

Figure 2. ^{19}F chemical shifts of element fluorides of the first and second period referenced to CCl_3F .

Results and Discussion

^{19}F NMR spectra of the product formed in the reaction of COS with F_2 in the gas phase are recorded repeatedly. A typical spectrum is shown in Figure 1. The intensity of the signal at -167 ppm corresponds well to the concentration of SF_2 , measured by FTIR spectroscopy. Since the resonance is close to that of SiF_4 , the IR spectrum of the gaseous product is checked for the presence of this compound, which is found to be present only in traces. Furthermore, the decrease of this signal and simultaneous increase of the signals of the dimer, SF_2SF_2 , is observed as expected.¹ Hence the signal at -167 ppm is attributed to SF_2 . All other signals can be assigned to other binary sulfur fluorides. The chemical shifts of these compounds in the liquid state are well established. The ^{19}F NMR spectrum reported here of the reaction products yields the chemical shifts in the gas phase. Some values show considerable phase-dependent shifts. The results are listed in Table I and compared to the values for the liquid compounds.

The experimental ^{19}F chemical shift of SF_2 of -167 ppm is in reasonable agreement with the predicted value of -182 ppm.¹¹ In Figure 2, chemical shifts of binary fluorides of p-block elements are compared. The fluorides in the first period exhibit the predicted decrease in their ^{19}F NMR shifts with increasing negative charge on the fluorine atoms caused by an increasing difference in electronegativity between the bonded element and fluorine (decreasing atomic number of central atom).

If one considers only these charges, the corresponding fluorine atoms in compounds of the second period should be more shielded. The lowest value should be that of SiF_4 , which should be similar to that of the fluoride ion. The experimental ^{19}F chemical shifts show that simple electronegativity arguments are not applicable for this series of compounds and that an increasing diamagnetic effect plays an important role in the series PF_3 , SF_2 , and ClF . The extremely negative ^{19}F shift of ClF corresponds to an extremely high shielding of the fluorine nucleus, which is attributable to a $\pi^* \rightarrow \sigma^*$ excitation, caused by the external magnetic field.²¹ It can be concluded from the curvature in the plot in Figure 2 that the same effect is also of considerable importance for SF_2 .

If we proceed from ClF via SF_2 and PF_3 to SiF_4 , the number of fluorine atoms competing for π orbitals with the central atom

Table II. ^{19}F NMR Chemical Shifts of SF_2 , PF_3 , SiF_4 , and Derivatives in ppm from CCl_3F

SF_2	-167	CF_3SF	-351^a		
PF_3	-33^b	$(\text{CF}_3)_2\text{PF}$	-218^b	$(\text{CH}_3)_2\text{PF}$	-196^c
SiF_4	-142^d			$(\text{CH}_3)_3\text{SiF}$	-155^d

^a Reference 16. ^b Reference 17. ^c Reference 18. ^d Reference 19.

increases. Therefore, the π -bond order to a specific F atom decreases in this series, and the diamagnetic effect attributed to the $\pi^* \rightarrow \sigma^*$ transition becomes less important. If F is replaced by CF_3 or CH_3 groups that are not capable of π -interaction with the central atom, the shielding of the remaining fluorine atom increases considerably (Table II) because of the higher π -bond order. The highest ^{19}F shielding of all compounds of the general type X-F listed in Table II is that of CF_3SF ($\text{X} = \text{CF}_3\text{S}$). Thus, the CF_3S group appears to be the best "parachlorine" in the sense of the element displacement principle.²⁰

Acknowledgment. Financial support by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

Registry No. SF_2 , 13814-25-0; SF_4 , 7783-60-0; SF_6 , 2551-62-4; S_2F_2 , 13709-35-8; S_2F_4 , 27245-05-2.

Contribution from the Departments of Chemistry, Southern Methodist University, Dallas, Texas 75275, and The Ohio State University, Columbus, Ohio 43210, and Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, California 90089

Synthesis and Spectroscopic Characterization of 1,2-Bis(trimethylsilyl)-1,2-dicarba-closo-hexaborane(6) Derived from closo-Stannacarborane and the X-ray Crystal Structure of the Precursor 1-Sn-2,3-(SiMe_3)₂-2,3- $\text{C}_2\text{B}_4\text{H}_4$

Narayan S. Hosmane,*[†] Reynaldo D. Barreto,[†] Michael A. Tolle,[†] John J. Alexander,[‡] William Quintana,[‡] Upali Siriwardane,[†] Sheldon G. Shore,*[‡] and Robert E. Williams[§]

Received December 14, 1989

It has been demonstrated that the C-SiMe₃-substituted stannacarboranes are important precursors in the production of a number of main-group and transition-metal metallacarboranes.¹ For example, the apical tin in the closo-stannacarboranes has been replaced by an $\text{Os}(\text{CO})_3$ unit in the production of closo-osmacarboranes.² The commo-germacarboranes³ were synthesized from the direct reaction of GeCl_4 with the corresponding stannacarboranes, while the reaction with a different molar ratio of reactants produced the mixed-valence germacarborane closo-1-Ge^{II}-2,3-(SiMe₃)₂-5-(Ge^{IV}Cl₃)-2,3- $\text{C}_2\text{B}_4\text{H}_3$.⁴ It has also been shown that the C,C'-dimethyl-substituted stannacarborane reacts with $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ to yield a cobaltacarborane via an air-sensitive intermediate $(\eta^5\text{-C}_5\text{H}_5)\text{CoSnMe}_2\text{C}_2\text{B}_4\text{H}_4$.⁵ In all of these cases there was no evidence of the oxidative closure of the carborane cage even when the apical tin was eliminated reductively as Sn^0 in some instances, such as in the production of the closo-osmacarborane² and the cyclopentadienylcobaltacarborane⁵ derivatives. However, it has been reported that the icosahedral stannacarborane analogue 1-Sn-2,3- $\text{C}_2\text{B}_9\text{H}_{11}$ eliminates the apical tin as Sn^0 at 450°C to produce the 11-vertex polyhedron closo-2,3- $\text{C}_2\text{B}_9\text{H}_{11}$.⁶ Furthermore, the reaction of SnCl_2 with the dianion $[1,7\text{-C}_2\text{B}_9\text{H}_{11}]^{2-}$ also produced closo-2,3- $\text{C}_2\text{B}_9\text{H}_{11}$ as the

(20) Haas, A. *Adv. Inorg. Chem. Radiochem.* **1984**, *28*, 167-202.

(21) Cornwell, C. D. *J. Chem. Phys.* **1966**, *44*, 874-880.

* Southern Methodist University.

[†] The Ohio State University.

[‡] University of Southern California.

sole product. This reaction was considered as an unusual instance of SnCl_2 functioning as an oxidizing agent that demonstrates the considerable reducing power of the $[\text{C}_2\text{B}_9\text{H}_{11}]^{2-}$ anion.⁶ The crystal structure of the stannacarborane precursor, *closo*-1-Sn-2,3-(SiMe_3)₂-2,3- $\text{C}_2\text{B}_4\text{H}_4$, has not been published to date. The ¹¹B NMR spectra indicated that the apical tin in the precursor should be symmetrically bonded to the C_2B_3 face. However, the crystal structures of the C-(trimethylsilyl)- and C-(trimethylsilyl)-C'-methylstannacarborane analogues were consistent with their solution spectra in that the apical tin is slipped toward the borons above the C_2B_3 face.¹⁷ In order to obtain more information about the relative importance of the effect of C-substitution on cage geometry, the X-ray structural investigation of the bis(trimethylsilyl)-substituted stannacarborane precursor was undertaken. Here, we describe the exclusive formation of 1,2-bis(trimethylsilyl)-1,2-dicarba-*closo*-hexaborane(6) from the corresponding stannacarborane precursor via platinum halide promoted oxidative closure of the C_2B_4 cage at ambient temperature and the spectroscopic characterization of this compound along with the X-ray crystal structure of its precursor, 2,3-bis(trimethylsilyl)-2,3-dicarba-1-stanna-*closo*-heptaborane(6).

Experimental Section

Materials. 2,3-Bis(trimethylsilyl)-2,3-dicarba-1-stanna-*closo*-heptaborane(6) was prepared by the methods of Hosmane et al.¹⁷ Prior to use, anhydrous PtCl_2 and PtCl_4 (Aldrich Chemical Co., Milwaukee, WI) were heated to 100 °C in vacuo overnight to remove any last traces of moisture. Chloroform was dried and stored over P_2O_5 and distilled before use. Tetrahydrofuran, benzene, and *n*-hexane were dried over LiAlH_4 and double-distilled before use. All other solvents were dried over 4–8-mesh molecular sieves (Davidson) and either saturated with dry argon or degassed before use.

Spectroscopic Procedures. Proton, boron-11, carbon-13, silicon-29, tin-119, and platinum-195 pulse Fourier transform NMR spectra, at 200, 64.2, 50.3, 39.76, 74.63, and 42.93 MHz, respectively, were recorded on an IBM-200 SY multinuclear NMR spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 283 infrared spectrometer and a Perkin-Elmer Model 1600 FT-IR spectrophotometer. Elemental analyses for C and H were performed on a Carlo Erba Strumentazione Model 1106 instrument.

Synthetic Procedures. All experiments were carried out in Pyrex glass round-bottom flasks of 250-mL capacity, containing magnetic stirring bars and fitted with high-vacuum Teflon valves. Nonvolatile substances were manipulated in either a drybox or evacuable glovebags under an atmosphere of dry nitrogen. All known compounds among the products were identified by comparing their infrared and ¹H NMR spectra with those of authentic samples.

Reaction of *closo*-1-Sn-2,3-(SiMe_3)₂-2,3- $\text{C}_2\text{B}_4\text{H}_4$ (I) with PtCl_4 . A chloroform (15 mL) solution of *closo*-1-Sn-2,3-(SiMe_3)₂-2,3- $\text{C}_2\text{B}_4\text{H}_4$ (I) (0.99 g, 2.94 mmol) was poured into a reaction flask containing anhydrous platinum(IV) chloride (PtCl_4) (0.51 g, 1.51 mmol) in vacuo at –23 °C. After warming to room temperature, the heterogeneous mixture of the reactants immediately turned dark brown. The ¹¹B NMR spectrum of this mixture, which was run after 10 min of reaction at room temperature, indicated that the stannacarborane (I) was completely consumed in the reaction. At this point, all the volatiles in the flask were moved to the vacuum line and were fractionated through traps held at –23, –45, and –196 °C. Nothing was collected in the trap held at –23 °C. The trap at –45 °C contained only the new product, identified as *closo*-1,2-(SiMe_3)₂-1,2- $\text{C}_2\text{B}_4\text{H}_4$ (II) (0.63 g, 2.89 mmol; 98% yield). The solvent, chloroform (not measured), passed through the trap at –45 °C

Table I. Crystallographic Data for *closo*-1-Sn-2,3-(SiMe_3)₂-2,3- $\text{C}_2\text{B}_4\text{H}_4$ (I)

chem form	$\text{C}_8\text{H}_{22}\text{B}_4\text{Si}_2\text{Sn}$
mol wt	336.37
color of cryst	transparent, colorless
space group	$P\bar{1}$
Z	2
<i>t</i> , °C	–50
<i>a</i> , Å	6.504 (4)
<i>b</i> , Å	9.334 (2)
<i>c</i> , Å	13.550 (4)
α , deg	95.63 (2)
β , deg	92.12 (4)
γ , deg	104.20 (4)
<i>V</i> , Å ³	792.1
cryst dims, mm	0.30 × 0.15 × 0.25
<i>d</i> (calcd), g cm ^{–3}	1.410
radiation λ (Mo K α), Å	0.710730
abs coeff, cm ^{–1}	17.4
transm, % (max, min)	99.02, 83.78
scan mode	ω –2 θ
data colln limits (2 θ), deg	4–50
no. of unique reflns	2772
no. of reflns used in struct	2492 [$\geq 3.0\sigma(I)$]
<i>hkl</i> collcd	$\pm 7.11, \pm 16$
no. of variables refined	136
$R_F = \sum F_o - F_c / \sum F_o $	0.050
$R_{wF} = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}$	0.072
$w = [\sigma(F_o)^2 + (k F_o)^2]^{-1}$	$k = 0.04$
GO F	2.525

and was collected in a trap at –196 °C. The dark brown residue, which remained in the reaction flask, was then dissolved in tetrahydrofuran (THF), the solution was filtered in vacuo, and the filtrate was concentrated. Although the proton and boron-11 NMR spectra showed the absence of any boron-containing compound, both the proton-decoupled and the proton-coupled tin-119 NMR spectra⁸ indicated the presence of SnCl_2 in the filtrate. The platinum-195 NMR spectrum did not show the presence of either any platinacarborane or unreacted PtCl_4 in the filtrate. After removal of THF from the filtrate, vacuum-drying of the residue at 80 °C gave 0.54 g of off-white solid SnCl_2 . The shiny gray metallic residue that remained on the sintered glass (0.29 g) was later identified by qualitative analyses as elemental platinum (Pt^0).

When the reaction was carried out in dry benzene or dry *n*-hexane, the products and their yields were identical with those described above.

The physical properties and characterization of II are as follows: colorless liquid, bp 151–152 °C; stable in air for a prolonged period of time; at 25 °C, highly soluble in both polar and nonpolar organic solvents; ¹H NMR (CDCl_3 , relative to external Me_4Si) δ 1.79 [q (br), 2 H, H_i , $^1J(\text{H}^{11}\text{B}) = 160$ Hz], 0.65 [q (br), 2 H, H_i , $^1J(\text{H}^{11}\text{B}) = 179$ Hz], –0.89 [s, 18 H, SiMe_3]; ¹¹B NMR (CDCl_3 , relative to external BF_3OEt_2) δ 9.98 [d, 2 B, BH, $^1J(\text{B}^{11}\text{B}^{11}\text{H}) = 159.5$ Hz], –9.85 [d, 2 B, BH, $^1J(\text{B}^{11}\text{B}^{11}\text{H}) = 179.5$ Hz]; ¹³C NMR (CDCl_3 , relative to external Me_4Si) δ 68.93 [s (br), cage carbons (SiCB)], –0.05 [q (br), SiMe_3 , $^1J(\text{C}^{13}\text{C}^{11}\text{H}) = 119.9$ Hz]; ²⁹Si NMR (CDCl_3 , relative to external Me_4Si) δ –4.49 [m, SiMe_3 , $^2J(\text{C}^{29}\text{Si}^{11}\text{H}) = 6.1$ Hz]; IR (CDCl_3 vs CDCl_3) 2961 (s), 2900 (m) [$\nu(\text{C}^{13}\text{H})$], 2588 (vs) [$\nu(\text{B}^{11}\text{H})$], 1949 (w), 1884 (w), 1712 (mw), 1518 (mw), 1456 (br, sh), 1410 (m) [$\delta(\text{C}^{13}\text{H})$, asym], 1335 (mw), 1269 (sh), 1252 (vs) [$\nu(\text{C}^{13}\text{H})$, sym], 1236 (ms), 1193 (s), 1144 (mw), 1121 (m), 1100 (mw), 1060 (m), 1048 (ms), 986 (mw), 974 (m), 962 (s), 935 (w), 840 (vvs) [$\rho(\text{C}^{13}\text{H})$], 791 (m), 783 (sh), 625 (s) [$\nu(\text{Si}^{29}\text{C})$] cm^{–1}. Anal. Calcd for $\text{C}_8\text{H}_{22}\text{B}_4\text{Si}_2$: C, 44.14; H, 10.19. Found: C, 44.71; H, 10.11.

Reaction of *closo*-1-Sn-2,3-(SiMe_3)₂-2,3- $\text{C}_2\text{B}_4\text{H}_4$ (I) with PtCl_2 . In a procedure identical with that employed in the above reaction, 1.1 g (3.27 mmol) of I was allowed to react with 0.88 g (3.31 mmol) of anhydrous platinum(II) chloride, PtCl_2 , in CHCl_3 (15 mL) at room temperature for 15 min. The fractionation of the volatile products gave only one carborane product, identified as II, in 94% yield (collected at –45 °C; 0.67 g, 3.08 mmol). The dark brown residue was identified by NMR spectroscopy and qualitative analyses as a mixture of SnCl_2 (0.59 g, 3.11 mmol) and elemental platinum (0.64 g, 3.28 mmol). The products and their yields were reproduced when the above reaction was carried out in either dry benzene, *n*-hexane, or dry THF.

X-ray Analysis of *closo*-1-Sn-2,3-(SiMe_3)₂-2,3- $\text{C}_2\text{B}_4\text{H}_4$ (I). Crystals of the stannacarborane precursor I were grown by sublimation onto a

- (1) (a) Hosmane, N. S.; Maguire, J. A. Recent Advances in the Chemistry of Main Group Heterocarboranes. In *Advances in Boron and the Boranes*; Greenberg, A., Liebman, J. F., Williams, R. E., Eds.; Molecular Structure and Energetics, Vol. 5; VCH Publishers: New York, 1988; Chapter 14, pp 297–328. (b) Hosmane, N. S.; Maguire, J. A. *Adv. Organomet. Chem.* **1990**, *30*, 99–150.
- (2) Hosmane, N. S.; Sirmokadam, N. N. *Organometallics* **1984**, *3*, 1119.
- (3) Islam, M. S.; Siriwardane, U.; Hosmane, N. S.; Maguire, J. A.; de Meester, P.; Chu, S. S. C. *Organometallics* **1987**, *6*, 1936.
- (4) Siriwardane, U.; Islam, M. S.; Maguire, J. A.; Hosmane, N. S. *Organometallics* **1988**, *7*, 1893.
- (5) Wong, K.-S.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 2053.
- (6) Chowdhry, V.; Pretzer, W. R.; Rai, D. N.; Rudolph, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 4560.
- (7) Hosmane, N. S.; Sirmokadam, N. N.; Herber, R. H. *Organometallics* **1984**, *3*, 1665.

- (8) Harris, R. K.; Kennedy, J. D.; McFarlane, W. *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: London, 1978; p 342.

Table II. Positional Parameters and Their Estimated Standard Deviations for 1-Sn-2,3-(SiMe₃)₂-2,3-C₂B₄H₄^a

atom	x	y	z	B, Å ²
Sn(1)	0.21647 (5)	0.34611 (4)	0.43220 (2)	2.892 (8)
C(2)	0.3100 (8)	0.1405 (5)	0.3254 (4)	2.29 (9)
C(3)	0.4191 (8)	0.2844 (5)	0.2894 (4)	2.33 (9)
B(4)	0.572 (1)	0.3913 (7)	0.3740 (5)	2.8 (1)
B(5)	0.557 (1)	0.2997 (7)	0.4749 (5)	3.2 (1)
B(6)	0.375 (1)	0.1366 (7)	0.4385 (5)	3.0 (1)
B(7)	0.579 (1)	0.2024 (7)	0.3581 (5)	2.9 (1)
Si(1)	0.4174 (2)	0.3346 (2)	0.1584 (1)	2.62 (3)
Si(2)	0.1516 (2)	-0.0427 (2)	0.2582 (1)	2.73 (3)
C(11)	0.492 (1)	0.1928 (7)	0.0699 (4)	3.8 (1)
C(12)	0.149 (1)	0.3630 (8)	0.1260 (5)	4.6 (1)
C(13)	0.618 (1)	0.5151 (7)	0.1527 (5)	4.4 (1)
C(21)	-0.022 (1)	-0.0301 (8)	0.1491 (5)	4.5 (2)
C(22)	0.340 (1)	-0.1574 (7)	0.2207 (6)	4.9 (2)
C(23)	-0.030 (1)	-0.1404 (8)	0.3477 (5)	4.7 (2)
H(4)	0.3320	0.5000	0.6445	6
H(5)	0.3320	0.6386	0.4570	6
H(6)	0.3320	0.0273	0.4785	6
H(7)	0.7089	0.1406	0.3125	6

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$.

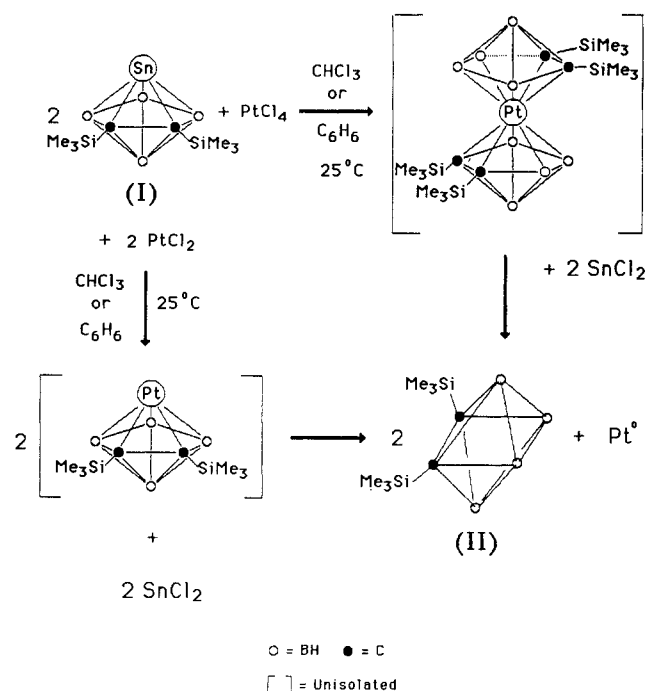
glass surface inside an evacuated, sealed tube. A crystal of suitable dimensions was mounted in a glass capillary. All crystallographic data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K α radiation. Unit cell parameters were obtained by a least-squares refinement of the angular settings from 25 reflections, obtained at -50 °C, well distributed in reciprocal space and lying in a 2θ range of 24–30°. Crystallographic data and positional parameters are given in Tables I and II, respectively.

All data were corrected for Lorentz and polarization effects, decay (2.4%), and absorption (empirically from ψ scan data). The structure was solved by employing a combination of the Patterson method, which yielded the location of the Sn atom, and Fourier techniques, which yielded the rest of the non-hydrogen atoms and the hydrogens bound to the cage borons. Positions of hydrogens bound to carbon were calculated, at a C–H distance of 0.95 Å. Analytical scattering factors were used throughout the structure refinement with both real and imaginary components included for the non-hydrogen atoms. Full-matrix least-squares refinements were employed. All crystallographic computations were carried out on a PDP 11/44 computer using the Structure Determination Package (SDP).⁹

Positions of the hydrogen atoms were kept fixed throughout the refinement, and the thermal parameters, arbitrarily assigned as 6.0 Å². The hydrogen atoms were not refined but were included in the final structure factor calculation.

Results and Discussion

Synthesis and Spectroscopic Characterization of II. The room-temperature reaction between the *closo*-stannacarborane 1-Sn-2,3-(SiMe₃)₂-2,3-C₂B₄H₄ (I) and PtCl₄ or PtCl₂ in both polar and nonpolar solvents was found to be instantaneous, as evidenced by the ¹¹B NMR spectra of the mixture of products that were run after a few minutes of reaction. The complete conversion of I into *closo*-1,2-(SiMe₃)₂-1,2-C₂B₄H₄ (II) along with the formation of SnCl₂ and elemental platinum (Pt⁰) suggests that the elimination of tin as SnCl₂ was a result of a simple substitution reaction, as in the production of *closo*- and *commo*-germacarboranes, and presumably the immediate step in the reaction.^{3,4} The carborane product of this substitution reaction could be the unisolatable and unstable platinacarborane species that would immediately eliminate the platinum from either the *commo* or *closo* position as platinum metal while forming the more energetically favored *closo*-carborane (II). The formation of a *nido*-platinacarborane intermediate could be ruled out since the stannacarborane precursor (I) is a *closo* species and possesses no bridge hydrogens. Apparently, the oxidative closure of the C₂B₄ cage occurred in

Scheme I

the final step of the reaction. When the stannacarborane (I) was allowed to react with a catalytic quantity of platinum chloride in chloroform there was no evidence of reaction to a measurable extent, since the ¹¹B NMR spectra of the products showed only the presence of the reactant I. Scheme I describes the proposed intermediates and a plausible mechanism of this reaction. The fact that the *closo*-carborane 1,2-(SiMe₃)₂-1,2-C₂B₄H₄ (II) was synthesized in almost quantitative yield from its stannacarborane precursor (I), and particularly at room temperature, makes this route a significant advance in the production of the 1,2-isomer of the *closo*-dicarba-hexaborane(6) derivatives, and hence a method of choice over the ones reported by Shapiro and co-workers,¹⁰ Spielman and Scott,¹¹ and McNeill and Scholer.¹² It is of interest that there have been no reports of the neutral platinacarboranes of the C₂B₄ system in which the "bare" platinum, formally in either +2 or +4 oxidation state, is π -bonded to the C₂B₃ pentagonal faces. However, insertion of zerovalent platinum species into bridging B–H–B bonds of 2,3-R₂-2,3-C₂B₄H₆ (R = Me, H) and subsequent pyrolysis of the resulting *nido*-platinacarborane to yield the corresponding *closo* species has been reported.¹³ Presently, there is no ready explanation for the anomalous behavior of the platinum reagents toward the C₂B₄ carborane system.

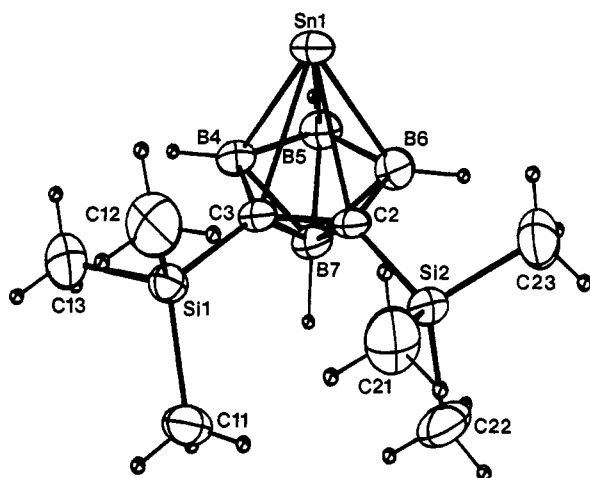
The carborane product 1,2-bis(trimethylsilyl)-1,2-dicarba-*closo*-hexaborane(6) (II) was characterized on the basis of ¹H, ¹¹B, ¹³C, and ²⁹Si pulse Fourier transform NMR spectra, IR spectra, and elemental analysis. The presence of a *closo*-carborane cage in addition to the SiMe₃ groups in II is substantiated by its proton, carbon-13, and silicon-29 NMR spectra. The presence of a 1,2-isomer (*cis*) in *closo*-dicarba-hexaborane(6) (II) is supported by its ¹¹B NMR spectra. The proton-coupled boron-11 NMR spectrum of II shows two doublets near +10 and -10 ppm, corresponding to a set of two equivalent BH units that are bonded to one carbon atom and three boron atoms, and another set of two equivalent BH units that are bonded to two carbons and two borons, respectively. For the 1,6-isomer (*trans*), all of the four

(9) SDP (developed by B. A. Frenz and Associates, Inc., College Station, TX 77840) was used to process X-ray data, apply corrections, solve and refine the structures, produce drawings, and print tables.

- (10) Shapiro, I.; Keilin, B.; Williams, R. E.; Good, C. D. *J. Am. Chem. Soc.* **1963**, *85*, 3167.
- (11) Spielman, J. R.; Scott, J. E. *J. Am. Chem. Soc.* **1965**, *87*, 3512.
- (12) McNeill, E. A.; Scholer, F. R. *Inorg. Chem.* **1975**, *14*, 1081.
- (13) (a) Barker, G. K.; Green, M.; Onak, T. P.; Stone, F. G. A.; Ungermann, C. B.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1978**, 169. (b) Barker, G. K.; Green, M.; Stone, F. G. A.; Welch, A. J.; Onak, T. P.; Siwapanoyos, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1687.

Table III. Bond Distances (Å) for 1-Sn-2,3-(SiMe₃)₂-2,3-C₂B₄H₄ and Their Estimated Standard Deviations

Sn(1)-C(2)	2.499 (5)	B(4)-B(5)	1.675 (9)
Sn(1)-C(3)	2.481 (6)	B(4)-B(7)	1.767 (9)
Sn(1)-B(4)	2.422 (6)	B(5)-B(6)	1.699 (9)
Sn(1)-B(5)	2.418 (8)	B(5)-B(7)	1.775 (9)
Sn(1)-B(6)	2.431 (7)	B(6)-B(7)	1.778 (9)
C(2)-C(3)	1.494 (7)	Si(1)-C(11)	1.862 (7)
C(2)-B(6)	1.582 (8)	Si(1)-C(12)	1.874 (7)
C(2)-B(7)	1.727 (8)	Si(1)-C(13)	1.870 (6)
C(2)-Si(2)	1.891 (4)	Si(2)-C(21)	1.859 (7)
C(3)-B(4)	1.583 (7)	Si(2)-C(22)	1.866 (9)
C(3)-B(7)	1.729 (9)	Si(2)-C(23)	1.868 (7)
C(3)-Si(1)	1.881 (5)		

**Figure 1.** Molecular structure of *closo*-1-Sn-2,3-(SiMe₃)₂-2,3-C₂B₄H₄ (I) (ORTEP plot with 50% thermal ellipsoids).

BH units would become equivalent and hence would show a single resonance in its proton-decoupled boron-11 NMR spectrum. The significant upfield shift of the cage carbon resonance from those of the corresponding *closo*-stannacarborane precursor (I)⁷ as well as the *nido*-2,3-dicarbahehexaborane(8)¹⁴ derivatives is consistent with the *closo* structure of II that is delocalized to some degree. The proton and the boron-11 NMR spectra and infrared spectra of II (see Experimental Section) are also consistent with those of the unsubstituted *closo*-1,2-dicarbahehexaborane(6) reported by Shapiro and co-workers.¹⁰

Crystal Structure of the Stannacarborane Precursor *closo*-1-Sn-2,3-(SiMe₃)₂-2,3-C₂B₄H₄ (I). The molecular structure of I (Figure 1, Tables III and IV) contains a distorted pentagonal-bipyramidal cluster core, SnC₂B₄, in which the Sn atom occupies a vertex site above the C₂B₃ plane and is "slipped" or displaced with respect to the centroid of this plane. The Sn-C distances [2.499 (5), 2.481 (6) Å] are longer than the Sn-B distances [2.422 (6), 2.418 (8), 2.431 (7) Å], suggesting weaker tin-carbon interaction than tin-boron interaction. B(7) occupies a vertex site below the C₂B₃ plane. Its distances to the C₂B₃ carbons [1.727 (8), 1.729 (9) Å] are shorter than the distances to the C₂B₃ boron atoms [1.767 (9), 1.775 (9), 1.778 (9) Å], which is consistent with the smaller radius of carbon than boron. The largest deviation from the least-squares plane defined by C₂B₃ is 0.017 Å for B(6). Distortions of the type observed in the structure of I have also been observed in other related main-group substituted carboranes: Sn(Me₃Si)C₂B₄H₅,¹⁵ Sn(Me₃Si)MeC₂B₄H₄,¹⁶ and 1-MeGaC₂B₄H₆.¹⁷

Table IV. Bond Angles (deg) for 1-Sn-2,3-(SiMe₃)₂-2,3-C₂B₄H₄ and Their Estimated Standard Deviations

C(2)-Sn(1)-C(3)	34.9 (2)	C(2)-C(3)-B(7)	64.3 (3)
C(2)-Sn(1)-B(4)	62.3 (2)	C(2)-C(3)-Si(1)	127.6 (3)
C(2)-Sn(1)-B(5)	64.6 (2)	B(4)-C(3)-B(7)	64.4 (4)
C(2)-Sn(1)-B(6)	37.5 (2)	B(4)-C(3)-Si(1)	120.4 (3)
C(3)-Sn(1)-B(4)	37.6 (2)	B(7)-C(3)-Si(1)	133.9 (4)
C(3)-Sn(1)-B(5)	64.5 (2)	Sn(1)-B(4)-C(3)	73.3 (3)
C(3)-Sn(1)-B(6)	62.3 (2)	Sn(1)-B(4)-B(5)	69.6 (3)
B(4)-Sn(1)-B(5)	40.5 (2)	Sn(1)-B(4)-B(7)	95.6 (3)
B(4)-Sn(1)-B(6)	66.3 (2)	C(3)-B(4)-B(5)	106.8 (4)
B(5)-Sn(1)-B(6)	41.0 (3)	C(3)-B(4)-B(7)	61.9 (3)
Sn(1)-C(2)-C(3)	71.9 (3)	B(5)-B(4)-B(7)	62.1 (4)
Sn(1)-C(2)-B(6)	69.0 (4)	Sn(1)-B(5)-B(4)	69.9 (3)
Sn(1)-C(2)-B(7)	94.0 (3)	Sn(1)-B(5)-B(6)	69.9 (3)
Sn(1)-C(2)-Si(2)	134.2 (2)	Sn(1)-B(5)-B(7)	95.5 (3)
C(3)-C(2)-B(6)	111.6 (4)	B(4)-B(5)-B(6)	103.8 (4)
C(3)-C(2)-B(7)	64.5 (3)	B(4)-B(5)-B(7)	61.5 (4)
C(3)-C(2)-Si(2)	132.4 (3)	B(6)-B(5)-B(7)	61.5 (3)
B(6)-C(2)-B(7)	64.8 (4)	Sn(1)-B(6)-C(2)	73.6 (3)
B(6)-C(2)-Si(2)	115.2 (3)	Sn(1)-B(6)-B(5)	69.1 (3)
B(7)-C(2)-Si(2)	130.3 (4)	Sn(1)-B(6)-B(7)	95.1 (3)
Sn(1)-C(3)-C(2)	73.1 (3)	C(2)-B(6)-B(5)	106.2 (4)
Sn(1)-C(3)-B(4)	69.2 (3)	C(2)-B(6)-B(7)	61.6 (3)
Sn(1)-C(3)-B(7)	94.5 (3)	B(5)-B(6)-B(7)	61.3 (3)
Sn(1)-C(3)-Si(1)	131.2 (3)	C(2)-B(7)-C(3)	51.2 (3)
C(2)-C(3)-B(4)	111.6 (4)	C(2)-B(7)-B(4)	93.5 (4)
C(2)-B(7)-B(5)	97.1 (4)	C(3)-Si(1)-C(13)	109.1 (2)
C(2)-B(7)-B(6)	53.6 (3)	C(11)-Si(1)-C(12)	113.0 (3)
C(3)-B(7)-B(4)	53.8 (3)	C(11)-Si(1)-C(13)	107.3 (3)
C(3)-B(7)-B(5)	96.6 (4)	C(12)-Si(1)-C(13)	107.8 (3)
C(3)-B(7)-B(6)	92.9 (4)	C(2)-Si(2)-C(21)	115.8 (3)
B(4)-B(7)-B(5)	56.5 (4)	C(2)-Si(2)-C(22)	108.5 (3)
B(4)-B(7)-B(6)	97.0 (4)	C(2)-Si(2)-C(23)	107.7 (3)
B(5)-B(7)-B(6)	57.1 (3)	C(21)-Si(2)-C(22)	110.1 (3)
C(3)-Si(1)-C(11)	111.8 (3)	C(21)-Si(2)-C(23)	105.7 (3)
C(3)-Si(1)-C(12)	107.8 (3)	C(22)-Si(2)-C(23)	108.7 (3)

Acknowledgment. This work was supported by grants to N.S.H. from the National Science Foundation (CHE-8800328), the Robert A. Welch Foundation (N-1016), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to S.G.S. from the National Science Foundation (CHE-8800515). W.Q. thanks the College of Mathematics and Physical Sciences of The Ohio State University for a postdoctoral fellowship, and J.J.A. thanks the University of Cincinnati for a sabbatical leave.

Supplementary Material Available: Listings of crystal data, bond distances, bond angles, positional parameters, and anisotropic thermal parameters (6 pages); a listing of calculated and observed structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

(17) Grimes, R. N.; Rademaker, W. J.; Denniston, M. L.; Bryan, R. F.; Greene, P. T. *J. Am. Chem. Soc.* **1972**, *94*, 1865.

Contribution from the School of Chemistry,
University of Bath, Claverton Down,
Bath BA2 7AY, U.K., and Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Synthetic, Electrochemical, and Structural Studies of Monoalkyne Complexes of Molybdenum(II) and Tungsten(II)

Brian J. Brisdon,^{*1a} Annabelle G. W. Hodson,^{1a}
Mary F. Mahon,^{1a} Kieran C. Molloy,^{1a}
and Richard A. Walton^{*1b}

Received December 27, 1989

Introduction

There is a diversity of chemistry centered around d⁴ metal complexes that contain an alkyne ligand acting as a 4-electron

(14) Hosmane, N. S.; Sirmokadam, N. N.; Mollenhauer, M. N. *J. Organomet. Chem.* **1985**, *279*, 359.

(15) Hosmane, N. S.; de Meester, P.; Mالدar, N. N.; Potts, S. B.; Chu, S. S. C. *Organometallics* **1986**, *5*, 772.

(16) Cowley, A. H.; Galow, P.; Hosmane, N. S.; Jutzi, P.; Norman, N. C. *J. Chem. Soc., Chem. Commun.* **1984**, 1564.