Chemistry of *C*-Trimethylsilyl-Substituted Heterocarboranes. 13. Synthesis of a Lithium Salt of 2,3-Dicarba-*nido*-hexaborate(1–). Crystal Structure of the First Discrete C_2B_4 Carborane Anion

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Summary: The reaction of nido-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ with 1 equiv of t-BuLi in TMEDA at 0 °C produces exclusively the solvated monolithium salt [Li(TMEDA)$_2$]$^+$[2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$]$^-$ (I) as an off-white solid in 84% yield. The ^1H, ^7Li, ^{11}B and ^{13}C NMR spectra and IR spectra of I are all consistent with its crystal structure that is composed of discrete cation and anion units within the unit cell with the closest contact of 5.09 Å between them. Compound I crystallizes in the monoclinic space group $P2_1/c$ with the following unit cell parameters: a = 11.606(5) Å, b = 13.459(6) Å, c = 20.622(9) Å, β = 96.94(3)°, V = 3198(2) Å^3, and Z = 4. Full-matrix least-squares refinements of I converged at R = 0.068, and R_w = 0.078 for 1497 observed reflections.

Introduction

Recently, we have reported the details of the syntheses and crystal structures of a number of monosodium, sodium lithium, and dilithium complexed "carbons adjacent" *nido*-carborane anions of the type [2-($SiMe_3$)-3-(*R*)-2,3-$C_2B_4H_{6-n}$]$^{n-}$ (R = $SiMe_3$, Me, H; *n* = 1, 2), as well as the disodium and dilithium complexed "carbons apart" *nido*-carborane anion [2,4-$(SiMe_3)_2$-2,4-$C_2B_4H_4$]$^{2-}$.[1-4] In all cases, a group 1 metal occupies an apical position of a pentagonal bipyramidal MC_2B_4 cage and interacts strongly with the carborane. In the bimetallic species a second group 1 metal atom interacts with the terminal H's of the carborane cage, forming two exopolyhedral M–H–B bridge bonds. From these studies it was concluded that the reactions of group 1 metal reagents with the *nido*-C_2B_4 carboranes do not produce a simple, discrete carborane anion; instead, they yield tightly bound ion pairs or ion clusters, which seem to determine their spectral properties and reactivity.[1-4] However, in a recent attempt to purify the mixed-valence trinuclear manganacarborane {[Li(THF)][Li(TMEDA)]$_2$}{*commo*-Mn_3[2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$]$_4$}[5] by column chromatographic separation on silica gel, an off-white solid was produced whose spectroscopic data showed it to be a new monolithium carborane species.[6] In order to provide a systematic and convenient method for the preparation of this compound, we have carried out a control reaction between *t*-BuLi and *nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$. We report herein the results of this investigation, including the crystal structure of the new salt, [Li(TMEDA)$_2$]$^+$[2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$]$^-$ (**I**).

Experimental Section

Materials. 2,3-Bis(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane(8) was prepared by the methods of Hosmane *et al.*[7] Prior to use, *N,N,N,N*-tetramethylethylenediamine, TMEDA (Aldrich), was distilled *in vacuo*, and stored over sodium metal. Purity was checked by IR and NMR spectra and boiling point measurements. Benzene and *n*-hexane were dried over $LiAlH_4$ and doubly distilled before use. All other solvents were dried over 4–8-mesh molecular sieves (Aldrich) and either saturated with dry argon or degassed before use. *tert*-Butyllithium, *t*-BuLi (1.7 M solution in pentane obtained from Aldrich), was used as received.

Spectroscopic and Analytical Procedures. Proton, lithium-7, boron-11, and carbon-13 pulse Fourier transform NMR spectra, at 200, 77.7, 64.2, and 50.3 MHz, respectively, were recorded on an IBM-WP200 SY multinuclear NMR spectrometer. Infrared spectra were recorded on a Perkin-Elmer Model 283 infrared spectrophotometer and a Perkin-Elmer Model 1600 FT-IR spectrophotometer. Elemental analyses were obtained from Oneida Research Services (ORS) Inc., Whitesboro, NY.

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 IR and NMR spectra with those of the authentic samples.

Synthesis of [Li(TMEDA)$_2$]$^+$[*nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$]$^-$ (I). A tetramethylethylenediamine (TMEDA) solution (10 mL) of *nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ (0.89 g, 4.05 mmol) was cooled to −78 °C, and to this solution was slowly added *t*-BuLi (1.7 M in pentane, 2.38 mL, 4.05 mmol) *in vacuo* with constant stirring. When the addition was complete, the mixture was warmed slowly to 0 °C and stirred further for 5 h at this temperature, during which time the solution became turbid and its color changed to pale yellow. The solvents and butane

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(6) A dark-red TMEDA solution (15 mL) of trinuclear manganacarborane {[Li(THF)][Li(TMEDA)]$_2$}{*commo*-Mn_3[2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$]$_4$} (1.12 g, 0.82 mmol)[5] was slowly poured, in an inert atmosphere, onto silica gel packed in a column of 15-cm length and was eluted with a solvent mixture of dry *n*-hexane (70%) and dry TMEDA (30%) to collect a clear, colorless solution. The colored band that remained in the column could not be eluted even after several elutions with a variety of organic solvents or their mixtures. After removal of solvents from the eluate *in vacuo*, an off-white solid remained in the flask whose spectroscopic data are identical to those of I discussed in this paper (0.49 g, 1.07 mmol, 43% yield). A recrystallization of the solid from a solution of *n*-hexane (80%) and benzene (20%) gave transparent platelike crystals: Wang, Y.; Zhang, H.; Oki, A. R.; Maguire, J. A.; Hosmane, N. S.; Ro, H.; Hatfield, W. E. Unpublished results.

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Table I. Crystallographic Data[a] for $[Li(TMEDA)_2]^+[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_5]^-$ (I)

formula	$C_{20}H_{55}N_4B_4LiSi_2$
fw	458.0
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	11.606(5)
b, Å	13.459(6)
c, Å	20.622(9)
β, deg	96.94(3)
V, Å^3	3198(2)
Z	4
D_{calcd}, g cm^{-3}	0.951
abs coeff, mm^{-1}	0.120
cryst dmns, mm	0.25 × 0.35 × 0.05
scan type	$\theta/2\theta$
min, max scan sp in ω, deg min^{-1}	6.01, 26.04
2θ range, deg	3.5–40.0
T, K	230
decay, %	0
no. of data collcd	2993
no. of obsd reflctns, $I > 3.0\sigma(I)$	1497
no. of params refined	280
GOF	2.22
g[c]	0.0005
$\Delta\rho_{max,\ min}$, e/Å^3	0.23, –0.18
R[b]	0.068
R_w	0.078

[a] Graphite monochromatized Mo Kα radiation, λ = 0.710 73 Å. [b] $R = \sum||R_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(F_o - F_c)^2/\sum w(F_o)^2]^{1/2}$. [c] $w = 1/[\sigma^2(F_o) + g(F_o)^2]$.

(not measured) were then pumped out of the reaction flask at room temperature to collect an off-white solid, identified as **I**, in 84% yield (1.56 g, 3.41 mmol). A recrystallization of the solid from a solution of dry *n*-hexane (80%) and anhydrous benzene (20%) gave transparent platelike crystals whose X-ray analysis confirmed the presence of discrete $[Li(TMEDA)_2]^+$ cations and [*nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5]^-$ anions, discussed in the following section. Since **I** is extremely sensitive to air and/or moisture, reproducible microanalytical data could not be obtained, even for single-crystal samples. The spectroscopic data for **I**: ^{1}H NMR (C_6D_6, relative to external Me_4Si) δ 3.32 [br, ill-defined peak, 2 H, basal H_t, $^1J(^1H\text{–}^{11}B)$ = unresolved], 1.84 [br, ill-defined peak, 1 H, basal H_t, $^1J(^1H\text{–}^{11}B)$ = unresolved], 0.83 [s (br), 8 H, CH_2, TMEDA], 0.76 [s (br), 24 H, CH_3, TMEDA], –0.67 [s, 18 H, CH_3, $SiMe_3$], –2.1 [q (br), 1 H, apical H_t, $^1J(^1H\text{–}^{11}B)$ = 144 Hz], –5.63 [s, 1 H, BHB (bridge)]; ^{7}Li NMR (C_6D_6, relative to external aqueous $LiNO_3$) δ –1.88 [s (v br), *exo*-cage $Li^+(TMEDA)_2$]; ^{11}B NMR (C_6D_6, relative to external $BF_3{\cdot}OEt_2$) δ 15.22 [br, ill-defined peak, 2 B, basal BH], –4.09 [br, ill-defined peak, 1 B, basal BH], –50.43 [d (br), 1 B, apical BH, $^1J(^{11}B\text{–}^1H)$ = 145 Hz]; ^{13}C NMR (C_6D_6, relative to external Me_4Si) δ 107.10 [s (br), 2 C, cage carbons (SiCB)], 56.94 [t, 4 C, CH_2, TMEDA, $^1J(^{13}C\text{–}^1H)$ = 134.04 Hz], 46.32 [q, 8 C, CH_3, TMEDA, $^1J(^{13}C\text{–}^1H)$ = 135 Hz], 3.81 [q, 6 C, CH_3, $SiMe_3$, $^1J(^{13}C\text{–}^1H)$ = 118.0 Hz]; IR (cm^{-1}, C_6H_6 vs C_6H_6) 3092 (s, s), 3067 (s, s), 3026 (s, s), 2952 (sh), 2895 (sh), 2830 (s, s), 2789 (s, s) [ν(C–H)], 2519 (s, br), 2470 (s, br), 2371 (sh) [ν(B–H)], 2314 (w, s), 2273 (m, s), 2207 (w, s), 1956 (vs, s) [B–H–B (bridge)], 1813 (vvs, s), 1751 (w, s), 1665 (w, s), 1612 (w, s), 1544 (m, br), 1507 (m, br), 1431 (s, br) [δ(C–H) asym], 1356 (w, s), 1240 (m, br) [δ(C–H) sym], 1158 (m, s), 1128 (m, s), 1098 (m, br), 1067 (m, br), 1015 (m, s), 948 (m, s), 864 (s, s), 834 (s, s) [ρ(C–H)], 794 (w, s), 748 (m, s), 675 (s, s), 496 (m, s).

Crystal Structure Analysis of $[Li\{(Me_2NCH_2)_2\}_2]^+[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_5]^-$ (I). Colorless, platelike crystals of **I** were grown from a saturated solution of *n*-hexane and benzene *in vacuo*. Since the crystals change to white amorphous powders upon brief exposure to air and/or moisture, they were sealed with an epoxy resin and mounted rapidly on a Siemens R3m/V diffractometer. The pertinent crystallographic data are summarized in Table I. The final unit cell parameters were obtained by a least-squares fit of 24 accurately centered reflections measured in the range $15° < 2\theta < 30°$ and the intensity data were collected at 230 K in the range $3.5° \le 2\theta \le 40.0°$ which were corrected for Lorentz and polarization effects. Three standard reflections monitored after every 150 reflections did not show any significant change in intensity during the data collection. The structure was solved by direct methods using the SHELXTL-Plus package.[8] Full-matrix least-squares refinements were performed, and the scattering factors were taken from ref 9. All non-H atoms were refined anisotropically. Carborane cage-H atoms were located in DF maps and were not refined. The methyl- and methylene-H atoms were calculated on the "ride mode" with fixed isotropic temperature factors (U = 0.08 Å^2). The final cycles of refinement converged at R = 0.068, R_w = 0.078, and GOF = 2.22 for 1497 observed reflections. Maximum and minimum residuals, 0.23 and –0.18 e/Å^3, respectively, were shown in the final difference Fourier maps. The final atomic coordinates are given in Table II, while bond lengths and bond angles are presented in Table III.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for I

	x	y	z	U(eq)[a]
Li	4848(11)	2353(9)	3701(6)	62(5)
Si(1)	878(3)	3390(2)	852(2)	99(1)
Si(2)	380(2)	859(2)	1539(1)	89(1)
C(1)	1947(7)	2456(6)	1187(4)	61(3)
C(2)	1766(6)	1473(6)	1467(3)	55(3)
B(3)	2883(9)	886(8)	1573(5)	77(5)
B(4)	3921(8)	1565(11)	1280(5)	93(5)
B(5)	3200(12)	2604(9)	1086(6)	102(6)
B(6)	2529(8)	1510(8)	829(4)	72(4)
C(7)	1554(10)	4609(7)	893(7)	215(9)
C(8)	–371(10)	3540(8)	1301(6)	179(7)
C(9)	316(8)	3154(7)	14(5)	135(5)
C(10)	608(9)	–477(7)	1693(6)	186(8)
C(11)	–218(8)	1281(10)	2257(5)	158(7)
C(12)	–701(8)	957(8)	816(5)	127(5)
N(21)	3741(8)	1112(7)	3762(4)	88(4)
N(22)	3397(7)	3217(6)	3436(4)	72(3)
C(23)	2629(11)	1566(12)	3570(7)	145(8)
C(24)	2531(10)	2542(13)	3500(7)	172(8)
C(25)	3735(11)	752(10)	4404(6)	205(9)
C(26)	3818(9)	271(8)	3354(6)	147(6)
C(27)	3306(9)	4045(10)	3844(6)	161(7)
C(28)	3251(8)	3578(8)	2790(5)	136(6)
N(31)	6215(6)	2164(6)	3139(4)	73(3)
N(32)	6073(7)	2815(7)	4478(4)	80(4)
C(33)	7250(8)	2268(8)	3637(6)	107(5)
C(34)	7089(9)	2953(9)	4133(6)	123(6)
C(35)	6214(8)	2948(7)	2656(5)	101(5)
C(36)	6315(7)	1235(7)	2796(5)	110(5)
C(37)	6277(9)	2066(7)	4973(5)	130(5)
C(38)	5902(8)	3745(8)	4799(5)	116(5)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results and Discussion

The reaction of *nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ with only 1 equiv of *t*-BuLi in TMEDA at 0 °C produces an off-white solid, identified as the solvated monolithium salt, $[Li(TMEDA)_2]^+$[*nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5]^-$ (**I**), in 84% yield. The analogous sodium compound can be obtained from the reaction of a TMEDA solution of the *nido*-carborane with solid NaH.[2] The monosodium compound shows no tendency to react further with NaH, even at elevated temperatures.[10] On the other hand, strong soluble bases, such as *t*-BuLi, can remove both of the bridged hydrogens from these same *nido*-carboranes, to give the corresponding dilithium compounds.[2,7a] Therefore, **I** can be considered as an intermediate in the double deprotonation reaction. The monosodium carboranes also react readily with *t*-BuLi to yield the corresponding

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Table III. Bond Lengths (Å) and Bond Angles (deg) for I

Li–N(21)	2.120(16)	Li–N(22)	2.065(15)
Li–N(31)	2.090(15)	Li–N(32)	2.103(14)
C(1)–C(2)	1.468(12)	C(1)–B(5)	1.506(16)
C(1)–B(6)	1.657(14)	C(2)–B(3)	1.512(13)
C(2)–B(6)	1.673(12)	B(3)–B(4)	1.682(16)
B(3)–B(6)	1.753(14)	B(4)–B(5)	1.654(18)
B(4)–B(6)	1.765(13)	B(5)–B(6)	1.720(16)
Si(1)–C(1)	1.842(8)	Si(1)–C(7)	1.815(10)
Si(1)–C(8)	1.823(13)	Si(1)–C(9)	1.799(10)
Si(2)–C(2)	1.830(8)	Si(2)–C(10)	1.839(10)
Si(2)–C(11)	1.802(11)	Si(2)–C(12)	1.835(9)
N(21)–C(23)	1.439(16)	N(21)–C(25)	1.410(15)
N(21)–C(26)	1.421(15)	N(22)–C(24)	1.373(17)
N(22)–C(27)	1.408(15)	N(22)–C(28)	1.410(14)
C(23)–C(24)	1.324(23)	N(31)–C(33)	1.490(12)
N(31)–C(35)	1.451(13)	N(31)–C(36)	1.448(13)
N(32)–C(34)	1.460(14)	N(32)–C(37)	1.435(13)
N(32)–C(38)	1.441(14)	C(33)–C(34)	1.405(17)
B(3)–H(34)	1.22	B(4)–H(34)	1.23
N(21)–Li–N(22)	88.8(6)	N(21)–Li–N(31)	116.3(7)
N(22)–Li–N(31)	124.8(7)	N(21)–Li–N(32)	123.1(7)
N(22)–Li–N(32)	119.3(7)	N(31)–Li–N(32)	88.3(6)
Si(1)–C(1)–C(2)	129.8(6)	Si(1)–C(1)–B(5)	118.4(7)
C(2)–C(1)–B(5)	111.1(8)	Si(1)–C(1)–B(6)	130.5(5)
C(2)–C(1)–B(6)	64.4(6)	B(5)–C(1)–B(6)	65.6(7)
Si(2)–C(2)–C(1)	127.4(6)	Si(2)–C(2)–B(3)	119.9(6)
C(1)–C(2)–B(3)	111.5(7)	Si(2)–C(2)–B(6)	129.1(5)
C(1)–C(2)–B(6)	63.3(6)	B(3)–C(2)–B(6)	66.6(6)
C(2)–B(3)–B(4)	107.6(8)	C(2)–B(3)–B(6)	61.1(6)
B(4)–B(3)–B(6)	61.8(6)	B(3)–B(4)–B(5)	100.5(8)
B(3)–B(4)–B(6)	61.1(6)	B(5)–B(4)–B(6)	60.3(7)
C(1)–B(5)–B(4)	108.9(9)	C(1)–B(5)–B(6)	61.4(7)
B(4)–B(5)–B(6)	63.1(7)	C(1)–B(6)–C(2)	52.3(5)
C(1)–B(6)–B(3)	92.5(6)	C(2)–B(6)–B(3)	52.3(5)
C(1)–B(6)–B(4)	97.4(7)	C(2)–B(6)–B(4)	97.2(6)
B(3)–B(6)–B(4)	57.1(6)	C(1)–B(6)–B(5)	53.0(6)
C(2)–B(6)–B(5)	92.6(7)	B(3)–B(6)–B(5)	95.2(7)
B(4)–B(6)–B(5)	56.6(7)	C(1)–Si(1)–C(7)	109.3(5)
C(1)–Si(1)–C(8)	115.2(5)	C(7)–Si(1)–C(8)	104.0(5)
C(1)–Si(1)–C(9)	112.9(4)	C(7)–Si(1)–C(9)	108.0(6)
C(8)–Si(1)–C(9)	106.8(5)	C(2)–Si(2)–C(10)	110.3(4)
C(2)–Si(2)–C(11)	110.7(4)	C(10)–Si(2)–C(11)	103.2(6)
C(2)–Si(2)–C(12)	115.0(4)	C(10)–Si(2)–C(12)	106.3(5)
C(11)–Si(2)–C(12)	110.6(4)	Li–N(21)–C(23)	100.3(8)
Li–N(21)–C(25)	113.5(8)	C(23)–N(21)–C(25)	107.4(10)
Li–N(21)–C(26)	120.7(8)	C(23)–N(21)–C(26)	107.0(9)
C(25)–N(21)–C(26)	106.8(9)	Li–N(22)–C(24)	100.7(8)
Li–N(22)–C(27)	114.0(7)	C(24)–N(22)–C(27)	111.0(10)
Li–N(22)–C(28)	116.5(7)	C(24)–N(22)–C(28)	108.2(9)
C(27)–N(22)–C(28)	106.4(8)	N(21)–C(23)–C(24)	120.9(12)
N(22)–C(24)–C(23)	127.7(12)	Li–N(31)–C(33)	102.0(7)
Li–N(31)–C(35)	110.8(7)	C(33)–N(31)–C(35)	109.8(7)
Li–N(31)–C(36)	119.1(7)	C(33)–N(31)–C(36)	108.2(7)
C(35)–N(31)–C(36)	106.6(7)	Li–N(32)–C(34)	100.3(7)
Li–N(32)–C(37)	111.9(7)	C(34)–N(32)–C(37)	111.3(8)
Li–N(32)–C(38)	119.3(7)	C(34)–N(32)–C(38)	106.1(8)
C(37)–N(32)–C(38)	107.6(8)	N(31)–C(33)–C(34)	113.4(8)
N(32)–C(34)–C(33)	117.1(9)	B(3)–H(34)–B(4)	87.0

sodium/lithium mixed species.[11] It has been suggested that the sensitivity of the stoichiometry of the deprotonation reaction to the base is more a function of the heterogeneous nature of the NaH reaction than it is of any difference in base strength;[2] the present results support that contention. The ^1H, ^{13}C, and ^{11}B NMR spectra of 1-Na(TMEDA)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$, are essentially the same as those found for **I**.[2] Except for those resonances due to the THF and TMEDA molecules, this similarity is also found in the THF-solvated 1-Na(THF)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$.[2]

Figure 1 shows the relative atom positions within the $Li(TMEDA)_2^+$ and [2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$]$^-$ ions, and Figure 2 shows the arrangement of these ions in the unit cell. The distance between the Li and the C_2B_3 centroid of the ion pair shown in Figure 1 is 5.27 Å, while the distance of closest approach between a lithium and a boron atom of the next closest cage is 5.49 Å. From these figures and distances it is apparent that the best description of the structure of **I** is that of an array of discrete cations and anions. This structure is quite different from that of either the THF- or the TMEDA-solvated monosodium carboranes in which the group 1 metal resides above the open face of the carborane and interacts directly with the cage atoms, without an intervening solvent molecule.[2] Direct metal–carborane interaction was also found in the TMEDA-solvated dilithium compound, *closo-exo*-4,5-[$(\mu$-H$)_2$Li(TMEDA)]-1-Li(TMEDA)-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_4$, in which an apical lithium interacts directly with a single TMEDA molecule and the carborane cage, while the other lithium occupies an exopolyhedral position above the trigonal face formed by three boron atoms equivalent to B(4), B(5), and B(6) in Figure 1. Evidence for nonequivalent lithiums was also found in the ^7Li NMR spectrum of the dilithium compound, in both C_6D_6 and TMEDA solutions. These spectra showed two resonances, one at $\delta = -1.60$ ppm, ascribed to the exopolyhedral lithium, and another at $\delta = -6.08$ ppm, due to the apical lithium which interacts directly with the π-electron system of the carborane.[2] The ^7Li NMR spectrum of **I** shows only a single resonance at $\delta = -1.88$ ppm, very close to that of the exopolyhedral lithium in the corresponding dilithiacarborane, indicating that in solution the lithium atom of **I** does not interact directly with the carborane ligand. In solvents of low dielectric constant, such as benzene and TMEDA, ion pairing should be prevalent; therefore, the ^7Li NMR spectrum of **I** indicates, at best, a solvent separated lithium–carborane ion pair. This is consistent with the solid state structure of **I** which shows the lithium participating in the equivalent of a solvent separated ion pair, in which the closest approaches of the lithium to any

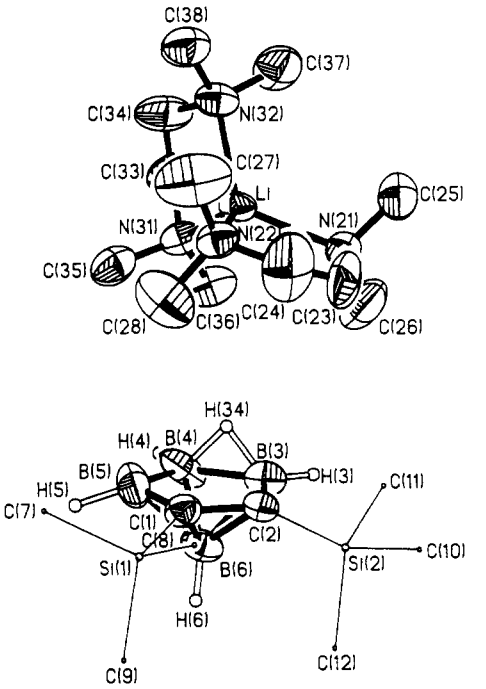

Figure 1. Perspective view of discrete $[Li(TMEDA)_2]^+$ cationic and [*nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$]$^-$ anionic units of **I** showing the atom numbering scheme with thermal ellipsoids, drawn at the 40% probability level. The atoms of the $SiMe_3$ groups are drawn with the circles of arbitrary radii, and the methyl and methylene H's are omitted for clarity.

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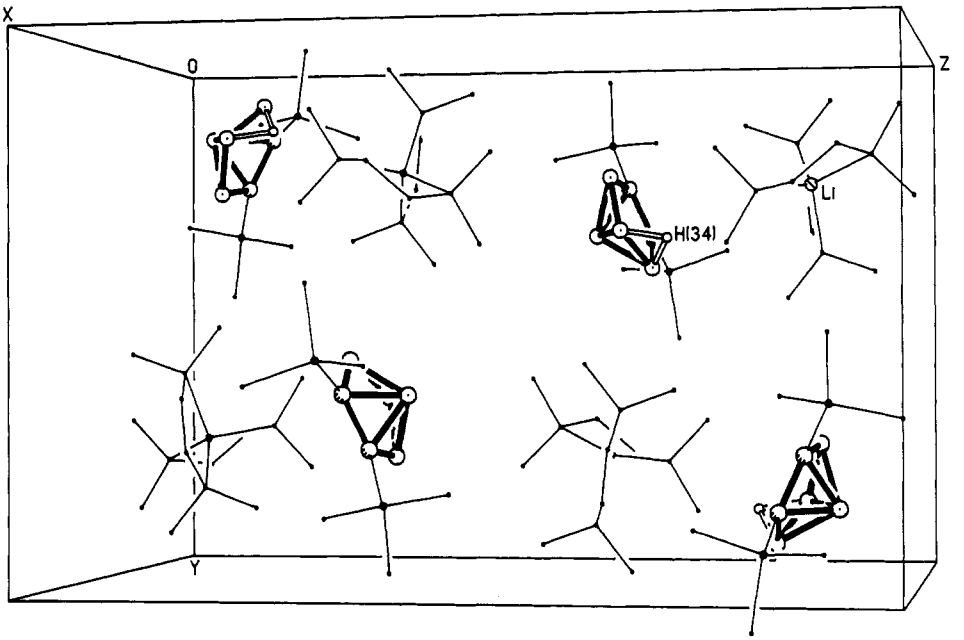

Figure 2. Packing diagram of **I** exhibiting discrete cationic and anionic units in the unit cell.

carborane cage atom are the Li–B(3) and Li–B(4) distances of 5.09 Å. The upfield ^{7}Li NMR resonance, in the $\delta = -5$ to −6 ppm region, may be taken as diagnostic for the existence of intimate ion pairing between the lithium and carborane ions. Such ion pairing exists in the dilithiacarborane, in either benzene or TMEDA solvents,[2] but is absent in the monolithium compound, **I**. It is of interest to note that in the formation of **I** by the protonation of the trinuclear manganacarborane, $\{[Li(THF)][Li(TMEDA)]_2\}\{commo\text{-}Mn_3[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_4\}$,[5] both THF and TMEDA molecules are available for coordination to the lithium but only the TMEDA-solvated compound was isolated. Therefore, unlike that found for monosodium carboranes, protonation of the lithiacarboranes in TMEDA destabilizes the ion pair to the extent that a more extensively solvated lithium, such as that shown in Figure 1, is more stable, despite the weaker, solvent separated ion pair. Compound **I**, dissolved in THF, undergoes rapid deprotonation in the presence of NaH to form the mixed-metal lithium/sodium carborane (**II**). Although the structure has not been confirmed by X-ray diffraction, its solution spectra are consistent with the formula shown in eq 1.[12] When TMEDA is used as a solvent, the second

$$\underset{\mathbf{I}}{[Li(TMEDA)_2]^+[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_5]^-} + NaH(s) \xrightarrow[25\ ^\circ C]{\text{THF or TMEDA}} H_2(g) + \underset{\mathbf{II}}{[Na(L)_n]^+[Li(TMEDA)_2]^+[2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]^{2-}}$$

$$n = 1\text{–}4;\ L = \text{THF or TMEDA} \qquad (1)$$

deprotonation is much slower, due to the low solubility of **I** in that solvent. As pointed out earlier, the 1:1 stoichiometry of the heterogeneous reaction of *nido*-$(CR)_2B_4H_6$ with excess NaH is a well-established and curious fact of carborane chemistry.[10] Use of stronger bases, such as KH, does not alter this stoichiometry.[13] The second deprotonation of **I** by NaH strongly supports the argument that steric factors, rather than base strength, dictate the stoichiometry of these heterogeneous reactions. When the neutral *nido*-carborane reacts with NaH, the product formed is a tight, intimate ion pair in which a partially solvated sodium interacts directly with the C_2B_3 carborane face.[2] The structure of this ion pair prevents the second bridged hydrogen from reacting with a hydride site on the solid base. On the other hand, the weaker solvent separated ion pair, as shown in Figure 1, can dissociate, or rearrange, so that the remaining bridge hydrogen can interact directly with a hydride site and be removed, as described in eq 1.

There is some question as to the relative solvating abilities of TMEDA and THF, with increasing evidence favoring the latter.[14] Therefore, it is probably an oversimplification to rationalize the differences in the extent of solvation of the metals of the group 1 metallacarboranes in terms of the relative solvating ability of THF and TMEDA. However, our results do show that ^{7}Li NMR spectroscopy can be used to probe the nature of the ion pair interactions that exist between lithium and carborane anions and that, as found in other organometallic systems, TMEDA reduces the extent of ion association which, in turn, affects their reactivity.[15]

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Supplementary Material Available: Tables of anisotropic displacement parameters (Table S-1) and H atom coordinates and isotropic displacement coefficients (Table S-2) for **I** (2 pages). Ordering information is given on any current masthead page.

OM9303257

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