Electron-Acceptor Behavior of 2,4,7,9-Tetracarba-*nido*-dodecaborane(12) with Group 1 and Group 2 Metals: Syntheses and Crystal Structures of $[(THF)_4Li][(SiMe_3)_4C_4B_8H_9]$ and $[(THF)_2Mg(SiMe_3)_4C_4B_8H_8]$[†]

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Summary: The room-temperature reaction between a THF solution of 2,4,7,9-tetracarba-nido-dodecaborane(12) $(SiMe_3)_4C_4B_8H_8$ and finely cut excess lithium or magnesium metal, in the absence of naphthalene and aromatic solvents, produced either $\{[(THF)_4Li][(SiMe_3)_4C_4B_8H_9]\}$ ***(1)*** *as an EPR-silent transparent crystalline solid in 41% yield or* $[(THF)_2Mg(SiMe_3)_4C_4B_8H_8]$ ***(2)*** *as an off-white crystalline solid in 88% yield. While the solid-state structure of* ***1*** *showed a single anionic* $[(SiMe_3)_4C_4B_8H_9]^-$ *unit that was well-separated from a discrete* $[Li(THF)_4]^+$ *cation, the structure of* ***2*** *is that of a novel magnesacarborane in which the carborane cage incorporates both electron-precise and electron-deficient carbon and boron atoms.*

It has been well-documented that the lithium or sodium naphthalenide mediated two-electron reductions of the *closo*-carboranes in either the C_2B_{10} or C_2B_4 cage systems result in cage openings to yield the corresponding *nido*-carborane dianions, in which the cage carbons are situated on the open faces of the carboranes and are separated by a boron atom.[1] A similar reduction process of the $C_{cage}-C_{cage}$-linked bis(carborane) $(1,2\text{-}C_2B_{10}H_{11})_2$ resulted in the formation of a much less opened species, in which the C−C bond on each triangular face of the carborane cages opened to produce two four-membered rings.[2] Grimes and co-workers studied the two-electron reduction of the neutral C-alkyl-substituted 2,3,7,8-tetracarba-*nido*-dodecaborane(12) $R_4C_4B_8H_8$ with excess sodium naphthalenide in THF.[3] Although the structure of the resulting dianion was not determined, the crystal structures of several of its metalla- and dimetallacarborane complexes suggested an *arachno*-C_4B_8 cage that can be envisioned as arising from the removal of two vertices from a 14-vertex hexagonal-antiprismic *closo*-carborane.[3] Since essentially all of the cited examples involve the use of metal naphthalenides as reducing agents,[4] the extent to which the exact nature of the reducing agent determines the course of these reactions is an open question. We report herein the results of an investigation of the reactivity of a *C*-$SiMe_3$-substituted 2,4,7,9-tetracarba-*nido*-dodecaborane(12), $(SiMe_3)_4C_4B_8H_8$, toward lithium and magnesium metals in the absence of naphthalene and aromatic solvents that indicate a significant dependence does exist. To our knowledge, the present synthetic and structural report describes the first examples of reactions in which a neutral carborane acts as a restricted electron acceptor, which removes only the valence electrons of a single group 1 or group 2 metal, even when a large excess of the particular metal is available.

As outlined in Scheme 1, treatment of a tetrahydrofuran (THF) solution of the 2,4,7,9-tetracarba-*nido*-dodecaborane(12) derivative $(SiMe_3)_4C_4B_8H_8$[5] with finely cut excess lithium metal at 25 °C resulted in the formation of a red-orange heterogeneous mixture, without any gas evolution. The initially formed compound was found to be EPR active with a g value of 2.0030, which suggests a π-type radical.[6] When the reaction mixture was stirred over a period of 5 days, a previously unknown monolithium compound, $\{[(THF)_4Li][(SiMe_3)_4C_4B_8H_9]\}$ (**1**), was produced as an EPR-silent transparent crystalline solid in 41% yield. A similar reaction of $(SiMe_3)_4C_4B_8H_8$ with the pure magnesium metal, over a period of 3 days, resulted in the formation of an off-white crystalline solid, identified as $[(THF)_2Mg(SiMe_3)_4C_4B_8H_8]$ (**2**), in 88% yield (see Scheme 1).[6] The driving forces for these reactions are not known, nor is it apparent why, even in the presence of excess lithium metal, compound **1** was formed over the expected two-electron-reduction product. It may be that the heterogeneous nature of the reaction mixture is a key factor in determining the courses of these reactions. Never-

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[†] Dedicated, with all best wishes, to Professor Sheldon G. Shore of The Ohio State University on the occasion of his 65th birthday.

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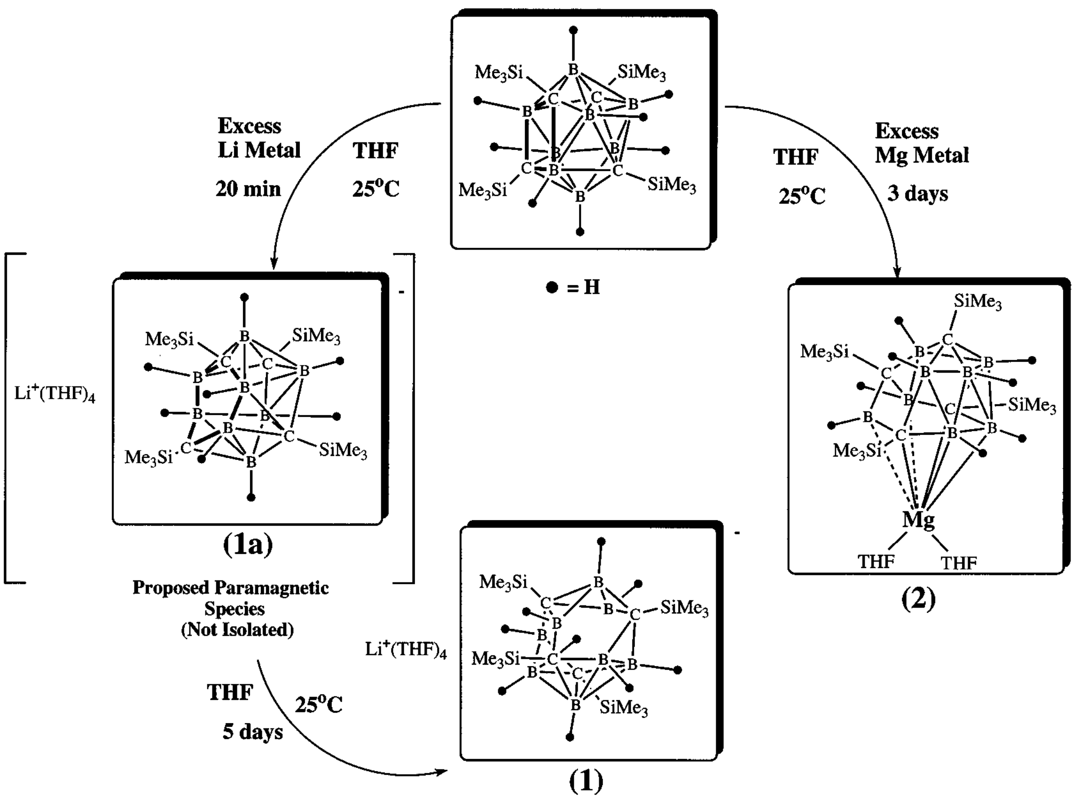
S0276-7333(95)00924-1 CCC: $12.00

Scheme 1



theless, the reasonable yields of **1** and **2** indicate that these are the major products in the reactions and suggest that the "carbons apart" C_4B_8 carborane can be effectively used to oxidize a single metal-atom species, thus facilitating the formation of the corresponding 1:1 ionic products, without the loss of any metal- or cage-bound moieties. If this is proven correct, the present method could constitute a general approach to the synthesis of a series of ionic (noncoordinating) or predominantly ionic (less coordinating) metallacarborane species, which would be of both theoretical and practical interest. The generality of this reaction is currently being explored in our laboratories.

The ^1H and ^{11}B NMR spectra[7] of **1** and **2** show the presence of solvating THF molecules, carborane cages, and C_{cage}-bound $SiMe_3$ groups. No evidence of B−H−B bridge H's was found in the δ 0 to −10 ppm regions of their ^1H NMR spectra, nor was there any evidence of such bridges in their IR spectra. The ^{11}B NMR of **1** exhibits three doublets of 6:1:1 peak area ratio at δ −24.59, −42.53, and −46.94 ppm, respectively, while **2** displays three doublets of 3:3:2 peak area ratio at δ −23.52, −25.13, and −44.6 ppm. The doublet structures indicate that the terminal B−H bonds remain intact. Both spectra differ significantly from that of the tetracarbon-carborane precursor, which exhibits only a single resonance at δ −5.57 ppm.[5] While these spectra show that **1** and **2** have structures that are quite different from that of their precursor carborane, they do not provide direct information as to the specific geometries of these compounds. Therefore, X-ray analyses were performed on both **1** and **2**; the resulting structures are shown in Figures 1 and 2, respectively.[8] Compound **1** (see the Supporting Information) consists of a discrete $[Li(THF)_4]^+$ cationic unit that is well-separated from a $[(SiMe_3)_4C_4B_8H_9]^-$ anion. If one takes the maximum

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(6) Synthesis of **1** and **2**: In separate experiments, a 1.08 mmol (0.469 g) or a 1.01 mmol (0.44 g) sample of the tetracarbon carborane $(SiMe_3)_4C_4B_8H_8$[5] was reacted *in vacuo* with an excess quantity of finely cut Li (0.036 g, 5.19 mmol) or Mg (0.3 g, 12.3 mmol) metal in dry THF (20 mL) at 25 °C, with constant stirring. In the case of the lithium reaction, the colorless heterogeneous mixture turned instantaneously to red-orange without any gas evolution. Its EPR spectrum indicated the coupling of four equivalent boron nuclei with an unpaired electron, giving a *g* value of 2.0030. After 20 min the reaction solution turned to a light brown with the formation of a pale yellow EPR-silent solid. On the other hand, the mixture of magnesium metal and $(SiMe_3)_4C_4B_8H_8$ in THF turned from a pale yellow to an off-white turbid solution. After they were stirred constantly for 5 days (lithium reaction) and 3 days (magnesium reaction), the reaction mixtures were filtered *in vacuo* and the residues washed repeatedly with a solvent mixture of *n*-hexane (15%) and benzene (85%) until clear filtrates were obtained. The unreacted metals left on the frits (not measured) were recovered and used in subsequent experiments. After slow removal of the solvents from the filtrates, slightly orange-yellow residues were obtained, which when further purified by recrystallization from benzene/hexane (4/1) solutions produced air-sensitive, transparent colorless crystals, identified as $\{[(THF)_4Li][(SiMe_3)_4C_4B_8H_9]\}$ (**1**; 0.323 g, 0.442 mmol; mp 187−189 °C), or off-white plate-like crystals, identified as $[(THF)_2Mg(SiMe_3)_4C_4B_8H_8]$ (**2**; 0.54 g, 0.89 mmol; mp 198 °C dec), in 41% and 88% yields, respectively. Both **1** and **2** are soluble in polar solvents but are less soluble in nonpolar organic solvents. Therefore, X-ray-quality crystals were grown from their respective benzene solutions.

(7) Compound **1**: ^1H NMR δ 3.87 (s, br, 16H, THF), 2.03 (s, br, 16H, THF), 0.40 (s, 9H, $SiMe_3$), 0.29 (s, 9H, $SiMe_3$), 0.17 (s, 18H, $SiMe_3$); ^{11}B NMR δ −24.59 (d, v br, 6B, ^1J(BH) = unresolved, cage BH), −42.53 (d, 1B, ^1J(BH) = 123 Hz, cage BH), −46.94 (d, 1B, ^1J(BH) = 133 Hz, cage BH); ^{13}C NMR δ 68.63 [t, CH_2, THF, $^1J(^{13}C-^1H)$ = 148.0 Hz], 34.87 [d(br), cage CH, $^1J(^{13}C-^1H)$ ~135 Hz], 25.18 [t, CH_2, THF, $^1J(^{13}C-^1H)$ = 133.2 Hz], 2.64 [q (br, overlapping), $SiMe_3$, $^1J(^{13}C-^1H)$ = 119−120 Hz], 2.17 [q (br, overlapping), $SiMe_3$, $^1J(^{13}C-^1H)$ = 119−120 Hz], 1.27 [q (br, overlapping), $SiMe_3$, $^1J(^{13}C-^1H)$ = 119−120 Hz], 0.14 [s, 1C, cage carbons (SiCB)], −0.82 [s, 2C, cage carbons (SiCB)]; ^7Li NMR δ −2.87 (s, br, *exo*-polyhedral cage-Li); IR data (C_6H_6; cm^{-1}) 2652 (s), 2597 (m) [ν(B−H)]. Anal. Calcd for $C_{32}H_{77}B_8Si_4O_4Li$: C, 52.53; H, 10.61. Found: C, 52.39; H, 10.12. Compound **2**: ^1H NMR δ 3.53 (s, br, 8H, THF), 1.33 (s, br, 8H, THF), 0.56 (s, 9H, $SiMe_3$), 0.45 (s, 9H, $SiMe_3$), 0.24 (s, 9H, $SiMe_3$), 0.12 (s, 9H, $SiMe_3$); ^{11}B NMR δ −23.52 (d, overlapping, 3B, ^1J(BH) unresolved, cage BH), −25.13 (d, overlapping, 3B, ^1J(BH) unresolved, cage BH), −44.60 (d, 2B, ^1J(BH) = 135 Hz, cage BH); ^{13}C NMR δ 69.70 [t, CH_2, THF, $^1J(^{13}C-^1H)$ = 147.6 Hz], 28.38 [t, CH_2, THF, $^1J(^{13}C-^1H)$ = 133.0 Hz], 3.11 [s, 2C, cage carbons (SiCB)], 5.07 [q (br, overlapping), $SiMe_3$, $^1J(^{13}C-^1H)$ = 119−120 Hz], 4.09 [q (br, overlapping), $SiMe_3$, $^1J(^{13}C-^1H)$ = 119−120 Hz], −1.37 [s, 2C, cage carbons (SiCB)]; IR data (THF; cm^{-1}) 2510 (vs, br), 2358 (m, br) [ν(B−H)]. Anal. Calcd for $C_{24}H_{60}B_8Si_4O_2Mg$: C, 47.73; H, 10.01. Found: C, 47.86; H, 10.28.

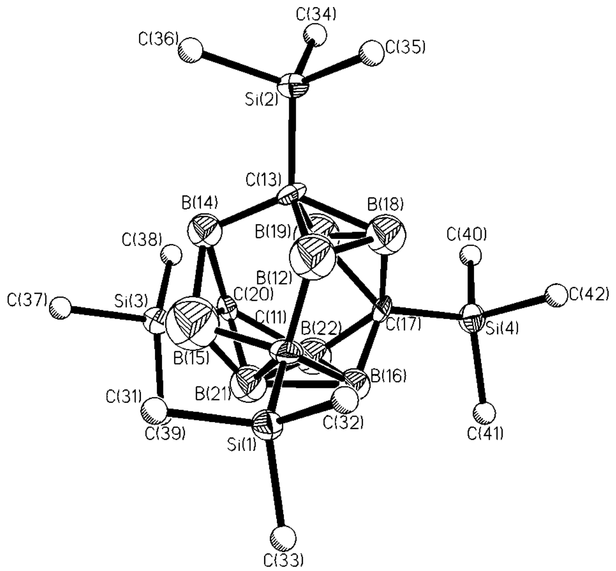

Figure 1. Perspective view of **1** drawn at the 40% probability level. Pertinent distances (Å) and angles (deg): C(11)−B(12,15,16,21) = 1.63(4), 1.81(5), 1.73(3), 1.69(3); B(12)−B(18) = 1.84(4); C(13)−B(12,14,18,19) = 1.67(4), 1.69(3), 1.73(4), 1.75(4); B(14)−B(15) = 1.70(5); B(14)−C(20) = 1.74(3); B(15)−C(20) = 1.81(5); B(15)−B(21) = 1.53(6); B(16)−C(17) = 1.63(3); B(16)−B(21) = 1.81(4); B(16)−B(22) = 1.80(4); C(17)−B(18,19,22) = 1.69(4), 1.73(5), 1.61(4); B(18)−B(19) = 1.87(4); C(20)−B(19,21,22) = 2.02(4), 1.70(3), 1.76(4); B(21)−B(22) = 1.78(4); Li−O(51,61,71,81) = 1.93(4), 1.96(4), 1.94(3), 1.84(4) (see Table S-2 in the Supporting Information for detailed bond lengths and angles). The silyl carbons are drawn with circles of arbitrary radii, and the discrete $[\mathrm{Li(THF)_4}]^+$ cationic unit has been omitted for clarity.

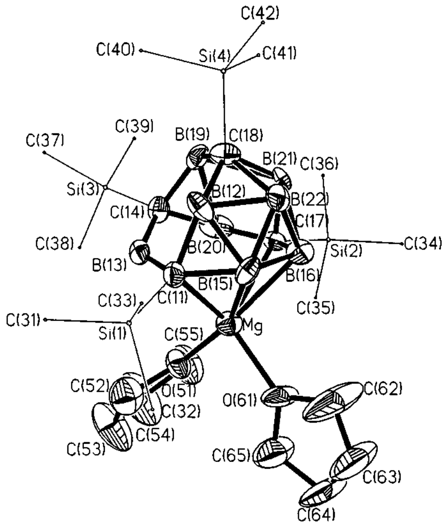

Figure 2. Perspective view of **2** drawn at the 40% probability level. Pertinent distances (Å) and angles (deg): Mg−C(11) = 2.315(10); Mg−B(13) = 2.644(12); Mg−B(15) = 2.393(12); Mg−B(16) = 2.402(11); Mg−C(17) = 2.326(9); Mg−B(20) = 2.687(14); Mg−O(51) = 2.034(7); Mg−O(61) = 2.027(8); C(11)−B(13) = 1.550(15); C(14)−B(13,19,20) = 1.568(15), 1.602(15), 1.573(17); B(19)−B(20,21) = 2.065(17), 2.064(16); B(13)−C(14)−B(19,20) = 111.7(8), 112.4(8) (see Table S-6 in the Supporting Information for detailed bond lengths and angles). The *exo*-polyhedral silyl moieties are drawn with circles of arbitrary radii, and all H atoms are omitted for clarity.

B−B "bonding distance" to be 2.000 Å, the structure of this monoanion shows three open faces; two five-membered rings (C(11)−B(12)−C(13)−B(14)−B(15) and C(11)−B(12)−B(18)−C(17)−B(16)) and one six-membered ring (C(13)−B(14)−C(20)−B(22)−C(17)−B(19)). This would give rise to three borons occupying 3*k* vertices, four occupying 4*k* vertices, and one occupying 5*k* vertices. However, this is somewhat arbitrary, especially in view of the indetermination in the structure. In addition, the 6:1:1 ^{11}B NMR spectral pattern indicates some fluxionality in solution. The structure of **1** shown in Scheme 1 shows a protonation of one of the cage carbons; this is inferred from the broad doublet at δ 34.87 ppm in the ^{13}C NMR spectrum.[7] Unfortunately, the cage hydrogens in **1** could not be located in its difference Fourier maps; however, the magnetic and NMR spectral data, coupled with the absence of bridged H's, make cage-carbon protonation the most reasonable assumption. The source of the proton is most likely the THF molecules. The structure of **2** (see Figure 2) shows that the Mg atom interacts strongly with the C(11), B(15), B(16), and C(17) atoms of one of the open faces of the carborane, giving rise to two six-membered rings (C(11)−B(13)−C(14)−B(20)−C(17)−Mg and C(11)−B(13)−C(14)−B(19)−C(18)−B(12)) and one four-membered ring (B(20)−B(19)−B(21)−C(17)). Compound **2** can be viewed as a fused polyhedron composed of an electron-precise three-coordinate boron atom (B(13)), a four-coordinate carbon atom (C(14)), a $\mathrm{(THF)_2Mg}$ unit, and an electron-deficient cluster that can be described as an *arachno*-$\mathrm{(CR)_3B_6H_9}$ fragment.[9] In this way, compound **2** represents the first example of a carborane cluster that contains both electron-precise and electron-deficient molecular units.

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Supporting Information Available: Tables of positional and thermal parameters and selected bond distances and bond angles for **1** and **2** and a figure of the structure of **1**, showing both the cationic and anionic units (14 pages). Ordering information is given on any current masthead page.

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[8] X-ray data for **1** ($\mathrm{C_{32}H_{77}B_8Si_4O_4Li}$; fw 731.7; orthorhombic, *Pca*2$_1$) and **2** ($\mathrm{C_{24}H_{60}B_8Si_4O_2Mg}$; fw 603.9; orthorhombic, *Pbca*): Data were collected at 220 and 230 K on a Siemens R3m/V diffractometer with a = 21.449(4) and 14.821(4) Å, b = 10.809(2) and 18.685(7) Å, c = 20.900(3) and 27.528(8) Å, V = 4845.6(14) and 7619(6) Å^3, Z = 4 and 8, and D_{calcd} = 1.003 and 1.053 g/cm^3 for **1** and **2**, respectively. Of the 3082 and 5301 reflections collected (2θ = 3.5−44 and 3.5−40°, respectively), 1550 and 1619 reflections were considered as observed ($F > 6.0\sigma(F)$) and were corrected for Lorentz and polarization effects. Both structures were solved by direct methods, and full-matrix least-squares refinements were performed using the SHELXTL-PLUS package of programs (Sheldrick, G. M. Structure Determination Software Programs; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990). The THF's in the cationic unit of **1** were disordered. All non-H atoms, except for those in the disordered groups in **1** and **2**, were refined anisotropically. Bonds in the disordered groups were restrained during the final cycles of refinements. Methyl and methylene H's in the nondisordered groups were placed in calculated positions in both **1** and **2**. The cage H's in only **2** could be located in difference Fourier maps and were not refined. The final refinements converged at R = 0.076 and 0.055, R_w = 0.093 and 0.060, and GOF = 2.14 and 1.19 for **1** and **2**, respectively.

[9] Williams, R. E. Personal communication to N.S.H.