5150 J. Am. Chem. Soc. **1996,** *118,* 5150−5151

The First Fully Sandwiched Lithiacarborane Complex: A Synthetic and Structural Investigation

Narayan S. Hosmane,* Jimin Yang, Hongming Zhang, and John A. Maguire

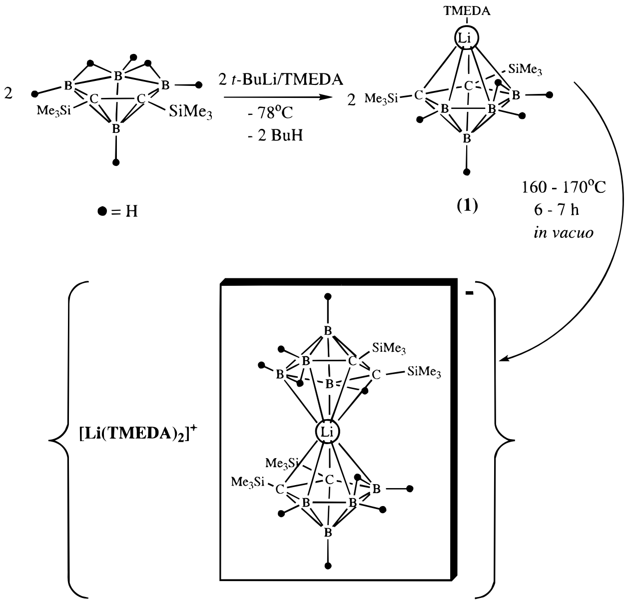
Department of Chemistry
Southern Methodist University
Dallas, Texas 75275

Received January 26, 1996

It is generally found that the monoanionic cyclopentadienides form stable sandwich complexes with metals in their lowest oxidation states, while the dianionic carborane (Cb^{2-}) ligands stabilize the higher oxidation states of the metals.[1] Consequently, the neutral Si(II) sandwiched complex is known only in the Cp (Cp = η^5-C_5R_5, R = hydrogen and an alkyl substituent) system,[2] but the corresponding Si(IV) species[3] exists exclusively in the Cb systems; a number of other examples of these oxidation state preferences are in the literature.[4] Therefore, the recent report of the formation of group 1 metal complexes in which the metal was sandwiched between π-electron Cp ligands to give the anionic full-sandwich $(Cp_2M)^-$ (M = Li, Na) complexes[5] raised the question as to whether lithium or sodium could form the analogous full-sandwich complex with the carborane ligands. If such complexes are stable, what synthetic method should be applied in their preparation? Our previous experience with the reactions of neutral and monoanionic *nido*-carboranes with group 1 bases,[6] plus our recent work on the magnesacarboranes in which it was found that the use of a monoalkyl Mg reagent produced the half-sandwich magnesacarborane while the synthesis of a full-sandwich Mg-(carborane)$_2$ complex was possible only with magnesium dialkyls,[7] indicated that the reactions of the monoalkyl lithiums with the neutral or monoanionic carborane ligands would not be profitable avenues to the synthesis of the full-sandwich group 1 metallacarborane species. Here, we report a new method for the synthesis of an anionic full-sandwich lithiacarborane complex, whose solid state structure closely resembles that of the $(Cp_2Li)^-$ complex. To our knowledge, this is the first example of a carborane species in which a group 1 metal is fully sandwiched between two carborane ligands.

Slow sublimation of the TMEDA[8] -solvated monolithium carborane complex, **1**,[9,10] at 160−170 °C over a period of 6−7 h *in vacuo* produced the full-sandwich lithiacarborane complex, $[Li^+(TMEDA)_2][$*commo*-1,1′-Li{2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5\}_2^-]$ (**2**), as a transparent crystalline solid (see Scheme 1).[10] The exactmechanism of the formation of **2** is not known. Since alkyllithiums have been shown to be sublimable,[11] it is possible that **1** is the subliming species which then disproportionates to give **2**. On the other hand, our experimental observations are also consistent with the disproportionation of **1** occurring prior to sublimation. The high yield for this reaction (61%) indicates that it may be a general method for the selective synthesis of a number of hitherto unknown full-sandwich metallacarboranes.

Scheme 1



Compound **2** was characterized by elemental analysis,[10] IR spectroscopy,[12] ^{1}H, ^{11}B, ^{13}C, and ^{7}Li NMR spectroscopy,[12] and

---

(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) Jutzi, P.; Kanne, D.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 164.

(3) (a) Siriwardane, U.; Islam, M. S.; West, T. A.; Hosmane, N. S.; Maguire, J. A.; Cowley, A. H. *J. Am. Chem. Soc.* **1987**, *109*, 4600. (b) Rees, W. S., Jr.; Schubert, D. M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 5369.

(4) (a) Hosmane, N. S.; Maguire, J. A. *Adv. Organomet. Chem.* **1990**, *30*, 99. (b) Hosmane, N. S.; Maguire, J. A. *J. Cluster Sci.* **1993**, *4*, 297 and references therein.

(5) (a) Harder, S.; Prosenc, M. H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1744. (b) Harder, S.; Prosenc, M. H.; Rief, U. *Organometallics* **1996**, *15*, 118.

(6) 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.

(7) Hosmane, N. S.; Zhu, D.; McDonald, J. E.; Zhang, H.; Maguire, J. A.; Gray, T. G.; Helfert, S. C. *J. Am. Chem. Soc.* **1995**, *117*, 12362.

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

(9) Hosmane, N. S.; de Meester, P.; Siriwardane, U.; Islam, M. S.; Chu, S. S. C. *J. Am. Chem. Soc.* **1986**, *108*, 6050. Wang, Y.; Zhang, H.; Maguire, J. A.; Hosmane, N. S. *Organometallics* **1993**, *12*, 3781.

(10) *Synthetic Procedure*: A TMEDA solution (30 mL) of *nido*-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_6$ (2.3 g, 10.5 mmol) (Hosmane, N. S.; Sirmokadam, N. N.; Mollenhauer, M. N. *J. Organomet. Chem.* **1985**, *279*, 359. Barreto, R. D.; Hosmane, N. S. *Inorg. Synth.* **1992**, *29*, 89) was slowly poured, *in vacuo*, onto a pentane solution of *t*-BuLi (8.5 mmol) in a reaction flask at −78 °C. The resulting mixture was then slowly warmed to room temperature and stirred for a short period of time (<1 h), thus avoiding the longer reaction times that gave rise to the corresponding TMEDA (solvent)-separated ion pairs.[9] During this time butane gas was evolved with concomitant formation of a pale yellow turbid solution. At this stage, all the volatile products, including solvents, were removed from the reaction flask by vacuum distillation to collect the off-white solid, *nido*-1-Li$[(Me_2NCH_2)_2]$-2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5$ (**1**) (2.86 g, 8.37 mmol),[9] in almost quantitative yield. Without further purification, the reaction flask containing **1** was attached to a detachable U-trap, whose side arm was wrapped with a heating tape, was then evacuated, and was immersed in an ice bath. Slow heating of the flask to 160−170 °C over a period of 6−7 h resulted in the deposition of colorless transparent crystals on the inside wall of the U-trap held at 0 °C; this sublimation was continued at this temperature for an additional 8 h period. The crystals were unambiguously identified as $[Li^+(TMEDA)_2][$*commo*-1,1′-Li{2,3-$(SiMe_3)_2$-2,3-$C_2B_4H_5\}_2^-]$ (**2**) (1.76 g, 2.57 mmol, 61% yield; mp 150−152 °C; soluble in both polar and nonpolar organic solvents). Compound **2** was recrystallized from a 1:1 mixture of hexane/benzene solution to give transparent rodlike X-ray quality crystals. Anal. Calcd for $C_{28}H_{78}B_8N_4Si_4Li_2$ (**2**): C, 49.19; H, 11.50; N, 8.09. Found: C, 49.32; H, 11.33; N, 8.04. The yellow polymeric mass that remained in the reaction flask after complete sublimation of **2** was insoluble in organic solvents and, therefore, was discarded.

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

(12) ^{1}H NMR (C_6D_6, relative to external Me_4Si) δ 1.75 (s, 4H, CH_2, TMEDA), 1.64 (s, 12H, Me, TMEDA), 0.55 (s, 18H, $SiMe_3$), −4.33 (s, br, 1H, B−H−B bridge); ^{11}B NMR (C_6D_6, relative to external $BF_3{\cdot}OEt_2$) δ 12.65 [br, 2B, basal BH, $^1J(^{11}B-^1H)$ = unresolved], −5.24 [br, 1B, basal BH, $^1J(^{11}B-^1H)$ = unresolved], −50.93 [d, 1B, apical BH, $^1J(^{11}B-^1H)$ = 158.2 Hz]; ^{13}C NMR (C_6D_6, relative to external Me_4Si) δ 112.60 [s(br), cage carbons (SiCB)], 55.70 [t, CH_2, TMEDA, $^1J(^{13}C-^1H)$ = 137.5 Hz], 44.86 [q, CH_3, TMEDA, $^1J(^{13}C-^1H)$ = 135.35 Hz], 3.15 [q, $SiMe_3$, $^1J(^{13}C-^1H)$ = 118.6 Hz]; ^{7}Li NMR (C_6D_6, relative to external aqueous $LiNO_3$) δ 0.29 [s, *exo*-polyhedral $Li^+(TMEDA)_2$], −2.60 [s(vbr), *commo*-cage-Li]; IR (cm^{-1}, C_6D_6 vs C_6D_6) 2552.1 (w, br), 2394.1 (m, s), 2288.8 (vvs) [ν-(B−H)], 1867.6 (m, br) [B−H−B (bridge)].

S0002-7863(96)00291-0 CCC: $12.00

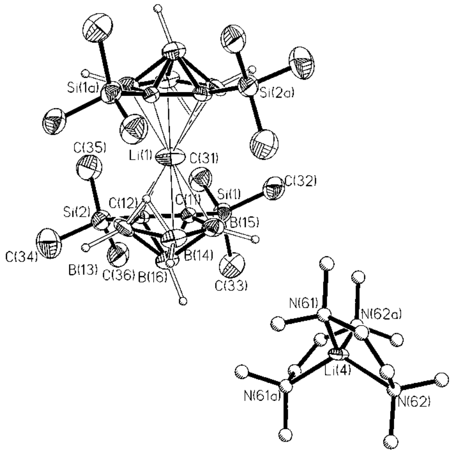


Figure 1. Perspective view of **2** drawn at the 40% probability level. Pertinent distances (Å) and angles (deg): Li(1,2)−(C_2B_3 centroid 1,2) 2.047, 2.071; Li(1,2)−C(11,21) 2.20 (1), 2.23 (2); Li(1,2)−C(12,22) 2.29 (1), 2.28 (2); Li(1,2)−B(13, 23) 2.55 (1), 2.55 (2); Li(1,2)−B(14,24) 2.74 (1), 2.74 (1); Li(1,2)−B(15, 25) 2.47 (2), 2.49 (2); Li(3,4)−N(51,61) 2.08 (2), 2.10 (2); Li(3,4)−N(52,62) 2.11 (2), 2.12 (2); (centroid 1)−Li(1)−(centroid 1a) 180.0; (centroid 2)−Li(2)−(centroid 2a) 175.0 (see supporting information, Tables S-2 and S-3, for detailed bond lengths and angles). For clarity, the methyl and methylene H's are omitted, and the discrete Li-bound TMEDA groups were drawn with circles of arbitrary radii.

X-ray crystallography.[13] The spectral data for **2** are consistent with the structure shown in Figure 1. The resonance at δ −4.33 ppm in its ^{1}H NMR spectrum can be assigned to the B−H−$B_{(bridge)}$ hydrogen, and the 2:1:1 peak pattern in the ^{11}B NMR spectra, due to basal and apical borons at δ 12.65, −5.24, and −50.93 ppm, respectively, as well as the cage carbon resonance (δ = 112.60 ppm) in the ^{13}C NMR spectra, are typical of those found for other group 1 compounds of this carborane.[6,9] The ^{7}Li NMR spectra shows resonances for both the *exo*-polyhedral Li (δ 0.29 ppm) and the *commo*-Li (δ −2.60 ppm) atoms.[12] The presence of B−H−$B_{(bridge)}$ H's are also apparent in the IR spectrum of **2**.[12] The X-ray analysis of **2** shows two independent half-molecules in the unit cell. While $(Cb)_2Li(1)$ possesses a center of symmetry, $(Cb)_2Li(2)$ (Cb = carborane) and each of the discrete cationic Li^+ units possess a 2-fold symmetry.[13] The unit cell of **2** reveals that each anionic lithiacarborane sandwich is associated with a discrete $Li(TMEDA)_2$ cation for charge balance. The Li−Cnt (Cnt = C_2B_3 centroid) distances in **2** (2.047 and 2.071 Å) are longer than the vlaue of 1.906 Å found in the half-sandwich dilithiacarborane[6] but are comparable to the Li−$Cp_{(Cnt)}$ distance of 2.008 Å found in the $[Cp_2Li]^-$ sandwich complex.[5a] This indicates that the presence of a B−H−$B_{(bridge)}$ hydrogen on each of the C_2B_3 faces does not significantly influence the bonding of the *commo*-Li metal to the cage atoms. The sensitivity of the metal−ligand distance to the ligand charge is consistent with a predominantly ionic interaction existing between the group 1 metal and the carborane cages. The slip distortion of the lithiums toward the cage carbons and one of the basal borons [Li(1)−C(11,12) = 2.20(1), 2.29(1); Li(1)−B(13,15) = 2.55(1), 2.47(2); Li(1)−B(14) = 2.74(1) Å] in the structure of **2** can be attributed to the presence of B−H−B bridge H's on the bonding faces. Such slippages have been observed in the solid state structures of a number of monosodium compounds of the neutral *nido*-carborane precursor.[6]

The utility of this approach to the syntheses of other s-block full-sandwich compounds is currently being explored in our laboratories. Preliminary results on the sodium analogue indicate that the present method may be of general use in the synthesis of a number of other full-sandwich alkali metal complexes. A detailed study of this work will be presented in a later report.

Acknowledgment. Dedicated, with all best wishes, to Professor Russell N. Grimes of University of Virginia on the occasion of his 60th birthday. This work was supported in part by grants from the National Science Foundation (CHE-9400672), the Robert A. Welch Foundation (N-1016), and the donors of the Petroleum Research Fund, administered by the American Chemical Society. N.S.H. thanks the Camille and Henry Dreyfus Foundation for a Scholar/Fellow Award.

Supporting Information Available: Tables of positional and thermal parameters and the selected bond distances and angles for **2** (9 pages). Ordering information is given on any current masthead page.

JA9602915

---

(13) X-ray data for **2** ($C_{28}H_{78}B_8Li_2N_4Si_4$; fw, 683.7; *Pccn*). Data were collected at 220 K on Siemens R3m/V diffractometer with a = 12.050(3) Å, b = 20.894(4) Å, c = 38.684(8) Å, V = 9740(4) Å^3, Z = 8, $D_{(calcd)}$ = 0.932 Mg/m^3. Of the 4507 reflections collected (2θ = 3.5−40.0°), 1723 reflections were considered as observed [$F > 4.0\sigma(F)$]. Data were corrected for Lorentz and polarization effects. The structure was solved by the 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 were refined anisotropically. While methyl and methylene H's were placed in calculated positions with fixed isotropic thermal parameters, the carborane cage terminal and the bridge H's were located in difference Fourier maps and were not refined. The final refinements converged at R = 0.0738, R_w = 0.079, and GOF = 1.58.