

## Magnesium Alkyls as Metalating Reagents in the Formation of Novel Half- and Full-Sandwich Magnesacarboranes

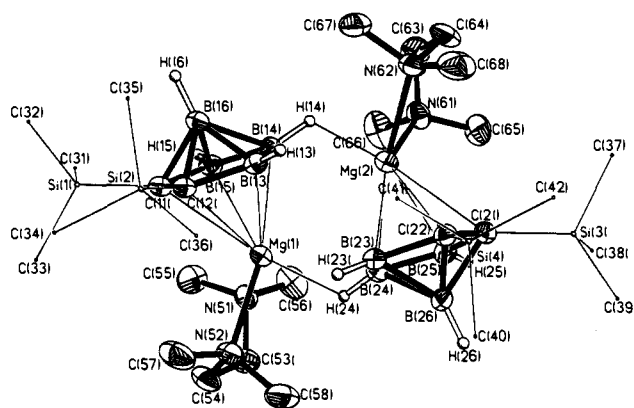
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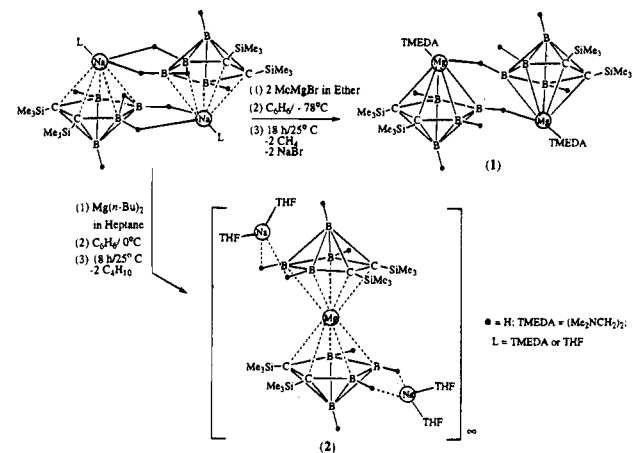
The most commonly encountered metallacarboranes are those in which a metal group is coordinated to the  $C_2B_3$  open face of either a  $[R_2C_2B_4H_4]^{2-}$  or a  $[R_2C_2B_9H_9]^{2-}$  carborane dianion, which is usually produced by removing B–H–B bridge hydrogens from the neutral *nido*-carboranes.<sup>1</sup> It is also well-known that alkylations of metal halides and other compounds are conveniently carried out using either magnesium dialkyls,  $R_2Mg$ , or Grignard reagents,  $RMgX$  ( $R$  = an alkyl group,  $X$  = a halide anion), in an ethereal solvent.<sup>2</sup> Since these alkylation reactions are believed to proceed via initial formation of alkyl bridges,<sup>3</sup> the question arose whether the magnesium alkyls could perturb the B–H–B bridges in a *nido*-carborane sufficiently to lead to either an alkylation or a metalation of the carborane. The latter result would afford the first magnesacarborane. This speculation led us to carry out the reactions between the TMEDA-solvated monosodium compound of the  $[2,3-(SiMe_3)_2-2,3-C_2B_4H_5]^-$  anion and alkylating agents,  $MeMgBr$  and  $(n-C_4H_9)_2Mg$ , in 1:1 and 2:1 stoichiometries in diethyl ether.<sup>4</sup> These reactions produced the novel half-sandwich magnesium complex *closo*-1-Mg(TMEDA)-2,3-( $SiMe_3$ )<sub>2</sub>-2,3- $C_2B_4H_4$  (**1**) and the full-sandwich dianionic magnesacarborane  $\{commo-1,1'-Mg[2,3-(SiMe_3)_2-2,3-C_2B_4H_4]_2\}^{2-}$  (**2**) in 87 and 82% yields, respectively, as outlined in Scheme 1.<sup>5</sup> No alkylations of the B–H bonds of the carborane cage were evident in the reaction. Although magnesocene has been known for some time<sup>6</sup> and an *exo*-polyhedrally bound magnesium has been reported in the metallaborane,  $(THF)_2Mg(B_6H_8)_2$ ,<sup>7</sup> to our knowledge, compounds **1** and **2** are the first reported *endo*-polyhedral magnesium complexes in any polyhedral borane or carborane system.

Recently, it has been established that the second B–H–B bridge hydrogen in  $[2,3-(SiMe_3)_2-2,3-C_2B_4H_5]^-$  monoanion is weakly acidic and, unlike in the  $C_2B_9$ -cage system, it does not readily undergo further deprotonation with strong heterogeneous bases, such as  $NaH$ .<sup>8</sup> The failure to further deprotonate with excess  $NaH$  has severely limited the use of this monosodium carborane compound in the syntheses of many targeted metallacarboranes.<sup>8</sup> The reaction of either the monosodium or the sodium/lithium compound of the carborane with  $MgX_2$  produced complex mixtures that could not be easily separated, and the



**Figure 1.** Perspective view of **1** drawn at the 40% probability level. Pertinent distances (Å) and angles (deg): Mg(1,2)–( $C_2B_3$  centroid) 1.2, 2.139, 2.124; Mg(1,2)–C(11,21) 2.649(3), 2.621(4); Mg(1,2)–C(12,22) 2.635(3), 2.596(3); Mg(1,2)–B(13,23) 2.493(3), 2.485(3); Mg(1,2)–B(14,24) 2.393(3), 2.404(3); Mg(1,2)–B(15,25) 2.472(4), 2.471(3); Mg(1,2)–B(24,14) 2.540(5), 2.534(5); Mg(1,2)–N(51,61) 2.327(2), 2.325(3); Mg(1,2)–N(52,62) 2.252(2), 2.256(2); (centroid 1)–Mg–N(51,52) 119.6, 127.5; (centroid 2)–Mg–N(61,62) 120.1, 127.2 (see supporting information, Tables S-2 and S-3, for detailed bond lengths and angles). For clarity, the *exo*-polyhedral  $SiMe_3$  groups were drawn with circles of arbitrary radii and the methyl and methylene H's were omitted.

### Scheme 1



neutral *nido*-2,3-( $SiMe_3$ )<sub>2</sub>-2,3- $C_2B_4H_6$  did not react with either  $R_2Mg$  or  $RMgX$ .<sup>9</sup> However, it seems that the formation of an alkane molecule is the driving force in Scheme 1, and is responsible for the high-yield formation of magnesacarboranes **1** and **2**. If this proves to be a general method, other metal alkyls could be used in the selective synthesis of a number of hitherto unknown half- or full-sandwich metallacarboranes. The generality of this reaction is currently being explored in our laboratories.

In addition to elemental analyses, both **1** and **2** were characterized by IR spectroscopy,<sup>10</sup>  $^1H$ ,  $^{11}B$ , and  $^{13}C$  NMR spectroscopy,<sup>10</sup> and X-ray crystallography.<sup>11</sup> The  $^{11}B$  NMR spectra of **1** showed resonances at  $\delta$  18.58, –0.28, and –49.77 ppm with peak area ratios of 2:1:1, which is quite similar to the 2:1:1 pattern at  $\delta$  15.68, 1.92, and –49.73 ppm, respectively, found for its monosodium precursor.<sup>8</sup> Such a similarity would be expected if the interaction of the Mg with the carborane was predominantly ionic. The X-ray analysis of **1** (see Figure 1)<sup>11</sup> shows a dimeric structure that is very similar to that of its precursor. However, a close examination of the metal–

(9) Unpublished results.

(10) Details given in the supporting information.

(1) (a) Grimes, R. N. *Chem. Rev.* **1992**, *92*, 251. (b) Grimes, R. N. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 1, Chapter 5.5, p 459.

(2) (a) Lindsell, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 1, Chapter 4. (b) Brandsma, L.; Verkruijse, H. In *Preparative Polar Organometallic Chemistry*; Trost, B. M., Ed.; Springer-Verlag: New York, 1986. (c) Lai, Y.-H. *Synthesis* **1981**, 585.

(3) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988.

(4) TMEDA = *N,N,N,N*-tetramethylethylenediamine,  $(CH_3)_2NCH_2CH_2N(CH_3)_2$ .

(5) Details of the syntheses are given in the supporting information.

(6) Bunder, W.; Weiss, E. *J. Organomet. Chem.* **1975**, *92*, 1.

(7) Denton, D. L.; Clayton, W. R.; Mangion, M.; Shore, S. G.; Meyers, E. A. *Inorg. Chem.* **1976**, *15*, 541.

(8) Hosmane, N. S.; Saxena, A. K.; Barreto, R. D.; Zhang, H.; Maguire, J. A.; Jia, L.; Wang, Y.; Oki, A. R.; Grover, K. V.; Whitten, S. J.; Dawson, K.; Tolle, M. A.; Siriwardane, U.; Demissie, T.; Fagner, J. S. *Organometallics* **1993**, *12*, 3001.

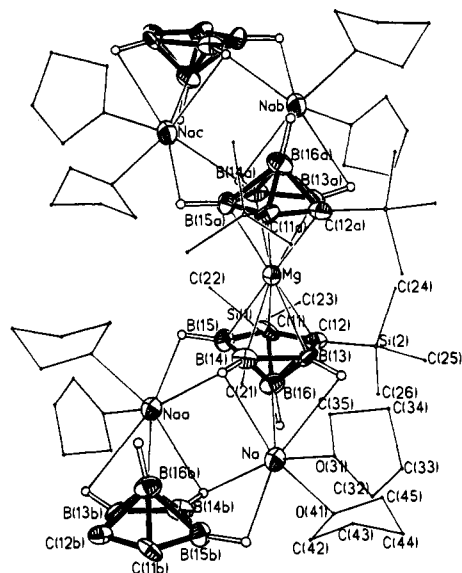
carborane bond distances [Mg–C(11,12) = 2.649(3), 2.635(3); Mg–B(13,15) = 2.493(3), 2.472(4); Mg–B(14) = 2.393(3) Å] reveals that the Mg atom in **1** is significantly slip-distorted toward the unique boron, B(14). Such slippages have been reported for the metallacarboranes of the group 13 and group 14 elements.<sup>12</sup> The terminal hydrogen on the unique boron forms a B–H–Mg bridge; therefore, it is possible that this interaction may be the cause of the slip-distortion of the apical Mg, rather than some Mg–carborane bonding preference. The X-ray structure of **2** (see Figure 2)<sup>11</sup> can be described as an extended array of dianionic magnesacarboranes,  $\{[2,3-(\text{SiMe}_3)_2-2,3-\text{C}_2\text{B}_4\text{H}_4]_2\text{Mg}\}^{2-}$ , in which the boron atoms of the bonding faces interact with *exo*-polyhedral sodium cations. No metal slip distortion can be detected in these complexes.

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**Supporting Information Available:** Experimental procedures, spectroscopic details, tables of positional and thermal parameters, selected bond distances, and bond angles for **1** and **2** (15 pages). This

(11) X-ray data for **1** ( $[\text{C}_{28}\text{H}_{76}\text{Na}_4\text{Si}_4\text{B}_8\text{Mg}_2] \cdot [\text{C}_6\text{H}_6]$ ; fw, 794.5;  $P\bar{1}$ ) and **2** ( $\text{C}_{32}\text{H}_{76}\text{O}_4\text{Si}_4\text{B}_8\text{Na}_2\text{Mg}$ ; fw, 794.1;  $C2/c$ ). Data were collected at 220 K on a Siemens R3m/V diffractometer with  $a = 13.609(2)$  and  $21.997(6)$  Å,  $b = 14.391(2)$  and  $13.417(4)$  Å,  $c = 15.021(2)$  and  $17.386(5)$  Å,  $\alpha = 89.44(1)^\circ$  and  $90^\circ$ ,  $\beta = 63.49(1)^\circ$  and  $91.28(2)^\circ$ ,  $\gamma = 81.28(1)^\circ$  and  $90^\circ$ ,  $V = 2596.4(7)$  and  $5137(4)$  Å<sup>3</sup>,  $Z = 2$  and  $4$ , and  $D_{\text{calcd}} = 1.016$  and  $1.027$  Mg/m<sup>3</sup> for **1** and **2**, respectively. Of the 5872 and 2862 reflections collected ( $2\theta = 3.0\text{--}42^\circ$ ), 4419 and 1139 reflections were considered as observed [ $F > 6.0\sigma(F)$ ]. Data were corrected for Lorentz and polarization effects. Both structures were solved by direct methods, and full-matrix least-squares refinements were performed by using SHELXTL-PLUS (Sheldrick, G. M. *Structure Determination Software Programs*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990). All non-H atoms, except for the C and O atoms of the disordered THF groups in **2**, were refined anisotropically. Bonds in the disordered groups were restrained during the final cycles of refinements. Methyl and methylene H's in the non-disordered groups were placed in calculated positions. The cage H's of **1** were isotropically refined, while those of **2** were located in difference Fourier maps without refinement. The final refinements for **1** and **2** converged at  $R = 0.039$  and  $0.095$ ,  $R_w = 0.057$  and  $0.12$ , with GOF = 1.50 and 2.50, respectively.

(12) Hosmane, N. S.; Maguire, J. A. *Adv. Organomet. Chem.* **1990**, *30*, 99 and references therein.



**Figure 2.** Perspective view of **2** drawn at the 40% probability level. This is a polymeric molecule which possesses a 2-fold symmetry axis passing through the Mg atoms. Pertinent distances (Å) and angles (deg): Mg–(C<sub>2</sub>B<sub>3</sub> centroid) 2.018; Mg–C(11) 2.446(13); Mg–C(12) 2.461(14); Mg–B(13) 2.420(16); Mg–B(14) 2.398(16); Mg–B(15) 2.405(18); B(13)–Na 2.976(17); B(14)–Na 2.867(17); B(16)–Na 3.055(18); B(14)–Na(a) ( $a = -x, -y, 1 - z$ ) 2.883(19); B(15)–Na(a) 2.831(19); Na–O(31) 2.234(23); Na–O(41) 2.308(14); (centroid)–Mg–(centroid') ( $i = -x, y, 3/2 - z$ ) 176.7 (see supporting information, Tables S-6 and S-7, for detailed bond lengths and angles). For clarity, the solvated THF molecules and the *exo*-polyhedral SiMe<sub>3</sub> units were drawn with circles of arbitrary radii.

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