2.124 (4) Å for II. The environment around each metal atom is essentially tetrahedral, with average C-Al-C and N-Al-C bond angles of 113.4 (2) and 105.2 (3)° and C-Ga-C and N-Ga-C bond angles of 114.3 (2) and 104.0 (3)°, respectively.

The fact that one would have expected I and II to have assumed a sterically less demanding trans conformation instead of the observed sterically crowded cis conformation is noteworthy and warrants closer examination. In this regard, it is interesting to consider two factors: (a) the dimeric nature of $M(CH_3)_3$ (M = Al, Ga) and (b) inversion of heterocyclic ring systems containing N-H fragments. Although the reaction chemistry of trimethylaluminum and trimethylgallium is largely dominated by monomeric units, these species are generally regarded to be predominantly dimeric in solution, being bridged by two μ-methyl groups.[15,16] In terms of the second factor, room-temperature inversion of heterocyclic ring systems containing N-H moieties is well documented.[17,18] Thus, it is reasonable that the endodentate conformation of [14]aneN_4 in I and II, while certainly stabilized by hydrogen bonding, was effectively trapped as it was approached by the dimeric form of the group 13 metal alkyl, $M_2(CH_3)_6$ (M = Al, Ga). The dimer could then be cleaved as each metal alkyl center approached nitrogen atoms on the same side of the azacrown.

Compound III results from the room-temperature reaction of I with 2 mol of trimethylgallium. The two $Ga(CH_3)_3$ units form adducts with two of the nitrogen atoms of the aza crown while the two trimethylaluminum units originally present in I participate in condensation with the aza hydrogen atoms of the aza crown. The most striking feature of III is the formation of the planar Al_2N_2 ring within the central cavity of the macrocycle and the formation of trimethylgallium adducts on the exterior of the macrocycle (Figure 3). The mean Al-N bond distance within the planar Al_2N_2 ring of 1.943 (8) Å compares to 1.888 (3) Å for the out-of-plane Al(1)-N(2) bond. The Ga(1)-N(2) bond distance is 2.136 (3) Å. The Al-N-Al and N-Al-N bond angles are 89.5 (1) and 92.67 (2)°, respectively. Compound III is very similar structurally to the condensation product $[Al(CH_3)]_2$-[14]ane$N_4[Al(CH_3)_3]_2$ (IV), a compound isolated from reaction of [14]aneN_4 with 4 mol of $Al(CH_3)_3$.[19] Interestingly, although III and IV proved to be isostructural, the twinning that occurred for IV was not observed for the heterobimetallic complex, III. Heating of I has been shown to produce IV in low yield. It appears that the first two $Al(CH_3)_3$ units that react with the aza crown become involved in the condensation while subsequently added $Ga(CH_3)_3$ species form adducts with the two remaining nitrogen atoms. Thus, it is reasonable to consider the greater Lewis acidity of trimethylaluminum (relative to trimethylgallium) as a contributing factor in the preparation of III.

Acknowledgment. We are grateful to the National Science Foundation for support of this work to G.H.R. (Grant RII-8520554).

Supplementary Material Available: Tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters and summaries of data collection and refinement (23 pages); listings of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Cage Opening of Parent Closo Cage Carboranes with Fluoride Ion: Formation of [5-F-*nido*-2,4-$C_2B_4H_6$]$^-$

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Received July 10, 1990

Fluoride ion, in aprotic solvents, has been found to be effective in the cage opening of *closo*-carboranes such as 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, 1,2-$C_2B_{10}H_{12}$, and 1,7-$C_2B_{10}H_{12}$. Nearly quantitative conversion to *nido*-carboranes is observed; in the case of 1,6-$C_2B_4H_6$ the product is the [5-F-*nido*-2,4-$C_2B_4H_6$]$^-$ ion. In the case of the higher carboranes the *nido*-carborane produced is that expected from the removal of a single vertex boron.

Introduction

Previous studies in our laboratories[1,2] demonstrated that fluoride ion can displace higher halogens in appropriately substituted *closo*-2,4-$C_2B_5H_7$ derivatives. Recently, we have discovered that it is not necessary to have a halogen attached to the cage of a *closo*-carborane in order for a reaction to be initiated with fluoride ion.[3] This report discusses the results of reactions involving the *closo*-carboranes 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, and 1,2- and 1,7-$C_2B_{10}H_{12}$.

Experimental Section

Materials and Handling of Chemicals. The reagents, (a) tetrabutylammonium fluoride (TBAF), as the trihydrate, (b) TBAF, as a 1 M solution in tetrahydrofuran (THF), (c) CaH_2, (d) deuterated THF, and (e) deuterated acetonitrile, were all obtained from Aldrich Chemical Co. The TBAF/THF solution was dried over CaH_2; the dried solution had to be used within several days, otherwise it separated into two phases (only the lower layer, a light tan color, appeared to contain fluoride ion, as assessed from fluorine-19 NMR spectroscopy and also by its reaction toward 1,6-$C_2B_4H_6$; vide infra). Upon the drying of TBAF/acetonitrile solutions with CaH_2, the solution remained as one layer. Standard high-vacuum and drybag techniques were employed in the handling of all chemicals.

Nuclear Magnetic Resonance. Proton (400.135 MHz), boron-11 (128.379 MHz), and fluorine-19 (376.503 MHz) spectra were gathered by using a Bruker AM400 FT-NMR instrument; the spectra were referenced to TMS, $Et_2O{\cdot}BF_3$, and $CFCl_3$, respectively, with negative chemical shift values upfield.

Reaction of TBAF with *closo*-1,6-$C_2B_4H_6$. Using THF as Solvent. A dried TBAF/THF solution (0.5 mL, 0.5 mmol of TBAF) was combined with *closo*-1,6-$C_2B_4H_6$ (0.25 mmol). After 1 h at room temperature about 90% of 1,6-$C_2B_4H_6$ disappeared, as monitored by ^{11}B NMR spectroscopy, with the concomitant formation of the [5-F-*nido*-2,4-$C_2B_4H_7$]$^-$ ion. After 17 days, the NMR spectrum of the solution showed essentially quantitative conversion to the [5-F-*nido*-2,4-$C_2B_4H_7$]$^-$ ion with no observable boron impurities in the boron-11 NMR spectrum. The ^{11}B NMR resonances assigned to the [5-F-*nido*-2,4-$C_2B_4H_7$]$^-$ ion are as follows: $\delta = -50.83$, $J(BH) = 158$ Hz, for B(1); $\delta = -9.75$, $J(BH_t) = 136$ Hz, $J(BH_\mu) =$ ca. 40 Hz, for B(6); $\delta = +17.9$ (broad singlet) for B(3); $\delta = +20.52$, $J(^{11}B^{19}F) =$ ca. 60 Hz, $J(BH_\mu) =$ ca. 45 Hz, for B(5) (note: the bridging hydrogen couplings to boron were obtained from resolution-enhanced spectra). Proton NMR data: $\delta = -2.22$, broad, for

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H_μ; $\delta = -1.00$, J(BH) = 156 Hz, for HB(1); $\delta = +2.38$ (singlet) for HC(2) or HC(4); $\delta = +2.56$ (singlet) for HC(4) or HC(2); also, $\delta = 0.87$ (triplet, J(HH) = 7 Hz, for CH_3), +1.28 (multiplet, CH_2-CH_3), +1.56 (multiplet, CH_2-C_2H_5), and +3.18 (triplet, J(HH) = 8 Hz, CH_2-C_3H_7) for tetrabutylammonium ion.

Using Acetonitrile as Solvent. A dried TBAF/CD_3CN solution (0.5 mL, 0.5 mmol of TBAF) was combined with *closo*-1,6-$C_2B_4H_6$ (0.25 mmol). After 2 h at ambient temperature a 72% conversion to the [5-F-*nido*-2,4-$C_2B_4H_7$]$^-$ ion was observed. After 3.5 days the conversion was 99%. The ^{11}B NMR resonances assigned to the [5-F-*nido*-2,4-$C_2B_4H_7$]$^-$ ion are as follows: $\delta = -50.74$, J(BH) = 158 Hz, for B(1); $\delta = -9.34$, $J(BH_t)$ = 139 Hz, $J(BH_\mu)$ = ca. 50 Hz, for B(6); δ +18.72, J(BH) = 125 Hz, for B(3); $\delta = +20.81$, $J(^{11}B^{19}F)$ = ca. 60 Hz, $J(BH_\mu)$ = ca. 50 Hz, for B(5) (note: the bridging hydrogen couplings to boron were obtained from resolution-enhanced spectra). Proton NMR data: $\delta = -1.83$, broad, for H_μ; $\delta = -0.63$, J(BH) = 158 Hz, for HB(1); $\delta = +2.83$ (singlet) for HC(2) or HC(4); $\delta = +3.01$ (singlet) for HC(4) or HC(2). The ^{19}F NMR spectrum showed a 1:1:1:1:1:1:1:1 octet of peaks centered at −196.7 ppm, which collapsed to a 1:1:1:1 quartet upon ^{1}H decoupling; $J(^{19}F^{11}B)$ = 57 Hz, and $J(FH_\mu)$ = 28 Hz.

When the THF was evaporated, in vacuo, from the THF solution of the [5-F-*nido*-2,4-$C_2B_4H_7$]$^-$ ion, and then CD_3CN was added, the same NMR spectrum was observed as when the formation of the [5-F-*nido*-2,4-$C_2B_4H_7$]$^-$ ion was carried out from *closo*-1,6-$C_2B_4H_6$ and TBAF in deuterated acetonitrile. Similarly, when the CD_3CN was evaporated from the THF solution of [5-F-*nido*-2,4-$C_2B_4H_7$]$^-$ ion, and then THF was added, the same NMR spectrum was observed as when the formation of the [5-F-*nido*-2,4-$C_2B_4H_7$]$^-$ ion was carried out from *closo*-1,6-$C_2B_4H_6$ and TBAF in THF. The only significant difference between the two spectra was found in the B(3)H resonance, which was well resolved into a 1:1 doublet in CD_3CN whereas it appeared as a somewhat broadened singlet in THF; otherwise, the two spectra were nearly identical.

Control Experiments. (a) A 5% H_2O in THF solution was dried with CaH_2. The dried solution (0.5 mL) was combined with *closo*-1,6-$C_2B_4H_6$ (0.25 mmol). No reaction was observed during a 35-day period at room temperature, as monitored by ^{11}B NMR spectroscopy. (b) In two separate experiments, solutions (0.5 mL) of 1% H_2O in THF, and 5% H_2O in THF, were added to *closo*-1,6-$C_2B_4H_6$ (0.25 mmol). No reaction was observed during a 35-day period at room temperature, as monitored by ^{11}B NMR spectroscopy. (c) A 1 M KOH/H_2O solution was combined with THF to give a 5% H_2O solution. A 0.5-mL quantity of this solution was added to *closo*-1,6-$C_2B_4H_6$. No reaction was observed during a 35-day period at room temperature, as monitored by ^{11}B NMR spectroscopy. (d) The above reactions were also carried out with CD_3CN, rather than THF, as the organic solvent. Essentially the same results were observed.

Reaction of TBAF with *closo*-2,4-$C_2B_5H_7$. A TBAF/CD_3CN solution (0.5 mL containing 0.5 mmol of TBAF) was combined with *closo*-2,4-$C_2B_5H_7$ and allowed to stand for 2 h at room temperature. A small quantity of noncondensable gas was liberated during this time. The ^{11}B NMR spectrum of the mixture after the 2-h period exhibited the resonances of the [*nido*-2,4-$C_2B_4H_7$]$^-$ ion ($\delta = -52.28$, J(BH) = 156 Hz, for B(1); $\delta = +0.88$, J(BH) = 128 Hz, for B(5,6); $\delta = +21.09$, J(BH) = 118 Hz, for B(3). ^{1}H NMR: $\delta = -5.2$ (broad) for H_μ; $\delta = -2.1$, J(BH) = 179 Hz, for HB(1)).[4,5] Additional resonances were observed at +2.3 and +32.6 ppm, which accounted for 20% of the total boron content. Nearly identical results were obtained when THF was used as the solvent. The primary differences were that the B(3) resonance of the ion was broader in the THF solvent and the doublet nature of the resonance could only be seen upon resolution enhancement. The ^{19}F NMR spectrum showed a myriad of singlet resonances (δ = −132.7, −137.4, and −138.2 among the strongest), a 1:1:1:1 quartet, $J(^{19}F^{11}B)$ = 15 Hz, centered at −142.9 ppm, and an apparent 1:1:1:1, $J(^{19}F^{11}B)$ = 69 Hz, multiplet centered at −128.7 ppm.

Conversion of *closo*-$C_2B_{10}H_{12}$ to [*nido*-$C_2B_9H_{12}$]$^-$ Using Fluoride Ion. Crystals of *closo*-1,2-$C_2B_{10}H_{12}$ and 1,7-$C_2B_{10}H_{12}$ (Dexsil Chemical Corp.) were dissolved in dry tetrahydrofuran as a 25% solution. A tetrabutylammonium fluoride solution in THF (1 M) solution with 5% water (Aldrich) was dried over CaH_2 (Aldrich) for 2 days. Mixtures of *closo*-$C_2B_{10}H_{12}$/TBAF in THF were prepared in various mole ratios (1:7, 1:3, 1:1, 3:1). Reactants (solutions containing ca. 2 mmol of carborane) were syringed into NMR tubes, each with an attached 1.5-mL glass bulb, in a drybag. The tubes were attached to a vacuum line, sealed, and subsequently warmed to room temperature. Similar mixtures were also prepared with CD_3CN, rather than THF, as the solvent. Upon warming of the solutions to room temperature, small amounts of gas bubbles (H_2?) were evolved from the *closo*-1,7-$C_2B_{10}H_{12}$ mixtures; by comparison, very small amounts of gas was were emitted from the 1,2-$C_2B_{10}H_{12}$ mixtures. The ^{11}B NMR spectra of the 3:1 fluoride ion/carborane solutions (after an overnight period at room temperature) showed nearly complete conversion to [*nido*-$C_2B_9H_{12}$]$^-$. The lower fluoride ion/carborane ratio mixtures showed only partial conversion to the [*nido*-$C_2B_9H_{12}$]$^-$ ion, and the amount of the [$C_2B_9H_{12}$]$^-$ ion did not substantially increase with additional time. In the case of *closo*-1,2-$C_2B_{10}H_{12}$ as the starting material, the ^{11}B NMR spectrum of the product exhibited resonances, and peak intensities, expected for [*nido*-7,8-$C_2B_9H_{12}$]$^-$: $\delta = -37.3$ (B(1), J = 134 Hz); $\delta = -32.5$ (B(10), J = 127 Hz); $\delta = -21.6$ (B(2,4), J = 147 Hz); $\delta = -17.2$ (B(3), J = 152 Hz); $\delta = -16.4$ (B(5,6), J = 139 Hz); $\delta = -10.7$ (B(9,11), J = 138 Hz).[6] There is also a 1:3:3:1 quartet (which does not change upon ^{1}H decoupling) centered at +1.26 ppm, J(BF) = 17 Hz. The ^{19}F NMR spectrum showed the presence of a 1:1:1:1, $J(^{19}F^{11}B)$ = 16 Hz, quartet centered at −143.5 ppm; this could be a BF_3 group bonded to Z, where Z might be solvent or an OH group. In the case of *closo*-1,7-$C_2B_{10}H_{12}$ as the starting material, the ^{11}B NMR spectrum of the product exhibited resonances expected for [*nido*-7,9-$C_2B_9H_{12}$]$^-$; $\delta = -35.1$ (B(1), J = 140 Hz); $\delta = -34.0$ (B(6), J = 134 Hz); $\delta = -22.5$ (B(10,11), $J(BH_t)$ = 135 Hz, $J(BH_\mu)$ = 53 Hz); $\delta = -21.2$ (B(3,4), J = 143 Hz); $\delta = -5.6$ (B(8), J = 136 Hz); $\delta = -4.3$ (B(2,5), J = 147 Hz).[7] There is also a 1:3:4:4:3:1 multiplet centered at +1.5 ppm in the ^{11}B NMR spectrum, which, upon ^{1}H decoupling, appeared as a 1:3:3:1 quartet, J = 71 Hz, assigned to a BF_3 grouping. A coupling constant J = 140 Hz is derived for H–B, and the J = 71 Hz coupling is assigned to fluorine–boron coupling. The ^{19}F NMR spectrum exhibited a singlet at $\delta = -112.8$ ppm, attributed to excess F^- ion, and a multiplet at $\delta = -136.2$ ppm, which was interpreted as a 1:1 doublet of 1:1:1:1 quartets with $J(^{19}F^1H)$ = 91 Hz and $J(^{19}H^{11}B)$ = 71 Hz. The area ratio of the $\delta = -112.8$ ppm peak to the $\delta = -136.2$ peak was approximately 1:2. The latter species could be either the HBF_3^- or $F_3BHF_3^-$ ion but more probably the former.

Results and Discussion

The parent *closo*-carboranes 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, 1,2-$C_2B_{10}H_{12}$, and 1,7-$C_2B_{10}H_{12}$ all react with tetrabutylammonium fluoride in the aprotic solvents acetonitrile or tetrahydrofuran to give *nido*-carborane products. Each reaction proceeds at a moderate rate at ambient temperatures and results in an essentially quantitative conversion to a single specific nido cage compound. In the case of *closo*-1,6-$C_2B_4H_6$ the cage product produced is the [5-F-*nido*-2,4-$C_2B_4H_6$]$^-$ ion (Figure 1). Somewhat surprisingly, fluoride ion (in the above-mentioned aprotic solvents) reacts considerably faster than does trimethylamine[5,8] with this same D_{4h} *closo*-carborane to give the substituted nido cage product, 5-Z-*nido*-2,4-$C_2B_4H_6$ (Z = $(CH_3)_3N$ and F, the latter as a mononegatively charged species). Unlike the 5-$(CH_3)_3N$-*nido*-2,4-$C_2B_4H_6$ zwitterion,[5] the [5-F-*nido*-2,4-$C_2B_4H_6$]$^-$ ion does not show any tendency at ambient temperature (in the solvents tested thus far, THF and aceonitrile) to rearrange to the corresponding 3-substituted nido isomer.

Several control experiments have been carried out in order to verify that fluoride ion, rather than a potential impurity, is the critical species for cage opening. In this regard it is noted that tetrabutylammonium fluoride, commercially available both in crystalline form and as a THF solution, comes as a hydrate. Solutions of this fluoride salt were dried with CaH_2 prior to reaction with the carborane; however, there is the possibility that some small quantity of water, and/or hydroxide, might be present along with the fluoride ion when used for the carborane reaction. However, only negative results were observed in attempted reactions between *closo*-1,6-$C_2B_4H_6$ and each of the following: (a) a THF solution containing either 1% or 5% of water, (b) a 5% H_2O/THF solution that was dried with CaH_2 prior to use, (c)

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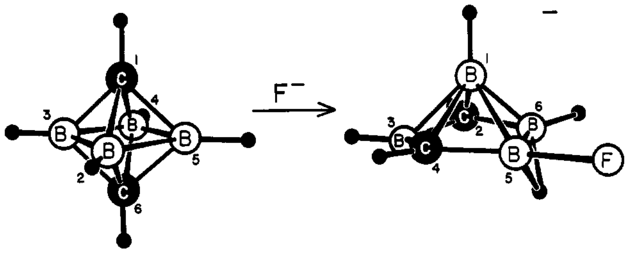

Figure 1. Reaction of *closo*-1,6-$C_2B_4H_6$ with fluoride ion to give the [5-F-*nido*-2,4-$C_2B_4H_6$]$^-$ ion. Bond distances for [5-F-*nido*-2,4-$C_2B_4H_6$]$^-$, as calculated from a GAUSSIAN-88 6-31G geometry optimization, are (in Å) B(1)–C(2) = 1.721, B(1)–B(3) = 1.898, B(1)–C(4) = 1.755, B(1)–B(5) = 1.786, B(1)–B(6) = 1.773, C(2)–B(3) = 1.534, B(3)–C(4) = 1.538, C(4)–B(5) = 1.523, B(5)–B(6) = 1.793, B(5)–F = 1.417, B(5)–H_μ = 1.346, and B(6)–H_μ = 1.342.

a THF solution that contained 5% of 1 M KOH/H_2O, and (d) the same as with parts a–c, except that acetonitrile was used instead of THF as the solvent.[9]

The ^{11}B and ^{19}F NMR spectra of the [5-F-*nido*-2,4-$C_2B_4H_6$]$^-$ ion are consistent with the pentagonal pyramidal structural assignment shown in Figure 1. The ^{11}B NMR spectrum of the ion exhibits four resonances in an area ratio of 1:1:1:1 with the highest field doublet resonance in the region expected for an apical BH group of a pyramidal structure.[10] Upon application of resolution measurement techniques to the spectrum, the lowest field resonance exhibits a well-resolved doublet of doublets. Proton decoupling of this resonance (eliminating the BH coupling) gives a single doublet of J = ca. 60 Hz, assigned to $^{11}B^{19}F$ coupling. The ^{19}F NMR pattern showed a 1:1:1:1:1:1:1:1 octet of peaks, which, upon proton decoupling, reveals a 1:1:1:1 ($^{19}F^{11}B$) quartet of J = 57 Hz. The remaining coupling, J = 28 Hz, in the undecoupled resonance is assigned to FBH_μ coupling. A 2D NMR spectrum showed connections between the resonances at −50.74 (B1) and −9.34 (B6) ppm and between −50.74 (B1) and +20.81 (B5) ppm. The lack of an observable 2D NMR connectivity between B(1) and B(3) is consistent with similar observations on the pentagonal pyramidal [*nido*-2,4-$C_2B_4H_7$]$^-$ ion and the pentagonal bipyramidal *closo*-2,4-$C_2B_5H_7$; the absence of B(5)/B(6) cross peaks is not inconsistent with the presence of a bridging hydrogen between these two borons. An ab initio calculation on the [5-F-*nido*-2,4-$C_2B_4H_6$]$^-$ ion gives a vibrationally stable species (Figure 1) with the expected pentagonal pyramidal geometry (optimized 6-31G total energy = −277.36406 au). Cage bond distances obtained from a 6-31G (GAUSSIAN-88) optimization are cited in Figure 1. It has been established that "IGLO" (individual gauge for localized molecular orbitals) NMR shift calculations on geometries obtained from reasonably high basis set optimizations can give satisfactory correlations to experimental data for a variety of organic systems[11,12] and have been used to correlate plausible B_5H_{11} structures with ^{11}B NMR data.[13] Bausch[14] was able to apply the IGLO method to our 6-31G-optimized coordinates of [5-F-*nido*-2,4-$C_2B_4H_6$]$^-$, and there appears to be a reasonably good match between the experimental (reported herein; see Experimental Section) and theoretically obtained values;[14] the average difference between experimental and theoretical chemical shifts is 3 ppm over a 71 ppm stretch of resonances. This magnitude of "error" is considered quite acceptable when one considers that the experimental data are obtained from a solution spectrum whereas the theoretical values are necessarily obtained from what amounts to an (unsolvated) "gas"-phase molecule.

The action of fluoride ion on *closo*-2,4-$C_2B_5H_7$ produces the [*nido*-2,4-$C_2B_4H_7$]$^-$ ion, a product expected from the removal of a single boron vertex. This reaction is analogous to the removal of a single vertex of *closo*-2,4-$C_2B_5H_7$ by amides[4] and the earlier reported removal of a single boron vertex from *closo*-1,2- and 1,7-$C_2B_{10}H_{12}$ using hydroxide ion, or alkoxide ion, in alcohol.[15-17]

Both the 1,2- and 1,7-isomers of *closo*-$C_2B_{10}H_{12}$ can be converted to the 7,8- and 7,9-isomers, respectively, of [*nido*-$C_2B_9H_{12}$]$^-$ by using tetrabutylammonium fluoride in THF or acetonitrile. It is to be noted that the conversion of *closo*-1,7-$C_2B_{10}H_{12}$ to [*nido*-7,9-$C_2B_9H_{12}$]$^-$ appears to be faster when carried out with tetrabutylammonium fluoride in THF than with the OH^-/ROH reagent combination. The temperature at which the production of [*nido*-7,9-$C_2B_9H_{12}$]$^-$ from *closo*-1,7-$C_2B_{10}H_{12}$/OH^-/ROH was reported[16] ranged from 150 to 160 °C, whereas the use of fluoride ion to effect the same conversion takes place at a reasonable rate at ambient temperature.

In order to effect quantitative conversions of *closo*-carboranes, $C_2B_5H_7$ and the $C_2B_{10}H_{12}$ isomers, to the respective nido anions, a 2-fold to 3-fold excess of F^- is required. Small quantities of gas (H_2?) are evolved during the reactions in which a single boron is removed from these *closo*-carboranes. This motivated us to think that the "anhydrous" tetrabutylammonium fluoride solutions we were employing were not as dry as originally thought (vide supra). However, an assessment of the quantity of moisture that may be present in the "dried" fluoride solutions has proven elusive.[18] Related to this problem is the question, what is the structure of the monoboron species that is extracted from the closo cage compound? Nuclear magnetic resonance data suggest that monoboron B–F_x-containing compounds are indeed formed (see Experimental Section), but the exact identity of these have not yet been unambiguously established.[19]

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(9) The relative unreactivity of 1,6-$C_2B_4H_6$ and sluggish reactivity of 2,4-$C_2B_5H_7$ (at ambient temperatures) toward water and OH^-/H_2O solutions have also been observed before: Dobbie, R. C.; Wan, E.; Onak, T. *J. Chem. Soc., Dalton Trans.* **1975**, 2603–2606. Wan, E.; Onak, T. Unpublished results.

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(19) An exercise in obtaining balanced equations from the reaction of *closo*-carboranes and fluoride ion, with either no water or various quantities of water present, to give "debor" reaction products can lead to the following possibilities, among others:

$$C_2B_xH_y + F^- \rightarrow [C_2B_{x-1}H_y]^- + (1/n)(BF)_n \qquad (1)$$

$$C_2B_xH_y + 2F^- + H_2O \rightarrow [C_2B_{x-1}H_y]^- + [(HO)(H)BF_2]^- \qquad (2)$$

$$C_2B_xH_y + 2F^- + 2H_2O \rightarrow [C_2B_{x-1}H_y]^- + H_2 + [(HO)_2BF_2]^- \qquad (3)$$

$$C_2B_xH_y + 3F^- + H_2O \rightarrow [C_2B_{x-1}H_y]^- + [HBF_3]^- + OH^- \qquad (4)$$

$$C_2B_xH_y + 3F^- + 2H_2O \rightarrow [C_2B_{x-1}H_y]^- + H_2 + [HOBF_3]^- + OH^- \qquad (5)$$

Note that eqs 2 and 3, and also eqs 4 and 5, only differ by the following:

$$[HBF_3]^- + H_2O \rightarrow H_2 + [HOBF_3]^-$$

The identification of the (presumably) monoboron species that represents the vertex atom that has been removed from the cage has not been forthcoming. Each of the *closo*-carboranes, 2,4-$C_2B_5H_7$ and 1,2- and 1,7-$C_2B_{10}H_{12}$, has given indications of producing somewhat different "monoboron" side products. The 2,4-$C_2B_5H_7$ reaction produced some undistinguished resonances in the fluorine and boron NMR spectra that could be monoboron compounds having at least one attached fluorine atom. The *closo*-1,2-$C_2B_{10}H_{12}$ reaction produced a resonance in the boron-11 NMR spectrum that suggested the presence of a BF_3 grouping (perhaps attached to a solvent molecule); 1,7-$C_2B_{10}H_{12}$ produced a species highly suggestive of a [HBF_3]$^-$ grouping.

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Control experiments with fluoride ion and each solvent have been carried out alongside the carborane experiments in order to assess potential problems of fluoride ion interaction with the solvent prior to carborane attack. It is to be noted, however, that preliminary studies with acetonitrile and tetrahydrofuran show no attack of solvent by fluoride ion under the conditions of the fluoride ion/carborane studies involving 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, or the 1,2- and 1,7-isomers of $C_2B_{10}H_{12}$.[20]

As mentioned above, attack of dialkylamide anion (in acetonitrile) on *closo*-2,4-$C_2B_5H_7$ also gives rise to *nido*-2,4-$C_2B_4H_7^-$ and along the way produces two intermediates, in which at least one is thought to represent progressive cage opening of the seven-atom cage system.[4] Thus far, we have not noticed intermediates during the fluoride ion/2,4-$C_2B_5H_7$ reaction or in the other fluoride/carborane reactions described in this report.

In closing, fluoride ion appears to be unique among the halides in that the higher halide ions do not appear to give cage-opened products by starting with the above *closo*-carboranes.[21]

Acknowledgment. We wish to thank the National Science Foundation, Grants CHE-8617068 and CHE-8922339, and the MBRS-NIH program for partial support of this study. We also thank California State University, Sacramento, CA, for access to the multiflow trace (NSF Grant CHE-8822716) minisupercomputer facilities and San Diego State University for access to the San Diego Supercomputer Regional Facility. The NMR data were obtained by the use of a Bruker AM-400 instrument at CSULA, funded by NIH Grant RR-08101-13S1, by NSF Grant DMB-8503839, and by the Keck and Dreyfus Foundations.

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(20) See the reference in footnote 18 for comments about the reactivity, or inertness, of fluoride ion with acetonitrile.

(21) It has come to our attention that others have noticed the action of fluoride ion on derivatives of 1,2-$C_2B_{10}H_{12}$, and results similar to those reported herein for the parent *o*-carborane were observed: Varadrajan, A.; Gomez, F.; Hawthorne, M. F. Unpublished studies.

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Tetranuclear Heterometallic Complexes of the General Types $[M\{(OH)_2CrA_4\}_3]^{5+}$ and $[M\{(OH)_2CoA_4\}_3]^{5+}$

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Received July 12, 1990

Series of tetranuclear heteronuclear complex ions of the general types $[M\{(OH)_2CrA_4\}_3]^{5+}$ and $[M\{(OH)_2CoA_4\}_3]^{5+}$, where M is a divalent metal ion and A_4 is a single tetradentate amine ligand, two bidentate amines, or four monodentate amines, have been synthesized and characterized. The structure of the cobalt(II)/chromium(III) complex $[Co\{(OH)_2Cr(bispictn)\}_3](ClO_4)_5\cdot 6H_2O$ (where bispictn is *N,N'*-bis(2-pyridylmethyl)-1,3-propanediamine, $C_{15}H_{20}N_4$) has been determined by single-crystal X-ray diffraction techniques. The complex crystallizes in the acentric space group *P*31*c* of the trigonal system with two tetranuclear species in a cell of dimensions $a = 16.144$ (5) Å and $c = 15.091$ (2) Å. The structure has been refined to a value of the weighted *R* factor of 0.046 based on 1604 independent observed reflections. The Co atom lies on the 3-fold axis and is surrounded by six bridging hydroxo groups. Hence, the complex can be viewed as consisting of three *cis*-$[Cr(bispictn)(OH)_2]^+$ units, which act as bidentate ligands to the central cobalt(II) core. The Co–O bond lengths are 2.050 (5) and 2.166 (5) Å, while the Cr–O distances are 1.902 (5) and 1.921 (5) Å. The Co–Cr distance in the tetramer is 3.064 (2) Å, comparable to the values in bis(μ-hydroxo)dichromium(III) dimers. The magnetic properties of the complexes have been investigated and are compared with the theoretical values obtained by fitting to the appropriate Hamiltonian. General energy diagrams illustrating the relation among energy, spin, and degeneracy for tetranuclear systems having S_1 between $^1/_2$ and $^5/_2$, $S_2 = S_3 = S_4 = {}^3/_2$, $J_{12} = J_{13} = J_{14} = J$, and $J_{23} = J_{34} = J_{42} = 0$ are given; these diagrams illustrate that in all cases, independent of S_1 and the sign of *J*, the ground state has a higher spin than the nearest excited states. This has important consequences for the variation of the effective magnetic moments with the temperature.

Introduction

During the past few years we[2-4] and others[5] have been interested in the development of polynuclear transition-metal ions formed from the interaction of 2 or more mol of *cis*-$[CrA_4(OH)_2]^+$ (where A_4 is a single tetradentate amine ligand, two bidentate amines, or four monodentate amines), or its cobalt(III) analogue, with metal halides. The resultant heteronuclear or homonuclear complex ion can be viewed as stemming from the interaction of the bidentate *ligand* $[CrA_4(OH)_2]^+$ with the central metal ion, and complexes with two, three, and four such ligands coordinated to a single metal have been isolated, characterized, and briefly described.[2-5] We have now undertaken a complete synthetic and physical study of the tetranuclear complexes of this type and have demonstrated the amazing versatility of our approach for the formation of tetranuclear species; virtually any central metal ion, M, can be coordinated to three bidentate $[CrA_4(OH)_2]^+$ moieties to form the complex.

We report here the synthetic approach, the magnetic and EPR properties, and the structures of this new series of tetranuclear heterometallic complexes.

Experimental Section

Syntheses. The following complexes were prepared according to procedures described in the literature: *N,N'*-bis(2-pyridylmethyl)-1,3-propanediamine (bispictn),[6] *cis*-β-$[Co(bispictn)Cl_2]Cl\cdot 0.5HCl$,[7] *cis*-$[Cr(NH_3)_4(OH)(H_2O)]S_2O_6\cdot H_2O$,[8] and *cis*-$[Co(NH_3)_4(H_2O)_2]Br_3$.[9] *cis*-$\beta$-$[Cr(bispictn)Cl_2]Cl\cdot 2H_2O$ and $[Cr(en)_2Cl_2]Cl$ were prepared from $CrCl_3$ and the appropriate amine in DMSO by following the method described for α-$[Cr(pico)_2Cl_2]Cl$.[10] The compounds were converted into the other starting materials as described below.

Starting Materials. 1. *cis*-β-$[Cr(bispictn)(OH)(H_2O)](ClO_4)_2\cdot 2H_2O$. *cis*-$\beta$-$[Cr(bispictn)Cl_2]Cl\cdot 2H_2O$ (0.41 g, 0.91 mmol) was dissolved in water (3 mL) and a solution of sodium hydroxide (1 mL, 2 M). The solution was heated briefly (80 °C) and then filtered. After the solution was cooled on ice, sodium perchlorate (2 g) was added, and the solution

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