

# Experimental and theoretical studies on group 1 metallacarboranes: Synthesis, structure and ab initio calculations of the NMR chemical shifts of the 1-(THF)-1-(TMEDA)-1-Na-2,4-(SiMe<sub>3</sub>)<sub>2</sub>-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub> and related carboranes<sup>1</sup>

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## Abstract

The reaction of gaseous HCl with either the disodium or dilithium compound of the [*nido*-2,4-(SiMe<sub>3</sub>)<sub>2</sub>-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]<sup>2-</sup> dianion (**I**) in 1:1 stoichiometry in THF produced the monoprotonated species 1-Na(THF)<sub>2</sub>-2,4-(SiMe<sub>3</sub>)<sub>2</sub>-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub> (**II**) or 1-Li(THF)<sub>2</sub>-2,4-(SiMe<sub>3</sub>)<sub>2</sub>-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub> (**III**), in 81% and 80% yields, respectively. This method proved superior to that involving the direct reduction of the *closo*-C<sub>2</sub>B<sub>4</sub> carborane by metal hydrides. **II** and **III** were characterized by elemental analysis, <sup>1</sup>H, <sup>11</sup>B and <sup>13</sup>C NMR and IR spectra. Compound **II** was recrystallized from a mixture THF, hexane and TMEDA (1:2:1) to isolate colorless crystals of the mixed solvated species, 1-(THF)-1-(TMEDA)-1-Na-2,4-(SiMe<sub>3</sub>)<sub>2</sub>-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub> (**IV**), which were subsequently used for X-ray diffraction studies. The structure of **IV** showed that the capping metal occupied the apical position above the open C<sub>2</sub>B<sub>3</sub> face of the carborane and that a hydrogen atom was bridging the two adjacent boron atoms on that face. The <sup>11</sup>B and <sup>13</sup>C NMR spectra calculated by GIAO (gauge independent atomic orbital) methods at the 6-311G\*\* level on the B3LYP/6-31G\* optimized geometries of **I–III**, and a number of related *nido*- and *closo*-carboranes, gave excellent agreement with experiment, even in compounds where electron correlation effects are known to be important. © 1998 Elsevier Science S.A.

**Keywords:** Crystal structure; X-ray diffraction; Carborane; GIAO computed <sup>13</sup>C; <sup>11</sup>B chemical shifts

## 1. Introduction

The dianions of the *nido*-(RC)<sub>2</sub>B<sub>4</sub>H<sub>4</sub> (R = an *exo*-polyhedral substituent or H) carboranes have been extensively employed as ligands in the synthesis of a variety of *closo*- and *commo*-metallacarboranes [1–4]. In all cases the carboranes bond to the metal using a set of π-type orbitals directed above their C<sub>2</sub>B<sub>3</sub> open pentagonal faces. In this way, the carborane dianions can be considered as six-electron π-donors similar to the cyclopentadienide ion. There are two different arrangements of the carbons atoms on the carborane face,

the so-called ‘carbons adjacent’ isomer, [*nido*-2,3-(RC)<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]<sup>2-</sup>, where the carbon atoms are next to one another and the ‘carbons apart’ isomer, [*nido*-2,4-(RC)<sub>2</sub>B<sub>4</sub>H<sub>4</sub>]<sup>2-</sup>, where these atoms are separated by a boron atom. A comparative study of the two isomeric stannacarboranes indicated that, while the carbons apart isomer is the thermodynamically more stable one, both seem to bond equally well with the metal [5]. The similarities in the ligating properties of the two carboranes have been confirmed through the syntheses and structure determinations of a number of metallacarboranes incorporating main group [1–13], *d*-block[[1,8]], and *f*-block[14–16] metals into both isomeric cages. The usual synthetic route to the metallacarboranes involves reacting a group 1 compound of the respective carborane with suitable metal halides. In the carbons adjacent system, the dianion is usually the preferred precursor to the metallacarboranes. However, it has recently been demonstrated that some metallacarboranes, such as the full-sandwich magnesium and lithium

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<sup>1</sup> Dedicated to Professor Kenneth Wade, with all best wishes, of University of Durham, UK, on the occasion of his 65th birthday.

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complexes,  $\{ \textit{commo-1,1'-Mg}[2,3-(\text{SiMe}_3)_2-2,3-\text{C}_2\text{B}_4\text{H}_4]_2 \}^{2-}$  [9] and  $\{ \textit{commo-1,1'-Li}[2,3-(\text{SiMe}_3)_2-2,3-\text{C}_2\text{B}_4\text{H}_5]_2 \}^-$  [17], could be synthesized only from the monoanionic species,  $[\textit{nido-2,3-(SiMe}_3)_2-2,3-\text{C}_2\text{B}_4\text{H}_5]^-$ . In the carbons adjacent system the monoanion is readily available and has been structurally and spectroscopically characterized [6,7,18,19]. However, such is not the case for the carbons apart isomers, there have been very few investigations of the properties and reactivities of the monoanion. This paucity of information is primarily due to the extreme difficulty in preparing the protonated carbons apart carborane isomers. To date, the only syntheses of such compounds were those described by Onak and coworkers that entailed either the opening of the corresponding *closo-1,6-(R)*<sub>2</sub>-1,6-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> with base [20,21] or the removal of one of the apical borons in *closo-2,4-C*<sub>2</sub>B<sub>5</sub>H<sub>7</sub> by reaction with LiNR<sub>2</sub> (R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub> and CH(CH<sub>3</sub>)<sub>2</sub>) [22]. These are extremely slow, low yield reactions that severely limit the supply of the corresponding monoanions. We describe herein an alternative, high yield synthesis of the 'carbons apart' monoanion,  $[\textit{nido-2,4-(SiMe}_3)_2-2,4-\text{C}_2\text{B}_4\text{H}_5]^-$ , its structural characterization as its  $[\text{Na}(\text{THF})(\text{TMEDA})]^+$  salt. Since <sup>11</sup>B NMR spectroscopy is extensively used in monitoring the extent of the reactions that lead from the group 1 salt to the heterocarborane product, a careful analysis of the factors affecting the NMR spectra of this anion and some related compounds, by a combined ab initio DFT/GIAO study was conducted and the results are also reported herein.

## 2. Experimental

### 2.1. Materials

Tetrahydrofuran (THF) and hexane were dried over LiAlH<sub>4</sub> and doubly distilled before use. *N,N,N,N*-tetramethylethylenediamine (TMEDA) (Aldrich) was distilled in vacuo and stored over sodium metal. Anhydrous HCl (Aldrich) was purified before use by passing it through a  $-78^\circ\text{C}$  trap on a vacuum line. Mineral oil-free NaH (Aldrich) was used as received. The group 1 'carbons apart' metallacarborane precursors, *exo-5,6-M*(THF)<sub>2</sub>-1-*M*(THF)<sub>2</sub>-2,4-(SiMe<sub>3</sub>)<sub>2</sub>-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> {M = Na [10] (**IA**) and Li [8] (**IB**)} were prepared by the reaction of 1,2-bis(trimethylsilyl)-1,2-dicarba-*closo*-hexacarborane(6) [8] with the corresponding group 1 metal in the presence of naphthalene in THF as described elsewhere [8,10].

### 2.2. 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-200

SY multinuclear NMR spectrometer. Infrared spectra were recorded on a Nicolet Magna-550 FT-IR spectrophotometer. Elemental analyses were obtained from E + R Microanalytical Laboratory, Corona, NY.

### 2.3. Synthetic procedures

All experiments were carried out in Pyrex glass round-bottom flasks of 50–100 ml capacity, containing magnetic stirring bars and fitted with high vacuum Teflon valves. Nonvolatile substances were manipulated in either a dry-box or evacuable glovebag under an atmosphere of dry nitrogen. All known compounds among the products were identified by comparing their <sup>1</sup>H and <sup>11</sup>B NMR spectra with those of authentic samples.

#### 2.3.1. Synthesis of 1-Na(THF)<sub>2</sub>-2,4-(SiMe<sub>3</sub>)<sub>2</sub>-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub> (**II**)

Anhydrous HCl (2.00 mmol) was condensed in vacuo into a reaction flask containing a THF solution (15 ml) of *exo-5,6-Na*(THF)<sub>2</sub>-1-*Na*(THF)<sub>2</sub>-2,4-(SiMe<sub>3</sub>)<sub>2</sub>-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> (**IA**) (1.104 g, 2.00 mmol) at  $-196^\circ\text{C}$ , and the resulting mixture was slowly warmed to  $-78^\circ\text{C}$  first and then to room temperature, with constant stirring over a period of 2–3 h. After additional stirring at room temperature for 2 h, the heterogeneous reaction mixture was filtered through a frit in vacuo to collect a clear filtrate. The off-white solid, that remained on the frit, was identified as NaCl by qualitative analysis and was discarded. After complete removal of THF from the filtrate in vacuo, the residue in the flask was washed several times with dry *n*-hexane to isolate a light yellow solid, identified as 1-*Na*(THF)<sub>2</sub>-2,4-(SiMe<sub>3</sub>)<sub>2</sub>-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub> (**II**) (0.618 g, 81% yield, m.p. 163–165°C). Anal. Calcd for C<sub>16</sub>H<sub>39</sub>O<sub>2</sub>B<sub>4</sub>Si<sub>2</sub>Na (**II**): C, 49.80; H, 10.19. Found: C, 49.61; H, 10.04. Spectroscopic data for **II**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, relative to external Me<sub>4</sub>Si)  $\delta$  3.46 [s (br), 8H, CH<sub>2</sub>, THF], 1.39 [s (br), 8H, CH<sub>2</sub>, THF], 0.43 [s, 18H, CH<sub>3</sub>, SiMe<sub>3</sub>],  $-4.07$  [s, 1H, B–H–B (bridge)]; <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub> or THF(*d*<sub>8</sub>), relative to external BF<sub>3</sub> · OEt<sub>2</sub>)  $\delta$  24.3 [br, 1B, basal BH, <sup>1</sup>*J*(<sup>11</sup>B–<sup>1</sup>H) = unresolved], 2.90 [d, 2B, basal BH, <sup>1</sup>*J*(<sup>11</sup>B–<sup>1</sup>H) = unresolved],  $-51.75$  [d, 1B, apical BH, <sup>1</sup>*J*(<sup>11</sup>B–<sup>1</sup>H) = 143.17 Hz]; <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, relative to external Me<sub>4</sub>Si)  $\delta$  83.64 [s, 2C, cage carbons], 68.47 [t, 4C, CH<sub>2</sub>, THF], 25.32 [t, 4C, CH<sub>2</sub>, THF], 1.61 [q, 6C, SiMe<sub>3</sub>, <sup>1</sup>*J*(<sup>13</sup>C–<sup>1</sup>H) = 115.6 Hz]; IR (cm<sup>-1</sup>, C<sub>6</sub>D<sub>6</sub> vs. C<sub>6</sub>D<sub>6</sub>) 2954 (s, br) 2894 (m, br) [ $\nu$  (C–H)], 2530 (m, br), 2487 (s, br) [ $\nu$  (B–H)], 1249 (s, s) [ $\delta$  (C–H)], 1200 (m, s), 1115.9 (s, s), 1049 (s, s), 848 (s, s), [ $\rho$  (C–H)], 685 (m, s).

#### 2.3.2. Synthesis of 1-Li(THF)<sub>2</sub>-2,4-(SiMe<sub>3</sub>)<sub>2</sub>-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub> (**III**)

In a procedure identical to that described above for the sodium compound, 2.00 mmol of *exo-5,6-*

Li(THF)<sub>2</sub>-1-Li(THF)<sub>2</sub>-2,4-(SiMe<sub>3</sub>)<sub>2</sub>-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> (**II**) (1.04 g) in THF (15 ml) was allowed to react with 2.00 mmol of anhydrous HCl with constant stirring at room temperature for 4–5 h to produce 1-Li(THF)<sub>2</sub>-2,4-(SiMe<sub>3</sub>)<sub>2</sub>-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub> (**III**) (0.59 g, 1.59 mmol) in 80% yield. Anal. Calcd for C<sub>16</sub>H<sub>39</sub>O<sub>2</sub>B<sub>4</sub>Si<sub>2</sub>Li: C, 51.96; H, 10.63. Found: C, 51.61; H, 10.81. Spectroscopic data for **III**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, relative to external Me<sub>4</sub>Si) δ 3.46 [s (br), 8H, CH<sub>2</sub>, THF], 1.39 [s (br), 8H, CH<sub>2</sub>, THF], 0.37 [s, 18H, CH<sub>3</sub>, SiMe<sub>3</sub>], -4.07 [s, 1H, B–H–B (bridge)]; <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub> or THF(*d*<sub>8</sub>), relative to external BF<sub>3</sub>·OEt<sub>2</sub>) δ 24.3 [br, 1B, basal BH, <sup>1</sup>J(<sup>11</sup>B–<sup>1</sup>H) = unresolved], 2.90 [d, 2B, basal BH, <sup>1</sup>J(<sup>11</sup>B–<sup>1</sup>H) = unresolved], -47.6 [d, 1B, apical BH, <sup>1</sup>J(<sup>11</sup>B–<sup>1</sup>H) = 143.17 Hz]; <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, relative to external Me<sub>4</sub>Si) δ 84.73 [s, 2C, cage carbons], 68.47 [t, 4C, CH<sub>2</sub>, THF], 25.32 [t, 4C, CH<sub>2</sub>, THF], 1.61 [q, 6C, SiMe<sub>3</sub>, <sup>1</sup>J(<sup>13</sup>C–<sup>1</sup>H) = 117.3 Hz]; <sup>7</sup>Li NMR (THF, relative to external aqueous LiNO<sub>3</sub>) δ 2.24 ppm; IR (cm<sup>-1</sup>, C<sub>6</sub>D<sub>6</sub> vs. C<sub>6</sub>D<sub>6</sub>) 2955 (s, br), 2874 (m, br), 2806 (s, sh) [ $\nu$  (C–H)], 2519 (m, br), 2466 (s, br) [ $\nu$  (B–H)], 1512 (s, s), 1466 (m, s), 1374 (m, s), 1301 (m, s), 1242 (m, s) [ $\delta$  (C–H)], 1199 (m, s), 1110 (s, s), 973 (s, s), 847 (s, s), [ $\rho$  (C–H)], 696 (m, s).

#### 2.4. Crystal structure analysis of 1-(THF)-1-(TMEDA)-1-Na-2,4-(SiMe<sub>3</sub>)<sub>2</sub>-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub> (**IV**)

Neither **II** nor **III** gave crystals suitable for single crystal X-ray analysis. Since it had been demonstrated that the solvation of the metal with TMEDA in group 1 metallacarboranes induces single-crystal growth [7,8], **II** was allowed to recrystallize from a mixture of THF, hexane and TMEDA (1:2:1) at room temperature, over a period of several days, to isolate colorless transparent crystals of the mixed solvated sodium species, 1-(THF)-1-(TMEDA)-1-Na-2,4-(SiMe<sub>3</sub>)<sub>2</sub>-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub> (**IV**), which were suitable for X-ray analysis. The crystal, coated with epoxy resin, was mounted on a Siemens R3m/V diffractometer under a low-temperature nitrogen stream. The pertinent crystallographic data are summarized in Table 1. The final unit cell parameters for **IV** were obtained by least-squares fits of 24 accurately centered reflections measured in the 2 $\theta$  range from 20° to 30°. Three standard reflections that were periodically monitored during the data collection showed no significant change in intensity. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using the SHELXTL-Plus package of programs [23]. The scattering factors were taken from Ref. [24]. Full-matrix least-squares refinement was performed for **IV**. All non-H atoms were anisotropically refined, the carborane-cage H atoms were located in difference Fourier maps and their sites were freely refined. The methyl and methylene-H's were placed using a riding model. Final values of  $R = \sum(|F_o| -$

Table 1  
Crystallographic data<sup>a</sup> for 1-(THF)-1-(TMEDA)-1-Na-2,4-(SiMe<sub>3</sub>)<sub>2</sub>-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>5</sub> (**IV**)

formula	C <sub>18</sub> H <sub>47</sub> N <sub>2</sub> B <sub>4</sub> NaOSi <sub>2</sub>
fw	430.0
crystal system	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>m</i>
<i>a</i> , Å	9.094 (2)
<i>b</i> , Å	17.276 (4)
<i>c</i> , Å	9.988 (2)
$\beta$ , deg.	112.19 (2)
<i>V</i> , Å <sup>3</sup>	1452.7 (7)
<i>Z</i>	2
$\rho_{\text{calcd}}$ , Mg/m <sup>3</sup>	0.983
abs coeff, mm <sup>-1</sup>	0.147
crystal dmns, mm	0.20 × 0.30 × 0.10
scan type	$\omega$
2 $\theta$ range, deg.	
<i>T</i> , K	220
decay, %	0
standard reflctns	3 after every 200 reflctns
data collected	1755
obsd reflctns, $F > 6.0\sigma(F)$	865
parameters refined	144
GOF	1.64
<i>g</i> <sup>c</sup>	0.001
$\Delta\rho_{(\text{max}, \text{min})}$ , e/Å <sup>3</sup>	0.27, -0.23
<i>R</i> <sup>b</sup>	0.062
<i>wR</i>	0.076

<sup>a</sup> Graphite monochromatized Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å.  
<sup>b</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR = [\sum w(F_o - F_c)^2 / \sum w(F_o)^2]^{1/2}$ .  
<sup>c</sup>  $w = 1 / [\sigma^2(F_o) + g(F_o)^2]$ .

$|F_c|) / \sum |F_o| = 0.062$ ,  $wR = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2} = 0.076$ , with  $w = [\sigma^2(F) + 0.001(F)^2]^{-1}$ . The atomic coordinates are given in Table 2. Selected interatomic distances and angles are listed in Table 3.

#### 2.5. Theoretical methods

Approximate density functional theory (DFT) [25] and Hartree Fock (HF) ab initio molecular orbital calculations, at various levels of theory, were carried out on either a Dec- $\alpha$ A or a Silicon Graphics Indigo2 RS10000 workstation using either the Gaussian 94 [26] or the SPARTAN [27] series of programs. It was found that good agreement could be obtained between the experimental <sup>11</sup>B and <sup>13</sup>C NMR spectra of various carboranes and those obtained using gauge-independent atomic orbital (GIAO) [28] calculations on structures whose geometries were optimized from DFT hybrid methods using Becke's three-parameter functional [29] with the 6-31G\* basis set (B3LYP/6-31G\*). For most compounds it was found that GIAO calculations at either the HF/6-311G\*\* or the B3LYP/6-311G\*\* level of theory were comparable and gave the best agreement with experiment; the latter method was found to be superior

Table 2

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^3$ ) for IV

	x	y	z	$U(\text{eq})^a$
Na	4220(4)	2500	1650(4)	51(2)
Si	1765(3)	801(1)	3131(2)	64(1)
C(11)	1700(7)	1768(4)	2353(7)	48(3)
B(12)	2454(15)	2500	3254(15)	57(6)
B(15)	604(10)	1982(6)	772(10)	55(4)
B(16)	392(15)	2500	2174(13)	50(6)
C(21)	2246(13)	832(6)	5106(9)	131(7)
C(22)	-65(11)	247(5)	2270(11)	142(7)
C(23)	3343(11)	211(6)	2871(11)	132(7)
O(31)	6476(8)	2500	3806(8)	69(4)
C(32)	7108(14)	1869(6)	679(11)	146(7)
C(33)	8255(17)	2125(6)	5997(13)	228(10)
N(34)	4684(11)	1652(4)	-141(8)	75(4)
C(35)	5021(17)	2159(4)	-1146(12)	169(9)
C(36)	6045(12)	1168(6)	624(11)	107(6)
C(37)	3349(11)	1140(5)	-885(9)	93(5)

<sup>a</sup> Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

only when electron correlation was unusually important. In all cases the final geometries were optimized under  $C_1$  symmetry starting from either the known X-ray structures or those obtained from optimizations at lower levels of theory. The  $^{13}\text{C}$  and  $^{11}\text{B}$  NMR chemical shifts are listed relative to  $\text{SiMe}_4$  and  $\text{BF}_3 \cdot \text{OEt}_2$  standards, respectively. In all cases these standards were subjected to the same optimization/GIAO cycle as the particular compound.

### 3. Results and discussion

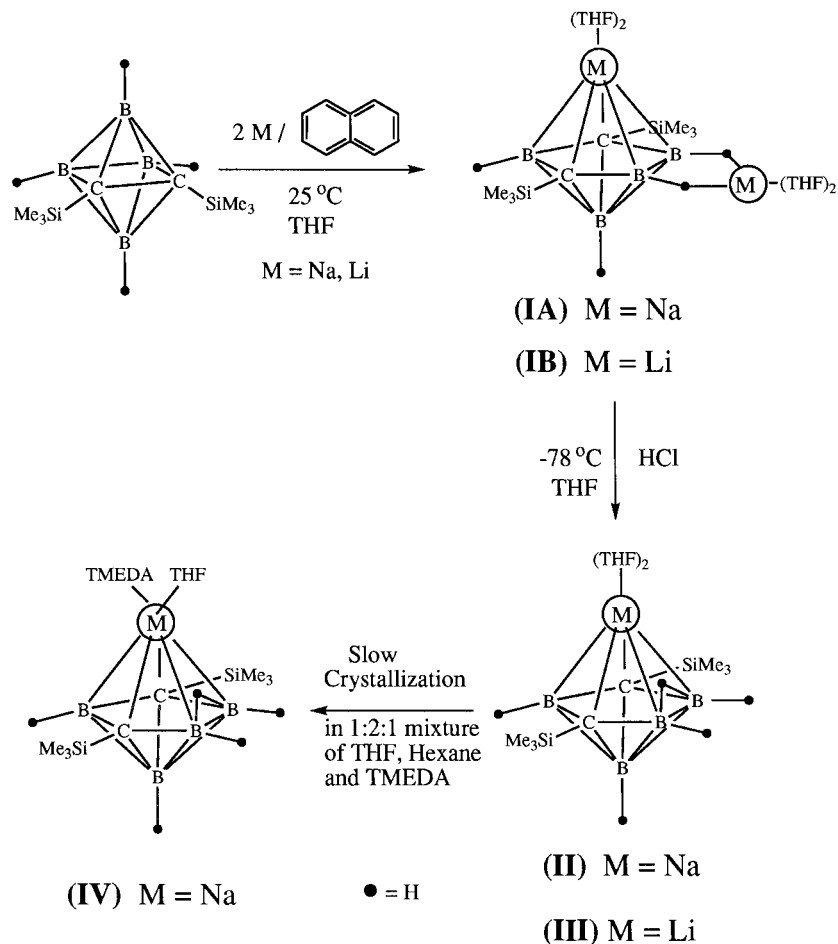
#### 3.1. Synthesis and structure

Direct protonation of either the disodium or dilithium compounds of the carborane dianion,  $[\text{nido-2,4}-(\text{SiMe}_3)_2\text{-2,4-C}_2\text{B}_4\text{H}_4]^{2-}$  (**I**) produced the corresponding monoanion in 81% and 80% yield, respectively. The general method is an indirect one involving the initial formation of the *closo*-1,2- $(\text{SiMe}_3)_2\text{-1,2-C}_2\text{B}_4\text{H}_4$  carborane, its reductive opening with the particular group 1 metal to give the dianion **I**, followed by protonation to give the final products (see Scheme 1). It has been reported that *closo*-1,6- $(\text{SiMe}_3)_2\text{-1,6-C}_2\text{B}_4\text{H}_4$  isomer can also be reduced to give **I** [10]. The more direct methods of preparation involving the reaction of the *closo*-carborane with bases, such as NaH, involve time consuming, low yield reactions [20,21], which is not the case for the method described in this report. All reactions described in Section 2 are high yield ones affording a ready supply of the pure monoanion. In addition, attempts to obtain the monoanion directly from *closo*-1,2- $(\text{SiMe}_3)_2\text{-1,2-C}_2\text{B}_4\text{H}_4$  by reaction with NaH proved unsuccessful. The  $^{11}\text{B}$  NMR spectra of THF mixtures of the *closo*-carborane and NaH showed a slow decomposition of the carborane such that after 3 days at 85°C about 75% of the *closo*-carborane had reacted. However, the resulting  $^{11}\text{B}$  NMR spectrum showed multiple resonances in the region of -10 to +30 ppm, indicating a complex mixture of products, with no apparent preference for the anticipated product, **II**. In the syntheses of **II** and **III**, care must be exercised to insure that the molar ratio of HCl-to-carborane does not exceed

Table 3

Bond lengths ( $\text{\AA}$ ) and bond angles (deg.) for IV

Bond lengths					
Na-H(1)	2.62 (7)	C(11)-B(15)	1.560 (10)	C(11)-B(12)	1.553 (9)
B(15)-H(1)	1.26 (7)	C(11)-B(16)	1.698 (12)	C(33)-C(33A)	1.296 (20)
Na-C(11)	2.925 (8)	B(12)-B(16)	1.776 (16)	N(34)-C(35)	1.450 (16)
Na-B(12)	2.662 (17)	B(15)-B(16)	1.733 (16)	N(34)-C(36)	1.449 (12)
Na-O(31)	2.347 (7)	B(15)-B(15A)	1.790 (20)	N(34)-C(37)	1.459 (11)
Na-N(34)	2.469 (9)	O(31)-C(32)	1.379 (11)	C(35)-C(35A)	1.179 (15)
Bond angles					
C(11)-Na-O(31)	105.8(3)	C(11)-B(12)-B(16)	60.9(5)		
B(12)-Na-O(31)	88.0(4)	C(11)-B(12)-C(11A)	109.0(8)		
C(11)-Na-N(34)	106.3(3)	C(11)-B(15)-B(16)	61.8(5)		
B(12)-Na-N(34)	138.0(3)	B(16)-B(15)-B(15A)	58.9(4)		
O(31)-Na-N(34)	109.6(3)	C(11)-B(16)-B(12)	53.1(4)		
N(34)-Na-C(11A)	142.6(3)	C(11)-B(16)-B(15)	54.1(5)		
N(34)-Na-N(34A)	72.8(4)	B(12)-B(16)-B(15)	94.4(8)		
B(15)-H(1)-B(15A)	91 (6)	C(11)-B(16)-C(11A)	96.2(8)		
B(12)-C(11)-B(15)	111.6(7)	B(12)-B(16)-B(15A)	94.4(8)		
B(12)-C(11)-B(16)	66.0(6)	B(15)-C(11)-B(16)	64.1(6)		



Scheme 1.

1:1; the use of excess HCl led to extended decomposition, with a number of unidentified products as observed by  $^{11}\text{B}$  NMR spectroscopy.

The structure of the mixed  $[\text{Na}(\text{THF})(\text{TMEDA})]$ -complexed  $\text{C}_2\text{B}_4$ -carborane monoanion, **IV**, is shown in Fig. 1, and some bond distances and bond angles are given in Table 3. The structure shows that the bridge hydrogen resides between the two adjacent facial boron atoms, B(15) and B(15a) in Fig. 1. This is consistent with the NMR spectra of **II** and **III**, as well as the  $^{11}\text{B}$  NMR spectrum of  $[\text{2,4-}\text{C}_2\text{B}_4\text{H}_7]^-$ , reported by Onak [22] (see Table 4). The  $\text{C}_2\text{B}_4\text{H}$  cage structure shown in Fig. 1 is quite similar to that found by Wrackmeyer and coworkers [36] for the alkyl-substituted  $\text{Na}[\text{nido-2,4-}\text{C}_2\text{B}_4\text{Et}_6\text{H}]$ , in that the bridging hydrogen resides between the two adjacent basal boron atoms of the  $\text{C}_2\text{B}_3$  open face of the carborane. The intracage bond distances given in Table 3 are quite similar to the analogous distances in the  $[\text{nido-2,4-}\text{C}_2\text{B}_4\text{Et}_6\text{H}]^-$  cage; the greatest difference being an elongation of the equivalent to the B(16)-B(12) distance by 0.050 Å, from the value of 1.776(16) Å in **IV** to 1.826(4) Å in the hexa-alkyl

substituted compound, all other distances being the same to within 0.010 Å, or better [36]. Comparison of the distances given in Tables 3 and 5 shows that, except for an elongation of the bond between the involved atoms, the presence of the bridge hydrogen has little effect on the overall cage geometry. In comparing the interatomic distances in **IV**, with the averages of the comparable distances found for the dianionic precursors, the only significant change is an increase of the B(15)-B(15a) distance in **IV** of 0.144 Å, the next largest change is a decrease by 0.032 Å in the B(16)-B(15,15a) bond distances, with all other distances being the same to within less than  $\pm 0.01$  Å (see Fig. 1).

Although relative stability or competitive proton binding studies have not been carried out on the carbons apart and carbons adjacent *nido*-carborane dianions, a measure of the relative energies and basicities of the two dianions can be obtained from the values of the change in energy,  $\Delta E$  (or  $\Delta H$ ), for the reactions shown in Eqs. (1) and (2), calculated using molecular orbital derived energies. Tables 5 and 6 list the B3LYP/6-31G\* calculated energies and geometries for several

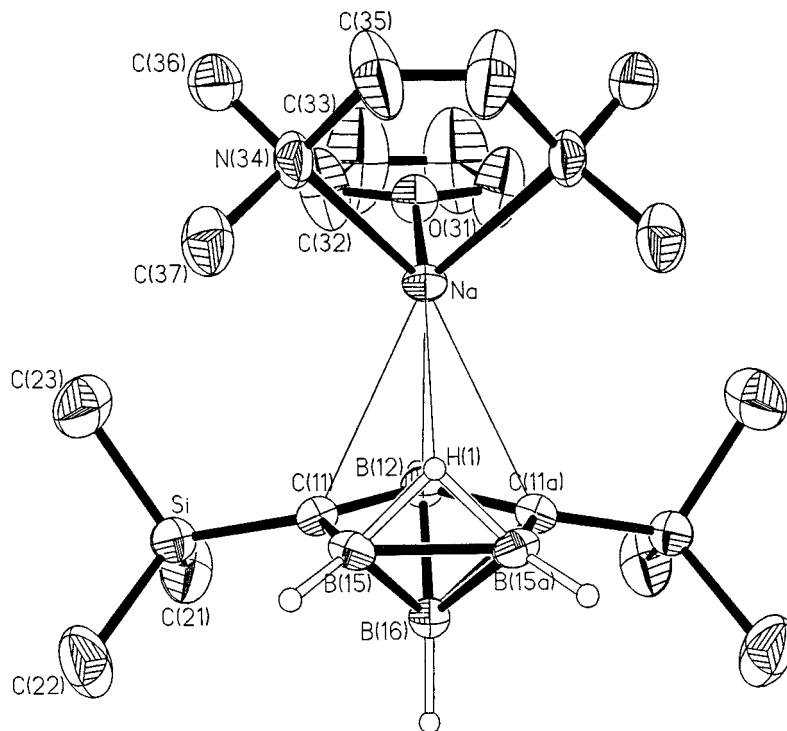
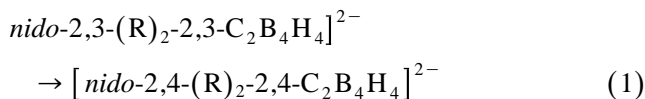


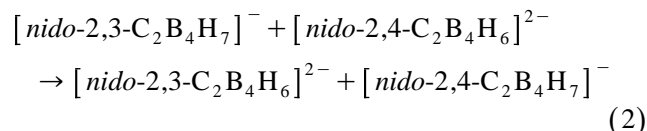
Fig. 1. Perspective view of **IV** with the thermal ellipsoids drawn at the 40% probability level. For clarity, the methyl and methylene H's are omitted.

*nido*-2,4- and *nido*-2,3- $C_2B_4$  carboranes. From these tables the calculated  $\Delta E$  values for Eq. (1) are  $-62.2$  kJ/mol for



R = H and  $-108.0$  kJ/mol for R = SiMe<sub>3</sub>. The greater relative stability of the 2,4-isomers over its 2,3- $C_2B_4$  analogues shown by these calculations are consistent with those obtained earlier from semiempirical calculations [5] and had been predicted by Williams<sup>4</sup> and generally born out experimentally. The change in  $\Delta E$  in going from R = H to R = SiMe<sub>3</sub> is not unexpected on steric grounds. The data listed in Table 6 shows an increase in both the experimental and calculated  $C_{\text{cage}}\text{-}C_{\text{cage}}$  bond distances as hydrogens are replaced by larger substituents, in the compounds *nido*-2-(R<sub>1</sub>)-3-(R<sub>2</sub>)-2,3- $C_2B_4H_6$  the relevant bond distances are: R<sub>1</sub> = R<sub>2</sub> = H, (exp) 1.418 Å, (calc) 1.424 Å; R<sub>1</sub> = R<sub>2</sub> = Me, (exp) 1.432 Å, (calc) 1.431 Å; R<sub>1</sub> = Me, R<sub>2</sub> = SiMe<sub>3</sub>, (exp) 1.460 Å, (calc) 1.438 Å and in  $[2,3\text{-}(\text{R})_2\text{-}2,3\text{-}C_2B_4H_4]^{2-}$  the distances are: R = H, (calc) 1.467 Å; R = SiMe<sub>3</sub>, (calc) 1.513 Å, (exp) 1.509 Å, a similar elongation was observed in the C–C bond distances in *closo*-1,2-(R)<sub>2</sub>-1,2- $C_2B_4H_4$  when going from R = H

(1.535 Å) to R = SiMe<sub>3</sub> (1.582 Å) [41]. These observations indicate a small but consistent influence of increasing the steric bulk of the cage carbon substituents. From the skeletal electron counting rules developed by Wade and others [42], one would not expect the nature of the cage substituents to materially affect the overall geometry of carborane cages. Since the effects of the SiMe<sub>3</sub> group appear to be small and unless such effects are thought to be important, theoretical analyses can be carried out safely on model compounds having hydrogen substituent on the cage carbons, the resulting saving in CPU time when using these model compounds is substantial.<sup>5</sup>



The value of calculated  $\Delta E$  for Eq. (2) is  $-4.56$  kJ/mol, indicating that, at least as measured by these calculated gas phase reaction energies, the 2,4-dianion is as basic as its 2,3-isomer, if not more so. Schleyer and coworkers [43] have succeeded in optimizing a structure for a neutral  $[ \textit{nido}\text{-}2,4\text{-}C_2B_4R_6H_2 ]$  (R = H,

<sup>5</sup> The CPU time required to optimize  $[2,4\text{-}(\text{R})_2C_2B_4H_4]^{2-}$  from their MNDO structures were: for R = SiMe<sub>3</sub>, 126.6 h; for R = H, 2.5 h.

<sup>4</sup> For a general discussion, see Refs. [39,40].

Table 4  
Calculated and experimental interatomic distances for some *nido*-2,4- $C_2B_4$  carboranes

Bond distances in Å <sup>a</sup>								Energy (A.U.)	Ref. or method
M	R	B(6)–B(4,5)	B(6)–B(2)	B(6)–C(1,2)	B(4,5)–C(1,2)	B(2)–C(1,2)	B(4)–B(5)		
<i>M</i> <sub>2</sub> [2,4-( <i>R</i> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ] <sup>2-</sup>									
[Li(THF) <sub>2</sub> ]	SiMe <sub>3</sub>	1.765	1.774	1.704	1.565	1.548	1.640	–	[8]
[Li(TMEDA)]	SiMe <sub>3</sub>	1.764	1.771	1.706	1.563	1.538	1.626	–	[8]
Na(THF) <sub>2</sub> ]	SiMe <sub>3</sub>	1.835	1.852	1.740	1.606	1.554	1.677	–	[10]
–	SiMe <sub>3</sub>	1.801	1.824	1.712	1.597	1.549	1.642	–996.51508	B3LYP/6-31G *
–	[1,2,4-LiC <sub>2</sub> B <sub>4</sub> H <sub>6</sub> ] <sup>-b</sup>	1.786	1.792	1.703	1.584	1.559	1.677	–186.85020	B3LYP/6-31G *
–	H	1.806	1.805	1.712	1.575	1.546	1.662	–179.09532	B3LYP/6-31G *
<i>M</i> [2,4-( <i>R</i> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>5</sub> ] <sup>-</sup>									
<b>IV</b>		1.733	1.776	1.698	1.560	1.553	1.790	–	This work
–	SiMe <sub>3</sub>	1.753	1.836	1.710	1.555	1.543	1.760	–997.26915	B3LYP/6-31G *
–	H	1.755	1.836	1.713	1.542	1.534	1.776	–179.89365	B3LYP/6-31G *

<sup>a</sup>B(6) is the apical boron, B(2) is the unique boron and B(4,5) are the basal borons.

<sup>b</sup>In compounds having several cations, one cationic group occupies the apical position above the C<sub>2</sub>B<sub>3</sub> face (position 1) and the other is exopolyhedrally bound.

Table 5  
Experimental and calculated interatomic distances for some *nido*-2,3- $C_2B_4$  carboranes

Bond distance in Å <sup>a</sup>								Energy (A.U.)	Ref. or method
M	R	B(6)–B(3,5)	B(6)–B(4)	B(6)–C(1,2)	C(1,2)–B(3,5)	B(4)–B(3,5)	C(1)–C(2)		
$M_2[2,3-(R)_2C_2B_4H_4]^{2-}$									
[Li(TMEDA)]	SiMe <sub>3</sub>	1.793	1.800	1.706	1.559	1.637	1.509	–	[7]
–	SiMe <sub>3</sub>	1.832	1.830	1.704	1.573	1.655	1.513	–996.47393	B3LYP/6-31G*
–	H	1.827	1.826	1.706	1.551	1.678	1.467	–179.07163	B3LYP/6-31G*
[1,2,3-LiC <sub>2</sub> B <sub>4</sub> H <sub>6</sub> ] <sup>–</sup>		1.801	1.795	1.706	1.562	1.690	1.485	–186.82552	B3LYP/6-31G*
$M[2,3-(R)_2C_2B_4H_5]^{-}$									
[Na(THF)]	SiMe <sub>3</sub> <sup>b</sup>	1.802	1.763	1.725	1.535	1.634	1.485	–	[6]
		1.747		1.704	1.536	1.770			
[Na(TMEDA)]	SiMe <sub>3</sub> <sup>b</sup>	1.787	1.760	1.725	1.528	1.642	1.490	–	[7]
		1.719		1.702	1.532	1.770			
[Na(TMEDA) <sub>2</sub> ]	SiMe <sub>3</sub> <sup>b,c</sup>	1.789	1.751	1.713	1.508	1.608	1.451	–	[19]
		1.735		1.692	1.522	1.753			
[Li(TMEDA) <sub>2</sub> ]	SiMe <sub>3</sub> <sup>b,c</sup>	1.720	1.765	1.657	1.506	1.654	1.468	–	[18]
		1.753		1.673	1.512	1.682			
–	H <sup>B</sup>	1.847	1.773	1.729	1.529	1.661	1.456	–179.86827	B3LYP/6-31G*
		1.757		1.708	1.528	1.800			
$[2,3-(R)_2C_2B_4H_6]$									
	H	1.772	1.714	1.750	1.499	1.790	1.418	–	[37]
	H	1.789	1.726	1.764	1.522	1.792	1.424	–180.43563	B3LYP/6-31G*
	Me	1.768	1.705	1.762	1.520	1.778	1.432	–	[37]
	Me	1.775	1.721	1.783	1.530	1.779	1.431	–259.07115	B3LYP/6-31G*
	SiMe <sub>3</sub> , Me <sup>d</sup>	1.761	1.687	1.832	1.544	1.758	1.460	–	[38]
	SiMe <sub>3</sub> , Me <sup>d</sup>	1.775	1.728	1.773	1.523	1.781	1.438	–	B3LYP/6-31G*

<sup>a</sup>B(6) is the apical boron, B(4) is the unique boron and B(3,5) are the basal borons. In compounds having several cations, one cationic group occupies the apical position above the  $C_2B_3$  face (position 1) and the other is exopolyhedrally bound.

<sup>b</sup>In those complexes in which protonation has removed symmetry, the first distance listed is for the unprotonated atoms (C(2) and B(3)).

<sup>c</sup>The crystal structure shows solvent separated ion pairing with the metal group being exopolyhedral.

<sup>d</sup>The [2-(SiMe<sub>3</sub>)-3-(Me)-2,3-B<sub>4</sub>H<sub>6</sub>] carborane.



Table 6  
 $^{11}\text{B}$  and  $^{13}\text{C}$  NMR chemical shifts of some *closo*- and *nido*-carboranes calculated at various levels from B3LYP/6-31G\* geometries<sup>a</sup>

Compound	$\delta^{13}\text{C}$	$\delta^{11}\text{B}$	Ref./Level
<i>nido</i> -[2,3- $\text{C}_2\text{B}_4\text{H}_8$ ]	122	-53.3(1)	-2.0(2) [30]
		-50.5(1)	-3.3(1) [31]
		-54.0(1)	-3.0(3) [32]
	127.30	-57.22(1)	-3.97(2) B3LYP/6-311G**
	115.34	-55.33(1)	-5.88(2) B3LYP/6-31G*
	123.43	-51.57(1)	0.79(2) 2.68(1) HF/6-311G**
	121.97	-52.01(1)	0.04(2) 1.64(1) HF/6-311G*
<i>nido</i> -[1,2- $\text{C}_2\text{B}_3\text{H}_7$ ]	117.94	-51.29(1)	-1.03(2) 1.94(1) HF/6-31G*
	-21.5	57.9	-13.39(2) -15.07(1) [33]
	-31.54	53.35	-10.73(2) -14.83(1) HF/6-311G**
<i>nido</i> -[2,3-(Me) $_2\text{C}_2\text{B}_4\text{H}_6$ ]	-22.90	64.21	-15.84(2) -20.22(1) B3LYP/6-311G**
			-47.7(1) -7.2(1) -3.7(2) [34]
	136.37	-46.26(1)	-1.01(2) 1.39(1) HF/6-311G**
<i>nido</i> -[2-(SiMe $_3$ )-3-(Me)-2,3- $\text{C}_2\text{B}_4\text{H}_6$ ]	141.98	-51.35(1)	-5.72(2) -4.76(1) B3LYP/6-311G**
	143	134	-48.3(1) -1.54(1) -0.73(1) 0.14(1) [35]
	150.76	140.91 <sup>b</sup>	-52.3(1) -3.98(1) -2.68(1) -2.39(1) B3LYP/6-311G**
<i>closo</i> -[1,5- $\text{C}_2\text{B}_3\text{H}_5$ ]	145.20	134.17 <sup>b</sup>	-47.18(1) 0.91(1) 2.06(1) 3.52(1) HF/6-311G**
		103.3	1.4 and 3.5 [30]
		106.41	1.34 B3LYP/6-311G**
<i>closo</i> -[1,2- $\text{C}_2\text{B}_4\text{H}_6$ ]		93.63	14.16 HF/6-311G**
		96.42	-0.23 B3LYP/6-31G*
			1.6 -16.3 <sup>c</sup> [30]
	41.80		3.15 -14.09 <sup>c</sup> HF/6-311G**
	53.82		-1.15 -17.26 <sup>c</sup> B3LYP/6-311G**

<sup>a</sup>The numbers in parentheses are the relative intensities.

<sup>b</sup>The C–Si cage carbon.

<sup>c</sup>Apical borons.

Me) species at the ab initio MP2(fc)/6-31G\* level of theory. The structure, whose energy was found to be about 19.2 kJ/mol (R = H) higher than that of the well known *nido*-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>8</sub> [31,32,34,30]. The optimized geometry showed an intact C<sub>2</sub>B<sub>4</sub>H cage, similar to that shown in Fig. 1, with the second hydrogen occupying an *endo*-position over one of the cage carbon atoms but is tilted towards one of the neighboring boron atoms to form a partial CHB bridge. The calculated ab initio/GIAO/NMR <sup>11</sup>B chemical shifts of the permethylated compound, [*nido*-2,4-C<sub>2</sub>B<sub>4</sub>Me<sub>6</sub>H<sub>2</sub>], were very similar to those found by Wrackmeyer and coworkers [36] for an intermediate in the decomposition of perethylated *arachno*-1-carba-pentaborane(10) derivatives to pentaethyl-1,5-dicarba-*closo*-pentaborane(5) [44]. Nonetheless, all of our attempts in producing the neutral [*nido*-2,4-(SiMe<sub>3</sub>)<sub>2</sub>-2,4-C<sub>2</sub>B<sub>4</sub>H<sub>6</sub>] by the further protonation of **II–IV** using anhydrous HCl, HBF<sub>4</sub> · OEt<sub>2</sub>, or CF<sub>3</sub>SO<sub>3</sub>H have proven unsuccessful.

### 3.2. NMR spectra

The <sup>11</sup>B NMR spectra of **II** and **III** are identical to each other and show no changes in switching solvent from benzene to THF. The <sup>11</sup>B NMR spectra of these compounds are similar to those of the other group 1 compounds in the *nido*-C<sub>2</sub>B<sub>4</sub> cage system in that all show an upfield resonance, in the δ –50 ppm range, due to the apical boron, with the resonances of the less shielded facial borons on the C<sub>2</sub>B<sub>3</sub> ring being shifted downfield by some 50–80 ppm [7,8]. In the 2,4-isomers the unique boron, which resides on the pseudo mirror plane of the cage [B(2) in Fig. 2], is the least shielded so that 1:2:1 peak area ratios are normally found [8], while in the 2,3-isomers the relative shielding of the facial borons is reversed giving rise to a pattern of 2:1:1 peak area ratios [7]. The <sup>11</sup>B NMR spectra of these *nido*-carboranes have been found to be sensitive to the nature of the metal group that is capped above its C<sub>2</sub>B<sub>3</sub> face and thus the <sup>11</sup>B NMR spectroscopy has routinely been used to monitor the progress of the formation of metal-carboranes. In those cases where X-ray quality crystals cannot be obtained, NMR is the major structural tool. In general, it has been found that the formation of a heterocarborane results in a deshielding of the cage atoms which has been rationalized in terms of the heteroatom withdrawing electron density from the cage when it bonds to the C<sub>2</sub>B<sub>3</sub> face of the carborane ligand [5,13]. However, there are large variations in such changes on complexation. For example, the <sup>11</sup>B NMR spectra of *closo*-1-Sn-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> shows two peaks at δ 24.5 ppm and –4.7 ppm with 3:1 peak area ratio, indicating a downfield shift of the apical boron resonance of about 40 ppm from its dianionic precursor resonances of δ –48.40 ppm, 3.18 ppm and 20.94 ppm for the apical, unique and basal borons,

respectively (see Table 4). Similar large downfield shifts have been observed on the formation of the germa-carboranes [38]. On the other hand, the <sup>11</sup>B NMR spectrum of 1-(C<sub>8</sub>H<sub>6</sub>N<sub>4</sub>)-1-(Me<sub>2</sub>CH)-1-In-2,3-(SiMe<sub>3</sub>)<sub>2</sub>-2,3-C<sub>2</sub>B<sub>4</sub>H<sub>4</sub> shows three resonances of 2:1:1 peak area ratios at δ 16.11, –0.12 and –51.81 ppm, respectively [45]. The opposing changes produced by metal complexation in the stanna- and indacarboranes is difficult to rationalize in terms of simple qualitative electron withdrawing arguments. Hermánek and coworkers have studied the <sup>11</sup>B NMR spectra of heterocarboranes of the form *closo*-EB<sub>11</sub>H<sub>11</sub> and EB<sub>9</sub>H<sub>9</sub> (E = a cage moiety bonded through a group 13, 14, 15 or 16 element) as a function of E and have found that the boron opposite to E is the one most affected [46,47], but that the distribution of electron density around the borons, rather than gross electron density, determined the chemical shift variations. Therefore, if NMR spectroscopy is to be generally useful in rationalizing the structures of the heterocarboranes, a better understanding of the significant aspects of the spectra of the starting carborane mono- and dianions must be established, as well as insight into what factors, other than hetero atom-carborane bonding, may affect the NMR spectra of these cages. To help establish such a basis, a combined experimental and theoretical study of the NMR spectra of mono- and dianions in the 2,3- and 2,4-C<sub>2</sub>B<sub>4</sub> cage systems was carried out, the results are given in Tables 4 and 7. The selection of the theoretical methods used in this study was based on the analyses of the calculated <sup>13</sup>C and <sup>11</sup>B NMR spectra of several *closo*- and *nido*-carboranes given in Table 4. The geometries of all the carboranes under investigation were those optimized at the 6-31G\* level of theory using approximate density functional theory with Becke's three-parameter hybrid method [29] and the correlation functional of Lee, Yang and Parr [48] (B3LYP/6-31G\*). It was found that this method provided geometries that yielded excellent agreement between the experimental and theoretical <sup>13</sup>C and <sup>11</sup>B NMR spectra of the test compounds listed in Table 4. This level of theory is the minimum suggested by Cheeseman and coworkers for predicting the <sup>13</sup>C NMR spectra of a number of large organic molecules [49]. The results in Table 4 show that, with the exception of *closo*-1,5-C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>, the <sup>13</sup>C and <sup>11</sup>B chemical shifts calculated from GIAO-HF/6-311G\*\* and GIAO-B3LYP/6-311G\*\* shielding constants agree quite well with experiment, and there seems to be no inherent advantage of one method over another. However, for the small *closo*-1,5-C<sub>2</sub>B<sub>3</sub>H<sub>5</sub>, where electron correlation effects are important [33], the DFT results are far superior to those obtained at the Hartree–Fock level. Schleyer and coworkers found that satisfactory <sup>13</sup>C and <sup>11</sup>B NMR chemical shifts could be calculated for *closo*-1,5-C<sub>2</sub>B<sub>3</sub>H<sub>5</sub> only at a correlated (GIAO-MP2/TZP') level

Table 7

Experimental and calculated  $^{11}\text{B}$  NMR chemical shifts for some *nido*- $\text{C}_2\text{B}_4$  carboranes<sup>a</sup>

Complex	$^{11}\text{B}$ NMR chemical shifts (relative intensities) $\delta$ , ppm			Ref. or method
<i>nido</i> -[2,4-( <i>R</i> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>5</sub> ] <sup>−</sup>				
<b>II–IV</b>				This work
[2,4-(SiMe <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>5</sub> ] <sup>−</sup>	−51.75(1);	2.90(2);	24.3(1)	HF/6-311G**
	−46.24(1)	6.85(2)	30.03(1)	B3LYP/6-311G**
	−53.24(1)	1.60(2)	24.16(1)	B3LYP/6-311G**
Li[2,4-C <sub>2</sub> B <sub>4</sub> H <sub>7</sub> ] <sup>b</sup>	−52.5(1);	0.8(2);	20.9(1)	[22]
Li[2,4-C <sub>2</sub> B <sub>4</sub> H <sub>7</sub> ] <sup>c</sup>	−51.9(1);	1.3(2);	21.1(1)	[21]
[2,4-C <sub>2</sub> B <sub>4</sub> H <sub>7</sub> ] <sup>−</sup>	−51.95(1);	2.29(2);	23.31(1)	HF/6-311G**
	−59.10(1)	−3.32(2)	17.68(1)	B3LYP/6-311G**
<i>nido</i> -[2,4-( <i>R</i> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ] <sup>2−</sup>				
[Na(THF)] <sub>2</sub> [2,4-(SiMe <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ] <sup>d</sup>	−45.86(1)	8.12(2)	30.02(1)	[10]
[Li(THF)] <sub>2</sub> [2,4-(SiMe <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ] <sup>d</sup>	−42.28(1)	13.94(2)	16.25(1)	[8]
[Li(TMEDA)] <sub>2</sub> [2,4-(SiMe <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ] <sup>e</sup>	−48.78(1)	6.56(2)	18.02(1)	[8]
[2,4-(SiMe <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ] <sup>2−</sup>	−52.80(1)	10.42(2)	18.81(1)	HF/6-311G**
	−58.63(1)	5.83(2)	10.97(1)	B3LYP/6-311G**
[2,4-C <sub>2</sub> B <sub>4</sub> H <sub>6</sub> ] <sup>2−</sup>	−60.11(1)	4.83(2)	9.97(1)	HF/6-311G**
	−66.17(1)	0.39(2)	2.93(1)	B3LYP/6-311G**
[1,2,4-LiC <sub>2</sub> B <sub>4</sub> H <sub>6</sub> ] <sup>−</sup>	−49.84(1)	9.81(2)	12.87(1)	HF/6-311G**
	−57.07(1)	5.33(2)	6.18(1)	B3LYP/6-311G**
<i>nido</i> -[2,3-( <i>R</i> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>5</sub> ] <sup>−</sup>				
Na[2,3-C <sub>2</sub> B <sub>4</sub> H <sub>7</sub> ] <sup>c</sup>	−55.0(1)	−5.5(1)	7.1(2)	[21]
Na[2,3-C <sub>2</sub> B <sub>4</sub> H <sub>7</sub> ] <sup>f</sup>	−56(1)	−11(1)	0.3(1)	[31]
[2,3-C <sub>2</sub> B <sub>4</sub> H <sub>7</sub> ] <sup>−g</sup>	−55.24(1)	−3.68(1)	3.27(1,BH)	HF/6-311G**
	−60.93	−8.18(1)	−2.53(1,BH)	B3LYP/6-311G**
Na[2,3(Me) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>5</sub> ] <sup>f</sup>	−48(1)	−9.8(1)	1.8(1)	[31]
[2,3(Me) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>5</sub> ] <sup>−</sup>	−48.64(1)	−5.35(1)	3.30(1,BH)	HF/6-311G**
	−53.61(1)	−10.21(1)	−1.93(1,BH)	B3LYP/6-311G**
[Na(THF)][2,3-(SiMe <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>5</sub> ] <sup>e</sup>	−50.76(1)		−3.78(1)	[6]
[Na(TMEDA)][2,3-(SiMe <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>5</sub> ] <sup>e</sup>	−49.73(1)		1.92(1)	[7]
[Na(TMEDA)] <sub>2</sub> [2,3-(SiMe <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>5</sub> ] <sup>e</sup>	−46.22(1)	0.00(1)	8.5(1)	[19]
[Li(TMEDA)] <sub>2</sub> [2,3-(SiMe <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>5</sub> ] <sup>e</sup>	−50.43(1)		−4.09(1)	[18]
<i>nido</i> -[2,3-( <i>R</i> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ] <sup>2−</sup>				
Li[1-Li-2,3-(SiMe <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ] <sup>f</sup>	−44.50(1)	2.36(1)	18.16(2)	[7]
Li(TMEDA)] <sub>2</sub> [2,3-(SiMe <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ] <sup>e</sup>	−48.40(1)	3.18(1)	20.94(2)	[7]
[2,3-(SiMe <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> B <sub>4</sub> H <sub>4</sub> ] <sup>2−</sup>	−54.67(1)	1.31(1)	21.51(2)	B3LYP/6-311G**
	−50.02(1)	2.99(1)	28.87(2)	HF/6-311G**
[2,3-C <sub>2</sub> B <sub>4</sub> H <sub>6</sub> ] <sup>2−</sup>	−60.34(1)	−1.17(1)	11.40(2)	HF/6-311G**
	−65.73(1)	−3.54(1)	5.63(2)	B3LYP/6-311G**
[1,2,3-LiC <sub>2</sub> B <sub>4</sub> H <sub>6</sub> ] <sup>−</sup>	−49.02(1)	6.59(1)	15.48(2)	HF/6-311G**
	−55.81(1)	3.70(1)	9.57(2)	B3LYP/6-311G**
Li[1,2,3-LiC <sub>2</sub> B <sub>4</sub> H <sub>6</sub> ] <sup>g</sup>	−48.76(1)	3.83(1)	8.52(1,BLi)	HF/6-311G**
	−54.99(1)	0.76(1)	2.24(1,BLi)	B3LYP/6-311G**

<sup>a</sup>The chemical shifts, in ppm, are relative to  $\text{BF}_3 \cdot \text{OEt}_2$ , geometries are optimized at the B3LYP/6-31G\* level, relative intensities are in parentheses.

<sup>b</sup>Solvent =  $\text{CH}_3\text{CN}$ .

<sup>c</sup>Solvent = Dimethoxyethane ( $\text{MeOCH}_2\text{CH}_2\text{OMe}$ ).

<sup>d</sup>Solvent = THF-*d*<sub>8</sub>.

<sup>e</sup> $\text{C}_6\text{D}_6$  or  $\text{C}_6\text{H}_6$ .

<sup>f</sup>Solvent = diglyme [ $(\text{MeOCH}_2\text{CH}_2)_2\text{O}$ ].

<sup>g</sup>The sequence in order of decreasing shielding is B(apical), B(unique), B(facial with H or Li atom), B(facial no bridge).

of ab initio theory [33,30]. GIAO-MP2/TZP' derived  $^{13}\text{C}$  and  $^{11}\text{B}$  chemical shifts calculated by these investigators were 104.2 ppm and 1.9 ppm, respectively, which can be compared to value of 106.4 ppm and 1.3 ppm at the B3LYP/6-311G\*\* level, given in Table 4, and experimental values of 103 ppm and 1.4 ppm, respectively [33,30]. It is gratifying that, at least for this test compound, correlation effect-corrections incorporated in

the more time efficient DFT-B3LYP approach works equally well as do the more extensive post Hartree–Fock MP2 methods. The use of MP2 derived geometries for the DFT based GIAO chemical shift calculations do not materially improve the results over those obtained from B3LYP/6-31G\* geometries; when a MP2/6-311G\* optimized geometry of *closo*-1,2- $\text{C}_2\text{B}_4\text{H}_6$  was used with a GIAO-B3LYP/6-311G\*\* chemical shift calcu-

lation, the results were:  $^{13}\text{C}$ ,  $\delta$  54.84 ppm;  $^{11}\text{B}$ ,  $\delta$  –1.00, –17.13 ppm, which are essentially the same as those listed in Table 4. Therefore, GIAO-BL3LYP/6-311G\*\*//B3LYP/6-311G\* calculations may provide an attractive alternative to the more exact and time intensive correlated GIAO methods, especially when the size of the molecule under study would make such calculations prohibitively expensive, both in terms of CPU time and memory/disk space requirements.

Table 7 lists the experimental and calculated  $^{11}\text{B}$  NMR chemical shifts for the mono- and dianions of the *nido*- $\text{C}_2\text{B}_4$  cage systems. The NMR spectra of the carbons apart monoanions,  $[\text{2,4-(R)}_2\text{C}_2\text{B}_4\text{H}_5]^-$  (R = H and  $\text{SiMe}_3$ ), are reproduced quite well by the GIAO calculations. The ab initio GIAO/B3LYP/6-311G\*\* calculated  $^{11}\text{B}$  NMR chemical shifts of  $[\text{2,4-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_5]^-$  reproduce the experimental values for compounds **II–IV** to within less than 2 ppm. The calculations also reproduce quite well the experimental shifts in the parent monoanion,  $[\text{2,4-C}_2\text{B}_4\text{H}_7]^-$ , with the HF/6-311G\*\* chemical shifts being somewhat superior. In general, the HF-based GIAO calculations predict less shielding than do the DFT-based ones, depending on the complex, this works either to its advantage or disadvantage. In the absence of strong electron correlation effects, such as was found in *closo*-1,5- $\text{C}_2\text{B}_3\text{H}_5$ , there is no reason to favor one method over another. On the other hand, the agreement between the calculated chemical shifts of the  $[\text{2,4-(R)}_2\text{C}_2\text{B}_4\text{H}_4]^{2-}$  dianions is not as good. All the experimental data are on the  $[\text{2,3-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4]^{2-}$  dianion with different cations [8] (see Table 7). Both DFT and HF calculations rather severely overestimate the shielding at the apical boron and predict chemical shifts that are too negative by about 10 ppm. In view of the good agreement between the calculated and observed chemical shifts of the neutral carboranes and monoanions, this discrepancy is most probably not a reflection of the limitations of the theory used in the calculations. A possible explanation for this is ion-pairing in the NMR solutions. The spectra of the dianionic species were obtained in low dielectric constant solvents ( $\text{THF-d}_8$  or  $\text{C}_6\text{D}_6$ ) in which ion pairing with the cation should be extensive. The crystal structures of the dianionic compounds show that one of the group 1 cations occupies the apical position above the  $\text{C}_2\text{B}_3$  face of the carborane, while the other is *exo*-polyhedrally bound to adjacent borons of the bonding face via two  $\text{B-H}_{(\text{terminal})}\text{-M}$  bonds [8,10]. The existence of two different lithium's was also evident in the  $^7\text{Li}$  NMR spectra of *exo*-5,6- $\text{Li}(\text{TMEDA})\text{-1-Li}(\text{TMEDA})\text{-2,4-(SiMe}_3)_2\text{C}_2\text{B}_4\text{H}_4$ , one with a  $^7\text{Li}$  NMR resonance at –2.13 ppm (relative to external aqueous  $\text{LiNO}_3$ ) and the other at –6.88 ppm [8]. The former was assigned to the exopolyhedral lithium while the latter was due to the *endo*-cage bonded metal group, so that a formulation

*closo-exo*-5,6- $[(\mu\text{-H})_2\text{Li}(\text{TMEDA})]\text{-1-Li}(\text{TMEDA})\text{-2,4-(SiMe}_3)_2\text{-2,4-C}_2\text{B}_4\text{H}_4$ ] was used in describing the compound [8]. The observation of two lithium resonances separated by about 4–5 ppm was also found in the  $^7\text{Li}$  NMR spectra of the corresponding TMEDA-solvated dilithium compound of the carbons adjacent carborane [7] (see Table 7). Since the apical boron resonances are those most affected by metal interactions, GIAO calculations on the model compounds  $[\text{2},n\text{-C}_2\text{B}_4\text{H}_6]^{2-}$  ( $n = 3, 4$ ) and their corresponding  $[\text{1},2,n\text{-LiC}_2\text{B}_4\text{H}_6]^-$  monoanions were undertaken. The results show that coordination of the dianion by a  $\text{Li}^+$  deshields the boron atoms and results in an upfield shift of the apical boron resonance of about 10 ppm, with the shifts of the more deshielded facial borons being progressively less affected. This 10 ppm change in the apical boron resonances is close to the discrepancies found between the calculated and observed  $^{11}\text{B}$  NMR resonances shown in Table 7. In addition, the GIAO calculated isotropic shielding parameters of the two lithium ions in  $\text{Li}[\text{1},2,3\text{-LiC}_2\text{B}_4\text{H}_6]$  indicates that the two  $^7\text{Li}$  resonances should be separated by  $\sim 7$  ppm, which is consistent with what is found experimentally [7].

The agreement between the experimental and calculated  $^{11}\text{B}$  NMR chemical shifts of the carbons adjacent monoanions, shown in Table 7, is not nearly as good as that found for the carbons apart isomers. Part of the problem is the complications arising for the asymmetry of the monoanion. Theory shows that the presence of the bridging hydrogen, as shown in Fig. 2, should lift the degeneracy of the two basal borons, with the boron involving in the hydrogen bridge being more heavily shielded (see Table 7). Calculations show that the splitting should be in the order of  $\sim 12\text{--}13$  ppm and should be detected experimentally. With the exception of  $\text{Na}[\text{2},3\text{-C}_2\text{B}_4\text{H}_7]$  and  $\text{Na}[\text{2},3\text{-(Me)}_2\text{C}_2\text{B}_4\text{H}_5]$  [31], all spectra show equivalent basal borons. This indicates that either a rapid proton exchange or some internal fluxional motion are equilibrating the two bridging sites. Schleyer and coworkers were able to identify a possible transition state for the migration of the bridge hydrogen in the model compound  $[\text{nido-2},3\text{-C}_2\text{B}_4\text{H}_7]^-$  that was 36.0 kJ/mol higher in energy than the single bridged anion [43], so fluxionality would not be unexpected. The two spectra in which nonequivalent borons were observed were run in diglyme, while the others were run in either dimethoxyethane or  $\text{C}_6\text{D}_6$ . However, in the diglyme solvent agreement between calculated and observed  $^{11}\text{B}$  NMR spectra is good. At present it is not apparent why diglyme should promote a more rigid stereochemistry than the other solvents. In cases where equilibration of the basal borons is found, the average of the bridged and unbridged resonances reproduces the measured values reasonably well. From the results on  $\text{Li}[\text{1},2,3\text{-LiC}_2\text{B}_4\text{H}_6]$  there is no reason to assume ion-aggregation greater than 1:1 need be considered in

rationalizing the spectra of these dianionic carborane compounds.

The results in Table 7 show that the  $^{11}\text{B}$  NMR chemical shifts of the mono- and dianions are not only functions of their cage structures, but also of their environment. It is also apparent that, under most circumstances, the parent carboranes, and metallocarboranes, can serve as useful guides for interpreting experimental chemical shifts of cages having cage-carbon substituents other than hydrogen.

#### 4. Supplementary material

A full listing of bond lengths and angles, thermal parameters, H atom parameters, observed and calculated structure factors for **IV** can be obtained from the authors (HZ).

#### 5. Unlinked References

[50]

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