Chemistry of *C*-Trimethylsilyl-Substituted Heterocarboranes. 16. Synthesis and Crystal Structure of a Discrete, Zwitterionic, Monomeric Monosodium Salt of 2,3-Dicarba-*nido*-hexaborate(1−): Conversion to the First "Carbons Adjacent" Disodium Compound

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*Summary: A TMEDA-solvated, zwitterionic monoso-
dium salt, nido-exo-4,5-[(μ-H)₂Na(TMEDA)₂]-2-(SiMe₃)-
3-(Me)-2,3-C₂B₄H₅ (II), was prepared and characterized
by ¹H, ¹¹B, and ¹³C NMR spectra, IR spectra and X-ray
crystallography. The presence of an exposed B—H—B
bridge hydrogen on the open C₂B₃ face of the carborane
in the discrete monomeric unit allowed II to undergo
further deprotonation by NaH to produce, in 94% yield,
the first disodium compound of the 2,3-C₂B₄ carborane
(carbons adjacent) dianion, closo-exo-4,5-[(μ-H)₂Na-
(TMEDA)]-1-Na(TMEDA)-2-(SiMe₃)-3-(Me)-2,3-C₂B₄H₄
(III).*

Introduction

The dianions of the C_2B_4 carboranes have been shown to be useful synthons in the preparation of both main group and transition metal metallacarboranes.[1] These dianions can be formed by the removal of the two bridged hydrogens of the neutral *nido*-$(CR)_2B_4H_6$ (R = *exo*-polyhedral substituent or H) with a suitable base. The monoanion is conveniently obtained by the heterogeneous reaction of the particular *nido*-carborane with the base NaH.[2,3] The unusual fact about this reaction is its 1:1 base-to-carborane stoichiometry. Neither the use of excess NaH at 200 °C nor the substitution of a stronger base, such as KH, gives any hint of the removal of the second bridge hydrogen of the carborane.[2–4] On the other hand, soluble bases, such as BuLi, react readily with either the monosodium salt or the neutral *nido*-carborane to form the dianion.[5] A possible explanation for this difference in behavior was provided by the recent reports on the structures of the monosodium compounds, 1-Na(L)-2,3-(SiMe₃)₂-2,3-C₂B₄H₅ [L = C₄H₈O (THF) or {(CH₃)₂NCH₂}₂ (TMEDA)], that showed the THF-solvated species to be an extended array of Na₂-(C₂B₄)₂ dimers that are stacked on top of one another to give a series of −[carborane]⁻−Na⁺−[carborane]⁻ chains, while the TMEDA-solvated analogue was a

discrete dimeric cluster (see Scheme 1).[6,7] Since previous work had shown that the deprotonation of the neutral *nido*-carborane by NaH occurred at the surface of the metal hydride through the direct reaction of a B—H—B$_{bridge}$ hydrogen of the carborane with a surface H⁻ site in the MH (M = Na or K) lattice,[4] it was assumed that a second deprotonation would also occur at the surface of MH.[7] It was argued that the monosodium carborane would exist in solution as an intimate ion pair and that the second bridge hydrogen in such an ion pair would be so effectively shielded from the metal surface by the capping metal unit and the terminal carborane hydrogens that it would not react further with the solid base. This steric shielding would not be important if the base was dispersed in solution. While this argument can account for the different carborane-base stoichiometries, it is not unassailable and raises several questions: (i) Would it be possible to prepare a discrete monomeric sodium salt, [Na]⁺[2,3-(CR)₂B₄H₅]⁻, in which the Na⁺ ion does not interact with the carborane in a capping position? (ii) If such species do exist, would they react further with NaH or KH in a heterogeneous reaction to undergo a second deprotonation and form the corresponding dianion? Here, we provide the answers, unequivocally, to these questions with the synthesis and crystal structure of a zwitterionic, TMEDA-separated, discrete, monomeric monosodium salt, *nido-exo*-4,5-[(μ-H)₂Na(TMEDA)₂]-2-(SiMe₃)-3-(Me)-2,3-C₂B₄H₅ (**II**), which could be converted to the corresponding disodium compound by reaction with NaH.

Experimental Section

Materials. 2-(Trimethylsilyl)-3-methyl-2,3-dicarba-*nido*-hexaborane(8) was prepared by the methods of Hosmane *et al.*[8] The synthetic route for the preparation of [*nido*-1-Na-(TMEDA)-2-(SiMe₃)-3-(Me)-2,3-C₂B₄H₅]₂ (**I**) was described elsewhere.[7] Prior to use, *N,N,N,N*-tetramethylethylenediamine, TMEDA (Aldrich), was distilled *in vacuo*, and stored over sodium metal. The purity was checked by IR and NMR spectra and boiling point measurements. Benzene and *n*-

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Scheme 1

● = H; TMEDA = (Me₂NCH₂)₂
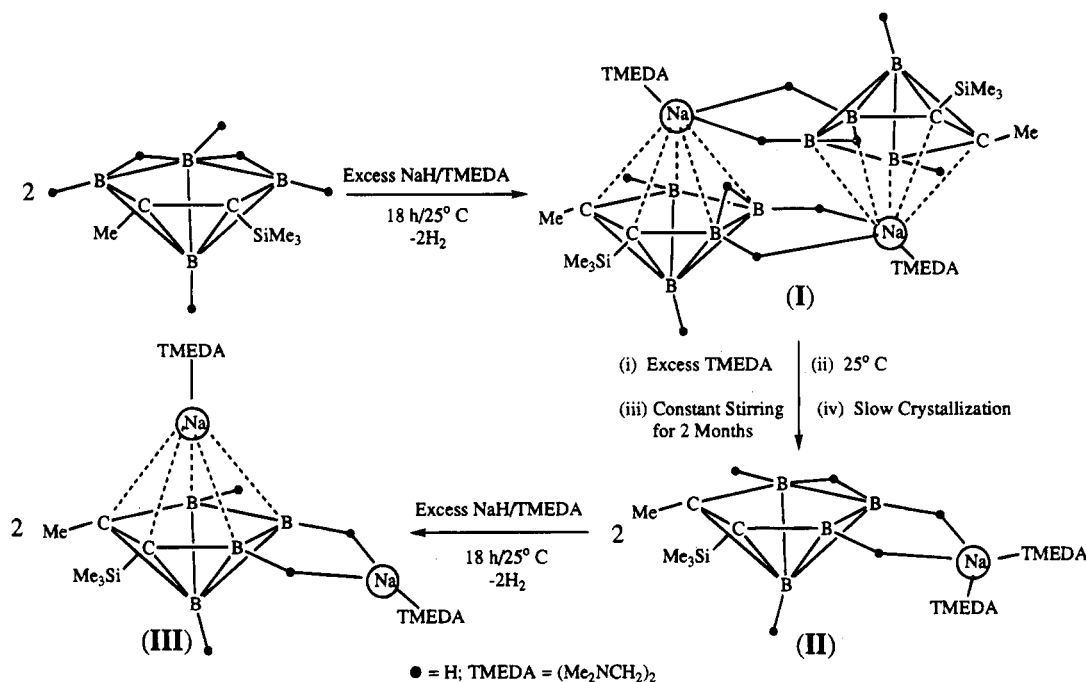
hexane were dried over LiAlH₄ and doubly distilled before use. All other solvents were dried over 4–8-mesh molecular sieves (Aldrich) and either saturated with dry argon or degassed before use. Prior to immediate use, NaH (Aldrich) in a mineral oil dispersion was washed repeatedly with dry *n*-pentane.

Spectroscopic and Analytical Procedures. Proton, boron-11, and carbon-13 pulse Fourier transform NMR spectra, at 200, 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 E+R Microanalytical Laboratory, Inc., Corona, 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 *nido-exo*-**4,5-[(μ-H)ₓNa(TMEDA)₂]-2-(SiMe₃)-3-(Me)-2,3-C₂B₄H₅ (II).** A 2.23-mmol (1.34-g) sample of dimeric [*nido*-1-Na(TMEDA)-2-(SiMe₃)-3-(Me)-2,3-C₂B₄H₅]₂ (I)[7] was dissolved in 15 mL of anhydrous TMEDA, and the resulting turbid solution was stirred constantly over a period of 2 months at room temperature, during which time the solution turned clear. At this point, the stirring was stopped and the solution was concentrated to 5-mL volume and allowed to stand at room temperature *in vacuo*. After several weeks, colorless needle-shaped crystals grew out of the TMEDA solution which were filtered out *in vacuo* and washed gently with a minimum quantity of anhydrous *n*-hexane to collect a colorless, extremely air-sensitive crystalline solid, identified as *nido-exo*-4,5-[(μ-H)₂Na(TMEDA)₂]-2-(SiMe₃)-3-(Me)-2,3-C₂-B₄H₅, **II**, in 99% yield (1.83 g, 4.41 mmol; sparingly soluble in TMEDA, C₆D₆, THF, and *n*-hexane). Spectroscopic data for **II**: ¹H NMR (C₆D₆, external Me₄Si) δ = 2.41 [s, 3H, C_cage—Me], 2.00 [s, 8H, CH₂, TMEDA], 1.92 [s, 24H, Me, TMEDA], 0.42 [s, 9H, SiMe₃], −4.41 [s (br), 1H, B—H—B_bridge] ; ¹¹B NMR (C₆D₆, external BF₃·OEt₂) δ = 16.30 [br, ill-defined peak, 1B, basal BH, ¹J(¹¹B—¹H) = unresolved], 10.64 [br, ill-defined peak, 1B, basal BH, ¹J(¹¹B—¹H) = unresolved], 0.00 [br, ill-defined peak, 1B, basal BH, ¹J(¹¹B—¹H) = unresolved], −45.5 [d (br),

1B, apical BH, ¹J(¹¹B—¹H) = 152.3 Hz]; ¹³C NMR (C₆D₆, external Me₄Si) δ = 126.7 [s (br), cage carbons (SiCB)], 101.9 [s (br), cage carbons (CCB)], 57.1 [t, 4C, CH₂, TMEDA, ¹J(¹³C—¹H) = 132.8 Hz], 46.0 [q, 8C, Me, TMEDA, ¹J(¹³C—¹H) = 134.8 Hz], 23.8 [q (br), 1C, C_cage—Me, ¹J(¹³C—¹H) = 125 Hz], 2.19 [q (br), 3C, SiMe₃, ¹J(¹³C—¹H) = 117.2 Hz]; IR (cm⁻¹; C₆D₆ vs C₆D₆) 2539 (vs), 2473 (vs, br), 2428 (sh), 2330 (sh) [ν(B—H)], 1928 (w, vbr) [B—H—B_bridge]. Anal. Calcd for C₁₈H₄₉B₄N₄-NaSi: C, 51.98; H, 11.88; N, 13.47. Found: C, 51.69; H, 11.92; N, 13.63.

Synthesis of *closo-exo*-**4,5-[(μ-H)ₓNa(TMEDA)]-1-Na(T-MEDA)-2-(SiMe₃)-3-(Me)-2,3-C₂B₄H₄ (III).** In a procedure identical with that employed for the synthesis of **I**,[7] a 4.0-mmol (1.66-g) sample of **II** was reacted with 8.3 mmol (0.2 g) of NaH in TMEDA at 25 °C for 18 h to isolate an extremely air- and moisture-sensitive off-white solid, identified as *closo-exo*-4,5-[(μ-H)₂Na(TMEDA)]-1-Na(TMEDA)-2-(SiMe₃)-3-(Me)-2,3-C₂B₄-H₄ (**III**), in 94% yield (1.65 g, 3.76 mmol; reasonably soluble in TMEDA and C₆D₆, and sparingly soluble in *n*-hexane, mp 99–101 °C). The solid product was then recrystallized from dry benzene solution to obtain air-sensitive microcrystals of **III**. The spectroscopic data for **III**: ¹H NMR (C₆D₆, external Me₄Si) δ = 2.29 [s, 3H, C_cage—Me], 2.02 [s, 8H, CH₂, TMEDA], 1.94 [s, 24H, Me, TMEDA], 0.29 [s, 9H, SiMe₃]; ¹¹B NMR (C₆D₆, external BF₃·OEt₂) δ = 15.0 [v br, ill-defined peak, 1B, basal BH, ¹J(¹¹B—¹H) = unresolved], 8.47 [br, ill-defined peak, 1B, basal BH, ¹J(¹¹B—¹H) = unresolved], 0.00 [br, ill-defined peak, 1B, basal BH, ¹J(¹¹B—¹H) = unresolved], −46.22 [d (br), 1B, apical BH, ¹J(¹¹B—¹H) = 148.4 Hz]; ¹³C NMR (C₆D₆, external Me₄Si) δ = 125.8 [s (br), cage carbons (SiCB)], 101.4 [s (br), cage carbons (CCB)], 57.5 [t, 4C, CH₂, TMEDA, ¹J(¹³C—¹H) = 130.9 Hz], 46.3 [q, 8C, Me, TMEDA, ¹J(¹³C—¹H) = 132.8 Hz], 23.9 [q (br), 1C, C_cage—Me, ¹J(¹³C—¹H) = 123 Hz], 2.62 [q (br), 3C, SiMe₃, ¹J(¹³C—¹H) = 115.2 Hz]; IR (cm⁻¹; C₆D₆ vs C₆D₆) 2530 (s, s), 2460 (m, br), 2430 (sh), 2360 (sh) [ν(B—H)]. Anal. Calcd for C₁₈H₄₈B₄N₄Na₂Si·C₆H₆: C, 55.87; H, 10.55; N, 10.86. Found: C, 56.01; H, 10.97; N, 11.13.

Crystal Structure Analysis of *nido-exo*-**4,5-[(μ-H)ₓNa-(TMEDA)₂]-2-(SiMe₃)-3-(Me)-2,3-C₂B₄H₅, (II).** Colorless, needle shaped crystals of **II** were grown from a saturated solution of TMEDA. 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

Table 1. Crystallographic Data[a] for *nido-exo*-4,5-[(μ-H)₂Na(TMEDA)₂]-2-(SiMe₃)-3-(Me)-2,3-C₂B₄H₅ (II)

formula	C₁₈H₄₉B₄N₄NaSi
fw	415.9
cryst syst	monoclinic
space group	P2₁/n
a, Å	14.569(4)
b, Å	13.593(4)
c, Å	14.593(5)
β, deg	94.11(2)
V, Å³	2887(1)
Z	4
D_calcd, g cm⁻³	0.957
abs coeff, mm⁻¹	0.106
crystal dmns, mm	0.10 × 0.30 × 0.05
scan type	ω
scan sp in ω: min, max	6.51, 29.30
2θ range, deg	3.5–42.0
T, K	230
decay, %	0
no. of data collected	3235
no of obsd reflctns, I > 3.0σ(I)	1788
no. of params refined	268
GOF	1.61
g[c]	0.0010
Δρ_max,min, e/Å³	+0.21, −0.25
R[b]	0.053
wR	0.070

[a] Graphite monochromatized Mo Kα radiation, λ = 0.710 73 Å. [b] R = Σ||F_o| − |F_c||/Σ|F_o|, wR = [Σw(F_o − F_c)²/Σw(F_o)²]^{1/2}. [c] w = 1/[σ²(F_o) + g(F_o)²].

Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³)

	x	y	z	U(eq)[a]
Na	5925(1)	5890(1)	7531(1)	54(1)
Si	3767(1)	1380(1)	7872(1)	63(1)
B(1)	4997(4)	3041(5)	7060(4)	54(2)
C(2)	4382(3)	2573(3)	7899(3)	46(2)
C(3)	4026(3)	3490(3)	7509(3)	51(2)
B(4)	4744(5)	4271(4)	7397(5)	60(3)
B(5)	5720(5)	3807(5)	7756(5)	59(3)
B(6)	5415(5)	2637(5)	8138(4)	60(3)
C(7)	3062(4)	3546(4)	7088(4)	74(2)
C(8)	4453(5)	459(5)	8530(6)	137(4)
C(9)	2674(5)	1491(4)	8441(4)	95(3)
C(10)	3514(5)	892(5)	6708(5)	113(3)
N(11)	5691(3)	7278(4)	6371(4)	75(2)
N(12)	6880(4)	5510(4)	6153(3)	70(2)
C(13)	6125(6)	6992(6)	5536(5)	113(4)
C(14)	6978(5)	6448(6)	5709(5)	101(3)
C(15)	4739(5)	7484(6)	6127(5)	124(4)
C(16)	6112(5)	8140(5)	6793(5)	118(4)
C(17)	7786(5)	5105(5)	6388(5)	101(3)
C(18)	6362(4)	4808(5)	5576(4)	92(3)
N(21)	7092(3)	6205(3)	8894(3)	60(2)
N(22)	5053(4)	6726(4)	8852(3)	73(2)
C(23)	6560(6)	6461(7)	9642(5)	116(4)
C(24)	5725(7)	6601(10)	9577(5)	253(10)
C(25)	7737(5)	6966(6)	8752(5)	116(3)
C(26)	7565(5)	5313(5)	9129(5)	111(3)
C(27)	4694(6)	7678(5)	8869(6)	146(5)
C(28)	4310(6)	6089(5)	8970(5)	130(4)

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

a Siemens *R3m/V* diffractometer. The pertinent crystallographic data are summarized in Table 1. The final unit cell parameters were obtained by a least-squares fit of 24 accurately centered reflections measured in the range 15° < 2θ < 30°, and the intensity data were collected at 230 K in the range 3.5° ≤ 2θ ≤ 42.0° 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.[9] Full-matrix least-squares refinements were performed, and the

Table 3. Bond Lengths (Å) and Bond Angles (deg)

Na–B(4)	2.792(7)	Na–B(5)	2.869(7)
Na–N(11)	2.541(5)	Na–N(12)	2.577(5)
Na–N(21)	2.559(5)	Na–N(22)	2.641(6)
Si–C(2)	1.852(5)	Si–C(8)	1.830(7)
Si–C(9)	1.854(7)	Si–C(10)	1.836(7)
B(1)–C(2)	1.692(8)	B(1)–C(3)	1.713(8)
B(1)–B(4)	1.789(9)	B(1)–B(5)	1.751(9)
B(1)–B(6)	1.734(9)	C(2)–C(3)	1.451(7)
C(2)–B(6)	1.522(8)	C(3)–B(4)	1.508(8)
C(3)–C(7)	1.494(7)	B(4)–B(5)	1.608(9)
B(5)–B(6)	1.753(10)	N(11)–C(13)	1.465(10)
N(11)–C(15)	1.435(9)	N(11)–C(16)	1.440(9)
N(12)–C(14)	1.443(9)	N(12)–C(17)	1.448(9)
N(12)–C(18)	1.448(8)	C(13)–C(14)	1.452(11)
N(21)–C(23)	1.426(9)	N(21)–C(25)	1.423(9)
N(21)–C(26)	1.424(9)	N(22)–C(24)	1.399(10)
N(22)–C(27)	1.397(9)	N(22)–C(28)	1.406(10)
C(23)–C(24)	1.229(14)		

B(4)–Na–B(5)	33.0(2)	B(4)–Na–N(11)	119.1(2)
B(5)–Na–N(11)	143.0(2)	B(4)–Na–N(12)	98.7(2)
B(5)–Na–N(12)	87.6(2)	N(11)–Na–N(12)	71.6(2)
B(4)–Na–N(21)	123.9(2)	B(5)–Na–N(21)	98.3(2)
N(11)–Na–N(21)	116.3(2)	N(12)–Na–N(21)	105.9(2)
B(4)–Na–N(22)	93.6(2)	B(5)–Na–N(22)	106.3(2)
N(11)–Na–N(22)	96.8(2)	N(12)–Na–N(22)	166.1(2)
N(21)–Na–N(22)	71.8(2)	C(2)–Si–C(8)	110.0(3)
C(2)–Si–C(9)	110.5(3)	C(8)–Si–C(9)	106.0(3)
C(2)–Si–C(10)	113.6(3)	C(8)–Si–C(10)	107.7(3)
C(9)–Si–C(10)	108.3(3)	C(2)–B(1)–C(3)	50.4(3)
C(2)–B(1)–B(4)	91.3(4)	C(3)–B(1)–B(4)	50.9(3)
C(2)–B(1)–B(5)	97.6(4)	C(3)–B(1)–B(5)	92.6(4)
B(4)–B(1)–B(5)	54.0(4)	C(2)–B(1)–B(6)	52.7(3)
C(3)–B(1)–B(6)	90.7(4)	B(4)–B(1)–B(6)	96.5(4)
B(5)–B(1)–B(6)	60.4(4)	Si–C(2)–B(1)	126.5(3)
Si–C(2)–C(3)	125.8(4)	B(1)–C(2)–C(3)	65.5(3)
Si–C(2)–B(6)	121.6(4)	B(1)–C(2)–B(6)	65.0(4)
C(3)–C(2)–B(6)	111.1(4)	B(1)–C(3)–C(2)	64.0(3)
B(1)–C(3)–B(4)	67.1(4)	C(2)–C(3)–B(4)	114.6(4)
B(1)–C(3)–C(7)	129.8(4)	C(2)–C(3)–C(7)	120.3(4)
B(4)–C(3)–C(7)	124.0(5)	Na–B(4)–B(1)	128.2(4)
Na–B(4)–C(3)	167.6(4)	B(1)–B(4)–C(3)	61.9(4)
Na–B(4)–B(5)	76.2(3)	B(1)–B(4)–B(5)	61.8(4)
C(3)–B(4)–B(5)	107.0(5)	Na–B(5)–B(1)	125.7(4)
Na–B(5)–B(4)	70.9(3)	B(1)–B(5)–B(4)	64.2(4)
Na–B(5)–B(6)	164.3(4)	B(1)–B(5)–B(6)	59.3(4)
B(4)–B(5)–B(6)	102.8(5)	B(1)–B(6)–C(2)	62.2(4)
B(1)–B(6)–B(5)	60.3(4)	C(2)–B(6)–B(5)	104.4(5)
Na–N(11)–C(13)	108.1(4)	Na–N(11)–C(15)	113.1(4)
C(13)–N(11)–C(15)	108.2(6)	Na–N(11)–C(16)	106.7(4)
C(13)–N(11)–C(16)	112.1(6)	C(15)–N(11)–C(16)	108.8(5)
Na–N(12)–C(14)	104.4(4)	Na–N(12)–C(17)	115.2(4)
C(14)–N(12)–C(17)	108.9(5)	Na–N(12)–C(18)	107.4(4)
C(14)–N(12)–C(18)	112.7(5)	C(17)–N(12)–C(18)	108.3(5)
N(11)–C(13)–C(14)	113.9(6)	N(12)–C(14)–C(13)	114.6(6)
Na–N(21)–C(23)	105.6(4)	Na–N(21)–C(25)	114.6(4)
C(23)–N(21)–C(25)	109.6(5)	Na–N(21)–C(26)	109.1(4)
C(23)–N(21)–C(26)	107.7(5)	C(25)–N(21)–C(26)	109.9(5)
Na–N(22)–C(24)	98.8(5)	Na–N(22)–C(27)	127.7(5)
C(24)–N(22)–C(27)	110.0(7)	Na–N(22)–C(28)	103.8(4)
C(24)–N(22)–C(28)	109.6(7)	C(27)–N(22)–C(28)	106.0(6)
N(21)–C(23)–C(24)	124.6(7)	N(22)–C(24)–C(23)	135.5(8)

scattering factors were taken from ref 10. All non-H atoms were refined anisotropically. Cage and bridge H atoms were located in difference Fourier maps and isotropically refined (U = 0.08 Å²), while the methyl and methylene H's were calculated. The final refinement of II converged at R = 0.053, wR = 0.070, and GOF = 1.61 for the 1788 observed reflections. The maximum and minimum residual electron densities are +0.21 and −0.25 e/Å³, respectively. The final atomic coordinates are given in Table 2, while bond lengths and bond angles are presented in Table 3.

(9) Sheldrick, G. M. *Structure Determination Software Programs*; Siemens X-ray Analytical Instruments Corp.: Madison, WI, 1991.
(10) *International Tables For X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.
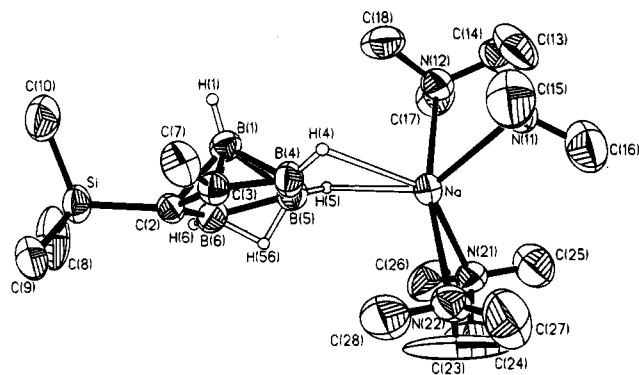
Figure 1. Perspective view of **II** with thermal ellipsoids drawn at the 40% probability level showing the atom numbering scheme. The hydrogen atoms of the SiMe₃ and Me groups and of the TMEDA molecules are omitted for clarity.

Results and Discussion

Constant stirring of the TMEDA solution of the dimeric [$nido$-1-Na(TMEDA)-2-(SiMe₃)-3-(Me)-2,3-C₂B₄-H₅]₂ (**I**)[7] over a period of 2 months at room temperature, followed by slow crystallization produced colorless crystals of $nido$-exo-4,5-[(μ-H)₂Na(TMEDA)₂]-2-(SiMe₃)-3-(Me)-2,3-C₂B₄H₅ (**II**) in 99% yield, indicating that a more extensively solvated sodium destabilizes the dimer formation and produces the weaker ion pair **II** (Scheme 1). Although the ¹H, ¹¹B, and ¹³C NMR spectra of **II** are all almost identical to those of the precursor **I**, its solid state structure (Figure 1) shows the compound to be a discrete monomer and that the [Na(TMEDA)₂]⁺ ion occupies an exo-polyhedral position halfway between B(4) and B(5) and directed down below the plane of the C₂B₃ face. While the packing diagram (Figure 2) of **II** shows the presence of four well-separated, identical monomeric units in the unit cell, the Na—B(4) and Na—B(5) distances of 2.792(7) and 2.869(7) Å in each unit are comparable to those of similar bonds in **I** (average 2.961(7) Å).[7] Since the metal—carborane interactions are essentially ionic, the similarities in the spectral properties of **I** and **II** are not surprising. In contrast to the inertness of **I**, compound **II** reacts readily with NaH in TMEDA, resulting in the isolation of an off-white, air-sensitive crystalline solid of the previously unknown disodium compound, $closo$-exo-4,5-[(μ-H)₂Na-(TMEDA)]-1-Na(TMEDA)-2-(SiMe₃)-3-(Me)-2,3-C₂B₄-H₄ (**III**), in 94% yield, as shown in Scheme 1. Although the structure of **III** has not been determined, the chemical analysis of **III** and the similarities in its
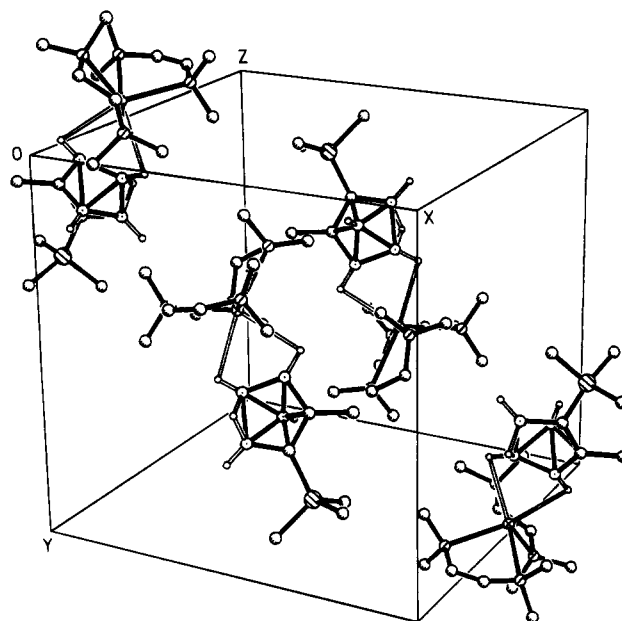

Figure 2. Packing diagram of **II**.

spectral properties and preparative routes to those of the mixed sodium lithium compounds, coupled with the structural determination of a dilithium complex,[7] leave little doubt as to the validity of the formula of **III**.

The results of the present study show that, in the absence of blockage of the second bridge hydrogen by the capping [Na(TMEDA)]⁺ unit, the monosodium compound (**II**) can react further with a H⁻ site in the NaH lattice to yield **III**. Thus, the role of the steric effects in determining the reactivity of the $nido$-carborane anions, rather than inherent acid/base strength alone, is hereby exemplified.

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

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