for modifying the synthetic procedure for $Ni^{II}L$.

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Synthesis of the New Boron Hydride *nido*-Undecaborane(15), $B_{11}H_{15}$, and the X-ray Structure of Its Conjugate Base Tetradecahydroundecaborate(1–), $[B_{11}H_{14}]^-$

Sir:

We recently reported[1] syntheses of alkali-metal (Li, Na, K) salts of the tetradecahydroundecaborate(1–) ion, $[B_{11}H_{14}]^-$, via a convenient, "one-pot", essentially quantitative procedure from the reaction of pentaborane(9), B_5H_9, with MH (M = Na, K) or (*t*-Bu)Li. In light of this new synthesis an investigation into the chemistry of $[B_{11}H_{14}]^-$ was begun. Reported, herein, is the preparation of *nido*-undecaborane(15), $B_{11}H_{15}$, from the protonation of $K[B_{11}H_{14}]$ and the subsequent deprotonation of $B_{11}H_{15}$ by $P(CH_3)_3$ to give $[P(CH_3)_3H][B_{11}H_{14}]$, the structure of which has been determined from single-crystal X-ray data.

Protonation of $NaB_{11}H_{14}\cdot 2.5C_4H_8O_2$ in $C_4H_8O_2$ has been reported[2] to produce $B_{11}H_{15}\cdot 2C_4H_8O_2$ and in $S(CH_3)_2$ to produce $B_{11}H_{13}\cdot S(CH_3)_2$ with the evolution of H_2 gas. We find that the reaction of $K[B_{11}H_{14}]$ with anhydrous HCl at –78 °C gives undecaborane(15), $B_{11}H_{15}$, in quantitative yield according to eq 1.

$$K[B_{11}H_{14}] + HCl \xrightarrow{-78\ ^\circ C} B_{11}H_{15} + KCl \qquad (1)$$

In a typical preparation, $K[B_{11}H_{14}]$ (125 mg, 0.725 mmol) was treated with excess HCl (25 mmol) at –78 °C for 12 h. No noncondensible gas was produced. The excess HCl was pumped away from the reactor at –78 °C over a period of 12 h. On the basis of the amount of recovered HCl (24.3 mmol), 0.7 mmol of HCl was consumed, indicating a 1:1 reactant ratio of HCl to $K[B_{11}H_{14}]$. Toluene-d_8 (0.7 mL) was condensed onto the product, and the resulting solution was filtered at low temperature into an NMR tube. The solid remaining on the frit was washed with tetrahydrofuran and identified as KCl by powder X-ray diffraction. Undecaborane(15) is not stable above 0 °C. In the solid state or in solution it decomposes with the evolution of about 0.5 mol of H_2/mol of $[B_{11}H_{14}]^-$ and the formation of a white solid,[3] insoluble in ethers, CH_3CN, toluene, and CH_2Cl_2.

The boron-11 NMR spectrum of $B_{11}H_{15}$ (96.3 MHz), obtained at –40 °C in toluene-d_8, consists of two resonances (–14.8 ppm (J = ~200 Hz, d) and –17.4 ppm (J = 145 Hz, d), $BF_3\cdot OEt_2$ at 0.00 ppm), which upon proton decoupling become singlets with relative areas of 6:5, respectively. This is consistent with a boron framework based upon an icosahedron with one vertex removed if it is assumed that the resonance due to the unique boron atom overlaps with the low-field signal that arises from one of the sets of five equivalent boron atoms. The proton NMR spectrum (300 MHz), with ^{11}B decoupling, in toluene-d_8 at –80 °C consists of two resonances in the terminal region at 2.43 and 1.29 ppm and only one resonance in the bridge hydrogen region at –3.53 ppm. The resonance due to the hydrogen atom on the unique boron atom was not observed and is believed to overlap the higher field terminal signal arising from one of the sets of five equivalent terminal hydrogen atoms. This is supported by the relative areas of the resonances, 1.2:1.4:1, which are consistent with the theoretical values of 1.25:1.5:1.

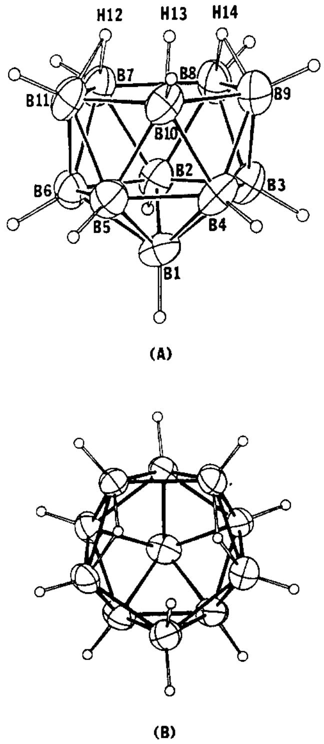

Figure 1. Views of the molecular structure of $[B_{11}H_{14}]^-$ (ORTEP plots with 50% probability ellipsoids).

Undecaborane(15) is readily deprotonated. It yields $[B_{11}H_{14}]^-$ in $(CH_3)_2O$, and the reaction (2) with $P(CH_3)_3$ yields an isolable salt. In a typical reaction $B_{11}H_{15}$ (0.60 mmol) prepared as above

$$B_{11}H_{15} + P(CH_3)_3 \xrightarrow{CH_2Cl_2} [P(CH_3)_3H][B_{11}H_{14}] \qquad (2)$$

was reacted with $P(CH_3)_3$ (0.70 mmol) at –35 °C, in CH_2Cl_2, with slow warming to room temperature over a period of 20 h. No noncondensible gas was formed, and the solid remaining after removal of the volatiles was washed twice with CH_2Cl_2 (~3 mL) and then extracted with acetonitrile. $[P(CH_3)_3H][B_{11}H_{14}]$ (64.8 mg, 0.36 mmol, 60%) was obtained and characterized, by spectroscopy and from a single-crystal X-ray study.[4]

Crystals of $[P(CH_3)_3H][B_{11}H_{14}]$ were obtained by slow diffusion of diethyl ether into a concentrated methylene chloride solution of $[P(CH_3)_3H][B_{11}H_{14}]$. The molecular structure of $[P(CH_3)_3H][B_{11}H_{14}]$ was determined from single-crystal X-ray diffraction data.[6] The boron framework of the $[B_{11}H_{14}]^-$ anion (Figure 1) is based upon a regular icosahedral structure with one vertex removed. The structure has pseudo-C_s symmetry. An interesting feature of this structure is the arrangement of the three hydrogen atoms associated with the open face of the cage that are not exo terminal hydrogens. Early in the development of polyhedral borane chemistry it was suggested[7] that the $[B_{11}H_{14}]^-$ ion could be described as a H_3^+ triangle interacting with a

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(1) Hosmane, N. S.; Wermer, J. R.; Hong, Z.; Getman, T. D.; Shore, S. G. *Inorg. Chem.* **1987**, *26*, 3638.

(2) Edwards, L. J.; Makhlouf, J. M. *J. Am. Chem. Soc.* **1966**, *88*, 4728.

(3) IR spectrum of the insoluble decomposition product (cm^{-1}): 2528 (br, s); 2211 (br, m); 2101 (br, m); 900–1500, broad absorption with maxima at 1384 (m), 1205 (m), 1100 (m), 1033 (m).

(4) NMR spectra are in accord with those reported previously for the $[P(CH_3)_3H]^+$ cation[5] and the $[B_{11}H_{14}]^-$ anion.[1]

(5) Moedritzer, K.; Maier, L.; Greonweghe, L. C. D. *J. Chem. Eng. Data* **1962**, *7*, 307.

(6) Crystal data for $[P(CH_3)_3H][B_{11}H_{14}]$: space group $P\bar{1}$, a = 7.296 (2) Å, b = 8.956 (5) Å, c = 10.673 (4) Å, α = 81.2 (5)°, β = 88.3 (3)°, γ = 85.0 (3)°, V = 686.3 Å^3, ρ(calcd) = 1.017 g cm^{-3}, M_r = 210.15, Z = 2, μ(Mo Kα) = 1.5 cm^{-1}. Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer. Crystallographic computations were carried out on a PDP 11/44 computer using SDP (Structure Determination Package). The structure was solved by a combination of the direct method MULTAN 11/82 and difference Fourier syntheses. Full-matrix least-squares refinements were employed. R_F = 0.054 and R_{wF} = 0.069 (232 variables refined) for 1570 reflections [$I > 3.0\sigma(I)$] of 2414 independent reflections collected over the range $4 < 2\theta < 50°$.

(7) Moore, E. B., Jr.; Lohr, L. L., Jr.; Lipscomb, W. N. *J. Chem. Phys.* **1961**, *35*, 1329.

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$[B_{11}H_{11}]^{2-}$ fragment, while a later structural prediction[8] 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 Å[8]). 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 Å[8]).

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]

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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.

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(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.

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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 sandwich (**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-$AlC_2B_9H_{11})_2]^-$ (**3**) was prepared from a variety of aluminum-containing reagents. The addition of any one of several aluminum alkyl derivatives to a suspension of $Tl_2[7,8\text{-}C_2B_9H_{11}]$ 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 $Tl_2[7,8\text{-}C_2B_9H_{11}]$ and $Al(C_2H_5)_2Cl$, $Al(C_2H_5)Cl_2$, or $Al(CH_3)_2Cl$ is immediate, while $Al(C_2H_5)_3$ requires approximately 1 h, $Al(i\text{-}C_4H_9)_3$ requires several hours, and $Al(CH_3)_3$ 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

$$2Tl_2[7,8\text{-}C_2B_9H_{11}] + 4AlR_2Cl \rightarrow Tl[Al(C_2B_9H_{11})_2] + 2Tl[AlR_3Cl] + Tl[AlR_2Cl_2]$$

$$R = CH_2CH_3$$

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 $3\cdot{}^2/_3C_7H_8$ was characterized by ^1H and ^{11}B NMR and IR spectroscopy[6] as well as by an X-ray diffraction study.[7]

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(4) In an oven-dried, 250-mL, round-bottom Schlenk flask fitted with a rubber septum, 500 mg (0.924 mmol) of $Tl_2[7,8\text{-}C_2B_9H_{11}]$ 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 $Al(CH_3)_2Cl$ in toluene, the $Tl_2[7,8\text{-}C_2B_9H_{11}]$ 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.

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