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Spirobis(pentagerma[1.1.1]propellane): A Stable Tetraradicaloid

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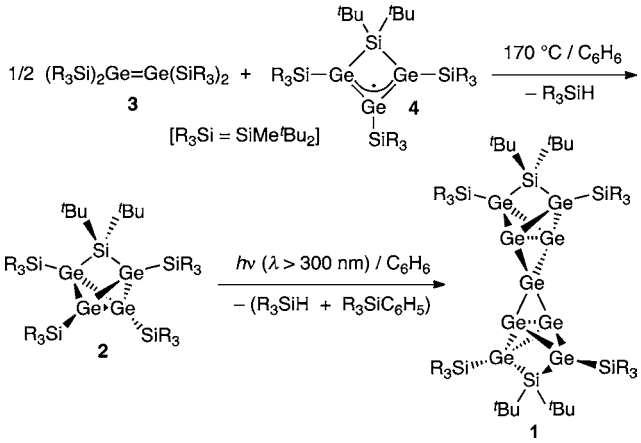
Supporting Information

ABSTRACT: In this contribution, we report a spirobis(pentagerma[1.1.1]propellane) derivative as a novel type of molecular architecture in cluster chemistry that features two spiro-fused [1.1.1]propellane units and represents a stable tetraradicaloid species. The crucial issue of the nature of the interaction between the germanium bridgeheads was probed computationally, revealing weak bonding interactions between the formally unpaired electrons.

[1.1.1]Propellanes, featuring a remarkable inverted tetrahedral geometry at the bridgehead carbons, are among the most challenging "nonclassical" compounds.[1] The central issue of the structure of [1.1.1]propellanes, the nature of the bond between their bridgehead carbons (covalent, charge-shift bond, singlet biradicaloid, or no bond), has been addressed in a number of theoretical and experimental studies, which sometimes led to controversial conclusions. However, the presence of a bonding path between the two bridgehead carbons has finally been acknowledged. Recent synchrotron crystallographic studies on a [1.1.1]propellane derivative showed the presence of such a bonding interaction with significant electron density at the bond critical point (BCP), corresponding to a bond order of 0.71.[2] According to a valence-bond theoretical treatment of [1.1.1]propellanes, their remarkably strong central bridging C−C bond is neither classically covalent nor classically ionic but rather a distinctive charge-shift bond.[3] As for the analogues of [1.1.1]propellane derivatives comprising group 14 elements heavier than carbon (Si, Ge, Sn), only a few examples have been reported to date.[4] Sita and co-workers pioneered this field by the synthesis of their milestone pentastannapropellane derivatives,[5] followed by the preparation of another pentastannapropellane by Drost and co-workers.[6] As the latest accomplishments, Breher and his group very recently reported the first pentasila-[7a] and pentagermapropellane[7b] derivatives. Hybrid [1.1.1]propellanes comprising different heavy group 14 elements, namely Ge_2Sn_3,[8] Ge_2Si_3,[9] and Sn_2Si_3,[9] were also recently reported. For all of these "heavy" [1.1.1]propellanes, a substantial amount of singlet biradicaloid character was assigned to a central bridging bond. In this contribution, we report a novel type of cluster compound, featuring two [1.1.1]propellane units joined together in a spiro fashion and representing a stable tetraradicaloid derivative. The crucial issue of the nature of the bridging Ge−Ge bond was addressed from the computational point of view.

The formation of a precursor for the spirobis([1.1.1]propellane) **1**, tricyclo[2.1.0.0^{2,5}]pentane cage **2**, isolated from the cothermolysis of tetra(silyl)digermene $(^tBu_2MeSi)_2Ge{=}Ge(SiMe^tBu_2)_2$ **3**[10] and the stable allylic-type cyclosilatrigermenyl radical **4** (for **4**, see the SI), came as a complete surprise (Scheme 1).[11]

Scheme 1. Preparation of the 3-Sila-1,2,4,5-tetragermatricyclo[2.1.0.0^{2,5}]pentane 2 by the Cothermolysis of the Digermene 3 and Stable Cyclic Radical 4, and Subsequent Photolysis of the $SiGe_4$ Cage 2 Forming the Si_2Ge_9 Cluster 1



The only isolable side product, the hydrosilane $^tBu_2MeSiH$, formed in an equimolar amount with cage **2**, could be readily separated from **2** by vacuum distillation (for the mechanism of formation of **2**, see the SI).

In contrast to organic tricyclo[2.1.0.0^{2,5}]pentanes featuring exceedingly short bridgehead bonds,[1b,12] their analogues containing the heavy group 14 elements showed a greater variation in the bridgehead-to-bridgehead bond length. Thus, a few examples of the stable tricyclo[2.1.0.0^{2,5}]pentane derivatives, fully (or partially) composed of heavy group 14 elements, can be categorized into two groups: (1) with normal bridging bond[13,14]

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or (2) with extraordinarily long bridging bond.[15] Our cage **2** showed the structural features of the classical organic tricyclopentanes: a remarkably acute interplanar angle Ge1−Ge2−Ge4/Ge1−Ge2−Ge3 of 95.48(1)°, wide Si1−Ge1−Ge2 and Si2−Ge2−Ge1 bond angles of 136.099(17)° and 136.514(17)°, and, as a consequence, a squeezed Ge1−Ge2 bridge of 2.4535(3) Å, which is shorter than any other skeletal Ge−Ge bond in **2** [2.4718(3)−2.5020(3) Å, av. 2.4846(3) Å] (Figure 1).[11]

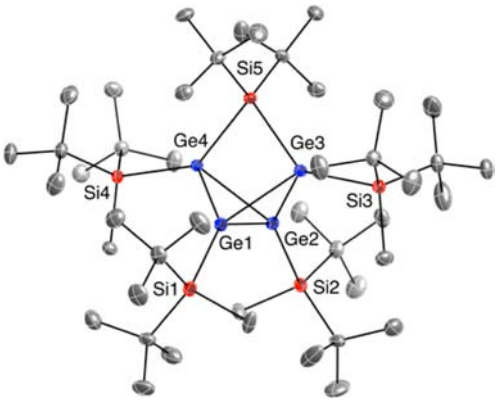

Figure 1. Molecular structure of cage **2** (ORTEP plot with thermal ellipsoids drawn at the 30% probability level). Hydrogen atoms are not shown. Selected bond lengths (Å): Ge1−Ge2, 2.4535(3); Ge1−Ge3, 2.4750(3); Ge1−Ge4, 2.5020(3); Ge2−Ge3, 2.4896(3); Ge2−Ge4, 2.4718(3); Ge3−Si5, 2.4201(5); Ge4−Si5, 2.4310(5). Selected bond angles (°): Ge3−Si5−Ge4, 82.493(17); Si1−Ge1−Ge2, 136.099(17); Si2−Ge2−Ge1, 136.514(17). Interplanar angle (°): Ge1−Ge2−Ge4/Ge1−Ge2−Ge3, 95.5.

The photolysis of cage **2** in benzene solution (λ > 300 nm) resulted in the formation of a totally unexpected, albeit extraordinarily interesting product, Si_2Ge_9 cluster **1** (Scheme 1 and Figure 2). For the moment, the mechanism for the formation of cluster **1** cannot be discussed in detail given the lack of any isolable (or even spectroscopically observable) reactive intermediates leading to the final **1**. One can only propose that the photolysis of the starting cage involves at least three molecules of $SiGe_4$ cage **2**, given the total of nine germanium atoms in the Si_2Ge_9 cluster **1**. The only identifiable side products of this complex process, involving the breaking and making of many Si−Ge and Ge−Ge bonds, are the hydrosilane $^tBu_2MeSiH$ and the phenylsilane $^tBu_2MeSiPh$, apparently formed by H abstraction and benzene (solvent) substitution reactions by the transient silyl radical $^tBu_2MeSi^\bullet$. Both ^1H and ^{13}C NMR spectra of the cluster **1** are rather simple, displaying only one set of signals for all $^tBu_2MeSi$ substituents along with a resonance of the ^tBu groups attached to the skeletal Si, and this spectral pattern agrees well with the high molecular symmetry of **1**. As in the case of cage **2**, the skeletal silicons in **1** are remarkably deshielded, being observed at +91.64 ppm. The reason for such atypical low-field shifted signals in both **1** and **2** is hard to rationalize considering only substituent effects; instead, we propose that such extreme deshielding results from the unusual bonding situations in **1** and **2**, which yield a particular charge distribution of the electrons (in fact, the spatial distribution of the electrons plays a more decisive role on the NMR chemical shifts than inductive effects[16]). Very recently, a similar extreme deshielding of the skeletal tetracoordinate Si atom in a pentasila[1.1.1]propellane derivative (+174.6 ppm) was described by Scheschkewitz and co-workers,

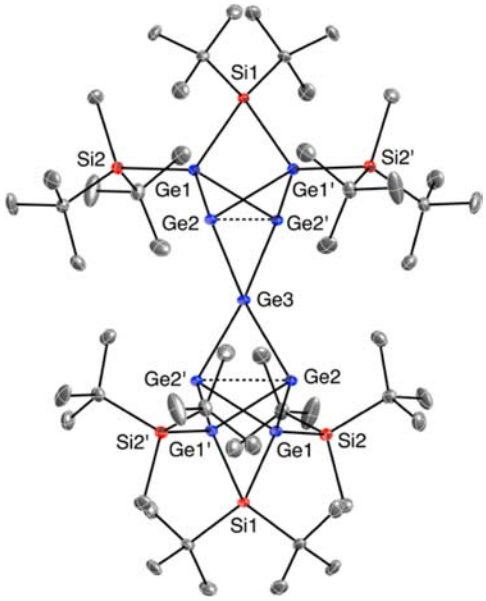

Figure 2. Molecular structure of cluster **1** (ORTEP plot with thermal ellipsoids drawn at the 30% probability level) [calculated values at the M05-2x/TZVPP level of the model compound **1H** are given in square brackets]. Hydrogen atoms and benzene molecule (as a crystallization solvent) are not shown. Selected bond lengths (Å): Ge1−Ge2, 2.4862(4) [2.488]; Ge1′−Ge2, 2.4709(3) [2.488]; Ge2−Ge3, 2.4849(3) [2.488]; Ge1−Si1, 2.4138(6) [2.405]; Ge1−Si2, 2.4322(11) [2.375]; Ge2···Ge2′, 2.8292(5) [2.869]. Selected bond angles (°): Ge1−Si1−Ge1′, 81.83(3) [81.5]; Ge3−Ge2−Ge2′, 55.301(6) [54.8]; Ge2−Ge3−Ge2′, 69.400(11) [70.4]. Interplanar angle (°): Ge2−Ge2′−Ge1/Ge2−Ge2′−Ge1′ = 101.9 [101.1].

who attributed this observation to the presence of the magnetically induced cluster ring current effects.[17]

The structural changes that take place upon photolysis on going from cage **2** to cluster **1** are quite instructive (Figure 2). Among them, the following are of paramount importance: (1) the interatomic distance between the two bridgehead germanium atoms dramatically increased on going from cage **2** to cluster **1**, from 2.4535(3) Å (Ge1−Ge2 in **2**) to 2.8292(5) Å (Ge2···Ge2′ in **1**), which corresponds to a huge elongation of ∼15%; (2) the interplanar angle widened, from 95.5° (Ge1−Ge2−Ge4/Ge1−Ge2−Ge3 in **2**) to 101.9° (Ge2−Ge2′−Ge1/Ge2−Ge2′−Ge1′ in **1**) (6.4° widening); (3) the bond angle involving two bridgehead germanium atoms and a substituent dramatically decreased, from 136.099(17) and 136.514(17)° (Si1−Ge1−Ge2 and Si2−Ge2−Ge1 in **2**) to 55.301(6)° (Ge3−Ge2−Ge2′ in **1**) (81.0° narrowing). The interatomic separation of 2.8292(5) Å between the two germanium bridgeheads in **1** is clearly outside the typical range of covalent interactions (the sum of the two germanium atoms' single-bond covalent radii is 2.42 Å[18]). This value of 2.8292(5) Å is reasonably comparable to that of the pentagermapropellane recently reported by Breher and co-workers (2.869(2) Å),[7b] although much shorter than that of Power's Ge_2Sn_3 cluster (3.363(1) Å)[8] (for both compounds cited above, a notable amount of singlet biradicaloid character was proposed on the basis of the experimental and computational data). Accordingly, in the case of our cluster **1**, featuring two exceedingly long bridgehead−bridgehead interatomic distances between the tricoordinate Ge2 and Ge2′ centers, the crucial question is the nature of their interaction: long covalent bond, weak interaction between singlet biradicaloid centers, or no bonding interaction at all. Answering this seemingly simple

question by considering only interatomic distance as the single criterion is not sufficiently reliable, given the rather subtle distinction between the above-mentioned types of interactions. We tried to approach this problem from the computational direction.

At first, we optimized the geometry of the model compound **1H** at the singlet electronic state, in which the ^{t}Bu$_2$MeSi substituents in **1** are replaced by H$_3$Si groups and the bridging ^{t}Bu$_2$Si units by H$_2$Si groups, using density functional theory with the M05-2x and BP86 functionals using TZVPP basis sets.[19] The M05-2x/TZVPP values, which are not very different from the BP86/TZVPP and B3LYP/TZVPP data (see Supporting Information), are shown in Figure 2. The calculated bond lengths and angles for **1H** are in very good agreement with the experimental values for **1** (Figure 2), except for the Ge1−Si2 bond to the terminal silyl group, where the calculated value of 2.375 Å is a bit shorter than the experimental value of 2.4322(11) Å. The difference may come from use of model silyl groups in **1H**. The optimized geometry is only slightly distorted from D_{2d} symmetry due to the presence of the H$_3$Si substituents. The triplet state of **1H** was calculated at M05-2x/def2-TZVPP to be 61.0 kcal/mol higher in energy than the singlet (37.5 kcal/mol at BP86/def2-TZVPP), while the quintet state was 75.6 kcal/mol (BP86/def2-TZVPP and 96.9 kcal/mol (M05-2x/def2-TZVPP) less stable than the singlet state.[20]

We first analyzed the bonding situation in **1H** using the Atoms-in-Molecules (AIM) method.[21] The contour line diagram of the Laplacian $\nabla^2\rho(r)$ of the molecule in one Ge3−Ge2−Ge2′ plane along with the bond paths is shown in Figure 3.

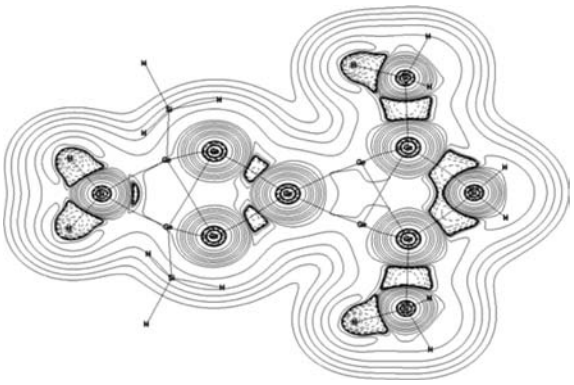

Figure 3. Contour line diagram showing the Laplacian $\nabla^2\rho(r)$ of the electron density of **1H** at M05-2x/def2-TZVPP. Solid lines indicate areas of charge depletion ($\nabla^2\rho(r) > 0$), and dashed lines indicate areas of charge accumulation ($\nabla^2\rho(r) < 0$). The solid lines that connect the atomic nuclei are the bond paths.

There are BCPs for all classical Ge−Ge bonds in **1H**; however, there are no bond paths for the Ge2−Ge2′ interaction between the bridgehead germanium atoms. We also carried out an AIM analysis for **1H′**, in which the Ge2−Ge2′ distance was frozen at the experimental value of 2.8292(5) Å while the rest of the molecule was optimized. Again, the latter calculation did not show a BCP for the Ge2−Ge2′ interaction. Thus, according to the AIM definition, there are no Ge2−Ge2′ chemical bonds in **1H**. However, it has been shown that the lack of a BCP does not necessarily imply the absence of a covalent interaction between two atoms.[22]

Inspection of the highest-lying occupied molecular orbitals of **1H** showed that there are two pairs of orbitals that are associated with the Ge2−Ge2′ interaction. The shapes and energies of the nearly degenerate HOMO−5 and HOMO−6 are depicted in Figure 4A,B. It becomes obvious that these two orbitals have

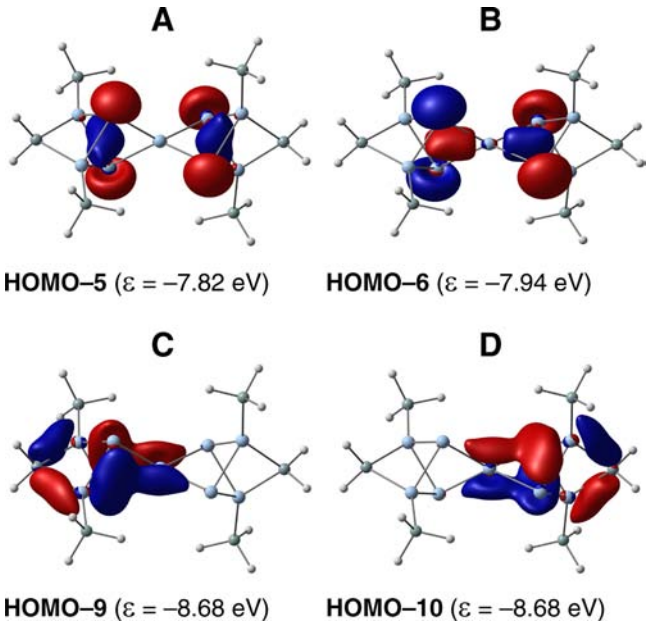

Figure 4. Shape and eigenvalues ε of selected occupied molecular orbitals of **1H**.

mainly nonbonded electron density character at Ge2 and Ge2′. However, the inner lobe of the sp^x atomic orbitals (AOs) at germanium are coupled in a bonding fashion, which is supported by small contributions from the valence p-AO of Ge3 (HOMO−6) or from sp-hybridized AOs of Ge1 and Ge1′ (HOMO−5). Because HOMO−5 and HOMO−6 describe the interactions of the four valence electrons of Ge2 and Ge2′, the bonding between these bridgehead atoms can be reasonably represented with the dashed lines, as depicted in Figure 2. The weak coupling of the inner lobes is not sufficiently strong to establish a BCP in the electron density map; however, it is clearly associated with some degree of orbital bonding. The weak coupling suggests that the Ge2−Ge2′ "bonds" could be easily attacked in a reaction, in which the cluster **1** exhibits features of a singlet biradical (biradicaloid).[23] We also identified a second pair of MOs that are associated with some Ge2−Ge2′ interaction: the shapes of HOMO−9 and HOMO−10, each of them exhibiting the features of three-center, two-electron π-bonding Ge3−Ge2−Ge2′, are shown in Figure 4C,D. Thus, the weak Ge2−Ge2′ σ-bonding, visible in HOMO−5 and HOMO−6, is somewhat enhanced by weak π-bonding.

In summary, the first spirobis([1.1.1]propellane), in the form of its germanium analogue, was synthesized by the photolysis of a tricyclo[2.1.0.0^{2,5}]pentane precursor. This unusual Si$_2$Ge$_9$ cluster represents a novel structural motif in polycyclic compounds chemistry, featuring two Ge$_5$-pentagerma[1.1.1]propellane fragments sharing a bridging germanium atom as a spiro center. The experimentally established very long separation between the germanium bridgehead atoms was explained in terms of the remarkable singlet biradicaloid character of these bridgehead-to-bridgehead interactions, which allows the classification of the spirobis([1.1.1]propellane) derivative as a singlet tetraradicaloid species.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details (including synthetic procedures and spectral and crystallographic data) for **1** and **2**; X-ray analysis data and tables of crystallographic data (including atomic positional and thermal parameters) for **1** and **2**; and description of the computational methods and all computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(19) All of the computations were carried out using the Gaussian 09 and Turbomole suite of programs (for the full reference, see the SI) at the DFT M05-2x/def2-TZVPP, BP86/def2-TZVPP, and B3LYP/def2-TZVPP levels of theory (for details, see the SI).

(20) One of the reviewers argued that the large singlet−triplet (S/T) energy gap does not support the classification of **1H** as a tetraradicaloid. But the S/T gap cannot be used as measure for the radicaloid character of the molecule, because heavier main group elements have an intrinsically higher stability for closed-shell configurations than for open-shell states compared with first-row elements. For example, CH_2 has a triplet ($^3B_1$) ground state which is 9.6 kcal/mol lower in energy than the singlet ($^1A_1$) ground state. In contrast, GeH_2 has a singlet ($^1A_1$) ground state which is 23 kcal/mol below the excited triplet ($^3B_1$) ground state [Mineva, T.; Russo, N.; Sicilia, E.; Toscano, M. *Int. J. Quantum Chem.* **1995**, *56*, 669.] For a discussion of the difference of chemical bonding between first-row elements and their heavier homologues, see: Kutzelnigg, W. *Angew. Chem., Int. Ed.* **1984**, *23*, 272.

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(23) Indeed, our preliminary studies showed that cluster **1** is selectively reactive toward radical trapping reagents, such as CCl_4, forming the corresponding products of the radical addition at the bridgehead Ge2 and Ge2′ atoms.