cannot happen to any great extent in the absence of Ti 4p functions) is important in stabilizing this complex and that the titanium prefers a more neutral environment. The large spatial extent of the diffuse orbitals[16] make a Mulliken population analysis for the DZP+ calculation virtually meaningless, and these are not reported in the table.

The DZP, DZP+, DZP+/MP2, and INDO/1 calculations all indicate that $[TiH_6]^{2-}$ is octahedral and the distortions from octahedral symmetry, during the course of a reaction or due to agostic M–H bonding in substituted complexes,[1,2] can occur without much cost in energy. This study, however, is motivated by the report that such a simple system as $[TiH_6]^2$ violated simple and very appealing crystal field concepts. The failure of the EH calculations to predict the same geometry as do the better ab initio and INDO calculations we attribute to the failure of that method to reproduce correctly the important electrostatics that form the octahedron. In the course of this study comes reinforcement of the observation that EH total energies should never really be taken too seriously, as the theory for doing so is but very qualitative.[17]

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(16) The Ti–H bond length is 1.85 Å, and for the diffuse 4s orbital on Ti $\langle r \rangle$ = 2.44 Å.

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closo-$[B_{11}H_{11}AlCH_3]^{2-}$, an Aluminaborane Analogue of the *closo*-$[B_{12}H_{12}]^{2-}$ Dianion: Synthesis, Characterization, and Molecular Structure

Sir:

Aluminacarboranes[1] and aluminum borohydride[2] have been characterized in some detail. Polyhedral aluminaboranes, on the other hand, have been examined less extensively.[3] There have been no reports of polyhedral aluminaboranes that are analogues of the *closo*-$[B_nH_n]^{2-}$ dianions. Described herein is the high-yield synthesis, characterization, and molecular structure (Figure 1) of the 1-methyl-1-aluminaundecahydrododecaborate(2–) dianion, $[B_{11}H_{11}AlCH_3]^{2-}$, an aluminaborane analogue of the *closo*-$[B_{12}H_{12}]^{2-}$ dianion.

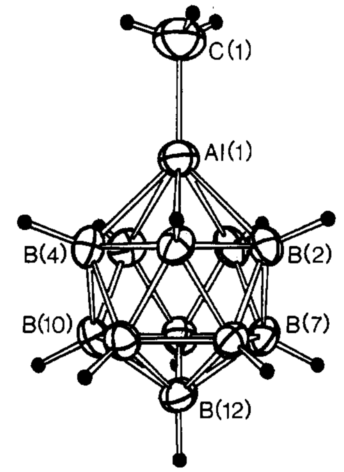

Figure 1. Molecular structure of *closo*-$[B_{11}H_{11}AlCH_3]^{2-}$ (ORTEP plot with 50% probability ellipsoids).

When $Na_2[B_{11}H_{13}]$ is heated in liquid $Al(CH_3)_3$ in the presence of 1 equiv of glyme, $Na_2[B_{11}H_{11}AlCH_3]$ is formed in greater than 90% yields according to eq 1. It is assumed that the glyme acts

$$Na_2[B_{11}H_{13}] + Al(CH_3)_3 \xrightarrow[\text{110 °C; 4 days}]{\text{glyme (1 equiv)}} Na_2[B_{11}H_{11}AlCH_3] + 2CH_4 \quad (1)$$

as a catalyst by cleaving the $[Al(CH_3)_3]_2$ dimer. In the absence of glyme, even after 8 days, the reaction is not complete. Progress of the reaction is followed by measuring the CH_4 evolved. The boron-11 NMR spectrum of $Na_2[B_{11}H_{11}AlCH_3]$ in THF-d_8 (BF_3·OEt_2 at 0.00 ppm) consists of the following resonances which have been assigned on the basis of a 2D ^{11}B–^{11}B NMR study: –17.8 ppm (d, J = 114 Hz), boron atoms 7–11; –18.8 ppm (d, J = 103 Hz), boron atoms 2–6; –25.5 ppm (d, J = 129 Hz), boron atom 12. The $^1H\{^{11}B\}$ NMR spectrum in THF-d_8 (TMS at 0.00 ppm) consists of the resonances 0.82 (B–H), 0.73 (B–H), and –0.64 ppm (C–H). Relative areas of these resonances are 6.2:5.2:3, respectively, in good agreement with the theoretical ratio 6:5:3, assuming that the signal due to the proton on the apical boron atom overlaps one of the other B-H signals.

$Na_2[B_{11}H_{11}AlCH_3]$ is air-sensitive and reacts with water, producing $Na_2[B_{11}H_{13}]$ and aluminum hydrolysis products. It also reacts with 1 equiv of methanol at 65 °C to yield $Na_2[B_{11}H_{13}]$ and unreacted $Na_2[B_{11}H_{11}AlCH_3]$. This indicates that complete cleavage of the aluminum atom from the cage is favored over the formation of species such as $Na_2[B_{11}H_{11}Al(OCH_3)]$. $Na_2[B_{11}H_{11}AlCH_3]$ does not react with diethylamine or dimethylamine. This is in contrast to the case for its carborane analogues $C_2B_9H_{11}AlR$ (R = CH_3, C_2H_5),[1a] which react with THF to form $C_2B_9H_{11}AlR$·THF and with stronger bases to cleave the aluminum atom from the cage.[1a,g] Solid $Na_2[B_{11}H_{11}AlCH_3]$ reacts with $^1/_3$ equiv of BCl_3 to yield only one polyhedral borane product and some unreacted starting material, as determined by boron-11 NMR spectroscopy. The product has resonances at –13.6 (d, $J \simeq$ 179 Hz) and –15.7 ppm (br d, J = 148 Hz). If excess BCl_3 is employed, a much more complex reaction mixture results with many overlapping resonances in the range –10 to –30 ppm being observed in the boron-11 NMR spectrum. During both reactions $B(CH_3)_3$ is evolved, indicating halide–alkyl exchange between BCl_3 and $Na_2[B_{11}H_{11}AlCH_3]$. The formation of $B(CH_3)_3$ and the simplicity of the boron-11 NMR spectrum indicate that the product formed when $^1/_3$ equiv of BCl_3 is employed may be the targeted compound, $Na_2[B_{11}H_{11}AlCl]$. Further investigation of this reaction is in progress.

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Crystals of $[As(C_6H_5)_4]_2[B_{11}H_{11}AlCH_3]$ were obtained by slow diffusion of diethyl ether into a concentrated acetonitrile solution. The molecular structure was determined from single-crystal X-ray diffraction data.[4] The structure of $[B_{11}H_{11}AlCH_3]^{2-}$ is that of an icosahedron (Figure 1). All hydrogen atoms bonded to boron atoms were located and refined. The boron-hydrogen distances range from 1.07 (3) to 1.16 (3) Å. Boron-boron distances in the plane of atoms B2-B6 range from 1.815 (5) to 1.856 (5) Å while the remaining boron-boron distances range from 1.760 (5) to 1.788 (5) Å. All the boron-boron distances and boron-hydrogen distances are within the normal range for boron hydrides.[5] Boron-aluminum distances range from 2.131 (4) to 2.140 (4) Å with the boron-aluminum-carbon angles ranging from 131.5 (2) to 134.7 (2)°. The aluminum-carbon distance is 1.942 (4) Å. The aluminum-carbon vector is essentially perpendicular to the plane formed by boron atoms B2-B6, tilting just 2° from perpendicularity.

$Na_2[B_{11}H_{13}]$ was prepared in a "one-pot" procedure from B_5H_9. By the literature procedure,[6] $Na[B_{11}H_{14}]$ (10.53 mmol) was prepared from NaH (287.1 mg, 88% activity, 10.53 mmol of active NaH) and B_5H_9 (2.53 mL, 0 °C, 26.45 mmol) in glyme. In order to ensure complete removal of excess B_5H_9, volatiles were removed from $Na[B_{11}H_{14}]$ for 12 h, under dynamic vacuum, and a yellow "gum" resulted. $Na_2B_{11}H_{13}$ was then prepared from this "gum" by using a modification of the literature preparation of the $[B_{11}H_{13}]^{2-}$ anion.[7] NaH was employed as the deprotonating agent, and glyme was used as the solvent. The product $Na_2[B_{11}H_{13}]$ was obtained in 74% yield based upon the amount of hydride employed in the preparation of $Na[B_{11}H_{14}]$.

The $[B_{11}H_{11}AlCH_3]^{2-}$ dianion is prepared from $Na_2[B_{11}H_{13}]$ and $Al(CH_3)_3$. In the glovebox, a reaction bulb, with a glass tube extending from its bottom and a Kontes stopcock attached to its top, was charged with a magnetic stirbar and $Na_2B_{11}H_{13}$ (253.0 mg, 1.42 mmol). The vessel was evacuated, and $Al(CH_3)_3$ (~3 mL) was condensed onto the $Na_2B_{11}H_{13}$ at −196 °C, followed by glyme (1.52 mmol). [*Caution*! Neat $Al(CH_3)_3$ is spontaneously flammable when in contact with air! Proper precautions must be taken.] The vessel was warmed to room temperature followed by slow warming of the slurry, with stirring, to 105-110 °C. This temperature was maintained for a period of 4 days. Methane gas formed during the reaction was measured (96% of theory). All volatiles were pumped from the reaction vessel, which was then transferred to the glovebox, and the solid reaction residue was rinsed with toluene (~20 mL) into another flask. This flask was attached to an extractor, and the solid was washed three times with toluene to remove any remaining $Al(CH_3)_3$ and glyme. Volatiles were removed, and the vessel taken into the glovebox, where the crude $Na_2[B_{11}H_{11}AlCH_3]$ was scraped from the frit (yield 294.3 mg, 95%; 4% of $Na_2[B_{11}H_{11}]$ formed by the thermal decomposition of $Na_2[B_{11}H_{13}]$ was present as an impurity).

The $N(C_2H_5)_4^+$ and $As(C_6H_5)_4^+$ salts of the $[B_{11}H_{11}AlCH_3]^{2-}$ dianion were obtained by metathesis reactions between tetraethylammonium or tetraphenylarsonium chloride and $Na_2[B_{11}H_{11}AlCH_3]$ in CH_3CN in 68% and 66% yields, respectively. Anal. Calcd for $[As(C_6H_5)_4]_2[B_{11}H_{11}AlCH_3]$: Al, 2.87; As, 15.96; B, 12.67; C, 62.69; H, 5.81. Found: Al, 2.79; As, 16.10; B, 12.45; C, 62.41; H, 5.63.

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Supplementary Material Available: Listings of selected bond distances, selected bond angles, positional parameters, and anisotropic thermal parameters (20 pages); a listing of calculated and observed structure factor amplitudes (42 pages). Ordering information is given on any current masthead page.

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[4] Crystal data for $[As(C_6H_5)_4]_2[B_{11}H_{11}AlCH_3]$: space group $P2_1/n$, $a = 10.2764$ (46) Å, $b = 21.7110$ (75) Å, $c = 21.9454$ (41) Å, $\beta = 98.68$ (2)°, $v = 4840.1$, ρ(calcd) = 1.290 g cm^{-3}, $M_r = 938.76$, $Z = 4$, μ(Mo Kα) = 1.5 cm^{-1}. Diffraction data were collected at −50 °C 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. $R_F = 0.028$ and $R_{wF} = 0.034$ (615 variables refined) for 4186 reflections $[I \geq 3.0\sigma(I)]$ of 6290 independent reflections collected over the range $4° \leq 2\theta \leq 45°$.

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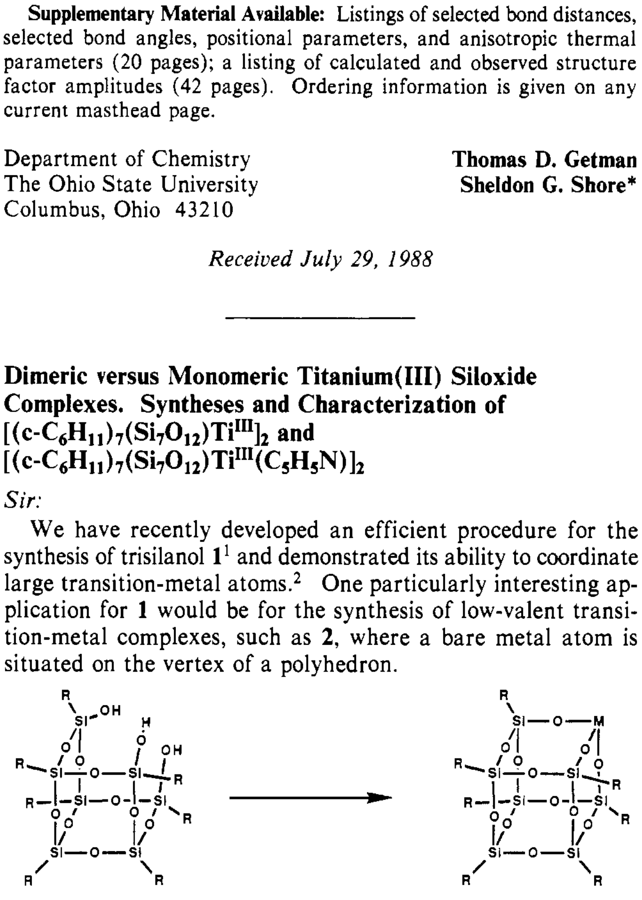
Dimeric versus Monomeric Titanium(III) Siloxide Complexes. Syntheses and Characterization of $[(c\text{-}C_6H_{11})_7(Si_7O_{12})Ti^{III}]_2$ and $[(c\text{-}C_6H_{11})_7(Si_7O_{12})Ti^{III}(C_5H_5N)]_2$

Sir:

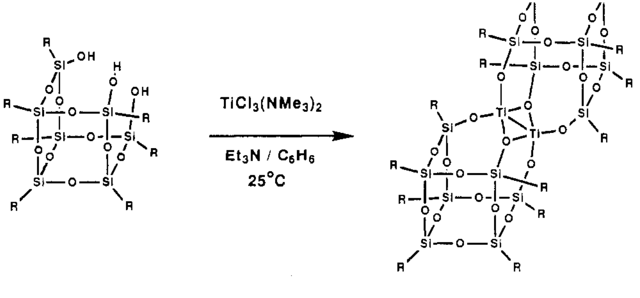
We have recently developed an efficient procedure for the synthesis of trisilanol **1**[1] and demonstrated its ability to coordinate large transition-metal atoms.[2] One particularly interesting application for **1** would be for the synthesis of low-valent transition-metal complexes, such as **2**, where a bare metal atom is situated on the vertex of a polyhedron.



1 **2**

This paper reports our efforts to synthesize Ti(III) complexes derived from **1**. Despite the unique steric and geometric requirements of **1** as a ligand, which present the best opportunity yet for the synthesis of pyramidalized ML_3 complexes, mononuclear complexes are not observed. Instead, siloxy-bridged dinuclear complexes are the thermodynamically preferred products.

The room-temperature reaction of **1** with $Ti[N(SiMe_3)_2]_3$[4] or $TiCl_3(NMe_3)_2$[4] in C_6H_6/Et_3N affords high yields of blue dinuclear complex **3**.[5]



1 **3**

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