covalent radii (280 pm).[9] Furthermore, the Sn–Si distance to the central silicon atom (Si9) of the capping $Si(SiMe_3)_2$ group (360 pm) is too long for a bond. This structure strongly suggests that an unusual bonding is to be expected for **3**.

Thereby it would be most interesting to see whether a bonding interaction exists between the two tin atoms with coordination number 3, which may be considered as radical centers at first glance. However, **3** is EPR silent, and quantum chemical calculations predict[10] the singlet state to be the ground state (ΔE singlet→triplet = 48.9 $kJ\,mol^{-1}$). Owing of these, **3** may be considered as a singlet biradicaloid,[11] as it is the case for propellane-type E_5R_6 compounds (E = Si, Ge, Sn; R = organic ligand such as, 1,3,5-Me_3-C_6H_2)[12] or related four membered P_2C_2[13] and B_2P_2[14] heterocycles.

A similar polyhedral arrangement of five Group 14 atoms was recently observed by Power et al. for the metalloid cluster compound $[Ge_5Ar_4]$ (**4**; Ar = 2,6-Mes_2-C_6H_3; Mes = 2,4,6-Me_3-C_6H_2).[15] A butterfly arrangement of four germanium atoms is capped by a naked germanium atom in **4**, also leading to two germanium atoms with coordination number three. Hence, such an arrangement seems favorable in the field of subvalent compounds of Group 14. However, a closer look at the molecular structure of **3** reveals significant differences with the Ge_5 compound **4** of Power et al.[15] (Figure 2). The geometry of the atoms with coordination number three is best described as nearly planar for **3** (sum of bonding angles: 350°), while it is pyramidal in the case of **4** (sum of bonding angles: 309°).[16]

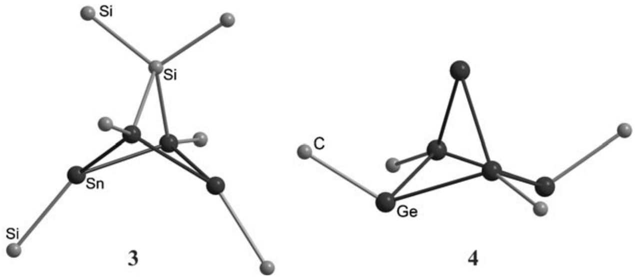

Figure 2. Comparison of the arrangement of central atoms inside **3** and **4**. Only those ligand atoms directly bound to metal centers are shown.

This different orientation of the ligands also leads to a different bonding inside the E_5 polyhedron, as supported by the results of quantum chemical calculations on **3** and **4**.

The most important difference between **3** and **4** is highlighted by an inspection of the shared electron number (SEN)[17] of the two center bonding component between the two tetrel atoms with coordination number three: there is a significant SEN of 0.21 in the case of **3** and a SEN close to zero (0.02) in the pyramidal form **4**. This result points to the existence of a bonding interaction between the two tin atoms with coordination number three inside **3**, even though the Sn–Sn distance (382 pm) is too long for a single bond. This result also shows that by changing the arrangement of the ligand (planar vs. pyramidal), a bonding path either is formed or destroyed.

To investigate the influence of the orientation of the ligands in more detail, we performed calculations on the model system $[(SiH_3)_4Sn_4SiH_2]$ (**3a**; in which every $SiMe_3$ group in **3** is substituted by a hydrogen atom). In this model compound the Sn-Sn-Si angle α (Figure 3) was systematically varied from 88° through 213°, while all other structural parameters were simultaneously optimized (for technical details, see “Quantum chemical calculation” section). CASSCF[18] (complete active space self consistent field) calculations for the singlet and the triplet state for each of these individual arrangements were carried out. The (2,2) active space (two electrons in two orbitals) that was used in all CASSCF calculations consisted of those two valence orbitals of the threefold coordinated Sn atoms that did not take part in the two-center two-electron (2c2e) bonds of these Sn atoms. Such a set up enables one to handle electronic states with more than one electronic configuration, which has been shown to be crucial in the treatment of biradicaloid compounds.[12d,19] The occupation numbers, n_1 and n_2, and orbital energies, ε_1 and ε_2, of the natural orbitals from the CASSCF-(2,2) calculation for the singlet ground state[20] provide much needed insight into the character of the bond between the threefold coordinated Sn centers. Three different regions (I–III) are identified in Figure 3, unexpectedly divided by sharp, first-order-like transitions around 135° and 185°; the experimental value for **3** ($\alpha = 126°$) is near the transition between regions I and II.[21]

The geometrical parameters and the electronic structure of **3a** are very different in the three regions illustrated in Figure 3. These three regions can be described as follows:

Region I: A typical singlet biradicaloid system is observed for angles smaller than 135°. That is, the occupation number of the bonding orbital n_1 is between 1.7 and 1.8, a value that is significantly reduced compared to the case of a 2c2e bond ($n_1 = 2$). Additionally, a singlet–triplet gap between 0.6 eV and 1.2 eV and a Sn1–Sn2 distance longer than 350 pm are obtained from calculations. The active orbitals are formed by sp^3-like hybrids which point away from each other (Figure 4a). The bonding situation is thus comparable to other biradicaloid systems.[12d,19,22] Interestingly, the biradicaloid character increases with an increasing angle α, that is, when the arrangement at the tin atom becomes increasingly planar. The active orbitals exhibit more and more *p*-character during this process.

Region II: the arrangement at the tin atoms becomes pyramidal once again with an increase in angle α. Consequently, the active orbitals regain sp^3 character and become facial (Figure 4b). The Sn–Sn distance is between 280 and 300 pm—typical for a single bond—and the occupation number n_1 is also equal to 2.0. Additionally, the singlet-triplet gap is larger than 2 eV, confirming the presence of a classical Sn–Sn single bond.

Region III: For angles greater than 185°, the active orbitals are oriented parallel to each other (Figure 4c), leading to a weaker interaction. The Sn–Sn distance is

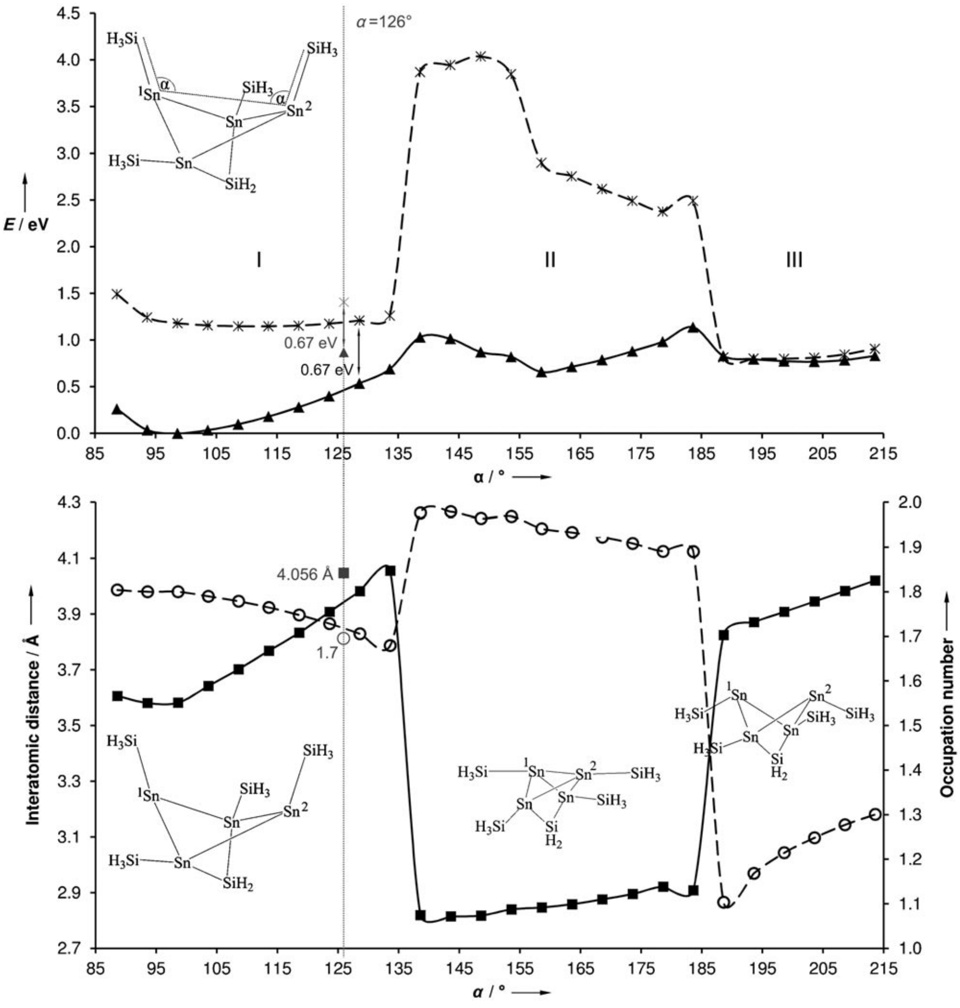

Figure 3. Top: Calculated energies of the model molecule **3a** in its singlet (▲) and triplet (*) state as a function of the Sn-Sn-Si angle α. Bottom: Angular dependence of the tin–tin bond distance between Sn1 and Sn2 (■) and the occupation number n_1 obtained from the CASSCF calculation of the singlet state (○) (the structure of **3a** in the different regions I, II, and III is also shown). The experimental values for **3** ($\alpha = 126°$) are given as a dotted line for comparison.

increased to values greater than 370 pm. The electronic structure is typical for a biradical, that is, the singlet–triplet gap is close to zero (around 0.01–0.1 eV) and both active orbitals are singly occupied.

These results clearly show that the orientation of the ligand directly affects the bonding between the two tin atoms with coordination number three.[22]

The calculations presented herein show that the transitions between regions I (singlet biradicaloid), II (2c2e bond), and III (triplet) are quite abrupt. That is, small changes in α lead to drastic change in bonding and, thus, in chemical behavior! This unexpected result is of general interest, for example, in biocatalytic processes where enzymes are in a so-called entatic state.[23] Whether the electronic ground state changes drastically with small changes in the ligand in catalytic systems remains an open question.

In summary, we synthesized the new compound **3**, in which the steric demand of the bulky $Si(SiMe_3)_3$ ligands forces the two threefold-coordinated tin atoms Sn(12) and Sn(14) into an almost planar arrangement. Between these tin atoms the very long bond of 382 pm is in accordance with a biradicaloid character. Quantum chemical calculations on the model compound **3a** show that by varying the Sn-Sn-Si bond angle α of the substituent, a first-order like transition between a singlet biradiacaloid and a classical system with a 2c2e bond, as well as a transition from the latter to a biradical compound, can take place. Because the Sn-Sn-Si angle α inside **3** (126°) is close to the critical angle of 136° between regions I and II, the polyhedral cluster **3** provides an ideal model system for further investigations on this general topic.[24]

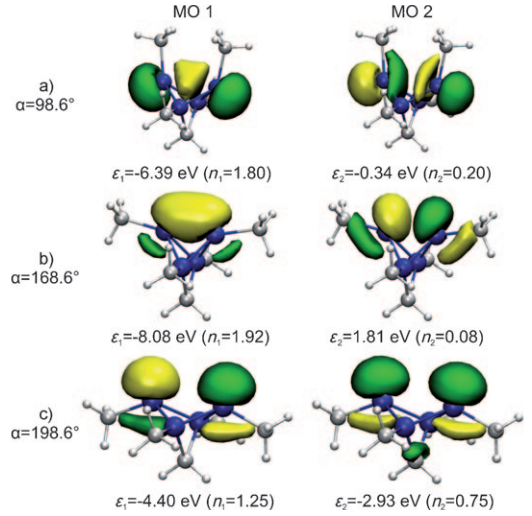

Figure 4. Natural orbitals of the CASSCF calculations for **3a** for three different angles α which are representative of regions a) I, b) II, and c) III. See text for details.

Experimental Section

All manipulations were carried out under nitrogen or in vacuo in Schlenk-type glassware on a dual manifold Schlenk line. Solvents were pre-dried over molecular sieves. THF was distilled from sodium benzophenone. SnBr was synthesized in a home-made co-condensation apparatus.[3,25]

Synthesis of **3·1**: A metastable Sn^IBr solution was prepared using a co-condensation technique, in which tin (1.88 g; 15.8 mmol) was treated with HBr (20 mmol) at 1240 °C. The resulting Sn^IBr was condensed at −196 °C with a mixture of toluene and NBu_3 in a volume ratio of 4:1. After warming to −78 °C a metastable solution of Sn^IBr was obtained. A solution of $LiSi(SiMe_3)_3·3THF$ (10.6 g, 22 mmol) in toluene (50 mL) was added to this metastable solution at −78 °C. The reaction mixture was then slowly warmed to room temperature, and a black reaction solution was obtained. Removing the solvent in vacuo leads to a black residue, which was extracted with pentane (ca. 150 mL). This, in turn, yielded a black pentane extract which, upon cooling to −30 °C, produced dark red rhombic crystals of $[(thf)LiSn\{Si(SiMe_3)_3\}_3]$(50 mg).

Removing half of the solvent and cooling to −30 °C yielded black rod-like crystals of the metalloid cluster compound $[Sn_{10}\{Si(SiMe_3)_3\}_6]$ (400 mg). Adding THF (1 mL) to the concentrated pentane extract led to the formation of black, diamond shaped crystals of $[Sn_4Si\{Si(SiMe_3)_3\}_4(SiMe_3)_2]·[Sn_{10}\{Si(SiMe_3)_3\}_6]$(**3·1**; 200 mg).

^1H NMR (400 MHz, $[D_8]THF$): $\delta = 0.03$ (s, 18 H, CH_3); 0.24 ppm (s, 108 H, CH_3). ^{13}C NMR: (100 MHz, $[D_8]THF$): $\delta = 5.4$ ($Si(SiMe_3)_3$) 5.6 ppm ($Si(SiMe_3)_2$). ^{29}Si-NMR (60 MHz, $[D_8]THF$): $\delta = -7.3$ ($Si(\mathit{Si}Me_3)_2$), −12 ($Si(\mathit{Si}Me_3)_3$), −117 ($\mathit{Si}(SiMe_3)_3$), −119 ppm ($\mathit{Si}(SiMe_3)_2$).

Technical details of the quantum chemical calculations on compound **3a**: To obtain a one-dimensional cut of the potential energy surface $E(\alpha)$ of model compound **3a**, a series of optimizations were carried out at the DFT level of theory for singlet, triplet, and broken symmetry states (Figure S1 in the Supporting Information). The gradient corrected BP86 functional[26] was used in conjunction with the def2-TZVP basis set[27] and the corresponding def2-ecp effective core potential[28] for tin atoms. The resolution of identity (RI)[29] approximation was applied to speed up the calculations. CASSCF (complete active space self consistent field) calculations were performed for each resulting geometry with the program package ORCA.[30] The starting orbitals were obtained from natural orbitals of a ground state MP2 calculation using the def2-TZVP basis set. Two orbitals having occupation numbers of 1.8 and 0.2 were chosen as orbitals for the active space. These orbitals, always located at the threefold coordinated Sn centers, correspond to linear combinations of the two valence orbitals which were not included in the bonds to the SiH_3 ligands. The final CASSCF calculations were thus always performed in a (2,2) active space with a def2-TZVP basis set.

X-ray crystal structure analysis: Crystal data and details of the single crystal X-ray diffraction analysis for $[Sn_4Si\{Si(SiMe_3)_3\}_4\{SiMe_3\}_2]•[Sn_{10}\{Si(SiMe_3)_3\}_6]$ (**3·1**): $Sn_{14}Si_{43}C_{96}H_{288}·C_5H_{12}$; $M_r = 4384.94\ g\,mol^{-1}$, crystal dimensions $0.35 \times 0.2 \times 0.1\ mm^3$, orthorhombic, space group $Pca2_1$, $a = 45.082(9)$, $b = 24.225(5)$, $c = 18.901(4)$ Å, $V = 20641(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.411\ g\,cm^{-3}$, $\mu_{Mo} = 1.942\ mm^{-1}$, $2\theta_{max} = 45.38°$, 185 827 measured, 27 492 independent reflections ($R_{int} = 0.0552$), absorptions correction: numerical (min./max. transmission 0.5890/0.8922), $R_1 = 0.0336$, $wR_2 = 0.0841$. The data were collected at 150 K on a Bruker IPDS II diffractometer equipped with an Oxford Cryosystems cryostat, employing monochromated $Mo_{K\alpha}$ (0.71073 Å) radiation from a sealed tube. The structure was solved by direct methods and refined by full-matrix least-square techniques (with the SHELXS and SHELXL[31] programs). The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were calculated using a riding model. CCDC 781709 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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[16] The change in orientation is induced by the steric bulk of the $Si(SiMe_3)_3$ ligands (similar to **3** in which the capping atom of the butterfly arrangement also involves bulky $SiMe_3$ groups).

[17] The shared electron numbers (SENs) for bonds are a reliable measure of the covalent bonding strength. For example, the SEN for the Sn–Sn single bond in $[(SiH_3)_3Sn{-}Sn(SiH_3)_3]$ is 1.11, while the SEN for the double bond in $[(SiH_3)_2Sn{=}Sn(SiH_3)_2]$ is 1.48.

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