drogens of the ethylene close to the two nearest-neighbor Pt atoms. The diosmacyclobutane 1 is thus not only a good vibrational[3] model for ethylene chemisorbed on Pt(111) but a good structural one as well.

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Supplementary Material Available: A stereoview of the unit cell for 1 (1 page); a listing of observed neutron structure factor amplitudes (31 pages). Ordering information is given on any current masthead page.

Theoretical Study of the Sandwich Compounds *commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11}$)$_2$ and *commo*-1,1′-Si(1,2,3-$SiC_2B_4H_6$)$_2$

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A theoretical study of the sandwich compounds *commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11}$)$_2$ (I) and *commo*-1,1′-Si(1,2,3-$SiC_2B_4H_6$)$_2$ (II) was conducted by using MNDO–SCF semiempirical molecular orbital theory. In agreement with experiment, the calculations show that the silicon atoms in both I and II are slipped toward the boron sides of the C_2B_3 carborane bonding faces. This slip distortion was found to be the result of Si(s)–cage carbon antibonding interactions and an enhancement in intracage bonding on slippage. Preference for a Si(IV) oxidation state in I and II and a Si(II) state in (η^5-C_5H_5)$_2$Si (III) could be explained on the basis of strong antibonding interactions in the LUMO's of I and II that are not present in the HOMO of III. A comparison of the MNDO results with Xα–scattered wave SCF molecular orbital calculations in which silicon harmonics up through $l = 2$ were used for II and III indicates that Si(d) orbital participation is not important in complex bonding.

Introduction

The number of main-group metallacarboranes that have been synthesized and structurally characterized has increased greatly in the past 5 years. Most of these compounds result from the reaction of a metal ion, or metal-containing group, with the dianions *nido*-1,2-$C_2B_9H_{11}^{2-}$, *nido*-2,3-$C_2B_4H_6^{2-}$, or their derivatives.[1,2] Depending on the metal and its oxidation state, the heteroatom can be incorporated into the polyhedral structure of the carborane to form either the respective closo or the commo complexes. In the icosahedral system, structures of the commo complexes of Al(III),[3,4] Ga(III),[5] and Si(IV)[6] have been reported, while, in the pentagonal-bipyramidal system, the structures of the commo complexes of Si(IV)[7,8] and Ge(IV),[9,10] with *nido*-2-[Si(CH_3)$_3$]-3-[R]-2,3-$C_2B_4H_4^{2-}$ (R = H, Si(CH_3)$_3$, CH_3), are known.

There have been numerous structural reports on *closo*-1-Sn-2-Si(CH_3)$_3$-3-R-2,3-$C_2B_4H_4$ (R = Si(CH_3)$_3$, CH_3, H)[1,11,12] and their adducts with monodentate,[13] bidentate,[12,14,15] bis(bidentate),[13] and tridentate[16] Lewis bases. Similar, though less extensive, studies have been reported for the analogous Ge(II)[17,18] and Pb(II)[19,20] metallacarboranes. In the icosahedral system, structural studies

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have been reported for the complexes 1-Sn(X)-2,3-$(CH_3)_2$-2,3-$C_2B_9H_9$ (X = C_4H_8O and $C_{10}H_8N_2$).[11,21]

All structures show that the metals bond to the C_2B_3 open faces of the carboranes. However, the metals are not necessarily symmetrically bonded to the atoms of these faces but are dislocated, or slipped, toward the boron side of the faces. The extent of slippage is a function of the metal, its coordination to other ligands, and the substituents on the cage atoms of the carborane.[22] While there have been a number of theoretical studies on the main-group *closo*-metallacarboranes and their Lewis base adducts,[15,16,22,23] there have been no parallel studies of *commo*-metallacarboranes. With the proper disclaimers, qualitative arguments based on cyclopentadienide (Cp^-) orbitals have been used to explain the bonding in both the icosahedral[6] and pentagonal-bipyramidal[8] main-group *commo*-metallacarboranes. Although the analogy between the carborane and cyclopentadienide anions provided a useful guide in the original synthesis of metallacarborane sandwich compounds by Hawthorne and co-workers[24] and theoretical calculations by Mingos[25] have also shown that the primary metal-binding orbitals of the two ligands are similar, striking structural and stoichiometric differences are found between the two classes of main-group metal sandwich complexes. In the group 14 cyclopentadienyl sandwich complexes, the metals are present in +2 oxidation states, and many of the complexes are bent so that the Cp rings are not parallel.[26,27] On the other hand, in the analogous *commo*-metallacarboranes, the metals are invariably in their +4 oxidation states and are sandwiched between essentially parallel faces of the two carborane ligands. The characteristic distortion found in the metallacarboranes is a slippage of the metal toward the boron side of the bonding C_2B_3 face.[1,2] In view of these differences, explanations of the geometries and stabilities of the *commo*-metallacarboranes based on cyclopentadienide-type orbitals would be highly qualitative and of questionable use. Therefore, theoretical calculations were carried out on *commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11})_2$, [$Si(C_2B_9H_{11})_2$], and *commo*-1,1′-Si(1,2,3-$SiC_2B_4H_6)_2$, [$Si(C_2B_4H_6)_2$], by using MNDO–SCF and Xα–scattered wave (Xα–SW) methods and are reported herein.

Calculations

MNDO–SCF semiempirical molecular orbital calculations were carried out by using version 2.10[28] of the MOPAC package[29] on an IBM 3081 computer. Unless otherwise noted, all geometric parameters were completely optimized with a modified[30] Davidson–Fletcher–Powell algorithm[31] incorporated as a standard part of the program. The parameters for carbon, boron, and hydrogen were those stored in the version. The older[32] parameters for silicon were used instead of the newer ones.[33] The former were found to give slightly better geometries than the latter. The starting geometry for $Si(C_2B_9H_{11})_2$ was its reported X-ray structure,[6] while that of $Si(C_2B_4H_6)_2$ was the X-ray structure of its C(cage)–$Si(CH_3)_3$ derivative.[7,8]

In analyzing some of the MNDO results, the total energy, E, was partitioned as the sum of one-center, E_A, and two-center, E_{AB}, terms such that[34-36]

$$\sum_{A} E_A + \sum\sum_{A<B} E_{AB}$$

E_{AB} has been found to provide a good quantitative measure of the A–B bond strength. A large negative value of E_{AB} indicates bonding, while a positive value implies antibonding.[35] Such analyses have proved useful in understanding the bonding interactions in several stannacarboranes and their Lewis base complexes.[15,22]

Molecular orbital calculations were also carried out on $Si(C_2B_4H_6)_2$ and $Si(C_5H_5)_2$ by using the spin-restricted Xα–SW method of Johnson and Slater.[37] In these calculations, the heavy-atom geometry of $Si(C_2B_4H_6)_2$ was taken as that of 2,2′,3,3′-$[Si(CH_3)_3]_4$-*commo*-1,1′-Si(1,2,3-$SiC_2B_4H_4)_2$,[7] while that of $Si(C_5H_5)_2$ was taken from the crystal structure of the $Si[C_5(CH_3)_5]_2$ isomer having D_{5d} symmetry.[27] The hydrogen positions in both complexes were the MNDO-optimized ones for the particular heavy-atom geometry. The statistical exchange parameter for hydrogen, α_H, was that given by Slater,[39] while the values for the other elements were the α_{HF} values calculated by Schwarz.[40] Because of the large silicon–ring atom distances, the usual methods of assigning the individual atomic sphere radii, on the basis of optimizing the virial ratio,[38] could not be directly applied. Instead, the ratios of the sphere radii of all atoms except silicon were taken as the ratios of the radii of spheres around each atom that just enclosed the number of electrons in the neutral atom, as suggested by Norman.[38] The silicon/carbon radius ratio was calculated by increasing the silicon radius until the silicon–carbon spheres were tangent. The absolute values of the radii were those that yielded a virial ratio closest to unity. The final viral ratios ($-2T/V$) were 1.00002 and 1.00341 for $Si(C_5H_5)_2$ and $Si(C_2B_4H_6)_2$, respectively. The sphere radii used for the unique atoms are listed in supplementary Table 1.

Results and Discussion

MNDO–SCF calculations were carried out on $Si(C_2B_9H_{11})_2$ and $Si(C_2B_4H_6)_2$ as described above. The MNDO-optimized geometries of both compounds yielded structures having C_{2h} symmetry, in which the silicon atoms were equally bonded to the two parallel C_2B_3 pentagonal faces of the carborane ligands. A comparison of the calculated structure of $Si(C_2B_9H_{11})_2$ with its X-ray structure[6] showed that MNDO tends to underestimate silicon–carborane bonding in that the optimized silicon–cage atom bond distances were all greater than the experimental ones.

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Table I. Selected Heavy-Atom Composition of the Molecular Orbitals of $Si(C_2B_4H_6)_2$ and $Si(C_2B_9H_{11})_2$ as the Percent of the MNDO Molecular Orbital

		Si		C		B(basal)[a]		B(unique)[a]		B(apical)[a]	
MO	energy[b]	s	p	s	p	s	p	s	p	s	p
					$Si(C_2B_4H_6)_2$						
$3a_g$	−21.65	25.30		0.11	2.83	0.02	2.66	0.02	3.01	17.98	0.17
$6a_g$	−15.62	24.01		0.13	1.01	0.57	0.54	1.66	1.02	4.41	10.42
$7b_u$	−13.34		6.41	0.04	11.58	0.04	1.47	0.04	0.39	0.02	8.77
$4a_u$	−12.30		20.75	0.01	5.67		9.09		0.48		7.47
$9b_u$	−11.31		26.86		1.81		2.60	0.16	15.42		8.81
$9a_g$	−11.17	12.58		0.57	14.91	0.18	0.54		2.09	0.28	6.66
$10a_g$	−3.23	19.63		0.01	0.41	1.27	4.45	2.39	12.60	1.98	6.68
					$Si(C_2B_9H_{11})_2$[c]						
$5a_g$	−21.32	11.80		0.28	1.08	1.06	2.58	5.48	1.32		
$9a_g$	−15.56	12.35		0.10	2.48	0.89	0.85	1.47	0.94		
$12b_u$	−13.29		1.90		4.05		1.47	0.09	1.04		
$14a_g$	−12.30	9.21		0.10	8.85	0.22	0.38	0.01	0.63		
$7a_u$	−12.25		12.96	0.01	4.00		8.30		0.67		
$15b_u$	−11.47		18.21	0.01	2.87	0.04	2.53	0.12	9.09		
$16a_g$	−4.25	18.84			0.49	0.94	3.98	2.69	13.32		

[a] B(basal) = the two borons off the mirro plane, B(unique) = the boron in the mirror plane, B(apical) = the apical boron. [b] In electron volts. [c] Only the atoms in the C_2B_3 pentagonal face are given.

[The calculated Si–C(cage), Si–B(basal), and Si–B(unqiue) bond distances are 2.45, 2.25, and 2.10 Å, respectively, while the corresponding experimental distances are 2.22, 2.14, and 2.05 Å.] The average difference between the other calculated and experimental intracage bond distances was 0.05 Å, indicating excellent agreement (see supplementary Table 2). A comparison of the calculated bond distances in $Si(C_2B_4H_6)_2$ with those found experimentally for its bis(trimethylsilyl) derivative[7] shows about the same extent of agreement as found in the icosahedral silacarborane system. That is, the silicon–cage atom distances are overestimated by about 0.1 Å, while other intracage distances agree to within about 0.05 Å (see supplementary Table 2). For both the icosahedral and pentagonal-bipyramidal *commo*-silacarboranes, the agreement between the calculated and experimental structures was close enough to warrant further analyses of the results.

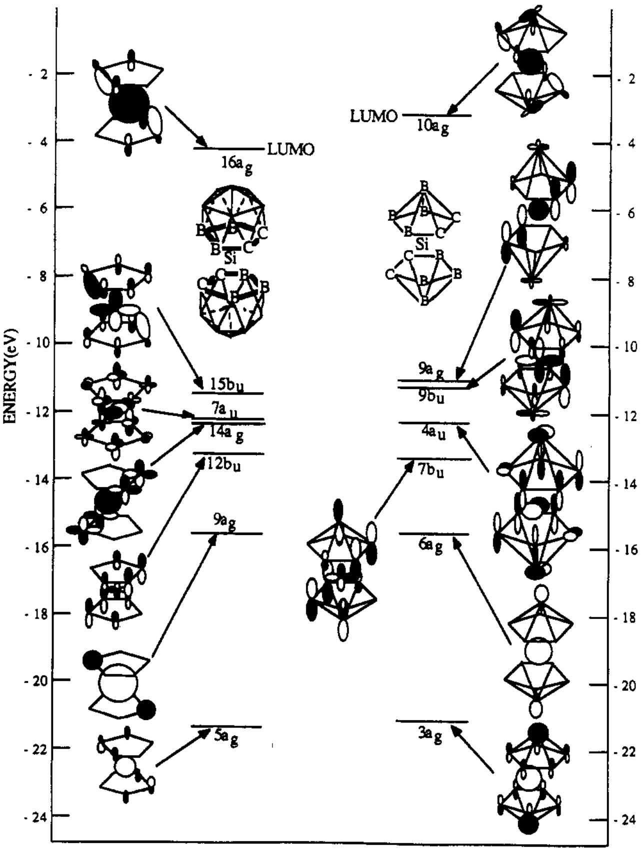

Figure 1. MNDO molecular orbital energies and heavy-atom orbital compositions for $Si(C_2B_9H_{11})_2$ and $Si(C_2B_4H_6)_2$. For $Si(C_2B_9H_{11})_2$ only the C_2B_3 face is shown.

Both calculations and experiment show that the silicons are not equally bonded to the atoms in the C_2B_3 open faces of the carboranes but are slipped toward the boron atoms. Such a slippage seems to be a common structural feature found in most main-group commo and closo metallacarboranes and their Lewis base complexes.[1,2]

The structures of the silacarboranes can be understood by considering the main silicon-containing molecular orbitals (MO's) of $Si(C_2B_9H_{11})_2$ and $Si(C_2B_4H_6)_2$ formed from the valence orbitals of the respective atoms. The $Si(C_2B_9H_{11})_2$ complex has 58 filled MO's and $Si(C_2B_4H_6)_2$ has 28 filled MO's. However, only seven MO's in each complex have significant silicon character; these are shown in Figure 1. Table I gives the pertinent heavy-atom compositions of these MO's. As can be seen, the strongest silicon–carborane bonding involves those carborane orbitals that extend above the pentagonal faces, that is, those having significant p_π character, relative to the C_2B_3 face.[41] In general, the $C_2B_9H_{11}^{2-}$ p_π orbitals are oriented more inward toward the silicon than are the analogous $C_2B_4H_6^{2-}$ orbitals. This difference in orientation has been noted by Mingos and co-workers.[25c] The silicon and C_2B_3 atomic orbital contributions and energies of the MO's of the two complexes shown in Figure 1 are remarkably similar. The major difference is in the ordering of the three highest energy MO's shown in Figure 1. The highest energy a_g MO in $Si(C_2B_9H_{11})_2$, MO $14a_g$, is relatively lower in energy than the analogous $Si(C_2B_4H_6)_2$ MO, MO $9a_g$. Both MO's are localized on the silicon atom and the cage carbons, and these two groups are antibonding to one another. Orbital compositions, given in Table I, show that $14a_g$ is more delocalized than is $9a_g$, should produce less antibonding silicon–cage interactions than are found in $9a_g$, and thus have a somewhat lower energy. However, in view of the overall similarities shown in Figure 1, the well-established parallel ligation chemistry of the $[C_2B_4H_6]^{2-}$ and $[C_2B_9H_{11}]^{2-}$ dianions (or their derivatives)[1,2] is under-

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[41] The C_2B_3 face is not planar but is folded such that the unique boron lies slightly below the plane of the other four atoms. In the coordinate system, the x axis is normal to this four-atom plane and the y axis is in the mirror plane of the complex.

Table II. One-Center (E_A) and Two-Center (E_{AB}) Energy Terms for Various Atomic Interactions in $Si(C_2B_4H_6)_2$ and $Si(C_2B_9H_{11})_2$ as a Function of Δ[a]

			$Si(C_2B_9H_{11})_2$				
Δ, Å	−0.37	−0.07	0.22	0.49[b]	0.79	1.09	1.41
ΔH_f, kcal/mol	68.82	38.19	20.44	15.54	19.41	27.90	38.80
$\sum E_{AB}$(cage),[c] eV	−296.14	−296.40	−296.94	−297.55	−298.18	−298.66	−298.85
$\sum E_{AB}$(Si–cage),[d] eV	−13.41	−15.44	−16.52	−16.97	−17.00	−16.69	−16.18
$\sum E_{AB}$(cage–cage),[e] eV	0.26	0.75	1.05	1.22	1.24	1.18	1.05
E_A(Si), eV	−80.41	−78.30	−76.60	−75.22	−74.07	−73.52	−73.51
$\sum E_A$(cage), eV	−739.97	−739.63	−739.38	−739.20	−739.05	−738.96	−738.97
E, eV	−2179.19	−2180.49	−2181.23	−2181.44	−2181.29	−2180.96	−2180.46
			$Si(C_2B_4H_6)_2$				
Δ, Å	−0.32	−0.14	−0.02	0.31[b]	0.49	0.66	0.86
ΔH_f, kcal/mol	87.68	74.90	66.09	59.79	61.66	66.12	72.33
$\sum E_{AB}$(cage),[c] eV	−158.43	−158.78	−159.16	−159.89	−160.30	−160.67	−161.03
$\sum E_{AB}$(Si–cage),[d] eV	−16.13	−16.70	−17.06	−17.40	−17.43	−17.39	−17.28
$\sum E_{AB}$(cage–cage),[e] eV	0.38	0.52	0.63	0.79	0.88	0.97	1.07
E_A(Si), eV	−78.56	−77.88	−77.28	−76.14	−75.43	−74.77	−74.13
$\sum E_A$(cage), eV	−453.69	−453.45	−453.31	−452.98	−452.88	−452.84	−452.83
E, eV	−1334.68	−1335.22	−1335.69	−1335.89	−1335.77	−1335.60	−1335.34

[a] Δ = the distance from the normal line from the C_2B_2 plane to the apical boron. In $Si(C_2B_9H1_1)_2$, Δ's for the cage carbons, basal borons, and unique boron are −1.08, 0.39, and 1.62, respectively. The analogous values in $Si(C_2B_4H_6)_2$ are −1.034, 0.37, and 1.41. [b] Optimized value. [c] The sum of the two-center terms for the atoms in a single $C_2B_4H_6$ or $C_2B_9H_{11}$ cage. [d] The sum of the two-center terms for the silicon and a carborane cage. [e] The sum of the two-center terms of the atoms in one carborane cage with the atoms of the other cage.

standable. It is apparent from Figure 1 that the main bonding between the silicon and the carboranes is accomplished through the Si(p) orbitals; the Si(s) orbital interactions in both complexes are either antibonding or nonbonding to the carborane atoms. These bonding preferences are reflected in the Mulliken overlap populations (MOP). In $Si(C_2B_4H_6)_2$ the MOP's for the Si(3s), Si($3p_x$), Si($3p_y$), and Si($3p_z$) orbitals[40] with the C_2B_3 orbitals are −0.7466, 0.1610, 0.2054, and 0.1694, respectively, while in $Si(C_2B_9H_{11})_2$ the analogous MOP's are −0.7790, 0.1588, 0.1694, and 0.1988, respectively. It is also apparent from Figure 1 that the Si(s) antibonding interactions involve cage carbon orbitals more than they do boron orbitals (see MO's $14a_g$ and $9a_g$). On the other hand, the generally bonding Si(p) interactions are found in those MO's more localized on the boron atoms (see Table I). Both of these characteristics would suggest that a slipped, rather than a centroidal, position of the silicon would be favored in these complexes; this turns out to be the case.

The detailed energy interactions accompanying slippage can be seen in Table II, which lists the one-center and two-center energy terms for $Si(C_2B_9H_{11})_2$ and $Si(C_2B_4H_6)_2$ as the silicon atom is moved across the C_2B_3 face of the carboranes. In these calculations the silacarboranes were constrained to maintain C_{2h} symmetry and the internal C_2B_4 and C_2B_9 cage geometries were fixed at their optimized configurations. The table shows the slippage is a result of several interactions. The silicon–cage two-center terms reach their largest negative values, signifying the most favorable silicon–carborane bonding, when the silicon is slightly slipped away from the centroidal position above the pentagonal face, toward the boron atoms. Analysis of the individual silicon–cage atom two-center energy terms shows that this slipped position affords the most favorable bonding to the two basal borons that are off the carborane mirror plane. Table I also shows one other interaction that is important in determining the extent of slippage. As the silicon moves toward the boron atoms, bonding within the carborane cages steadily increases. This increased intracage bonding on slippage of the metal toward the boron side of the C_2B_3 face has also been found for the *closo*-stannacarboranes and their Lewis base adducts.[22] In all cases the main contribution to the enhanced intracage bonding is an increase in C(cage)–C(cage) bonding on slippage. Figure 1 shows that $Si(C_2B_9H_{11})_2$ MO $14a_g$ and $Si(C_2B_4H_6)_2$ MO $9a_g$, while antibonding in Si(s), are responsible for some of the strongest C(cage)–C(cage) bonding in the complexes. Therefore, slippage of the silicon away from the cage carbons not only relieves antibonding interactions in these MO's, but also promotes C(cage)–C(cage) bonding. Both of these effects are important in determining the extent of slip distortion of the silacarborane sandwich compounds. Similar calculations on $Si(C_5H_5)_2$ show that the centroidal position of the silicon above the Cp faces is determined solely by Si–Cp bonding interactions (see supplementary Table 3).

Figure 1 also shows the orbital sketches of the LUMO's of $Si(C_2B_9H_{11})_2$ (MO $16a_g$) and $Si(C_2B_4H_6)_2$ (MO $10a_g$). These are heavily localized on the unique boron and the silicon atoms, which are strongly antibonding to one other. While both $16a_g$ and $10a_g$ are vacant when Si(IV) bonds to the carboranes, they would be occupied if Si(II) were bonded to form complexes such as $[Si(C_2B_4H_6)_2]^{2-}$ or $[Si(C_2B_9H_{11})_2]^{2-}$. In view of the strongly antibonding nature of the LUMO orbitals found for the silacarboranes, it is not surprising that, in the group 14 *commo*-metallacarboranes, the metals are present exclusively in their higher oxidation states.[1,2]

The above arguments are based on theoretical calculations that utilize limited basis sets comprising only the valence s and p silicon atomic orbitals. The HOMO's of $Si(C_2B_9H_{11})_2$ and $Si(C_2B_4H_6)_2$ are π-type carborane orbitals with b_g symmetry that could interact with the silicon d orbitals. In MNDO these MO's are treated as nonbonding. It is an open question to what extent vacant Si(d) valence orbitals could interact directly with the b_g carborane MO's and ameliorate the silicon–carborane interactions in orbitals such as $14a_g$ and $9a_g$. In order to ascertain the extent to which specific Si(d) interactions would alter the explanations arrived at from MNDO studies, Xα–SW SCF calculations were carried out on $Si(C_2B_4H_6)_2$ and (η^5-$C_5H_5)_2$Si, using spherical harmonics on silicon through $l = 2$. Xα–SW was chosen because it has been applied successfully to a number of main group η^5-cyclopentadienyl[42] and bis(η^5-cyclopentadienyl)[43] complexes. The Xα–SW calculated ionization potentials of (η^5-C_5H_5)In, (η^5-C_5H_5)BeCl, and (η^5-$C_5H_5)_2$M (M = Sn, Pb) were found to agree quite well with ultraviolet photo-

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Table III. Composition of Xα–SW Silicon-Containing Molecular Orbitals as a Percent of the Charge Density for $Si(C_2B_4H_6)_2$ and $(\eta^5-C_5H_5)_2Si$

		Si			C		B(unique)		B(basal)		B(apical)				
MO	energy, eV	s	p	d	s	p	s	p	s	p	s	p	H total	outer total	inner total
							$Si(C_2B_4H_6)_2$								
$3a_g$	−14.76	18.03		0.18	0.31	15.15	0.29	3.14	0.01	5.69	25.47	1.12	19.43	0.35	10.84
$6a_g$	−11.92	14.26		0.18	0.20	4.17	9.63	5.40	2.07	3.68	1.69	16.61	41.00	0.68	4.08
$7b_u$	−9.95		14.67		0.39	38.35	0.02	0.28	0.06	5.79	0.74	13.88	10.37	0.26	15.57
$4a_u$	−8.57		25.78		0.22	12.17		1.99	0.02	23.85		5.45	1.93	0.08	24.24
$9b_u$	−8.28		19.32		0.23	3.78	0.53	22.75	0.02	10.87	1.21	17.58	3.17	0.16	20.38
$9a_g$	−7.38	3.87		6.34	0.89	38.13		11.35	0.09	1.45		15.44	0.19	0.18	22.06
$5b_g$	−6.27			9.79	3.44	20.31		3.45	27.79	0.35		2.24	32.68	0.27	23.85
$10a_g$[a]	−1.55	11.23		13.12	0.52	8.24	2.03	24.48	0.90	1.99	0.31	2.21	1.37	2.87	30.72
							$(\eta^5-C_5H_5)_2Si$								
$3a_{1g}$	−11.07	55.32		0.03	2.09	23.78							0.01	0.37	18.40
$3a_{2u}$	−8.58		17.89		0.37	55.79							0.03	1.23	24.69
$3e_{1u}$	−5.40		32.63		0.66	33.64							0.08	1.21	31.77
$4a_{1g}$	−4.73	33.56		4.67	1.49	43.73							0.22	2.50	17.98
$3e_{1g}$	−3.81			7.39	0.04	61.72							0.01	2.46	28.39

[a] From a spin-restricted calculation with single occupancies of $5b_g$ and $10a_g$.

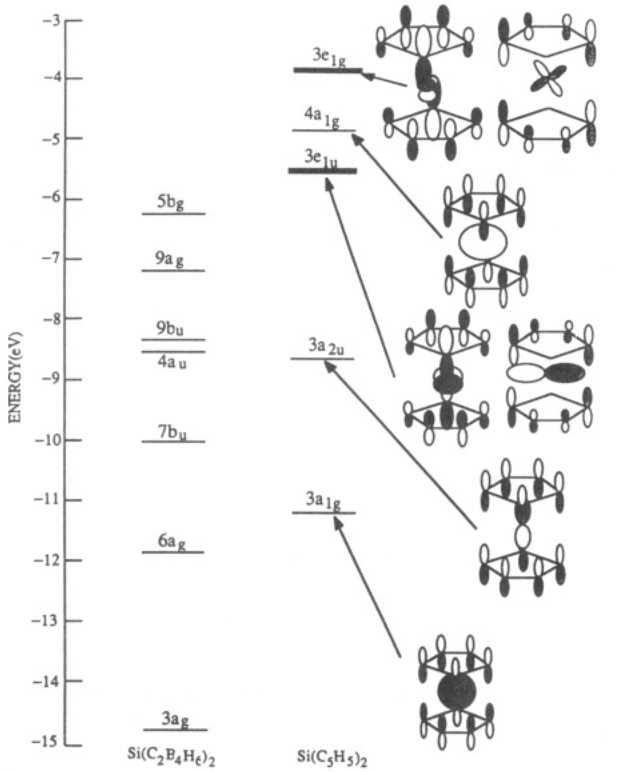

Figure 2. Xα–SW molecular orbital energies of $Si(C_2B_4H_6)_2$ and $(\eta^5-C_5H_5)_2$ with heavy-atom LCAO projections for $(\eta^5-C_5H_5)_2Si$.

electron spectroscopy data.[42,43] Figure 2 shows the energies of the major silicon-containing MO's of $Si(C_2B_4H_6)_2$ and $(C_5H_5)_2Si$, and Table III lists their compositions. For purposes of comparison, Figure 2 also shows the atomic orbital sketches of the $(C_5H_5)_2Si$ MO's, projected as LCAO's of the silicon and cyclopentadienide valence orbitals.[44] A comparison of the results summarized in Figures 1 and 2 shows that MNDO and Xα–SW calculations give the same sequence of MO's. Except for the presence of small amounts of Si(d) functions in several of the Xα–SW-generated orbitals, the MO's given by the two methods are of very similar composition. The only difference in the spacings of the MO's is that MNDO predicts that the $9a_g$ and $9b_u$ orbitals are about equal in energy, while the Xα–SW results show a much larger energy spread. This difference is more an inherent function of the two calculation methods rather than the influence of d functions on the energy of MO $9a_g$. When Xα–SW calculations were carried out on $Si(C_2B_4H_6)_2$ with silicon spherical harmonics truncated at $l = 1$, the resulting energy level sequence was very similar to that found in Figure 2. The largest energy decrease on inclusion of Si(d) harmonics was found in MO $5b_g$ (1 eV), followed by that of $9a_g$ (0.5 eV). These are the MO's with the highest Si(d) character (see Table III). The effect in $9a_g$ is to distort electron density so as to moderate the silicon–carborane antibonding interactions. While the presence of d functions in $5b_g$ does allow for delocalization of electron density onto the silicon, its contribution to bonding is minor compared to those of the silicon s and p orbitals (see Table III). Therefore, while inclusion of d functions would undoubtedly improve energy calculations, it gives little additional insight into the bonding and structural distortions found in the main-group metallacarboranes. This is in general agreement with ab initio calculations by Magnusson,[45] who found that d function involvement in hypercoordinate molecules, such as PF_5 and SF_6, was not fundamentally different from those found in normal valency compounds. In the silacarboranes the silicon bonds through its s and p valence orbitals and specific d orbital interactions are not important; the HOMO's in these sandwich complexes can be viewed as nonbonding between silicon and the carborane ligands.

Figure 2 shows the LCAO projections for the main silicon-containing orbitals for the $(C_5H_5)_2Si$ complex having D_{5d} symmetry.[46] In comparison of the silicon bonding in the cyclopentadienyl complex with that in the silacarboranes, one important difference that is apparent is the enhanced Si(s) bonding with the totally symmetric ligand orbital in $(C_5H_5)_2Si$, MO $3a_g$, compared to the analogous MO's in $Si(C_2B_4H_6)$ and $Si(C_2B_9H_{11})_2$, MO's $3a_g$ and $5a_g$, respectively (see Figure 1 and Table II).

A +2, rather than a +4, oxidation state of silicon in $Si(C_5H_5)_2$ can be understood by noting that the HOMO in $Si(C_5H_5)_2$, MO $3e_{1g}$, while not containing much silicon character, at least compared to the other orbitals in Table II, is responsible for a major part of the intracyclopentadienyl bonding. Therefore, depopulation of this state would not be expected. Thus, the preferences for different oxidation states of silicon in forming carborane and cy-

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[44] Bursten, B. E.; Fenske, R. F. *J. Chem. Phys.* **1977**, *67*, 3138.

[45] Magnusson, E. *J. Am. Chem. Soc.* **1990**, *112*, 7940.

[46] Reference 2 states that the crystal structure of $(C_5Me_5)_2Si$ contained two independent molecules: one having the C_5Me_5 rings planar (D_{5d}) and the other having the rings bent (C_s).

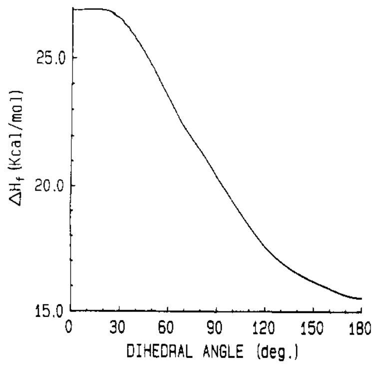

Figure 3. ΔH_f of $Si(C_2B_9H_{11})_2$ as a function of the B(unique)-B(apical)-B′(unique)-B′(apical) dihedral angle.

clopentadienyl sandwich complexes are understandable after considering the nature of the HOMO of $Si(C_5H_5)_2$ and the LUMO's of the silacarboranes.

One persistent structural feature of the *commo*-silacarboranes, and other main-group metallacarboranes,[1,2] is that the cage carbons of the two carborane ligands are positioned opposite to one another across the silicon atom. The presence of bulky trimethyl silyl groups on the cage carbons in the pentagonal-bipyramidal carboranes would favor this arrangement. However, $Si(C_2B_9H_{11})_2$ also shows a trans orientation of the cage carbons, so other factors must also be important. The MNDO energy of the $Si(C_2B_9H_{11})_2$ complex was calculated as a function of the dihedral angle of the lines connecting the B(unique)-B(apical) atoms of the two carborane cages. At a dihedral angle of 180° the cage carbons would occupy the experimentally found trans positions, and at a dihedral angle of 0° the cage carbons would be cis and the carborane cages would be eclipsed. Figure 3 shows a plot of energy, expressed as ΔH_f, versus the dihedral angle. While both the 180 and 0° structures were found to be local minima on the potential energy surface, the energies of the intermediate angles were calculated by assuming that each cage maintained its intracage mirror plane and that the silicon was equidistant from both cages.[47] As can be seen from Figure 3, the trans (180°) structure resides at the bottom of a very broad minimum of energy so that fairly large changes in dihedral angles can be accomplished by very small energy inputs. For example, a dihedral angle of 160° would have an energy of about 0.5 kcal above that of the optimized structure. It is of interest to note that while $Si(C_2B_9H_{11})_2$[9] and the $[Al(C_2B_9H_{11})_2]^-$ complex[3,4] have their cage carbons in trans positions, the dihedral angle found for the isoelectronic $[Ga(C_2B_9H_{11})_2]^-$ complex is about 160°. In view of the very broad minima found in our calculations and the fact that gallium uses the same type of orbitals as does silicon in bonding to the carborane, a partially eclipsed structure is not surprising.

Conclusion

The stabilities, structures and stoichiometries of the *commo*-silicarboranes can be understood in terms of the interactions of the silicon 3s and 3p valence orbitals with π-type orbitals on the C_2B_3 open faces of the carborane ligands. The major bonding interactions are between the silicon 3p orbitals and carborane orbitals that are localized on the boron atoms of the carborane face, while the silicon 3s orbital is either nonbonding or antibonding to the carborane orbitals. These orbitals, while antibonding with respect to the silicon, are heavily localized on the cage carbons and are responsible for some very strong intracage bonding. The driving forces for the slip distortions found in the silacarboranes are the relief of Si(s)-C(cage) antibonding interactions and an enhancement of intracage bonding. These interactions are fundamentally different from those that govern slip distortion in transition-metal carborane sandwich compounds.[48] A preference for a +4 rather than a +2 oxidation state of the metal is dictated by the compositions of the LUMO's of the *commo*-silacarboranes. In these MO's the silicon (3s) and carborane orbitals are strongly antibonding and their occupation would greatly destabilize the sandwich compounds.

Using the silacarboranes as a guide, this investigation shows that, while the stabilities of the main-group carborane sandwich complexes are governed by metal p orbital bonding, their structures and stoichiometries are dictated by antibonding interactions involving the metal's s orbital.

Acknowledgment. I thank Professor Michael Lattman for invaluable help with the Xα-SW calculations and also Southern Methodist University for furnishing time on the IBM 3081 computer.

Supplementary Material Available: Tables of atomic sphere radii for Xα–SW calculations of $Si(C_2B_4H_6)_2$ and $(C_5H_5)_2Si$, MNDO optimized and experimental bond distances in $Si(C_2B_9H_{11})_2$ and $Si(C_2B_4H_6)_2$, and MNDO one- and two-center terms for $(C_5H_5)_2Si$ as a function of Δ (3 pages). Ordering information is given on any current masthead page.

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[47] In calculations in which no restrictions were imposed, ΔH_f changed very little near 180° but, as the dihedral angle decreased, one Si–cage distance increased to the extent that the complex could better be discribed as a $[SiC_2B_9H_{11}]^{2+}$,$[C_2B_9H_{11}]^{2-}$ ion pair.

[48] Mingos, D. M. P.; Forsyth, M. I. *J. Organomet. Chem.* **1978**, *146*, C37.