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Synthesis, Structural Characterization, and Reactivity of the Bis(η^5-dicarbollide)silicon Sandwich Compound *commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11}$)$_2$

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The bis(dicarbollide)silicon sandwich compound *commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11}$)$_2$ (1) has been prepared and structurally characterized by a single-crystal X-ray diffraction study. Complete details of this study as well as the results of reactivity studies of 1 are reported. Compound 1 reacts with Lewis bases. Structures of products resulting from the reaction of 1 with pyridine, (10-*exo*-η^1-7,8-$C_2B_9H_{11}$)(10-*endo*-η^1-7,8-$C_2B_9H_{11}$)Si(C_5H_5N)$_2$ (4), and trimethylphosphine, [η^5-10-{(Me_3P)$_2$BH}$C_2B_8H_{10}$]Si(η^1-$C_2B_9H_{11}$) (5), have been determined by X-ray diffraction studies. Species 1 crystallizes in the space group $P2_1/n$ with a = 6.9956 (6) Å, b = 9.6804 (10) Å, c = 12.2838 (22) Å, β = 91.800 (11)°, V = 831 Å^3, and Z = 2. Data were collected to a maximum of 2θ = 54°, giving 1818 unique reflections. The final discrepancy indices were R = 0.050 and R_w = 0.068 for 1282 independent reflections. Compound 4 crystallizes in the space group $P2_1/c$ with a = 10.645 (1) Å, b = 12.437 (2) Å, c = 19.256 (2) Å, β = 94.333 (4)°, V = 2537 Å^3, and Z = 4. Data were collected to a maximum of 2θ = 50°, giving 4482 unique reflections. The final discrepancy indices were R = 0.052 and R_w = 0.068 for 3065 independent reflections. Derivative 5 crystallizes in the space group $P2_1/n$ with a = 8.640 (1) Å, b = 12.690 (2) Å, c = 23.626 (3) Å, β = 92.549 (5)°, V = 2588 Å^3, and Z = 4. Data were collected to a maximum of 2θ = 50°, giving 4560 unique reflections. The final discrepancy indices were R = 0.048 and R_w = 0.057 for 2925 independent reflections.

Introduction

The structure and bonding patterns of π-complexes of the transition metals are now fairly well understood. Complexes that feature multihapto bonding between the main-group elements, however, are considerably fewer in number and not well understood. The best known representatives of the main-group-element π-complexes are the group 14 formal E(II) species Cp^*_2E (E = Si,[1] Ge,[2] Sn,[2] Pb,[2] Cp* = C_5Me_5). Stable sandwich complexes that contain formal [Ne]-core group 13 and group 14 centers (e.g. Al(III), Si(IV)) are known at this time only for those complexes which contain carborane donor ligands.[3-8]

The synthesis and X-ray structural characterization of the novel silicon sandwich complex *commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11}$)$_2$ (1), which contains a formal silicon(IV) center, has been reported previously in a brief communication.[3] The full details of the synthesis, structural characterization, and further reactivity studies of compound 1 are reported herein. At the time of our initial report of compound 1, the bis-η^5-bonding mode exhibited by this species was unprecedented among p-block-element compounds featuring a central atom in its highest formal oxidation state. Subsequent to our report of compound 1, the synthesis of a related silacarborane sandwich species, 2,2′,3,3′-[(SiMe$_3$)]$_4$-*commo*-1,1′-Si(1,2,3-$SiC_2B_4H_4$)$_2$ (2), was reported by Hosmane et al.[8] Notably, compound 1 is also isoelectronic and essentially isostructural with the anionic aluminacarborane sandwich complex [*commo*-3,3′-Al-(3,1,2-$AlC_2B_9H_{11}$)$_2$]$^-$ ([3]$^-$), which we have also recently described.[5]

Results

The reaction of silicon tetrachloride with 2 molar equiv of Li_2[*nido*-7,8-$C_2B_9H_{11}$] in refluxing benzene or toluene results in the formation of the bis(dicarbollide)silicon sandwich compound *commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11}$)$_2$ (1), according to eq 1. Compound 1 is a white crystalline solid

$$2\mathrm{Li_2[7,8\text{-}C_2B_9H_{11}]} + \mathrm{SiCl_4} \rightarrow \underset{1}{commo\text{-}3,3'\text{-}\mathrm{Si(3,1,2\text{-}SiC_2B_9H_{11})_2}} + 4\mathrm{LiCl} \tag{1}$$

that can be isolated in greater than 78% yield. This compound is very soluble in aromatic hydrocarbons and moderately soluble in aliphatic hydrocarbons, from which large crystals can be readily obtained. The compound will sublime slowly under high-vacuum conditions at ca. 200 °C. This species is moderately stable and can be handled for prolonged periods of time in dry air. Slow hydrolytic decomposition occurs in moist air.

Compound 1 was characterized by a combination of ^{1}H, ^{11}B, and ^{13}C NMR, IR, and mass spectroscopy, as well as by X-ray diffraction. The ^{1}H NMR spectrum of 1 in benzene or toluene solution displays a single carboranyl C–H resonance in addition to broad, complex B–H resonances characteristic of the dicarbollide cage. The ^{11}B NMR spectrum exhibits resonances consistent with the presence of two symmetry-equivalent dicarbollide cages. The IR spectrum contains characteristic bands at 3047 and 2592 cm^{-1}, assigned to the carboranyl C–H and B–H stretching modes, respectively, while the mass spectrum exhibits a strong parent ion envelope. The structure of 1 was determined by a single-crystal X-ray diffraction study.

Description of the Molecular Structure of 1. The structure of 1 is shown in Figure 1 along with selected interatomic distances and angles. The silicon atom in 1 occupies a center of crystallographic symmetry and is bound in an η^5 fashion to the five-membered face of each of two dicarbollide cages. The mean planes of the bonding

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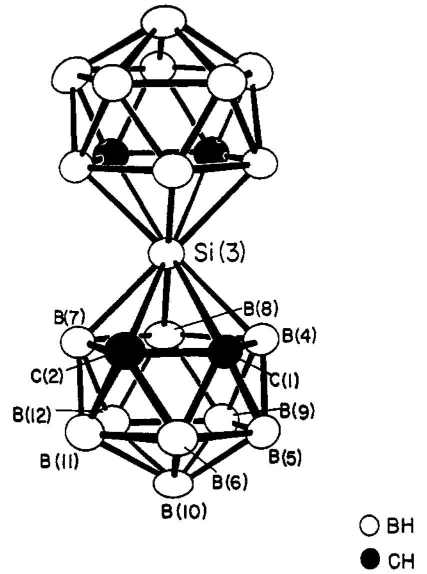

Figure 1. Structure of *commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11})_2$ (1) with hydrogen atoms omitted for clarity. Interatomic distances (Å): Si(3)–C(1,2), 2.22; Si(3)–B(4,7), 2.14; Si(3)–B(8), 2.05 (1).

faces of the two dicarbollide cages are thus required crystallographically to be both parallel and equidistant from silicon. The distance of the silicon atom to each mean plane of the dicarbollide cage faces is 1.57 Å.

Carborane complexes containing the [*nido*-7,8-$C_2B_9H_{11}]^{2-}$ ligand and its C-substituted derivatives, as well as the [*nido*-2,3-$C_2B_4H_6]^{2-}$ ligand and its derivatives, may exhibit varying degrees of distortion from idealized closo geometry by undergoing a slipping of the heteroatom parallel to the plane of the C_2B_3 cage face. This slippage generally occurs in a direction away from the two carbon atoms and in the direction of the unique boron atom of the cage face. The slip distortion for dicarbollide ligand derivatives has been quantified in terms of the slip parameter Δ,[9] which is a measure of the displacement of the heteroatom from the normal to the centroid of the least-squares plane of the B(5,6,9,11,12) atoms of the dicarbollide cage. The silicon atom in 1 shows a moderate slip (Si–C(1,2)/Si–B(8) = 1.08), with respect to the cage face of each dicarbollide cage, in the direction of the unique boron atom (B(8),B(8′)). The slip parameter Δ[9] for 1 is 0.26 Å, which is intermediate between typical fully slipped and unslipped parameters. This value is comparable with the slip distortion exhibited by $[3]^-$.[10] While the slip distortion for compound 2 is technically undefined in terms of the Δ parameter, this species also displays a similar moderate slip distortion (Si–C(1,2)/Si–B(4) = 1.10). A projection of the silicon atom of 1 on the plane of the dicarbollide cage face is shown in Figure 2a. In addition to the slip distortion, dicarbollide complexes may also undergo "folding" distortions. The degree of nonplanarity of the dicarbollide cage bonding face has been defined in terms of the folding parameters θ and ϕ.[9] Compound 1 exhibits small θ and ϕ distortion parameters, as listed in Table I.

Table I. Distortion Parameters

compd	Δ/Å[a]	θ/deg	ϕ/deg	M–cage dist/Å[b]
1	0.26	1.4	0.3	1.57
4				
endo cage	1.04	2.8	2.0	1.91
exo cage	NA[c]	1.5	1.9	NA
5				
dicarbollide	0.77	1.7	1.2	1.81
dicarbacanastide	NA	NA	NA	1.42

[a] Δ is the displacement of the metal from the normal to the centroid of the least-squares plane of the lower B_5 ring of the dicarbollide cage. [b] Calculated as the distance of the metal from the least-squares plane of the upper C_2B_3 ring of the dicarbollide cage. [c] NA = not applicable.

Survey of the Chemical Reactivity of *commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11})_2$ (1). The hydrolysis of 1 can be monitored by ^1H and ^{11}B NMR spectroscopy. This reaction is rapid at room temperature in wet THF or acetone but occurs much more slowly in neat water, presumably because of the hydrophobic nature of 1. Hydrolysis in water is accompanied by a decrease in pH, formation of a white precipitate, and the appearance of ^{11}B NMR signals characteristic of the *nido*-[7,8-$C_2B_9H_{12}]^-$ anion, indicating that hydrolysis apparently occurs according to eq 2. The $Si(OH)_4$ written for convenience in eq 2 undoub-

$$\textit{commo}\text{-}3,3'\text{-Si}(3,1,2\text{-SiC}_2\text{B}_9\text{H}_{11})_2 + 4\text{H}_2\text{O} \rightarrow 2[\textit{nido}\text{-}7,8\text{-C}_2\text{B}_9\text{H}_{12}]^- + \text{“Si(OH)}_4\text{”} + 2\text{H}^+ \quad (2)$$

tedly disproportionates under the reaction conditions to the usually complex oxysilicon species, leading to the observed white precipitates. Compound 1 undergoes relatively slow alcoholysis when dissolved in dry alcohols including methanol, ethanol, and ethylene glycol. Such reactions can be monitored by ^1H and ^{11}B NMR spectroscopy and appear to occur in a stepwise fashion involving intermediate species of the type $[C_2B_9H_{11}Si(OR)_2]$. Unfortunately, these intermediates have proven to be relatively unstable and have thus far eluded isolation as pure species.

The carboranyl C–H groups of 1 are sufficiently acidic to allow deprotonation by strong bases. The reaction of 1 with 2 equiv of *n*-butyllithium followed by the addition of D_2O results in the formation of 1-d_2, $[Si(C_2B_9H_{10}D)_2]$, in ca. 30% yield, as illustrated in Figure 3. The infrared spectrum of the deuteriated product exhibits a C–D stretching band at 2276 cm^{-1} in addition to the 3047-cm^{-1} carboranyl C–H stretching band.

Adduct formation between main-group-element carborane derivatives and Lewis bases has been the subject of recent studies.[11] Compound 1 reacts with a variety of Lewis bases to form adducts that demonstrate a variety of structural types. The addition of excess pyridine to a toluene solution of 1 results in the immediate precipitation of an amorphous yellow solid. The extremely low solubility of this species has precluded the acquisition of NMR data or the growth of crystals that could provide structural information by X-ray diffraction studies. However, when this material was heated at 100 °C in vacuo, the adduct slowly changed from yellow to white with loss of pyridine,

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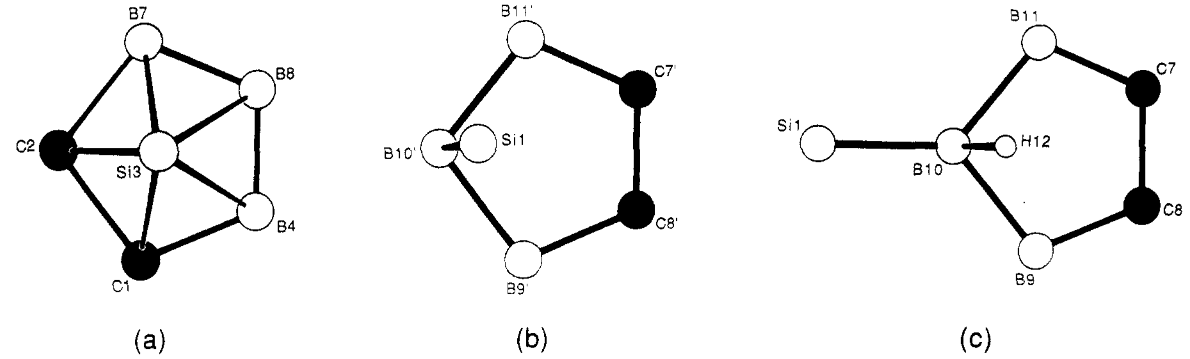
(9) (a) Mingos, D. M. P.; Forsyth, M. I.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 605. (b) Mingos, D. M. P.; Forsyth, M. I.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1363.

(10) The X-ray structure of Tl[3] features two ordered and crystallographically nonequivalent $[3]^-$ anions having Δ parameters of 0.24 and 0.29 Å. A third $[3]^-$ anion was crystallographically disordered.

(11) See for example: (a) Hosmane, N. S.; Maguire, J. A. In *Molecular Structures and Energetics*; Liebman, J. F., Greenberg, A., Williams, R. E., Eds.; VCH: New York, 1987; Vol. 5, Chapter 14, and references therein. (b) Barreto, R. D.; Fehlner, T. P.; Hosmane, N. S. *Inorg. Chem.* **1988**, *27*, 453. (c) Jutzi, P.; Galow, P.; Abu-Orabi, S.; Arif, A. F.; Cowley, A. H.; Norman, N. C. *Organometallics* **1987**, *6*, 1024. (d) Jutzi, P.; Galow, P. *J. Organomet. Chem.* **1987**, *319*, 139. (e) Hosmane, N. S.; Islam, M. S.; Pinkerton, B. S.; Siriwardane, U.; Banewicz, J. J.; Maguire, J. A. *Organometallics* **1988**, *7*, 2340. (f) Hosmane, N. S.; de Meester, P.; Maldar, N. N.; Potts, S. B.; Chu, S. S. C.; Herber, R. H. *Organometallics* **1986**, *5*, 772. (g) Maguire, J. A.; Ford, G. P.; Hosmane, N. S. *Inorg. Chem.* **1988**, *27*, 3354.



(a) (b) (c)

Figure 2. Projections viewed along the normals to the least-squares planes of (a) the dicarbollide cage face of 1, (b) the endo dicarbollide cage face of 4, and (c) the exo dicarbollide cage face of 4.

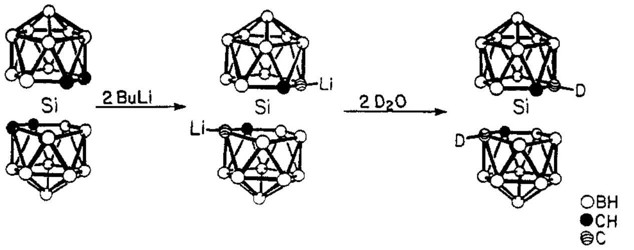


Figure 3. Metalation and subsequent deuteriation of 1.

suggesting that the yellow solid is a Lewis acid–base adduct. The remaining white solid was found to be 1 by NMR, IR, and mass spectral analysis. The pyridine distillate was collected in a −98 °C U-trap and identified by its IR spectrum. Gravimetric analysis applied to this adduct dissociation process indicates the formation of a bis(pyridine) adduct of 1 as shown in eq 3.

$$\textit{commo}\text{-}3,3'\text{-Si}(3,1,2\text{-SiC}_2\text{B}_9\text{H}_{11})_2 + 2\text{C}_5\text{H}_5\text{N} \rightarrow \underset{4}{(\text{C}_5\text{H}_5\text{N})_2\text{Si}(\text{C}_2\text{B}_9\text{H}_{11})_2} \quad (3)$$

When 1 is allowed to stand in the presence of excess neat pyridine for several days, the initially formed yellow precipitate slowly dissolves to produce a yellow solution. Addition of *n*-pentane to this solution results in the precipitation of yellow crystals and a yellow oil. The crystalline product, 4, which was isolated in 72% yield, was found to be the bis(pyridine) adduct $(C_5H_5N)_2Si(C_2B_9H_{11})_2$. Compound 4 was characterized by a combination of elemental analysis, spectroscopic techniques, and a single-crystal X-ray diffraction study. The yellow oil gave NMR spectral patterns indicative of a complex mixture of uncharacterized products.

The addition of excess trimethylphosphine to a toluene solution of 1 at room temperature results in the immediate formation of an amorphous white precipitate that was not sufficiently soluble to allow the acquisition of NMR data. However, when the reaction mixture containing excess trimethylphosphine was allowed to stand for several days, the initially formed precipitate slowly dissolved and colorless crystals were deposited on the sides of the flask. This crystalline product, formed by the reaction shown in eq 4, was identified as a unique 2:1 phosphine–1 species,

$$\textit{commo}\text{-}3,3'\text{-Si}(3,1,2\text{-SiC}_2\text{B}_9\text{H}_{11})_2 + 2\text{Me}_3\text{P} \rightarrow \underset{5}{[(\text{Me}_3\text{P})_2\text{BH}(\text{C}_2\text{B}_8\text{H}_{10})]\text{Si}(\text{C}_2\text{B}_9\text{H}_{11})} \quad (4)$$

5. Compound 5 has been characterized by a combination of elemental analysis, spectroscopic techniques, and a single-crystal X-ray diffraction study.

When 1 was passed through a quartz tube heated at 450 °C under dynamic vacuum, a characteristic silicon mirror deposited in the tube and a white solid was collected in a cooled trap at the exit of the reaction zone. Small amounts of tan decomposition products were deposited at the ends of the heated region of the tube under these conditions. The collected white solid was identified as *closo*-1,8-$C_2B_9H_{11}$ by its characteristic mass spectrum, thus indicating the reductive-elimination reaction shown in eq 5 as a plausible thermal decomposition pathway for 1. This result suggests the possible use of 1 as an MOCVD source of thin elemental Si films under appropriate conditions.

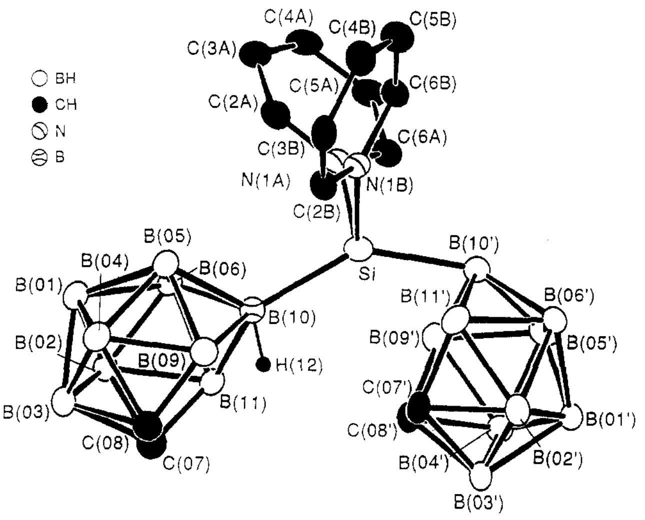


Figure 4. Structure of 4 with hydrogen atoms omitted for clarity.

$$\underset{1}{\textit{commo}\text{-}3,3'\text{-Si}(3,1,2\text{-SiC}_2\text{B}_9\text{H}_{11})_2} \rightarrow \text{Si} + 2\,\textit{closo}\text{-}1,8\text{-C}_2\text{B}_9\text{H}_{11} \quad (5)$$

When dilute solutions (ca. 0.1 M) of 1 in THF are allowed to stand for several days, a slow increase in viscosity occurs, eventually leading to a clear, colorless, elastomeric solid. This product, when dissolved in toluene-d_8 solution, revealed broad ^1H NMR resonances characteristic of poly(alkylene oxide) species and unreacted 1, which suggests the catalytic polymerization of THF through ring opening, possibly preceded by THF·1 adduct formation. The elastomeric product was found to be hygroscopic, slowly decreasing in viscosity when exposed to moist air.

Despite the instability of 1 with respect to hydrolysis, no reaction occurs between 1 and glacial acetic acid under mild conditions. Compound 1 is similarly unreactive toward electrophiles. For example, prolonged heating of 1 at 60 °C in glacial acetic acid in the dark and in the presence of excess bromine results in no reaction, nor does reaction occur with excess trimethylaluminum.

Description of the Molecular Structure of 4. The structure of 4 is shown in Figure 4, and selected intera-

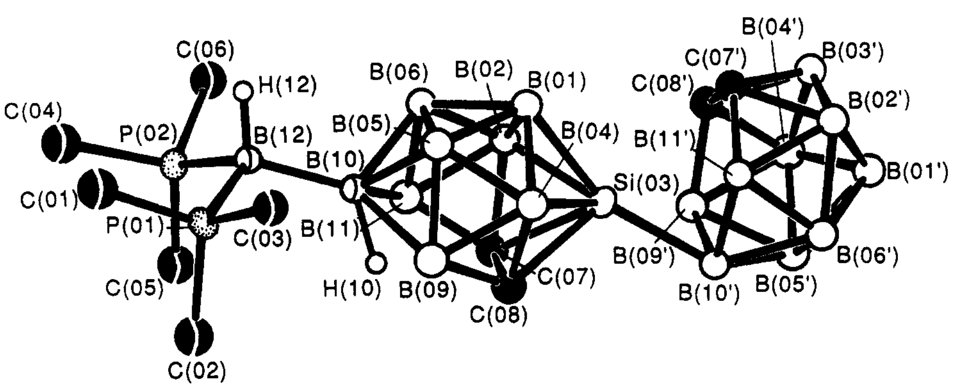


Figure 5. Structure of 5 with hydrogen atoms omitted for clarity.

Table II. Interatomic Distances (Å) and Angles (deg) for $(C_5H_5N)_2Si(C_2B_9H_{11})_2$ (4)

Si(01)-N(1A)	1.923 (3)	Si(01)-N(1B)	1.923 (3)
Si(01)-B(10′)	2.008 (4)	Si(01)-B(10)	2.020 (4)
Si(01)-B(09′)	2.475 (4)	Si(01)-B(11′)	2.416 (4)
Si(01)-C(07′)	2.943 (4)	Si(01)-C(08′)	2.972 (4)
C(07)-C(08)	1.592 (4)	C(08)-B(09)	1.606 (5)
B(09)-B(10)	1.849 (5)	B(10)-B(11)	1.856 (5)
C(07)-B(11)	1.605 (5)	B(10)-H(12)	1.142 (40)
C(07′)-C(08′)	1.553 (4)	C(08′)-B(09′)	1.615 (5)
B(09′)-B(10′)	1.820 (5)	B(10′)-B(11′)	1.822 (5)
C(07′)-B(11′)	1.619 (5)	B(10′)-H(10′)	1.103

N(1A)-Si(01)-N(1B)	89.67 (11)	B(10)-Si(01)-B(10′)	140.44 (15)
B(09′)-B(10′)-Si(01)	80.43 (19)	B(11′)-B(10′)-Si(01)	78.07 (19)
B(09)-B(10)-Si(01)	126.64 (23)	B(11)-B(10)-Si(01)	125.79 (22)
C(08)-C(07)-B(11)	113.10 (25)	C(07)-C(08)-B(09)	113.18 (26)
C(08)-B(09)-B(10)	106.44 (26)	B(09)-B(10)-B(11)	100.77 (24)
B(10)-B(11)-C(07)	106.38 (25)	C(08′)-C(07′)-B(11′)	113.60 (26)
C(07′)-C(08′)-B(09′)	113.94 (26)	C(08′)-B(09′)-B(10′)	104.41 (26)
B(09′)-B(10′)-B(11′)	103.37 (25)	B(10′)-B(11′)-C(07′)	104.44 (25)

tomic distances and angles are given in Table II. Compound 4 features a silicon atom that is bound to two dicarbollide cages as well as to two pyridine molecules. One of the two dicarbollide cages is bound to the silicon atom in the exo configuration via a σ bond, 2.01 Å long, involving B(10). A hydrogen atom that occupies the endo position at B(10) was located crystallographically. The second dicarbollide cage is bound in the slipped-endo configuration via a Si-B(10′) bond, 2.01 Å in length. The interatomic distances between the silicon atom and the endo dicarbollide cage face atoms B(09′) and B(11′) are 2.48 and 2.42 Å, respectively. The two pyridine molecules are coordinated to the silicon atom in a σ fashion, making an N(1A)-Si(01)-N(1B) angle of 89.7°. The angle between the normals to mean planes of the two pyridine rings is 112.4°. The two silicon-nitrogen distances are 1.92 Å and are equivalent within error. The endo dicarbollide cage is highly slipped (Si-C(7′,8′)/Si-B(10′) = 1.47) with a Δ parameter[9] of 1.04 Å, and the distance of silicon to the mean plane of the cage face is 1.91 Å. The θ and ϕ parameters[9] for the exo and endo cages of 4 are listed in Table I. Projections of the silicon atom of 4 along the normals to the planes of the two unique dicarbollide cages are shown in Figure 2b,c.

Description of the Molecular Structure of 5. The structure of 5 is shown in Figure 5, and Table III lists selected interatomic distances and angles. Compound 5 features a silicon atom that is bound to two structurally dissimilar carborane cages. One of these cages is a normal dicarbollide unit which is bound to the silicon atom in the slipped-endo configuration similar to that seen for one of the dicarbollide cages in compound 4. The shortest interatomic distance, 2.00 Å, for this silicon-cage interaction occurs between silicon and B(10′). The Si-B(09′) and Si-B(11′) distances are 2.32 and 2.31 Å, respectively. The second carborane cage to which the silicon atom in 5 is bound is formally a substituted dicarbacanastide $[C_2B_8H_{10}]^{4-}$ cage[12] that has resulted from the partial degradation of one of the dicarbollide cages of 1 by nucleophilic attack of trimethylphosphine at one of its B-H vertices. The silicon atom is bound to this cage in an η^5 fashion and has two carbon and three boron atom nearest neighbors, as in 1. An open five-membered face exists that shares an edge (occupied by the two carbon atoms) with the silicon-bound cage face. The boron atom B(10), which occupies a position in the open face opposite the carbon atoms, is a formal BH_2 vertex in which a proton has been replaced by $[(PMe_3)_2BH]^{2+}$. The BH group of this substituent presumably originated as part of the dicarbollide cage to which it remains attached. The exopolyhedral boron-boron interatomic distance is 1.74 Å, and the P(1)-B(12)-P(2) angle is 113.2°. The hydrogen atom of the substituent group was located crystallographically and

Table III. Interatomic Distances (Å)[a] and Angles (deg)[a] for $[(Me_3P)_2BH](C_2B_8H_{10})Si(C_2B_9H_{11})$ (5)

Si(03)-C(07)	2.054 (4)	Si(03)-C(08)	2.042 (4)
Si(03)-B(01)	2.045 (4)	Si(03)-B(02)	2.036 (4)
Si(03)-B(04)	2.063 (4)	Si(03)-C(07′)	2.673 (4)
Si(03)-C(08′)	2.692 (4)	Si(03)-B(09′)	2.325 (4)
Si(03)-B(10′)	2.004 (4)	Si(03)-B(11′)	2.311 (4)
C(07)-C(08)	1.562 (5)	B(02)-C(07)	1.724 (5)
B(04)-C(08)	1.730 (6)	B(01)-B(02)	1.826 (6)
B(01)-B(04)	1.805 (6)	C(07′)-C(08′)	1.560 (5)
C(07′)-B(11′)	1.630 (5)	C(08′)-B(09′)	1.639 (5)
B(09′)-B(10′)	1.830 (6)	B(10′)-B(11′)	1.852 (6)
C(08)-B(09)	1.614 (6)	C(07)-B(11)	1.594 (6)
B(09)-B(10)	1.860 (6)	B(10)-B(11)	1.862 (6)
B(09)-H(10)	1.61 (3)	B(10)-H(10)	1.27 (3)
B(11)-H(10)	1.68 (3)	B(10)-B(12)	1.744 (5)
B(12)-P(01)	1.917 (4)	B(12)-P(02)	1.931 (4)
P(01)-C(02)	1.786 (4)	P(01)-C(01)	1.808 (4)
P(02)-C(04)	1.804 (4)	P(01)-C(03)	1.801 (4)
P(02)-C(05)	1.799 (4)	P(02)-C(06)	1.798 (4)
B(12)-H(12)	1.09 (3)		

B(02)-B(01)-B(04)	106.7 (3)	C(07)-B(02)-B(01)	103.7 (3)
C(08)-B(04)-B(01)	103.5 (3)	B(02)-C(07)-C(08)	112.5 (3)
C(08)-C(07)-B(11)	113.4 (3)	B(04)-C(08)-C(07)	113.5 (3)
C(07)-C(08)-B(09)	112.0 (3)	C(08)-B(09)-B(10)	108.4 (3)
B(09)-B(10)-B(11)	97.5 (3)	B(09)-B(10)-B(12)	130.4 (3)
B(11)-B(10)-B(12)	128.0 (3)	C(07)-B(11)-B(10)	108.4 (3)
B(10)-B(12)-P(01)	112.9 (2)	B(10)-B(12)-P(02)	111.7 (2)
P(01)-B(12)-P(02)	113.2 (2)	C(08′)-C(07′)-B(11′)	114.4 (3)
C(07′)-C(08′)-B(09′)	113.2 (3)	C(08′)-B(09′)-B(10′)	105.1 (3)
B(09′)-B(10′)-B(11′)	102.9 (3)	B(10′)-B(11′)-C(07′)	104.3 (3)
C_n-Si(03)-C_n'[b]	159.7 (2)		

[a] Standard deviations in parentheses. [b] C_n and C_n' denote the centroids of the silicon-bound C_2B_3 faces of the nonprimed and primed carborane cages, respectively.

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(12) Francis, J. N.; Hawthorne, M. F. *Inorg. Chem.* **1971**, *10*, 863.

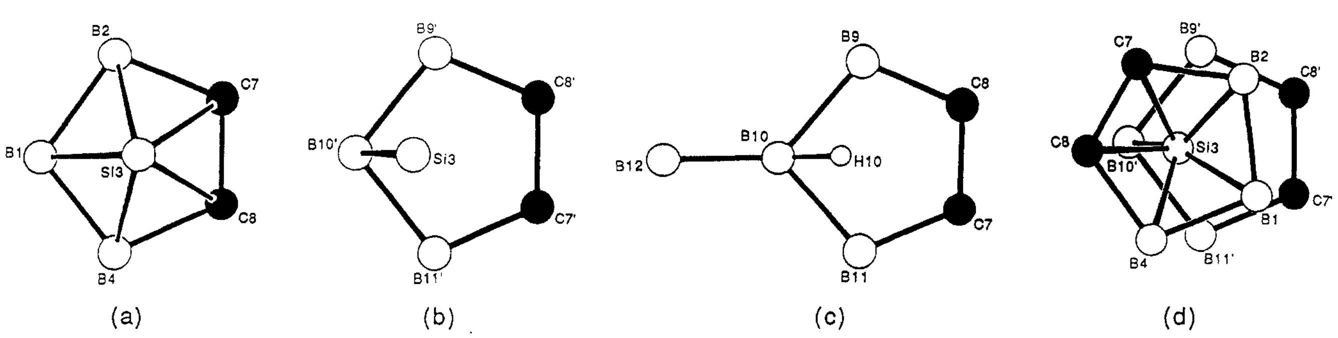

Figure 6. Projections along the normal to the five-membered carborane cage faces of **5** for (a) the silicon-containing dicarbacanastide cage face, (b) the dicarbollide cage, (c) the open dicarbacanastide cage face, and (d) the silicon-containing dicarbacanastide cage face superimposed on the dicarbollide cage face.

defines an essentially tetrahedral geometry about this boron atom. A hydrogen atom attached to B(10) was also located crystallographically in a position somewhat over the open cage face. The B(9)–H(10) and B(11)–H(10) distances average 1.48 Å. Projections along the normals to the mean planes of the various carborane cage faces are shown in Figure 6. The slip parameter Δ^9 for the silicon atom with respect to the dicarbollide cage is 0.77 Å (Si–C(7′,8′)/Si–B(10′) = 1.34). The distance between the silicon atom and the mean plane of this cage face is 1.42 Å. The slip parameter Δ^9 for the dicarbacanastide cage face cannot be defined; however, the silicon atom is unslipped (Si–C(7,8)/Si–B(1) = 1.00) and exhibits the η^5 bonding mode. The distance of silicon to the mean plane of this cage face is 1.81 Å.

The base-promoted degradation of carborane compounds is well-known,[13] and this process formally results in the complete removal of a BH^{2+} vertex from the polyhedral cage framework. For example, the primary or secondary amine-promoted degradation of *closo*-1,2-$C_2B_{10}H_{12}$ results in the corresponding ammonium salts of the [*nido*-7,8-$C_2B_9H_{12}$]$^-$ anion along with an aminoborane. The formation of **5** represents a unique example of the incomplete removal of a BH vertex from a carborane cage by a Lewis base.

Discussion

Compound **1** is an unusual example of a π-sandwich complex that contains a central main-group element in its highest formal oxidation state (i.e. [Ne]-core electron configuration). Unlike the more familiar ECp^*_2 (E = Si, Ge, Sn, Pb; Cp* = C_5Me_5) compounds, which are 14-interstitial-electron systems,[14,15] **1** can be considered to be a 12-interstitial-electron system. In the absence of any quantitative or qualitative data that might be obtained from detailed molecular orbital calculations, any discussion of bonding in **1** must be speculative. Nevertheless, some attempt to rationalize the bonding in this species can be made.[3] A pair of dicarbollide cages prepared for bonding[16] with silicon possess the filled ligand orbital (LO) combinations a_g, a_u, e_{1g}, and e_{1u}. The e_{1u} LO set is of appropriate symmetry to combine with the degenerate silicon p_x and p_y atomic orbitals (AO's), affording possible π-bonding interactions.[9] The a_g and a_u LO set may interact with the silicon s and p_z AO's, respectively, to provide σ-bonding interactions.[16] This scheme employs eight of the 12 available interstitial electrons in silicon–ligand bonding interactions. Further bonding via silicon d_{xz}, d_{yz} orbital interactions with the e_{1g} LO set might be considered at this point; however, it is likely that the disparity between the energy levels of the occupied LO sets and silicon d orbitals is prohibitively large. Consequently, it is more likely that the remaining four electrons occupy essentially nonbonding e_{1g} LO's. A similar rationalization can be made for the bonding present in the related aluminacarborane sandwich[5] compound [**3**]$^-$. It has been noted that the complex $Mg(\eta^5\text{-}C_5H_5)_2$[17] also possesses 12 interstitial electrons and a sandwich type structure.[8] In the case of transition-metal dicarbollide complexes, the dicarbollide cage in η^5, η^3, and η^1 bonding modes is generally found to be a six-electron, four-electron, and two-electron donor, respectively. It now appears that each η^5-dicarbollide cage in **1** and [**3**]$^-$ donates four electrons to metal–ligand bonding and retains two electrons in nonbonding orbitals.

Compound **5** features a slipped (Δ = 0.77 Å) essentially η^1-dicarbollide cage, as well as an η^5-carborane cage. The partial degradation of one of the dicarbollide cages of **1** results in a lowering of molecular symmetry and a probable change in the electron density at silicon. These changes are apparently sufficient to give rise to the observed slip of the other dicarbollide cage to an η^1 two-electron interaction with silicon, while the η^5 face becomes a six-electron donor. This scheme provides silicon with its requisite octet of electrons. Distortions of the type exhibited by **5** may result from the optimization of silicon s- and p-orbital interactions with the dissimilar carborane cage boron and carbon atomic orbitals. The distortion exhibited by **5** thus may be attributable to factors similar to those that are thought to give rise to the tilting distortions of *closo*-3-Et-3,1,2-$AlC_2B_9H_{11}$ (**6**)[18] and *closo*-3-Me-3,1,2-$GaC_2B_4H_6$ (**7**),[19] which feature M–R groups that are tilted away from the normal to the plane of the dicarbollide cage bonding faces in the direction of the carboranyl carbon atoms at angles of 19.5 and 14°, respectively. In the case of compound **4**, the two pyridine ligands and the exo dicarbollide cage are each clearly two-electron σ donors to silicon. The endo cage in **4** is highly slipped (Δ = 1.08 Å) and may be regarded as an η^1 2e donor to silicon. The $Si\text{–}B_{endo}$ distance

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[13] See for example: (a) Wiesboeck, R. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1964**, *86*, 1642. (b) Hawthorne, M. F.; Wegner, P. A.; Stafford, R. C. *Inorg. Chem.* **1965**, *4*, 1675.

[14] Collins, J. B.; Schleyer, P. v. R. *Inorg. Chem.* **1977**, *16*, 152.

[15] It may be noted that $Si(C_5Me_5)_2$[1] is the only member of this series which displays the parallel bonding mode for one of its stable conformations, as was predicted previously by molecular orbital calculations; see: Baxter, S. G.; Cowley, A. H.; Lasch, J. G.; Lattman, M.; Sharum, W. P.; Stewart, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 4064.

[16] The fact that compound **1** does not possess true D_{5d} symmetry and the LO's designated as e_1 are not strictly degenerate in the case of the dicarbollide ligand is ignored for the purpose of discussion. These deficiencies should not alter the qualitative result.

[17] Bunder, W.; Weiss, E. *J. Organomet. Chem.* **1975**, *92*, 1.

[18] (a) Young, D. A. T.; Willey, G. R.; Hawthorne, M. F.; Reis, A. H., Jr.; Churchill, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 6663. (b) Young, D. A. T.; Wiersema, R. J.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1971**, *93*, 5687. (c) Schubert, D. M.; Bandman, M. A.; Rees, W. S., Jr.; Knobler, C. B.; Lu, P.; Nam, W.; Hawthorne, M. F. *Organometallics* **1990**, *9*, 2046.

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Table IV. Details of Crystallographic Data Collections[a]

	1[b]	4[c]	5[d]
temp/K	298	128	128
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a/Å	6.9956 (6)	10.645 (1)	8.640 (1)
b/Å	9.6804 (10)	12.437 (2)	12.690 (2)
c/Å	12.2838 (22)	19.256 (2)	23.626 (3)
β/deg	91.800 (11)	94.333 (4)	92.549 (5)
V/Å^3	831	2537	2588
Z	2	4	4
ρ(calcd)/g cm^{-3}	1.17	1.18	1.14
μ/cm^{-1}	1.14	0.98	1.79
scan width			
below $K\alpha_1$	1.3	1.3	1.3
above $K\alpha_2$	1.5	1.6	1.6
scan rate/deg min^{-1}	1.5	3	3
no. of unique rflns	1818	4482	4560
no. of obsd ($I > 3\sigma(I)$) rflns	1282	3065	2925
$2\theta_{max}$/deg	54	50	50
data collected	$h,k,\pm l$	$h,k,\pm l$	$h,k,\pm l$
no. of params refined	106	319	162
R	0.050	0.052	0.047
R_w	0.068	0.068	0.055
GOF	1.997	2.20	1.75

[a] Conditions: radiation (graphite monochromator), Mo $K\alpha$; wavelength, 0.7107 Å. [b] $C_4H_{22}B_{18}Si$. [c] $C_{14}H_{32}B_{18}N_2Si$. [d] $C_{10}H_{40}B_{18}P_2Si$.

in 4 is 2.008 (4) Å, which is essentially the same as the Si–B_{endo} distance in 5, 2.004 (4) Å. Thus, the silicon atom in 4 is supplied with an octet of electrons in a straightforward manner.

Experimental Section

General Considerations. Standard glovebox and Schlenk-line techniques were employed for all manipulations of air- and moisture-sensitive compounds.[20] Reaction solvents were reagent grade and were distilled from appropriate drying agents under nitrogen before use. Benzene and toluene were distilled from potassium and sodium, respectively; tetrahydrofuran was distilled from sodium benzophenone ketyl. Deuteriated solvents were obtained from Cambridge Isotope Laboratories in sealed ampules under argon and were used without further purification. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points were measured in sealed tubes and are uncorrected.

Physical Measurements. NMR spectra were recorded with Bruker AF 200 (^{1}H, ^{13}C), WP 200 (^{1}H, ^{31}P, ^{13}C), and AM 500 (^{11}B, ^{1}H, ^{13}C) spectrometers, as well as a JEOL FX 90Q (^{31}P) instrument. Chemical shift values for ^{11}B and ^{31}P NMR spectra were referenced relative to external $BF_3{\cdot}OEt_2$ and H_3PO_4, respectively. Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced to $SiMe_4$ and measured with respect to residual protons and carbon in deuteriated solvents. Resonances observed upfield of the references were assigned negative chemical shift values in all cases. Infrared spectra were obtained as Nujol mulls or neat samples between NaCl plates and were recorded on a Beckman FT-1100 instrument. Mass spectra were obtained on an AEI limited, MS-902 sector-filled, double-focusing spectrometer.

***commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11}$)$_2$ (1).** A 2.5 M solution of *n*-BuLi (12.5 mL, 31.25 mmol) was added slowly under nitrogen to a suspension of 3.00 g (15.5 mmol) of dry [$HNMe_3$][*nido*-7,8-$C_2B_9H_{12}$] in 200 mL of dry toluene. After it was stirred for 30 min at 40 °C, the mixture was cooled and the supernatant solution was decanted from the resulting Li_2[*nido*-7,8-$C_2B_9H_{11}$] precipitate via cannula. Residual NMe_3 was removed by washing the precipitate with three 75-mL portions of dry, degassed toluene. This material was held in vacuo for 30 min and then resuspended in 200 mL of dry, degassed toluene. To this suspension was added dropwise 1.32 mL (7.75 mmol) of freshly vacuum-distilled $SiCl_4$. This mixture was refluxed for 4 h. After the mixture was cooled, precipitated LiCl was allowed to settle and the clear solution was decanted and filtered through a 1-cm plug of Celite. Solvent was removed in vacuo to give crude 1 as a tan solid. Further purification by recrystallization from hot heptane gave 1.84 g (81%) of 1: $^{11}B\{^1H\}$ NMR (C_6H_6, ambient temperature) δ −8.5 (area 2), −11.2 (area 1), −20.4 (area 1), −24.7 (area 1) ppm; ^{1}H NMR (C_6D_6, ambient temperature) δ 2.4 (singlet, C–H), ca. 0.0–4.0 ppm (broad, B–H); $^{13}C\{^1H\}$ NMR (C_6D_6, ambient temperature) δ 30.02 ppm; characteristic IR (cm^{-1}) 3047 (m, C–H str), 2592 (s, B–H), 1227 (m), 1103 (m), 1099 (m), 969 (s), 666 (m); mass spectrum, parent ion at *m/e* 296, $[^{12}C_4{}^{11}B_{18}H_{22}{}^{28}Si]^+$. Anal. Calcd for $C_4B_{18}H_{22}Si$: C, 16.40; H, 7.57; Si, 9.59. Found: C, 16.61; H, 7.81; Si, 9.95.

(C_5H_5N)$_2$Si($C_2B_9H_{11}$)$_2$ (4). The addition of 20 mL of pyridine to 200 mg (0.68 mmol) of 1 under argon resulted in an immediate reaction, which produced an amorphous yellow solid. The mixture was stirred for 1 week at room temperature, during which time the yellow solid gradually dissolved to give a clear yellow solution. Layering of this solution with *n*-pentane resulted in the formation of yellow crystals of 4 (220 mg, 72%) and the separation of a yellow oil. Anal. Calcd for $C_{14}H_{32}B_{18}N_2Si$: C, 37.28; H, 7.15; N, 6.21. Found: C, 40.72; H, 7.12; N, 6.75.

[(Me_3P)$_2$BH]($C_2B_8H_{10}$)Si($C_2B_9H_{11}$) (5). The addition of 0.80 mL (ca. 2 mmol) of PMe_3 to 300 mg (1.0 mmol) of 1 in 50 mL of toluene under argon resulted in the immediate formation of 5 (420 mg, 94%) as an amorphous white solid. X-ray-quality crystals of 5 were obtained by allowing the reaction mixture to stand undisturbed for 10 days, during which time colorless crystals gradually grew on the walls of the flask. The solution was then decanted away, and the crystals were scraped from the walls of the flasks, washed with toluene followed by *n*-pentane, and allowed to dry. Because of this compound's insolubility, it could not be purified by further recrystallizations. Anal. Calcd for $C_{10}H_{40}B_{18}SiP_2$: C, 26.99; H, 9.06; P, 13.92; Si, 6.31. Found: C, 27.09; H, 9.36; P, 12.45; Si, 7.02.

General Methods of Crystallographic Analyses. All data were collected on an automated diffractometer in the θ–2θ scan mode using Mo $K\alpha$ radiation. Data for 4 and 5 were collected on a modified Picker FACS-1 diffractometer. Data for 1 were collected on a Huber diffractometer. All calculations were performed by using the DEC VAX 11/750 computer of the J. D. McCullough Crystallographic Laboratory and the UCLA crystallographic programs listed in ref 21. Data were corrected for Lorentz and polarization effects. Structure 1 was solved with use of statistical methods (MULTAN80). Structures 4 and 5 were solved with use of heavy-atom methods. Remaining atoms were located

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(20) (a) Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969. (b) Jolly, W. L. *The Synthesis and Characterization of Inorganic Compounds*; Prentice Hall: Englewood Cliffs, NJ, 1970.

(21) Programs: CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis and Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least-squares refinement; MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declerq, and Woolfson), direct methods; ORTEP (Johnson), figure plotting.

by use of difference electron density maps. In the course of refinement all cage C and B atoms were initially assigned scattering factors for boron. After refinement, carboranyl carbon atom positions could be distinguished by their anomalously low temperature factors and by shorter interatomic distances. Reported R and R_w values are defined as $R = [\sum(|F_o| - |F_c|)/\sum|F_o|]$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = 1/\sigma^2(F_o)$, and "goodness of fit" is defined by $[\sum w(|F_o| - |F_c|)^2/(N_{\text{observns}} - N_{\text{variables}})]^{1/2}$. Scattering factors for hydrogen were obtained from Stewart et al.,[22] and those for other atoms were taken from ref 23. Details of the individual data collections are given in Table IV.

***commo*-3,3′-Si(3,1,2-SiC$_2$B$_9$H$_{11}$)$_2$ (1).** A colorless crystal was affixed to a fiber. Systematic absences were found for reflections $0k0$ ($k = 2n + 1$) and for $h0l$ ($h + l = 2n + 1$). Unit cell parameters were determined from a least-squares fit of 13 accurately centered reflections (13.9° < 2θ < 16.2°). Three intense reflections (2,1,−5, 210, 1,3,−1) were monitored every 97 reflections to check stability. Intensities of these reflections fluctuated only slightly, ca ±3%, with decay less than 2% during the course of the experiment (71.4-h exposure). Anisotropic thermal parameters were refined for all non-hydrogen atoms. All carboranyl H atoms were kept in located positions with assigned B values of 4 Å^2. Anomalous dispersion terms were applied to the scattering of Si. A final difference electron density map was essentially featureless; maximum and minimum peaks were ca. 0.4 e Å^{-3}. Positional parameters for 1 are given in the supplementary material (Table 2s).

(C$_5$H$_5$N)$_2$Si(C$_2$B$_9$H$_{11}$)$_2$ (4). A colorless parallelepiped was sealed in an argon-filled capillary. Systematic absences were found for reflections $0k0$ ($k = 2n + 1$) and for $h0l$ ($l = 2n + 1$). Unit cell parameters were determined from a least-squares fit of 34 accurately centered reflections (9.6° < 2θ < 25.9°). Three intense reflections (108, 433, 053) were monitored every 97 reflections to check stability. Intensities of these reflections fluctuated only slightly, ca. ±4.5%, during the course of the experiment (89.9-h exposure). Anisotropic thermal parameters were refined for all non-hydrogen atoms. All carboranyl H atoms except H(12) were kept in located positions; all carboranyl H atoms were assigned B values of 2 Å^2. Positional parameters were refined for H(12). All other hydrogen atoms were kept in calculated positions and were assigned B values of 3 Å^2. Anomalous dispersion terms were applied to the scattering of Si. A final difference electron density map was essentially featureless; maximum and minimum peaks were ca. 0.8 e Å^{-3}, near Si. Positional parameters for 4 are given in the supplementary material (Table 5s).

[(Me$_3$P)$_2$BH](C$_2$B$_8$H$_{10}$)Si(C$_2$B$_9$H$_{11}$) (5). A colorless crystal was sealed in an argon-filled capillary. Systematic absences were found for reflections $0k0$ ($k = 2n + 1$) and for $h0l$ ($h + l = 2n + 1$). Unit cell parameters were determined from a least-squares fit of 29 accurately centered reflections (7.6° < 2θ < 20.2°). Three intense reflections (014, 1,−2,1, 1,2,−1) were monitored every 97 reflections to check stability. Intensities of these reflections fluctuated only slightly, ca. ±4%, during the course of the experiment (91.8-h exposure). Anisotropic thermal parameters were refined for Si and P. All carboranyl H atoms were refined (positions) with assigned U values of 0.03 Å^2. All other hydrogen atoms were kept in calculated positions with assigned U values of 0.05 Å^2 (CH$_3$). Anomalous dispersion terms were applied to the scattering of Si and P. A final difference electron density map was essentially featureless; maximum and minimum peaks were ca. 0.2 e Å^{-3}. Positional parameters for 5 are given in the supplementary material (Table 8s).

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Supplementary Material Available: Tables of positional and thermal parameters and complete interatomic distances and angles for 1, 4, and 5 (23 pages); listings of observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page.

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Synthesis and Molecular and Crystal Structures of (3-Methyl-3-benzoborepin)chromium Tricarbonyl

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(3-Methyl-3-benzoborepin)chromium tricarbonyl was obtained by treating the free ligand with tris(acetonitrile)chromium tricarbonyl in refluxing tetrahydrofuran. Red crystals of the complex C$_{14}$H$_{11}$BCrO$_3$ form in the $P2_1/n$ space group with $Z = 4$, $a = 9.421$ (2) Å, $b = 14.046$ (3) Å, $c = 9.949$ (2) Å, and $\beta = 98.63$ (1)°. The full structure has been determined and indicates that chromium is η^7-coordinated to the borepin rather than the benzo ring.

Introduction

Unsaturated boron–carbon heterocycles can serve as versatile π-ligands toward transition metals.[1-3] Thus, the five-membered rings borole 1 and 1,3-diborolyl 2 form η^5-complexes 6[4] and 7.[5] Similarly, the six-membered ring heterocycles boratabenzene 3 and 1,4-diboracyclohexadiene 4 are known to form η^6-complexes 8[6] and 9,[7] respectively. On the other hand, the chemistry of the seven-membered ring borepin 5 has been less well explored,[8-12] and only a

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