Synthesis and X-ray Structure of a Novel Bis(*nido*-carboranyl)aluminate Complex, $[Al(\eta^2\text{-}6,9\text{-}C_2B_8H_{10})_2]^-$

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Summary: Synthesis of the anionic bis(*nido*-carboranyl)aluminate complex $[Al(\eta^2\text{-}6,9\text{-}C_2B_8H_{10})]^-$ (**[2]**$^-$) is outlined. Spectroscopic data for **[2]**$^-$ are reported, and the results of a single-crystal X-ray structure determination of the air-stable salt PPN**[2]** are presented. The bonding in **[2]**$^-$ is discussed.

Synthesis and characterization of the aluminacarborane complex *nido*-$[\mu\text{-}6,9\text{-}AlEt(OEt_2)\text{-}6,9\text{-}C_2B_8H_{10}]$ (1) was described in the preceding communication.[1] Here we wish to report the synthesis and structural characterization of a related anionic aluminacarborane complex, $[Al(\eta^2\text{-}6,9\text{-}C_2B_8H_{10})_2]^-$ (2).

Reaction of diethylaluminum chloride with 2 molar equiv of $Na[5,6\text{-}C_2B_8H_{11}]$[2] in refluxing toluene resulted in evolution of gas and the formation of $Na[Al(\eta^2\text{-}6,9\text{-}C_2B_8H_{10})_2]$ (Na[2]).[3] This reaction presumably occurs according to eq 1. The product Na[2] was a pale yellow,

$$2Na[5,6\text{-}C_2B_8H_{11}] + Et_2AlCl \xrightarrow[\textit{reflux}]{\text{toluene}} \underset{Na[2]}{Na[Al(\eta^2\text{-}6,9\text{-}C_2B_8H_{10})_2]} + NaCl + 2C_2H_6 \quad (1)$$

microcrystalline solid (mp >300 °C), isolated in 81% yield. While Na[2] was found to be moderately stable to dry air, it hydrolyzed slowly when dissolved in water and decomposed gradually in moist air. Cation exchange with [PPN]Cl resulted in nearly quantitative conversion to PPN[2], a white crystalline solid (mp >300 °C).[4] This salt was found to be stable to air for at least several weeks, and it could also be recovered unchanged after suspension in water for several hours. Slow hydrolysis did occur, however, when PPN[2] was dissolved in wet acetone.

The 160.5-MHz ^{11}B NMR spectra of both Na[2] and PPN[2] in CH_2Cl_2 solution exhibited three doublet resonances in a 2:1:1 area ratio (2.7, 0.9, and −28.7 ppm, respectively). These resonances collapsed to singlets upon ^1H decoupling. The 200.1-MHz ^1H NMR spectrum of PPN[2] in toluene-d_8 solution displayed a single carboranyl C–H proton resonance (4.8 ppm, area 2) and a set of broad, complex B-H resonances (ca. 5.1–0.1 ppm, area ca. 10), in addition to resonances characteristic of the PPN$^+$ cation (6.9–7.3 ppm, area 15). The ^1H NMR spectrum of Na[2] in toluene-d_8 solution showed an identical resonance at 4.8 ppm and similar broad B–H resonances. The IR spectrum of Na[2][5] showed bands characteristic of a carborane anion complex. The IR spectrum of PPN[2] was essentially identical except for the presence of additional bands characteristic of the PPN$^+$ cation.

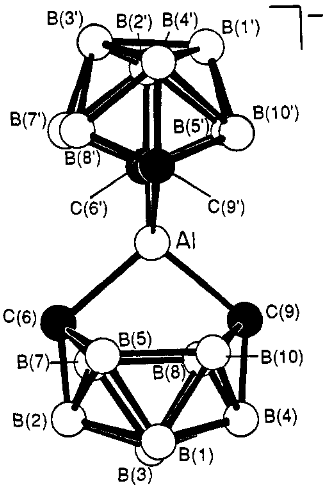

Figure 1. Structure of $[Al(\eta^2\text{-}6,9\text{-}C_2B_8H_{10})_2]^-$ anion ($[2]^-$) with hydrogen atoms omitted for clarity.

A single-crystal X-ray diffraction study was carried out on PPN[2].[6] The structure of the carboranylaluminate anion $[2]^-$ is shown in Figure 1. Unfortunately, the structure was found to be disordered. Although the PPN$^+$ cation did not exhibit disorder and no disorder is required by the space group symmetry, the $[2]^-$ anion was found to be disordered with respect to a fourfold rotation about the noncrystallographic twofold axis of the complex. This disorder resulted in the occurrence of two crystallographic forms of $[2]^-$, a major [52.5 (6)%] and a minor occupant. Both of these forms of $[2]^-$ were considered to be identical and to differ only in their orientation; hence they will be treated here as one complex.

The overall geometry of $[2]^-$ is that of two mutually orthogonal octadecahedral clusters which share the unique aluminum vertex. The aluminum atom occupies the unique position common to both cages and is surrounded

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[3] Preparation of Na[2]: the $Na[5,6\text{-}C_2B_8H_{11}]$ reagent was prepared by reaction of *nido*-$5,6\text{-}C_2B_8H_{12}$ with excess NaH in diethyl ether (see ref 2). For removal of residual ether prior to use, the $Na[5,6\text{-}C_2B_8H_{11}]$ was ground to a fine powder in a glovebox and then heated at 40 °C in vacuo for ca. 12 h. To a 200-mL toluene suspension of $Na[5,6\text{-}C_2B_8H_{11}]$ (1.18 g, 8.16 mmol) in a 500-mL Schlenk flask under dry nitrogen was added 4.10 mL of a 1.0 M hexane solution of Et_2AlCl (4.1 mmol). After the mixture was stirred at room temperature for 1 h, a water-cooled reflux condenser was attached and the mixture was refluxed for 16 h. Evolution of gas was observed initially upon warming. The cooled mixture was then filtered to remove precipitated NaCl. The filtrate volume was reduced in vacuo, and the product Na[2] was precipitated by addition of 200 mL of *n*-pentane. Further purification by recrystallization from methylene chloride/*n*-pentane produced pale yellow microcrystalline Na[2] (0.98 g, 81% yield).

[4] Preparation of PPN[2] by cation exchange: to a suspension of Na[2] (0.50 g, 1.72 mmol) in 500 mL of dry methylene chloride under dry nitrogen was added 0.99 g (1.72 mmol) of [PPN]Cl (PPN$^+$ = bis(triphenylphosphine)nitrogen(1+) cation). After being stirred for 24 h at room temperature, the mixture was filtered through a medium frit and the collected precipitate was washed with three 75-mL portions of methylene chloride. Removal of solvent from the combined filtrate in vacuo resulted in a nearly quantitative yield (1.37 g, 1.70 mmol) of white, crystalline PPN[2].

[5] Na[2]: characteristic IR (Nujol mull, cm^{-1}) 2543 (vs, B-H str.), 1092 (m), 1064 (s), 723 (s), 693 (s).

[6] Crystallographic data: suitable crystals of PPN[2] were grown from toluene/heptane. PPN[2] crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions a = 16.378 (3) Å, b = 18.781 (3) Å, c = 14.806 (3) Å, β = 90.197 (5)°, and V = 4554 Å^3 with Z = 4. The data were collected at −100 °C on a modified Picker automated diffractometer (Mo Kα, λ = 0.7107 Å, max 2θ = 45°). The structure was solved by direct methods using MULTAN 80 and was refined by full-matrix least-squares methods to an R value of 0.078 (R_w = 0.088, GOF = 2.0) by using 2128 reflections for which $I > 3\sigma(I)$ (a total of 5909 unique reflections were measured). The $[2]^-$ anion was disordered. In order to treat the disorder, all like distances within the two anions were constrained to be equal and all like atoms were constrained to have a single thermal parameter; e.g., distances Al–C(6), Al–C(6'), Al–C(9), Al–C(9'), Al''–C(6C), Al''–C(6D), Al''–C(9C), and Al''–C(9D) were constrained to be equal. Some H positions for the anion were not located. Those which are reported were not refined but were included in structure factor calculations. For the cation, which was ordered, all phenyl groups were constrained to be rigid C6 hexagons; C–C = 1.395 Å; C–H = 1.0 Å.

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by an approximately tetrahedral array of four carbon atoms, each of which in turn occupies an apical position in one of the two $C_2B_8H_{10}$ carborane moieties. The four aluminum–carbon interatomic distances average 2.06 Å while the eight aluminum–boron distances average 2.53 Å.

The bonding in $[2]^-$ can be rationalized in a manner similar to that applied to complex **1**.[1] The geometry and interatomic distances in $[2]^-$ suggest that the aluminum atom participates in four electron precise bonds with the nearby tetrahedrally disposed carbon atoms. The relatively long aluminum–boron distances are indicative of a lack of bonding interaction between aluminum and boron. In this bonding description, each of the 6,9-$C_2B_8H_{10}$ cluster fragments in $[2]^-$ are formally regarded as dianionic *nido*-carborane cages, each of which donate four electrons via two carbon-based orbitals to sp^3 hybrid orbitals of the formal aluminum(III) metal center having suitable symmetry. It may be noted that this bonding description allows the $[2]^-$ anion to be regarded as a spiro-aluminate complex.

The mechanism by which $[2]^-$ is formed is not known but may involve successive loss of NaCl and cleavage of the two ethyl groups from aluminum concomitant with deprotonation of each carborane cage resulting in formation of ethane. Migration of the carbon atoms to the 6,9-positions of the $C_2B_8H_{10}$ cage is, as with compound **1**, the expected thermal rearrangement for this system.[7] This rearrangement also appears to result in the most favorable arrangement of carbon-based orbitals for bonding to the aluminum center. Continuous heating of Na[**2**] in refluxing toluene for 3 weeks resulted neither in decomposition nor further rearrangement.

Synthesis of other new aluminacarborane compounds are under investigation and will be reported later.

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Supplementary Material Available: Tables of positional and thermal parameters and interatomic distances and angles (12 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Formation of Metallo Hydride, Formyl, and Alkyl Complexes of Rh(TMTAA)

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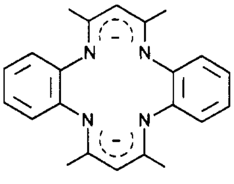
Summary: The dimeric complex $(Rh^{II}(TMTAA))_2$ (**1**) (TMTAA = dibenzotetramethylaza[14]annulene dianion) reacts with mixtures of hydrogen and carbon monoxide gases to produce a metallo hydride, $Rh^{III}(TMTAA)(H)$ (**2**), and an η^1-metallo formyl complex, $Rh^{III}(TMTAA)(CHO)$. Compounds **1** and **2** react with ethene to produce bridging and terminal alkyl complexes, respectively.

Reactions of metallo hydrides with carbon monoxide that result in the transfer of hydrogen to the carbon center have been accomplished with the transition-metal hydride species $(Cp^*{}_2)V(H)$,[1] $(Cp^{*2})Zr(H)_2$,[2] Rh(porphyrin)(H),[3] and actinide complexes $(Cp^*{}_2)Th(OR)(H)$[4] [$Cp^* = \eta^5$-$C_5(CH_3)_5$]. Metal-site catalyzed hydrogenation of CO to organic products is thought to require the formation of a metallo hydride complex, through the reaction of molecular hydrogen, and the formation of either an η^1-carbon-bonded or η^2-carbon- and oxygen-bonded, metallo formyl complex.[5] Rhodium porphyrin dimer complexes are at present the only molecular species reported to react with hydrogen and carbon monoxide to produce both the metallo hydride and metallo formyl complexes.[3] This communication reports on several key features of the organometallic chemistry of a Rh–Rh bonded macrocyclic complex, $(Rh(TMTAA))_2$



TMTAA

(TMTAA = dibenzotetramethylaza[14]annulene dianion), including the reactions with H_2 and CO to produce both metallo hydride and η^1-formyl complexes (reactions 1 and 2).

$$(Rh(TMTAA))_2 + H_2 \rightleftarrows 2Rh(TMTAA)(H) \tag{1}$$

$$(Rh(TMTAA))_2 + H_2 + 2CO \rightleftarrows 2Rh(TMTAA)(CHO) \tag{2}$$

$(Rh(TMTAA))_2$ (**1**) is prepared by refluxing rhodium acetate dimer with the free base ligand H_2TMTAA[6] in ethanol (24 h) and collecting the precipitate by filtration under nitrogen gas. The product obtained is an ethanol solvate and can be converted to the ethanol free form by recrystalization from benzene followed by vacuum drying. Complex **1** has been characterized by ^1H NMR as well as mass spectral analyses.[7]

Solutions of **1** (5×10^{-3} M) in THF-d_8 react with hydrogen gas (P = 0.2–0.8 atm), over a period of 48 h at 298 K, to form a monomeric metallo hydride complex, Rh(TMTAA)(H) (**2**) (reaction 1). Formation of **2** is conveniently observed by the appearance of a diagnostic high-field doublet in the ^1H NMR (δ_{Rh-H} −20.2, $J_{^{103}Rh-^1H}$ = 47.6 Hz).[8]

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(7) (a) ^1H NMR (C_6D_6): δ +7.09 (d of d, 8 H, *m*-phenyl), +6.76 (d of d, 8 H, *o*-phenyl), +3.68 (s, 4 H, methene), +2.00 (s, 24 H, methyl). MS: *m/e* 890 (exptl) vs. 890.6 (calcd) (M^+). (b) Footnote in ref 6 alludes to an unpublished structure determination.

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