Silicon(IV) and Germanium(IV) Moieties Stabilized by the Charge-Compensated Carborane Ligand $[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$: Synthetic and Structural Investigation

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Reaction of the charge-compensated carborane anion $[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ ($\mathbf{1}^-$) with Me_2ECl_2 and Me_3ECl (E = Si, Ge) leads to the carboranes η^1-8-EMe_2Cl-9-SMe_2-7,8-$C_2B_9H_{10}$ (**2a**,**b**) and (EMe_3)-(9-SMe_2-7,8-$C_2B_9H_{10}$) (**3a**,**b**), respectively. Compound **3a** was found to react readily with $FeCl_2$ to form $Fe(\eta^5$-9-SMe_2-7,8-$C_2B_9H_{10})_2$ (**4**). All products were characterized by NMR spectroscopy and chemical analysis. Compounds **2a**,**b** were additionally characterized by X-ray crystallography. The two compounds are isostructural with the carborane η^1-bonded to the Si or Ge through the cage carbon adjacent to the boron having the SMe_2 substituent.

Introduction

The reactions of both the large (C_2B_9) and small (C_2B_4) cage *nido*-carborane dianions with the heavier group 14 elements have been studied for the last 40 years.[1] Depending on the element and reaction conditions, the heterocarboranes can have either half- or full-sandwich structures with the group 14 elements in oxidation states of II or IV, respectively. The structures show that the C_2B_3 faces of the carboranes are essentially η^5-bonded to the lighter group 14 elements (Si, Ge), whereas with the heavier elements there is an increasing tendency to be slip distorted away from the cage carbons.[2,3] There is one report of η^1-bonding of carboranes to an atom of silicon. These were products formed in the reaction of *commo*-3,3′-Si(3,1,2-$C_2B_9H_{11})_2$ with either C_5H_5N or Me_3P; in both cases the silicon was bonded through one of the cage borons.[2b] Herein, we report the syntheses of η^1-8-EMe_2Cl-9-SMe_2-7,8-$C_2B_9H_{10}$ (**2a**, E = Si; **2b**, E = Ge), which are the products of the reactions of the charge-compensated carborane monoanion $[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_{10}\text{-}H_{10}]^-$ (**1**)[4] with Me_2ECl_2. Structural studies show these to be the first examples of group 14 heterocarboranes in which the carborane is η^1-bonded through one of its cage carbons. We also report the synthesis and some chemical properties of trimethylsilyl and germyl derivatives (EMe_3)(9-SMe_2-7,8-$C_2B_9H_{10}$) (**3a**, E = Si; **3b**, E = Ge). From their structures and properties, it is an open question as to how to describe the nature of these carborane−E interactions.

Experimental Section

General Synthetic Procedures. All operations were carried out on a double-manifold Schlenk vacuum line under a dry argon atmosphere or in a nitrogen-filled glovebox. The starting charge-compensated carborane, 9-SMe_2-7,8-$C_2B_9H_{11}$ (**1**), was prepared and then converted into its sodium salt ($\mathbf{1}^-$), as described in the literature.[4d] Prior to use, Me_3SiCl and Me_2SiCl_2 (Aldrich) were purified by distillation under argon with fractionation by dephlegmator (30 cm) in the presence of *N*,*N*-dimethylaniline to remove any HCl; the silyl chlorides were stored at −20 °C. Me_3GeCl and Me_2GeCl_2 (Gelest Inc.) were used as purchased. THF and petroleum ether were dried over Na/benzophenone and Na/K alloy, respectively. THF-d_8 (Aldrich) for NMR studies was purified by shaking with Na/K alloy and was stored at −20 °C. The ^1H, ^{11}B, and ^{13}C NMR spectra (δ in ppm, J in Hz) were recorded on a Bruker Fourier transform multinuclear spectrometer operating at 200.13, 64.21, and 50.32 MHz, respectively. Elemental analyses were determined in house at Northern Illinois University using a Perkin-Elmer 2400 CHN elemental analyzer.

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Synthesis of η^1-8-SiMe$_2$Cl-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$ (2a). A mixture of 266 mg (2.06 mmol) of Me_2SiCl_2 and 8.1 mL of a 0.25 M solution of 1^- in THF (2 mmol) was stirred for 3 days at room temperature. The precipitate of NaCl, formed in the reaction, was removed by filtration. The solvent was then removed by evaporation, *in vacuo*, yielding η^1-8-SiMe$_2$Cl-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$ (**2a**), which was then dissolved in THF and reprecipitated by the addition of petroleum ether. This recrystallization process was repeated twice to produce colorless crystals that were dried overnight under vacuum. Yield: 585.10 mg, 1.99 mmol (99.7%). Mp: 130−132 °C. Crystals for X-ray analysis were grown by slow diffusion of petroleum ether into a saturated solution of **2a** in THF in a NMR tube. ^{1}H NMR (THF-d_8): δ 2.61 (s, 3H, SMe$_2$), 2.57 (s, 3H, SMe$_2$), 2.18 (br s, 2H, cage CH), 0.90 (s, 3H, SiMe$_2$), 0.82(s, 3H, SiMe$_2$). ^{11}B NMR (THF-d_8): δ −5.79 (s, B-SMe$_2$, 1B), −8.15 (d, 140, 2B), −13.23 (d, 150, 1B), −14.89 (d, 150, 1B), −16.38 (d, 151, 1B), −21.41 (d, 156, 1B), −33.09 (d, 141, 1B), −34.74 (d, 82, 1B). ^{13}C NMR (THF-d_8): δ 49.67(d, 135, 1C), 46.69 (d, 164, 1C), 20.00−0.00 (m, 4C, SMe$_2$ and SiMe$_2$). Anal. Calc for $C_6H_{22}B_9SSiCl$: C, 24.48; H, 7.47. Found: C, 25.19; H, 7.74.

Synthesis of η^1-8-GeMe$_2$Cl-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$ (2b). A mixture of 208.28 mg (1.2 mmol) of Me_2SiCl_2 and 9.1 mL of a 0.11 M solution of 1^- in THF (1 mmol) was stirred for 1 week at room temperature, during which time a precipitate of NaCl formed. The solution was filtered, and then the solvent was removed *in vacuo*. The resulting compound was purified by first dissolving it in THF and then reprecipitating it by the slow addition of petroleum ether. This recrystallization process was repeated twice. The resulting solid was identified as η^1-8-GeMe$_2$Cl-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$ (**2b**). Yield: 205.65 mg, 0.62 mmol (62.01%). Mp: 133−135 °C. Crystals for X-ray analysis were grown similarly to **2a**. ^{1}H NMR (THF-d_8): δ 2.57 (s, 3H, SMe$_2$), 2.56 (s, 3H, SMe$_2$), 2.17 (br s, 2H, cage CH), 1.13 (s, 3H, SiMe$_2$), 1.01(s, 3H, SiMe$_2$). ^{11}B NMR (THF-d_8): δ −4.38 (s, B-SMe$_2$, 1B), −7.84 (d, 134, 2B), −12.95 (d, 160, 1B), −15.15 (d, 132, 1B), −17.14 (d, 146, 1B), −21.89 (d, 156, 1B), −32.07 (d, 139, 1B), −33.80 (d, 97, 1B). ^{13}C NMR (THF-d_8): δ 47.91(d, 150, 1C), 44.82(d, 162, 1C), 20.00−0.00 (m, 4C, SMe$_2$ and GeMe$_2$). Anal. Calc for $C_6H_{22}B_9SGeCl$: C, 21.72; H, 6.69. Found: C, 21.70; H, 6.49.

Synthesis of (SiMe$_3$)(9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$) (3a). A mixture of 256.80 mg (2.36 mmol) of Me_3SiCl and 8.1 mL of a 0.25 M solution of 1^- in THF (2 mmol) was stirred for 3 days at room temperature, during which time a solid (NaCl) formed. While the precipitate was removed by filtration, the solvent and the unreacted Me_3SiCl, if any, were removed from the filtrate *in vacuo*. The solid was recrystallized three times by dissolving in THF, then reprecipitating by the addition of petroleum ether, and was dried *in vacuo* overnight. The final product, identified as (SiMe$_3$)(9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$) (**3a**), was a colorless oil. Yield: 502.12 mg, 1.88 mmol (94.2%). ^{1}H NMR (THF-d_8): δ 2.72 (s, 3H, SMe$_2$), 2.59 (s, 3H, SMe$_2$), 2.00 (br s, 1H, cage CH), 1.41 (br s, 1H, cage CH), from 0.14 to −0.12 (m, 9H, SiMe$_3$). ^{11}B NMR (THF-d_8): δ −5.84 (d, 171, 1B), −7.93 (s, B-SMe$_2$, 1B), −13.96 (d, 160, 1B), −18.31 (d, 96, 1B), −19.99 (d, 154, 1B), −24.93 (d, 193, 1B), −28.03 (d, 156, 1B), −31.57 (d, 150, 1B), −38.44 (d, 145, 1B). Anal. Calc for $C_7H_{25}B_9SSi$: C, 31.54; H 9.38. Found: C, 30.39; H, 8.23.

Synthesis of (GeMe$_3$)(9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$) (3b). A mixture of 269.40 mg (1.10 mmol) of Me_3GeCl and 9.1 mL of a 0.11 M solution of 1^- in THF (1 mmol) was stirred for 1 week at room temperature. The precipitate that formed (NaCl) was removed; the solvent and excess Me_3GeCl were removed by evaporation, and the product was purified as described above. A colorless semisolid substance, identified as (GeMe$_3$)(9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$) (**3b**), was obtained after vacuum drying overnight. Yield: 258.42 mg, 0.83 mmol (83.02%). ^{1}H NMR (THF-d_8): δ 2.75 (s, 3H, SMe$_2$), 2.61 (s, 3H, SMe$_2$), 2.07 (br s, 2H, cage CH), from 0.1 to −0.2 (m, 9H, SiMe$_3$). ^{11}B NMR (THF-d_8): δ −5.74 (d, 176, 1B), −7.82 (s, B-SMe$_2$, 1B), −13.76 (d, 165, 1B), −18.27 (d, 92, 1B), −19.99 (d, 164, 1B), −24.91 (d, 142, 1B), −28.00 (d, 159, 1B), −31.57 (d, 160, 1B), −38.40 (d, 144, 1B). Anal. Calc for $C_7H_{25}B_9GeS$: C, 27.01; H 8.10. Found: C, 26.85; H, 7.89.

Structure Determination. Single crystals of the compounds were selected under Na-dried paraffin oil and transferred quickly to a glass fiber mounted on the goniometer of a Bruker SMART CCD diffractometer. The glass fiber was kept under a nitrogen steam of *ca.* −70 °C to prevent the decay of the crystals in air. Data were then collected by the diffractometer. Absorption corrections were applied to the data through the program SADABS.[9] The structures were solved with direct methods using the SIR97 program.[10] Full matrix least-squares refinement on F^2 was carried out using the SHELXTL package.[11] The structures have been checked for possible existence of higher symmetry by the program ADDSYM in the PLATON package.[12] No additional symmetry element was found. The crystallographic information including selected bond lengths of the compounds is listed in Tables 1 to 3.

Results and Discussion

Synthesis and Characterization of η^1-8-EMe$_2$Cl-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$ (2a,b). The reaction of the charge-compensated carborane monoanion [9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$]$^-$ (1^-), with Me_2ECl_2 in THF produced the carborane complexes η^1-8-EMe$_2$Cl-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$ (**2a**, E = Si; **2b**, E = Ge) as a colorless, microcrystalline solids in yields of 99% and 62%, respectively (see Scheme 1). The reaction with Me_2SiCl_2 proceeded more rapidly (3 days for **2a** vs 1week for **2b**) and in higher yields than did the same reaction with Me_2GeCl_2. A similar reactivity pattern was found for the corresponding Me_3ECl (E = Si, Ge) reactions. These results parallel the increased ease of hydrolysis of R_nSiCl_{4-n} compared to its germanium congeners.

The presence of the −Me$_2$ECl groups on complexes **2a** and **2b** suggests that they might prove to be interesting precursors for further reactions through the E−Cl bond. However, the Cl atom is surprisingly inert; **2a** and **2b** did not react with an excess of the monocarborane anion 1^-. This lack of further reactivity could be a consequence of steric effects. In both compounds, the Cl atom is surrounded by two methyl groups as well as the carborane ligand, which would make further reactions by bulky anions, such as 1^-, difficult. It is also consistent with a Me_2ECl^+ being less reactive than the neutral Me_2ECl_2. On the other hand, both **2a** and **2b** are sensitive to moisture, with the hydrolysis products being the neutral *nido*-carborane 9-SMe$_2$-7,8-C$_2$B$_{10}$H$_{11}$ (**1**) and a silicon or germanium polymer (oils); this suggests reaction at the E-Cl site. A study of the reactions of **2a** and **2b** with less sterically demanding anionic groups is currently underway in our laboratories.

The solid-state structures of **2a** and **2b** were established by single-crystal X-ray crystallography and are shown in Figures 1 and 2. Table 1 lists the pertinent crystallographic data, and some selected bond distances and bond angles are given in Tables 2 (**2a**) and 3 (**2b**). The two compounds are essentially isostructural and show the −EMe$_2$Cl groups bonded primarily to the cage carbon next to the SMe$_2$ group (C(8)), but slightly

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Table 1. Crystal Data for η^1-8-$SiMe_2Cl$-9-SMe_2-7,8-$C_2B_9H_{10}$ (2a) and η^1-8-$GeMe_2Cl$-9-SMe_2-7,8-$C_2B_9H_{10}$ (2b)

	compound **2a**	compound **2b**
empirical formula	$C_6H_{22}B_9ClSSi$	$C_6H_{22}B_9ClGeS$
fw	287.13	331.63
temperature	203(2) K	203(2) K
wavelength	0.71073 Å	0.71073 Å
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
unit cell dimens	a = 8.9214(5) Å	a = 8.8368(8) Å
	b = 14.2968(8) Å	b = 12.812(1) Å
	c = 13.1606(7) Å	c = 14.184(1) Å
	β = 106.972(1)°	β = 90.913(1)°
volume	1605.5(2) $Å^3$	1605.6(2) $Å^3$
Z	4	4
density (calcd)	1.184 Mg/m^3	1.368 Mg/m^3
absorp coeff	0.414 mm^{-1}	2.175 mm^{-1}
F(000)	596	668
cryst size	0.50 × 0.42 × 0.40 mm^3	0.50 × 0.40 × 0.30 mm^3
θ range for data collection	2.16 to 25.00°	2.14 to 25.00°
index ranges	$-10 \le h \le 10$, $-17 \le k \le 17$, $-15 \le l \le 15$	$-10 \le h \le 10$, $-15 \le k \le 15$, $-16 \le l \le 16$
no. of reflns collected	11 388	11 726
no. of indep reflns	2821 [R(int) = 0.0201]	2818 [R(int) = 0.0168]
completeness to θ = 25.00°	99.8%	99.9%
absorp corr	semiempirical from equivalents	semiempirical from equivalents
max. and min. transmn	1.000 and 0.590321	1.000 and 0.721746
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	2821/0/184	2818/0/177
goodness-of-fit on F^2	1.098	1.128
final R indices [$I > 2\sigma(I)$]	R1 = 0.0562, wR2 = 0.1821	R1 = 0.0341, wR2 = 0.1109
R indices (all data)	R1 = 0.0572, wR2 = 0.1850	R1 = 0.0352, wR2 = 0.1120
largest diff peak and hole	0.747 and −0.527 e $Å^{-3}$	0.821 and −0.487 e $Å^{-3}$

Table 2. Selected Bond Distances (Å) and Angles (deg) for η^1-8-$SiMe_2Cl$-9-SMe_2-7,8-$C_2B_9H_{10}$ (2a)

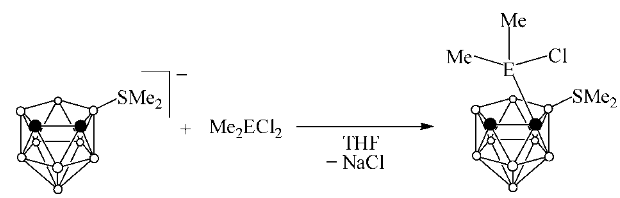
Distances			
Si−C(12)	1.854(3)	S−C(22)	1.802(3)
Si−C(11)	1.864(3)	C(7)−B(11)	1.606(5)
Si−Cl	2.1214(13)	C(7)−C(8)	1.817(5)
Si−C(8)	2.026(3)	C(8)−B(9)	1.788(4)
S−B(9)	1.907(3)	B(10)−B(11)	1.555(4)
S−C(21)	1.791(3)		
Angles			
C(21)−S−C(22)	101.6(2)	C(11)−Si−C(8)	112.97(17)
C(21)−S−B(9)	104.28(16)	C(12)−Si−Cl	103.15(13)
C(22)−S−B(9)	105.30(15)	C(11)−Si−Cl	101.02(15)
B(10)−B(9)−S	118.1(2)	C(8)−Si−Cl	101.09(10)
B(4)−B(9)−S	125.3(2)	B(9)−C(8)−Si	95.06(17)
B(5)−B(9)−S	117.3(2)	B(3)−C(8)−Si	136.8(2)
C(8)−B(9)−S	125.4(2)	B(4)−C(8)−Si	152.8(2)
C(12)−Si−C(11)	110.58(19)	C(7)−C(8)−Si	80.54(17)
C(12)−Si−C(8)	124.13(15)		

Table 3. Selected Bond Distances (Å) and Angles (deg) for η^1-8-$GeMe_2Cl$-9-SMe_2-7,8-$C_2B_9H_{10}$ (2b)

Distances			
Ge−C(12)	1.946(4)	S−C(22)	1.798(3)
Ge−C(11)	1.934(3)	C(7)−B(11)	1.604(4)
Ge−Cl	2.2324(9)	C(7)−C(8)	1.840(5)
Ge−C(8)	2.121(3)	C(8)−B(9)	1.793(4)
S−B(9)	1.905(3)	B(10)−B(11)	1.559(4)
S−C(21)	1.794(3)		
Angles			
C(21)−S−C(22)	101.64(18)	C(12)−Ge−C(8)	115.39(15)
C(21)−S−B(9)	104.19(16)	C(12)−Ge−Cl	100.06(13)
C(22)−S−B(9)	105.67(14)	C(11)−Ge−Cl	101.65(11)
B(10)−B(9)−S	118.1(2)	C(8)−Ge−Cl	98.06(9)
B(4)−B(9)−S	125.9(2)	B(9)−C(8)−Ge	91.87(17)
B(5)−B(9)−S	117.65(19)	B(3)−C(8)−Ge	134.8(2)
C(8)−B(9)−S	125.1(2)	B(4)−C(8)−Ge	149.2(2)
C(11)−Ge−C(12)	110.82(16)	C(7)−C(8)−Ge	78.17(16)
C(11)−Ge−C(8)	125.03(14)		

tilted to the center of the open five-membered C_2B_3 ring. The C(8)−Si bond distance in **2a** (2.026 Å) is longer than the two Si−Me distances (Si−C(11) 1.864 Å, Si−C(12) 1.854 Å), but

Scheme 1



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2a: E = Si, 99 %
2b: E = Ge, 62 %

shorter than the Si−C atom distances found in decamethylsilicocene (2.324−2.541 Å),[5a] where the Cp* ligand is η^5-bonded to the silicon. In the same way, the Ge−C(8) distance in **2b** (2.122 Å) is smaller than the shortest Ge−C distance in Cp_2Ge (2.347 Å).[5b] There are, at best, only weak interactions between the Si/Ge atoms in **2a** and **2b** with the adjacent cage carbon, C(7), with E−C(7) distances of 2.49 and 2.51 Å, respectively.

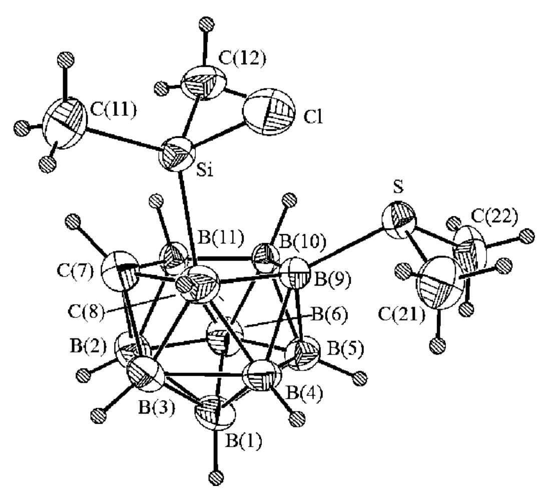

Figure 1. Structure of η^1-8-$SiMe_2Cl$-9-SMe_2-7,8-$C_2B_9H_{10}$ (**2a**). The 50% probability density surfaces are shown for all atoms.

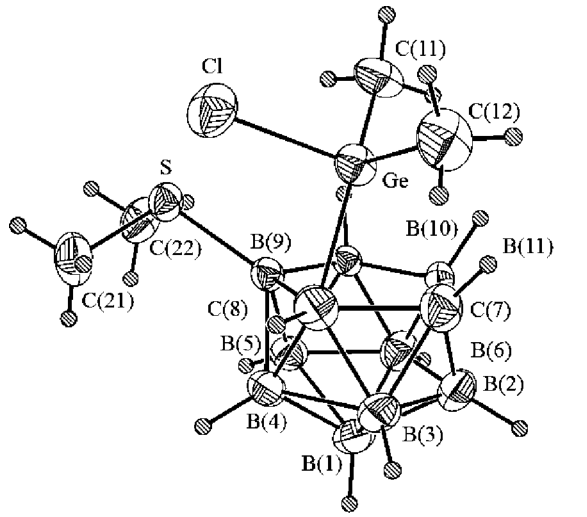

Figure 2. Structure of η^1-8-GeMe$_2$Cl-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$ (**2b**). The 50% probability density surfaces are shown for all atoms.

A comparison of the structure of the sodium salt of [9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$]$^-$, reported by Lyssenko and co-workers,[4g] with those of compounds **2a** and **2b** shows that coordination by the EClMe$_2$ causes a lengthening of the cage carbon bonds from 1.535 Å to 1.818 and 1.844 Å, respectively; the C(7)−B(9) bonds are also elongated, from 1.598 Å to 1.792 and 1.794 Å. Such C$_c$−C$_c$ elongations have been observed in both charge-compensated and noncompensated metallacarboranes and have been explained in terms of both increased steric repulsion between derivative groups on the cage carbons[6] and electron donation from lone pairs on the derivative groups to the LUMO, which is antibonding between the cage carbons.[7] Neither of these interactions seems to be operative in the case of **2a** and **2b**. The additional bond formed by the EClMe$_2$ moieties would withdraw electron density from the vicinity of C(7), thereby weakening its adjacent bonds. Sila- and germacarboranes have been reported in both the large, C$_2$B$_9$, and small, C$_2$B$_4$, cage systems.[2,3] In these complexes, the C$_2$B$_3$ pentagonal faces of the carboranes are η^5-bonded to the group 14 element, with a slight slip distortion away from the cage carbons.[2,3] For example, in *commo*-3,3′-Si(3,1,2-SiC$_2$B$_9$H$_{11}$)$_2$,[2a] the Si−C$_{cage}$ bond distances were 2.22 Å, compared to Si−B$_{facial}$ distances of 2.14−2.08 Å; similar distances were found in 2,2′,3,3′-(SiMe$_3$)$_4$-*commo*-1,1′-E(1,2,3-EC$_2$B$_4$H$_4$)$_2$ (E = Si, Ge).[3a] The η^1-bonding modes of the carboranes, through their cage carbons, with the group 14 atoms in **2a** and **2b** have not been observed in the other sila- and germacarboranes.

The ^{1}H NMR spectra of **2a** and **2b** in THF-d_8 show characteristic doublets from the two nonequivalent methyl groups of the SMe$_2$ substituent in the δ 2.61−2.56 ppm region and broad singlets for the two H−C(cage) protons at δ 2.18−2.17 ppm. These resonances are close to the equivalent proton signals found in the neutral *nido*-carborane **1** (δ 2.78 2.61 ppm for the SMe$_2$ protons and 2.20 ppm for the C−H protons)[4a] and for other related *nido*-carboranes.[4b,d,8] Nonequivalent proton resonances on the SiMe groups were also observed in the δ 1.13−0.82 region. This indicates restricted rotations about both the E−C(8) and S−B(9) bonds. The ^{1}H NMR spectrum of the neutral *nido*-carborane **1**[4d] also showed proton nonequivalence in SMe$_2$. It is surprising that the presence of the EMe$_2$Cl on one of the cage carbons exerts such a small influence on the shielding of the attached proton. The ^{11}B NMR spectra of compounds **2a** and **2b** show nine doublets in the region from δ −4.38 to −34.74 ppm that are similar to those found for the neutral carborane **1**.[4d] Although the presence of the C(8)−H(8) bond could not be verified by X-ray diffraction, the ^{13}C NMR spectra of **2a** and **2b** showed coupling of both of the C$_{cage}$ resonances with attached protons. The ^{13}C spectra show doublets from C$_{cage}$−H in the region δ 49.67−44.82 ppm, compared to the region δ 52.40−38.00 ppm for the same signals in **1**. The C−H coupling constant (J_{C-H}) is between 135 and 165 Hz, which is also comparable to that found for the carborane **1**.[4d]

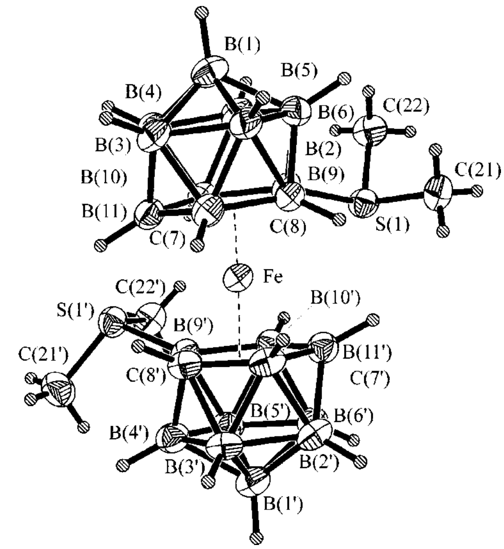

Figure 3. Structure of Fe(η^5-9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$)$_2$ (**4**). The 50% probability density surfaces are shown for all atoms. The numbering of atoms for the carborane ligands is similar to that of **1** for clarity. For all distances see ref 4c.

The nature of the bonding is unclear; the fact that the chemical shifts of the ^{1}H NMR resonances of the two H−C$_{cage}$ protons are the same for both C(7) and C(8) in **2a** and **2b** indicates a fairly weak interaction between E and C(7), at least as measured by their proton NMR spectra. On the other hand, bonding by the EClMe$_2$ produces significant distortions into the carborane cage.

Synthesis and Characterization of (EMe$_3$)(9-SMe$_2$-7,8-C$_2$B$_9$H$_{10}$) (3a,b). The reaction of carborane monoanion **1**$^-$ with Me$_3$ECl (E = Si, Ge) in THF produced the carboranes **3a** and **3b** in yields of 94% and 83%, respectively, as seen in Scheme 2. The reaction proceeds only slowly, especially when E = Ge. Both **3a** and **3b** are colorless oil-like materials that are very sensitive to moisture and oxygen.

The ^{11}B NMR spectra of compounds **3a** and **3b** are almost identical, consisting of nine resonances in the region δ −5.80 to −38.44 ppm. The spectra are very similar to the neutral **1** and **1**$^-$. Given the broadness of the resonance signals, **3a** and **3b** are the same as **1**$^-$. The ^{1}H NMR spectra of **3a** and **3b** in THF-d_8 show characteristic doublets from nonequivalent methyl groups on SMe$_2$ in the region δ 2.75−2.59 ppm and broad singlets from the two C$_{cage}$−H protons of the carborane cluster

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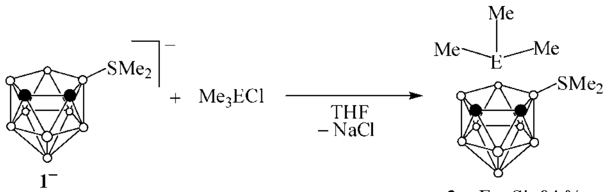
Scheme 2



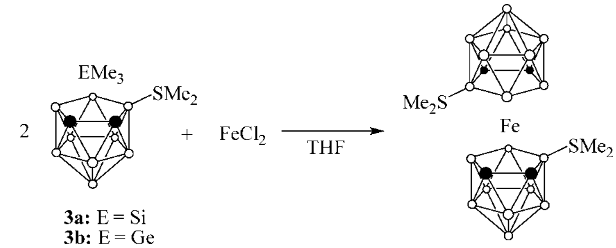
1$^-$

3a: E = Si, 94 %
3b: E = Ge, 83 %

at δ 2.07−2.00 ppm. These shifts are close to the analogous signals from the neutral carborane **1** (δ 2.78−2.61 ppm for SMe_2 and 2.20 ppm for $C-H_{cage}$) as well as for similar carboranes.[4d,8] The resonances from the $SiMe_3$ protons appear as multiplets in the region from δ 0.14 to −0.2 ppm, which are very similar to the shifts of the nine protons from the $SiMe_3$ group in Cp*$SiMe_3$ (δ −0.14 ppm).[5b] As was found in **2a** and **2b**, the multiplicity indicates restricted rotation of the Me groups. Scheme 2 shows compounds **3a** and **3b** to be half-sandwich complexes with the EMe_3 groups occupying apical positions over the C_2B_3 open faces of the carboranes. This is just for convenience; there is no experimental evidence for either aspect of these structures. Indeed, the striking similarities between the ^{11}B NMR spectrum of **1**$^-$ and **3a** and **3b** could well indicate a significant ionic interaction between a $[EMe_3]^+$ and a $[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_{10}H_{10}]^-$. To further test this possibility, **3a** and **3b** were mixed with a THF solution of $FeCl_2$, as shown in Scheme 3.

In the case of **3a** the reaction proceeds instantly with a yield of the iron complex Fe(η^5-9-SMe_2-7,8-$C_2B_9H_{10}$)$_2$ (**4**) (60%). This yield is higher than that reported in the original synthesis

Scheme 3



3a: E = Si
3b: E = Ge

meso, DD/LL
15 - 60 %

of the ferracarborane **4** (36%)[4c] from sodium derivative **1**$^-$. These results indicate that **3a** could prove to be a very useful carborane transfer agent. The reaction of $FeCl_2$ with **3b** proceeds very slow (one month) and with a low yield (15%). The less reactivity of **3b** can be explained by its higher stability than **3a** according to the position of silicon and germanium in the periodic table.

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Supporting Information Available: X-ray crystallographic files in CIF format for η^1-8-$SiMe_2Cl$-9-SMe_2-7,8-$C_2B_9H_{10}$ (**2a**) and η^1-8-$GeMe_2Cl$-9-SMe_2-7,8-$C_2B_9H_{10}$ (**2b**) are available free of charge via the Internet at http://pubs.acs.org.

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