Ligand Exchange and Alkyl Abstraction Involving (Perfluoroaryl)boranes and -alanes with Aluminum and Gallium Alkyls

Jerzy Klosin,*,† Gordon R. Roof, and Eugene Y.-X. Chen*,‡

Catalysis Laboratory, The Dow Chemical Company, Midland, Michigan 48674

Khalil A. Abboud

Department of Chemistry, University of Florida, Gainesville, Florida 32611

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Summary: Reaction between $M(C_6F_5)_3$ (M = B, Al) and AlR_3 in hydrocarbons leads to facile aryl/alkyl group exchange and formation of aluminum dimers, while reaction of (perfluoroaryl)boranes $B(C_6F_5)_3$ and $B(C_{12}F_9)_3$ with AlR_3 (R = Me, Et, octyl) or $GaMe_3$ in ether solvents produces alumocenium or gallocenium borates. Neutral aluminum dimers and cationic alumocenium species have been found to be very effective as catalyst activators in ethylene/1-octene copolymerization.

Group 13 based activators such as methylaluminoxane (MAO),[1] $B(C_6F_5)_3$,[2] $[Ph_3C]^+[B(C_6F_5)_4]^-$,[3] and $[HNRR'_2]^+[B(C_6F_5)_4]^-$ [4] are key components of homogeneous single-site olefin polymerization[5] catalyst systems. Aluminum alkyls, being less efficient activators themselves, are often used in a polymerization system as scavengers or in situ alkylating reagents.[6] Certain reactions occurring between AlR_3 and the abovementioned activators have been observed in many catalytic systems,[7−9] which raises a question regarding the true structure of the activator when more than one cocatalytic component is present. In this communication we report[10] ligand exchange and alkyl abstraction reactions involving (perfluoroaryl)boranes and -alanes with AlR_3[11] or GaR_3, as well as the use of the products of these reactions, neutral dimeric aluminum species and cationic alumocenium borates, as efficient activators for ethylene and 1-octene copolymerization catalyzed by $Me_2Si(\eta^5\text{-}Me_4C_5)(t\text{-}BuN)Ti(1,3\text{-pentadiene})$.[12]

Stirring equimolar amounts of $B(C_6F_5)_3$ and $AlMe_3$ in hydrocarbon solvents leads to facile aryl/alkyl group exchange, offering a convenient and efficient synthesis of $Al(C_6F_5)_3$.[7] However, monitoring this reaction by NMR in toluene-d_8 reveals stepwise CH_3/C_6F_5 ligand exchange to produce a solution mixture, containing $Al(C_6F_5)_3$, dimeric aluminum species $[Al(C_6F_5)_x(CH_3)_{3-x}]_2$ ($x = 1-2$), and borane species $B(C_6F_5)_x(CH_3)_{3-x}$ ($x = 0-2$) (Scheme 1).[9,13,14] This exchange reaction does not go to completion under the conditions of the NMR experiment to form $Al(C_6F_5)_3$ in a pure form for over a 24 h time period. In a preparative-scale reaction the equilibrium can be shifted toward $Al(C_6F_5)_3$ formation either by precipitation of the product with aliphatic solvents or by vacuum removal of BMe_3. Other AlR_3 species undergo similar ligand exchange reactions.

Scheme 1

$$B(C_6F_5)_3 + AlMe_3 \xrightarrow{\text{fast}} MeB(C_6F_5)_2 + 1/2\ (C_6F_5)_2Al_2Me_4 \rightleftharpoons$$

$$Me_2B(C_6F_5) + 1/2\ (C_6F_5)_4Al_2Me_2 \rightleftharpoons BMe_3 + Al(C_6F_5)_3$$

Use of a superstoichiometric amount of $AlMe_3$ accelerates the ligand exchange considerably, and the final

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† E-mail: klosin@dow.com.

‡ Current address: Department of Chemistry, Colorado State University, Fort Collins, CO 80523. E-mail: eychen@lamar.colostate.edu.

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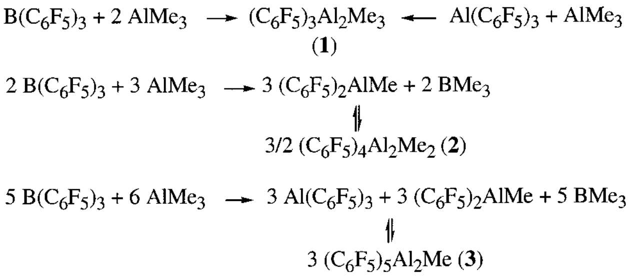
exchange products are the various dimeric aluminum species **1**−**3** (Scheme 2).[14]

Scheme 2



$$B(C_6F_5)_3 + 2\,AlMe_3 \longrightarrow \underset{(\mathbf{1})}{(C_6F_5)_3Al_2Me_3} \longleftarrow Al(C_6F_5)_3 + AlMe_3$$

$$2\,B(C_6F_5)_3 + 3\,AlMe_3 \longrightarrow 3\,(C_6F_5)_2AlMe + 2\,BMe_3 \rightleftharpoons 3/2\,(C_6F_5)_4Al_2Me_2\,(\mathbf{2})$$

$$5\,B(C_6F_5)_3 + 6\,AlMe_3 \longrightarrow 3\,Al(C_6F_5)_3 + 3\,(C_6F_5)_2AlMe + 5\,BMe_3 \rightleftharpoons 3\,(C_6F_5)_5Al_2Me\,(\mathbf{3})$$

Alternatively, these dimeric Al species can also be obtained by more rapid ligand exchange between $Al(C_6F_5)_3$ and an appropriate molar ratio of $AlMe_3$. The CH_3/C_6F_5 group scrambling in these dimeric species is fast on the NMR time scale. For instance, at ambient temperature dimer **1** exhibits only one broad signal ($\Delta\nu_{1/2} \approx 60$ Hz in toluene-d_8, $\Delta\nu_{1/2} > 167$ Hz in hexane) for *p*-F of the C_6F_5 group in the ^{19}F NMR spectrum, which then becomes sharp at 80 °C. Addition of an excess of Et_2O to the isolated $(C_6F_5)_3Al_2Me_3$ results in the formation of the two ether adducts $(C_6F_5)_2AlMe\cdot OEt_2$ and $(C_6F_5)AlMe_2\cdot OEt_2$,[9] plus a trace amount of $(C_6F_5)_3Al\cdot OEt_2$ and $AlMe_3\cdot OEt_2$. The molecular structure of **1** has been determined by single-crystal X-ray analysis,[15] and its thermal ellipsoid drawing is presented in Figure 1. The overall molecular structure of $(C_6F_5)_3Al_2(CH_3)_3$ features two methyl groups unsymmetrically bridging two aluminum centers with noticeably shorter Al−Me (bridge) distances for Al(2), the more highly Lewis acidic aluminum site.

Interestingly, the exchange chemistry described above is completely suppressed in coordinating solvents such as, for example, diethyl ether and THF. When $B(C_6F_5)_3$ is reacted with $AlMe_3$ in diethyl ether, a colorless oil is formed after solvent removal. Multinuclear NMR analyses indicated formation of a single product, the structure of which was identified as the alumocenium borate salt $[Me_2Al(OEt_2)_2]^+[MeB(C_6F_5)_3]^-$ (**4**) (Scheme 3).[16] The most notable spectroscopic evidence supporting this assignment comes from ^{19}F and $^{11}B\{^1H\}$ NMR data, which are the same as those reported in the literature for the $[MeB(C_6F_5)_3]^-$ anion.[2a,b,17] The noncoordinating nature of the $[MeB(C_6F_5)_3]^-$ anion in solution is established by the small chemical shift difference (2.7 ppm) between the *para* and *meta* fluorines in ^{19}F NMR.[18] Triethyl- and trioctylaluminum and trimethylgallium undergo analogous reactions with $B(C_6F_5)_3$ in diethyl ether, producing the corresponding borate salts **5**−**7**, respectively, as colorless oils (Scheme 3).

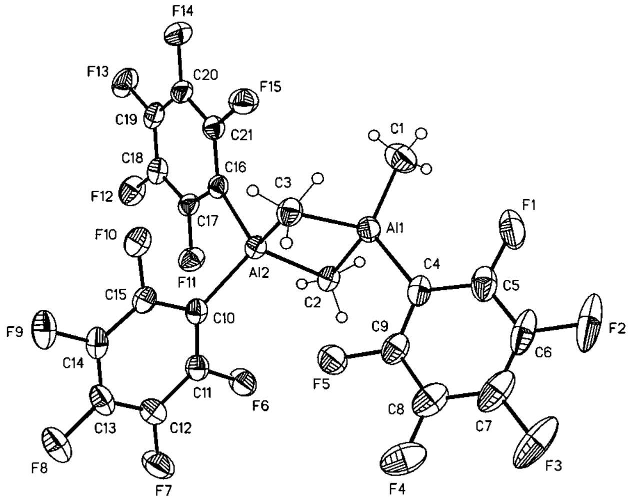
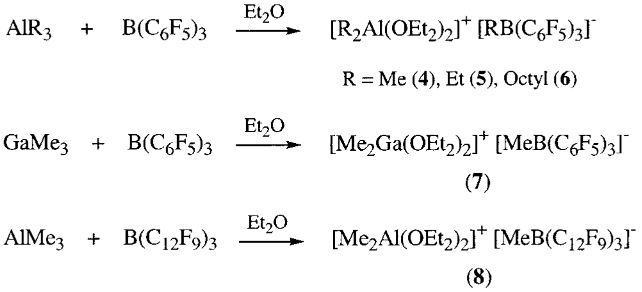


Figure 1. Thermal ellipsoid drawing of $(C_6F_5)_3Al_2(CH_3)_3$ (**1**) shown at the 40% probability level. Selected bond lengths (Å) and angles (deg): Al(1)−Al(2) = 2.5723(8); Al(1)−C(1) = 1.920(3); Al(1)−C(2) = 2.145(2); Al(1)−C(3) = 2.127(2); Al(2)−C(2) = 2.067(2); Al(2)−C(3) = 2.083(2); Al(1)−C(2)−Al(2) = 75.26(7); Al(1)−C(3)−Al(2) = 75.31(7).

Scheme 3



$$AlR_3 + B(C_6F_5)_3 \xrightarrow{Et_2O} [R_2Al(OEt_2)_2]^+ [RB(C_6F_5)_3]^-$$

R = Me (**4**), Et (**5**), Octyl (**6**)

$$GaMe_3 + B(C_6F_5)_3 \xrightarrow{Et_2O} \underset{(\mathbf{7})}{[Me_2Ga(OEt_2)_2]^+ [MeB(C_6F_5)_3]^-}$$

$$AlMe_3 + B(C_{12}F_9)_3 \xrightarrow{Et_2O} \underset{(\mathbf{8})}{[Me_2Al(OEt_2)_2]^+ [MeB(C_{12}F_9)_3]^-}$$

To gain insight into relative alkyl abstraction rates, $B(C_6F_5)_3$ was reacted with a mixture of 0.5 $AlMe_3$ and 0.5 $AlEt_3$ in ether. The ^{19}F NMR and LSIMS analysis showed formation of $[MeB(C_6F_5)_3]^-$ and $[EtB(C_6F_5)_3]^-$ in a 9:1 ratio, demonstrating a higher propensity of $B(C_6F_5)_3$ for methyl vs ethyl group abstraction. All the salts synthesized are soluble in THF and CH_2Cl_2, but only the octyl derivative **6** is completely soluble in aromatic solvents. Because of the very high reactivity of alumocenium and gallocenium borates, their mass spectra have proven difficult to obtain. We have found that tetraglyme can be used successfully for LSIMS

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[14] See the Supporting Information for synthetic details. *Caution! All of the neutral (perfluorophenyl)aluminum species described in this report have been found to be highly heat and shock sensitive.* **1**: ^1H NMR (toluene-d_8, 23 °C) δ 0.01 (s, br, AlCH_3); ^{19}F NMR (toluene-d_8, 23 °C) δ −160.73 (t, 6F, $^3J_{F-F}$ = 18.7 Hz, *m*-F), −151.38 (s br, 3F, *p*-F), −122.26 (d, 6F, $^3J_{F-F}$ = 27.3 Hz, *o*-F); $^{13}C\{^1H\}$ NMR (toluene-d_8, 23 °C) δ −7.25 (Al−Me), 135−152 (series of multiplets). **2**: ^1H NMR (toluene-d_8, 23 °C) δ −0.01 (s, br, AlCH_3); ^{19}F NMR (toluene-d_8, 23 °C) δ −160.67 (br, 8F, *m*-F), −150.84 (s, br, 4F, *p*-F), −122.29−123.04 (s, br, 8F, *o*-F). **3**: ^1H NMR (toluene-d_8, 23 °C) δ 0.15 (s, AlCH_3); ^{19}F NMR (toluene-d_8, 23 °C) δ −160.45 (s, br, 10F, *m*-F), −150.50 (s, br, 5F, *p*-F), −122.30 (s, br, 10F, *o*-F).

[15] Crystallographic data for **1**: $C_{21}H_9Al_2F_{19}$, M_w = 676.24, triclinic, space group $P\bar{1}$, a = 9.119(1) Å, b = 9.919(1) Å, c = 13.029(2) Å, α = 95.601(2)°, β = 98.379(2)°, γ = 101.148(2)°, V = 1134.3(3) Å^3, Z = 2, D_{calcd} = 1.980 Mg/m^3, absorption coefficient 0.297 mm^{-1}, $F(000)$ = 664, number of reflections collected 7881, number of independent reflections 5028, GOF = 1.038, R1 = 0.0356 ($I > 2\sigma(I)$), wR2 = 0.0733 (all data).

[16] Analytical data for **4**. ^1H NMR (CD_2Cl_2): δ −0.48 (s, 6H, $(CH_3)_2$-Al−), 0.51 (s, br, CH_3B−), 1.46 (t, 12H, $^3J_{H-H}$ = 7.1 Hz, $(CH_3CH_2)_2O$), 4.27 (q, 8H, $^3J_{H-H}$ = 7.1 Hz, $(CH_3CH_2)_2O$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ −11.4 (br, $(CH_3)_2$Al−), 10.5 (CH_3B−), 13.75 ($(CH_3CH_2)_2O$), 70.64 ($(CH_3CH_2)_2O$), 129.6 (br, ipso), 138.23 (dm, $^1J_{C-F}$ = 244 Hz), 137.94 (dm, $^1J_{C-F}$ = 242 Hz), 148.77 (dm, $^1J_{C-F}$ = 232 Hz). ^{19}F NMR (CD_2Cl_2): δ −167.78 (t, 6F, $^3J_{F-F}$ = 21.4 Hz, *m*-F), −165.10 (t, 3F, $^3J_{F-F}$ = 19.9 Hz, *p*-F), −133.15 (d, 6F, $^3J_{F-F}$ = 18.3 Hz, *o*-F). $^{11}B\{^1H\}$ NMR (C_6D_6): δ −14.9 Hz (s, br). $^{27}Al\{^1H\}$ NMR (CD_2Cl_2) δ 164.2 ($\Delta\nu_{1/2}$ = 2017 Hz). HRMS (LSIMS, negative mode): *m*/*z* calcd for $C_{19}H_3F_{15}B$, 527.0088 (100, M^-); found, 527.0146. HRMS (LSIMS, positive mode): *m*/*z* calcd for $C_{12}H_{28}O_5Al$, 279.1752 (32.6, $M^+ - 2\,Et_2O$ + tetraglyme); found, 279.1777.

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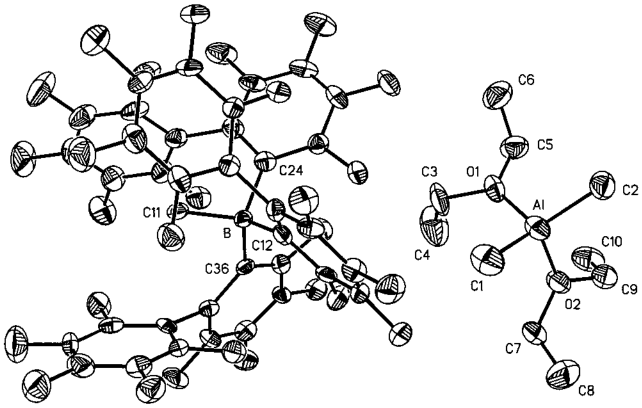

Figure 2. Thermal ellipsoid drawing of $[Me_2Al(OEt_2)_2]^+[MeB(C_{12}F_9)_3]^-$ (**8**) shown at the 40% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Al−B = 7.305(7); B−C(11) = 1.667(7); Al−C(1) = 1.933(6); Al−C(2) = 1.939(6); Al−O(1) = 1.904(5); Al−O(2) = 1.878(5); C(1)−Al−C(2) = 126.4(3); O(1)−Al−O(2) = 99.9(2).

measurements. In addition to being a good matrix, tetraglyme displaces both ether molecules coordinated to aluminum, giving rise to a very strong peak in the positive mode of LSIMS from the $[R_2Al(tetraglyme)]^+$ fragment. Tris(nonafluoro-1,1′-biphenyl-2-yl)borane[19] ($B(C_{12}F_9)_3$) also reacts with $AlMe_3$ in diethyl ether, producing $[Me_2Al(OEt_2)_2]^+[MeB(C_{12}F_9)_3]^-$ (**8**) as a crystalline white solid in 85% yield. The molecular structure of $[Me_2Al(OEt_2)_2]^+$ $[MeB(C_{12}F_9)_3]^-$ (**8**) is presented in Figure 2 along with selected bond lengths and angles.[20] The structure features a borate anion and a four-coordinate alumocenium cation with a distance between boron and aluminum atoms of 7.305 Å. The geometry around aluminum is that of a distorted tetrahedron with C(1)−Al−C(2) and O(1)−Al−O(2) bond angles of 99.9(2) and 126.4(3)°, respectively.

Unlike $B(C_6F_5)_3$, reaction of $Al(C_6F_5)_3$ with $AlMe_3$ (1:1 ratio) carried out in diethyl ether generates $[Me_2Al(OEt_2)_2]^+[MeAl(C_6F_5)_3]^-$ (**9**), but only in about 20% yield as seen by ^{19}F NMR.[21] This compound then decomposes within days via perfuoroaryl transfer to give a mixture of $(C_6F_5)AlMe_2{\cdot}OEt_2$ and $(C_6F_5)_2AlMe{\cdot}OEt_2$. The propensity of aluminum alkyls and halides to form cationic species when reacted with Lewis basic substrates is well-documented,[22] although these reactions usually require either polydentate bases or/and good leaving groups such as chloride anion to proceed to completion. This reactivity pattern can be illustrated, for example, by reaction of $AlCl_3$ with excess of THF, which yields $[AlCl_2(THF)_4]^+[AlCl_4]^-$.[22e,f] Recently, methyl group abstraction from Cp_2AlMe and trimethylaluminum adducts of silylphosphimines by $B(C_6F_5)_3$ has also been reported.[23] Diethyl ethers can be easily displaced from the aluminum coordination sphere with stronger bases. For example, reaction of gallium salt **7** with tetramethylethylenediamine (TMEDA) in diethyl ether gives $[Me_2Ga(TMEDA)]^+[MeB(C_6F_5)_3]^-$ (**10**) as the only product, the structure of which has been determined by single-crystal X-ray analysis.[24] The molecular structure of **10** shows well-separated ions, with a distance between gallium and boron atoms of 5.663 Å. Two fluorine atoms originating from two different borate molecules are directed toward the gallium cation, with Ga−F distances between 3.280(2) and 3.408(2) Å.[24]

The ability of the dimeric aluminum species and alumocenium borates to act as efficient activators for olefin polymerization has been demonstrated in ethylene−1-octene copolymerization studies using the constrained-geometry catalyst $Me_2Si(\eta^5\text{-}Me_4C_5)(t\text{-}BuN)Ti$-(1,3-pentadiene).[25] Compounds **1**−**3** give somewhat lower polymerization efficiencies as compared to a control run with $B(C_6F_5)_3$. They produce similar low-density copolymers having significantly higher molecular weights (70−100% higher) than those produced by $B(C_6F_5)_3$. Alumocenium borate salts are also very effective activators, producing ethylene−octene copolymers with efficiencies higher than those obtained with $B(C_6F_5)_3$. To our knowledge, this is the first time cationic aluminum species have been reported as effective activators for olefin polymerization.

In conclusion, these results demonstrate two distinctive pathways involving the reaction of (perfluoroaryl)boranes and -alanes with AlR_3 or GaR_3. While facile aryl/alkyl ligand exchange occurs in hydrocarbon solvents, leading to formation of dimeric aluminum species, abstraction of the alkyl group from AlR_3 or GaR_3 by (perfluoroaryl)boranes is observed in polar solvents, affording alumocenium or gallocenium borates. These neutral aluminum dimers as well as ionic alumocenium borate species exhibit interesting cocatalytic activities for olefin polymerization. Further reactivity studies of these species are in progress.

Supporting Information Available: Experimental procedures, polymerization results, stereoviews of thermal ellipsoid drawings, and tables of atomic positions, anisotropic thermal parameters for non-hydrogen atoms, and comprehensive bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Crystallographic data for **8**: $C_{47}H_{29}AlBF_{27}O_2$, two independent salt molecules in unit cell, M_w = 1176.49, monoclinic, space group $P2_1/n$, a = 25.908(1) Å, b = 15.6457(9) Å, c = 26.146(1) Å, β = 115.234(1)°, V = 9587(1) Å^3, Z = 8, D_{calcd} = 1.630 Mg/m^3, absorption coefficient 0.188 mm^{-1}, F(000) = 4704, number of reflections collected 40 981, number of independent reflections 12 525, GOF = 0.887, R1 = 0.0553 ($I > 2\sigma(I)$), wR2 = 0.1165 (all data).

(21) $[Me_2Al(OEt_2)_2]^+[MeAl(C_6F_5)_3]^-$ (**9**): ^1H NMR (toluene-d_8, 23 °C) δ 3.57 (s br, 8H, $(CH_2CH_3)_2O$), 0.66 (t, 12H, $^3J_{H-H}$ = 7.1 Hz, $(CH_2CH_3)_2O$), −0.52 (s, 6H, $(CH_3)_2Al$−), −0.95 (s, 3 H, $[(C_6F_5)_3AlMe]^-$); ^{19}F NMR (toluene-d_8, 23 °C) δ −164.15 (t, 6F, $^3J_{F-F}$ = 18.3 Hz, *m*-F), −158.89 (t, 3F, $^3J_{F-F}$ = 20.8 Hz, *p*-F), −121.59 (d, 6F, $^3J_{F-F}$ = 18.7 Hz, *o*-F).

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(24) See the Supporting Information for structural details of **10**.

(25) See the Supporting Information for polymerization results and procedures.