J. Am. Chem. Soc. **1998,** *120,* 8277−8278

Cationic Aluminum Alkyl Complexes Incorporating Aminotroponiminate Ligands

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Received May 19, 1998

Three-coordinate cationic aluminum alkyls $(L-X)AlR^+$ that are stabilized by appropriate monoanionic bidentate $L-X^-$ ligands are attractive candidates for catalytic applications because the combination of the electrophilic Al center and reactive Al−R bond should promote insertion chemistry.[1] We recently reported that the neutral amidinate complex $\{MeC(N^iPr)_2\}AlMe_2$ (**1**) reacts with 0.5 equiv of $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ to afford dinuclear cation **2**, in which the $\{MeC(N^iPr)_2\}AlMe^+$ cation is stabilized by coordination of **1** (Scheme 1).[1a] Base-stabilized 4-coordinate $\{MeC(N^iPr)_2\}Al(Me)L^+$ species (**3**, L = NMe_2Ph or PMe_3) have also been prepared. However, to date, base-free $(L-X)AlR^+$ cations have not been obtained with amidinate ligands, in part because of the high steric unsaturation resulting from the four-membered chelate structure (N−Al−N angle = ca. 69°).[2] We have investigated two strategies to favor the formation of base-free cations: (i) the use of $L-X^-$ ligands that form larger chelate rings (and hence have larger bite angles than amidinates) to increase the steric crowding around Al and (ii) the use of higher alkyls (R > methyl) to disfavor alkyl bridging. Here we describe the application of these strategies to the synthesis of new aluminum alkyls based on the (*N*,*N*-diisopropylamino)troponiminate $\{(^iPr)_2ATI)\}^-$ ligand.

Neutral $\{(^iPr)_2ATI\}AlR_2$ compounds (**4a**, R = Me; **4b**, R = H; Scheme 2) have been prepared by Dias and adopt five-membered chelate structures (N−Al−N angles = ca. 84°).[3] The reaction of **4a**,**b** with 0.5 equiv of $[Ph_3C][B(C_6F_5)_4]$[4] at 23 °C in C_6D_6 results in the quantitative formation of dinuclear cationic aluminum complexes **5a**,**b**.[5] Compounds **5a**,**b** phase separate from benzene as liquid clathrates, i.e., oils containing **5a**,**b** and solvent,[6] and have been isolated (**5a**, pale green powder; **5b**, yellow powder) by washing the liquid clathrates with hexane. At −90 °C, the ^1H NMR spectrum of **5a** (CD_2Cl_2) contains two singlets at δ 0.63 and −0.38 in a 1:2 intensity ratio, which are assigned to the bridging and terminal methyl groups, respectively. These signals coalesce to a broad singlet (δ 0.00) at −60 °C, indicating that bridge/terminal exchange is rapid at this temperature. The ^1H NMR spectrum of a C_6D_5Cl solution of **5a** containing 2 equiv of **4a** contains a single set of resonances at the average chemical shifts of the two components down to −40 °C, implying that intermolecular exchange between **5a** and **4a** is rapid. Thus **5a** is clearly more labile than **2**, for which exchange with free **1** is slow on the NMR time scale at 23 °C.[1a] The −90 °C ^{13}C NMR spectrum of **5a** contains separate resonances for the bridging (δ −0.8) and terminal (δ −5.2) methyl carbons. The μ-Me $^1J_{C-H}$ value (133 Hz) is consistent with a large Al−C−Al angle, trigonal bipyramidal (*tbp*) geometry at C, and substantial sp^2-C character in the C−H bonds.[7] The terminal Me $^1J_{C-H}$ value (118 Hz) is normal. Crystals of **5a** suitable for X-ray crystallographic analysis were obtained by slow (months) crystallization from a C_6D_6 liquid clathrate in an NMR tube. Compound **5a** crystallizes as discrete ions.[8] Consistent with the NMR data, the cation contains two $\{(^iPr)_2ATI\}AlMe$ units linked by a nearly linear Al−Me−Al bridge (Al(1)−C(1)−Al(2) angle = 167.8(2)°; Figure 1). The μ-CH_3 hydrogens were located in the equatorial plane of the nearly *tbp* carbon center (sum of H−C(1)−H angles = 357°). As a result of the 3c−2e Al−Me−

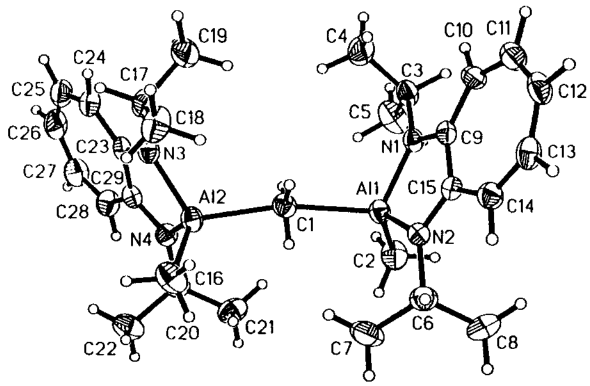
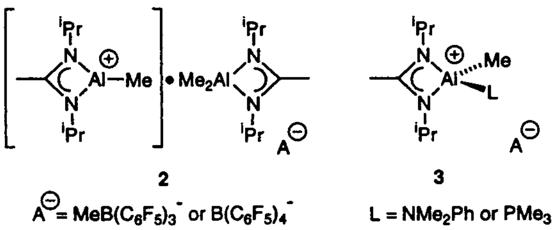
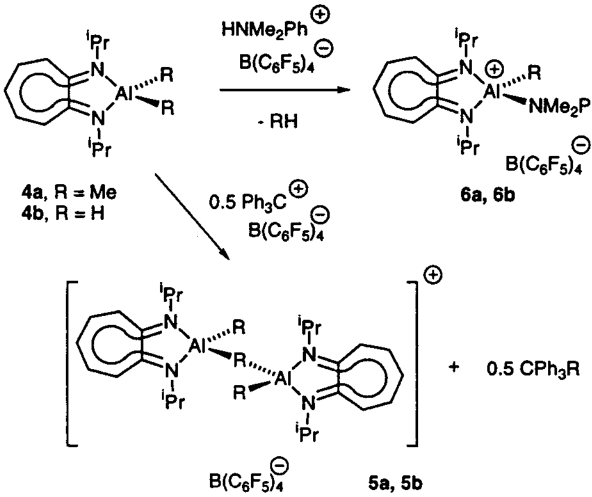


Figure 1. Molecular structure of the cation of **5a**.

Scheme 1



Scheme 2



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[1] (a) Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1997**, *119*, 8125. (b) For cationic polymerization of isobutylene and isobutylene/isoprene initiated by Cp_2Al^+, see: Bochmann, M.; Dawson, D. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2226.

[2] Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1997**, *16*, 5183.

[3] Dias, H. V. R.; Jin, W.; Ratcliff, R. E. *Inorg. Chem.* **1995**, *34*, 6100.

[4] The synthesis of $[Ph_3C][B(C_6F_5)_4]$ was described in the following: Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570. We describe a modified synthesis and full characterization data of this activator in the Supporting Information.

[5] **5a** does not react with excess $[Ph_3C][B(C_6F_5)_4]$ at 23 °C in C_6D_6. **5b** does react with excess $[Ph_3C][B(C_6F_5)_4]$ under these conditions, but the products have not been identified.

[6] The liquid clathrates contain sufficient C_6D_6 to allow NMR locking and afford sharp NMR spectra.

[7] Waymouth, R. M.; Santarsiero, B. D.; Coots, R. J.; Bronikowski, M. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 1427.

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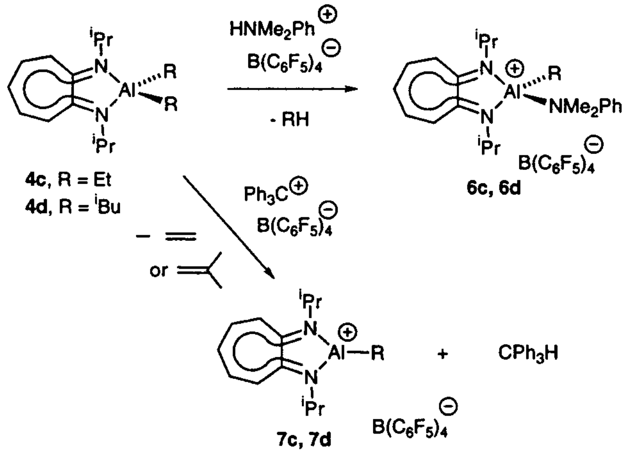
Published on Web 07/29/1998

Scheme 3

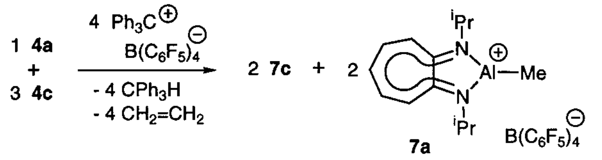


Al bonding, the Al−C$_{bridge}$ distances (Al(1)−C(1), 2.177(3) Å; Al(2)−C(1), 2.120(3) Å) are significantly longer than the Al−C$_{terminal}$ distances (Al(1)−C(2), 1.949(3) Å; Al(2)−C(16), 1.953(3) Å). The structure of the {(^{i}Pr)$_2$ATI}Al framework of **5a** is very similar to that in **4a**.[9]

The ^{1}H NMR spectra of **5b** (CD_2Cl_2) contain a single hydride resonance (δ 4.6) and a single set of {(^{i}Pr)$_2$ATI} resonances characteristic of time-averaged C_{2v} symmetry over the temperature range 0 to −90 °C. It is likely that **5b** has a structure analogous to that of **5a** and bridge/terminal H exchange is rapid. The reaction of **4a**,**b** with [HNMe$_2$Ph][B(C_6F_5)$_4$] affords amine adducts **6a**,**b**.

Neutral higher alkyl complexes **4c**,**d** were prepared by the reaction of {(^{i}Pr)$_2$ATI}H and AlR$_3$ (Scheme 3). Compounds **4c**,**d** react with 1 equiv of [Ph$_3$C][B(C_6F_5)$_4$] in C_6D_6 at 23 °C via β-hydride abstraction to afford base-free cationic complexes **7c**,**d** as liquid clathrates, along with Ph$_3$CH and ethylene (**4c**) or isobutylene (**4d**) as coproducts.[10] Analytically pure **7c**,**d** were obtained as yellow powders by washing the liquid clathrates with hexane, confirming the base-free composition of these complexes. The NMR data for **7c**,**d** (C_6D_6, liquid clathrate) are consistent with effective C_{2v} symmetry and the $^1J_{C-H}$ values for the Al-Et and Al-^{i}Bu groups are in the normal range, indicating that agostic interactions are weak or absent (**7c**: $^1J_{C\alpha-H} = 120$, $^1J_{C\beta-H} = 128$; **7d**: $^1J_{C\alpha-H} = 115$, $^1J_{C\beta-H} = 125$, $^1J_{C\gamma-H} = 125$). Variable-temperature ^{1}H and ^{13}C NMR spectra (CD_2Cl_2) establish that **7c**,**d** retain effective C_{2v} symmetry down to −90 °C. These results establish that coordination of solvent or B(C_6F_5)$_4^-$ to the cations of **7c**,**d** (if present) is sufficiently labile to allow the Al−R group to move rapidly between the two available tetrahedral coordination sites. ^{11}B, ^{13}C, and ^{19}F NMR data for the anion of **7c**,**d** (C_6D_6 or C_6D_5Cl at 23 °C) are identical to data for **5a** and [Ph$_3$C][B(C_6F_5)$_4$], consistent with the absence of strong cation/anion interactions in **7c**,**d**. It is conceivable that **7c**,**d** adopt dinuclear dicationic structures, i.e., [{(^{i}Pr)$_2$ATI}Al(μ-R)$_2$Al{ATI(^{i}Pr)$_2$}]$^{2+}$.[11] However, the ^{1}H and ^{13}C NMR spectra of a mixture of **4c**, **4d**, and [Ph$_3$C][B(C_6F_5)$_4$] in a 1:1:2 molar ratio contain resonances for only **7c**,**d**. Resonances attributable to a mixed alkyl species, i.e., [{(^{i}Pr)$_2$ATI}Al(μ-Et)(μ-^{i}Bu)Al{ATI(^{i}Pr)$_2$}]$^{2+}$, are not observed. Additionally, the reaction of **4a**, **4c**, and [Ph$_3$C][B(C_6F_5)$_4$] in a 1:3:4 molar ratio affords a 1:1 mixture of **7c** and [{(^{i}Pr)$_2$ATI}AlMe][B(C_6F_5)$_4$] (**7a**) along with 4 equiv of Ph$_3$CH; again, mixed alkyl species are not detected (Scheme 4). In this case, a 1:1 **7c**/**7a** mixture is generated because Al-Et β-hydride abstraction is much faster than Al-Me methyl abstraction, and methyl transfer from **4a** to **7c** is rapid.[12] These observations strongly support the formulation of **7a**,**c**,**d** as monomeric species. The reaction of **4c**,**d** with [HNMe$_2$Ph][B(C_6F_5)$_4$] yields NMe$_2$Ph adducts **6c**,**d**.

Scheme 4



Base-free compounds **7c**,**d** exhibit polymerization activity for ethylene,[13] while dinuclear cations **5a**,**b** show only trace activity. Dinuclear hydride cation **5b** polymerizes methyl methacrylate (MMA) to predominantly syndiotactic poly(MMA).[14,15] In contrast, neither neutral hydride **4b**, dinuclear methyl cation **5a**, nor base-free cation **7c** polymerizes MMA under these conditions. While the active species and mechanisms of these polymerizations are not yet established, it is clear that the reactivity of cationic Al species is strongly influenced by their structures (nuclearity, identity of Al-R).

This work shows that labile {(L−X)AlR}$_2$(μ-R)$^+$ and base-free (L−X)AlR$^+$ cations can be obtained cleanly by proper choice of L−X$^-$ and R ligands. We are currently investigating the reactivity of these novel species with a variety of substrates.

Acknowledgment. This work was supported by Department of Energy Grant DE-FG02-88ER13935 and Eastman Chemical Co. E.I. was partially supported by the Yamada Science Foundation. We thank H. Yasuda for assistance with PMMA analyses, Asahi Glass for a gift of [Ph$_3$C][B(C_6F_5)$_4$], and Boulder Scientific for a gift of [HNMe$_2$Ph][B(C_6F_5)$_4$].

Supporting Information Available: Synthetic procedures, characterization data for new compounds, and details of the X-ray structure determination of **5a** (30 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(8) X-ray data for **5a**: triclinic, space group $P\bar{1}$, $a = 10.4815(2)$ Å, $b = 14.0422(3)$ Å, $c = 18.7747(4)$ Å, $\alpha = 104.450(1)°$, $\beta = 94.848(1)°$, $\gamma = 96.639(1)°$, $V = 2639.44(9)$ Å^3, $Z = 2$, $R1 = 0.0447$, w$R2 = 0.0891$, data/parameters = 9012/740. Non-hydrogen atoms were refined anisotropically. The μ-CH$_3$ hydrogen atoms were located in the difference map and positionally refined with relative isotropic displacement factors. The remaining hydrogens were placed in idealized positions and refined as riding atoms with relative isotropic displacement parameters. The structure of the B(C_6F_5)$_4^-$ anion of **5a** is normal.

(9) For analogous dinuclear zirconocene cations, see: (a) Bochmann, M.; Lancaster, S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1634. (b) Chen, Y.-X.; Stern, C. L.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 12451. (c) For related M−Me−M species, see: Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 5853 and references therein.

(10) The reaction of Cp$_2$HfEt$_2$ with [Ph$_3$C][B(C_6F_5)$_4$] proceeds by β-hydride abstraction, yielding [(Cp$_2$HfEt)$_2$(μ-Et)][B(C_6F_5)$_4$], Ph$_3$CH, and ethylene. Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **1995**, *497*, 55.

(11) Related dinuclear dicationic Zr species have been observed or proposed. (a) [{(Me$_8$taa)Zr(μ-X)}$_2$][B(C_6F_5)$_4$]$_2$ (Me$_8$taa = octamethyldibenzotetraazaannulene; X = OH, OEt, C≡CR); Martin, A.; Uhrhammer, R.; Gardner, T. G.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1998**, *17*, 382. (b) [{Me$_2$Si(NCMe$_3$)$_2$}$_2$Zr$_2$Bz$_2$][B(C_6F_5)$_4$]$_2$; Horton, A. D.; With, J. D. *Organometallics* **1997**, *16*, 5424.

(12) The reaction of **4a**, **4c**, and [Ph$_3$C][B(C_6F_5)$_4$] in 1:1:2 ratio affords **7a** exclusively.

(13) Representative results: **7c** (toluene, 80 °C, 1 atm of ethylene), activity = 2600 g of PE/(mol·h·atm); **7c** (toluene, 100 °C, 5 atm of ethylene), activity = 1000 g of PE/(mol·h·atm), $M_n = 106\,500$, $M_w/M_n = 2.4$, mp (DSC) = 137.8 °C; **7d** (toluene, 80 °C, 1 atm of ethylene), activity = 900 g of PE/(mol·h·atm).

(14) Representative results: (a) toluene, 23 °C: 100% yield, $M_n = 228\,000$, $M_w/M_n = 1.8$, *mm*:*mr*:*rr* = 1:22:77; (b) chlorobenzene, 23 °C: 80% yield, $M_n = 187\,000$, $M_w/M_n = 1.8$, *mm*:*mr*:*rr* = 1:22:88.

(15) For polymerization of MMA initiated by a combination of cationic and neutral zirconocene compounds, see: Li, Y.; Ward, D. G.; Reddy, S. S.; Collins, S. *Macromolecules* **1997**, *30*, 1875.