

$[B_{11}H_{11}]^{2-}$ fragment, while a later structural prediction⁸ assumed that two of the three hydrogens would bridge boron atoms while the third hydrogen would be an endo terminal hydrogen. The structural results confirm this later prediction. Figure 1B clearly shows that H(13) is an endo terminal hydrogen and H(12) and H(14) are bridge hydrogens. Such an endo terminal hydrogen has recently been reported for the *nido*-3,4- $[Et_2C_2B_5H_8]^-$ anion, which also has a pentagonal face.⁹

The boron–boron bond distances within the cage of $[B_{11}H_{14}]^-$ range from 1.747 to 1.775 Å with an average of 1.762 (10) Å. These distances are similar to the average boron–boron bond distance found within the cage of tridecahydroundecaborate(2-), $[B_{11}H_{13}]^{2-}$ (average 1.79 Å⁸). Boron–boron bond distances about the open face of the cage range from 1.875 to 1.895 Å with an average of 1.886 (8) Å, which also are similar to the corresponding distances in $[B_{11}H_{13}]^{2-}$ (average 1.84 Å⁸).

The exo terminal boron–hydrogen bond distances range from 0.99 to 1.16 Å with an average of 1.08 (5) Å. The endo terminal, B(10)–H(13), boron–hydrogen bond distance is 1.13 Å. Bridge boron–hydrogen bond distances range from 1.19 to 1.38 Å with an average of 1.30 (9) Å. These distances are all within the normal range for boron–hydrogen bond distances of their respective types.¹⁰

The spectral data indicate that the boron framework of $B_{11}H_{15}$ is similar to that of $[B_{11}H_{14}]^-$. However, the exact nature of the hydrogen atoms associated with the open face of the cage could not be determined, since they remain fluxional even at –80 °C. Attempts to obtain NMR spectra at lower temperatures failed due to the low solubility of $B_{11}H_{15}$ in CF_2Cl_2 (Freon 12) and the dissociation of $B_{11}H_{15}$ in $(CH_3)_2O$. Since the five boron orbitals associated with the open face of the cage are occupied in binding bridging and endo hydrogens in $[B_{11}H_{14}]^-$, an additional bridging hydrogen cannot be accommodated on the face. Therefore, it is conceivable that protonation results in the opening of an edge of the pentagonal face as suggested by R. E. Williams.¹¹

Acknowledgment. This work was supported by the Army Research Office through Grant DAAG29-85-K-0187. We thank the NSF for a grant (CHE84-11630) for an X-ray diffractometer. NMR spectra were obtained at The Ohio State University Campus Chemical Instrument Center (funded in part by NSF Grant 79-10019 and NIH Grant 1 S10 PRO140518-01A).

Supplementary Material Available: Listings of selected bond distances, selected bond angles, positional parameters, and anisotropic thermal parameters (6 pages); a listing of calculated and observed structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

(8) Fritchie, C. J., Jr. *Inorg. Chem.* **1967**, *6*, 1199.

(9) Beck, J. S.; Quintana, W.; Sneddon, L. G. *Organometallics* **1988**, *7*, 1015.

(10) Muetterties, E. L. *The Chemistry of Boron and Its Compounds*; Wiley: New York, 1967; p 231.

(11) Williams, R. E., private communication.

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Received April 29, 1988

Synthesis and X-ray Structure of a Symmetrical Bis(η^5 -dicarbollide)aluminum Sandwich

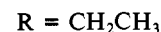
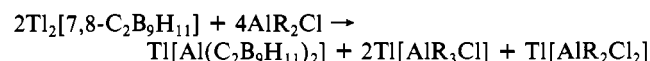
Sir:

Previously, we have reported the syntheses and structures of two *commo*-[Ne]-core bis(η^5 -dicarbollide) main group element sandwich compounds: a symmetric, neutral silacarborane sand-

wich (1)¹ and a formally zwitterionic complex containing an aluminacarborane sandwich (2).² Hosmane et al. have also reported the syntheses of bis(η^5 -metallacarboranes) containing silicon and germanium in a seven-vertex closo framework.³ While compound 1 is a "naked" sandwich (the carborane cages contain no exopolyhedral substituent), 2 contains an exopolyhedral diethylaluminum cation bound to one of the carborane cages by a pair of B–H–Al bridge bonds. Here we relate the synthesis and characterization of the first symmetric system incorporating an aluminum atom η^5 -bound to two π -donor ligands: the anion that is isoelectronic with 1.

The Tl(I) salt of the new aluminacarborane [*commo*-3,3'-Al(3,1,2-AlC₂B₉H₁₁)₂]⁻ (3) was prepared from a variety of aluminum-containing reagents. The addition of any one of several aluminum alkyl derivatives to a suspension of Tl₂[7,8-C₂B₉H₁₁] in toluene, in a mole ratio of 2:1 aluminum to carborane cage, generated the desired $[Al(C_2B_9H_{11})_2]^-$ anion, which precipitated as the thallium (I) salt 3 upon addition of heptane. The time required for complete reaction at room temperature is affected by the choice of the aluminum alkyl. For example, the reaction between Tl₂[7,8-C₂B₉H₁₁] and Al(C₂H₅)₂Cl, Al(C₂H₅)Cl₂, or Al(CH₃)₂Cl is immediate, while Al(C₂H₅)₃ requires approximately 1 h, Al(*i*-C₄H₉)₃ requires several hours, and Al(CH₃)₃ must be heated to 60 °C to produce a reaction. The method of choice (96% yield) utilizes dimethylaluminum chloride, in which case the reaction mixture becomes homogeneous and contains no suspended solids.⁴ Addition of heptane to this solution results in the crystallization of small, colorless needles of 3. A gray contaminant, presumably thallium metal, was observed in those preparations that involved the other aluminum alkyls.

The ¹H NMR spectra of the reaction mixtures in which ethylaluminum and diethylaluminum chloride reagents were used contain broadened peaks attributable to ethyl groups bound to aluminum, a characteristic of alkylaluminates.⁵ Thallium(I) aluminate species such as Tl⁺[AlR_{4-x}Cl_x]⁻ (R = alkyl, x = 0, 1, 2, 3), can be postulated as products on the basis of the species that remain in solution. For example, when diethylaluminum chloride is used, the reaction may proceed as



The difficulty experienced in isolating pure product from reactions that did not employ dimethylaluminum chloride may stem from the decomposition of these potentially unstable thallium aluminate byproducts to form thallium metal and uncharacterized aluminum-containing species.

The species $3^{2/3}C_7H_8$ was characterized by ¹H and ¹¹B NMR and IR spectroscopy⁶ as well as by an X-ray diffraction study.⁷

- (1) Rees, W. S., Jr.; Schubert, D. M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 5369.
- (2) Rees, W. S., Jr.; Schubert, D. M.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 5367.
- (3) (a) Hosmane, N. S.; de Meester, P.; Siriwardane, U.; Islam, M. S.; Chu, S. S. C. *J. Chem. Soc., Chem. Commun.* **1986**, 1421. (b) Hosmane, N. S.; de Meester, P.; Siriwardane, U.; Islam, M. S.; Chu, S. S. C. *J. Am. Chem. Soc.* **1986**, *108*, 6050. (c) Siriwardane, U.; Islam, M. S.; West, T. A.; Hosmane, N. S.; Maguire, J. A.; Cowley, A. H. *J. Am. Chem. Soc.* **1987**, *109*, 4600.
- (4) In an oven-dried, 250-mL, round-bottom Schlenk flask fitted with a rubber septum, 500 mg (0.924 mmol) of Tl₂[7,8-C₂B₉H₁₁] was suspended in 75 mL of dry, freshly distilled toluene under Ar. Upon addition of 0.20 mL (2.0 mmol) of a 1 M solution of Al(CH₃)₂Cl in toluene, the Tl₂[7,8-C₂B₉H₁₁] immediately dissolved, producing a clear solution. Addition of 150 mL of heptane precipitated pure 3, which was isolated by Schlenk filtration. The yield was 220 mg (96%) of white, microcrystalline solid.
- (5) (a) Williams, K. C.; Brown, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 4134. (b) Oliver, J. P.; Wilkie, C. A. *J. Am. Chem. Soc.* **1967**, *89*, 163. (c) Westmoreland, T. D., Jr.; Bhacca, N. S.; Wander, J. D.; Day, M. C. *J. Organomet. Chem.* **1972**, *38*, 1.

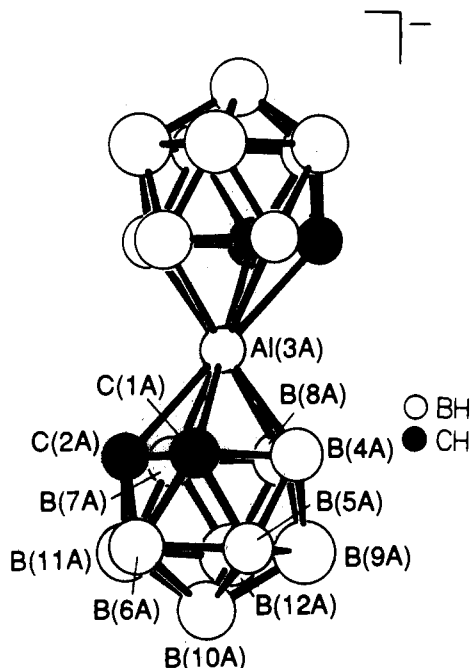


Figure 1. ORTEP representation of one of the three anionic $[\text{Al}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ sandwiches (A) showing the numbering scheme. These three sandwich anions are nearly superposable. Aluminum to C_2B_3 face distances for each of the crystallographically unique sandwiches are shown below. In sandwich C only one of the carbon atoms was identified; the

	A	B	C
Al(3)···C(1)	2.30 (2)	2.28 (2)	2.24 (2)
C(2)	2.29 (2)	2.26 (2)	2.29 (2)
B(4)	2.22 (2)	2.21 (2)	2.18 (3)
B(7)	2.24 (2)	2.19 (2)	2.29 (2)
B(8)	2.14 (2)	2.14 (2)	2.14 (3)

two adjacent atoms [C(1) and B(7)] were disordered.

The ^{11}B NMR spectrum at room temperature of **3** in toluene exhibits peaks characteristic of a single type of $[\text{nido-7,8-C}_2\text{B}_9\text{H}_{11}]^{2-}$ ligand. The ^1H NMR spectrum shows only one carboranyl C–H resonance as well as broad B–H resonances characteristic of the carborane skeleton. Compound **3** is slightly moisture sensitive, although not as reactive as **2** or *closo-3-(C₂H₅)-3,1,2-AIC₂B₉H₁₁* (**4**), which react violently with water.⁸

This added stability may be attributed to the sterically hindered environment of the aluminum atom, which is between two η^5 -dicarbollide ligands, in contrast to the tetrahedral exopolyhedral aluminum in **2** and to the $(\text{C}_2\text{H}_5)_3\text{Al}$ vertex in **4**.

The unit cell of **3** (supplementary figure) consists of three crystallographically unique anionic aluminacarborane sandwiches, three Tl^+ cations, and two disordered toluene solvate molecules, each of which is situated near a thallium ion [$\text{Tl}(2)\text{--C}(1\text{T}) = 3.22$ (2), $\text{Tl}(2)\text{--C}(2\text{T}) = 3.18$ (3), $\text{Tl}(2)\text{--C}(3\text{T}) = 3.17$ (3), $\text{Tl}(2)\text{--C}(4\text{T}) = 3.20$ (3), $\text{Tl}(2)\text{--C}(5\text{T}) = 3.23$ (3), $\text{Tl}(2)\text{--C}(6\text{T}) = 3.24$ (3) Å]. In addition, the two thallium ions $\text{Tl}(2)$ are close to all three cages [$\text{Tl}(2)\text{--H}(4\text{A}) = 2.94$, $\text{Tl}(2)\text{--H}(9\text{A}) = 3.01$, $\text{Tl}(2)\text{--H}(4\text{B}) = 2.79$, $\text{Tl}(2)\text{--H}(9\text{B}) = 2.75$, $\text{Tl}(2)\text{--H}(8\text{C}) = 2.79$, $\text{Tl}(2)\text{--H}(9\text{C}) = 2.79$ Å], while the third thallium, which lies at a special position, is near only one cage [$\text{Tl}(1)\text{--H}(8\text{B}) = 3.02$, $\text{Tl}(1)\text{--H}(9\text{B}) = 2.88$ Å]. Shown in Figure 1 is the ORTEP representation of the structure of one of the aluminacarborane sandwiches of **3**. Unlike the case of the structure of **2**, in which the distance of the sandwiched aluminum to each of the two planar C_2B_3 faces is unique, the aluminum atom of **3** lies at a crystallographic center of symmetry and thus is equidistant from the two planar, parallel faces of the dicarbollide ligands. The distances from the aluminum atom to the cage atoms in **3** are quite similar to the corresponding distances in **2** involving that cage which contains the exopolyhedral diethylaluminum.⁹ The bond distance from the aluminum to B(8) in **3** coincides with the corresponding distance in **4**; however, all of the other aluminum to dicarbollide distances are longer.¹⁰ Thus, the aluminum atom in **3**, relative to that in **4**, is further from the plane of the dicarbollide ligand face and slipped closer to the three boron atoms.

Previously reported syntheses of aluminacarboranes have involved the loss of aluminum-bound alkyl groups as alkanes such as CH_4 or C_2H_6 in protolysis reactions.^{8,11} However, that route is obviously inaccessible to this system. A reductive and/or salt elimination mechanism appears to be unlikely, since thallium halides and/or thallium metal are not observed as products. Thus, the detailed mechanism is unknown at this time and is currently under investigation. The results of this study, as well as the reactivity of **3**, will be reported elsewhere.

Acknowledgment. The support of this work by the National Science Foundation (Grant CHE-84-01433) is gratefully acknowledged. We also thank Andrea Oweyung for the illustrations.

Supplementary Material Available: An ORTEP drawing of the unit cell of **3** and tables of positional and thermal parameters and interatomic distances and angles (8 pages). Ordering information is given on any current masthead page.

- (6) Spectroscopic data for **3**: $^{11}\text{B}\{^1\text{H}\}$ NMR (160.463 MHz) (C_7H_8 ; referenced to external $\text{BF}_3\cdot\text{OEt}_2$ in C_6D_6) -12.5 (area 2), -14.9 (area 1), -17.9 (area 3), -19.8 (area 2), -32.7 (area 1) ppm; ^1H NMR (200.133 MHz) (C_6D_6 ; referenced to residual solvent protons = 7.15 ppm) 2.09 (s, toluene CH_3), 2.84 (s, carborane CH), 6.94–7.08 (ill defined, toluene CH protons) ppm; IR (KBr) 3035 (m, C–H stretch), 2510 (s, B–H stretch), 1030 (m), 746 (m), 657 (m) cm^{-1} .
- (7) Colorless X-ray-quality crystals were grown by layering the reaction mixture with pentane. The crystals were placed in 0.3 mm capillary tubes in a drybox under Ar and sealed. Data collection was carried out at 25 °C, by using a locally designed automated diffractometer (Mo $\text{K}\alpha$ radiation). The space group is $P\bar{1}$ with $a = 11.347$ (2) Å, $b = 11.748$ (2) Å, $c = 12.708$ (2) Å, $\alpha = 92.429$ (6)°, $\beta = 90.876$ (6)°, $\gamma = 93.343$ (5)°, and $V = 1689$ Å³. A total of 1891 reflections with $I > 3\sigma(I)$ were used for structure solution and refinement using the heavy-atom method and the UCLA crystallographic package and SHELX 76. The unit cell contains three $\text{Tl}^+[\text{Al}(\text{C}_2\text{B}_9\text{H}_{11})_2]^-$ and two toluene molecules. The last cycle of least-squares refinement gave residuals of $R = 0.057$, $R_w = 0.064$, and $\text{GOF} = 1.57$.
- (8) Young, D. A. T.; Willey, G. R.; Hawthorne, M. F.; Churchill, M. R.; Reis, A. H. *J. Am. Chem. Soc.* **1970**, *92*, 6663.

- (9) Compound **2**: Al–C(1) = 2.288 (5), Al–C(1′) = 2.240 (4), Al–C(2) = 2.271 (5), Al–C(2′) = 2.254 (5), Al–B(4) = 2.234 (5), Al–B(4′) = 2.175 (5), Al–B(7) = 2.230 (5), Al–B(7′) = 2.165 (5), Al–B(8) = 2.175 (5), Al–B(8′) = 2.130 (5) Å. The primes designate the cage with the exopolyhedral aluminum.
- (10) Churchill, M. R.; Reis, A. H. *J. Chem. Soc., Dalton Trans.* **1972**, 1317. Bond distances in **4** are as follows: Al–C(1,2) = 2.173 (7), Al–B(4,7) = 2.138 (8), Al–B(8) = 2.136 (9) Å.
- (11) (a) Schubert, D. M.; Knobler, C. B.; Rees, W. S., Jr.; Hawthorne, M. F. *Organometallics* **1987**, *6*, 201. (b) Schubert, D. M.; Knobler, C. B.; Rees, W. S., Jr.; Hawthorne, M. F. *Organometallics* **1987**, *6*, 203.
- (12) Hardy, G. E.; Callahan, K. P.; Strouse, C. E.; Hawthorne, M. F. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *B32*, 264.

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Received May 6, 1988