In the ^{13}C NMR of complexes **3**,[5,6] the C_3 carbon which is bonded to molybdenum was found to resonate at considerably higher field as compared with the reported value for the same carbon in $(\eta^5\text{-}C_5Me_5)_2TiCH_2CH_2CH(Me)O$ (55.8 ppm).[7] This implies that the higher electron density at the metal center in the molybdenum(IV) complexes than in titanium(IV) in spite of the opposite order of the propensity for the electron-donating ability between cyclopentadienyl and pentamethylcyclopentadienyl ligands.

The neutral oxametallacycle derivatives **3a** and **3b** revert to the parent cyclic (γ-hydroxyalkyl)molybdenum cations **1a** and **1b**, respectively, on treatment with an equimolar amount of TsOH in Et_2O. Similarly, the reaction of **3a** with anhydrous hydrogen chloride in Et_2O yields the chloride analogue of **1a** $[Cp_2MoCH_2CH(CH_3)CH_2OH]^+Cl^-$.

Acknowledgment. We thank Dr. F. Ozawa, Tokyo Institute of Technology, for the measurement of mass spectroscopy.

Registry No. **1a**, 103822-69-1; **1a**-d_1, 105517-88-2; **1b**, 103822-61-3; **2**, 103822-61-3; **3a**, 105472-71-7; **3b**, 105472-72-8; **4**, 105472-70-6; $[Cp_2Mo(D)(EtOD)]^+TsO^-$, 105472-69-3; $[Cp_2MoCH_2CH(CH_3)CH_2OH]Cl$, 105472-73-9; allyl alcohol, 107-18-6; β-methallyl alcohol, 513-42-8.

Synthesis and Molecular Structure of a Novel Aluminacarborane, *nido*-[μ-6,9-AlEt(OEt$_2$)-6,9-$C_2B_8H_{10}$]

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Received July 29, 1986

Summary: Synthesis and characterization of *nido*-[μ-6,9-AlEt(OEt$_2$)-6,9-$C_2B_8H_{10}$] (**2**) is outlined, and the results of a single-crystal X-ray structure determination for **2** are presented. Ligand exchange of OEt_2 in **2** for THF to produce [μ-6,9-AlEt(THF)-6,9-$C_2B_8H_{10}$] (**3**) is reported, and direct synthesis of **3** is described. Spectroscopic data for **2** and **3** are reported, and bonding in these species is discussed.

Interest in hetero- and metallacarboranes derived from the main-group elements stems from the unusual structures and bonding modes exhibited by these compounds. Characterizations of 12-vertex aluminacarboranes of composition $C_2B_9H_{11}AlR$ (R = Me, **1a**; R = Et, **1b**) in which an aluminum atom is bound to the five-membered face of the dicarbollide ligand have been described previously.[1] Synthesis of **1a** and **1b** was accomplished by direct reaction of $C_2B_9H_{13}$ with the appropriate trialkylaluminum reagent. Preparation of the bis(tetrahydrofuran) (THF) adduct of **1b** by reaction of $Na_2C_2B_9H_{11}$ with $EtAlCl_2$ in THF has been reported.[2] Here we wish to describe the synthesis by a related reaction of an aluminacarborane derived from the formal $[C_2B_8H_{10}]^{2-}$ ligand and its structural characterization.

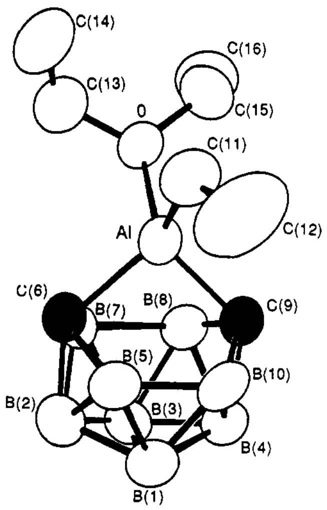

Figure 1. Molecular structure of **2**, with hydrogen atoms omitted for clarity and thermal ellipsoids drawn at 50% probability level. Interatomic distances (Å) and angles (deg): Al–C(6) = 2.030 (3), Al–C(9) = 2.025 (3), Al–B(5) = 2.500 (4), Al–B(7) = 2.509 (4), Al–B(8) = 2.499 (3), Al–B(10) = 2.514 (4), Al–C(1) = 1.966 (3), Al–O(1) = 1.909 (2); C(6)–Al–C(9) = 99.44 (12), C(1)–Al–O(1) = 99.87 (13), C(13)–O(1)–C(15) = 115.88 (25).

Reaction of diethylaluminum chloride–diethyl etherate with an equimolar amount of $Na[5,6\text{-}C_2B_8H_{11}]$[3] in refluxing toluene resulted in evolution of gas and formation of [μ-6,9-AlEt(OEt$_2$)-6,9-$C_2B_8H_{10}$] (**2**).[4] This reaction presumably occurs according to eq 1.

$$Na[5,6\text{-}C_2B_8H_{11}] + Et_2AlCl\cdot OEt_2 \xrightarrow[\text{reflux}]{\text{toluene}} nido\text{-}[\mu\text{-}6,9\text{-}AlEt(OEt_2)\text{-}6,9\text{-}C_2B_8H_{10}] + NaCl + C_2H_6 \quad (1)$$

Purification by high vacuum fractional distillation afforded **2**, a colorless, viscous liquid, in 77% yield.[5] Complex **2** is air- and water-sensitive, decomposing visibly within seconds upon exposure to the atmosphere and reacting vigorously with water. Crystals (mp 28–30 °C) could be obtained by layering benzene solutions of **2** with pen-

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(4) Preparation of **2**: All manipulations were carried out under dry N_2 or in vacuo by using standard Schlenk line, glovebox, and vacuum line apparatus. In a typical experiment, 16.6 mL of a 0.5 M toluene solution of $Et_2AlCl\cdot OEt_2$ (8.3 mmol) was added rapidly to a stirred suspension of freshly prepared $Na[5,6\text{-}C_2B_8H_{11}]$ (1.2 g, 8.3 mmol) in 200 mL of toluene at 0 °C in a 500-mL, round-bottom Schlenk flask. The mixture was stirred at room temperature for 1 h. The flask was then fitted with a condenser and solution was refluxed under N_2 for 16 h. The resulting mixture was filtered and the volume of the filtrate reduced in vacuo to ca. 20 mL. Product **2** was precipitated from the filtrate as a pale yellow oil by addition of 150 mL of dry *n*-pentane. The product was precipitated twice more from benzene/*n*-pentane. Further purification was accomplished by distillation under high vacuum at 60 °C to a 0 °C U-trap to give liquid **2** (1.6 g, 77% yield) as a colorless distillate.

(5) Spectroscopic data for **2**: 160.5 MHz ^{11}B NMR (C_6D_6; referenced to external $BF_3\cdot OEt_2$ at 0 ppm with chemical shift values upfield of 0 ppm reported as negative; ambient temperature; splitting patterns and areas given in parentheses) δ 4.3 (d, 1), 2.9 (d, 2), −25.3 (d, 1), singlets upon ^1H decoupling; 200.1-MHz ^1H NMR (C_6D_6; referenced to residual protons in C_6D_6 at 7.15 ppm; ambient temperature) δ 4.69 (s, 2, carboranyl C–H), 2.97 (q, 4, coordinated OEt_2), 0.95 (t, 2, Al-bound ethyl group), 0.51 (t, 6, coordinated OEt_2), −0.38 (q, 3, Al-bound ethyl group), broad B–H resonances in the 5.1–0.1 ppm region; characteristic IR (NaCl; neat press; cm^{-1}) 2943 (vs), 2793 (m), 2548 (vs, B–H stretch), 1468 (s), 1392 (s), 1327 (m), 1287 (m), 1192 (s), 1150 (s), 1090 (s), 1053 (m), 1012 (vs), 953 (m), 890 (s), 833 (m), 770 (s).

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tane. The ^1H NMR spectra of these crystals dissolved in deuteriated solvent indicated incorporation of benzene solvent in a ratio of one benzene molecule for each two molecules of **2**. When subjected to vacuum, these crystals lost benzene, melting to liquid **2**. At no time was loss of diethyl ether observed.

A single-crystal X-ray diffraction study was carried out on $\mathbf{2}\cdot{}^1/_2C_6H_6$.[6] A projection of the aluminacarborane **2** is shown in Figure 1 together with significant interatomic distances and angles. The polyhedral portion of the structure of **2** is that of a nearly regular octadecahedron, since no unique open face is present. The aluminum atom occupies a position on the pseudo-twofold axis of the cluster, being nearly equidistant from the four boron atoms as well as the two carbon atoms of the six-membered face of the carborane fragment, and thus can be regarded as occupying the eleventh octadecahedral vertex. Diethyl ether is coordinated to the metal center as evidenced by the relatively short Al–O distance (1.909 (2) Å). The carboranyl carbon atoms occupy the 6- and 9-positions of the formal $[C_2B_8H_{10}]^{2-}$ ligand in agreement with the observed spectroscopic data. The angles through the metal between the two exopolyhedral groups and between the two carboranyl carbon atoms are roughly those anticipated for the accommodation of the tetrahedral bonding geometry of aluminum. The aluminum–boron interatomic distances average 2.51 Å while the aluminum–carbon distances average 2.03 Å.

A rationalization of the observed geometry of **2** involves the description of the formally dianionic $[6,9\text{-}C_2B_8H_{10}]^{2-}$ cage as a nido η^2-ligand. This ligand can be viewed as donating four electrons to the metal via two carbon-based orbitals directed at two formal coordination sites of the tetrahedral aluminum center. The aluminum atom with its substituents is treated in this description as a bridging, exopolyhedral moiety that does not participate in the polyhedral framework of the cluster.

The structure of **2** contrasts with that of other known main-group element substituted, 11-vertex, 26-electron clusters [e.g., $[(Me_2M(\eta^4\text{-}B_{10}H_{12})]$ (M = Si, Ge, Sn)[7]] which adopt nido structures having a single open face at which two bridging hydrogen atoms reside. Transition-metal complexes of the type $[\mu\text{-}6,9\text{-}ML_2\text{-}6,9\text{-}C_2B_8H_{10}]$ (M = Pt, L = PPh_3, SEt_2; M = Ni, L = *cis*-1,2-$(NH_2)_2C_6H_4$), which bear structural similarity to **2**, have been reported recently; however, these involve square planar rather than tetrahedral metal centers.[8]

The apparent C_{2v} symmetry of **2** indicated by the ^{11}B NMR data can be attributed to rapid exchange of diethyl ether in solution. Upon addition of 1 equiv of diethyl ether to a toluene-d_8 solution of **2**, only one set of diethyl ether ethyl resonances was observed in the ^1H NMR spectrum. These resonances occurred at chemical shift positions intermediate between free and coordinated diethyl ether, indicating the occurrence of a rapid exchange process. Variable-temperature NMR studies carried out down to −90 °C failed to reveal any significant change in either the ^1H or $^{11}B\{^1H\}$ NMR spectra of **2** in toluene solution. Furthermore, the low-temperature ^1H NMR spectrum of **2** containing added ether did not show two sets of diethyl ether resonances but rather exhibited only one broad set of resonances. The kinetic lability of coordinated diethyl ether in **2** was further demonstrated by facile exchange with tetrahydrofuran (THF) which was accomplished by dissolving a sample of **2** in a 50% solution of THF-d_8 in toluene-d_8. The ^1H NMR spectrum of the resulting solution indicated complete displacement of diethyl ether by excess THF-d_8. Removal of volatiles in vacuo resulted in the isolation of a colorless liquid identified spectroscopically as $[\mu\text{-}6,9\text{-}AlEt(C_4D_8O)\text{-}6,9\text{-}C_2B_8H_{10}]$ (**3**-d_8). The nondeuteriated analogue **3**[9] was prepared independently by reaction of $Na[5,6\text{-}C_2B_8H_{11}]$ with $Et_2AlCl\cdot THF$ by the same procedure as described for the synthesis of **2**. Compounds **3** and **3**-d_8 gave identical ^{11}B and ^1H NMR data with the exception of the expected absence of THF resonances in the ^1H NMR spectrum of **3**-d_8.

The mechanism of formation of **2** is not known but may involve initial formation of an intermediate with composition $[C_2B_8H_{11}AlEt_2(OEt_2)]$ (**4**) having a bridging B–H–B moiety. Elimination of ethane from **4** would then lead to **2** or a species isomeric with **2**, but differing in the positions of the carboranyl carbon atoms. Thermal rearrangement of the $C_2B_8H_{10}$ ligand to produce the observed 6,9-isomer is that expected for this system under the reaction conditions as established by previous studies[10] and is consistent with the general pattern for neutral polyhedral carborane thermal rearrangements in which carbon atoms tend to migrate to positions which are separated from one another and of low connectivity.[11] This rearrangement also apparently provides the most suitable orbital arrangement for bonding with the tetrahedral metal center. The $Na[5,6\text{-}C_2B_8H_{11}]$ used in the synthesis of **2** was prepared by deprotonation of $5,6\text{-}C_2B_8H_{12}$ with excess NaH.[3] The ^{11}B NMR spectra of $Na[C_2B_8H_{11}]$ thus obtained confirmed that carbon atom migration did not occur upon deprotonation.

The synthesis and structural characterization of the related anion complex $[Al(\eta^2\text{-}6,9\text{-}C_2B_8H_{10})_2]^-$ is described in the following communication.

Acknowledgment. The support of the National Science Foundation (Grant CHE-84-01433) is gratefully acknowledged. We also thank NSF for use of the Bruker WM 500 FTNMR spectrometer at the Southern California Regional Magnetic Resonance Facility (Grant CHE-79-16324).

Supplementary Material Available: Tables of positional and thermal parameters and interatomic distances and angles (9 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

(6) $\mathbf{2}\cdot{}^1/_2C_6H_6$ crystallizes in the triclinic space group $A\bar{1}$ with cell dimensions a = 13.964 (3) Å, b = 15.966 (4) Å, c = 8.550 (2) Å, α = 92.227 (8)°, β = 86.689 (7)°, γ = 102.060 (8)°, and V = 1862 Å^3 with Z = 4 (reduced cell: $P\bar{1}$, Z = 2, a = 8.5525 Å, b = 8.9099 Å, c = 13.9674 Å, α = 99.172°, β = 93.323°, γ = 116.428°, V = 930.9 Å^3). The data were collected at 25 °C on a modified Picker automated diffractometer (Mo Kα, λ = 0.7107 Å, max 2θ = 50°). The structure was solved by direct methods using SHELX 76 and refined by full-matrix least squares to an R factor of 0.061 (R_w = 0.081, GOF = 2.85) by using 2338 reflections for which $I > 3\sigma(I)$ (a total of 3273 unique reflections).

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(9) Spectroscopic data for **3**: 160.5-MHz ^{11}B NMR (C_7H_8; referenced to external $BF_3\cdot OEt_2$ at 0 ppm with chemical shift values upfield of 0 ppm reported as negative; ambient temperature; splitting patterns and areas given in parentheses) δ 3.3 (d, 2), 2.4 (d, 1), −25.8 (d, 1), singlets upon ^1H decoupling; 200.1-MHz ^1H NMR (C_7D_8; referenced to residual benzyl protons in C_7D_8 at 2.09 ppm; ambient temperature) δ 4.69 (s, 2, carboranyl C–H), 3.81 (m, 4, coordinated THF), 1.50 (m, 4, coordinated THF), 0.943 (t, 3, Al-bound ethyl group), broad B–H resonances in the 5.1–0.1 ppm region; characteristic IR (cm^{-1}) 2940 (s), 2902 (s), 2867 (s), 2540 (vs), 1458 (m), 1377 (m), 1149 (m), 1090 (s), 1056 (s), 948 (s), 758 (s).

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