Synthesis and Molecular Structure of a Novel Bis(η^5-dicarbollide) Silicon Sandwich Compound: *commo*-3,3′-Si(3,1,2-$SiC_2B_9H_{11}$)$_2$

William S. Rees, Jr.,[1] David M. Schubert,
Carolyn B. Knobler, and M. Frederick Hawthorne*

Department of Chemistry and Biochemistry
University of California—Los Angeles
Los Angeles, California 90024

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In the preceding paper we reported the synthesis and structural characterization of a formally zwitterionic aluminacarborane complex (1),[2] containing a *commo* aluminum bis(η^5-dicarbollide) moiety, $[Al(\eta^5\text{-}C_2B_9H_{11})_2]^-$.[3] The existence of this complex suggested to us the possibility of preparing an isoelectronic series of commo-[Ne]-core bis(η^5-dicarbollide) sandwich compounds, $[M(\eta^5\text{-}C_2B_9H_{11})_2]^n$, where M = Al(III), n = 1−; M = Si(IV), n = 0; and M = P(V), n = 1+. While complex **1** effectively represents the first member of this series, each of the other members would have great novelty and would be expected to exhibit unusual bonding modes for these main-group elements. Here we wish to report the synthesis and structural characterization of the second member of this proposed series, commo-3,3′-Si(3,1,2-$SiC_2B_9H_{11}$)$_2$ (**2**). Reaction of silicon tetrachloride with 2 molar equiv of dilithio-7,8-dicarbollide in benzene at the reflux temperature resulted in the desired product, **2**, according to eq 1.[4]

$$2Li_2[\textit{nido}\text{-}7,8\text{-}C_2B_9H_{11}] + SiCl_4 \xrightarrow[\text{reflux}]{\text{benzene}} \textit{commo}\text{-}3,3'\text{-}Si(3,1,2\text{-}SiC_2B_9H_{11})_2 + 4LiCl \quad (1)$$

Compound **2** was isolated and purified by sublimation in 78% yield. This species was found to be stable to dry air but gradually decomposed in moist air. Compound **2** is soluble in most organic solvents and sparingly soluble in saturated hydrocarbons such as heptane.

Compound **2** was characterized by a combination of ^1H, ^{11}B, and ^{13}C NMR, IR, and mass spectroscopy[5] and by a single-crystal X-ray diffraction study.[6] The ^{11}B NMR spectrum of **2** in benzene solution exhibited resonances attributable to a single kind of dicarbollide ligand. The ^1H NMR spectrum showed a single carboranyl C-H resonance in addition to broad B-H resonances characteristic of the $[\textit{nido}\text{-}7,8\text{-}C_2B_9H_{11}]^{2-}$ ligand. The IR spectrum contained a single carboranyl C-H stretching band in addition to bands typically observed for the dicarbollide cage.

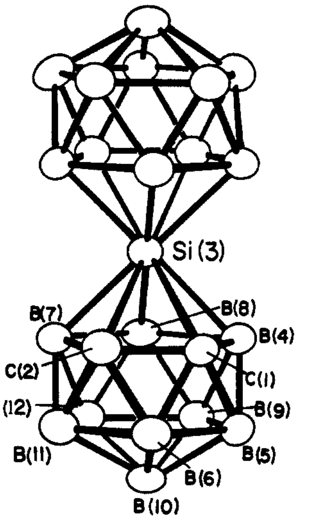

Figure 1. ORTEP representation of the structure of commo-3,3′-Si-(3,1,2-$SiC_2B_9H_{11}$)$_2$ (**2**), with hydrogen atoms omitted for clarity and thermal ellipsoids at 50% probability level. Si–C(1,2) 2.22 (1), Si–B(4,7) 2.14 (1), Si–B(8) 2.05 (1) Å.

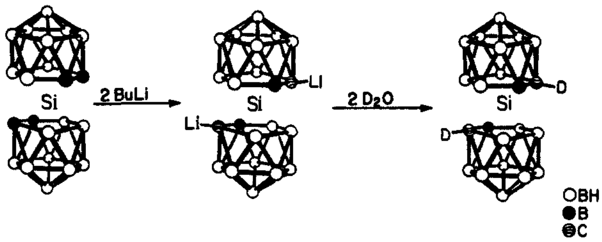

Figure 2. Deuteration of **2**.

The ORTEP representation of the structure of **2** is shown in Figure 1 together with selected bond lengths. The silicon atom in **2** resides at a crystallographic center of symmetry in the molecular structure of **2**, being equidistant between each of the planar, parallel C_2B_3 faces of the two dicarbollide ligands.

While the exact nature of silicon–ligand bonding in **2** is uncertain, we can rationalize this 12 interstitial electron interaction as follows. A pair of dicarbollide cages prepared for bonding with silicon possess the filled ligand orbital combinations (LO sets) a_g, a_u, e_{1g}, and e_{1u} with which to form bonds to silicon.[7] The e_{1u} LO set is of proper symmetry to combine with the p_x and p_y atomic orbitals (AO's) of silicon, affording possible π-bonding interactions while the a_u LO may interact with the p_z AO to form a bond of σ symmetry. At this point one might speculatively invoke the participation of silicon d-orbitals in commo bonding. The d_{xz} and d_{yz} αO's are of the proper symmetry to provide orbital overlap with the e_{1g} LO set to produce π bonds between silicon and each dicarbollide ligand. Alternatively, the disparity in energies between

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[2] Compound **1** is: *commo*-3,3′-Al[[*exo*-8,9-(μ-H)$_2$Al(C_2H_5)$_2$-3,1,2-$AlC_2B_9H_9$](3′,1′,2′-$AlC_2B_9H_{11}$)].

[3] Rees, W. S., Jr.; Schubert, D. M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.*, preceding paper in this issue.

[4] In a typical experiment, 3.00 g (15.5 mmol) of dry $[HNMe_3][\textit{nido}\text{-}7,8\text{-}C_2B_9H_{12}]$ was suspended in 150 mL of dry, freshly distilled benzene under N_2 in an oven-dried, 250-mL, three-neck, round-bottom flask fitted with a stir bar, reflux condenser, Schlenk line attachment , and rubber septum. After the mixture was heated to 40 °C, 2 equiv (31.0 mmol) of newly titrated *n*-BuLi in hexane was added via syringe to liberate NMe_3 and form sparingly soluble $Li_2[\textit{nido}\text{-}7,8\text{-}C_2B_9H_{11}]$. The mixture was heated at the reflux temperature for 30 min and then evaporated to dryness in vacuo. The white solid residue was washed 5 times with benzene to remove the last traces of NMe_3, which were found to interfere with the next step in the synthesis. The $Li_2[\textit{nido}\text{-}7,8\text{-}C_2B_9H_{11}]$ was placed under a vacuum of 2×10^{-3} mmHg at 80 °C for 1 h and then suspended in 150 mL of freshly distilled benzene at ambient temperature. Freshly vacuum distilled $SiCl_4$ (1.32 g, 7.75 mmol) was diluted with 50 mL of freshly distilled benzene and cannulated into the reaction flask over a 5-min period. Immediate precipitation of LiCl occurred. The solution was heated at the reflux temperature for 4 h, cooled to ambient temperature, filtered through a medium-porosity glass frit to remove the LiCl, and evaporated to dryness in vacuo. The light tan residue which resulted was purified by sublimation at 120 °C to a dry ice-cooled cold finger, under a dynamic vacuum of 10^{-5} mmHg. This afforded 1.78 g (78%) pure **2** as a white solid (mp >300 °C).

[5] Spectroscopic data for **2**: $^{11}B\{^1H\}$ NMR (C_6D_6; referenced to external $BF_3{\cdot}OEt_2$ δ 0; chemical shifts upfield of δ 0 reported as negative; ambient temperature) δ −8.5 (area 2), −11.2 (area 1), −12.9 (area 4), −20.4 (area 1), −24.7 (area 1); ^1H NMR (C_6D_6, referenced to residual protons in C_6D_6, 7.15 ppm; ambient temperature) δ 2.10 (singlet, carboranyl C–H protons), δ 0.0–4.0 (br, B–H protons); $^{13}C\{^1H\}$ NMR (C_6D_6; referenced to C_6D_6 128.0 ppm; ambient temperature) δ 30.02; characteristic IR (cm^{-1}; NaCl, Nujol mull) 3047 (m, C–H stretch), 2592 (s, B–H stretch), 1227 (m), 1103 (m), 1099 (m), 969 (s), 905 (m), 666 (m); mass spectrum, parent at m/e 296, $^{12}C_4{}^{11}B_{18}H_{22}{}^{28}Si^+$.

[6] Crystallographic data: suitable crystals of **2** ($C_4H_{22}B_{18}Si$) were grown from toluene/heptane. Data collection was carried out at 25 °C, using a modified Huber automated diffractometer, Mo Kα radiation. The space group is $P2_1/n$ with a = 6.9956 (6) Å, b = 9.6804 (10) Å, c = 12.2838 (22) Å, β = 91.800 (11)°. Intensity data for 1282 reflections which measured $I > 3\sigma(I)$ were used for structure solution and refinement using MULTAN 80 and the UCLA Crystallographic Package. The last cycle of least-squares refinement gave residuals of R = 0.050, R_w = 0.068, and GOF = 1.997.

[7] The fact that the molecular orbitals designated as e_1 are not strictly degenerate in the case of the dicarbollide ion is ignored for purposes of discussion. See: (a) Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1977**, 602. (b) Mingos, D. M. P.; Forsyth, M. I.; Welsh, A. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1363.

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the d_{xz} and d_{yz} orbitals and the e_{1g} set may require that two electron pairs remain nonbonding and essentially ligand electrons reside in the e_{1g} orbital set. Finally, either the combination of s and d_{z^2} AO's or the s orbital alone may interact with the a_g LO to form a bonding interaction of σ symmetry.

Preliminary reactivity studies indicate that **2** is sufficiently stable to undergo a conventional carborane cage nucleophilic derivatization reaction at carbon. Treatment of **2** with 2 molar equiv of *n*-butyllithium in benzene at 25 °C resulted in precipitation of white solid presumed to be dilithio-**2**. Subsequently, reaction of this material with D_2O resulted in formation of $[Si(C_2B_9H_{10}D)_2]$[8] in ca. 30% yield, as shown in Figure 2. The relatively low yield of this reaction may be a consequence of competing nucleophilic attack by the *n*-butyl reagent at silicon. The reactivity of **2** with respect to nucleophilic and electrophilic substitution and hydrolysis is currently under investigation.

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Registry No. 2, 103303-90-8; $[HNMe_3]$[*nido*-7,8-$C_2B_9H_{12}$], 12543-22-5; $SiCl_4$, 10026-04-7.

Supplementary Material Available: Tables of positional and thermal parameters, interatomic distances and angles, and observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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[8] IR (cm^{-1}; NaCl, Nujol mull) 3047 (m, C–H stretch), 2276 (m, C–D stretch); mass spectrum, parent at *m/e* 298, $^{12}C_4{}^{11}B_{18}H_{20}D_2{}^{28}Si^+$.

Synthesis and Structural Characterization of the $[H_{6-n}Ni_{34}(CO)_{38}C_4]^{n-}$ (n = 6, 5) and $[Ni_{35}(CO)_{39}C_4]^{6-}$ Clusters: Molecular Models for Carbidized Metal Crystallites

Alessandro Ceriotti, Anna Fait, Giuliano Longoni,*
Giampietro Piro, and Luigi Resconi

Dipartimento di Chimica Inorganica e Metallorganica
20133 Milano, Italy

Francesco Demartin, Mario Manassero,*
Norberto Masciocchi, and Mirella Sansoni

Istituto di Chimica Strutturistica Inorganica
20133 Milano, Italy

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We wish here to report a series of nickel polycarbide clusters of formula $[H_{6-n}Ni_{34}(CO)_{38}C_4]^{n-}$ (n = 6, 5) and $[Ni_{35}(CO)_{39}C_4]^{6-}$, whose structural features can be of relevance in envisioning the structural changes which may occur in compactly packed metal crystallites[1] on carbidization.[2,3] In contrast to previously reported nickel polycarbides, e.g., $[Ni_{10}(CO)_{16}C_2]^{2-}$ and $[Ni_{16}(CO)_{23}(C_2)_2]^{4-}$,[4,5] the new compounds contain four isolated carbide atoms imbedded in a complex metal framework derived from the fusion of compact, simple-hexagonal, pentagonal-bipyramidal, and polytetrahedral metal packing[6] moieties.

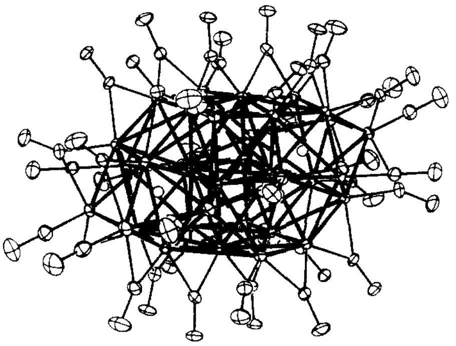

Figure 1. ORTEP drawing of $[HNi_{34}(CO)_{10}(\mu_2\text{-}CO)_{26}(\mu_3\text{-}CO)_2C_4]^{5-}$.

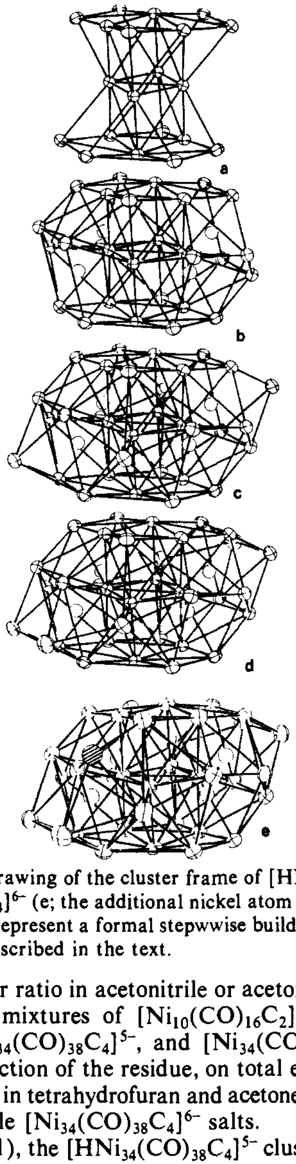

Figure 2. ORTEP drawing of the cluster frame of $[HNi_{34}(CO)_{38}C_4]^{5-}$ (d) and $[Ni_{35}(CO)_{39}C_4]^{6-}$ (e; the additional nickel atom is shown as hatched circle). Parts a–c represent a formal stepwwise building procedure of the two clusters, as described in the text.

The $[H_{6-n}Ni_{34}(CO)_{38}C_4]^{n-}$ (n = 6, 5) derivatives are obtained directly from reactions of tetrasubstituted ammonium salts ($[NEt_4]^+$, $[NMe_3CH_2Ph]^+$, $[NBu_4]^+$) of $[Ni_6(CO)_{12}]^{2-}$ with C_2Cl_6 in a ca. 2:1 molar ratio in acetonitrile or acetone. The reactions afford variable mixtures of $[Ni_{10}(CO)_{16}C_2]^{2-}$,[4] $[Ni_{16}(CO)_{23}(C_2)_2]^{4-}$,[5] $[HNi_{34}(CO)_{38}C_4]^{5-}$, and $[Ni_{34}(CO)_{38}C_4]^{6-}$ clusters. Sequential extraction of the residue, on total evaporation of the reaction mixture, in tetrahydrofuran and acetone allows separation of the less soluble $[Ni_{34}(CO)_{38}C_4]^{6-}$ salts.

As shown in (1), the $[HNi_{34}(CO)_{38}C_4]^{5-}$ cluster is obtained by protonation of the hexaanion with dilute H_3PO_4 in acetonitrile.[7]

$$[Ni_{34}(CO)_{38}C_4]^{6-} \underset{Me_2SO}{\overset{H^+,\ CH_3CN}{\rightleftharpoons}} [HNi_{34}(CO)_{38}C_4]^{5-} \tag{1}$$

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[5] Ceriotti, A.; Longoni, G.; Piro, G.; Resconi, L.; Manassero, M.; Masciocchi, N.; Sansoni, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1402–1403.

[6] Wells, A. F. *Structural Inorganic Chemistry*, 4th ed.; Clarendon Press: Oxford, England, 1975.

[7] Infrared carbonyl absorptions of $[Ni_{34}(CO)_{38}C_4]^{6-}$ in CH_3CN at 1992 s and 1853 s cm^{-1}. Analytical results for $[NEt_4]_6[Ni_{34}(CO)_{38}C_4]$: Found $[NEt_4]^+$ 19.92, Ni 51.02, $[NEt_4]^+$:Ni = 1:5.67. Calcd $[NEt_4]^+$ 20.06; Ni 51.13; $[NEt_4]^+$:Ni = 1:5.66. Infrared carbonyl absorptions of $[HNi_{34}(CO)_{38}C_4]^{5-}$ in acetone at 2008 s and 1862 s cm^{-1}. Analytical results for $[NMe_3CH_2Ph]_5[HNi_{34}(CO)_{38}C_4]$: Found $[NMe_3CH_2Ph]^+$ 19.27; Ni 51.43; $[NMe_3CH_2Ph]^+$:Ni = 1:6.82. Calcd $[NMe_3CH_2Ph]^+$ 19.44; Ni 51.72; $[NMe_3CH_2Ph]^+$:Ni = 1:6.8. Infrared carbonyl absorptions of $[Ni_{35}(CO)_{39}C_4]^{6-}$ in CH_3CN at 1998 s, 1864 s, and 1850 sh cm^{-1}. Analytical results for $[NEt_4]_6[Ni_{35}(CO)_{39}C_4]$: Found $[NEt_4]^+$ 19.12; Ni 51.32; $[NEt_4]^+$:Ni = 1:5.94. Calcd $[NEt_4]^+$ 19.63; Ni 51.69; $[NEt_4]^+$:Ni = 1:5.83.

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