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Gas-Phase Positive-Ion Chemistry of Trimethylboron and Trimethylaluminum

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Me_2B^+ and Me_2Al^+ are the principal ions produced by electron impact on Me_3B and Me_3Al, respectively. Study of halide transfer to these species leads to determination of the halide affinities: $D(Me_2B^+–F^-)$ = 238.5 ± 3 kcal/mol, $D(Me_2B^+–Cl^-)$ = 192.5 ± 3 kcal/mol, $D(Me_2Al^+–F^-)$ = 228 ± 8 kcal/mol, and $D(Me_2Al^+–Cl^-)$ = 185 ± 5 kcal/mol. These show about 9 kcal/mol greater stability for Me_2Al^+ compared to Me_2B^+. Me_3B reacts by methyl anion transfer with CF_3^+ and CF_2Cl^+ but not with CCl_3^+, $C_3H_7^+$, or $CHCl_2^+$, establishing a value for the methyl anion affinity of Me_2B^+ of $D(Me_2B^+–CH_3^-)$ = 250 ± 15 kcal/mol. In a related reaction also involving carbon–carbon bond formation, $CHCl_2^+$ and $CFCl_2^+$ are alkylated by Me_3Al to $C_2H_4Cl^+$ and $C_2H_3FCl_+$, respectively. Other thermochemical determinations include the hydride affinity of $Me_2B{=}CH_2^+$: $D(Me_2BCH_2^+–H^-)$ = 260.5 ± 5 cal/mol. A variety of molecules (L) condense with Me_2B^+ to yield one-ligand complexes and with Me_2Al^+ to yield two-ligand complexes. The relative order of ligand binding energies for these molecules to both species is determined from the preferred direction of displacement reactions: for $Me_2B(L)^+$, $Me_2S < MeCN < C_6H_5OMe < Me_2O < C_6H_5CN <$ pyridine, and for $Me_2Al(L)_2^+$, $Me_3Al < Me_2S < C_6H_5OMe < Me_2O < MeCN < Et_2O \simeq (i\text{-}C_3H_7)_2O < C_6H_5CN < Me_3N <$ pyridine. The relative position of MeCN in these series indicates that Me_2Al^+ is a relatively softer acid than Me_2B^+ or Al^+.

Introduction

Alkylboron and alkylaluminum compounds behave as Lewis acids in that they readily form adducts with Lewis bases such as Me_3N. In some respects these molecules have quite different chemistries, however. For example, alkylboron compounds do not form dimeric species while alkylaluminum compounds do.[2] Furthermore, X_3Al compounds can form pentacoordinate adducts, $X_3Al(Y)_2$, while boron has not been observed to have coordination exceeding four.[2]

Much work has been done on the neutral chemistry of alkylboron and alkylaluminum compounds. Alkylaluminum compounds in particular have been the subject of intense study because of their important role in industrial Ziegler–Natta polymerization catalysts, an area which is still not well understood.[3]

Studies of the gas-phase ion chemistry of these molecules have been rather limited in spite of the potential of such studies for providing useful bond-energy data. Reported work in this field to data has dealt mainly with the ion chemistry of boron alkyls.[4] In one of these studies, some aspects, mainly negative ion chemistry, of the gas-phase ion chemistry of Me_3B were presented.[5]

This paper examines the gas-phase positive-ion chemistry of trimethylboron (Me_3B) and trimethylaluminum (Me_3Al). Variations in reactivity between analogous aluminum and boron-containing ionic species are observed and discussed. Several useful thermodynamic results are also obtained.

Experimental Section

This study was carried out by using an ion cyclotron resonance (ICR) spectrometer built at MIT. General features of the instrumentation and procedures used have been previously described.[6] Studies of Me_3Al chemistry were carried out using a three-section drift cell with marginal oscillator detection. The Me_3B experiments were performed by using a one-section trapped-ion cell with bridge circuit detection.[7] Pressures were measured by using a Bayard-Alpert ionization gauge. Because of variations in ionization cross section from one gas to another, absolute pressures and rate constants are only accurate to a factor of 2.

Me_3B and Me_3Al were obtained from Alfa Inorganics. Other chemicals used were reagent grade and were obtained from commercially available sources. All reactant gases were purified by repeated freeze–pump–thaw cycles.

Electron-beam energies used were normally less than 15 eV. Throughout the Me_3B study, boron-containing species were observed to have the correct natural isotope abundances: ^{10}B, 19.8%; ^{11}B, 80.2%. All reactions were confirmed by double-resonance experiments.

Results

Trimethylboron. Low-pressure ICR mass spectra of Me_3B at 70 eV agree well with published results.[5] Electron-impact ionization at this energy produces Me_3B^+, Me_2B^+, $C_2H_4B^+$, $C_2H_2B^+$, and CH_4B^+ in relative abundance of 2%, 69%, 13%, 5%, and 11%, respectively. The experiments reported in this paper were carried out at electron energies of 15 eV and below where only Me_2B^+ and Me_3B^+ are produced in significant amounts. Studies with only Me_3B^+ present confirm the previous observation,[5] that Me_3B^+ is unreactive toward the parent neutral. Me_2B^+ also does not react with Me_3B except for methyl anion transfer (reaction 1). Dimeric species such as Me_5B_2 or $Me_6B_2^+$ are not observed.

$$Me_2{}^{10}B^+ + Me_3{}^{11}B \rightleftarrows Me_2{}^{11}B^+ + Me_3{}^{10}B \qquad (1)$$

A number of alkyl halides, RX, react with Me_2B^+ by halide transfer. Chloride transfer (reaction 2) is observed

$$Me_2B^+ + RCl \rightarrow Me_2BCl + R^+ \qquad (2)$$

$$Me_2B^+ + RF \rightarrow Me_2BF + R^+ \qquad (3)$$

for CCl_4, $CHCl_3$, *n*-PrCl, *i*-PrCl, and EtCl, while fluoride transfer (reaction 3) occurs for CCl_3F, $CHFCl_2$, CCl_2F_2, and

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(2) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Wiley: New York, 1980.

(3) Boor, J., Jr. "Ziegler-Natta Catalysts and Polymerizations"; Academic Press: New York, 1979.

(4) See, for example: Pasto, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 136.

(5) Murphy, M. K.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 1433.

(6) Uppal, J. S.; Staley, R. H. *J. Am. Chem. Soc.* **1980**, *103*, 508–511.

(7) For a general discussion of ICR techniques see: Bursey, M. M. "Ion Cyclotron Resonance Spectrometry"; M. Wiley: New York, 1976.

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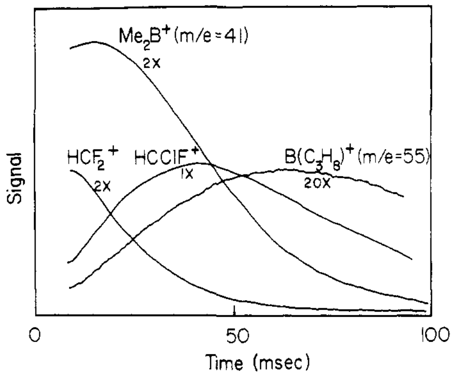

Figure 1. Variation of ion abundance with time following a 10-ms, 14-eV electron beam pulse in a 1:1 mixture of Me_3B and CHF_2Cl at 5×10^{-6} torr. The reactions occurring are quite complicated. In addition to being produced by electron impact on Me_3B, Me_2B^+ is formed by dissociative proton transfer from CHF_2^+ and $CHFCl^+$. $CHFCl^+$ results from fluoride transfer. Chloride transfer to produce CHF_2^+ is not observed. This ion is produced by electron impact on CHF_2Cl. $B(C_3H_8)^+$ is formed as a result of hydride transfer to CHF_2^+ and $CHFCl^+$. The *m/z* value for the isotopic peak which was followed for each species is indicated in parentheses.

CHF_2Cl. Dehydrochlorination is not observed with EtCl or any other chlorocarbon studied with Me_2B^+. CH_2Cl_2 and CF_3Cl do not react with Me_2B^+. Methyl anion transfer, from Me_3B to R^+ (reaction 4) is observed for R^+

$$R^+ + Me_3B \rightarrow MeR + Me_2B^+ \qquad (4)$$

$= CF_3^+$ and CF_2Cl^+. $CHCl_2^+$, CHF_2^+, $CHFCl^+$, and $C_2H_5^+$ also react with Me_3B to give Me_2B^+. These reactions could occur either by dissociative proton transfer (reaction 5) or

$$MH^+ + Me_3B \rightarrow Me_2B^+ + CH_4 + M \qquad (5)$$

methyl anion transfer. Me_3B does not react with CCl_3^+, $C_3H_7^+$, or $CHCl_2^+$. Hydride transfer from Me_3B to R^+ (reaction 6) occurs with $R^+ = CF_3^+$, CF_2Cl^+, CH_2Cl^+, CHF_2^+, $CHFCl^+$, $CHCl_2^+$, and $C_2H_5^+$. CCl_3^+ and $C_3H_7^+$

$$R^+ + Me_3B \rightarrow RH + (C_3H_8)B^+ \qquad (6)$$

do not undergo hydride transfers. Where both halide transfer and hydride transfer occur for a particular cation with Me_3B, hydride transfer is a relatively minor channel (typically ~10%). Figure 1 is an example of the type of data obtained in this study. Shown is a plot of ion abundance vs. time for all major ionic species that are observed in a mixture of Me_3B and CHF_2Cl. This time plot provides evidence, which is confirmed by double-resonance spectra, for the occurrence in this system of fluoride transfer (reaction 3), dissociative proton transfer (reaction 5), and hydride transfer (reaction 6).

The ligand molecules pyridine, C_6H_5CN, Me_2O, C_6H_5OMe, MeCN, and Me_2S condense once with Me_2B^+ to give $Me_2B(L)^+$ (reaction 7). A second condensation to

$$Me_2B^+ + L \rightarrow Me_2B(L)^+ \qquad (7)$$

form $Me_2B(L)_2^+$ is not observed. Mass spectra at short reaction times show no evidence for neutral–neutral reaction of Me_3B with any of the ligands studied.

Observation of ligand displacement (reaction 8), in mixtures of Me_3B with two different ligands L_1 and L_2, indicates that the binding energy of L_1 to Me_2B^+ is less than the binding energy of L_2. As a result, it is possible

$$Me_2B(L_1)^+ + L_2 \rightleftarrows Me_2B(L_2)^+ + L_1 \qquad (8)$$

to determine an order for ligand bond energies to Me_2B^+. The binding energies to Me_2B^+ of the ligands studied increase in the order $Me_2S < MeCN < C_6H_5OMe < Me_2O < C_6H_5CN <$ pyridine.

Trimethylamine, rather than condensing with Me_2B^+, reacts by proton transfer (reaction 9) and therefore could not be included on the ligand binding energy scale.

$$Me_2B^+ + Me_3N \rightarrow MeB{=}CH_2 + Me_3NH^+ \qquad (9)$$

Trimethylaluminum. The positive-ion ICR mass spectrum of Me_3Al, taken at low pressure ($<10^{-6}$ torr) and 70-eV electron energy, is in agreement with the previously reported conventional mass spectrum.[8] Ions observed are Me_3Al^+, Me_2Al^+, $MeAl^+$, and Al^+ in relative abundances of 8%, 65%, 6%, and 21%, respectively. At an electron energy of 17 eV, only Me_3Al^+ and Me_2Al^+ are observed in abundances of 11% and 89%, respectively. Me_2Al^+ condenses with Me_3Al to give $Me_5Al_2^+$ (reaction 10) with an

$$Me_2Al^+ + Me_3Al \rightarrow Me_5Al_2^+ \qquad (10)$$

apparent rate constant of 1.7×10^{-10} cm^3 $molecule^{-1}$ s^{-1} at a pressure of 6×10^{-6} torr. Me_3Al^+ also reacts with Me_3Al eliminating a radical to form Me_5Al_2 (reaction 11). $Me_5Al_2^+$ does not react with Me_3Al.

$$Me_2Al^+ + Me_3Al \rightarrow Me_5Al_2^+ + Me \qquad (11)$$

Me_2Al^+ dehydrochlorinates EtCl. Both possible product channels are observed: retention of C_2H_4 (reaction 12) and

$$Me_2Al^+ + EtCl \rightarrow Me_2Al(C_2H_4)^+ + HCl \qquad (12)$$
$$ \rightarrow Me_2Al(HCl)^+ + C_2H_4 \qquad (13)$$

retention of HCl (reaction 13). The branching ratio is 2:1 in favor of C_2H_4 retention. In a subsequent reaction step, EtCl displaces C_2H_4 or HCl to give $Me_2Al(EtCl)^+$ (reactions 14 and 15). Me_3Al displaces EtCl to yield $Me_5Al_2^+$ as the final product in this system (reaction 16).

$$Me_2Al(C_2H_4)^+ + EtCl \rightarrow Me_2Al(EtCl)^+ + C_2H_4 \qquad (14)$$

$$Me_2Al(HCl)^+ + EtCl \rightarrow Me_2Al(EtCl)^+ + HCl \qquad (15)$$

$$Me_2Al(EtCl)^+ + Me_3Al \rightarrow Me_5Al_2^+ + EtCl \qquad (16)$$

Dehydrochlorination is not observed with n-C_3H_7Cl or i-C_3H_7Cl. Instead, Me_2Al^+ reacts by chloride transfer to produce $C_3H_7^+$ (reaction 22; see below). $C_3H_7^+$ reacts with Me_3Al by dissociative proton transfer to regenerate Me_2Al^+ (reaction 17; Scheme I) and complete a two-step reaction sequence that converts Me_3Al and C_3H_7Cl to Me_2AlCl, CH_4, and C_3H_6. The same net conversion is also observed to occur by another route. $Me_5Al_2^+$ reacts with C_3H_7Cl (either n-propyl chloride or isopropyl chloride) to give $Me_4Al_2Cl^+$ (reaction 18). This species regenerates $Me_5Al_2^+$ upon reaction with Me_3Al (reaction 19). Some $Me_3Al_2Cl_2^+$ is also formed in these systems (reaction 20); this also reacts with Me_3Al to regenerate $Me_4Al_2Cl^+$ (reaction 21) and complete the same net reaction.

Scheme I

$$Me_3Al + C_3H_7^+ \rightarrow Me_2Al^+ + CH_4 + C_3H_6 \qquad (17)$$

$$Me_5Al_2^+ + C_3H_7Cl \rightarrow Me_4Al_2Cl^+ + CH_4 + C_3H_6 \qquad (18)$$

$$Me_4Al_2Cl + Me_3Al \rightarrow Me_5Al_2^+ + Me_2AlCl \qquad (19)$$

$$Me_4Al_2Cl^+ + C_3H_7Cl \rightarrow Me_3Al_2Cl_2^+ + CH_4 + C_3H_6 \qquad (20)$$

$$Me_3Al_2Cl_2^+ + Me_3Al \rightarrow Me_4Al_2Cl^+ + Me_2AlCl \qquad (21)$$

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(8) Tanaka, J.; Smith, S. R. *Inorg. Chem.* **1969**, *8*, 265.

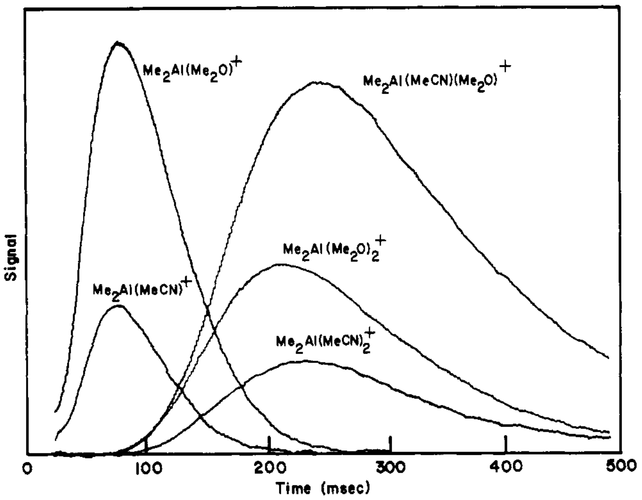

Figure 2. Variation of ion abundance with time in a 5:1:3 mixture of Me_2O, MeCN, and Me_3Al at a total pressure of 9.6×10^{-6} torr following a 10-ms, 14-eV electron energy pulse. Diffusional ion loss from the ICR cell results in a decrease in *total* ion abundance with time in this figure. Following initial formation reactions, the ionic abundances of $Me_2Al(MeCN)(Me_2O)^+$, $Me_2Al(Me_2O)_2^+$, and $Me_2Al(MeCN)_2^+$ approach equilibrium. For the overall reaction (reaction 31; $L_1 = Me_2O$, $L_2 = MeCN$) the equilibrium constant is $K = 13.9$ corresponding to $\Delta G = -1.56$ kcal/mol.

Me_2Al^+ reacts with a number of alkyl halides by halide transfer. Chloride transfer (reaction 22) is seen for 1,2-dichloroethane, $CHCl_3$, CCl_4, $n\text{-}C_3H_7Cl$, and $i\text{-}C_3H_7Cl$. Fluoride transfer (reaction 23) occurs with $CFCl_3$, CF_2Cl_2, and $CHFCl_2$.

$$Me_2Al^+ + RCl \rightarrow Me_2AlCl + R^+ \qquad (22)$$

$$Me_2Al^+ + RF \rightarrow Me_2AlF + R^+ \qquad (23)$$

$CHCl_2^+$ and $CFCl_2^+$ react with Me_3Al to form $C_2H_4Cl^+$ and $C_2H_3FCl^+$, respectively (reactions 24 and 25). CCl_3^+ is not alkylated by Me_3Al. CH_3F, CH_3Cl, C_6H_5Cl, CH_2Cl_2, CHF_2Cl, and CF_3Cl are unreactive toward Me_2Al^+.

$$CHCl_2^+ + Me_3Al \rightarrow C_2H_4Cl^+ + Me_2AlCl \qquad (24)$$

$$CFCl_2^+ + Me_3Al \rightarrow C_2H_3FCl^+ + Me_2AlCl \qquad (25)$$

The molecules Me_2O, Et_2O, $(i\text{-}C_3H_7)_2O$, C_6H_5OMe, Me_2S, MeCN, C_6H_5CN, Me_3N, and pyridine each condense twice with Me_2Al^+ to form the two-ligand complex $Me_2Al(L)_2^+$ (reactions 26 and 27). Each of these ligand molecules displaces Me_3Al from $Me_5Al_2^+$ (reaction 28). If Me_2Al^+ is generated in the presence of two ligands, L_1 and L_2, three different two-ligand complexes of Me_2Al^+ are formed. Ligand displacement reactions are observed in these systems (reactions 29 and 30). In a few of these systems, ligand displacement is reversible and equilibrium is approached. Figure 2 shows an example of such a system ($L_1 = Me_2O$, $L_2 = MeCN$). The equilibrium constant for the overall reaction 31 is measured to be 13.9 corresponding to a free energy different of 1.56 kcal/mol ($T = 298$ K). Equilibrium constants can also be determined separately for reactions 29 and 30 with these ligands: $K_{29} = 14.1$ and $K_{30} = 0.97$. The forward rate constant for ligand displacement obtained by a pulsed double-resonance experiment for reaction 29 is $k = 5.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} in this system.

$$Me_2Al^+ + L \rightarrow Me_2Al(L)^+ \qquad (26)$$

$$Me_2Al(L)^+ + L \rightarrow Me_2Al(L)_2^+ \qquad (27)$$

$$Me_5Al_2^+ + L \rightarrow Me_2Al(L)^+ + Me_3Al \qquad (28)$$

$$Me_2Al(L_1)_2^+ + L_2 \rightleftarrows Me_2Al(L_1)(L_2)^+ + L_1 \qquad (29)$$

$$Me_2Al(L_1)(L_2)^+ + L_2 \rightleftarrows Me_2Al(L_2)_2^+ + L_1 \qquad (30)$$

$$Me_2Al(L_1)_2^+ + 2L_2 \rightleftarrows Me_2Al(L_2)_2^+ + 2L_1 \qquad (31)$$

Other ligand exchange equilibria were not observed in this study. The preferred direction of reaction 29 and 30 could be measured, however, and consequently ligands could be ordered by their ability to displace other ligands from Me_2Al^+. The binding energies (to Me_2Al^+) of the ligands studied increase in the order $Me_3Al < Me_2S < C_6H_5OMe < Me_2O < MeCN < Et_2O \approx (i\text{-}C_3H_7)_2O < C_6H_5CN < Me_3N <$ pyridine.

Even at the low pressures used ($\sim 5 \times 10^{-6}$ torr), certain compounds were found to undergo neutral–neutral reactions with Me_3Al to a sufficient extent to hinder studying their ion chemistry. In particular, $TiCl_4$, MeOH, MeCHO, and Me_2CO reacted to a large extent, and mixtures of these compounds with Me_3Al could not be studied. Other alcohols, ketones, aldehydes, and esters were not studied because neutral–neutral reactions were expected as a result of these observations.

Neutral–neutral reactions are also a slight problem in mixtures of Me_3Al with Me_3N or pyridine (py); nuetral complexes such as $Me_3Al(Me_3N)$ and $Me_3Al(py)$ are formed in these mixtures. Ions such as $Me_5Al_2(Me_3N)_2^+$ and $Me_5Al_2(py)_2^+$ are observed.

In mixtures of Me_3Al with Et_2O, small amounts of $MeAlOEt^+$, $Me_4Al_2OEt^+$, and $Me_2Al(EtOH)^+$ are observed. The total abundance of these ions is about 10% of the total abundance of the condensation products. Similar ions are also observed in the $Me_3Al/i\text{-}Pr_2O$ mixture.

Discussion

Halide Transfers. Both Me_2B^+ and Me_2Al^+ react with alkyl halides by halide transfer (reactions 2, 3, 22, and 23). This reaction occurs only if the halide affinity of Me_2B^+ or Me_2Al^+ is greater than that of the product carbonium ion. Nonoccurrence of halide transfer indicates an endothermic reaction.[9] Chloride transfer to Me_2B^+ is observed to produce $C_2H_5^+$ (190), $CHCl_2^+$ (180), $i\text{-}C_3H_7^+$ (169), and CCl_3^+ (165). Chloride transfer with the appropriate neutral does not occur to generate CF_3^+ (207), CHF_2^+ (201), or CH_2Cl^+ (195). Chloride affinities, $D(R^+\text{–}Cl^-)$, for each R^+ are given in parentheses from Table I. These results place the chloride affinity of Me_2B^+ between that of $C_2H_5^+$ and CH_2Cl^+: $D(Me_2B^+\text{–}Cl^-) = 192.5 \pm 3$ kcal/mol. Fluoride transfer from RF to Me_2B^+ produces CCl_3^+ (208), $CFCl_2^+$ (214), $CHCl_2^+$ (220), and $CHFCl^+$ (236). Me_2B^+ does not react with CF_3Cl to give CF_2Cl^+ (241). Fluoride affinities from Table I are given in parentheses. The above results place the fluoride affinity of Me_2B^+ at $D(Me_2B^+\text{–}F^-) = 238.5 \pm 3$ kcal/mol.

Me_2Al^+ reacts by chloride transfer to produce $CHCl_2^+$ (180), $i\text{-}C_3H_7^+$ (169), $CFCl_2^+$ (168), and CCl_3^+ (165). Chloride transfer to Me_2Al^+ is not observed for $R^+ = Me^+$ (228), CHF_2^+ (201), CH_2Cl^+ (195), CF_2Cl^+ (192), $CHFCl^+$ (191), or $C_2H_5^+$ (190). These observations place the chloride affinity of Me_2Al^+ between that of $CHCl_3^+$ and Et^+: $D(Me_2Al^+\text{–}Cl^-) = 185 \pm 5$ kcal/mol. Chloride transfer

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[9] Halide transfer is a kinetically facile process if thermodynamically allowed, and therefore nonoccurrence is assumed to indicate a thermodynamic barrier. This was confirmed for a number of these systems in which endothermic double resonance spectra were obtained when R^+ was observed while Me_2B^+ was excited. No competing reactions occur with these reactants in these systems.

Table I. Heterolytic Bond Dissociation Energies for Relevant Ions[a]

R^+	$\Delta H_f(R^+)$	$D(R^+-Cl^-)$[h,i]	$D(R^+-F^-)$[i,k]	$D(R^+-Me^-)$[l]	$D(R^+-H^-)$[n]
CH_3^+	264[b]	228[j]	260[j]	277	315
CH_2F^+	199.5 ± 6[c]	206	248[j]	255[m]	290
CHF_2^+	142 ± 5[c]	201	250[j]	254	283
CF_3^+	93.8 ± 2[c]	207	257	265	293
CH_2Cl^+	228.5 ± 0.4[e]	195	233	247	281
$CHCl_2^+$	211.2 ± 0.4[e,g]	180	220	235	265
CCl_3^+	198 ± 7[c]	165	208		256
$CHFCl^+$	179 ± 5[c]	191	236		275
$CFCl_2^+$	155 ± 5[c]	168	214		256
CF_2Cl^+	130 ± 2[f]	192	241		278
$C_2H_5^+$	219[b]	190	222[j]	237	272[o]
i-$C_3H_7^+$	191[b]	169	202	216	249[o]
n-$C_3H_7^+$	207[b]	182			

[a] All data in kcal/mol for the gas phase at 298 K. [b] Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, T. J. *J. Phys. Chem. Ref. Data* **1977**, *6*, Suppl. 1. [c] Lias, S. G.; Ausloos, P. *Int. J. Mass Spectrom. Ion Phys.* **1977**, *23*, 273. [d] Johnstone, R. A. W.; Mellon, F. A. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1209. [e] Werner, A. S.; Tsai, B. P.; Baer, T. *J. Chem. Phys.* **1974**, *60*, 3650. [f] Ajello, J. M.; Huntress, W. T.; Rayerman, P. *Ibid.* **1976**, *64*, 4746. [g] Lossing, F. P. *Bull. Soc. Chim. Belg.* **1972**, *81*, 125. [h] $\Delta H_f(Cl^-) = -55.9$ kcal/mol from: Stull, D. R.; Prophet, H. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* **1971**, *NSRDS–NBS 37*. [i] $\Delta H_f(RX)$ except as noted from: Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. [j] $\Delta H_f(RX)$ from: Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley-Interscience: New York, 1976. [k] $\Delta H_f(F^-) = -58.5$ kcal/mol.[b] [l] $\Delta H_f(CH_3^-) = -7.2$ kcal/mol from $\Delta H_f(CH_3) = 34.3$ kcal/mol[j] and EA(CH_3) = 1.8 eV.[b] $\Delta H_f(RMe)$ from footnote *i*, except where noted. [m] $\Delta H_f(RMe)$ estimated in footnote *c*. [n] $\Delta H_f(H^-) = 33.2 \pm 0.5$ kcal/mol.[h] $\Delta H(RH)$ from footnote *c*, except as noted. [o] $\Delta H_f(RH)$ from footnote *j*.

was also observed to generate n-$C_3H_7^+$ (182) and $C_2H_4Cl^+$ (179).[10] The n-$C_3H_7^+$ result appears to set a lower limit on $D(Me_2Al^+-Cl^-)$; it is likely that n-$C_3H_7^+$ rearranges to i-$C_3H_7^+$ during the reaction, however.[11] Consequently, this result is not used to further define the chloride affinity of Me_2Al^+. While the result for 1,2-dichloroethane is consistent with other data, it also has not been included due to uncertainty about the structure and thermochemistry of $C_2H_4Cl^+$.

The fluoride affinity of Me_2Al^+ can be inferred from fluoride transfer results. Fluoride transfer produces $CHCl_2^+$ (220), $CFCl_2^+$ (214), and CCl_3^+ (208) but not Me^+ (260), CF_2Cl^+ (241), or $CHFCl^+$ (236). Therefore, one obtains $D(Me_2Al^+-F^-) = 228 \pm 8$ kcal/mol.

Dehydrochlorination. A common reaction between metal cations and alkyl halides (HYX) is dehydrohalogenation.[12,13] Typically one or both of the possible reaction channels (HX or Y elimination) are observed. In mixtures of Me_3B with n-C_3H_7Cl, i-C_3H_7Cl, or C_2H_5Cl, Me_2B^+ was not observed to react by dehydrohalogenation. Me_2Al^+, on the other hand, readily dehydrochlorinates EtCl to give $Me_2Al(HCl)^+$ and $Me_2Al(C_2H_4)^+$ (reactions 12 and 13). This result implies that the bond energies of Me_2Al^+ to C_2H_4 and to HCl are greater than the energy required to convert EtCl into HCl and C_2H_4: $D(Me_2Al^+-HCl)$ and $D(Me_2Al^+-C_2H_4) > 17.1$ kcal/mol.[14]

The displacement of HCl or C_2H_4 by EtCl in $Me_2Al(HCl)^+$ and $Me_2Al(C_2H_4)^+$, followed by displacement of EtCl by Me_3Al, implies that $D(Me_2Al^+-Me_3Al) > D(Me_2Al^+-EtCl)$, $D(Me_2Al^+-HCl)$.

Hydride Transfer. H^- transfer from Me_3B to R^+ is observed for $R^+ = CF_3^+$ (293), CHF_2^+ (283), CH_2Cl^+ (281), CF_2Cl^+ (278), $CHFCl^+$ (275), $C_2H_5^+$ (272), and $CHCl_2^+$ (265). No reaction was seen for $CFCl_2^+$ (256), CCl_3^+ (256), and i-$C_3H_7^+$ (249). Given in parentheses are the heterolytic $D(R^+-H^-)$ bond dissociation energies from Table I. The above results place the hydride affinity of $Me_2BCH_2^+$ between that of CCl_2F^+ and CCl_2H^+: $D(Me_2BCH_2^+-H^-) = 260.5 \pm 5$ kcal/mol. Hydride transfer was not observed in the reactions of Me_3Al with R^+.

Alkylation Reactions. Me_3B can react with R^+ by transferring a methyl anion (reaction 4). The reaction is seen to occur for $R^+ = CF_3^+$ and CF_2Cl^+. No reaction to produce Me_2B^+ is seen with $R^+ = CCl_3^+$, i-Pr^+, or $CHCl_2^+$. These results together with known values for $D(R^+-CH_3^-)$, Table I, set limits on $D(Me_2B^+-CH_3^-)$. Reaction with CF_3^+ sets an upper limit of 265 kcal/mol. Nonreaction with $CHCl_2^+$ sets a lower limit of 235 kcal/mol. Reactions of $CHCl_2^+$, CHF_2^+, and $C_2H_5^+$ with Me_3B to give Me_2B^+ and of $C_3H_7^+$ with Me_3Al to give Me_2Al^+ may proceed by methyl anion transfer or by dissociative proton transfer (reaction 17). Since their interpretion is ambiguous, these results are not used to infer relative methyl anion affinities. No case of simple methyl anion transfer is observed with Me_3Al. Reactions 24 and 25, in which Cl is exchanged for methyl to give Me_2AlCl, may well proceed via initial methyl anion transfer giving an intermediate Me_2Al^+-halocarbon complex in which chloride transfer to give Me_2AlCl precedes dissociation.

Ligand-Exchange Reactions. Me_2B^+ and Me_2Al^+ react with various ligand molecules to form one- and two-ligand complexes, respectively. Quantitative determination of relative ligand binding energies, as have been obtained for various metal cations from ligand-exchange equilibria,[15-17] is generally not possible in these systesm. In only one case is a ligand-exchange equilibrium successfully measured. For $L_1 = Me_2O$ and $L_2 = MeCN$ the equilibrium constant of reaction 31 is measured as 14 corresponding to a free energy difference between

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(10) $\Delta H_f(CH_2ClCH_2Cl) = -30.7$ kcal/mol: Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. $\Delta H_f(C_2H_4Cl^+) = 204$ kcal/mol from: Hodges, R. V.; Armentrout, P.; Beauchamp, J. L. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *29*, 375.

(11) This rearrangement also appears to occur in the reactions of Al^+ with n-C_3H_7Cl and the butyl chlorides.[12]

(12) Uppal, J. S.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1229–34.

(13) See, for example: Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3794.

(14) Calculated by using heats of formation from: Benson, S. W. "Thermochemical Kinetics"; 2nd ed.; Wiley: New York, 1976.

(15) Uppal, J. S.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1235–38, 1238–43.

(16) Jones, R. W.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 2296–2300. Jones, R. W.; Staley, R. H. *J. Phys. Chem.* **1982**, *86*, 1387–92.

(17) Kappes, M. M.; Staley, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 1813–19, 1819–23.

Table II. Summary of Thermochemical Results[a]

X^-	$D(Me_2B^+-X^-)$	$D(Me_2Al^+-X^-)$
CH_3^-	250 ± 15	
F^-	238.5 ± 3	228 ± 8
Cl^-	192.5 ± 3	185 ± 5

[a] All data in kcal/mol for the gas phase at 298 K.

$Me_2Al(Me_2O)_2^+$ and $Me_2Al(MeCN)_2^+$ of 1.6 kcal/mol. Ordering of ligands by their binding energies is possible, however. The $Me_2B(L)^+$ ligand-binding energies increase in the order Me_2S < MeCN < C_6H_5OMe < Me_2O < C_6H_5CN < pyridine. For Me_2Al^+ the order is Me_3Al < Me_2S < C_6H_5OMe < Me_2O < MeCN < $Et_2O \approx i\text{-}Pr_2O$ < C_6H_5CN, Me_3N < pyridine.

Comparison of Me_2B^+ and Me_2Al^+ Results. A comparison of the Me_2B^+ ligand order to that obtained for Me_2Al^+ shows one reversal: MeCN binds more strongly to Me_2Al^+ than Me_2O and C_6H_5OMe, whereas with Me_2B^+, MeCN is a weaker ligand than these ethers. It is interesting to compare both scales to the measured ligand binding energies for one-ligand complexes of Al^+, $D(Al^+-L)$.[15] For Al^+ the binding energy order for some relevant ligands is Me_2S < MeCN < Me_2O < C_6H_5CN < Et_2O. Thus, Al^+ behaves like Me_2B^+ in that it binds MeCN less strongly than Me_2O. MeCN and other nitriles have been useful and consistent indicators of relative acid softness (in the terminology of hard–soft acid–base theory) in ligand binding energy studies of complexes of Cu^+, Co^+, Ni^+, and $FeBr^+$.[16,17] Thus Me_2Al^+ in binding MeCN relatively more strongly than Me_2B^+ and Al^+ is seen to be a relatively softer acid.

In summary, this study has revealed a number of thermodynamic, structural, and mechanistic similarities and differences between the chemistry of Me_3B and Me_3Al. Fluoride and chloride affinities show about 9 kcal/mol greater stability for Me_2Al^+ compared to Me_2B^+, Table II. Formation of two-ligand complexes with Me_2Al^+ is facile, whereas with Me_2B^+ only one-ligand complexes form. Dehydrochlorination of alkyl chlorides by Me_2Al^+ but not Me_2B^+ may be related since this reaction proceeds through an intermediate in which two ligands, HCl and an alkene, are both bound to Me_2Al^+. Ligand displacement results suggest that Me_2Al^+ is a softer acid than Me_2B^+. Proton transfer from Me_2B^+ giving $MeB{=}CH_2$ and hydride abstraction from Me_3B to give $Me_2B{=}CH_2$ are observed, but the corresponding reactions with Me_2Al^+ and Me_3Al are not. This is consistent with the expectation that boron should more readily form double bonds with carbon than will aluminum.

Registry No. Me_3B, 593-90-8; Me_3Al, 75-24-1; Me_2B^+, 59414-81-2; CCl_4, 56-23-5; $CHCl_3$, 67-66-3; *n*-PrCl, 540-54-5; *i*-PrCl, 75-29-6; EtCl, 75-00-3; CCl_3F, 75-69-4; CCl_2F_2, 75-71-8; CHF_2Cl, 75-45-6; CF_3^+, 18851-76-8; CF_2Cl^+, 40640-71-9; $CHCl_2^+$, 56932-33-3; CHF_2^+, 35398-31-3; $CHFCl^+$, 40640-66-2; $C_2H_5^+$, 14936-94-8; C_6H_5CN, 100-47-0; Me_2O, 115-10-6; C_6H_5OMe, 100-66-3; MeCN, 75-05-8; Me_2S, 75-18-3; C_5H_5N, 110-86-1; Me_3N, 75-50-3; Me_2Al^+, 82614-01-5; Me_3Al^+, 82614-02-6; $C_3H_7^+$, 19252-53-0; $Me_5Al_2^+$, 82614-03-7; $Me_3Al_2Cl_2^+$, 82614-04-8; $C_2H_4Cl_2$, 107-06-2; $CFCl_2^+$, 40640-70-8; $(i\text{-}Pr)_2O$, 108-20-3; Et_2O, 60-29-7; $TiCl_4$, 7550-45-0; MeOH, 67-56-1; MeCHO, 75-07-0; Me_2CO, 67-64-1; $CHFCl_2$, 75-43-4; CH_2Cl^+, 59000-00-9.

Crystal and Molecular Structure of Tetra-*o*-tolylbis(*μ*-*o*-tolyl)dialuminum and Tri-*o*-tolylaluminum Diethyl Etherate

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The crystal and molecular structures of tetra-*o*-tolylbis(*μ*-*o*-tolyl)dialuminum (I) and of tri-*o*-tolylaluminum diethyl etherate (II) have been determined by single-crystal X-ray diffraction techniques. I crystallizes in the monoclinic space group $P2_1/c$ with two molecules per unit cell. The cell dimensions are a = 10.319 (3) Å, b = 10.201 (5) Å, c = 16.544 (5) Å, and β = 105.84 (3)°. Full-matrix least-squares refinement for I gave final discrepancy factors of $R_F = 0.038$ and $R_{wF} = 0.052$ for 1634 counter data for which $I \geq 2.5\sigma(I)$. II also crystallizes in the monoclinic system but was solved in the nonconventional space group $P2_1/n$ to bring β closer to 90°. The cell contains four molecules and has dimensions a = 11.648 (2) Å, b = 14.033 (2) Å, c = 14.209 (2) Å, and β = 106.48 (1)°. Full-matrix least-squares refinement for II gave final discrepancy factors of $R_F = 0.052$ and $R_{wF} = 0.064$ for 2487 counter data for which $I \geq 2.5\sigma(I)$. The structure of I consists of discrete bridged dimeric molecules similar in form to the structures of Al_2Ph_6, $Al_2(c\text{-}C_3H_5)_6$, and Al_2Me_6 with the only unusual feature being the increase in the Al–Al distance from ~2.6 Å commonly observed in bridged dimers to 2.817 (2) Å. The structure of II is similar to other trialkylaluminum adducts with the aluminum bound to three carbon atoms, one from each tolyl ring, and the ether oxygen atom providing a pseudotetrahedral environment for the aluminum atom.

Introduction

The structures of organoaluminum derivatives have been of interest to chemists for many years as a result of their formation of electron-deficient, three-center bridge bonds.[1,2] Our interest in this area has been renewed as a result of the observation that organic groups which contain electron-rich regions tend to form more stable bridged bonds through interaction of these regions and the nonbonding orbitals centered on the metal atoms in a symmetrical fashion. This type of interaction has been invoked to account for the more stable bridge bonds observed in vinyl-,[3] phenyl-,[4] and cyclopropylaluminum[5]

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