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Will an η^3-Si_3H_3 Ligand Form Sandwich Compounds with Main Group Elements?

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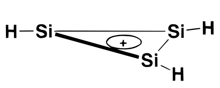
Abstract: η^3-Si_3H_3 sandwich compounds **5** and **6**, with classical and H-bridged ligands, respectively, having the main group elements boron and carbon as central atoms are minima at B3LYP/6-311++G(2d,2p). The stability of these systems is assisted by transfer of charge from the ligands to the central atom and is reversed from that of cyclopentadienyl sandwiches. The C and B containing pyramidal complexes **7**, containing both a η^3-Si_3H_3 and a μ^2-Si_3H_3 ligand, are more stable than **5** by 20.7 and 8.5 kcal/mol, respectively. The spiro compounds **8**, in which the C and B atoms are sandwiched by two allylic μ^2-Si_3H_3 ligands, are still more stable by 29.6 and 21.9 kcal/mol, respectively. All three types (face-face, face-side, side-side) of sandwich structures are considered viable targets for synthetic pursuit. The Be complexes deviate from the C and B analogues because Be is much more electropositive. In the preferred cluster structure **9** the Be atom sits in a Si_6H_6 basket.

Introduction

Sandwich compounds have become important structural elements in chemistry. The discovery of ferrocene in 1951[1] led to the development of sandwiched transition metals and actinides and even main group metals such as Cp_2Li^-, Cp_2Na^-, and Cp_2Mg.[2,3] All have electropositive metals sandwiched by η^5-cyclopentadienyl anion (Cp) rings. Extension to larger rings led to the involvement of f-orbitals such as in bis-cyclooctatetraenyluranium, while similar attempts at smaller η^3-ligands have been limited to mixed systems such as $CpNi(C_3Ph_3)$.[2,4]

It has been suggested that sandwiches with cyclopropenyl cation ligands and a central atom from the first-row elements are feasible.[5] Formally, each η^3-ring provides 3π electrons with two coming from the central atom (charge adjusted) leading to eight interstitial valence electrons to fill the bonding orbitals. The cationic ligands require the central atom to be less electropositive, giving a reversed polarity from that of the Cp_2M sandwiches. It is then not surprising that an early theoretical study showed the cyclopropenyl ($C_3H_3^+$) sandwiches of Be and B to be unstable.[5] We now explore the heavier congener, the trisilacyclopropenium cation $Si_3H_3^+$, as a sandwich ligand for the main group elements Be, B, and C.

$Si_3H_3^+$ has been detected in the gas phase.[6] Its ring structure **1** (D_{3h}) is 23.7 kcal/mol more stable at B3LYP/6-311++G-(2d,2p) than the triply H-bridged isomer **2** (C_{3v})[7] and has shown potential as a η^3-ligand in pyramidal structures **3** (C_{3v}) and **4** (C_{3v}).[8] We are unaware of reports on sandwiches with two such ligands. Cyclic $Si_3H_3^+$ is a weakly delocalized 2π system and may function as a η^3-ligand (face-on) and as a μ^2-ligand (side-on) resulting in the face-face (**I**, π-complex), face-side (**II**, σ,π-complex), and side-side (**III**, σ-complex) structural arrangements. Of these, **I** relates to the Cp_2M systems, **III** relates to the spiro structures, and **II** is an extension of pyramidal structure **3**. We will show remarkable examples of these three forms for the main group elements boron and carbon, i.e., $(Si_3H_3)_2B^+$ and



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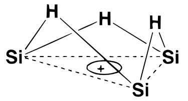

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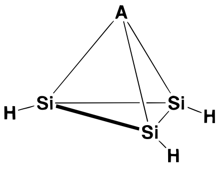

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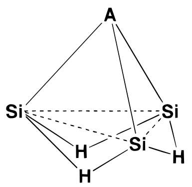

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A = BH^-, CH, N, NH^+, NO, SiH, P, PH^+ and PO

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$(Si_3H_3)_2C^{2+}$, as well as the limited ability of beryllium to play a similar role. The focus is on ligand **1** because its derivatives are more amenable for synthetic pursuit. For the low-energy structures, permethyl substitution is also studied to explore experimental feasibility.

Computational Methods

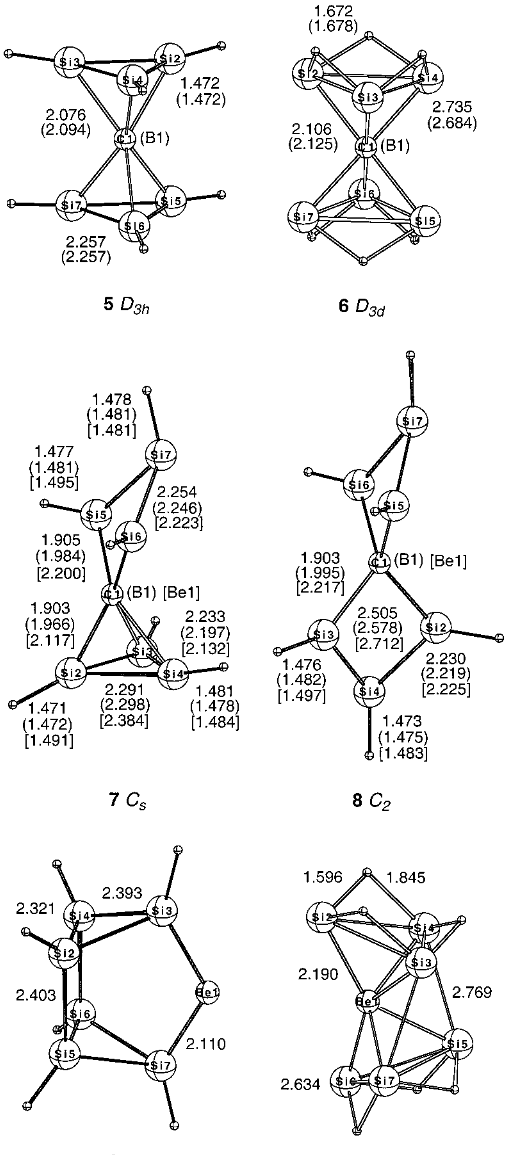
Structures **5X**−**10X** (X = Be, B, C) were first optimized and characterized by their Hessian signature at the HF and B3LYP levels using the 6-31G(d) basis set.[9−11] We next optimized sandwiches **I**, **II**, and **III** at B3LYP/6-311++G(2d,2p).[9,12] Correlation effects were computed by energy evaluation at MP2/6-311++G(2d,2p) using the B3LYP /6-311++G(2d,2p) geometries.[13] All the calculations were done using the GAUSSIAN94 suite of programs.[14] The permethyl-substituted systems were optimized at the HF/6-31G(d) level using PQS (Parallel Quantum Solutions)[15] on a 4-node QS4-450 Quantum Station. The nature of the stationary points was determined by evaluating the second derivatives of the energy using GAUSSIAN94. Figure 1 shows the relevant structures with selected geometrical parameters. The total and relative energies are given in Table 1. We use natural charges obtained from the natural bond orbital (NBO) analysis.[16] Emphasis is given to the "classical" sandwich forms, and particularly to those with boron and carbon, to stimulate their experimental pursuit as the propensity for bridging may not go beyond hydrogen.[7,8,17]

Results and Discussions

***π*-Sandwiches (I).** Given the unusual coordination number of carbon and boron with $Si_3H_3^+$ ligands in structures **5C** and **5B**, it was quite surprising to find that both structures were minima in the D_{3h} point group. Also, structures **6B** and **6C** (D_{3d}) with the H-bridging "nonclassical" $Si_3H_3^+$ ligand **2** are minima. The π-stabilization in these systems must be very effective in light of boron and carbon's high propensity for covalent bonding. Why do these structures exist as minima?

Molecular orbital analysis of dication **5C** shows the valence 2e′ and 2a″ MOs to contain contributions from both the $Si_3H_3^+$ rings (requiring D_{3h} symmetry) and from the C-center, indicating transfer of charge from the rings to the carbon. The NBO charges (SCF) of −2.16, 0.77, and −0.08 e for C, Si, and H support this interpretation. The charges for B, Si, and H in monocation **5B** (D_{3h}) of −2.04, 0.61, and −0.11 e are analogous. This transfer of charge reduces the antibonding interactions between the rings, but only for the elements B (2.04) and C (2.55) because of their higher electronegativity than Si (1.90).[18] Since Be (1.57) is more electropositive a destabilizing transfer of charge from the central atom to the rings would be favored instead. With an NBO charge of +1.03 e for Be in neutral **5Be** (D_{3h}) it is not surprising that the Be-sandwich structures are not minima. Likewise, the earlier investigated $(\eta^3\text{-}C_3H_3)_2Be$ and $(\eta^3\text{-}C_3H_3)_2B^+$ sandwiches[5] are higher order saddle points with corresponding Be and B charges of 1.53 and 0.02 e.

The short C−Si distances of 2.076 Å in **5C** (D_{3h}) reflect a strong π-complex, but it is less tight (1.904 Å) than pyramidal **3** (A = CH).[8] The Si−Si bond lengths of 2.257 Å in **5C** are



5 D_{3h} **6** D_{3d}

7 C_s **8** C_2

9 C_{2v} **10** C_1

Figure 1. Optimized geometries at B3LYP/6-311++G(2d,2p). For **5**−**8** the C-sandwiches are shown with those for B complexes in parentheses and Be complexes in brackets.

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Table 1. Total (in au), Zero Point (ZPE, in kcal/mol), and Relative Energies (in kcal/mol)[a]

structure	level	total energy	ZPE	NIF	rel energy	structure	level	total energy	ZPE	NIF
5-C^{2+}, D_{3h}	HF/A	−1774.01409	40.16	0	0.0	**7**-B^{+}, C_s	HF/A	−1761.24106	39.09	0
	B3LYP/A	−1777.82176	36.09	0	0.0		B3LYP/A	−1765.02060	35.68	0
	B3LYP/B	−1777.98909			0.0		B3LYP/B	−1765.18445		
	MP2/B	−1774.90504			0.0		MP2/B	−1762.10633		
6-C^{2+}, D_{3d}	HF/A	−1773.96897	38.91	0	27.2	**8**-B^{+}, C_2	HF/A	−1761.28670	39.35	0
	B3LYP/A	−1777.83236	36.29	0	−6.5		B3LYP/A	−1765.05637	36.21	0
	B3LYP/B	−1778.01948			−18.9		B3LYP/B	−1765.22032		
	MP2/B	−1774.94176			−24.2		MP2/B	−1762.13449		
7-C^{2+}, C_s	HF/A	−1774.04461	40.02	1	−19.3	**5**-Be, D_{3h}	HF/A	−1751.38578	37.05	4
	B3LYP/A	−1777.85340	36.40	0	−19.6		B3LYP/A	−1755.15389	33.45	2
	B3LYP/B	−1778.02263			−20.7	**7**-Be, C_s	HF/A	−1751.41728	36.46	0
	MP2/B	−1774.93206			−17.1		B3LYP/A	−1755.16760	33.62	0
8-C^{2+}, C_2	HF/A	−1774.09924	40.62	0	−53.0		B3LYP/B	−1755.32762		
	B3LYP/A	−1777.90063	37.18	0	−48.4		MP2/B	−1752.24745		
	B3LYP/B	−1778.07091			−50.3	**8**-Be, C_2	HF/A	−1751.45253	36.72	0
	MP2/B	−1774.97556			−43.8		B3LYP/A	−1755.19557	34.02	0
5-B^{+}, D_{3h}	HF/A	−1761.22843	39.40	0	0.0		B3LYP/B	−1755.35525		
	B3LYP/A	−1765.00769	35.37	0	0.0		MP2/B	−1752.26880		
	B3LYP/B	−1765.17038			0.0	**9**, C_{2v}	HF/A	−1751.52868	39.05	0
	MP2/B	−1762.10268			0.0		B3LYP/A	−1755.25142	35.69	0
6-B^{+}, D_{3d}	HF/A	−1761.19432	38.60	0	20.7		B3LYP/B	−1755.40648		
	B3LYP/A	−1765.02612	35.96	0	−11.0		MP2/B	−1752.32655		
	B3LYP/B	−1765.20388			−20.4	**10**, C$_1$	HF/A	−1751.35420	35.98	0
	MP2/B	−1762.14381			−26.5		B3LYP/A	−1755.17066	33.83	0
							B3LYP/B	−1755.34404		

[a] A: 6-31G(d). B: 6-311++G(2d,2p). NIF indicates the number of imaginary frequencies. Relative energies include ZPE corrections, scaled by 0.9135 for HF and by 0.9806 for B3LYP.[29] ZPE's calculated at B3LYP/A and HF/A are used for the B3LYP/B and MP2/B relative energies, respectively.

elongated from those of the free ligand (2.198 Å) and shortened with respect to **3** (A = CH, 2.337 Å),[8] trisilacyclopropane (2.332 Å),[19] and disilane (2.334 Å);[20] the nonbonded SiSi distance of 3.232 Å is much longer than that in hexasilaprismane (2.375 Å).[21] Interestingly, the hydrogens of **5C** are tilted inward, toward the carbon, by as much as 7°. Structure **5B** (D_{3h}) has B−Si distances of 2.094 Å, marginally longer than the C−Si bond lengths of **5C**, and has its hydrogens tilted outward by 4°. Such tilting of peripheral hydrogens is common in 3D-aromatics,[22] bridged olefins, and alkynes,[23] and indicates strong π-interactions.

Sandwich structures **6B** and **6C** (D_{3d}) are both about 19 kcal/mol more stable than their "classical" isomers at B3LYP/6-311++G(2d,2p). This difference in stability is not even half the related preference of pyramidal **4** over **3** (44.0 kcal/mol (A = CH), B3LYP/6-31G(d)). However, we note that the energy difference is rather sensitive to the basis set employed, which is not surprising in light of the multitude of H-bridges. D_{3d} structures are preferred due to the arrangement of the Si lone pair (the D_{3h} forms are transition structures for ligand rotation).

***σ,π*-Sandwiches (II).** Replacing one η^3-Si_3H_3 (**1**) unit for a μ^2-ligand results in the kinetically stable structures **7B** and **7C**. These are remarkably similar to pyramidal structure **3** in which the C−H/B−H cap is formally replaced by a cyclic $CSi_3H_3^{2+}$/$BSi_3H_3^{+}$ group, maintaining the six interstitial electrons for 3D aromaticity. However, the mixed inward (−22.8°) and outward (7.0°) tilting of the peripheral hydrogens of **7C** illustrates a distortion from such ideal behavior. The distortion is caused by puckering (141°) of the 4-ring bridge, which is similar to that of the cyclobutadienyl dication (137°).[9,24] The equal C−Si(2) and C−Si(5,6) bond lengths of 1.903 Å with longer C−Si(3,4) bonds of 2.204 Å suggests carbonium ion character for the central carbon and thus C−Si σ-bonds in its bridge.[20] Structure **7B** shows a similar puckering (145°) of its $BSi_3H_3^{+}$ bridge and corresponding boronium ion properties. It is interesting to note that the σ−π sandwich structure is a minimum for Be. The puckering (153°) of the 4-ring bridge is much less compared to that of **7C** and **7B**. Structure **7C** is 20.7 kcal/mol more stable than the **5C** sandwich and for the boron analogue this energy difference is 8.5 kcal/mol.

***σ*-Sandwiches (III).** Replacing both η^3-Si_3H_3 (**1**) units for μ^2-ligands gives spiro compounds **8C** and **8B** (C_2), which are 50.3 and 30.5 kcal/mol, respectively, more stable than sandwich structures **5C** and **5B** (the D_{2d} structures are second-order saddle points with imaginary frequencies for ring puckering). σ-Bonding is evident from the 1.903 Å C−Si and 1.995 Å B−Si bond lengths, which is in line with the corresponding 2.505 and 2.578 Å Si(2,5)−Si(3,6) distances that suggest opening of the $Si_3H_3^{+}$ rings to "allylic" units. The XSi_3H_3 rings are puckered, 143.1° for **8C** and 148.8° for **8B**, but less than in the σ,π-sandwich (II) structures. Also **8Be** is a minimum with properties similar to **8C** and **8B**. This isomer is 17.0 kcal/mol more stable than **7Be**: its $BeSi_3H_3$ ring puckering (152°) is similar to that of **7Be**. The energetic preference of these spiro compounds is a reflection of the σ-bonding that the central atoms favor. Cp_2C is also reported to show similar behavior.[25]

Isomer **9Be** is obtained by following the imaginary vectors in **5Be**. This cluster type structure, in which Be is sitting in a Si_6H_6 basket, is more stable than the sandwich type structures (**I**, **II**, and **III**) discussed above. Structure **10Be**, the Be-

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embedded basket with H-bridges, is 37.4 kcal/mol less stable than the conventional form **9Be**.

Are the discussed sandwich structures viable synthetic targets? The "classical" form may be a reasonable possibility if substituted with adequately large groups. The analogy with tetrasilatetrahedrane Si_4H_4 is instructive. While **3SiH** is 20.6 kcal/mol less stable than its H-bridged **4SiH** isomer at MP2/6-31G(d) and even 49.3 kcal/mol compared to a four-membered ring structure,[8,17c,d] its "super silyl" ($^tBu_3Si$) substituted derivative has nevertheless been synthesized.[17e] To present a more tangible picture, the permethylated structures of **5** and **8** (i.e., **5′** and **8′**) were studied for B and C and found to be minima. at HF/6-31G(d) isomers **8B′** and **8C′** are 37.6 and 57.3 kcal/mol more stable than **5B′** and **5C′**, respectively.[26] These relative energies of these permethyl derivatives are very close to those of the parent molecules at the same level of theory. The recent experimental preparation and X-ray analysis of the trisilacyclopropenium ion Si_3R_4 (R = $SiMe^tBu_2$) is illustrative of the importance of bulky substituents.[27] Therefore, we feel that any of the three sandwich structures are intriguing targets for experimental pursuit, with that of structure **5C** being the greatest challenge. If anything, silyl substituents will only increase the donation of electron density into the Si_3 ring and strengthen the π bonding as in disilenes.[28]

Conclusions

The η^3-Si_3H_3 sandwich compounds with boron and carbon as central atoms are found to be minima. The stability of these systems is due to charge transfer from the ligands to the central atom, which is a reversed flow compared to the cyclopentadienyl sandwiches. With Be as the central atom, the sandwich structures are found to be unstable due to the higher electropositive nature of Be. However, the pyramidal complex **7Be**, containing both a η^3-Si_3H_3 and a μ^2-Si_3H_3 ligand, is a minimum. The C- and B-containing pyramidal complexes (**7C** and **7B**) are more stable than **5** by 20.7 and 8.5 kcal/mol, respectively. Spiro compounds **8**, in which the central atom is sandwiched by two allylic μ^2-Si_3H_3 ligands, are still more stable by 21.9 and 29.6 kcal/mol for B and C, respectively. Calculations on the permethylated sandwiches **5′** and **8′** reveal these structures to be minima with relative energies similar to those of the parent molecules. The preferred Be complex is a cluster type molecule **9** where the Be atom sits in a Si_6H_6 basket.

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Supporting Information Available: Cartesian coordinates of the structures in Figure 1 (PDF). This information is available free of charge via the Internet at http://pubs.acs.org.

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[26] Total energies at HF/6-31G(d) level; **8C′,** −2008.46153 au; **8B′**, −1995.59881 au.

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