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Et_2Al^+ Alumenium Ion-like Chemistry. Synthesis and Reactivity toward Alkenes and Alkene Oxides

Kee-Chan Kim and Christopher A. Reed*

Department of Chemistry, University of California, Riverside, California 92521-0304

Gregory S. Long and Ayusman Sen*

Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802

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Alumenium ions, R_2Al^+, are attractive targets as electrophilic catalysts. Since the initial reports by Ziegler[1] on the "aufbau" reaction, the possibility of synthesizing polyolefins by aluminum-only systems has been investigated.[2-4] Neutral $AlCl_3$ is one of the most widely used Lewis acids. Cationic analogues[5] may be more active.

The $Cp^*{}_2Al^+$ ion has been prepared with perfluorinated tetraphenylborate ($F_{20}{-}BPh_4^-$) as the counterion.[6] With simple alkyl ligands, however, cleavage of an anion $B{-}C_6F_5$ bond occurs.[7] Electrophilic attack by transient R_2Al^+ was implicated.

Icosahedral carboranes of the type $CB_{11}H_6X_6^-$ (X = halide) outperform fluorinated tetraphenylborates in sustaining Brønsted acidity.[8] Indeed, they sustain superacidity[9] and are among the most inert, least coordinating anions known.[10,11] Herein, we show that they stabilize the high level of Lewis acidity anticipated for the R_2Al^+ ion.

Treatment of Et_3Al with trityl salts of carboranes (X = Cl, Br) leads to ethyl group abstraction via β-hydrogen elimination.

$$Et_3Al + [Ph_3C][CB_{11}H_6X_6] \rightarrow Et_2Al(CB_{11}H_6X_6)\ Ph_3CH + C_2H_4$$

The byproducts were identified by ^1H NMR spectroscopy. The product, $Et_2Al(CB_{11}H_6X_6)$ (X = Cl (**1a**), Br (**1b**)), is produced very cleanly in benzene solution and isolated in excellent yield by the addition of hexanes (90%). The ^1H NMR signals of the ethyl groups are sharp [0.27 (4H, q, CH_2), 0.87 (6H, t, CH_3) ppm for X = Br] and show the reverse ordering of methyl and methylene resonances that is common to ethyl groups attached to electrophilic aluminum.[4,12] The boron quadrupole-broadened carborane anion signals [1.6 (1H, CH), 1.9−3.3 (5H, BH) ppm for X = Br] are essentially unchanged from those of the free ion.

The benzene solubility of $Et_2Al(CB_{11}H_6X_6)$ suggests overall electroneutrality or tight ion pairing. This is illuminated in the X-ray crystal structures for X = Cl, Br. The carborane anion shows weak bidentate coordination to the Et_2Al^+ fragment via halo substituents from the 7,8 positions of the pentagonal belt of the anion (see Figure 1 for X = Br). The Al- - -Br bond distances (2.58, 2.54 Å) are ca. 0.3 Å longer than typical Al−Br bonds (2.25−2.30 Å).[13] The coordinated B−Br bonds are only ca. 0.03 Å longer than equivalent uncoordinated bonds. These dimensional aspects are mirrored in the chloro derivative (Al- - -Cl = 2.44, 2.43 Å). They reflect the weakly coordinating nature of the carborane anion and the development of considerable R_2Al^+ ionic character. The C−Al−C angles of 130.0° and 136.6° for X = Br, Cl, respectively, are considerably larger than either the tetrahedral (sp^3) or trigonal (sp^2) ideals, further suggesting the development of alumenium ion character (sp). The larger angle for X = Cl suggests the chloro anion is less coordinating.

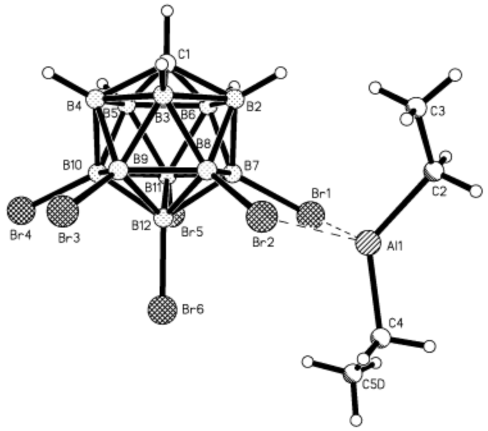

Figure 1. Perspective view of $Et_2Al(CB_{11}H_6Br_6)$, **1b.** Selected bond distances (Å): Al−Br1 = 2.581(2), Al−Br = 2.542(2), Al−C = 1.927(6), Al−C4 = 1.924(6), B7−Br1 = 1.981(5), B8−Br2 = 1.982(5), B9−Br3 = 1.944(5), B10−Br4 = 1.948(5), B11−Br5 = 1.943(5).

The structure is reminiscent of silylium species with very weakly coordinating anions. Predominant ionic bonding between R_3Si^+ and $CB_{11}H_6X_6^-$ is reflected in Si- - -X bonds that are similarly ca. 0.3 Å longer than typical Si−X bonds and the C−Si−C angles are much greater than the sp^3 ideal.[14] Indeed, they are about 75% of the way to the sp^2 ideal.[15] They are written $R_3Si^{\delta+}(CB_{11}H_6X_6)^{\delta-}$ to reflect this ion-like character. A similar designation for the present alumenium species, $Et_2Al^{\delta+}(CB_{11}H_6X_6)^{\delta-}$, is appropriate from both structure and reactivity considerations (see below). Although ion-like species are not free ions they can behave like free ions.

Silylium ion-like species such as $Et_3Si^{\delta+}(F_{20}{-}BPh_4)^{\delta-}$ and electron-deficient neutral aluminum species such as $Al(C_6F_5)_3$ react with arenes to form novel species that lie along the $\pi{-}\sigma$ complex continuum.[14,16-18] To date we have found no evidence for a related $[Et_2Al(arene)]^+$ species, presumably because the solvation energy cost of forming free ions is too great in low dielectric media. However, reaction with alkenes is rapid.

When a high-pressure NMR tube containing a benzene-d_6 solution of $Et_2Al(CB_{11}H_6Cl_6)$, **1a**, was charged with ethene (150 psi), a mixture of butenes and alkylated benzenes was observed, i.e., the products of ethene dimerization and electrophilic aromatic substitution. GC analysis confirmed the formation of ethylbenzene and *sec*-butylbenzene in ~1:10 ratio. The likely chemistry giving rise to these products involves the Lewis acid activation of ethene

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* Corresponding author. E-mail: chris.reed@ucr.edu.

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Scheme 1

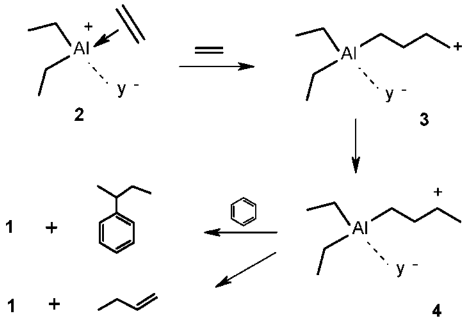

Table 1. Reaction of Ethene with Aluminum Compounds[a]

Al compd	yield (g)	M_w[b]	M_w/M_n[b]	branching[c] (H_{Me}/H_{tot})
triethylaluminum	trace			
diethylaluminum chloride	trace			
ethylaluminum dichloride	0.37	620	1.5	0.43
diethylaluminum hexachlorocarborane[d]	0.90	525	2.3	0.51
trichloroaluminum	2.3			0.50

[a] Standard conditions: 125 mL stainless steel autoclave, 10 mL of chlorobenzene, 700 psi of ethene (constant pressure), 0.1 mmol of aluminum compound, 60 °C, 24 h. [b] Determined by GPC relative to polystyrene standards. [c] By ^{1}H NMR integration. [d] 0.05 mmol used.

to produce $Et_2Al(\eta^2\text{-}C_2H_4)^{\delta+}(CB_{11}H_6Cl_6)^{\delta-}$, **2**. This strong electrophile could attack either benzene or ethene. Reaction with benzene would lead to ethylbenzene via straightforward electrophilic substitution. When the alkene is changed to norbornene, the product is phenylnorbornane. As expected, reactivity toward aromatic substitution is diminished with less electron-rich arenes such as chloro- or dichlorobenzene.

Reaction of activated ethene in **2** with further ethene is more interesting. If a primary butyl carbocation **3** is produced (see Scheme 1), rapid rearrangement via 1,2 H shifts to a secondary cation, such as **4,** would be expected. Subsequent elimination of butene or electrophilic attack on benzene would rationalize the formation of the observed products.

Significantly, the ethyl groups on aluminum remain unaltered throughout the course of these reactions. When carried out with C_2D_4 to multiple turnovers, there is no significant diminution of the ^{1}H NMR signals of the ethyl groups in **1**. Apparently, there is no aufbau insertion of ethene into the Al−Et bond in **2**. Instead, the chemistry of **1** appears to be dominated by the Lewis acidity of the aluminum center.

To further probe the electrophilicity of **1** relative to other common aluminum species, the catalytic oligomerization of ethene was carried out in comparative studies with chlorobenzene as solvent (see Table 1). Compound **1a** was more active than $EtAlCl_2$, and some products arising from the alkylation of the solvent were also observed. The activity of $AlCl_3$ was higher than that of **1a** with proportionately more alkylated chlorobenzene being formed. On this basis, it is possible to propose the following order of increasing electrophilicity: $Et_3Al < Et_2AlCl < EtAlCl_2 < Et_2Al(\text{carborane}) < AlCl_3$. Evidently, the electron-withdrawing effect of three chloride groups more than compensates for the lack of a positive charge on the metal. Given the observed noninvolvement of the ethyl groups on the aluminum and the activity of aluminum trichloride, it is likely that the branched oligoethenes arise from a carbocationic oligomerization/rearrangement pathway.[19]

Compound **1a** is an extremely efficient catalyst for the polymerization of cyclohexene oxide. Adding a solution containing 1 g of cyclohexene oxide in 5 mL of chlorobenzene to one containing 0.02 mmol of **1a** in 5 mL of chlorobenzene at room temperature resulted in an immediate exothermic reaction and the quantitative formation of the polymer ($M_w = 7600$; $M_w/M_n = 1.5$, relative to polystyrene standards).

As expected,**1** reacts with bases such as pyridine to form mono- and bis-adducts. The tetrahedrally coordinated cation, $[Et_2Al(\text{pyridine})_2]^+$, has been characterized by X-ray crystallography (see Supporting Information) and is inactive for ethene oligomerization or cyclohexene oxide polymerization.

In summary, carborane anions are sufficiently inert that they allow an exploration of the Lewis acidity of the $Et_2Al^{\delta+}$ moiety. Mechanistic studies should lead to insight into the challenging problem of finding effective non-transition-metal catalysts for alkene polymerization and understanding the factors that control alkene insertion into an aluminum alkyl bond.[2−4,20]

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Supporting Information Available: Synthetic procedures and X-ray crystallographic data (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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