Cationic Aluminum Alkyl Complexes Incorporating Aminotroponiminate Ligands

Andrey V. Korolev,[†] Eiji Ihara,[†] Ilia A. Guzei,[‡] Victor G. Young, Jr.,[§] and Richard F. Jordan*,[†]

Contribution from the Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637, Department of Chemistry, Iowa State University, Ames, Iowa 50011, and Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received January 29, 2001. Revised Manuscript Received May 17, 2001

Abstract: The synthesis, structures, and reactivity of cationic aluminum complexes containing the *N*,*N*′-diisopropylaminotroponiminate ligand (^{i}Pr$_2$-ATI$^-$) are described. The reaction of (^{i}Pr$_2$-ATI)AlR$_2$ (**1a**−**e**,**g**,**h**; R = H (**a**), Me (**b**), Et (**c**), Pr (**d**), ^{i}Bu (**e**), Cy (**g**), CH$_2$Ph (**h**)) with [Ph$_3$C][B(C$_6$F$_5$)$_4$] yields (^{i}Pr$_2$-ATI)AlR$^+$ species whose fate depends on the properties of the R ligand. **1a** and **1b** react with 0.5 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$] to produce dinuclear monocationic complexes [{(^{i}Pr$_2$-ATI)AlR}$_2$(μ-R)][(C$_6$F$_5$)$_4$] (**2a**,**b**). The cation of **2b** contains two (^{i}Pr$_2$-ATI)AlMe$^+$ units linked by an almost linear Al−Me−Al bridge; **2a** is presumed to have an analogous structure. **2b** does not react further with [Ph$_3$C][B(C$_6$F$_5$)$_4$]. However, **1a** reacts with 1 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$] to afford (^{i}Pr$_2$-ATI)Al(C$_6$F$_5$)(μ-H)$_2$B(C$_6$F$_5$)$_2$ (**3**) and other products, presumably via C$_6$F$_5^-$ transfer and ligand redistribution of a [(^{i}Pr$_2$-ATI)AlH][(C$_6$F$_5$)$_4$] intermediate. **1c**−**e** react with 1 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$] to yield stable base-free [(^{i}Pr$_2$-ATI)AlR][B(C$_6$F$_5$)$_4$] complexes (**4c**−**e**). **4c** crystallizes from chlorobenzene as **4c**(ClPh)·0.5PhCl, which has been characterized by X-ray crystallography. In the solid state the PhCl ligand of **4c**(ClPh) is coordinated by a dative PhCl−Al bond and an ATI/Ph π-stacking interaction. **1g**,**h** react with [Ph$_3$C][B(C$_6$F$_5$)$_4$] to yield (^{i}Pr$_2$-ATI)Al(R)(C$_6$F$_5$) (**5g**,**h**) via C$_6$F$_5^-$ transfer of [(^{i}Pr$_2$-ATI)AlR][(BC$_6$F$_5$)$_4$] intermediates. **1c**,**h** react with B(C$_6$F$_5$)$_3$ to yield (^{i}Pr$_2$-ATI)Al(R)(C$_6$F$_5$) (**5c**,**h**) via C$_6$F$_5^-$ transfer of [(^{i}Pr$_2$-ATI)AlR][RB(C$_6$F$_5$)$_3$] intermediates. The reaction of **4c**−**e** with MeCN or acetone yields [(^{i}Pr$_2$-ATI)Al(R)(L)][B(C$_6$F$_5$)$_4$] adducts (L = MeCN (**8c**−**e**), acetone (**9c**−**e**)), which undergo associative intermolecular L exchange. **9c**−**e** undergo slow β-H transfer to afford the dinuclear dicationic alkoxide complex [{(^{i}Pr$_2$-ATI)Al(μ-O^{i}Pr)}$_2$][B(C$_6$F$_5$)$_4$]$_2$ (**10**) and the corresponding olefin. **4c**−**e** catalyze the head-to-tail dimerization of *tert*-butyl acetylene by an insertion/σ-bond metathesis mechanism involving [(^{i}Pr$_2$-ATI)Al(C≡C^{t}Bu)][B(C$_6$F$_5$)$_4$] (**13**) and [(^{i}Pr$_2$-ATI)Al(CH=C(^{t}Bu)C≡C^{t}Bu)][B(C$_6$F$_5$)$_4$] (**14**) intermediates. **13** crystallizes as the dinuclear dicationic complex [{(^{i}Pr$_2$-ATI)Al(μ-C≡C^{t}Bu)}$_2$][B(C$_6$F$_5$)$_4$]$_2$·5PhCl from chlorobenzene. **4e** catalyzes the polymerization of propylene oxide and **2a** catalyzes the polymerization of methyl methacrylate. **4c**,**e** react with ethylene-d_4 by β-H transfer to yield [(^{i}Pr$_2$-ATI)AlCD$_2$CD$_2$H][B(C$_6$F$_5$)$_4$] initially. Polyethylene is also produced in these reactions by an unidentified active species.

Introduction

Neutral aluminum AlX$_3$ complexes (X = halide, alkyl, alkoxide, etc.) are widely used as Lewis acid reagents and catalysts (Friedel−Crafts, Diels−Alder, etc.), alkylating and reducing agents, initiators for cationic polymerizations, catalysts for the oligomerization of ethylene to α-olefins, and cocatalysts/activators in transition-metal-catalyzed olefin polymerizations.[1,2] *Cationic* aluminum alkyl complexes are potentially interesting for these and other applications because the charge may enhance the Lewis acidity of the Al center and influence the reactivity of the Al−R group.[3] Low-coordinate cationic Al species which contain vacant coordination sites or labile ligands are particularly attractive for applications in catalysis.

Bochmann has reported that transient "R$_2$Al$^+$" (R = Me, ^{i}Bu) species can be generated in toluene-d_8, but abstract C$_6$F$_5^-$ from B(C$_6$F$_5$)$_4^-$ to form neutral Al and B complexes.[4] Aluminocenium cations, (C$_5$R$_5$)$_2$Al$^+$, which can be considered to be 6-coordinate complexes, are more stable than AlR$_2^+$ alkyl species, and [(C$_5$H$_5$)$_2$Al][MeB(C$_6$F$_5$)$_3$] has been exploited as an initiator for the cationic polymerization of isobutylene and the synthesis of butyl rubber.[5] Nöth has investigated [Al(NR$_2$)$_2$(L)][AlX$_4$] salts (NR$_2$ = 2,2,6,6-tetramethylpiperidide; L = pyridine bases; X = Br, I) and concluded on the basis of ^{27}Al NMR,

* Address correspondence to this author.
† The University of Chicago.
‡ Iowa State University.
§ University of Minnesota.

(1) (a) Starowieyski, K. B. In *Chemistry of Aluminium, Gallium, Indium and Thallium*; Downs, A. J., Ed.; Chapman & Hall: London, UK, 1993; pp 322−371. (b) Eisch, J. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier: Oxford, UK, 1995; Vol. 11, Chapter 6. (c) Matyjaszewski, K., Ed. *Cationic Polymerizations: Mechanisms, Synthesis and Applications*; Marcel Dekker: New York, 1996. (d) Kennedy, J. P.; Marechal, E. *Carbocationic Polymerization*; Wiley-Interscience: New York, 1982. (e) Eisch, J. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Elsevier: Oxford, UK, 1995; Vol. 1, Chapter 10.

(2) (a) Ziegler, K.; Gellert, H. G. *Ann.* **1950**, *567*, 195. (b) Skinner, W. A.; Bishop, E.; Cambour, P.; Fuqua, S.; Lim, P. *Ind. Eng. Chem.* **1960**, *52*, 695. (c) Skupínska, J. *Chem. Rev.* **1991**, *91*, 613. (d) Al-Jarallah, A. M.; Anabtawi, J. A.; Siddiqui, M. A. B.; Aitani, A. M.; Al-Sa'doun, A. W. *Catal. Today* **1992**, *14*, 42. (e) Grünig, H.; Luft, G. *Angew. Makromol. Chem.* **1986**, *142*, 161.

(3) Atwood, D. A. *Coord. Chem. Rev.* **1998**, *176*, 407.

(4) Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908.

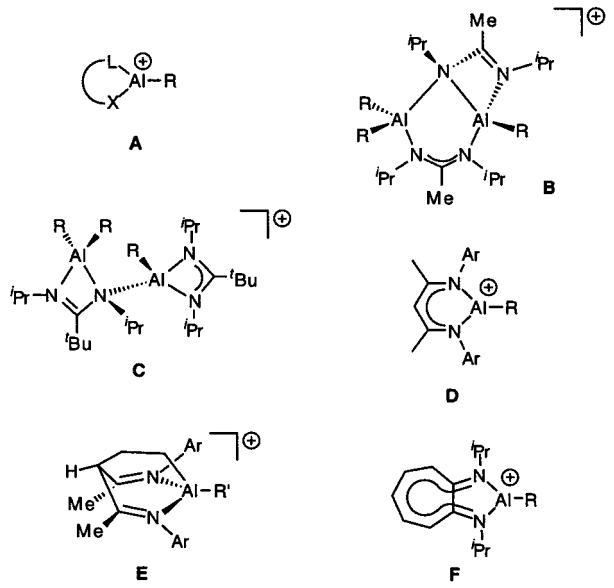
10.1021/ja010242e CCC: $20.00
Published on Web 08/02/2001

conductivity, and computational results that the Al cations have three-coordinate structures.[6] Several classes of four-coordinate Al cations have also been reported.[7] Bertrand showed that bisaminoamide complexes $\{\eta^3\text{-HRN(CH}_2)_2\text{N(R}')(\text{CH}_2)_2\text{NR}\}\text{-AlCl}^+$ adopt trigonal monopyramidal geometries with a vacant axial coordination site and catalyze the polymerization of propylene oxide, probably by an anionic-coordination mechanism.[8] Gibson reported that pyridylaminoamide complexes $\{\eta^3\text{-2-(ArNCRMe),6-(ArN=CR)-C}_3\text{H}_3\text{N}\}\text{AlMe}^+$ and pendant arm Schiff base complexes $\{3,5\text{-}^t\text{Bu}_2\text{-2-(O)C}_6\text{H}_2\text{CH=NL}\}\text{AlMe}^+$ (L = $\text{CH}_2\text{CH}_2\text{NMe}_2$, 8-quinolinyl) polymerize ethylene.[9,10] Atwood has prepared several 6-coordinate Shiff base complexes that contain labile axial ligands, including $(\text{salen})\text{Al(MeOH)}_2^+$ and $(\text{acen})\text{Al(MeOH)}_2^+$, and has shown that these species polymerize propylene oxide, probably by a cationic mechanism.[11]

Our work in this area is focused on the chemistry of 3-coordinate $(\text{L}-\text{X})\text{AlR}^+$ cations (**A**, Chart 1) or weakly solvated/ion-paired versions thereof, which contain chelating monoanionic L-X^- ancillary ligands. These species are expected to be more stable than AlR_2^+ species but may be highly reactive due to the combination of the low coordination number and the charge at Al. The use of chelating $\text{L}-\text{X}^-$ ligands minimizes complications from ligand exchange/redistribution reactions. In our initial approach to $(\text{L-X})\text{AlR}^+$ species we investigated the synthesis of cationic amidinate complexes $\{\text{RC(NR}')_2\}\text{AlR}^+$, via alkyl abstraction from $\{\text{RC(NR}')_2\}\text{AlR}_2$ precursors.[10d,12] The reaction of $\{\text{RC(NR}')_2\}\text{AlMe}_2$ (R = Me or ^{t}Bu, R′ = ^{i}Pr or Cy) with $[\text{Ph}_3\text{C}][\text{B(C}_6\text{F}_5)_4]$ or $\text{B(C}_6\text{F}_5)_3$ yields amidinate-bridged dinuclear species (**B**, **C**), the structures and stability of which depend on the steric properties of the amidinate substituents and the reactivity of the anion ($\text{B(C}_6\text{F}_5)_4^- < \text{RB(C}_6\text{F}_5)_3^-$). Dinuclear species are formed in these reactions because the initially generated $\{\text{RC(NR}')_2\}\text{AlR}^+$ cation is trapped by the starting $\{\text{RC(NR}')_2\}\text{AlMe}_2$ complex. Alkyl abstraction from the "super bulky" amidinate complex $\{^t\text{BuC(N}^t\text{Bu)}_2\}\text{AlMe}_2$ yields a thermally unstable mononuclear cation $\{^t\text{BuC(N}^t\text{Bu)}_2\}\text{AlMe}^+$ that could not be isolated. The difficulty in generating stable mononuclear $\{\text{RC(NR}')_2\}\text{AlR}^+$ species is due to the small bite angle of the amidinate ligand (N−Al−N angles ca. 70° in $\{\text{RC(NR}')_2\}\text{AlR}_2$ complexes),[13] which results in sterically open and hence highly reactive Al centers. To circumvent this problem, we investigated alkyl abstraction reactions of *N*,*N*-diaryldiketiminate complexes $\{\text{HC(CMeNAr)}_2\}\text{AlMe}_2$ (Ar = 2,6-^{i}Pr$_2$-C$_6$H$_3$), in which the larger ligand bite angle (N−Al−N angle ca. 96°) and bulky *N*-aryl substituents provide increased steric protection at Al.[14] These reactions yield stable 3-coordinate $\{\text{HC(CMeNAr)}_2\}\text{AlR}^+$ cations (**D**), several salts of which have been characterized by X-ray crystallography. Cationic $\{\text{HC(CMeNAr)}_2\}\text{AlR}^+$ species readily coordinate Lewis bases to form 4-coordinate $\{\text{HC(CMeNAr)}_2\}\text{Al(R)(L)}^+$ adducts, but react with ethylene by reversible cycloaddition across the Al-diketiminate ring to yield products of type **E**. Smith has also investigated the synthesis of $\{\text{diketiminate}\}\text{AlR}^+$ species.[15]

In our studies of cationic Al amidinate and diketiminate complexes, three reagents were investigated for the conversion of $(\text{L}-\text{X})\text{AlR}_2$ complexes to $(\text{L}-\text{X})\text{AlR}^+$ cations: $[\text{Ph}_3\text{C}][\text{B(C}_6\text{F}_5)_4]$,[16] $\text{B(C}_6\text{F}_5)_3$,[17] and $[\text{NMe}_2\text{Ph}][\text{B(C}_6\text{F}_5)_4]$.[18] Each of these "activators" has been used successfully to generate reactive transition-metal L_nMR^+ cations from L_nMR_2 precursors.[19] Our work shows that $[\text{Ph}_3\text{C}][\text{B(C}_6\text{F}_5)_4]$ is the most useful of these reagents for the generation of $(\text{L-X})\text{AlR}^+$ species because the $\text{B(C}_6\text{F}_5)_4^-$ anion is very stable and the organic byproducts (Ph_3CR or Ph_3CH) do not react with $(\text{L-X})\text{AlR}^+$ cations.

Chart 1



(5) (a) Dohmeier, C.; Schnöckel, H.; Robl, C.; Schneider, U.; Ahlrichs, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1655. (b) Bochmann, M.; Dawson, D. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2226. (c) Burns, C. T.; Stelck, D. S.; Shapiro, P. J.; Vij, A.; Kunz, K.; Kehr, G.; Concolino, T.; Rheingold, A. L. *Organometallics* **1999**, *18*, 5432.

(6) Krossing, I.; Nöth, H.; Schwenk-Kircher, H. *Eur. J. Inorg. Chem.* **1998**, 927.

(7) (a) Coslédan, F.; Hitchcock, P. B.; Lappert, M. F. *Chem. Commun.* **1999**, 705. (b) Atwood, D. A.; Jegier, J. *Inorg. Chem.* **1996**, *35*, 4277. (c) Atwood, D.; Jegier, J. *Chem. Commun.* **1996**, 1507. (d) Uhl, W.; Wagner, J.; Fenske, D.; Baum, G. *Z. Anorg. Allg. Chem.* **1992**, *612*, 25. (e) Self, M. F.; Pennington, W. T.; Laske, J. A.; Robinson, G. H. *Organometallics* **1991**, *10*, 36. (f) Kynast, U.; Kelton, B. W.; White, A. H.; Henderson, M. J.; Raston, C. L. *J. Organomet. Chem.* **1990**, *384*, C1. (g) Engelhardt, L. M.; Kynast, U.; Raston, C. L.; White, A. H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 681. (h) Bourget, L.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1999**, 2645.

(8) (a) Emig, N.; Nguyen, H.; Krautscheid, H.; Réau, R.; Cazaux, J.-B.; Bertrand, G. *Organometallics* **1998**, *17*, 3599. (b) Emig, N.; Réau, R.; Krautscheid, H.; Fenske, D.; Bertrand, G. *J. Am. Chem. Soc.* **1996**, *118*, 5822.

(9) (a) Bruce, M.; Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 2523. (b) Cameron, P. A.; Gibson, V. C.; Redshaw, C.; Segal, J. A.; Bruce, M. D.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1999**, 1883.

(10) For other reports of ethylene polymerization by Al catalysts see: (a) Kim, J. S.; Wojcinski, L. M., II; Liu, S.; Sworen, J. C.; Sen, A. *J. Am. Chem. Soc.* **2000**, *122*, 5668. (b) Soga, K.; Shiono, T.; Doi, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 840. (c) Martin, H.; Bretinger, H. *Makromol. Chem.* **1992**, *193*, 1283. (d) Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1997**, *119*, 8125.

(11) (a) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *J. Am. Chem. Soc.* **1995**, *117*, 6779. (b) Jegier, J. A.; Atwood, D. A. *Inorg. Chem.* **1997**, *36*, 2034. (c) Munoz-Hernandez, M.-A.; Sannigrahi, B.; Atwood, D. A. *J. Am. Chem. Soc.* **1999**, *121*, 6747. (d) Jegier, J. A.; Munoz-Hernandez, M.-A.; Atwood, D. A. *J. Chem. Soc., Dalton Trans.* **1999**, 2583.

(12) Dagorne, S.; Guzei, I. A.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 274.

(13) (a) Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1997**, *16*, 5183. (b) Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1998**, *17*, 4042. (c) Edelmann, F. T. *Coord. Chem. Rev.* **1994**, *137*, 403. (d) Barker, J.; Kilner, M. *Coord. Chem. Rev.* **1994**, *133*, 219

(14) (a) Radzewich, C. E.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 9384. (b) Radzewich, C. E.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 8673.

(15) Qian, B.; Ward, D. L.; Smith, M. R., III *Organometallics* **1998**, *17*, 3070.

(16) Use of $[\text{Ph}_3\text{C}][\text{B(C}_6\text{F}_5)_4]$ to generate zirconocene species: (a) Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570. (b) Ewen, J. A.; Elder, M. J. European Patent Application 0,426,637, 1991; *Chem. Abstr.* **1991**, *115*, 136988d.

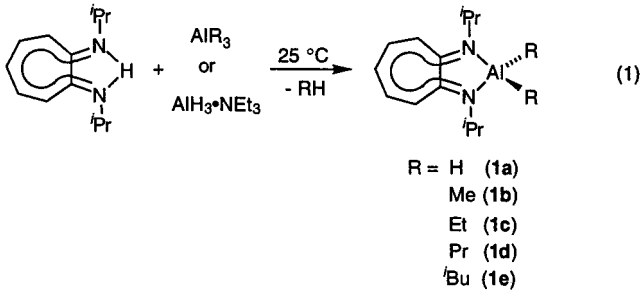
(17) Use of $\text{B(C}_6\text{F}_5)_3$ for alkyl abstraction: (a) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015 and references therein. (b) Ewen, J. A.; Elder, M. J. U.S. Patent Application 419,017, 1989; *Chem. Abstr.* **1991**, *115*, 136998g.

$B(C_6F_5)_3$ is also efficient at abstracting R^- groups from (L-X)-AlR_2 compounds; however, the resulting $RB(C_6F_5)_3^-$ anions are often incompatible with (L-X)AlR^+ species due to R^- or $C_6F_5^-$ transfer leading to neutral products.[15,19a,20] Ammonium salts $[HNR_3][B(C_6F_5)_4]$ generally react with (L-X)AlR_2 to produce stable 4-coordinate (L-X)Al(R)$(NR_3)^+$ amine adducts.

The specific objective of the work described here is to prepare and study the reactivity of cationic (^{i}Pr$_2$-ATI)AlR^+ complexes (**F**) which contain the *N*,*N*′-diisopropylaminotroponiminate ligand (^{i}Pr$_2$-ATI$^-$). This ligand was introduced in main group chemistry by Dias and forms stable 5-membered chelate ring complexes with aluminum.[21] The bite angle of the ^{i}Pr$_2$-ATI$^-$ ligand is intermediate between that of the amidinate and diketiminate ligands discussed above (N−Al−N = 83.3(1)° in (^{i}Pr$_2$-ATI)AlMe_2),[21a] and thus (^{i}Pr$_2$-ATI)AlR^+ species are expected to be moderately stable and reactive. Additionally, the fused ring structure of (^{i}Pr$_2$-ATI)AlR^+ species may disfavor cycloaddition reactions analogous to those observed in the diketiminate systems. Here we describe the synthesis, structures, and reactivity of several novel families of mononuclear and dinuclear cationic Al alkyls which incorporate the ^{i}Pr$_2$-ATI$^-$ ligand.[22]

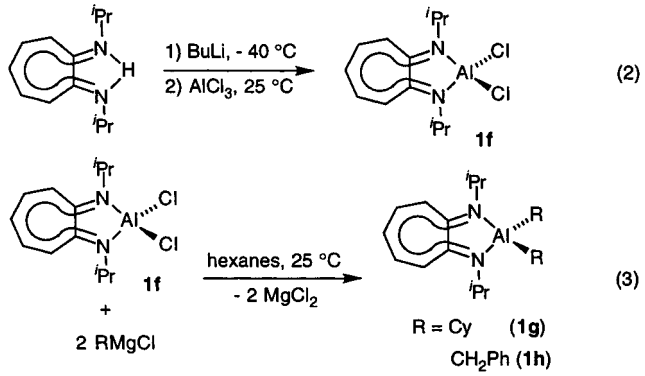
Results

Synthesis of (^{i}Pr$_2$-ATI)AlR_2 Complexes. The (^{i}Pr$_2$-ATI)H ligand precursor was synthesized from 2-tropolone using the procedure described by Dias et al.[21a] Dialkyl complexes (^{i}Pr$_2$-ATI)AlR_2 (**1a**−**e**, R = H, Me, Et, Pr, ^{i}Bu) are easily prepared in moderate to high yield by the alkane elimination procedure described by Dias for **1a**,**b** (eq 1).[21a] Alternatively,



(1)

the reaction of Li[^{i}Pr$_2$-ATI] with $AlCl_3$ yields (^{i}Pr$_2$-ATI)$AlCl_2$ (**1f**, eq 2), which can be cleanly alkylated by Grignard reagents. This approach was used to prepare (^{i}Pr$_2$-ATI)$AlCy_2$ (**1g**) and (^{i}Pr$_2$-ATI)Al$(CH_2Ph)_2$ (**1h**, eq 3), for which the corresponding AlR_3 compounds are not commercially available.

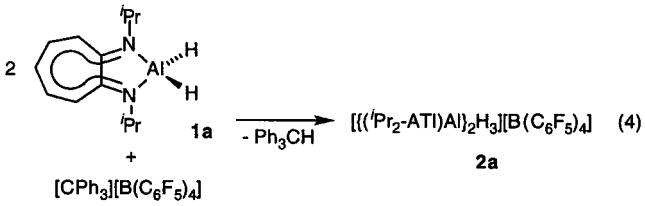


(2)

(3)

Compounds **1a**−**g** are isolated as red to yellow crystalline solids while **1h** is isolated as a red oil. The dialkyl derivatives are stable in solution to well above 100 °C, do not react with Lewis bases such as nitriles, amines, or ethers, but enflame when exposed to air. The ^{1}H and ^{13}C NMR spectra of **1a**−**h** are consistent with C_{2v} structures.

Synthesis of Cationic Al Hydrides. The reaction of **1a** with 0.5 equiv of $[Ph_3C][B(C_6F_5)_4]$ yields a cationic Al hydride species $[\{(^i$Pr$_2$-ATI)Al$\}_2H_3][B(C_6F_5)_4]$ (**2a**, eq 4). Compound

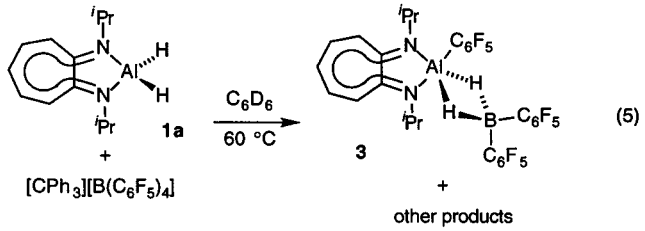


(4)

2a separates as an oil (liquid clathrate)[23] from benzene solution and can be isolated in high yield as a solid after extensive washing of the oil with hexanes. **2a** is stable at room temperature in benzene and toluene clathrates and in chlorobenzene solution.

The ^{1}H NMR spectrum of **2a** in C_6D_6 contains a broad signal at δ 4.54 (3H) and one ^{i}Pr-methyl doublet at δ 0.92 (24H), corresponding to three hydride ligands and two C_{2v}-symmetric (^{i}Pr$_2$-ATI)Al units, respectively. The same pattern is observed at −90 °C in CD_2Cl_2. These data are insufficient to establish the structure of **2a**; however, by analogy to the structurally characterized Me analogue (**2b**, vide infra), we propose that the cation of **2a** has a dinuclear mono-H-bridged structure, $\{(^i$Pr$_2$-ATI)AlH$\}_2(\mu$-H)$^+$, and undergoes fast bridge/terminal H exchange resulting in time-averaged C_{2v} symmetry.

The reaction of **1a** with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ at 60 °C in benzene produces a mixture of Al species, one of which, (^{i}Pr$_2$-ATI)Al$(C_6F_5)(\mu$-H$)_2$B$(C_6F_5)_2$ (**3**), crystallizes from solution (eq 5). It is probable that the formation of **3** involves generation of (^{i}Pr$_2$-ATI)AlH^+ which abstracts a $C_6F_5^-$ group from the $B(C_6F_5)_4^-$ anion.[24] Subsequent ligand redistribution reactions produce **3**.



(5)

(18) Use of HNR_3^+ reagents for the generation of $L_nM(R)^+$ species: (a) Bochmann, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1610. (b) Lin, Z.; Le Marechal, J.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 4127. (c) Turner, H. W.; Hlatky, G. G. European Patent Application 0,277,003, 1988. (d) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (e) Turner, H. W. European Patent Application 0,277,004, 1988. (f) Hlatky, G. G.; Eckman, R. R.; Turner, H. W. *Organometallics* **1992**, *11*, 1413.

(19) (a) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391. (b) Piers, W. E.; Chivers, T. *Chem. Soc. Rev.* **1997**, *26*, 345. (c) Guram, A. S.; Jordan, R. F. In *Comprehensive Organometallic Chemistry*; Lappert, M. F., Ed.; Pergamon: Oxford, UK, 1995; Vol. 4, pp 589−626.

(20) For a recent example of $C_6F_5^-$ transfer from $RB(C_6F_5)_3^-$ to a cationic transition metal species see: Deckers, P. J. W.; van der Linden, A. J.; Meetsma, A.; Hessen, B. *Eur. J. Inorg. Chem.* **2000**, 929.

(21) (a) Dias, H. V. R.; Jin, W.; Ratcliff, R. E. *Inorg. Chem.* **1995**, *34*, 6100. (b) Dias, H. V. R.; Jin, W. *Inorg. Chem.* **1996**, *35*, 6546. (c) Dias, H. V. R.; Jin, W.; Wang, Z. *Inorg. Chem.* **1996**, *35*, 6074. (d) Dias, H. V. R.; Wang, Z.; Jin, W. *Coord. Chem. Rev.* **1998**, *176*, 67. (e) Roesky, P. W. *Chem. Soc. Rev.* **2000**, *29*, 335. (f) Bailey, P. J.; Dick, C. M. E.; Fabre, S.; Parsons, S. *J. Chem. Soc., Dalton Trans.* **2000**, 1655.

(22) Aspects of this work were communicated previously: (a) Ihara, E.; Young, V. G., Jr.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 8277. (b) Korolev, A. V.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 11606.

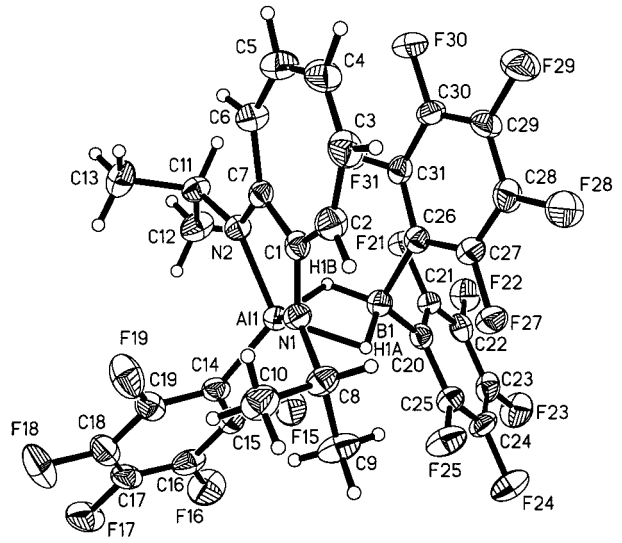
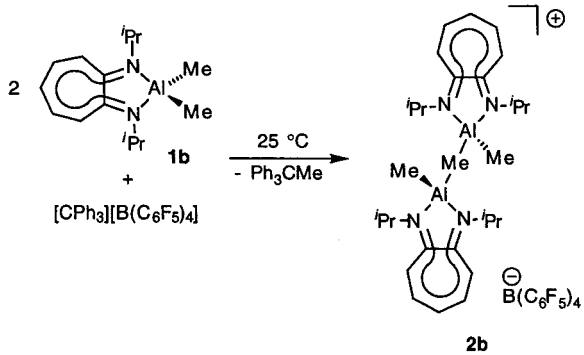


Figure 1. Molecular structure of (^{i}Pr$_2$-ATI)Al(C$_6$F$_5$)(μ-H)$_2$B(C$_6$F$_5$)$_2$ (**3**). Selected bond distances (Å) and angles (deg): Al(1)−N(1) 1.870(2), Al(1)−N(2) 1.864(2), Al(1)−H(1A) 1.82(2), Al(1)−H(1B) 1.93(2), Al(1)−C(14) 1.976(3), Al(1)−B(1) 2.283(3), B(1)−C(20) 1.605(4), B(1)−C(26) 1.620(4); N(1)−Al(1)−N(2) 86.28(9), N(1)−Al(1)−C(14) 122.4(1), N(2)−Al(1)−C(14) 117.7(1), N(1)−Al(1)−H(1A) 88.2(8), N(1)−Al(1)−H(1B) 130.8(8), N(2)−Al(1)−H(1A) 131.8(8), N(2)−Al(1)−H(14B) 89.3(7), H(1A)−Al(1)−H(1B) 59.8(1), H(1A)−B(1)−H(1B) 106(2), C(20)−B(1)−C(26) 117.3(2).

The molecular structure of **3** was established by X-ray crystallography (Figure 1). The Al and B atoms in **3** are linked by two bridging hydride ligands. The Al−H distances (Al−H(1A) 1.82(2) Å, Al−H(1B) 1.93(2) Å) are longer than those in Al{(μ-H)$_2$BH$_2$}$_3$ (gas phase, 1.801(6) Å)[25a] and (tmp)$_2$Al(μ-H)$_2$(9-BBN) (tmp = 2,2,6,6-tetramethylpiperidinyl, 9-BBN = 9-borabicyclononane; 1.738 Å).[25b] The B−H bond distances (B−H(1A) 1.18(2) Å and B−H(1B) 1.17(2) Å) are shorter than those in Al{(μ-H)$_2$BH$_2$}$_3$ (B−(μ-H) 1.28(1) Å), but close to those in (tmp)$_2$Al(μ-H)$_2$(9-BBN) (1.208 Å). The 5-coordinate geometry at Al is made possible by the compactness of the η^2-H$_2$B(C$_6$F$_5$)$_2^-$ ligand; the H−Al−H angle (59.8(11)°) is smaller than those in Al{(μ-H)$_2$BH$_2$}$_3$ and (tmp)$_2$Al(μ-H)$_2$(9-BBN) (73.4(8) and 65.4°, respectively)). The Al−C$_6$F$_5$ bond distance (Al−C(14), 1.976(3) Å) is similar to that in {^{t}BuC(NCy)$_2$}-AlMe(C$_6$F$_5$) (2.011(3) Å)[12] and the terminal Al−Ph bond distance in Al$_2$Ph$_6$ (1.95(8) Å average).[26]

Synthesis of Cationic Al Alkyls. The reaction of (^{i}Pr$_2$-ATI)-AlMe$_2$ (**1b**) with 0.5 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$] at ambient temperature in benzene or chlorobenzene yields the dinuclear Me-bridged species [{(^{i}Pr$_2$-ATI)AlMe}$_2$(μ-Me)][B(C$_6$F$_5$)$_4$] (**2b**) and Ph$_3$CMe (eq 6). **2b** separates as an oil from benzene and can be isolated as a pale green precipitate when the reaction mixture is washed with hexanes. No further reaction occurs when **2b** is mixed with excess [Ph$_3$C][B(C$_6$F$_5$)$_4$] in benzene at 23 °C for several days. Compound **2b** is stable at room temperature as a benzene or toluene liquid clathrate and in C$_6$H$_5$-Cl solution, but decomposes in CH$_2$Cl$_2$ to unidentified species.



(6)

The ^{1}H NMR spectrum of **2b** at −90 °C in CD$_2$Cl$_2$ 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. The −90 °C ^{13}C NMR spectrum of **2b** contains separate resonances for the bridging (δ −0.8) and terminal (δ −5.2) methyl carbons. A large $^1J_{C-H}$ (133 Hz) is observed for the μ-Me group, which is consistent with a large Al−C−Al angle and substantial sp^2-C character in the C−H bonds.[27] The terminal Me $^1J_{C-H}$ value (118 Hz) is normal for an Al-Me group. The bridge and terminal Me signals coalesce to a broad singlet (δ 0.00) at −60 °C, indicating that bridge/terminal exchange is rapid at this temperature. The free energy barrier for this process is $\Delta G^{\ddagger} = 9.5(3)$ kcal/mol.[28]

The ^{1}H NMR spectrum of a C$_6$D$_5$Cl solution of **2b** containing 2 equiv of **1b** contains a single set of resonances at the weighted average chemical shifts of the two components down to −40 °C, implying that intermolecular exchange between **2b** and **1b** is rapid. It is unlikely that **2b** reversibly dissociates to **1b** and (^{i}Pr$_2$-ATI)AlMe$^+$, because, as noted above, **2b** does not react further with [Ph$_3$C][B(C$_6$F$_5$)$_4$] even at 25 °C. Hence, the exchange between **2b** and **1b** probably occurs by an associative mechanism.

Crystals of **2b** suitable for X-ray crystallographic analysis were obtained by slow (months) crystallization from a C$_6$D$_6$ liquid clathrate. Compound **2b** crystallizes as discrete ions (Figure 2). Consistent with the NMR data, the cation contains two (^{i}Pr$_2$-ATI)AlMe units linked by a nearly linear Al−Me−Al bridge (Al(1)−C(1)−Al(2) angle = 167.8(2)°). The μ-CH$_3$ hydrogens were located in the equatorial plane of the nearly trigonal bipyramidal (*tbp*) carbon center (sum of H−C(1)−H angles = 357°). The μ-CH$_3$ carbon is sp^2-hybridized and the remaining p orbital is used for 3-center, 2-electron bonding to the two Al atoms. This bonding description is consistent with the large $^1J_{CH}$ value observed in the ^{13}C NMR spectrum.[29] The Al−C$_{bridge}$ distances are ca. 0.2 Å longer than the Al−C$_{term}$ distances as expected. The structure of the (^{i}Pr$_2$-ATI)Al framework of **2b** is very similar to that in **1b**.[21a]

In contrast to the behavior of **1b**, complexes **1c**−**e**, which contain higher primary alkyl groups, react with 1 equiv of [Ph$_3$C]-[B(C$_6$F$_5$)$_4$] in benzene, toluene, hexanes, or pentane at 25 °C by net β-H abstraction to give base-free [(^{i}Pr$_2$-ATI)AlR]-

(23) Leading references to liquid clathrate phenomena: (a) Atwood, J. L. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH: New York, 1993; pp 197−232. (b) Lambert, J. B.; Zhao, Y.; Wu, H.; Tse, W. C.; Kuhlmann, B. *J. Am. Chem. Soc.* **1999**, *121*, 5001.

(24) For examples of C$_6$F$_5^-$ transfer from the B(C$_6$F$_5$)$_4^-$ anion to the metal center see ref 4 and: Gómez, R.; Green, M. L. H.; Haggitt, J. L. *J. Chem. Soc., Dalton Trans.* **1996**, 939.

(25) (a) Almenningen, A.; Gundersen, G.; Haaland, A. *Acta. Chem. Scand.* **1968**, *22*, 328. (b) Knabel, K; Krossing, I.; Nöth, H.; Schwenk-Kircher, H.; Schmidt-Amelunxen, M.; Seifert, T. *Eur. J. Inorg. Chem.* **1998**, 1095. (c) Holloway, C. E.; Melnik, M. *J. Organomet. Chem.* **1997**, *543*, 1.

(26) Malone, J. F.; McDonald, W. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2646.

(27) Waymouth, R. M.; Santarsiero, B. D.; Coots, R. J.; Bronikowski, M. J.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 1427.

(28) The free energy barrier for bridge/terminal methyl exchange of **2b** was determined using the graphical method described in the following: Shanan-Atidi, H.; Bar-Eli, K. H. *J. Phys. Chem.* **1970**, *74*, 961. $T_C = 213$ K; $\Delta\nu = 364$ Hz at 360 MHz.

(29) Analogous dinuclear zirconocene cations have been reported. (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.

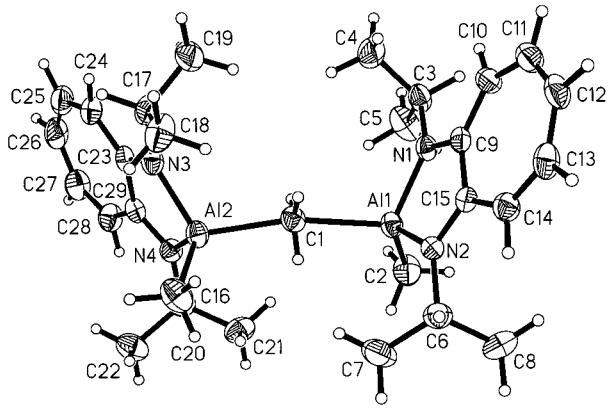
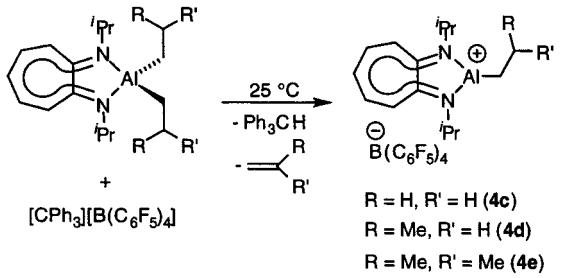


Figure 2. Structure of the $\{(^{i}Pr_2\text{-ATI})AlMe\}_2(\mu\text{-Me})^+$ cation in **2b**. Selected bond distances (Å) and angles (deg): Al(1)−N(1) 1.865(2), Al(1)−N(2) 1.876(2), Al(2)−N(3) 1.881(2), Al(2)−N(4) 1.884(2), Al(1)−C(1) 2.177(3), Al(2)−C(1) 2.120(3), Al(1)−C(2) 1.949(3), Al(2)−C(16) 1.953(3), C(1)−H(1A) 0.92(3), C(1)−H(1B) 0.89(3), C(1)−H(1C) 0.96(3); N(1)−Al(1)−N(2) 86.07(9), N(3)−Al(2)−N(4) 85.58(9), Al(1)−C(1)−Al(2) 167.8(2), N(1)−Al(1)−C(1) 109.0(1), N(1)−Al(1)−C(2) 122.2(1), N(2)−Al(1)−C(1) 110.2(1), N(2)−Al(1)−C(2) 119.0(1), C(1)−Al(1)−C(2) 108.5(1), N(3)−Al(2)−C(1) 112.7(1), N(3)−Al(2)−C(16) 120.4(1), N(4)−Al(2)−C(1) 110.3(1), N(4)−Al(2)−C(16) 118.0(1), C(1)−Al(2)−C(16) 108.3(1).

$[B(C_6F_5)_4]$ salts (**4c**−**e**) and the corresponding olefin (eq 7). Pale yellow-green powders of **4c**−**e** precipitate after extensive



(7)

washing of the benzene (toluene) clathrates which form during the reaction, or when the reaction is conducted in hexane or pentane. Compounds **4c**−**e** are stable at room temperature as benzene or toluene clathrates and in C_6H_5Cl solution, but decompose to unidentified species in CH_2Cl_2.

Recrystallization of **4c** from chlorobenzene at −40 °C yields yellow crystals of the PhCl complex $[(^{i}Pr_2\text{-ATI})Al(Et)(ClPh)][B(C_6F_5)_4]$ (**4c**(ClPh)) which also contain 0.5 equiv of noncoordinated PhCl of crystallization. This material readily loses PhCl and is converted to base-free **4c** upon exposure to vacuum. The structure of the **4c**(ClPh) unit (Figure 3) consists of a distorted tetrahedral $(^{i}Pr_2\text{-ATI})Al(Et)(ClPh)^+$ cation that is weakly ion-paired to the $B(C_6F_5)_4^-$ anion. The Al−Cl distance (2.540(3) Å) is somewhat longer than the Al−(μ-Cl) distances in Cl-bridged dialuminum complexes (2.2−2.5 Å)[1a,30] or the sum of the Al and Cl covalent radii (2.24 Å), but is far shorter than the sum of Al and Cl van der Waals (vdW) radii (3.8 Å),[31] consistent with a dative Al−ClPh bond. The Al−ClPh interaction does not significantly perturb the C−Cl bond distance

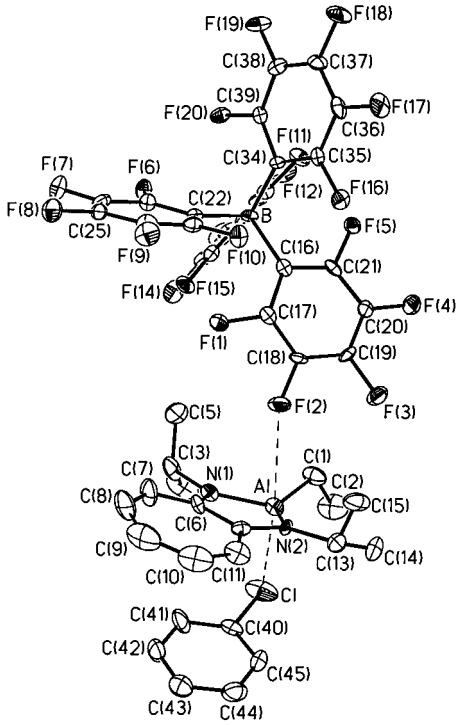


Figure 3. Structure of the $[(^{i}Pr_2\text{-ATI})Al(Et)(ClPh)][B(C_6F_5)_4]$ unit in **4c**(ClPh)·0.5PhCl. Selected bond distances (Å) and angles (deg): Al−N(1) 1.827(6), Al−N(2) 1.850(5), Al−C(1) 1.919(7), Al−Cl 2.540(3), C(40)−Cl 1.774(7); N(1)−Al−N(2) 87.8(2), Al−Cl−C(40) 102.7(2), Al−C(1)−C(2) 119.4(6), N(1)−Al−C(1) 129.3(3), N(1)−Al−Cl 99.4 (2), N(2)−Al−C(1) 133.8(3), N(2)−Al−Cl 99.3(2), C(1)−Al−Cl 99.9(2). Hydrogen atoms are omitted.

(1.774(7) Å vs 1.737(5) Å in free PhCl in the gas phase)[32] but does induce a significant displacement (0.31 Å) of the Al atom out of the N(1)−N(2)−C(1) plane (Σ of the angles at Al = 350.9°). Additionally, the PhCl phenyl ring is positioned close to the $^{i}Pr_2$-ATI ligand in an orientation that permits an attractive π-stacking interaction.[33] The distances between PhCl carbon atoms and the plane of the $^{i}Pr_2$-ATI ligand are between 3.3 and 4.0 Å, and the PhCl ring is shifted to one side of the $^{i}Pr_2$-ATI ligand such that the electron-deficient PhCl ipso carbon lies under the electron-rich N(2) atom (C(40)- - -N(2) 3.39 Å), and the centroid of the PhCl phenyl ring lies under one of the electron-deficient $^{i}Pr_2$-ATI iminato carbon atoms (centroid- - -C(12) = 3.66 Å). The Al−Cl−Ph angle is 102.7(2)° and the angle between the PhCl and $^{i}Pr_2$-ATI planes is 17.1°. The closest Al−F contact to the anion (Al- - -F(2); 3.23 Å) is close to the sum of the Al and F vdW radii (3.52 Å),[31] indicating that the cation−anion interaction is extremely weak.[34,35]

Variable-temperature multinuclear NMR spectra of **4c** in C_6D_5Cl (to −40 °C) and CD_2Cl_2 (to −90 °C) establish that the $(^{i}Pr_2\text{-ATI})AlEt^+$ cation retains effective C_{2v} symmetry and that ion-pairing interactions are not significant enough to perturb the spectra of the $B(C_6F_5)_4^-$ anion in these chlorocarbon

(30) Representative examples: (a) $[(BHT)AlMe(\mu\text{-Cl})]_2$ (BHT = 2,6-bis-*tert*-butyl-4-methylphenoxide; Al−Cl 2.277(3) and 2.291(3) Å): Healy, M. D.; Ziller, J. W.; Barron, A. R. *Organometallics* **1992**, *11*, 3041. (b) $[(ArO)AlMe(\mu\text{-Cl})]_2$ (Ar = 2,6-bis-*tert*-butylphenyl; Al−Cl 2.298(2) Å): Jegier, J. A.; Atwood, D. A. *Bull. Soc. Chim. Fr.* **1996**, *133*, 965.

(31) The covalent and van der Waals radii for Al (1.25 and 2.05 Å) were taken from ref 1a, p 2, and those for F (0.64 and 1.47 Å) and Cl (0.99 and 1.75 Å) were taken from the following: Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89.

(32) Penionzhkevich, N. P.; Sadova, N. I.; Vilkov, L. V. *Zh. Struct. Khim.* **1979**, *20*, 527.

(33) Hunter, C. A.; Sanders, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.

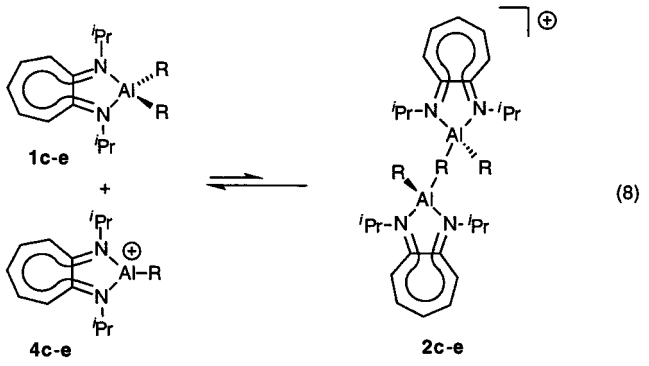
(34) The Re PhCl complexes $[(C_5R_5)Re(NO)(PPh_3)(ClPh)][BF_4]$ (C_5R_5 = C_5H_5, C_5Me_5) have been characterized in C_6H_5Cl/C_6D_5Cl solution by multinuclear NMR. These species exist predominantly as Cl-ligated isomers at −45 °C, but other isomers are also observed at higher temperatures. (a) Peng, T.-S.; Winter, C. H.; Gladysz, J. A. *Inorg. Chem.* **1994**, *33*, 2534. (b) Kowalczyk, J. J.; Agbossou, S. K.; Gladysz, J. A. *J. Organomet. Chem.* **1990**, *397*, 333.

(35) For a review of fluorocarbon coordination chemistry see: Plenio, H. *Chem. Rev.* **1997**, *97*, 3363.

solvents.[36] On the basis of the X-ray and solution NMR data we conclude that in chlorocarbon solution the (^{i}Pr$_2$-ATI)AlR$^+$ cations of **4c**−**e** exist as RCl adducts which undergo fast RCl exchange.

The structures of "base-free" **4c**−**e** in aromatic solvents or in the solid state are uncertain.[37] The most likely situation is that these cations are monomeric and weakly solvated and/or ion-paired in aromatic solvents and more strongly ion-paired in the solid state. However, dinuclear dicationic structures with bridging ^{i}Pr$_2$-ATI or R ligands are also possible. Two lines of evidence suggest that **4c**−**e** are monomeric in aromatic solvents. First, the $^1J_{CH}$ values for the Al-*C*H$_2$ carbons of **4c**−**e** in C_6D_6 or toluene-d_8 liquid clathrates are in the same range as those in chlorinated solvents (115−120 Hz). In particular, the Al-*C*H$_2$ $^1J_{CH}$ value for **4c** (119 Hz, C_6D_6 or toluene-d_8, 25 °C) is close to the $^1J_{CH}$ value of the Al-Et$_{term}$ methylene carbon of (Et$_2$Al)$_2$-(μ-Et)$_2$ (114 Hz, CD_2Cl_2, −90 °C) rather than to that of the Al-Et$_{bridge}$ (106 Hz).[38] These data support the presence of terminal alkyl ligands in **4c**−**e**. Additional evidence against dinuclear dicationic structures is provided by experiments in which **1c**, **1e**, and [Ph$_3$C][B(C$_6$F$_5$)$_4$] were mixed in 1:1:2 ratio in C_6D_5Cl and C_6D_6. In both cases, *only* signals of **4c** and **4e** were observed by NMR; if these species were dimeric, new resonances or shifts in resonances due to the presence of the "mixed" species [(^{i}Pr$_2$-ATI)$_2$Al$_2$(Et)(^{i}Bu)]$^{2+}$ would be expected. There is no evidence for agostic Al- - -HC interactions in these cationic Al alkyls.

The ^{1}H and ^{13}C NMR spectra of CD_2Cl_2 solutions of **4c**−**e** containing 1 equiv of **1c**−**e**, respectively, each contain only one set of ^{i}Pr$_2$-ATI and Al-R signals which are very close to the weighted average of the corresponding signals of the two components down to −90 °C. Similar results are obtained for solutions of **4c**−**e** and **1c**−**e** generated in situ by the reaction of **1c**−**e** with 0.5 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$]. These results are indicative of fast alkyl exchange between the (^{i}Pr$_2$-ATI)AlR$^+$ cations and (^{i}Pr$_2$-ATI)AlR$_2$ dialkyls, presumably via μ-R intermediates (**2c**−**e**, eq 8). It is possible to separate **1c**−**e** from



(8)

1c−**e**/**4c**−**e** mixtures simply by washing the mixture with hexanes to extract the neutral dialkyl complex. The poorer bridging ability of the higher alkyls versus Me is responsible for the lower stability of **2c**−**e** versus the Me-bridged analogue **2b**.

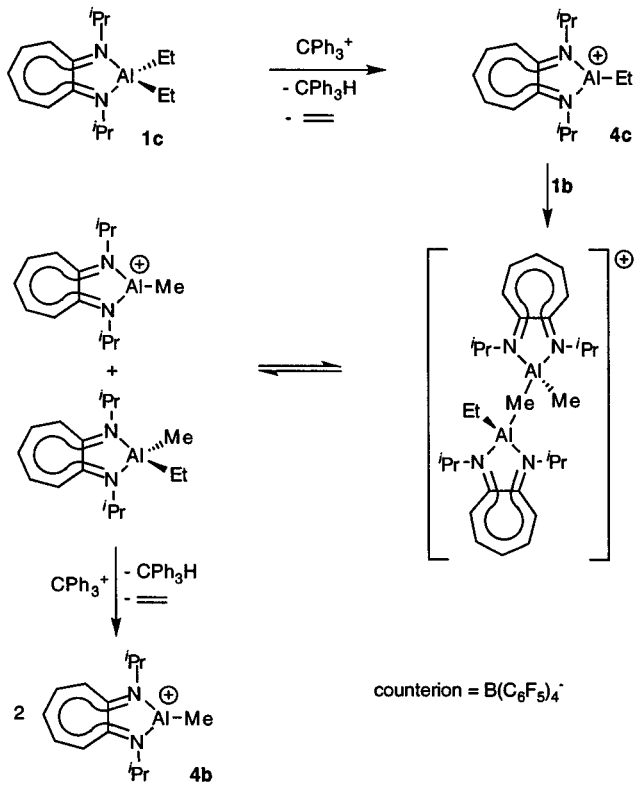
Synthesis of [(^{i}Pr$_2$-ATI)AlMe][B(C$_6$F$_5$)$_4$] (4b). It is possible to exploit the poorer bridging ability of the Et group (vs Me) and the β-H abstraction from Al-Et groups by Ph$_3$C$^+$ to prepare

(36) The ^{13}C, ^{11}B, and ^{19}F NMR spectra for the B(C$_6$F$_5$)$_4^-$ anion in **4c**−**e** are identical to those for [Ph$_3$C][B(C$_6$F$_5$)$_4$].

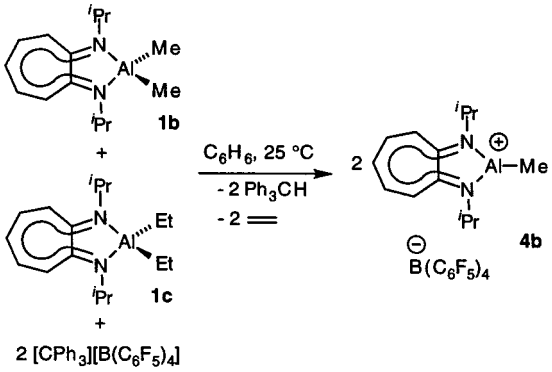
(37) Cryoscopic molecular weight and conductivity studies of **4c**−**e** in benzene are precluded by the formation of clathrates.

(38) Olah, G. A.; Prakash, G. K. S.; Liang, G.; Henold, K. L.; Haigh, G. B. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *74*, 5217.

Scheme 1



the mononuclear (^{i}Pr$_2$-ATI)AlMe$^+$ cation. Thus, [(^{i}Pr$_2$-ATI)-AlMe][B(C$_6$F$_5$)$_4$] (**4b**) forms when **1b**, **1c**, and [CPh$_3$][B(C$_6$F$_5$)$_4$] are mixed in 1:1:2 stoichiometry (eq 9). As summarized in



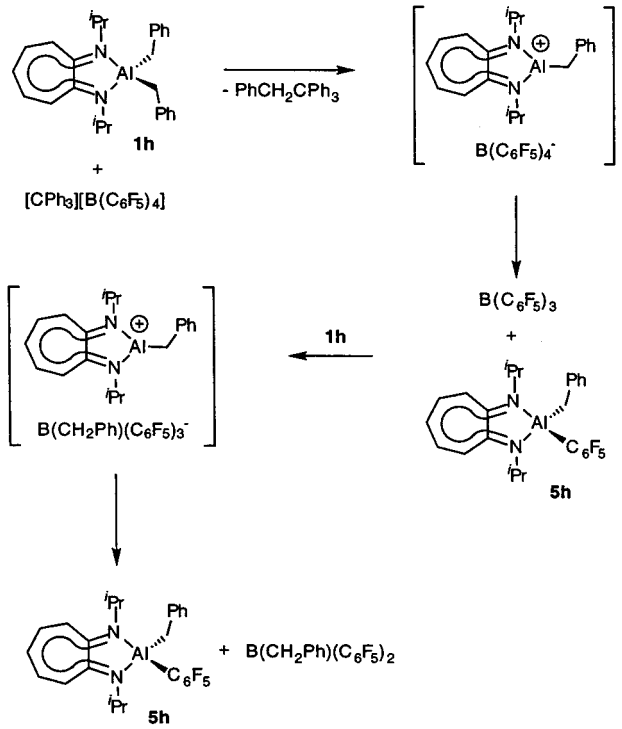
(9)

Scheme 1, this reaction probably proceeds by initial β-H abstraction from **1c** by Ph$_3$C$^+$ to produce (^{i}Pr$_2$-ATI)AlEt$^+$, methyl transfer from **1b** to produce (^{i}Pr$_2$-ATI)AlMe$^+$ and (^{i}Pr$_2$-ATI)Al(Me)(Et), and β-H abstraction from the latter species by Ph$_3$C$^+$ to produce a second equivalent of (^{i}Pr$_2$-ATI)AlMe$^+$.[39] **4b** separates as a clathrate from benzene solution and can be isolated in high yield as a solid after extensive washing of the clathrate with hexanes. The properties of **4b** are very similar to those of **4c**−**e**.

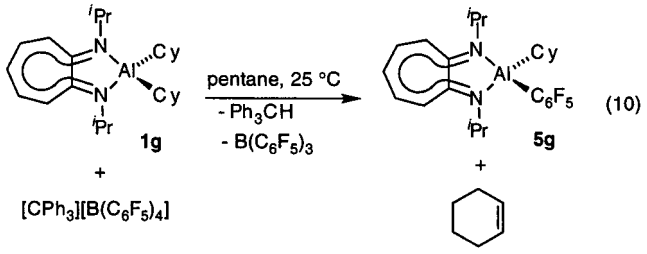
Generation and Fate of Cationic Al Cyclohexyl and Benzyl Species. Compound **1g** reacts with [Ph$_3$C][B(C$_6$F$_5$)$_4$] in pentane at 25 °C to give pentane-soluble (^{i}Pr$_2$-ATI)Al(Cy)(C$_6$F$_5$) (**5g**, eq 10). This reaction proceeds by initial formation of the transient base-free complex [(^{i}Pr$_2$-ATI)AlCy][B(C$_6$F$_5$)$_4$],[40] followed by abstraction of a C$_6$F$_5^-$ group from the anion.[24] No

(39) It is also possible that the Me-bridged intermediate (^{i}Pr$_2$-ATI)Al-(Me)(μ-Me)Al(Et)(^{i}Pr$_2$-ATI)$^+$ is stable and undergoes reaction with Ph$_3$C$^+$ without dissociation.

Scheme 2

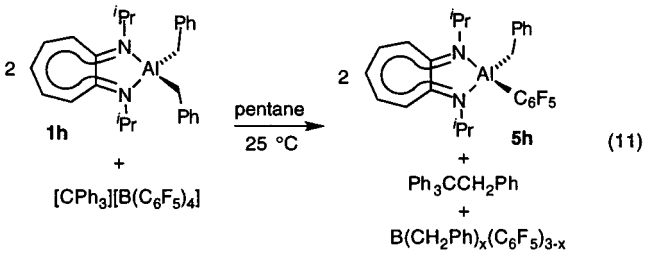


further reaction between **5g** and $B(C_6F_5)_3$ is observed at 25 °C in benzene. The ^{1}H and ^{13}C NMR spectra of **5g** are consistent with C_s symmetry. The ^{19}F NMR spectrum of the product



(10)

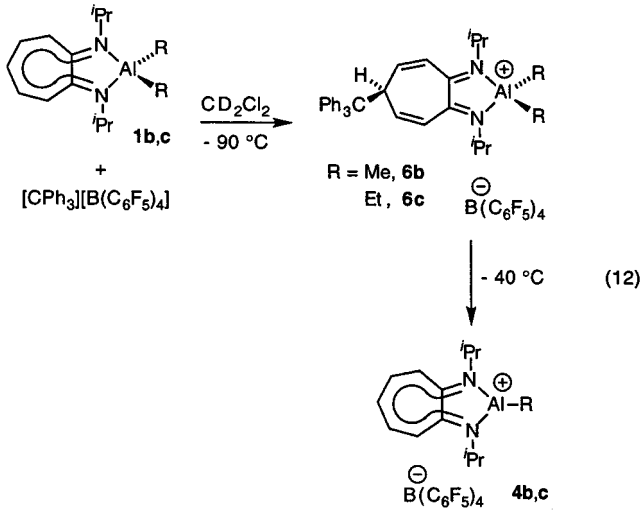
mixture contains two sets of C_6F_5 signals in 1:3 intensity ratio which are assigned to **5g** and $B(C_6F_5)_3$, respectively. The reaction of **1h** and $[Ph_3C][B(C_6F_5)_4]$ in 2:1 stoichiometry results in the formation of pentane-soluble (^{i}Pr$_2$-ATI)Al(CH_2Ph)(C_6F_5) (**5h**, eq 11). As summarized in Scheme 2, this reaction proceeds



(11)

by initial abstraction of a benzyl group from **1h** by Ph_3C^+ to form 1 equiv of the transient base-free complex [(^{i}Pr$_2$-ATI)-Al(CH_2Ph)][$B(C_6F_5)_4$], which undergoes rapid $C_6F_5^-$ transfer to yield **5h** and $B(C_6F_5)_3$. The $B(C_6F_5)_3$ coproduct reacts with the second equivalent of **1h** to give the unstable intermediate [(^{i}Pr$_2$-ATI)Al(CH_2Ph)][$B(CH_2Ph)(C_6F_5)_3$], which decomposes by $C_6F_5^-$ transfer to **5h** and $B(CH_2Ph)(C_6F_5)_2$. In the 1:1 stoichiometric reaction, 0.5 equiv of $[Ph_3C][B(C_6F_5)_4]$ remains unreacted and can be separated from the pentane-soluble products. In this case, $B(C_6F_5)_3$ reacts more rapidly with **1h** than does $[Ph_3C][B(C_6F_5)_4]$ because the latter reagent is insoluble in the reaction solvent (pentane), resulting in the 2:1 stoichiometry of the reaction. Under the reaction conditions, $B(CH_2Ph)(C_6F_5)_2$ undergoes ligand redistribution reactions resulting in a mixture of all possible $B(CH_2Ph)_x(C_6F_5)_{3-x}$ (x = 0−3) boranes with $B(CH_2Ph)(C_6F_5)_2$ being the major species.[41] No further reaction of **5h** and $[Ph_3C][B(C_6F_5)_4]$ or $B(C_6F_5)_3$ is observed at room temperature. The ^{1}H and ^{13}C NMR spectra of **5h** are consistent with C_s symmetry. The boranes $B(CH_2Ph)_x(C_6F_5)_{3-x}$ (x = 0−3) were identified by ^{1}H and ^{19}F NMR spectra of the reaction mixture.

Observation of an Intermediate in Reaction of (^{i}Pr$_2$-ATI)-AlR$_2$ Complexes with [Ph$_3$C][B(C$_6$F$_5$)$_4$]. Low-temperature NMR experiments show that **1b** and **1c** react with $[Ph_3C][B(C_6F_5)_4]$ at ca. −90 °C in CH_2Cl_2 via electrophilic attack of Ph_3C^+ at the ^{i}Pr$_2$-ATI C5 carbon to yield thermally unstable diimine intermediates {1,2-(N^{i}Pr)$_2$-5-CPh$_3$-cyclohepta-3,6-diene}AlR$_2^+$ (R = Me, **6b**; R = Et, **6c**; eq 12). The structures



(12)

of these species were assigned on the basis of the following key observations: (i) The C5 ^{13}C NMR resonance of **6b** appears at δ 51.8 with $^1J_{CH}$ = 138 Hz indicative of the loss of unsaturation at C5. Similarly the C5 resonance of **6c** appears at δ 52.0. In contrast, the C5 resonances of **1b**,**c** both appear at δ 119.2 with $^1J_{CH}$ = 159 Hz. (ii) The NMR spectra of **6b**,**c** each contain two ^{i}Pr Me resonances and one ^{i}Pr methine resonance, and resonances for two inequivalent Al−R groups, consistent with C_s symmetry. (iii) Signals corresponding to Ph_3CMe (reaction of **1b**) or Ph_3CH and ethylene or Ph_3CEt (reaction of **1c**) are not observed. (iv) The NMR spectra of **6b**,**c** are similar to those of analogous Ga and In complexes {1,2-(N^{i}Pr)$_2$-5-CPh$_3$-cyclohepta-3,6-diene}MMe$_2^+$ (M = Ga, In), which have been characterized by X-ray crystallography.[42]

In the temperature range −40 to −30 °C, **6b**,**c** decompose to **4b**,**c**, most likely via dissociation of Ph_3C^+ followed by Me or β-H abstraction. In the case of R = Me, the ratio of **1b** and $[Ph_3C][B(C_6F_5)_4]$ was set to 2:1, and a 1:1 mixture of **6b** and **1b** was formed at −90 °C; warming this mixture to −30 °C produced dinuclear **2b** rather than base-free **4b**. It is likely that

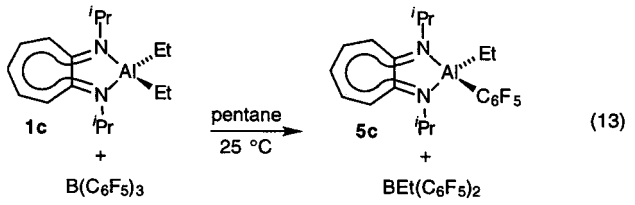
(40) The reaction of (^{i}Pr$_2$-ATI)AlCy$_2$ with $[Ph_3C][B(C_6F_5)_4]$ in pentane produces a transient yellow precipitate that dissolves after ca. 1 h. The yellow compound may be [(^{i}Pr$_2$-ATI)AlCy][$B(C_6F_5)_4$].

(41) The ligand redistribution reaction of $B(CH_2Ph)(C_6F_5)_2$ was observed previously: Horton, A. D.; de With, J. *Organometallics* **1997**, *16*, 5424.

(42) Dagorne, S.; Delpech, F.; Guzei, I. A.; Jordan, R. F. Unpublished results.

analogous intermediates are formed in the reactions of **1d**,**e**,**g**,**h** and Ph_3C^+.

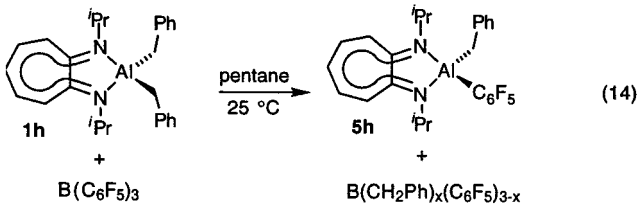
Reaction of (^{i}Pr$_2$-ATI)AlR$_2$ Complexes with B(C$_6$F$_5$)$_3$. We tested the utility of $B(C_6F_5)_3$ as an alkyl abstraction reagent in the (^{i}Pr$_2$-ATI)AlR$_2$ systems by investigating two representative cases. The reaction of diethyl complex **1c** with 1 equiv of $B(C_6F_5)_3$ in pentane yields a 1:1 mixture of (^{i}Pr$_2$-ATI)Al(Et)-(C_6F_5) (**5c**) and B(Et)(C_6F_5)$_2$ (eq 13). Presumably, [(^{i}Pr$_2$-ATI)-



(13)

AlEt][BEt(C_6F_5)$_3$] forms in this reaction initially, but decomposes to the observed products by $C_6F_5^-$ transfer. No further reaction of **5c** and B(Et)(C_6F_5)$_2$ is observed at 25 °C in benzene. The ^{1}H and ^{13}C NMR spectra of **5c** are consistent with C_s symmetry. The ^{19}F NMR spectrum of the product mixture contains two sets of C_6F_5 signals in 1:2 intensity ratio which are assigned to **5c** and B(Et)(C_6F_5)$_2$, respectively.[43]

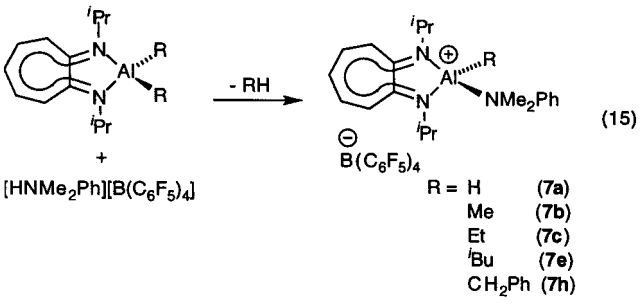
Similarly, the reaction of dibenzyl compound **1h** with 1 equiv of $B(C_6F_5)_3$ in pentane yields a mixture of **5h** and B(CH_2Ph)$_x$-(C_6F_5)$_{3-x}$ ($x = 0-3$, eq 14). Compound **5h** is much more soluble



(14)

than the borane coproducts in toluene/pentane solution at −37 °C, and was isolated in 70% yield. The Al and B species formed in eq 14 are identical to those formed in eq 11. This result facilitates assignment of the NMR signals of the mixture obtained in reaction 11 and supports the mechanism proposed in Scheme 2. These results show that RB(C_6F_5)$_3^-$ anions (R = Et, CH_2Ph) are too reactive to be compatible with (^{i}Pr$_2$-ATI)-AlR$^+$ cations.

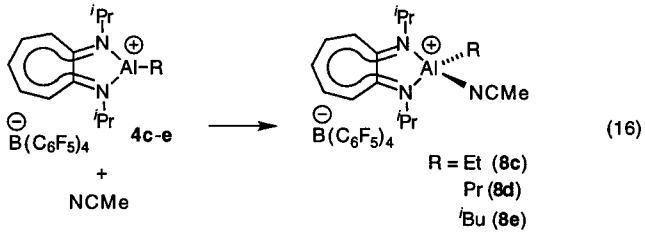
Reaction of (^{i}Pr$_2$-ATI)AlR$_2$ Complexes with [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]. The reaction of (^{i}Pr$_2$-ATI)AlR$_2$ complexes **1a**−**c**,**e**,**h** with [$HNMe_2Ph$][B(C_6F_5)$_4$] proceeds by clean Al−R bond protonolysis to afford [(^{i}Pr$_2$-ATI)AlR(NMe_2Ph)][B(C_6F_5)$_4$] (**7a**−**c**,**e**,**h**, eq 15). These amine complexes are soluble and very



(15)

stable in C_6D_5Cl and CD_2Cl_2 at ambient temperature. The ^{1}H and ^{13}C NMR spectra of **7a**−**c**,**e**,**h** are consistent with C_s symmetry. These cationic species do not react further with excess $HNMe_2Ph^+$ at ambient temperature.

Reaction of (^{i}Pr$_2$-ATI)AlR$^+$ Cations with Acetonitrile. The reaction of **4c**−**e** with acetonitrile yields simple [(^{i}Pr$_2$-ATI)Al-(R)(NCMe)][B(C_6F_5)$_4$] adducts (**8c**−**e**, eq 16). Compound **8c**



(16)

is isolated as a yellow crystalline solid. Unlike the base-free precursor **4c**, **8c** is stable in CH_2Cl_2 solution at 25 °C. Remarkably, chlorobenzene solutions of **8c** show no sign of reaction after 16 h at 180 °C (sealed tube). In contrast, neutral alkylaluminum compounds generally react with nitriles by insertion, C−H activation, or β-H transfer under similar conditions.[44,45] For example, $AlEt_3$(NC^tBu) undergoes β-H transfer to produce {$AlEt_2$(μ-N=CH^tBu)}$_2$ (80% yield) and ethylene at 155 °C. The MeCN adduct, $AlEt_3$(NCMe), reacts at 110−130 °C predominantly by ethane elimination to produce polymeric ($Et_2AlCH_2C{\equiv}N)_n$; the insertion product {$AlEt_2$-(μ-N=CMeEt)}$_2$ is formed as a minor product (18%).[44b]

The ^{1}H and ^{13}C NMR spectra of **8c** in C_6D_5Cl in the absence of excess MeCN each exhibit two ^{i}Pr Me resonances, one ^{i}Pr methine resonance and a resonance for coordinated MeCN (^{1}H: δ 1.77), consistent with C_s symmetry. However, in the presence of even trace amounts of excess MeCN, the two ^{i}Pr Me resonances are collapsed to a single resonance, and only a single MeCN resonance is observed, which is indicative of time-averaged C_{2v} symmetry due to fast exchange of free and coordinated MeCN by an associative mechanism. For example, **8c** exhibits time-averaged C_{2v} symmetry in the presence of less than 1 mol % excess MeCN even at −90 °C in CD_2Cl_2 solution.

The molecular structure of the (^{i}Pr$_2$-ATI)Al(Et)(NCMe)$^+$ cation of **8c** is shown in Figure 4. The Al−NCMe bond in **8c** (Al−N(3) 1.955(1) Å) is ca. 0.06 Å shorter and the C(16)−Al−N(3) angle (103.82(7)°) is nearly identical with the corresponding parameters in Me_3Al(NCMe) (2.02(1) Å, 102.0-(5)°).[46] The Al−N(1) (1.856(1) Å) and Al−N(2) (1.854(1) Å) bonds involving the ^{i}Pr$_2$-ATI ligand of **8c** are ca. 0.06 Å shorter than corresponding bonds in (^{i}Pr$_2$-ATI)$AlMe_2$ (1.915(1) Å),[21a] but are very close to those in the dinuclear cation [{(^{i}Pr$_2$-ATI)-AlMe}$_2$(μ-Me)]$^+$ of **2b**.[22a] The structure of the B(C_6F_5)$_4^-$ anion is normal.

Reaction of (^{i}Pr$_2$-ATI)AlR$^+$ Cations with Acetone. Compound **4c** reacts with 1 equiv of acetone to yield the acetone adduct **9c** (Scheme 3). The solution behavior of **9c** is similar to that of MeCN adduct **8c**. Thus, the ^{1}H and ^{13}C NMR spectra of **9c** in the absence of excess acetone each exhibit two ^{i}Pr Me resonances, one ^{i}Pr methine resonance, and a resonance for coordinated acetone, while in the presence of even a slight (4%) excess of acetone, the two ^{i}Pr Me resonances collapse to a single resonance, and only one acetone resonance is observed. This results are consistent with associative intermolecular acetone exchange. Compound **9c** is slowly (3 days, 23 °C, CD_2Cl_2)

(43) B(Et)(C_6F_5)$_2$ was characterized previously: Parks, D. J.; Piers, W. E.; Yap, G. P. A. *Organometallics* **1998**, *17*, 5492.

(44) (a) Lloyd, J. E.; Wade, K. *J. Chem. Soc.* **1965**, 2662. (b) Jennings, J. R.; Lloyd, J. E.; Wade, K. *J. Chem. Soc.* **1965**, 5083. (c) Jensen, J. A. *J. Organomet. Chem.* **1993**, *456*, 161.

(45) McDonald, W. S. *Acta Crystallogr.* **1969**, *B25*, 1385.

(46) Atwood, J. L.; Seale, S. K.; Roberts, D. H. *J. Organomet. Chem.* **1973**, *51*, 105.

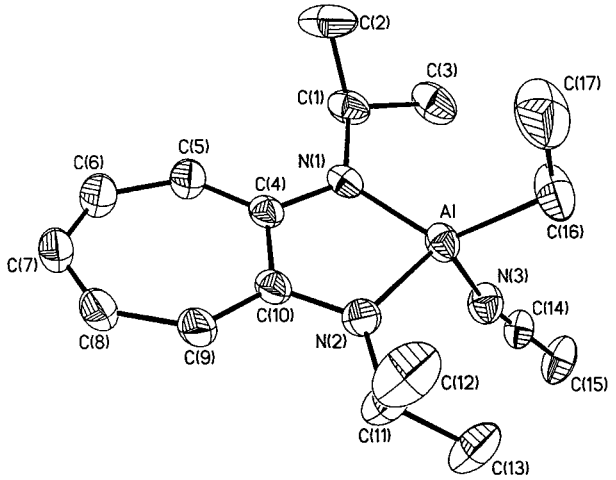
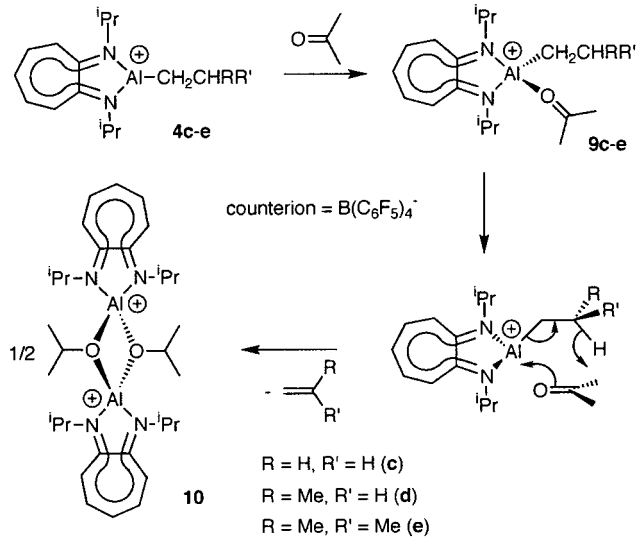


Figure 4. Structure of the (^{i}Pr$_2$-ATI)Al(Et)(NCMe)$^+$ cation in **8c**. Selected bond distances (Å) and angles (deg): Al−N(1) 1.856(1), Al−N(2) 1.854(1), Al−N(3) 1.955(1), Al−C(16) 1.942(2), N(3)−C(14) 1.135(2); N(1)−Al−N(2) 87.04(5), Al−N(3)−C(14) 169.9(1), Al−C(16)−C(17) 116.0(1), N(1)−Al−C(16) 125.68(8), N(1)−Al−N(3) 106.50(6), N(2)−Al−C(16) 122.60(8), N(2)−Al−N(3) 109.88(6), C(16)−Al−N(3) 103.82(7). Hydrogen atoms are omitted.

Scheme 3



converted to isopropoxide complex **10** in quantitative yield by net β-H transfer with release of ethylene (Scheme 3). Complexes **4d** and **4e** react with acetone in a similar manner; however, the corresponding intermediates **9d** and **9e** are less stable than **9c**, and are completely converted to **10** within 5 h at 23 °C in C_6D_5Cl.

For comparison, $AlEt_3$ reacts with diethyl ketone by competitive ketone insertion into the Al−Et bond, β-H transfer, and enolization; the product ratio depends on the $AlEt_3$/ketone ratio.[47] The monomeric Al alkyls $(BHT)_xAlEt_{3-x}$ (BHT = 2,6-di-*tert*-butyl-4-methylphenoxide) react with enolizable ketones by enolization and subsequent aldol condensation.[48]

Unlike **9c**,**d**, **10** is insoluble in C_6H_5Cl and only sparingly soluble in CH_2Cl_2. An X-ray crystallographic analysis established that **10** crystallizes from CH_2Cl_2 as the complex salt

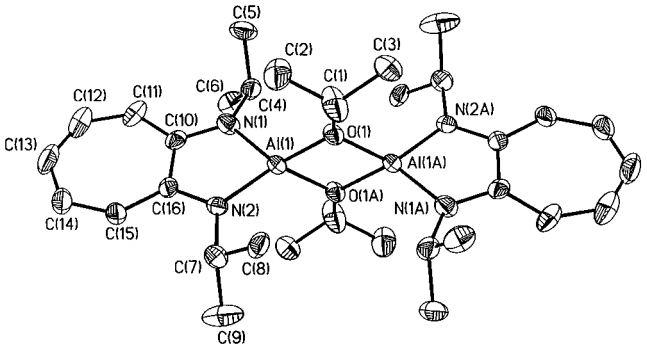


Figure 5. Structure of the {(^{i}Pr$_2$-ATI)Al(μ-O^{i}Pr)}$_2^{2+}$ dication in **10**·$2CD_2Cl_2$. Selected bond distances (Å) and angles (deg): Al(1)−N(1) 1.820(3), Al(1)−N(2) 1.832(3), Al(1)−O(1) 1.809(2), Al(1)−O(1A) 1.817(3), Al(1)−Al(1A) 2.774(2), O(1)−C(1) 1.508(5); N(1)−Al(1)−N(2) 89.0(1), O(1)−Al(1)−O(1A) 80.2(1), N(1)−Al(1)−O(1) 123.3-(1), N(1)−Al(1)−O(1A) 118.4(1), N(2)−Al(1)−O(1) 124.3(1), N(2)−Al(1)−O(1A) 126.3(1), Al(1)−O(1)−Al(1A) 99.8(1), Al(1)−O(1)−C(1) 131.0(2), Al(1A)−(1)−C(1) 127.6(2). Hydrogen atoms are omitted.

[{(^{i}Pr$_2$-ATI)Al(μ-O^{i}Pr)}$_2$][B(C$_6$F$_5$)$_4$]$_2$·$2CH_2Cl_2$ (**10**·$2CH_2Cl_2$). The structure of the dinuclear cation of **10** is shown in Figure 5. The planar Al_2O_2 ring features an acute O(1)−Al(1)−O(1A) angle (80.2(1)°) and an obtuse Al(1)−O(1)−Al(1A) angle (99.8-(1)°), and is nearly perpendicular to the ATI rings (angle between planes 93.2°). The Al−N bond distances (Al(1)−N(1) 1.820(3), Al(1)−N(2) 1.832(3) Å) are ca. 0.05 Å shorter than those in {(^{i}Pr$_2$-ATI)AlMe}$_2$(μ-Me)$^+$,[22a] and ca. 0.09 Å shorter than those in (^{i}Pr$_2$-ATI)AlMe$_2$.[21a] The Al−O bond distances (Al(1)−O(1) 1.809(2), Al(1)−O(1A) 1.817(3) Å) are similar to those in neutral aluminum μ-OR compounds.[25c,49] The geometry at the oxygens is almost planar (sum of angles around O(1) = 358.4°) as normally observed in alkoxy-bridged aluminum compounds.[49,50] The dinuclear structure of the cation explains the low solubility of **10**.

Reactions of (^{i}Pr$_2$-ATI)AlR$^+$ Cations with *tert*-Butyl Acetylene. Compounds **4c**−**e** catalytically dimerize *tert*-butyl acetylene to the head-to-tail dimer 2-*tert*-butyl-5,5-dimethyl-1-hexen-3-yne (**11**, C_6D_5Cl, 23 °C, ca. 4 t.o./h, >90% selectivity for **11**) as shown in Scheme 4.[51] Support for the mechanism in Scheme 4 is provided by the following observations from NMR and GC-MS studies of stepwise reactions. (i) **4c** reacts with 1 equiv of ^{t}BuC≡CH by β-H transfer to yield cationic vinyl compound **12** and ethylene quantitatively. **12** is stable in C_6D_5Cl solution at 23 °C in the absence of ^{t}BuC≡CH. The trans stereochemistry is established by a vinyl $^3J_{HH}$ value of 21 Hz.[52] (ii) **12** reacts with additional ^{t}BuC≡CH by σ-bond metathesis to yield alkynyl complex **13** and *tert*-butyl ethylene, followed by ^{t}BuC≡CH insertion to yield **14**. When **12** is reacted with 1 equiv of ^{t}BuC≡CH, a 4:1:1 mixture of **13**, **14**, and unreacted **12** is formed, indicating that the two reactions occur at similar rates. Removal of the volatiles from this reaction mixture followed by addition of C_6H_5Cl affords yellow crystalline **13**

(47) (a) Pasynkiewicz, S.; Dluzniewski, T.; Sonnek, G. *J. Organomet. Chem.* **1987**, *321*, 1. (b) Pasynkiewicz, S.; Sliwa, E. *J. Organomet. Chem.* **1965**, *3*, 121.

(48) (a) Power, M. B.; Bott, S. G.; Clark, D. L.; Atwood, J. L.; Barron, A. R. *Organometallics* **1990**, *9*, 3086. (b) Power, M. B.; Apblett, A. W.; Bott, S. G.; Atwood, J. L.; Barron, A. R. *Organometallics* **1990**, *9*, 2529.

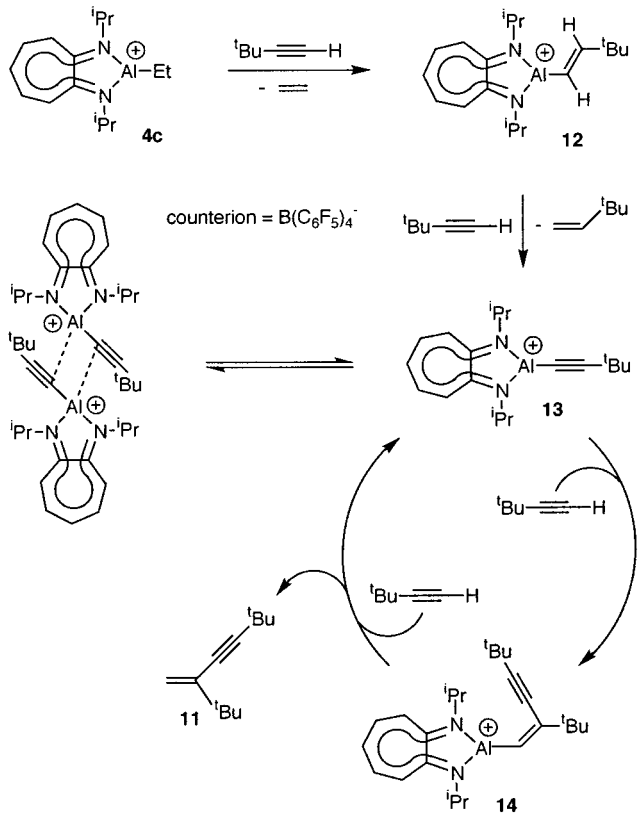
(49) (a) Turova, N. Ya.; Kozunov, V. A.; Yanovskii, A. I.; Bokii, N. G.; Struchkov, Yu. T.; Tarnopol'skii, B. L. *J. Inorg. Nucl. Chem.* **1979**, *41*, 5. (b) Wengrovius, J. H.; Garbauskas, M. F.; Williams, E. A.; Going, R. C.; Donahue, P. E.; Smith, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 982. (c) Cayton, R. H.; Chisholm, M. H.; Davidson, E. R.; DiStasi, V. F.; Du, P.; Huffman, J. C. *Inorg. Chem.* **1991**, *30*, 1020. (d) Kunicki, A.; Sadowski, R.; Zachara, J. *J. Organomet. Chem.* **1996**, *508*, 249.

(50) The preliminary communication (ref 22b) reported erroneous data on the sum of the angles around O(1).

(51) Small amounts of trimer and tetramer products were detected by GC-MS.

(52) Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*, 6th ed.; Wiley: New York, 1998.

Scheme 4



in 55% isolated yield (vide infra). (iii) The reaction of **12** with excess ^{t}BuC≡CH results in catalytic formation of **11**. (iv) Isolated **13** is insoluble in C_6D_5Cl, but dissolves in the presence of excess ^{t}BuC≡CH yielding **14** with catalytic formation of **11**. (v) The only Al species detected by NMR under catalytic conditions is **14**, indicating that this species is the resting state of the catalytic cycle.

The neutral bis-amidinate compound $\{PhC(NSiMe_3)_2\}_2AlH$,[53] MAO,[54] and a variety of early transition metal species[55] catalytically dimerize terminal alkynes by analogous mechanisms. For comparison, $AlEt_3$ reacts with RC≡CH (R = C_4H_9, C_5H_{11} and C_6H_{13}) at 20 °C predominantly by σ-bond metathesis to give $\{AlEt_2(\mu\text{-}C{\equiv}CR)\}_2$ (>80% yield) and RH along with minor amounts of insertion (both Markovnikov and *anti*-Markovnikov) and β-H transfer products.[56]

13 crystallizes from C_6H_5Cl as $[\{(^i Pr_2\text{-ATI})Al(\mu\text{-}C{\equiv}C^tBu)\}_2][B(C_6F_5)_4]_2\cdot 5PhCl$ (**13**·5PhCl). The dinuclear dication of **13**·5PhCl (Figure 6) consists of two (^{i}Pr$_2$-ATI)Al units linked by two unsymmetrical σ,π-alkynyl bridges. The short Al−C σ-bonds (Al(1)−C(14) 1.971(2) Å) are associated with a slightly bent Al−C≡C unit (Al(1)−C(14)−C(15) = 163.6(2)°). The long Al−C bonds (Al(1)−C(14A) 2.151(2) Å) are formed by donation of alkynyl π-electrons to an empty Al p orbital.[57] The C(14)−C(15) bond (1.217(3) Å) retains triple bond character. The Al_2C_2 plane is almost perpendicular to the ATI rings (angle between planes 93.6°). Similar structures have been observed for neutral dinuclear aluminum alkynyl compounds.[58,59]

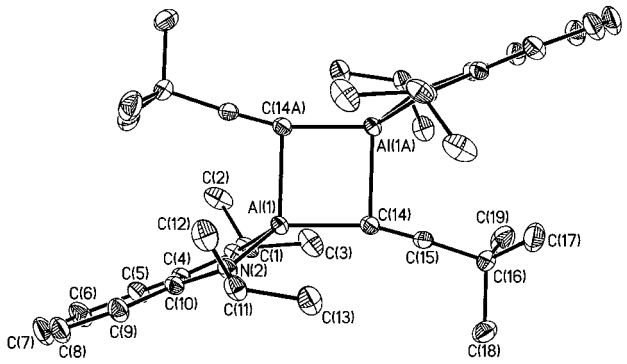


Figure 6. Structure of the $\{(^i Pr_2\text{-ATI})Al(\mu\text{-}C{\equiv}C^tBu)\}_2^{2+}$ dication in **13**·5C_6D_5Cl. Selected bond distances (Å) and angles (deg): Al(1)−N(1) 1.834(2), Al(1)−N(2) 1.837(2), Al(1)−C(14) 1.971(2), Al(1)−C(14A) 2.151(2), C(14)−C(15) 1.217(3); N(1)−Al(1)−N(2) 88.86(7), N(1)−Al(1)−C(14) 125.98(7), N(1)−Al(1)−C(14A) 112.12(7), N(2)−Al(1)−C(14) 125.01(7), N(2)−Al(1)−C(14A) 118.91(7), C(14)−Al(1)−C(14A) 88.49(7), Al(1)−C(14)−Al(1A) 91.51(7), Al(1)−C(14)−C(15) 163.6(2), Al(1A)−C(14)−C(15) 103.9(1), C(14)−C(15)−C(16) 176.8(2). Hydrogen atoms are omitted.

It is not established if the cations of **12**, **13**, and **14** exist in C_6D_5Cl solution as solvated mononuclear species (cf. **4c**(ClPh)) or dinuclear dicationic species with bridging alkynyl or alkenyl ligands (cf. solid-state structure of **13**); however, the former possibility is most probable given the catalytic activity observed.[59]

Reactions of (^{i}Pr$_2$-ATI)AlR$^+$ Cations with Olefins. It was observed that when **4c** was generated in benzene or toluene in closed vessels, the ethylene byproduct was completely polymerized after several hours at room temperature. These results prompted further studies of the reactions of (^{i}Pr$_2$-ATI)AlR$^+$ cations with ethylene. Neither the base-stabilized complexes (^{i}Pr$_2$-ATI)Al(R)(NMe$_2$Ph)$^+$ (**7a**−**c**,**e**) and (^{i}Pr$_2$-ATI)Al(R)(NCMe)$^+$ (**8c**) nor the dinuclear cationic species [{(^{i}Pr$_2$-ATI)Al}$_2$H$_3$]$^+$ and [{(^{i}Pr$_2$-ATI)AlMe}$_2$(μ-Me)]$^+$ react with ethylene (1 atm) at 25−80 °C in toluene or C_6H_5Cl. However, the base-free complexes **4c**,**e** (generated in situ, toluene, 80−100 °C, 1−5 atm of ethylene) polymerize ethylene with low activity (900−2600 g PE/mol·h·atm, M_n = 106 500 and M_w/M_n = 2.4). The yield and M_n values imply that, at most, only a small fraction (<1%) of Al centers produce polymer chains. The fate of the (^{i}Pr$_2$-ATI)AlR$^+$ species and the identity of the active catalyst species in bench scale polymerization experiments was not established. To probe the mechanism of the ethylene polymerization further, reactions were monitored by NMR.

^{1}H NMR monitoring of the reaction of **4c** with ethylene (1−8 equiv) in C_6D_5Cl at 25 °C shows that polyethylene is formed, but the spectrum of **4c** is not significantly changed and no significant new Al species are observed. However, NMR monitoring of the reaction of **4c** with ethylene-d_4 (ca. 8 equiv, 25 °C, 3 days) showed that the intensity of the Al-CH_2 signal of **4c** was reduced by ca. 22% due to deuterium incorporation at this site,[60] and a small broad peak appeared at δ 5.26 that was assigned to ethylene. Similarly, the reaction of **4e** and

(53) Duchateau, R.; Meetsma, A.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1996**, 223.

(54) Dash, A. K.; Eisen, M. S. *Org. Lett.* **2000**, *2*, 737.

(55) (a) Yoshida, M.; Jordan, R. F. *Organometallics* **1997**, *16*, 4508. (b) Horton, A. D. *J. Chem. Soc., Chem. Commun.* **1992**, 185 and references therein.

(56) Rienäcker, R.; Schwengers, D. *Liebigs Ann. Chem.* **1970**, *737*, 182.

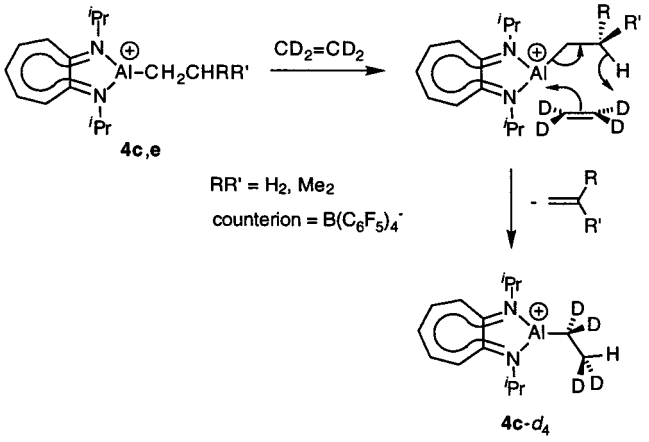
(57) Erker, G.; Albrecht, M.; Kruger, C.; Nolte, M.; Werner, S. *Organometallics* **1993**, *12*, 4979 and references therein.

(58) (a) Almenningen, A.; Fernholt, L.; Haaland, A. *J. Organomet. Chem.* **1978**, *155*, 245. (b) Stucky, G. D.; McPherson, A. M.; Rhine, W. E.; Eisch, J. J.; Considine, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 1941.

(59) The neutral dinuclear Al alkenyl complex $\{Al(^iBu)_2(\mu\text{-}CH{=}CH^tBu)\}_2$ was characterized by X-ray crystallography. Albright, M. J.; Butler, W. M.; Anderson, T. J.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1976**, *98*, 3995.

(60) The intensities of the ATI-ring ^{1}H NMR resonances of **4c** are unchanged. Due to the presence of poly(ethylene-d_4) gel in the NMR tube, the $AlCH_2CH_3$, $NCHMe_2$ (and probably polyethylene) signals were overlapped in a broad peak, preventing accurate integration.

Scheme 5

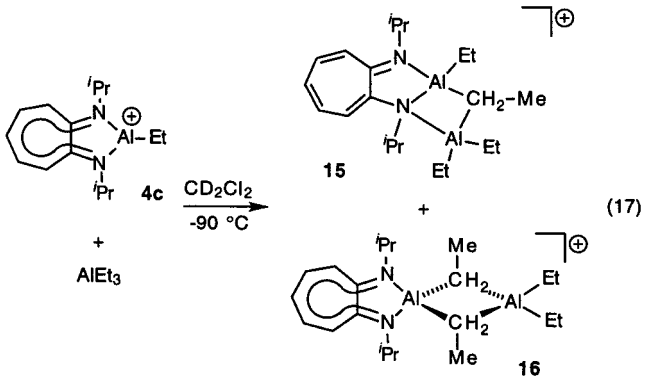


ethylene-d_4 (3 equiv, 25 °C) yields [(^{i}Pr$_2$-ATI)AlCD$_2$CD$_2$H][B(C$_6$F$_5$)$_4$] (**4c**-d_4), poly(ethylene-d_4), and polyisobutylene. The ^{1}H NMR spectrum of this reaction after 8 h contains signals for **4c**-d_4, but not for **4e**, and the ^{13}C NMR spectrum contains an AlCD$_2$*C*D$_2$H resonance at δ 6.9 with a characteristic $^1J_{CD}$ of 20 Hz for **4c**-d_4, which is isotopically shifted ca. 0.7 ppm upfield versus the corresponding signal for **4c**.[52] Control experiments show that **4c** polymerizes isobutylene under these conditions, presumably by a cationic mechanism, without formation of **4e**. These results show that the predominant reaction of **4c** and **4e** with ethylene-d_4 is β-H transfer to yield **4c**-d_4 and ethylene or isobutylene (Scheme 5). This observation is consistent with recent ab initio calculations for a model aluminum amidinate complex {HC(NH)$_2$}AlCH$_2$CH$_3^+$, which showed that β-H transfer from the Al-Et group to ethylene has a lower energy barrier than ethylene insertion, β-H transfer to Al to produce {HC(NH)$_2$}AlH$^+$ and ethylene, or σ-bond metathesis to produce {HC(NH)$_2$}AlCH=CH$_2^+$ and ethane.[61] Computational studies also predict a high barrier to ethylene insertion in {MeC(NMe)$_2$}AlMe$^+$.[62] We conclude that intact (^{i}Pr$_2$-ATI)AlR$^+$ are not active ethylene polymerization catalysts, and that the observed polymerization is due to a minor as yet unidentified species in solution. Further work on this issue is in progress.

Polymerization of Propylene Oxide by (^{i}Pr$_2$-ATI)AlR$^+$ Cations. Compound **4e** polymerizes propylene oxide (PO). The reaction of **4e** with a ca. 500-fold excess of PO in toluene is very exothermic and yields atactic poly(propylene oxide) with activity of 240 t.o./h. The neutral diethyl complex **1c** does not polymerize PO under these conditions. This reaction was not studied in further detail.

Polymerization of Methyl Methacrylate by {(^{i}Pr$_2$-ATI)Al}$_2$H$_3^+$ (2a). The dinuclear cationic hydride complex **2a** completely polymerizes a ca. 450-fold excess of methyl methacrylate (MMA) in 3 h in toluene at room temperature in an exothermic reaction. The poly(MMA) is moderately syndiotactic with *mm*:*mr*:*rr* = 1:22:77. In contrast, the neutral dihydride complex **1a** and the cationic alkyl species **2b** and **4c**,**e** do not polymerize MMA under these conditions. The polymerization by **2a** may occur by a group transfer mechanism, similar to that established for MMA polymerization catalyzed by transition metal complexes.[63]

Reaction of (^{i}Pr$_2$-ATI)AlEt$^+$ with AlEt$_3$. In all of the neutral and cationic Al aminotroponiminate complexes described to this point, the ^{i}Pr$_2$-ATI ligand coordinates in a chelating (nonbridging) mode, as seen in previous *p*-, *d*-, and *f*-block metal aminotroponiminate complexes.[21d–f] However, given the tendency of amidinate ligands to coordinate in a bridging mode in cationic Al species,[12] it is reasonable to expect that the ^{i}Pr$_2$-ATI ligand might also function as a bridging ligand in suitably electron deficient and sterically open systems. This is in fact the case. The reaction of **4c** and 1 equiv of AlEt$_3$ in CD$_2$Cl$_2$ at −78 °C yields a 2:1 mixture of [AlEt(μ-η^2,η^1-^{i}Pr$_2$-ATI)(μ-Et)AlEt$_2$][B(C$_6$F$_5$)$_4$] (**15**) and an isomer tentatively identified as [(^{i}Pr$_2$-ATI)Al(μ-Et)$_2$AlEt$_2$][B(C$_6$F$_5$)$_4$] (**16**, eq 17). The C_1-symmetric mixed-bridge isomer **15** was isolated from the reaction of **4c** and AlEt$_3$ in toluene, which results in separation of an oil from which **15** crystallizes. Compound **15** was characterized by X-ray crystallography. The C_{2v}-symmetric isomer **16** was detected by NMR analysis of mixtures of **15** and **16**.



Compound **15** crystallizes as discrete ions (Figure 7). The two Al centers of the cation of **15** are bridged by one nitrogen

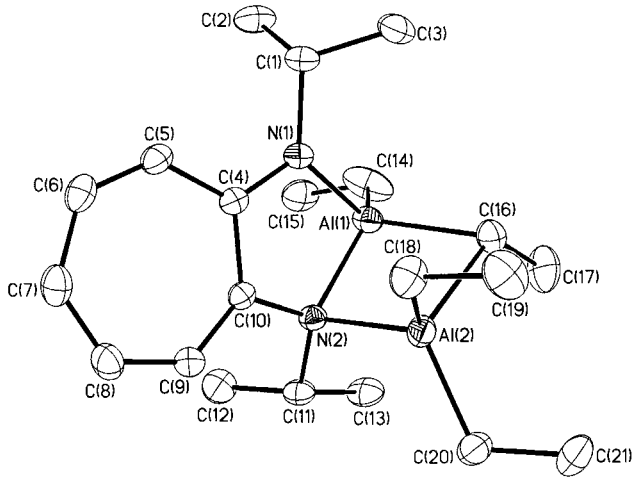


Figure 7. Structure of the {AlEt(μ-^{i}Pr$_2$-ATI)(μ-Et)AlEt$_2$}$^+$ cation in **15**. Selected bond distances (Å) and angles (deg): Al(1)−N(1) 1.904(2), Al(1)−N(2) 1.937(2), Al(1)−C(14) 1.896(2), Al(1)−C(16) 2.095(2), Al(2)−C(16) 2.208(2), Al(2)−C(18) 1.963(2), Al(2)−C(20) 1.957(2), Al(2)−N(2) 2.050(2), Al(1)−Al(2) 2.6927(8); N(1)−Al(1)−N(2) 84.87(6), N(1)−Al(1)−C(14) 116.0(1), N(1)−Al(1)−C(16) 112.68(8), N(2)−Al(1)−C(14) 129.61(9), N(2)−Al(1)−C(16) 100.65(8), Al(1)−N(2)−Al(2) 84.92(6), Al(1)−C(16)−Al(2), 77.41(7), Al(1)−C(16)−C(17) 112.3(2), Al(2)−C(16)−C(17) 119.3(2), N(2)−Al(2)−C(16) 93.57(7), C(18)−Al(2)−C(20) 119.1(1), C(18)−Al(2)−C(16) 106.2(1), C(18)−Al(2)−N(2) 112.22(8), C(20)−Al(2)−C(16) 110.18(9), C(20)−Al(2)−N(2) 112.32(8). Hydrogen atoms are omitted.

(61) Talarico, G.; Budzelaar, P. H. M.; Gal, A. W. *J. Comput. Chem.* **2000**, *21*, 398.

(62) Reinhold, M.; McGrady, J. E.; Meier, R. J. *J. Chem. Soc., Dalton Trans.* **1999**, 487.

(63) Leading references to polymerization of MMA by a group transfer mechanism: (a) Collins, S.; Ward, D. G. *J. Am. Chem. Soc.* **1992**, *114*, 5460. (b) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223. (c) Cameron, P. A.; Gibson, V. C.; Graham, A. J. *Macromolecules* **2000**, *33*, 4329.

Table 1. ^{27}Al NMR Data for Neutral (^{i}Pr$_2$-ATI)Al(R^1)(R^2) Complexes

compd	R^1, R^2	δ	$\Delta\nu_{1/2,\,Hz}$	solvent
1a	H, H	126	1900	C_6D_6
1b	Me, Me	154	3200	C_6D_6
1c	Et, Et	153	2700	$C_6D_5CD_3$
1d	Pr, Pr	152	5000	C_6D_5Cl
1e	*i*Bu, *i*Bu	150	5900	C_6D_5Cl
1f	Cl, Cl	109	490	C_6D_6
1g	Cy, Cy	147	4900	C_6D_6
1h	CH_2Ph, CH_2Ph	146	3500	C_6D_6
5c	Et, C_6F_5	137	4100	C_6D_6
5g	Cy, $C6F_5$	138	5100	C_6D_6
5h	CH_2Ph, C_6F_5	130	3600	C_6D_5Cl

of the ^{i}Pr$_2$-ATI ligand and one Et group. The ^{i}Pr$_2$-ATI ligand is thus coordinated in an "imine, μ-amide" mode and has a localized π-system, which is manifested by a pronounced alternation of bond lengths. The N(1)−C(4) (1.333(2) Å) and C(5)−C(6), C(7)−C(8), and C(9)−C(10) (1.364 Å average) bonds have significant double bond character while the N(2)−C(10) (1.427(2) Å) and C(4)−C(5), C(6)−C(7), and C(8)−C(9) (1.414 Å average) bonds have significant single bond character. The Al(1)−N$_{imine}$ distance (Al(1)−N(1) (1.904(2) Å) is shorter than the Al−N$_{imine}$ distance in {η^2-(p-tolyl)NCH$_2$CMe=N(p-tolyl)}AlMe$_2$ (1.979(6) Å),[64] and the Al−N$_{\mu-amide}$ distances (Al(1)−N(2) 1.937(2) Å; Al(2)−N(2) 2.050(2) Å) are comparable to those in {Me$_2$Al(μ-NH(adamantyl))}$_2$ (1.97(2) Å average).[65] The Al(1)−C distances to the bridging and terminal Et groups (Al(1)−C(16) 2.095(2) Å; Al(1)−C(14) 1.896(2) Å) are significantly shorter than the corresponding distances involving Al(2) (Al(2)−C(16) 2.208(2) Å; Al(2)−C(20) 1.957(2) Å; Al(2)−C(18) 1.963(2) Å). These differences suggest that the positive charge is more localized on Al(1) than on Al(2). The Al(1)−N(2)−Al(2)−C(16) ring is puckered (torsion angles C(16)−Al(2)−N(2)−Al(1) −13.95(7)° and N(2)−Al(1)−C(16)−Al(2) −14.15(7)°). The structure of the B(C$_6$F$_5$)$_4^-$ anion is normal.

^{27}Al NMR Spectra of (^{i}Pr$_2$-ATI)AlR$_2$ Complexes. The ^{27}Al NMR spectra of neutral four-coordinate (^{i}Pr$_2$-ATI)AlR^{1}R^2 complexes contain one broad peak in the δ 100−160 region (Table 1). For the hydrocarbyl derivatives, the signal shifts downfield as the electron-donating ability of the R groups increases. The peak width for (^{i}Pr$_2$-ATI)AlCl$_2$ (**1f**, $\Delta\nu_{1/2}$ = 490 Hz) is much narrower than those for the (^{i}Pr$_2$-ATI)AlR$_2$ complexes ($\Delta\nu_{1/2}$ = 1900−6000 Hz). This difference is ascribed to the smaller differences in the ionic character of the Al−N bonds versus the Al−Cl or Al−R bonds which results in a smaller electric field gradient at Al in the former species.[66] No ^{27}Al NMR signals in the δ −200−900 region were observed for the cationic species **2b** or **4c**−**e** in C_6D_6 clathrates or C_6D_5-Cl solutions, so ^{27}Al NMR is not a useful probe of the structures of these species.

Discussion

The reaction of (^{i}Pr$_2$-ATI)AlR$_2$ complexes with [Ph$_3$C][B(C$_6$F$_5$)$_4$] proceeds by net R abstraction (R = H, Me, CH_2Ph) or, if β-hydrogens are present on the alkyl group (R = Et, Pr, ^{i}Bu, Cy), β-H abstraction/alkene elimination to produce the corresponding (^{i}Pr$_2$-ATI)AlR$^+$ cations (**4a**−**e**,**g**,**h**). The preference for β-H abstraction is ascribed to the greater steric accessibility of the β-C−H unit versus the Al−R bond to the bulky Ph$_3$C$^+$ electrophile. NMR monitoring studies of two cases (R = Et, Me) indicate that these reactions proceed by initial addition of Ph$_3$C$^+$ to the ^{i}Pr$_2$-ATI C5 carbon to generate {1,2-(N^{i}Pr)$_2$-5-CPh$_3$-cyclohepta-3,6-diene}AlR$_2^+$ diimine intermediates **6**, which decompose at ca. −30 °C to (^{i}Pr$_2$-ATI)AlR$^+$ species by dissociation of Ph$_3$C$^+$ followed by R or β-H abstraction. Base-free (^{i}Pr$_2$-ATI)AlR$^+$ cations are very reactive, as expected for 6-electron cationic Al species, and their stability depends on (i) the steric properties, electron donating ability, and bridging tendency of the Al−R group, (ii) the reactivity of the counterion, and (iii) the availability of Lewis bases which coordinate to Al to produce stable 4-coordinate adducts.

The primary alkyl complexes **4b**−**e** are thermally stable and have been isolated as base-free materials. The (^{i}Pr$_2$-ATI)AlR$^+$ cations in **4b**−**e** are most likely monomeric in the solid state and in benzene/toluene liquid clathrates, and form (^{i}Pr$_2$-ATI)Al(R)(ClR)$^+$ solvent adducts in chlorocarbon solution. An X-ray crystallographic analysis of one such adduct, [(^{i}Pr$_2$-ATI)Al(Et)(ClPh)][B(C$_6$F$_5$)$_4$] (**4c**(ClPh)·0.5PhCl), shows that the PhCl is coordinated by a dative PhCl- -Al interaction and an attractive Ph/ATI π-stacking interaction.

In contrast, the mononuclear hydride complex [(^{i}Pr$_2$-ATI)AlH][B(C$_6$F$_5$)$_4$] is thermally unstable and decomposes by transfer of a C$_6$F$_5^-$ group from B to Al and subsequent ligand redistribution reactions to produce (^{i}Pr$_2$-ATI)Al(C$_6$F$_5$)(μ-H)$_2$B(C$_6$F$_5$)$_2$ (**3**) and other products. The Al center in (^{i}Pr$_2$-ATI)AlH$^+$ is more sterically accessible and perhaps more electrophilic than those in **4c**−**e**, due to the smaller size and poorer electron donating ability of H versus R, which facilitates C$_6$F$_5^-$ abstraction from the anion. The benzyl complex [(^{i}Pr$_2$-ATI)AlCH_2Ph][B(C$_6$F$_5$)$_4$] is also thermally unstable and decomposes by C$_6$F$_5^-$ abstraction to (^{i}Pr$_2$-ATI)Al(CH_2Ph)(C$_6$F$_5$) (**5h**). The (^{i}Pr$_2$-ATI)AlCH_2Ph$^+$ cation is probably more electrophilic than primary alkyl (^{i}Pr$_2$-ATI)AlR$^+$ species due to the poorer electron donating ability of CH_2Ph versus R. Similarly, the (^{i}Pr$_2$-ATI)AlCy$^+$ cation abstracts a C$_6$F$_5^-$ group from B(C$_6$F$_5$)$_4^-$ to produce (^{i}Pr$_2$-ATI)Al(Cy)(C$_6$F$_5$) (**5g**). In this case, steric interactions between the Cy ring and ^{i}Pr groups of the (^{i}Pr$_2$-ATI)$^-$ ligand may weaken the Al−C bond and enhance the electrophilic character of the Al center. The stability of [(^{i}Pr$_2$-ATI)AlR][B(C$_6$F$_5$)$_4$] compounds containing primary Al−R groups is thus quite fortuitous, as the cations in these salt species must be near the limit of compatibility with the B(C$_6$F$_5$)$_4^-$ anion.

In cases where the Al−R group can form a strong 3-center, 2-electron bridge (i.e. R = Me, H), stable dinuclear monocationic {(^{i}Pr$_2$-ATI)AlR}$_2$(μ-R)$^+$ species are formed. The dinuclear Me complex **2b** forms unavoidably in the reaction of **1b** with Ph$_3$C$^+$ (regardless of the **1b**/Ph$_3$C$^+$ ratio) because **1b** is trapped by (^{i}Pr$_2$-ATI)AlMe$^+$ faster than it reacts with Ph$_3$C$^+$, and because **2b** does not react with Ph$_3$C$^+$ due to steric crowding and does not dissociate into **1b** and **4b**, the former of which could react with Ph$_3$C$^+$. Similarly, the dinuclear hydride **2a** is formed in the reaction of 2 equiv of **1a** with 1 equiv of Ph$_3$C$^+$, but reacts further with excess Ph$_3$C$^+$ to produce the unstable (^{i}Pr$_2$-ATI)AlH$^+$ cation. In contrast, dinuclear {(^{i}Pr$_2$-ATI)AlR}$_2$(μ-R)$^+$ cations are not stable for the higher alkyls which are poorer bridging ligands than Me or H, although these species are probably intermediates in alkyl exchange reactions between (^{i}Pr$_2$-ATI)AlR$_2$ and (^{i}Pr$_2$-ATI)AlR$^+$. In cases where the Al−R group can form a strong 3-center, 4-electron bridge (R = −OR, −C≡CR), unique dinuclear *dicationic* {(^{i}Pr$_2$-ATI)Al(μ-R)}$_2^{2+}$

(64) Kanters, J. A.; Van Mier, G. P. M.; Nijs, R. L. L. M.; Van Der Steen, F.; Van Koten, G. *Acta Crystallogr. C* **1988**, *44*, 1391.
(65) Waggoner, K. M.; Power, P. P. *J. Am. Chem. Soc.* **1991**, *113*, 3385.
(66) (a) Delpuech, J. J. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 2, p 153. (b) Mason, J. *Multinuclear NMR*; Plenium Press: New York and London, 1987; pp 259−278.

Table 2. Average Al−N Bond Distances in (^{i}Pr$_2$-ATI)Al Complexes

compd	d_{Al-N}, Å
(^{i}Pr$_2$-ATI)AlMe$_2$ (**1b**)[a]	1.915
(iPr$_2$-ATI)AlH$_2$ (**1a**)[a]	1.890
(iPr$_2$-ATI)Al(C$_6$F$_5$)(μ-H)$_2$B(C$_6$F$_5$)$_2$ (**3**)	1.867
[{(iPr$_2$-ATI)AlMe}$_2$(μ-Me)][B(C$_6$F$_5$)$_4$] (**2b**)	1.876
[(iPr$_2$-ATI)Al(Et)(NCMe)][B(C$_6$F$_5$)$_4$] (**8c**)	1.855
[(iPr$_2$-ATI)AlEt][B(C$_6$F$_5$)$_4$] (**4c**)	1.838
[{(iPr$_2$-ATI)Al(μ-C≡CtBu)}$_2$][B(C$_6$F$_5$)$_4$] (**13**)	1.836
[{(iPr$_2$-ATI)Al(μ-OiPr)}$_2$][B(C$_6$F$_5$)$_4$] (**10**)	1.826

[a] Taken from ref 21a.

species are formed.[67] The driving force to achieve an 8-electron configuration at Al overcomes the Coulombic repulsion between the two cationic centers in the formation of these dications.[68]

The steric and electronic properties of the ^{i}Pr$_2$-ATI ligand both contribute to the stability of the (^{i}Pr$_2$-ATI)AlR$^+$ cations. As pointed out by Dias, steric interactions between the ATI ring and the isopropyl groups favor a conformation in which the ^{i}Pr methyl groups point toward the Al center in (^{i}Pr$_2$-ATI)-Al complexes.[21a] Also, the N−Al−N bite angle in cationic (^{i}Pr$_2$-ATI)Al complexes (83−89°) is larger than those in amidinate complexes (ca. 70°).[12,13] These factors provide a moderate degree of steric protection to the unsaturated Al center in (^{i}Pr$_2$-ATI)AlR$^+$ cations. The strong electron donor ability and polarizability of the ^{i}Pr$_2$-ATI ligand stabilizes the electron deficient Al center in (^{i}Pr$_2$-ATI)AlR$^+$ species. As summarized in Table 2, the Al−N bond distances are significantly shorter in (^{i}Pr$_2$-ATI)Al(R)(L)$^+$ than in (^{i}Pr$_2$-ATI)AlR$_2$ complexes, which reflects stronger N−Al bonding in the former systems.

The reactivity of (^{i}Pr$_2$-ATI)AlR$^+$ species is dominated by their Lewis acidity. These cations form robust adducts with Lewis bases such as NMe$_2$Ph, Me$_2$C═O, MeCN, and even PhCl, which undergo associative rather than dissociative ligand exchange. For R = H, Cy, and CH$_2$Ph, the base-free cations are so electrophilic that they abstract a C$_6$F$_5^-$ group from the B(C$_6$F$_5$)$_4^-$ anion. The formation of dinuclear monocations {(^{i}Pr$_2$-ATI)-AlR}$_2$(μ-R)$^+$ (R = H, Me) and dinuclear dications {(^{i}Pr$_2$-ATI)-Al(μ-R)}$_2^{2+}$ (R = −OR, −C≡CR) by coordination of (^{i}Pr$_2$-ATI)AlR$_2$ or (^{i}Pr$_2$-ATI)AlR$^+$ to (^{i}Pr$_2$-ATI)AlR$^+$ also reflects the Lewis acidity at aluminum. Cationic (^{i}Pr$_2$-ATI)AlR$^+$ species initiate the polymerization of isobutylene and propylene oxide, and the dinuclear hydride complex {(^{i}Pr$_2$-ATI)AlH}$_2$(μ-H)$^+$ catalyzes the polymerization of MMA. While the mechanisms of these polymerizations have not yet been studied, the Lewis acid character of the cationic Al species is probably important.

The predominant reaction of the higher alkyl (^{i}Pr$_2$-ATI)Al-(CH$_2$CHRR′)$^+$ species (RR′ = H$_2$, HMe, Me$_2$) with unsaturated substrates is β-H transfer to the substrate. Thus, (^{i}Pr$_2$-ATI)Al(CH$_2$CHRR′)$^+$ species react with Me$_2$C═O, ^{t}BuC≡CH, and ethylene to yield (^{i}Pr$_2$-ATI)Al(O^{i}Pr)$^+$, (^{i}Pr$_2$-ATI)Al-(CH═CH^{t}Bu)$^+$, and (^{i}Pr$_2$-ATI)AlEt$^+$, respectively, with extrusion of the corresponding CH$_2$═CRR′ olefin. These reactions proceed in high yield and therefore probably do not involve β-H transfer to Al to produce a (^{i}Pr$_2$-ATI)AlH$^+$ intermediate, since this species (at least in base-free form) decomposes to **3**. Rather these reactions probably involve direct hydride transfer to coordinated substrate via six-membered transition states (Schemes 3−5). The (^{i}Pr$_2$-ATI)AlR$^+$ species do not exhibit high insertion reactivity. Complexes **4c**,**e** react with ethylene by β-H transfer rather than insertion, and the acetonitrile adducts **8c**−**e** do not undergo MeCN insertion, even at very high temperature for **8c**. The preference for β-H transfer over insertion in the reactions with unsaturated substrates is more pronounced for cationic Al alkyls than for neutral AlR$_3$ compounds which may reflect, at least in part, increased Al−R bond strengths due to the charge at Al. However, the alkynyl complex [(^{i}Pr$_2$-ATI)Al(C≡C^{t}Bu)][B(C$_6$F$_5$)$_4$] (**13**) does insert ^{t}BuC≡CH to produce vinyl complex **14**. This reaction is a key step in catalytic dimerization of ^{t}BuC≡CH, which occurs by an insertion/σ-bond metathesis cycle.

Conclusions

The ^{i}Pr$_2$-ATI ligand, which was originally used for neutral Al alkyls by Dias,[21a] permits the synthesis of several novel classes of cationic Al species, including mononuclear (^{i}Pr$_2$-ATI)-AlR$^+$ and (^{i}Pr$_2$-ATI)Al(R)(L)$^+$ complexes and dinuclear {(^{i}Pr$_2$-ATI)AlR}$_2$(μ-R)$^+$ and {(^{i}Pr$_2$-ATI)Al(μ-R)}$_2^{2+}$ complexes. The (^{i}Pr$_2$-ATI)AlR$^+$ cations are potent Lewis acids and undergo facile β-H transfer to unsaturated substrates. These reactivity properties are important in the polymerization of isobutylene and propylene oxide by (^{i}Pr$_2$-ATI)AlR$^+$, the dimerization of ^{t}BuC≡CH catalyzed by (^{i}Pr$_2$-ATI)AlR$^+$, and the polymerization of methyl methacrylate by {(^{i}Pr$_2$-ATI)AlH}$_2$(μ-H)$^+$. However, the present systems exhibit several complications which must be addressed before this catalytic chemistry can be fully developed. Neutral (^{i}Pr$_2$-ATI)AlR$_2$ complexes are susceptible to electrophilic attack by Ph$_3$C$^+$ at the ATI C5 position, which suggests that similar reactions may provide a decomposition pathway for (^{i}Pr$_2$-ATI)AlR$^+$ cations. Additionally, the Al−N bonds in (^{i}Pr$_2$-ATI)AlR$^+$ species are susceptible to attack by AlR$_3$ (and presumably other reactive alkyls), which can lead to dinuclear species and complicate the chemistry. Finally, and perhaps most importantly, (^{i}Pr$_2$-ATI)AlR$^+$ species are clearly near the limit of compatibility with B(C$_6$F$_5$)$_4^-$, which is one of the most stable anions known. Our future work in this area will address these issues by modification of the ^{i}Pr$_2$-ATI ligand and utilization of other anions.[69,70]

Experimental Section

General Procedures. All manipulations were performed in a glovebox filled with purified nitrogen or on a high-vacuum line. Pentane, hexane, toluene, benzene (Fisher), toluene-d_8, and benzene-d_6 (Cambridge) were distilled under nitrogen from sodium/benzophenone ketyl and stored in flasks sealed with Teflon valves. Acetone (Fisher) and *tert*-butyl acetylene (Aldrich) were distilled under nitrogen from P$_2$O$_5$. Acetonitrile, methylene chloride (Fisher), chlorobenzene (Aldrich), and acetonitrile-d_3, methylene chloride-d_2, and chlorobenzene-d_5 (Cambridge) were dried over CaH$_2$ for 24 h, degassed by freeze−pump−thaw cycles, and vacuum transferred to a storage vessel. [CPh$_3$][B(C$_6$F$_5$)$_4$] (Boulder Scientific) was recrystallized from toluene/pentane. B(C$_6$F$_5$)$_3$ (Boulder Scientific) was purified by sublimation and the purity was confirmed by ^{19}F and ^{11}B NMR. [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]

(67) Several dinuclear dicationic Al compounds incorporating 5-coordinate Al centers have been reported: (a) [(EtAl)$_2$·diaza-18-crown-6]-[EtAlCl$_3$]$_2$: Self, M. F.; Pennington, W. T.; Laske, J. A.; Robinson, G. H. *Organometallics* **1991**, *10*, 36. (b) [{Salpen(^{t}Bu)$_4$Al}$_2$][GaCl$_4$]$_2$ and [{Salomphen(^{t}Bu)$_3$Al}$_2$][GaCl$_4$]$_2$: ref 11c.

(68) Dinuclear dicationic Zr compounds have been proposed or characterized. See ref 41 and the following: (a) Martin, A.; Uhrhammer, R.; Gardner, T. G.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1998**, *17*, 382. (b) Cuenca, T.; Royo, P. *J. Organomet. Chem.* **1985**, *293*, 61.

(69) We have prepared *N*-*tert*-butyl-2-(*tert*-butylamino)troponimine (^{t}Bu$_2$-ATI)H and the Al complexes (^{t}Bu$_2$-ATI)AlEt$_2$ and [(^{t}Bu$_2$-ATI)AlEt]-[B(C$_6$F$_5$)$_4$]. Korolev, A. V.; Jordan, R. F. Unpublished results.

(70) (a) Lancaster, S. J.; Walker, D. A.; Thornton-Pett, M.; Bochmann, M. *Chem. Commun.* **1999**, 1533. (b) Metz, M. V.; Schwartz, D. J.; Stern, C. L.; Nickias, P. N.; Marks, T. J. *Angew. Chem. Int. Ed.* **2000**, *39*, 1312. (c) Li, L.; Stern, C. L.; Marks, T. J. *Organometallics*, **2000**, *19*, 3332. (d) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133. (e) Lupinetti, A. J.; Strauss, S. H. *Chemtracts-Inorg. Chem.* **1972**, *11*, 565.

(Boulder Scientific) were used as received. ^{n}BuLi (1.6 M solution in hexanes), $PhCH_2MgCl$ (1.0 M solution in Et_2O), CyMgCl (2.0 M solution in Et_2O), and $AlCl_3$ were purchased from Aldrich and used as received. $Mg(CH_2Ph)_2 \cdot 2THF$ was synthesized by a literature procedure,[71] and the purity was checked by ^1H and ^{13}C NMR. *N*-Isopropyl-2-(isopropylamino)troponimine ((^{i}Pr$_2$-ATI)H), **1a**, and **1b** were prepared using procedures described by Dias,[21a] and **1c**−**e** were prepared by analogous procedures.

^1H, ^{13}C, ^{19}F, and ^{11}B NMR spectra were recorded in sealed tubes at ambient probe temperature unless otherwise indicated. ^1H and ^{13}C chemical shifts are reported versus $SiMe_4$ and were determined by reference to the residual ^1H and ^{13}C solvent peaks. The residual ^1H NMR resonances for C_6D_5Cl appear at δ 7.14, 7.00, and 6.97, and the ^{13}C NMR resonances for C_6D_5Cl appear at δ 134.2, 129.3(t), 128.3(t), and 126.0(t). ^{11}B chemical shifts are reported versus $BF_3 \cdot Et_2O$ in C_6D_5Cl. ^{19}F chemical shifts are reported versus neat $CFCl_3$. Coupling constants are reported in Hz. Elemental analyses were performed by Desert Analytics Laboratory (Tucson, AZ) or Midwest Microlabs (Indianapolis, IN).

The $B(C_6F_5)_4^-$ salts studied in this work separate from $C_6D_5CD_3$ and C_6D_6 as oily phases (liquid clathrates) which contain the salt and sufficient solvent to allow NMR locking. In these cases, NMR spectra were recorded for the liquid clathrate directly.

The NMR spectra of cationic Al compounds contained signals of the free $B(C_6F_5)_4^-$ anion. ^{13}C NMR (C_6D_5Cl) δ 148.9 (d, $^1J_{CF}$ = 238), 138.7 (d, $^1J_{CF}$ = 246), 136.9 (d, $^1J_{CF}$ = 245), 126.5 (br, C_{ipso}). ^{13}C NMR (liquid clathrate, C_6D_6) δ 149.0 (d, $^1J_{CF}$ = 243), 138.8 (d, $^1J_{CF}$ = 233), 137.0 (d, $^1J_{CF}$ = 245), 124.8 (br, C_{ipso}). ^{13}C NMR (CD_2Cl_2) δ 148.7 (d, $^1J_{CF}$ = 237), 138.8 (d, $^1J_{CF}$ = 244), 136.8 (d, $^1J_{CF}$ = 241). ^{13}C NMR (CD_2Cl_2, −90 °C) δ 147.0 (d, $^1J_{CF}$ = 241), 137.3 (d, $^1J_{CF}$ = 246), 135.4 (d, $^1J_{CF}$ = 244), 122.5 (br, C_{ipso}). ^{11}B NMR (C_6D_5Cl) δ −16.4 (s). ^{19}F NMR (C_6D_5Cl) δ −132.2 (d, $^3J_{FF}$ = 10.5, 8F, F_o), −162.7 (t, $^3J_{FF}$ = 21, 4F, F_p), −166.7 (t, $^3J_{FF}$ = 18.5, 8F, F_m). ^{19}F NMR (liquid clathrate, C_6D_6) δ −131.9 (8F, F_o), −162.6 (4F, F_p), −166.7 (8F, F_m). In cases where cationic Al compounds were analyzed by NMR spectroscopy without isolation, the spectra contain signals for Ph_3CMe or Ph_3CH coproducts (see Supporting Information).

(^{i}Pr$_2$-ATI)AlMe$_2$ (1b). The preparation and ^1H and ^{13}C NMR data in C_6D_6 have been reported by Dias.[21a] ^1H NMR (C_6D_5Cl) δ 6.91 (t, $^3J_{HH}$ = 10.5, 2H, H4 and H6), 6.41 (d, $^3J_{HH}$ = 12, 2H, H3 and H7), 6.32 (t, $^3J_{HH}$ = 9.0, 1H, H5), 3.64 (sept, $^3J_{HH}$ = 6.5, 2H, Me_2CHN), 1.24 (d, $^3J_{HH}$ = 6.5, 12H, Me_2CHN), −0.41 (s, 6H, AlMe). ^{13}C NMR (C_6D_5Cl) δ 160.9 (s, C1 and C2), 136.5 (d, $^1J_{CH}$ = 153, C4 and C6), 119.2 (d, $^1J_{CH}$ = 159, C5), 113.4 (d, $^1J_{CH}$ = 151, C3 and C7), 47.5 (d, $^1J_{CH}$ = 135, Me_2CHN), 22.5 (q, $^1J_{CH}$ = 126, Me_2CHN), −4.3 (q, $^1J_{CH}$ = 112, $AlCH_3$).

(^{i}Pr$_2$-ATI)AlEt$_2$ (1c). A hexanes solution (ca. 20 mL) of (^{i}Pr$_2$-ATI)H (2.04 g, 9.98 mmol) was added to a hexanes solution of $AlEt_3$ (1.52 g, 13.3 mmol) at 0 °C. The mixture was allowed to warm to 23 °C and stirred overnight. A small amount of insoluble solid was removed by filtration. The volatiles were removed under vacuum leaving a yellow solid, which was recrystallized from pentane to afford (^{i}Pr$_2$-ATI)$AlEt_2$ as a yellow powder (1.20 g, 42%). ^1H NMR (C_6D_6) δ 6.76 (t, $^3J_{HH}$ = 10.5, 2H, H4 and H6), 6.35 (d, $^3J_{HH}$ = 11.5, 2H, H3 and H7), 6.22 (t, $^3J_{HH}$ = 9.5, 1H, H5), 3.55 (sept, $^3J_{HH}$ = 6.5, 2H, Me_2CHN), 1.34 (t, $^3J_{HH}$ = 8, 6H, $AlCH_2CH_3$), 1.23 (d, $^3J_{HH}$ = 6.5, 12H, Me_2CHN), 0.38 (q, $^3J_{HH}$ = 8, 4H, $AlCH_2CH_3$). ^1H NMR (C_6D_5Cl) δ 6.90 (t, $^3J_{HH}$ = 10, 2H, H4 and H6), 6.45 (d, $^3J_{HH}$ = 11, 2H, H3 and H7), 6.30 (t, $^3J_{HH}$ = 9, 1H, H5), 3.70 (sept, $^3J_{HH}$ = 6.5, 2H, Me_2CHN), 1.27 (d, $^3J_{HH}$ = 6.5, 12H, Me_2CHN), 1.14 (t, $^3J_{HH}$ = 8, 6H, $AlCH_2CH_3$), 0.17 (q, $^3J_{HH}$ = 8, 4H, $AlCH_2CH_3$). ^{13}C NMR (C_6D_6) δ 161.6 (s, C1 and C2), 136.5 (d, $^1J_{CH}$ = 153, C4 and C6), 119.1 (d, $^1J_{CH}$ = 160, C5), 113.6 (d, $^1J_{CH}$ = 151, C3 and C7), 47.5 (d, $^1J_{CH}$ = 135, Me_2CHN), 22.2 (q, $^1J_{CH}$ = 125, Me_2CHN), 9.9 (q, $^1J_{CH}$ = 124, $AlCH_2CH_3$), 4.2 (t, $^1J_{CH}$ = 114, $AlCH_2CH_3$). ^{13}C NMR (C_6D_5Cl) δ 161.5 (s, C1 and C2), 136.5 (d, $^1J_{CH}$ = 153, C4 and C6), 119.2 (d, $^1J_{CH}$ = 158, C5), 113.5 (d, $^1J_{CH}$ = 151, C3 and C7), 47.5 (d, $^1J_{CH}$ = 134, Me_2CHN), 22.2 (q, $^1J_{CH}$ = 126, Me_2CHN), 9.7 (q, $^1J_{CH}$ = 124, $AlCH_2CH_3$), 4.1 (t, $^1J_{CH}$ = 109, $AlCH_2CH_3$). Anal. Calcd for $C_{17}H_{29}AlN_2$: C, 70.80; H, 10.13; N, 9.71. Found: C, 70.69; H, 9.95; N, 9.53.

(71) Schrock, R. R. *J. Organomet. Chem.* **1976**, *122*, 209.

(^{i}Pr$_2$-ATI)AlPr$_2$ (1d). A pentane solution (ca. 20 mL) of (^{i}Pr$_2$-ATI)H (1.08 g, 5.29 mmol) was added to a solution of $AlPr_3$ (827 mg, 5.29 mmol) in pentane at −37 °C. The mixture was allowed to warm to 25 °C and stirred for 3 h. The volatiles were removed under vacuum leaving a yellow solid. Recrystallization of this solid from pentane afforded (^{i}Pr$_2$-ATI)$AlPr_2$ as a yellow powder (1.58 g, 95%). ^1H NMR (C_6D_6) δ 6.77 (m, 2H, H4 and H6), 6.35 (d, $^3J_{HH}$ = 8, 2H, H3 and H7), 6.22 (t, $^3J_{HH}$ = 9, 1H, H5), 3.56 (sept, $^3J_{HH}$ = 6.5, 2H, Me_2CHN), 1.63 (m, 4H, $AlCH_2CH_2CH_3$), 1.23 (d, $^3J_{HH}$ = 6.5, and t, $^3J_{HH}$ = 7, 18H, Me_2CHN and $AlCH_2CH_2CH_3$), 0.37 (m, 4H, $AlCH_2CH_2CH_3$). ^1H NMR (C_6D_5Cl) δ 6.90 (m, 2H, H4 and H6), 6.45 (d, $^3J_{HH}$ = 12, 2H, H3 and H7), 6.30 (t, $^3J_{HH}$ = 9, 1H, H5), 3.70 (sept, $^3J_{HH}$ = 6.5, 2H, Me_2CHN), 1.48 (m, 4H, $AlCH_2CH_2CH_3$), 1.27 (d, $^3J_{HH}$ = 6.5, 12H, Me_2CHN), 1.07 (t, $^3J_{HH}$ = 7, 6H, $AlCH_2CH_2CH_3$), 0.20 (m, 4H, $AlCH_2CH_2CH_3$). ^{13}C NMR (C_6D_6) δ 161.6 (s, C1 and C2), 136.4 (d, $^1J_{CH}$ = 151, C4 and C6), 119.1 (d, $^1J_{CH}$ = 161, C5), 113.7 (d, $^1J_{CH}$ = 150, C3 and C7), 47.5 (d, $^1J_{CH}$ = 135, Me_2CHN), 22.3 (q, $^1J_{CH}$ = 127, Me_2CHN), 21.4 (q, $^1J_{CH}$ = 122, $AlCH_2CH_2CH_3$), 20.1 (t, $^1J_{CH}$ = 127, $AlCH_2CH_2CH_3$), 17.0 (t, $^1J_{CH}$ = 113, $AlCH_2CH_2CH_3$). ^{13}C NMR (C_6D_5Cl) δ 161.4 (s, C1 and C2), 136.5 (d, $^1J_{CH}$ = 153, C4 and C6), 119.1 (d, $^1J_{CH}$ = 160, C5), 113.5 (d, $^1J_{CH}$ = 151, C3 and C7), 47.5 (d, $^1J_{CH}$ = 134, Me_2CHN), 22.2 (q, $^1J_{CH}$ = 126, Me_2CHN), 21.2 (q, $^1J_{CH}$ = 126, $AlCH_2CH_2CH_3$), 19.9 (t, $^1J_{CH}$ = 124, $AlCH_2CH_2CH_3$), 17.1 (t, $^1J_{CH}$ = 109, $AlCH_2CH_2CH_3$).

(^{i}Pr$_2$-ATI)Al^{i}Bu$_2$ (1e). A hexanes solution (ca. 20 mL) of (^{i}Pr$_2$-ATI)H (1.17 g, 5.73 mmol) was added to a hexanes solution (10 mL) of Al^{i}Bu$_3$ (1.27 g, 6.40 mmol) at 0 °C. The mixture was allowed to warm to 23 °C and was stirred overnight. A small amount of insoluble solid was removed by filtration. The volatiles were removed under vacuum leaving a yellow solid. Recrystallization of this solid from pentane afforded (^{i}Pr$_2$-ATI)Al^{i}Bu$_2$ as yellow crystals (0.95 g, 48%). ^1H NMR (C_6D_6) δ 6.76 (dd, $^3J_{HH}$ = 11.5, 9.0, 2H, H4 and H6), 6.36 (d, $^3J_{HH}$ = 11.5, 2H, H3 and H7), 6.20 (t, $^3J_{HH}$ = 9.0, 1H, H5), 3.58 (sept, $^3J_{HH}$ = 6.5, 2H, Me_2CHN), 2.01 (nonet, $^3J_{HH}$ = 6.5, 2H, $AlCH_2CHMe_2$), 1.27 (d, $^3J_{HH}$ = 6.5, 12H, Me_2CHN), 1.12 (d, $^3J_{HH}$ = 6.5, 12H, $AlCH_2CHMe_2$), 0.38 (d, $^3J_{HH}$ = 6.5, 4H, $AlCH_2CHMe_2$). ^1H NMR (C_6D_5Cl) δ 6.90 (t, $^3J_{HH}$ = 10.5, 2H, H4 and H6), 6.46 (d, $^3J_{HH}$ = 11, 2H, H3 and H7), 6.29 (t, $^3J_{HH}$ = 9, 1H, H5), 3.70 (sept, $^3J_{HH}$ = 6.5, 2H, Me_2CHN), 1.89 (nonet, $^3J_{HH}$ = 6.5, 2H, $AlCH_2CHMe_2$), 1.31 (d, $^3J_{HH}$ = 6.5, 12H, Me_2CHN), 0.99 (d, $^3J_{HH}$ = 6.5, 12H, $AlCH_2CHMe_2$), 0.23 (d, $^3J_{HH}$ = 6.5, 4H, $AlCH_2CHMe_2$). ^{13}C NMR (C_6D_6) δ 161.6 (s, C1 and C2), 136.4 (d, $^1J_{CH}$ = 151, C4 and C6), 119.2 (d, $^1J_{CH}$ = 158, C5), 114.2 (d, $^1J_{CH}$ = 151, C3 and C7), 47.5 (d, $^1J_{CH}$ = 135, Me_2CHN), 28.7 (q, $^1J_{CH}$ = 124, $AlCH_2CHMe_2$), 27.3 (d, $^1J_{CH}$ = 124, $AlCH_2CHMe_2$), 26.5 (t, $^1J_{CH}$ = 107, $AlCH_2CHMe_2$), 22.3 (q, $^1J_{CH}$ = 126, $NCHMe_2$). $^{13}C\{H\}$ NMR (C_6D_5Cl) δ 161.4 (s, C1 and C2), 136.5 (C4 and C6), 119.3 (C5), 114.1 (C3 and C7), 47.5 (Me_2CHN), 28.6 ($AlCH_2CHMe_2$), 27.2 ($AlCH_2CHMe_2$), 26.3 ($AlCH_2CHMe_2$), 22.3 (Me_2CHN). Anal. Calcd for $C_{21}H_{37}AlN_2$: C, 73.21; H, 10.82; N, 8.13. Found: C, 73.07; H, 11.04; N, 8.01.

Li[^{i}Pr$_2$-ATI]. A solution of (^{i}Pr$_2$-ATI)H (1.25 g, 6.12 mmol) in hexanes (10 mL) was cooled to −37 °C, and BuLi (5 mL of 1.6 M solution in hexanes, 8 mmol) was added dropwise by syringe. A yellow precipitate formed. The mixture was stirred for 2 h, and the precipitate was collected by filtration, washed with hexanes (3 × 5 mL) and dried under vacuum to give 1.27 g (98%) of Li[^{i}Pr$_2$-ATI]. ^1H NMR (CD_3CN) δ 6.48 (m, 2H, H4 and H6), 5.96 (d, $^3J_{HH}$ = 12, 2H, H3 and H7), 5.49 (t, $^3J_{HH}$ = 9, 1H, H5), 3.69 (sept, $^3J_{HH}$ = 6, 2H, Me_2CHN), 1.14 (d, $^3J_{HH}$ = 6, 12H, Me_2CHN).

(^{i}Pr$_2$-ATI)AlCl$_2$ (1f). $AlCl_3$ (116 mg, 870 μmol) was suspended in toluene (4 mL) and solid Li[^{i}Pr$_2$-ATI] (183 mg, 870 μmol) was slowly added. The mixture was stirred for 36 h at room temperature, filtered through Celite, and evaporated under vacuum leaving a yellow-green solid. Recrystallization of this material from hexanes at −37 °C afforded 257 mg (98%) of a yellow crystalline product. ^1H NMR (C_6D_6) δ 6.74 (m, 2H, H4 and H6), 6.38 (d, $^3J_{HH}$ = 12, 2H, H3 and H7), 6.33 (t, $^3J_{HH}$ = 9, 1H, H5), 3.45 (sept, $^3J_{HH}$ = 6, 2H, Me_2CHN), 1.37 (d, $^3J_{HH}$ = 6, 12H, Me_2CHN). ^{13}C NMR (C_6D_6) δ 159.8 (s, C1 and C2), 137.2 (d, $^1J_{CH}$ = 154, C4 and C6), 123.0 (d, $^1J_{CH}$ = 159, C5), 116.2 (d, $^1J_{CH}$ = 153, C3 and C7), 47.7 (d, $^1J_{CH}$ = 135, Me_2CHN), 22.4 (q, $^1J_{CH}$ = 126, Me_2CHN).

(^{i}Pr$_2$-ATI)AlCy$_2$ (1g). A solution of (^{i}Pr$_2$-ATI)AlCl$_2$ (350 mg, 1.16 mmol) in hexanes (5 mL) was cooled to −37 °C, and CyMgCl (1.2 mL of 2 M solution in Et$_2$O, 2.4 mmol) was added by syringe. The solution was stirred for 16 h, filtered through Celite, and evaporated under vacuum to give a dark red oily residue. The residue was dissolved in pentane, ca. 0.2 mL of dioxane was added, and the solution was cooled to −37 °C for 16 h. A white precipitate formed. The mixture was filtered and the filtrate was evaporated under vacuum leaving a dark red oily residue. The residue was dissolved in a minimum amount of pentane and kept at −37 °C for 16 h. Red crystals formed and were isolated by filtration (yield 317 mg, 74%). ^{1}H NMR (C$_6$D$_6$) δ 6.77 (m, 2H, H4 and H6), 6.40 (d, $^3J_{HH}$ = 12, 2H, H3 and H7), 6.21 (t, $^3J_{HH}$ = 9, 1H, H5), 3.59 (sept, $^3J_{HH}$ = 6.5, 2H, Me$_2$C*H*N), 1.95 (br m, 10H, C$_6$H$_{11}$ ring), 1.47 (br m, 10H, C$_6$H$_{11}$ ring), 1.27 (d, $^3J_{HH}$ = 6.5, 12H, *Me*$_2$CHN), 0.53 (br t, $^3J_{HH}$ = 11, 2H, AlCH). ^{13}C NMR (C$_6$D$_6$) δ 162.0 (C1 and C2), 136.5 (d, $^1J_{CH}$ = 155, C4 and C6), 119.1 (d, $^1J_{CH}$ = 160, C5), 114.0 (d, $^1J_{CH}$ = 152, C3 and C7), 47.4 (d, $^1J_{CH}$ = 135, Me$_2$*C*HN), 31.2 (t, $^1J_{CH}$ = 123, *C*H$_2$, C$_6$H$_{11}$ ring), 30.9 (t, $^1J_{CH}$ = 125, *C*H$_2$, C$_6$H$_{11}$ ring), 28.7 (t, $^1J_{CH}$ = 131, *C*H$_2$, C$_6$H$_{11}$ ring), 26.6 (d, $^1J_{CH}$ = 96, Al*C*H), 22.2 (q, $^1J_{CH}$ = 126, *Me*$_2$CHN).

(^{i}Pr$_2$-ATI)Al(CH$_2$Ph)$_2$ (1h). A solution of (^{i}Pr$_2$-ATI)AlCl$_2$ (212 mg, 704 μmol) in ca. 10 mL of hexanes was prepared and Mg(CH$_2$Ph)$_2$·2THF (322 mg, 918 μmol) was added as a powder. The mixture was stirred for 16 h at room temperature, filtered through Celite, and evaporated under vacuum leaving a red oily residue. The residue was dissolved in hexanes (ca. 5 mL), and ca. 0.5 mL of dioxane was added. The solution was kept at −37 °C for 16 h, and a white precipitate formed. The mixture was filtered and the filtrate was evaporated under vacuum giving a red oily product (221 mg, 76%). ^{1}H NMR (C$_6$D$_6$) δ 7.10 (m, 8H, H$_o$, H$_m$), 6.91 (t, $^3J_{HH}$ = 7, 2H, H$_p$), 6.70 (m, 2H, H4 and H6), 6.30 (d, $^3J_{HH}$ = 12, 2H, H3 and H7), 6.18 (t, $^3J_{HH}$ = 9, 1H, H5), 3.42 (sept, $^3J_{HH}$ = 6.5, 2H, Me$_2$C*H*N), 2.04 (s, 4H, AlC*H*$_2$), 1.05 (d, $^3J_{HH}$ = 6.5, 12H, *Me*$_2$CHN). ^{13}C NMR (C$_6$D$_6$) δ 161.6 (s, C1 and C2), 146.9 (s, C$_{ipso}$), 136.6 (d, $^1J_{CH}$ = 152, C4 and C6), 128.3 (d, $^1J_{CH}$ = 158, C$_m$), 127.9 (d, $^1J_{CH}$ = 154, C$_o$), 122.1 (d, $^1J_{CH}$ = 158, C$_p$), 120.2 (d, $^1J_{CH}$ = 160, C5), 114.8 (d, $^1J_{CH}$ = 152, C3 and C7), 47.3 (d, $^1J_{CH}$ = 134, Me$_2$*C*HN), 25.1 (t, $^1J_{CH}$ = 113, Al*C*H$_2$), 22.0 (q, $^1J_{CH}$ = 126, *Me*$_2$CHN).

[{(^{i}Pr$_2$-ATI)Al}$_2$H$_3$][B(C$_6$F$_5$)$_4$] (2a). A vial was charged with (^{i}Pr$_2$-ATI)AlH$_2$ (54 mg, 230 μmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (90 mg, 98 μmol). Toluene (ca. 0.5 mL) was added and the mixture was stirred for 0.5 h. Hexanes (ca. 5 mL) was added, the mixture was stirred, and a yellow precipitate formed. The supernatant was removed using a pipet. The yellow solid was washed with hexanes (3 × 5 mL), collected by filtration, and dried under vacuum affording [{(^{i}Pr$_2$-ATI)Al}$_2$H$_3$)][B(C$_6$F$_5$)$_4$] as a yellow powder (76 mg, 68%). ^{1}H NMR (C$_6$D$_5$Cl) δ 7.14 (t, $^3J_{HH}$ = 10.5, 4H, H4 and H6), 6.72 (d, $^3J_{HH}$ = 11, 4H, H3 and H7), 6.69 (t, $^3J_{HH}$ = 10, 2H, H5), 4.59 (br, 3H, AlH), 3.51 (sept, $^3J_{HH}$ = 6.5, 4H, Me$_2$C*H*N), 1.05 (d, $^3J_{HH}$ = 6.5, 24H, *Me*$_2$CHN). ^{13}C{H} NMR (C$_6$D$_5$Cl) δ 160.7 (C1 and C2), 138.6 (C4 and C6), 126.2 (C5), 118.3 (C3 and C7), 47.0 (Me$_2$*C*HN), 22.5 (*Me*$_2$CHN). ^{13}C, ^{11}B, and ^{19}F NMR spectra in C$_6$D$_5$Cl confirmed that the B(C$_6$F$_5$)$_4^-$ anion is free. Anal. Calcd for C$_{26}$H$_{41}$Al$_2$BF$_{20}$N$_4$: C, 52.56; H, 3.62; N, 4.90. Found: C, 52.64; H, 3.93; N, 4.69.

[{(^{i}Pr$_2$-ATI)AlMe}$_2$(μ-Me)][B(C$_6$F$_5$)$_4$] (2b). A mixture of (^{i}Pr$_2$-ATI)AlMe$_2$ (153 mg, 588 μmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (252 mg, 273 μmol) in toluene (ca. 0.5 mL) was stirred for 0.5 h at room temperature. Hexanes (ca. 5 mL) was added, the mixture was stirred for 1 h, and a pale green precipitate formed. The supernatant was removed using a pipet. The pale green solid was washed with hexanes (4 × 5 mL), collected by filtration, and dried under vacuum affording [{(^{i}Pr$_2$-ATI)-AlMe}$_2$(μ-Me)][B(C$_6$F$_5$)$_4$] as a pale green powder (235 mg, 73%). ^{1}H NMR (C$_6$D$_5$Cl) δ 7.06 (t, $^3J_{HH}$ = 10.5, 4H, H4 and H6), 6.63 (d, $^3J_{HH}$ = 11.5, 4H, H3 and H7), 6.59 (t, $^3J_{HH}$ = 9.5, 2H, H5), 3.60 (sept, $^3J_{HH}$ = 6.5, 4H, Me$_2$C*H*N), 1.08 (d, $^3J_{HH}$ = 6.5, 24H, *Me*$_2$CHN), −0.09 (s, 9H, AlMe). ^{1}H NMR (CD$_2$Cl$_2$, −90 °C, slow bridge/terminal exchange) δ 7.35 (t, $^3J_{HH}$ = 10.5, 4H, H4 and H6), 6.95 (d, $^3J_{HH}$ = 11.5, 4H, H3 and H7), 6.80 (t, $^3J_{HH}$ = 9.5, 2H, H5), 3.97 (br, 4H, Me$_2$C*H*N), 1.25 (br, 24H, *Me*$_2$CHN), 0.63 (br s, 3H, AlMe$_{bridge}$), −0.38 (br s, 6H, AlMe$_{terminal}$). ^{1}H NMR (CD$_2$Cl$_2$, −15 °C, fast bridge/terminal Me exchange) δ 7.41 (t, $^3J_{HH}$ = 10.5, 4H, H4 and H6), 7.00 (d, $^3J_{HH}$ = 11, 4H, H3 and H7), 6.87 (t, $^3J_{HH}$ = 9, 2H, H5), 4.02 (sept, $^3J_{HH}$ = 6.5, 4H, Me$_2$C*H*N), 1.30 (d, $^3J_{HH}$ = 6.5, 24H, *Me*$_2$CHN), 0.00 (s, 9H, AlMe). ^{13}C NMR (C$_6$D$_5$Cl) δ 160.5 (s, C1 and C2), 138.1 (d, $^1J_{CH}$ = 157, C4 and C6), 124.6 (d, $^1J_{CH}$ = 153, C5), 116.9 (d, $^1J_{CH}$ = 154, C3 and C7), 47.3 (d, $^1J_{CH}$ = 137, NCHMe$_2$), 22.7 (q, $^1J_{CH}$ = 126, *Me*$_2$CHN), −3.0 (q, $^1J_{CH}$ = 122, AlMe). ^{13}C NMR (CD$_2$Cl$_2$, −90 °C, slow bridge/terminal Me exchange) δ 159.7 (s, C1 and C2), 137.4 (d, $^1J_{CH}$ = 153, C4 and C6), 123.2 (d, $^1J_{CH}$ = 164, C5), 115.9 (d, $^1J_{CH}$ = 153, C3 and C7), 46.5 (d, $^1J_{CH}$ = 135, Me$_2$*C*HN), 22.4 (q, $^1J_{CH}$ = 127, *Me*^{A}Me^{B}CHN), 22.1 (q, $^1J_{CH}$ = 127, Me^A*Me*^{B}CHN), −0.8 (q, $^1J_{CH}$ = 133, AlMe$_{bridge}$), −5.2 (q, $^1J_{CH}$ = 118, AlMe$_{terminal}$). ^{13}C, ^{11}B, and ^{19}F NMR spectra in C$_6$D$_5$Cl confirmed that the B(C$_6$F$_5$)$_4^-$ anion is free. Anal. Calcd for C$_{53}$H$_{47}$Al$_2$BF$_{20}$N$_4$: C, 53.73; H, 4.00; N, 4.73. Found: C, 53.52; H, 3.95; N, 4.51.

Observation of an Intermediate in the Reaction of (^{i}Pr$_2$-ATI)-AlMe$_2$ and [Ph$_3$C][B(C$_6$F$_5$)$_4$] in CD$_2$Cl$_2$ at Low Temperature. An NMR tube was charged with (^{i}Pr$_2$-ATI)AlMe$_2$ (55 mg, 210 μmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (97 mg, 110 μmol). CD$_2$Cl$_2$ (ca. 0.5 mL) was added by vacuum transfer at −78 °C. The tube was sealed at that temperature and inserted into the pre-cooled (−90 °C) NMR probe and spectra were recorded at −90 °C. The NMR spectra established the presence of a 1:1 mixture of (^{i}Pr$_2$-ATI)AlMe$_2$ and [{1,2-(N^{i}Pr)$_2$-5-CPh$_3$-cyclohepta-3,6-diene}AlMe$_2$][B(C$_6$F$_5$)$_4$]. ^{1}H NMR (CD$_2$Cl$_2$, −90 °C) δ 7.70−6.60 (m, 19H, Ph ring and H3 and H7 and H4 and H6), 6.01 (br, 1H, H5), 3.85 (br, 2H, Me$_2$C*H*N), 1.26 (br, 12H, *Me*$_2$CHN), −0.46 (br, 3H, AlMe), −0.65 (br, 3H, AlMe). ^{13}C NMR (CD$_2$Cl$_2$, −90 °C) δ 161.6 (s, C1 and C2), 151.0 (d, $^1J_{CH}$ = 159, C4 and C6), 143.6 (s, Ph$_{ipso}$), 132.6 (d, $^1J_{CH}$ = 159, Ph), 128.6 (d, $^1J_{CH}$ = 166, Ph), 127.1 (d, $^1J_{CH}$ = 144, Ph), 126.5 (d, $^1J_{CH}$ = 152, Ph), 126.1 (d, $^1J_{CH}$ = 149, Ph), 121.4 (d, $^1J_{CH}$ = 165, C3 and C7), 66.9 (s, Ph$_3$*C*), 51.8 (d, $^1J_{CH}$ = 138, C5), 46.6 (d, $^1J_{CH}$ = 134, Me$_2$*C*HN), 22.2 (q, $^1J_{CH}$ = 127, *Me*^{A}Me^{B}CHN), 21.0 (q, $^1J_{CH}$ = 126, Me^A*Me*^{B}CHN), −7.6 (d, $^1J_{CH}$ = 115, Al*Me*^{A}Me^B), −8.6 (t, $^1J_{CH}$ = 116, AlMe^A*Me*^{B}). The presence of six Ph signals in the ^{13}C NMR spectrum is ascribed to restricted rotation around Ph$_3$C−C5 bond. These spectra also contained signals of (^{i}Pr$_2$-ATI)-AlMe$_2$. ^{13}C, ^{11}B, and ^{19}F NMR spectra in CD$_2$Cl$_2$ confirmed that the B(C$_6$F$_5$)$_4^-$ anion is free.

(^{i}Pr$_2$-ATI)Al(C$_6$F$_5$)(μ-H)$_2$B(C$_6$F$_5$)$_2$ (3). An NMR tube was charged with (^{i}Pr$_2$-ATI)AlH$_2$ (40 mg, 170 μmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (159 mg, 170 μmol), and C$_6$D$_6$ (ca. 0.5 mL) was added by vacuum transfer at −78 °C. The tube was sealed and warmed to 25 °C, and a dark red oil separated from solution. The tube was heated to 60 °C and a homogeneous solution formed. NMR spectra at 60 °C indicated that a complex mixture of unidentified products had formed. The tube was cooled to 25 °C and crystals of **3** formed. The structure of **3** was established by X-ray crystallography.

[(^{i}Pr$_2$-ATI)AlMe][B(C$_6$F$_5$)$_4$] (4b). A solution of (^{i}Pr$_2$-ATI)AlEt$_2$ (62 mg, 220 mmol) and (^{i}Pr$_2$-ATI)AlMe$_2$ (56 mg, 220 mmol) in ca. 5 mL of toluene was prepared and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (397 mg, 430 mmol) was added at room temperature. The mixture was stirred for 0.5 h. Pentane (ca. 10 mL) was added and a yellow solid precipitated. The solid was collected by filtration, washed with pentane (4 × 5 mL), and dried under vacuum affording [(^{i}Pr$_2$-ATI)AlMe][B(C$_6$F$_5$)$_4$] as a yellow powder (356 mg, 89%). ^{1}H NMR (C$_6$D$_5$Cl) δ 7.18 (t, $^3J_{HH}$ = 10.5, 2H, H4 and H6), 6.79 (t, $^3J_{HH}$ = 9, 1H, H5), 6.77 (d, $^3J_{HH}$ = 12, 2H, H3 and H7), 3.53 (sept, $^3J_{HH}$ = 6.5, 2H, Me$_2$C*H*N), 1.08 (d, $^3J_{HH}$ = 6.5, 12H, *Me*$_2$CHN), −0.16 (s, 3H, AlMe). ^{13}C NMR (C$_6$D$_5$Cl) δ 159.9 (s, C1 and C2), 138.9 (d, $^1J_{CH}$ = 158, C4 and C6), 128.2 (d, $^1J_{CH}$ = 173, C5), 119.5 (d, $^1J_{CH}$ = 153, C3 and C7), 47.4 (d, $^1J_{CH}$ = 138, Me$_2$*C*HN), 22.9 (q, $^1J_{CH}$ = 127, *Me*$_2$CHN), −6.7 (q, $^1J_{CH}$ = 120, AlMe). ^{13}C, ^{11}B, and ^{19}F NMR spectra in C$_6$D$_5$Cl confirmed that the B(C$_6$F$_5$)$_4^-$ anion is free.

[(^{i}Pr$_2$-ATI)AlEt][B(C$_6$F$_5$)$_4$] (4c). **Procedure A.** A vial was charged with (^{i}Pr$_2$-ATI)AlEt$_2$ (104 mg, 361 μmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (303 mg, 328 μmol) and benzene (ca. 0.5 mL) was added. The mixture was stirred for 0.5 h at room temperature. Hexanes (ca. 5 mL) was added, the mixture was stirred, and a yellow precipitate formed. The supernatant was removed using a pipet. The yellow solid was washed with hexanes (4 × 5 mL), collected by filtration, and dried under vacuum affording [(^{i}Pr$_2$-ATI)AlEt][B(C$_6$F$_5$)$_4$] as a yellow powder (226 mg, 74%). **Procedure B**. (^{i}Pr$_2$-ATI)AlEt$_2$ (395 mg, 1.37 mmol) was

dissolved in ca. 20 mL of pentane. A finely divided powder of $[Ph_3C][B(C_6F_5)_4]$ (1.25 g, 1.35 mmol) was added and the mixture was stirred for 2 days at room temperature. A yellow precipitate formed and was collected by filtration, washed with pentane (3 × 20 mL), and dried under vacuum affording $[(^i Pr_2\text{-ATI})AlEt][B(C_6F_5)_4]$ as a pale yellow powder (1.25 g, 99%). ^1H NMR (C_6D_5Cl) δ 7.16 (t, $^3J_{HH}$ = 10.5, 2H, H4 and H6), 6.78 (t, $^3J_{HH}$ = 10, 1H, H5), 6.74 (d, $^3J_{HH}$ = 11, 2H, H3 and H7), 3.51 (sept, $^3J_{HH}$ = 6.5, 2H, Me_2CHN), 1.09 (d, $^3J_{HH}$ = 6.5, 12H, Me_2CHN), 1.04 (t, $^3J_{HH}$ = 8, 3H, $AlCH_2CH_3$), 0.44 (q, $^3J_{HH}$ = 8, 2H, $AlCH_2CH_3$). ^{13}C NMR (C_6D_5Cl) δ 159.9 (s, C1 and C2), 139.0 (d, $^1J_{CH}$ = 157, C4 and C6), 128.7 (d, $^1J_{CH}$ = 160, C5), 119.7 (d, $^1J_{CH}$ = 155, C3 and C7), 47.3 (d, $^1J_{CH}$ = 139, Me_2CHN), 22.8 (q, $^1J_{CH}$ = 126, Me_2CHN), 7.6 (q, $^1J_{CH}$ = 127, $AlCH_2CH_3$), 3.3 (t, $^1J_{CH}$ = 116, $AlCH_2CH_3$). ^{13}C, ^{11}B, and ^{19}F NMR spectra in C_6D_5Cl confirmed that the $B(C_6F_5)_4^-$ anion is free. Anal. Calcd for $C_{39}H_{24}N_2AlF_{20}B$: C, 49.92; H, 2.58; N, 2.99. Found: C, 50.08; H, 2.73; N, 2.90.

Observation of an Intermediate in the Reaction of (^{i}Pr$_2$-ATI)AlEt$_2$ and [Ph$_3$C][B(C$_6$F$_5$)$_4$] at Low Temperature. An NMR tube was charged with $(^i Pr_2\text{-ATI})AlEt_2$ (32.4 mg, 112 μmol) and $[Ph_3C][B(C_6F_5)_4]$ (102 mg, 110 μmol), and CD_2Cl_2 (ca. 0.5 mL) was added by vacuum transfer at −78 °C. The tube was sealed at that temperature and inserted into a pre-cooled (−90 °C) NMR probe. The probe was warmed gradually to −30 °C, and spectra were recorded at several temperatures during the warm-up period. These spectra indicated that an intermediate formed between −90 and −45 °C that was identified as $[\{1,2\text{-}(N^iPr)_2\text{-}5\text{-}CPh_3\text{-cyclohepta-}3,6\text{-diene}\}AlEt_2][B(C_6F_5)_4]$ by NMR. ^1H NMR (CD_2Cl_2, −75 °C) δ 7.60−6.90 (m, 17H, H of Ph ring and H4 and H6), 6.57 (d, $^3J_{HH}$ = 13.0, H3 and H7), 6.00 (br, 1H, H5), 3.93 (br, 2H, Me_2CHN), 1.37 (br, 12H, Me_2CHN), 1.07 (t, $^3J_{HH}$ = 8, 3H, $AlCH_2CH_3^A$), 0.72 (t, $^3J_{HH}$ = 8, 3H, $AlCH_2CH_3^B$), 0.17 (q, $^3J_{HH}$ = 8, 4H, $AlCH_2^ACH_3$), 0.17 (q, $^3J_{HH}$ = 8, 4H, $AlCH_2^BCH_3$). $^{13}C\{H\}$ NMR (CD_2Cl_2, −75 °C) δ 162.2 (s, C1 and C2), 151.0 (C4 and C6), 143.7 (s, Ph_{ipso}), 132.6 (Ph), 128.8 (Ph), 127.2 (Ph), 126.7 (Ph), 126.5 (Ph), 121.7 (C3 and C7), 66.8 (s, Ph_3C), 52.0 (C5), 46.9 (Me_2CHN), 22.2 (Me^AMe^BCHN), 20.7 (Me^AMe^BCHN), 8.4 ($AlCH_2C^AH_3$), 7.4 ($AlCH_2C^BH_3$), 1.8 ($AlC^AH_2CH_3$), 0.2 ($AlC^BH_2CH_3$). The presence of six Ph signals in the ^{13}C NMR spectrum is ascribed to restricted rotation around the Ph_3C−C5 bond. ^{13}C, ^{11}B, and ^{19}F NMR spectra in CD_2Cl_2 confirmed that the $B(C_6F_5)_4^-$ anion is free.

$[\{1,2\text{-}(N^iPr)_2\text{-}5\text{-}CPh_3\text{-cyclohepta-}3,6\text{-diene}\}AlEt_2][B(C_6F_5)_4]$ was converted to $[(^i Pr_2\text{-ATI})AlEt][B(C_6F_5)_4]$ at −30 °C. Then, the probe was cooled to −90 °C and the spectra of this species were recorded. ^1H NMR (CD_2Cl_2, −90 °C) δ 7.69 (t, $^3J_{HH}$ = 10.5, 2H, H4 and H6), 7.41 (d, $^3J_{HH}$ = 12, 2H, H3 and H7), 4.14 (sept, $^3J_{HH}$ = 5.5, 2H, Me_2CHN), 1.44 (d, $^3J_{HH}$ = 5.5, 12H, Me_2CHN), 1.18 (t, $^3J_{HH}$ = 7.5, 3H, $AlCH_2CH_3$), 0.74 (q, $^3J_{HH}$ = 7.5, 2H, $AlCH_2CH_3$). The H5 resonance is obscured by a Ph_3CH resonance. $^{13}C\{H\}$ NMR (CD_2Cl_2, −90 °C) δ 159.1 (C1 and C2), 138.8 (C4 and C6), 123.3 (C5), 119.8 (C3 and C7), 46.6 (Me_2CHN), 22.1 (Me_2CHN), 7.2 ($AlCH_2CH_3$), 3.0 ($AlCH_2CH_3$). These spectra also contained resonances for Ph_3CH and ethylene. ^{13}C, ^{11}B, and ^{19}F NMR spectra in CD_2Cl_2 confirmed that the $B(C_6F_5)_4^-$ anion is free. $[(^i Pr_2\text{-ATI})AlEt][B(C_6F_5)_4]$ decomposed at −15 °C in CD_2Cl_2.

[(^{i}Pr$_2$-ATI)AlPr][B(C$_6$F$_5$)$_4$] (4d). This compound was synthesized from $(^i Pr_2\text{-ATI})AlPr_2$ in 96% yield using procedure B described above for **4c**. ^1H NMR (C_6D_5Cl) δ 7.16 (t, $^3J_{HH}$ = 10.5, 2H, H4 and H6), 6.79 (t, $^3J_{HH}$ = 9.5, 1H, H5), 6.75 (d, $^3J_{HH}$ = 11.5, H3 and H7), 3.52 (sept, $^3J_{HH}$ = 6.5, 2H, Me_2CHN), 1.46 (sext, $^3J_{HH}$ = 7.5, 2H, $AlCH_2CH_2CH_3$), 1.12 (d, $^3J_{HH}$ = 6.5, 12H, Me_2CHN), 0.95 (t, $^3J_{HH}$ = 7, 3H, $AlCH_2CH_2CH_3$), 0.55 (t, $^3J_{HH}$ = 8, 2H, $AlCH_2CH_2CH_3$). ^{13}C NMR (C_6D_5Cl) δ 160.0 (s, C1 and C2), 138.9 (d, $^1J_{CH}$ = 159, C4 and C6), 128.7 (d, $^1J_{CH}$ = 163, C5), 119.7 (d, $^1J_{CH}$ = 155, C3 and C7), 47.4 (d, $^1J_{CH}$ = 137, Me_2CHN), 22.8 (q, $^1J_{CH}$ = 126, Me_2CHN), 20.0 (q, $^1J_{CH}$ = 125, $AlCH_2CH_2CH_3$), 18.0 (t, $^1J_{CH}$ = 126, $AlCH_2CH_2CH_3$), 14.6 (t, $^1J_{CH}$ = 115, $AlCH_2CH_2CH_3$). ^{13}C, ^{11}B, and ^{19}F NMR spectra in C_6D_5Cl confirmed that the $B(C_6F_5)_4^-$ anion is free.

[(^{i}Pr$_2$-ATI)Al^{i}Bu][B(C$_6$F$_5$)$_4$] (4e). This compound was synthesized using procedure A (244 mg, 67%) or procedure B (1.10 g, 98%) described above for **4c**. ^1H NMR (C_6D_5Cl) δ 7.16 (dd, $^3J_{HH}$ = 11.5, 9.5, 2H, H4 and H6), 6.79 (d, $^3J_{HH}$ = 9.5, 2H, H5), 6.75 (t, $^3J_{HH}$ = 11.5, 2H, H3 and H7), 3.53 (sept, $^3J_{HH}$ = 6.5, 2H, Me_2CHN), 1.94 (nonet, $^3J_{HH}$ = 7, 2H, $AlCH_2CHMe_2$), 1.15 (d, $^3J_{HH}$ = 6.5, 12H, Me_2CHN), 0.95 (d, $^3J_{HH}$ = 7, 6H, $AlCH_2CHMe_2$), 0.60 (d, $^3J_{HH}$ = 8, 2H, $AlCH_2CHMe_2$). ^1H NMR (CD_2Cl_2, −90 °C) δ 7.70 (t, $^3J_{HH}$ = 10.5, 2H, H4 and H6), 7.41 (d, $^3J_{HH}$ = 12, 2H, H3 and H7), 7.26 (t, $^3J_{HH}$ = 9, 1H, H5), 4.13 (br, 2H, Me_2CHN), 2.10 (br, 2H, $AlCH_2CHMe_2$), 1.41 (d, $^3J_{HH}$ = 4.5, 12H, Me_2CHN), 0.98 (d, $^3J_{HH}$ = 4.5, 6H, $AlCH_2CHMe_2$), 0.79 (d, $^3J_{HH}$ = 7, 2H, $AlCH_2CHMe_2$). $^{13}C\{H\}$ NMR (C_6D_5Cl) δ 160.0 (C1 and C2), 139.0 (C4 and C6), 128.7 (C5), 119.7 (C3 and C7), 47.4 (Me_2CHN), 27.9 ($AlCH_2CHMe_2$), 25.7 ($AlCH_2CHMe_2$), 24.1 ($AlCH_2CHMe_2$), 22.8 (Me_2CHN). $^{13}C\{H\}$ NMR (CD_2Cl_2, −90 °C) δ 159.1 (C1 and C2), 147.0 138.8 (C4 and C6), 128.2 (C5), 119.9 (C3 and C7), 46.7 (Me_2CHN), 27.1 ($AlCH_2CHMe_2$), 25.0 ($AlCH_2CHMe_2$), 23.2 ($AlCH_2CHMe_2$), 22.0 (Me_2CHN). ^{13}C, ^{11}B, and ^{19}F NMR spectra in C_6D_5Cl confirmed that the $B(C_6F_5)_4^-$ anion is free. Anal. Calcd for $C_{41}H_{28}AlBF_{20}N_2$: C, 50.95; H, 2.92; N, 2.90. Found: C, 51.04; H, 3.15; N, 2.92.

Reaction of (^{i}Pr$_2$-ATI)AlEt$_2$ with B(C$_6$F$_5$)$_3$. A solution of $B(C_6F_5)_3$ (126 mg, 246 μmol) in pentane (6 mL) was added to a solution of $(^i Pr_2\text{-ATI})AlEt_2$ (71 mg, 250 μmol) in pentane (2 mL) at room temperature producing a cloudy mixture. A small amount of a red oil separated and the mixture was stirred for 36 h. The supernatant was decanted from the oil and evaporated under vacuum leaving a red oily residue that was dissolved in ca. 0.5 mL of C_6D_6. NMR spectra were taken. Signals of $(^i Pr_2\text{-ATI})AlEt(C_6F_5)$ (**5c**) and $BEt(C_6F_5)_2$ were observed.[43]

Data for **5c**: ^1H NMR (C_6D_6) δ 6.83 (m, 2H, H4 and H6), 6.47 (d, $^3J_{HH}$ = 11.5, 2H, H3 and H7), 6.31 (t, $^3J_{HH}$ = 9, 1H, H5), 3.55 (sept, $^3J_{HH}$ = 6.5, 2H, Me_2CHN), 1.26 (t, $^3J_{HH}$ = 8, 3H, $AlCH_2CH_3$), 1.14 (d, $^3J_{HH}$ = 6.5, 6H, Me^AMe^BCHN), 1.03 (d, $^3J_{HH}$ = 6.5, 6H, Me^AMe^BCHN), 0.65 (q, $^3J_{HH}$ = 8, 2H, $AlCH_2CH_3$). ^{13}C NMR (C_6D_6) δ 161.7 (s, C1 and C2), 150.0 (d, $^1J_{CF}$ = 231, AlC_6F_5), 141.5 (d, $^1J_{CF}$ = 253, AlC_6F_5), 137.2 (d, $^1J_{CF}$ = 252, AlC_6F_5), 137.1 (d, $^1J_{CH}$ = 154, C4 and C6), 121.0 (d, $^1J_{CH}$ = 160, C5), 115.2 (d, $^1J_{CH}$ = 152, C3 and C7), 47.5 (d, $^1J_{CH}$ = 135, Me_2CHN), 22.3 (q, $^1J_{CH}$ = 126, Me^AMe^BCHN), 22.1 (q, $^1J_{CH}$ = 126, Me^AMe^BCHN), 8.1 (q, $^1J_{CH}$ = 125, $AlCH_2CH_3$), 5.6 (br t, $^1J_{CH}$ = 112, $AlCH_2CH_3$). The signal corresponding to C_{ipso} of AlC_6F_5 was not observed. ^{19}F NMR (C_6D_6) δ −122.7 (2F, F_o, AlC_6F_5), −155.3 (1F, F_p, AlC_6F_5), −162.6 (2F, F_m, AlC_6F_5).

Data for $BEt(C_6F_5)_2$: ^1H NMR (C_6D_6) δ 1.80 (q, $^3J_{HH}$ = 8, 2H, BCH_2CH_3), 0.95 (t, $^3J_{HH}$ = 8, 3H, BCH_2CH_3). ^{13}C NMR (C_6D_6) δ 147.1 (d, $^1J_{CF}$ = 247, BC_6F_5), 143.5 (d, $^1J_{CF}$ = 258, BC_6F_5), 137.6 (d, $^1J_{CF}$ = 252, BC_6F_5), 24.2 (t, $^1J_{CH}$ = 115, BCH_2CH_3), 9.1 (q, $^1J_{CH}$ = 125, BCH_2CH_3). The signal corresponding to C_{ipso} of BC_6F_5 was not observed. ^{11}B NMR (C_6D_6) δ 72.2 (br s). ^{19}F NMR (C_6D_6) δ −131.0 (4F, F_o, BC_6F_5), −148.2 (2F, F_p, BC_6F_5), −161.7 (4F, F_m, BC_6F_5),

Reaction of (^{i}Pr$_2$-ATI)AlCy$_2$ with [Ph$_3$C][B(C$_6$F$_5$)$_4$]. A solution of $(^i Pr_2\text{-ATI})AlCy_2$ (23 mg, 62 μmol) in pentane (2 mL) was prepared and $[Ph_3C][B(C_6F_5)_4]$ (54 mg, 59 μmol) was added as a powder. The mixture was stirred for 24 h at 25 °C. A yellow precipitate formed during the first hour and then disappeared leaving a green-yellow solution and a small amount of a dark green oily residue. The supernatant was decanted from the oily residue and evaporated under vacuum leaving a dark green solid that was dissolved in ca. 0.5 mL of C_6D_6. The NMR spectra of this solution contained resonances for $(^i Pr_2\text{-ATI})AlCy(C_6F_5)$ (**5g**), Ph_3CH, and $B(C_6F_5)_3$.

Data for **5g**: ^1H NMR (C_6D_6) δ 6.81 (m, 2H, H4 and H6), 6.46 (d, $^3J_{HH}$ = 12, 2H, H3 and H7), 6.29 (t, $^3J_{HH}$ = 9, 1H, H5), 3.52 (sept, $^3J_{HH}$ = 6.5, 2H, Me_2CHN), 2.13 (br m, 2H, Cy), 1.93 (br m, 3H, Cy), 1.48 (br m, 5H, Cy), 1.15 (d, $^3J_{HH}$ = 6.5, 6H, Me^AMe^BCHN), 1.02 (d, $^3J_{HH}$ = 6.5, 6H, Me^AMe^BCHN), 0.81 (br m, 1H, AlCH). ^{13}C NMR (C_6D_6) δ 161.7 (C1 and C2), 149.9 (d, $^1J_{CF}$ = 233, C_6F_5), 141.4 (d, $^1J_{CF}$ = 250, C_6F_5), 137.2 (d, $^1J_{CH}$ = 251, C_6F_5), 137.0 (d, $^1J_{CH}$ = 154, C4 and C6), 120.9 (d, $^1J_{CH}$ = 160, C5), 115.2 (d, $^1J_{CH}$ = 152, C3 and C7), 47.5 (d, $^1J_{CH}$ = 135, Me_2CHN), 30.6 (t, $^1J_{CH}$ = 125, $2CH_2$, Cy), 28.6 (t, $^1J_{CH}$ = 127, CH_2, Cy), 27.1 (d, $^1J_{CH}$ = 111, AlCH), 22.5 (q, $^1J_{CH}$ = 126, Me^AMe^BCHN), 21.9 (q, $^1J_{CH}$ = 126, Me^AMe^BCHN). The signal for C_{ipso} of AlC_6F_5 was not observed. ^{19}F NMR (C_6D_6) δ −122.7 (2F, F_o), −154.9 (2F, F_p), −162.2 (2F, F_m).

Data for $B(C_6F_5)_3$: ^{13}C NMR (C_6D_6) δ 148.4 (d, $^1J_{CF}$ = 250, C_6F_5), 145.1 (d, $^1J_{CF}$ = 260, C_6F_5), 137.7 (d, $^1J_{CF}$ = 255, C_6F_5), 113.1 (br,

C_{ipso}). ^{19}F NMR (C_6D_6) δ −129.1 (6F, F_o), −142.0 (3F, F_p), −160.4 (6F, F_m).

Reaction of (^{i}Pr$_2$-ATI)Al(CH$_2$Ph)$_2$ with [Ph$_3$C][B(C$_6$F$_5$)$_4$]. A solution of (^{i}Pr$_2$-ATI)Al(CH$_2$Ph)$_2$ (262 mg, 635 μmol) in hexanes (10 mL) was prepared and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (536 mg, 581 μmol) was added as a powder. The suspension was stirred for 48 h at room temperature producing a slurry of a brown solid in a yellow solution. The solid was collected by filtration, washed with pentane, and dried under vacuum to give 243 mg (45% of the starting amount) of unreacted [Ph$_3$C][B(C$_6$F$_5$)$_4$] that was identified by ^1H NMR. The pentane washes were combined with the hexane filtrate and evaporated under vacuum to yield a yellow residue. The NMR spectra of this material contained signals for (^{i}Pr$_2$-ATI)Al(CH$_2$Ph)(C$_6$F$_5$) (**5h**) and Ph$_3$CCH$_2$Ph in ca. 2:1 molar ratio, and signals for a mixture of boranes B(CH$_2$Ph)$_x$(C$_6$F$_5$)$_{3-x}$ ($x = 0-3$).[40] Trace amounts of B(C$_6$F$_5$)$_4^-$ were detected by ^{19}F NMR. The Ph ring ^1H resonances were not assigned due to the complexity of the spectrum in the aromatic region.

Data for **5h**: ^1H NMR (C_6D_6) δ 6.40 (d, $^3J_{HH}$ = 12, 2H, H3 and H7), 6.25 (t, $^3J_{HH}$ = 9, 1H, H5), 3.44 (sept, $^3J_{HH}$ = 6.5, 2H, Me$_2$C*H*N), 2.40 (s, 2H, PhC*H*$_2$Al), 0.97 (d, $^3J_{HH}$ = 6.5, 6H, Me^A*Me*^{B}CHN), 0.95 (d, $^3J_{HH}$ = 6.5, 6H, *Me*^{A}Me^{B}CHN). The H4 and H6 resonance was obscured by Ph ring ^1H resonances. ^{19}F NMR (C_6D_6) δ −122.4 (2F, F_o), −154.3 (1F, F_p), −162.0 (2F, F_m).

Data for Ph$_3$CCH$_2$Ph: ^1H NMR (C_6D_6) δ 3.79 (s, 2H, Ph$_3$CC*H*$_2$Ph).

Data for B(CH$_2$Ph)(C$_6$F$_5$)$_2$: ^1H NMR (C_6D_6) δ 3.26 (s, C*H*$_2$Ph). ^{19}F NMR (C_6D_6) δ −129.8 (2F, F_o), −147.0 (1F, F_p), −161.4 (2F, F_m).

Data for B(CH$_2$Ph)$_2$(C$_6$F$_5$): ^1H NMR (C_6D_6) δ 2.88 (s, C*H*$_2$Ph). ^{19}F NMR (C_6D_6) δ −133.0 (4F, F_o), −152.3 (2F, F_p), −162.0 (4F, F_m).

Data for B(CH$_2$Ph)$_3$: ^1H NMR (C_6D_6) δ 2.09 (s, C*H*$_2$Ph).

Generation of [(^{i}Pr$_2$-ATI)Al(R)(NMe$_2$Ph)][B(C$_6$F$_5$)$_4$] (7a,b,c,e,h; R = H, Me, Et, ^{i}Bu, CH$_2$Ph). The following procedure for **7a** is representative; details for the other examples are provided in the Supporting Information. An NMR tube was charged with (^{i}Pr$_2$-ATI)AlH$_2$ (15 mg, 65 μmol) and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (59 mg, 74 μmol), and C$_6$D$_5$Cl (ca. 0.5 mL) was added by vacuum transfer at −78 °C. The tube was warmed to 23 °C and a rapid reaction occurred affording a homogeneous solution after a few seconds. The NMR spectra indicated that quantitative formation of [(^{i}Pr$_2$-ATI)AlH(NMe$_2$Ph)][B(C$_6$F$_5$)$_4$] had occurred. ^1H NMR (C_6D_5Cl) δ 7.22 (t, $^3J_{HH}$ = 11, 2H, H4 and H6), 7.17 (t, $^3J_{HH}$ = 7.5, 2H, H$_m$), 7.11 (t, $^3J_{HH}$ = 7.5, 1H, H$_p$), 6.96 (d, $^3J_{HH}$ = 7.5, 2H, H$_o$), 6.84 (d, $^3J_{HH}$ = 11.5, 2H, H3 and H7), 6.79 (t, $^3J_{HH}$ = 9.5, 1H, H5), 4.33 (br s, 1H, AlH), 3.34 (sept, $^3J_{HH}$ = 6.5, 2H, Me$_2$C*H*N), 2.40 (s, 6H, N*Me*$_2$Ph), 0.93 (br s, 6H, *Me*^{A}Me^{B}CHN), 0.79 (br s, 6H, Me^A*Me*^{B}CHN). ^{13}C NMR (C_6D_5Cl) δ 161.7 (s, C1 and C2), 144.1 (s, C_{ipso}), 138.8 (d, $^1J_{CH}$ = 157, C4 and C6), 130.5 (d, $^1J_{CH}$ = 169, C_m), 129.0 (d, $^1J_{CH}$ = 165, C_o), 127.4 (d, $^1J_{CH}$ = 161, C5), 121.0 (d, $^1J_{CH}$ = 165, C_p), 119.6 (d, $^1J_{CH}$ = 154, C3 and C7), 48.7 (d, $^1J_{CH}$ = 134, Me$_2$*C*HN), 45.9 (q, $^1J_{CH}$ = 142, N*Me*$_2$Ph), 23.9 (q, $^1J_{CH}$ = 126, *Me*^{A}Me^{B}CHN), 21.4 (q, $^1J_{CH}$ = 126, Me^A*Me*^{B}CHN). ^{13}C, ^{11}B, and ^{19}F NMR spectra in C_6D_5Cl confirmed that the B(C$_6$F$_5$)$_4^-$ anion is free.

[(^{i}Pr$_2$-ATI)Al(R)(NCMe)][B(C$_6$F$_5$)$_4$] (8c,d,e; R = Et, Pr, ^{i}Bu). The following procedure for **8c** is representative; details for the other examples are provided in the Supporting Information. A sample tube was charged with [(^{i}Pr$_2$-ATI)AlEt][B(C$_6$F$_5$)$_4$] (330 mg, 352 μmol) and toluene (ca. 5 mL). Phase separation to a yellow liquid clathrate and a pale-yellow solution occurred. Acetonitrile (ca. 1 mL) was added by vacuum transfer at −78 °C, and the tube was warmed to room temperature. The clathrate dissolved. The volatiles were removed under vacuum leaving a red-yellow oil that crystallized over a 12 h period to give 340 mg (99%) of the product. The NMR spectra of isolated material indicated that intermolecular NCMe exchange is fast on the NMR time scale which is ascribed to an associative exchange with a trace amount of free MeCN. ^1H NMR (C_6D_5Cl) δ 7.13 (m, 2H, H4 and H6), 6.73 (d, $^3J_{HH}$ = 11, 2H, H3 and H7), 6.67 (t, $^3J_{HH}$ = 9, 1H, H5), 3.62 (sept, $^3J_{HH}$ = 6.5, 2H, Me$_2$C*H*N), 1.74 (s, 3H, *Me*CN), 1.11 (d, $^3J_{HH}$ = 6.5, 12H, *Me*$_2$CHN), 1.03 (t, $^3J_{HH}$ = 8, 3H, AlCH$_2$C*H*$_3$), 0.23 (q, $^3J_{HH}$ = 8, 2H, AlC*H*$_2$CH$_3$). ^1H NMR (CD_2Cl_2) δ 7.52 (m, 2H, H4 and H6), 7.16 (d, $^3J_{HH}$ = 11.5, 2H, H3 and H7), 7.01 (t, $^3J_{HH}$ = 9, 1H, H5), 4.08 (sept, $^3J_{HH}$ = 6.5, 2H, Me$_2$C*H*N), 2.56 (s, 3H, *Me*CN), 1.41 (d, $^3J_{HH}$ = 6.5, 12H, *Me*$_2$CHN), 1.14 (t, $^3J_{HH}$ = 8, 3H, AlCH$_2$C*H*$_3$), 0.42 (q, $^3J_{HH}$ = 8, 2H, AlC*H*$_2$CH$_3$). ^1H NMR (CD_2Cl_2, −90 °C) δ 7.44 (t, $^3J_{HH}$ = 10, 2H, H4 and H6), 7.05 (d, $^3J_{HH}$ = 11.5, 2H, H3 and H7), 6.93 (t, $^3J_{HH}$ = 9.5, 1H, H5), 3.97 (br m, 2H, Me$_2$C*H*N), 2.58 (s, 3H, *Me*CN), 1.31 (br d, 12H, *Me*$_2$CHN), 1.01 (t, $^3J_{HH}$ = 8, 3H, AlCH$_2$C*H*$_3$), 0.29 (q, $^3J_{HH}$ = 8, 2H, AlC*H*$_2$CH$_3$). $^{13}C\{H\}$ NMR (C_6D_5Cl) δ 160.6 (C1 and C2), 138.5 (C4 and C6), 125.9 (C5), 123.1 (Me*C*N), 117.8 (C3 and C7), 47.0 (Me$_2$*C*HN), 22.5 (*Me*$_2$CHN), 7.9 (AlCH$_2$*C*H$_3$), 1.6 (Al*C*H$_2$CH$_3$), 0.7 (*Me*CN). $^{13}C\{H\}$ NMR (CD_2Cl_2) δ 161.4 (C1 and C2), 139.0 (C4 and C6), 126.2 (C5), 120.7 (Me*C*N), 118.4 (C3 and C7), 47.6 (Me$_2$*C*HN), 23.2 (*Me*$_2$CHN), 8.1 (AlCH$_2$*C*H$_3$), 3.3 (*Me*CN), the Al*C*H$_2$CH$_3$ resonance was not observed. $^{13}C\{H\}$ NMR (CD_2Cl_2, −90 °C) δ 159.9 (C1 and C2), 137.9 (C4 and C6), 124.7 (C5), 122.5 (br, Me*C*N), 117.1 (C3 and C7), 46.4 (Me$_2$*C*HN), 22.1 (*Me*$_2$CHN), 7.7 (AlCH$_2$*C*H$_3$), 3.4 (*Me*CN), 0.9 (Al*C*H$_2$CH$_3$). ^{13}C, ^{11}B, and ^{19}F NMR spectra in CD_2Cl_2 confirmed that the B(C$_6$F$_5$)$_4^-$ anion is free. Anal. Calcd for $C_{41}H_{27}N_3F_{20}BAl$: C, 50.30; H, 2.78; N, 4.21. Found: C, 50.44; H, 2.80; N, 4.22.

To generate **8c** in the complete absence of free MeCN, the above reaction was carried out with 10 mol % deficiency of MeCN. NMR spectra indicated that **8c** formed quantitatively (based on MeCN) and signals for the expected ca. 10% unreacted **4c** were also observed. Due to the presence of **4c**, no free MeCN is present and intermolecular MeCN exchange is thus slow. ^1H NMR (C_6D_5Cl) δ 7.13 (m, 2H, H4 and H6), 6.73 (d, $^3J_{HH}$ = 11, 2H, H3 and H7), 6.67 (t, $^3J_{HH}$ = 9, 1H, H5), 3.62 (sept, $^3J_{HH}$ = 6.5, 2H, Me$_2$C*H*N), 1.77 (s, 3H, *Me*CN), 1.16 (d, $^3J_{HH}$ = 6.5, 6H, Me^A*Me*^{B}CHN), 1.06 (d, $^3J_{HH}$ = 6.5, 6H, *Me*^{A}Me^{B}CHN), 1.03 (t, $^3J_{HH}$ = 8, 3H, AlCH$_2$C*H*$_3$), 0.22 (q, $^3J_{HH}$ = 8, 2H, AlC*H*$_2$CH$_3$). ^{13}C NMR (C_6D_5Cl) δ 160.7 (s, C1 and C2), 138.5 (d, $^1J_{CH}$ = 156, C4 and C6), 125.9 (d, $^1J_{CH}$ = 162, C5), 123.3 (s, Me*C*N), 117.8 (d, $^1J_{CH}$ = 153, C3 and C7), 47.0 (d, $^1J_{CH}$ = 137, Me$_2$*C*HN), 22.8 (q, $^1J_{CH}$ = 125, Me^A*Me*^{B}CHN), 22.3 (q, $^1J_{CH}$ = 125, *Me*^{A}Me^{B}CHN), 7.9 (q, $^1J_{CH}$ = 126, AlCH$_2$*C*H$_3$), 1.7 (t, $^1J_{CH}$ = 116, Al*C*H$_2$CH$_3$), 0.7 (q, $^1J_{CH}$ = 140, *Me*CN). ^{13}C, ^{11}B, and ^{19}F NMR spectra in C_6D_5Cl confirmed that B(C$_6$F$_5$)$_4^-$ anion is free.

[(^{i}Pr$_2$-ATI)Al(R)(O=CMe$_2$)][B(C$_6$F$_5$)$_4$] (9b,c,d; R = Me, Et, Pr). The following procedure for **9c** is representative; details for the other examples are provided in the Supporting Information. An NMR tube was charged with [(^{i}Pr$_2$-ATI)AlEt][B(C$_6$F$_5$)$_4$] (50 mg, 53 μmol), and C$_6$D$_5$Cl (0.5 mL) and acetone (20.3 mL at 44 Torr and 25 °C, 48 μmol) were added by vacuum transfer at −78 °C. The tube was warmed to room temperature and a yellow solution formed. NMR spectra were obtained after ca. 5 min at 23 °C and indicated that **9c** had formed quantitatively (based on Me$_2$CO); signals for the expected ca. 10% unreacted **4c** were also observed. **9c** is stable in C$_6$D$_5$Cl solution for ca. 1 day at 23 °C. Due to the presence of **4c**, no free Me$_2$CO is present and intermolecular Me$_2$CO exchange is thus slow. ^1H NMR (C_6D_5Cl) δ 7.15 (m, 2H, H4 and H6), 6.77 (d, $^3J_{HH}$ = 12, 2H, H3 and H7), 6.68 (t, $^3J_{HH}$ = 9, 1H, H5), 3.62 (sept, $^3J_{HH}$ = 6.5, 2H, Me$_2$C*H*N), 2.02 (s, 6H, *Me*$_2$CO), 1.05 (d, $^3J_{HH}$ = 6.5, 6H, *Me*^{A}Me^{B}CHN), 1.01 (m, 9H, d of Me^A*Me*^{B}CHN and t of AlCH$_2$C*H*$_3$), 0.26 (q, $^3J_{HH}$ = 8.3, 2H, AlC*H*$_2$CH$_3$). $^{13}C\{H\}$ NMR (C_6D_5Cl) δ 236.7 (Me$_2$*C*O), 160.3 (C1 and C2), 138.5 (C4 and C6), 126.0 (C5), 117.8 (C3 and C7), 46.9 (Me$_2$*C*HN), 32.3 (*Me*$_2$CO), 22.9 (*Me*^{A}Me^{B}CHN), 22.1 (Me^A*Me*^{B}CHN), 8.0 (AlCH$_2$*C*H$_3$), 1.6 (Al*C*H$_2$CH$_3$).

The above reaction was also carried out with 4 mol % excess acetone. NMR spectra indicated that quantitative formation of **9c** occurred and that intermolecular Me$_2$CO exchange is fast on the NMR time scale at 23 °C. ^1H NMR (C_6D_5Cl) δ 7.15 (m, 2H, H4 and H6), 6.77 (d, $^3J_{HH}$ = 12, 2H, H3 and H7), 6.68 (t, $^3J_{HH}$ = 9, 1H, H5), 3.62 (sept, $^3J_{HH}$ = 6.5, 2H, Me$_2$C*H*N), 2.00 (s, 6H, *Me*$_2$CO), 1.03 (m, 15H, d of *Me*$_2$CHN and t of AlCH$_2$C*H*$_3$), 0.27 (q, $^3J_{HH}$ = 8.3, 2H, AlC*H*$_2$CH$_3$). $^{13}C\{H\}$ NMR (C_6D_5Cl) δ 160.3 (C1 and C2), 138.5 (C4 and C6), 126.0 (C5), 117.8 (C3 and C7), 46.8 (N*C*HMe$_2$), 32.1 (*Me*$_2$CO), 22.5 (NCH*Me*$_2$), 8.0 (AlCH$_2$*C*H$_3$), 1.6 (Al*C*H$_2$CH$_3$); the Me$_2$*C*O resonance was not observed.

[{(^{i}Pr$_2$-ATI)Al(μ-O^{i}Pr$_2$)}$_2$][B(C$_6$F$_5$)$_4$]$_2$·2CD$_2$Cl$_2$ (10·2CD$_2$Cl$_2$). A resealable NMR tube was charged with [(^{i}Pr$_2$-ATI)AlEt][B(C$_6$F$_5$)$_4$] (62 mg, 66 μmol), and C_6D_6 (1 mL) was added by pipet at 25 °C. Phase separation occurred to produce a pale yellow solution above a dark red oil. Acetone (20.3 mL at 61 Torr and 25 °C, 66 μmol) was added by vacuum transfer at −78 °C. The tube was continuously shaken and was warmed to room temperature. The lower oil layer did not dis-

solve. The volatiles were removed under vacuum leaving a yellow solid. CD_2Cl_2 (0.5 mL) was added by vacuum transfer producing a yellow solution. The tube was maintained at 25 °C for 3 days. NMR spectra were obtained periodically and established that **9c** was gradually converted to **10** during this period. The volatiles were removed under vacuum leaving a yellow oil that was washed with pentane (3 × 1 mL) to afford 59 mg (94%) of a yellow powder. This material was recrystallized from CH_2Cl_2 to yield yellow crystalline **10**·$2CH_2Cl_2$. **10** was also synthesized from **4d** using the above procedure. ^{1}H NMR (CD_2Cl_2) δ 7.95 (m, 2H, H4 and H6), 7.79 (d, $^3J_{HH}$ = 11, 2H, H3 and H7), 7.58 (t, $^3J_{HH}$ = 9, 1H, H5), 4.86 (sept, $^3J_{HH}$ = 6, 1H, Me_2CHO), 4.32 (sept, $^3J_{HH}$ = 7, 2H, Me_2CHN), 1.68 (d, $^3J_{HH}$ = 7, 12H, Me_2CHN), 1.44 (d, $^3J_{HH}$ = 6, 6H, Me_2CHO). ^{13}C{H} NMR (CD_2Cl_2) δ 159.5 (C1 and C2), 140.9 (C4 and C6), 132.4 (C5), 124.3 (C3 and C7), 78.0 (Me_2CHO), 48.6 (Me_2CHN), 25.7 (Me_2CHO), 23.1 (Me_2CHN). ^{13}C, ^{11}B, and ^{19}F NMR spectra confirmed that the $B(C_6F_5)_4^-$ anion is free. **Anal.** Calcd for **10**·$2CD_2Cl_2$ ($C_{41}H_{26}D_2AlBCl_2F_{20}NO$): C, 46.66; H + D, 2.86; N 2.65. Found: C, 46.76; H + D 2.70; N, 2.67.

[(^{i}Pr$_2$-ATI)Al(CH═CH^{t}Bu)][B(C_6F_5)$_4$] (12). A resealable NMR tube was charged with [(^{i}Pr$_2$-ATI)AlEt][B(C_6F_5)$_4$] (42 mg, 45 μmol), and C_6D_5Cl (0.5 mL) was added by vacuum transfer to produce a yellow solution. ^{t}BuC≡CH (20.3 mL at 42 Torr and 25 °C, 45 μmol) was added by vacuum transfer at −78 °C. The tube was continuously shaken and was warmed to room temperature. NMR spectra were obtained after 5 min at room temperature and indicated that quantitative formation of **12** and ethylene had occurred. The volatiles were removed under vacuum leaving a dark red oil, and C_6D_5Cl (0.5 mL) was added by vacuum transfer. ^{1}H and ^{13}C NMR spectra confirmed the presence of **12** and the absence of ethylene. Compound **12** was generated in similar experiments from **4d** and **4e**; in these cases propylene and isobutylene are formed. ^{1}H NMR (C_6D_5Cl) δ 7.19 (t, $^3J_{HH}$ = 10, 2H, H4 and H6), 6.81 (m, 3H, H3 and H7 and H5), 6.45 (d, $^3J_{HH}$ = 21, 1H, AlCH═C*H*CMe$_3$), 5.56 (d, $^3J_{HH}$ = 21, 1H, AlC*H*═CHCMe$_3$), 3.57 (sept, $^3J_{HH}$ = 6.5, 2H, Me_2CHN), 1.16 (d, $^3J_{HH}$ = 6.5, 12H, Me_2CHN), 0.95 (s, 9H, AlCH═CHCMe_3). ^{13}C{H} NMR (C_6D_5Cl) δ 169.9 (AlCH═*C*HCMe$_3$), 160.0 (C1 and C2), 139.1 (C4 and C6), 128.7 (C5), 119.8 (C3 and C7), 118.0 (br, Al*C*H═CHCMe$_3$), 47.6 (Me_2CHN), 37.0 (AlCH═CH*C*Me$_3$), 28.2 (AlCH═CHCMe_3), 23.1 (Me_2CHN). ^{13}C, ^{11}B, and ^{19}F NMR spectra confirmed that the $B(C_6F_5)_4^-$ anion is free.

[{(^{i}Pr$_2$-ATI)Al(μ-C≡C^{t}Bu)}$_2$][B(C_6F_5)$_4$]$_2$·$2C_6H_5Cl$ (13·$2C_6H_5Cl$). A resealable NMR tube was charged with [(^{i}Pr$_2$-ATI)AlPr][B(C_6F_5)$_4$] (131 mg, 138 μmol), and C_6H_5Cl (0.5 mL) and ^{t}BuC≡CH (20.3 mL at 64 Torr and 25 °C, 140 μmol) were added by vacuum transfer at −78 °C. The tube was warmed to room temperature and shaken for 5 min. A second equivalent of ^{t}BuC≡CH (20.3 mL at 64 Torr and 25 °C, 140 μmol) was added by vacuum transfer at −78 °C. The tube was warmed to room temperature and shaken for 5 min. The volatiles were removed under vacuum leaving a yellow-red glass. C_6H_5Cl (0.5 mL) was added by vacuum transfer at −78 °C. A yellow crystalline precipitate formed upon dissolution of the glass at room temperature. The mother liquor was decanted, and the precipitate was washed with benzene (7 × 0.5 mL) and pentane (5 × 0.5 mL) and dried under vacuum to give 83 mg (55%) of **13**·$2C_6H_5Cl$. **Anal.** Calcd for **13**·$2C_6H_5Cl$ ($C_{49}H_{33}$-$AlBClF_{20}N_2$): C, 53.36; H, 3.02; N, 2.54. Found: C, 53.48; H, 3.13; N 2.71. X-ray analysis of crystals from the yellow precipitate established that this material is **13**·$5C_6H_5Cl$ (prior to drying). The crystals crumble in the absence of C_6H_5Cl solvent with loss of 3 equiv of C_6H_5Cl molecules forming **13**·$2C_6H_5Cl$. **13** is insoluble in toluene, benzene, and chlorobenzene, and decomposes to unidentified species in CH_2Cl_2.

^{1}H NMR Spectrum of 13 Before Precipitation. The ^{1}H NMR spectrum of **13** in C_6D_5Cl was assigned by comparison of the spectra recorded for reaction of **12** with ^{t}BuC≡CH before and after precipitation of **13**·$5C_6D_5Cl$. As noted in the text, the nuclearity of the [(^{i}Pr$_2$-ATI)Al(C≡C^{t}Bu)]$^+$ cation in solution (i.e. mononuclear vs dinuclear) is not established. ^{1}H NMR (C_6D_5Cl) δ 7.41 (m, 2H, H4 and H6), 7.25 (m, 3H, H3 and H7 and H5), 3.98 (br, 2H, Me_2CHN), 1.48 (d, $^3J_{HH}$ = 6.5, 12H, Me_2CHN), 0.84 (s, 9, AlC≡CCMe_3).

[(^{i}Pr$_2$-ATI)Al(CH═C(^{t}Bu)C≡C^{t}Bu)][B(C_6F_5)$_4$] (14) was observed by NMR as an intermediate in the catalytic reaction of **4c**−**e** with ^{t}BuC≡CH. ^{1}H NMR (C_6D_5Cl) δ 7.25 (t, $^3J_{HH}$ = 11, 2H, H4 and H6), 6.93 (d, $^3J_{HH}$ = 11, 2H, H3 and H7), 6.83 (t, $^3J_{HH}$ = 9, 1H, H5), 6.07 (s, 1H, AlC*H*), 3.62 (sept, $^3J_{HH}$ = 6.5, 2H, Me_2CHN), 1.22 (d, $^3J_{HH}$ = 6.5, 12H, Me_2CHN), 1.06 (s, 9H, AlCH═C(CMe_3)), 0.71 (s, 9H, AlCH═C(CMe$_3$)C≡CCMe_3). ^{13}C NMR (C_6D_5Cl) δ 159.7 (C1 and C2), 159.0 (AlCH═*C*H(CMe$_3$)C≡CCMe$_3$), 148.9 (d, $^1J_{CF}$ = 240, $B(C_6F_5)_4^-$), 139.1 (C4 and C6), 138.7 (d, $^1J_{CF}$ = 245, $B(C_6F_5)_4^-$), 136.8 (d, $^1J_{CF}$ = 240, $B(C_6F_5)_4^-$), 128.7 (C5), 126.5 (br, *ipso*-$B(C_6F_5)_4^-$), 119.9 (C3 and C7), 118.0 (br, Al*C*), 86.0 (AlCH═C(CMe$_3$)C≡*C*), 59.8 (AlCH═C(CMe$_3$)*C*≡C), 47.7 (Me_2CHN), 31.5 (AlCH═C(*C*Me$_3$)), 29.8 (AlCH═C(CMe$_3$)C≡CCMe_3), 28.0 (AlCH═C(CMe_3)), 22.6 (Me_2CHN); the AlCH═C(CMe$_3$)C≡C*C*Me$_3$ resonance was not assigned. ^{13}C, ^{11}B, and ^{19}F NMR spectra in C_6D_5Cl confirmed that the $B(C_6F_5)_4^-$ anion is free.

Catalytic Dimerization of ^{t}BuC≡CH. An NMR tube was charged with [(^{i}Pr$_2$-ATI)AlEt][B(C_6F_5)$_4$] (30 mg, 32 μmol). C_6D_5Cl (0.5 mL) was added by vacuum transfer at −78 °C and the mixture was warmed to room temperature to produce a yellow solution. ^{t}BuC≡CH (ca. 8 equiv) was added by vacuum transfer at −78 °C. The mixture was warmed to room temperature and monitored by NMR. The formation of ethylene and ^{t}BuCH═CH_2 (1 equiv) was observed. After 3 days at ambient temperature, the signals corresponding to ^{t}BuC≡CH had completely disappeared, and the resonances for the head-to-tail dimer, 2-*tert*-butyl-5,5-dimethyl-1-hexen-3-yne (**11**), were observed. Hexanes (ca. 2 mL) and a few drops of 5% aqueous HCl solution were added to the solution. The mixture was shaken for 5 min. The clear colorless organic layer was separated and analyzed by GC-MS. **11** was observed as the major organic product (>90%). The data for **11** are consistent with those reported by Eisen.[72] Characterization of **11**: **^{1}H NMR** (C_6D_5Cl) δ 5.22 (d, 1H, $^2J_{HH}$ = 1.8, H^AHBC═C), 5.09 (d, 1H, $^2J_{HH}$ = 1.8, HAH^BC═C), 1.19 (s, 9H, H_2C═C(CMe_3)), 1.12 (s, 9H, C≡CCMe_3). ^{13}C NMR (C_6D_5Cl) δ 142.3 (H_2C═*C*(CMe$_3$)), 115.9 (H_2C═C), 99.2 (C≡*C*CMe$_3$), 79.4 (*C*≡CCMe$_3$), 31.1 (C≡CCMe_3), 29.1 (H_2C═C(CMe_3)); the H_2C═C(*C*Me$_3$)C≡C*C*Me$_3$ resonances were not assigned. GCMS *m*/*e*: 164 (M^+), 149 (100%, M^+ − Me), 134 (M^+ − 2 Me), 133 (M^+ − Me − CH_4), 121 (M^+ − Me − CH_2═CH_2), 108 (M^+ − CH_2═CMe_2), 107 (M^+ − ^{t}Bu), 93 (M^+ − Me − CH_2═CMe_2).

Reaction of [(^{i}Pr$_2$-ATI)AlEt][B(C_6F_5)$_4$] with $AlEt_3$. An NMR tube was charged with [(^{i}Pr$_2$-ATI)AlEt][B(C_6F_5)$_4$] (128 mg, 140 μmol) and $AlEt_3$ (15 mg, 140 μmol), and CD_2Cl_2 (ca. 0.5 mL) was added by vacuum transfer at −78 °C. The tube was sealed at −78 °C and inserted into a pre-cooled (−90 °C) NMR probe. NMR spectra at this temperature indicated that two compounds had formed in a 2:1 ratio, which were assigned as [AlEt(μ-^{i}Pr$_2$-ATI)(μ-Et)$AlEt_2$][B(C_6F_5)$_4$] (**15**) and [(^{i}Pr$_2$-ATI)Al(μ-Et)$_2AlEt_2$][B(C_6F_5)$_4$] (**16**), respectively. Crystals of **15** were obtained after slow evaporation of a 1:1 mixture of [(^{i}Pr$_2$-ATI)AlEt][B(C_6F_5)$_4$] and $AlEt_3$ in toluene. ^{1}H NMR (CD_2Cl_2, −90 °C) δ 8.41 (t, 2H, H4 and H6 of **16**), 8.16 (t, 1H, H5 of **16**), 8.05 (d, 2H, H3 and H7 of **16**), 7.74 (t, 2H, H4 or H6 of **15**), 7.53 (t, 2H, H4 or H6 of **15**), 7.39 (m, 6H, H3, H5, H7 of **15**), 4.01 (br, 6H, Me_2CHN of both), 2.00−1.00 (m, 96H, Me_2CHN, $AlCH_2CH_3$, $AlCH_2CH_3$ of both). ^{13}C NMR (CD_2Cl_2, −90 °C) δ 168.1, 164.9, 155.4 (s, C1 and C2 of both), 147.0 (d, $^1J_{CH}$ = 161), 142.9 (d, $^1J_{CH}$ = 157), 139.2 (d, $^1J_{CH}$ = 165), 137.4 (d, $^1J_{CH}$ = 152), 134.4 (d, $^1J_{CH}$ = 160) (C4, C5, C6 of both), 130.3 (d, $^1J_{CH}$ = 155), 129.0 (d, $^1J_{CH}$ = 157), 125.9 (d, $^1J_{CH}$ = 158) (C3 and C7 of both), 49.8 (d, $^1J_{CH}$ = 134), 48.5 (d, $^1J_{CH}$ = 134), 48.2 (d, $^1J_{CH}$ = 137) (Me_2CHN of both), 23.1 (q, $^1J_{CH}$ = 129), 22.3 (q, $^1J_{CH}$ = 126, 2 overlapping signals), 21.3 (q, $^1J_{CH}$ = 128), 20.5 (q, $^1J_{CH}$ = 129) (Me_2CHN of both), 8.7, 8.3, 8.2, 8.0, 7.5, 7.1 (q, $AlCH_2CH_3$ terminal and bridging of both), 5.6 (t, $^1J_{CH}$ = 119), 3.4 (t, $^1J_{CH}$ = 105), 1.6 (t, $^1J_{CH}$ = 113), 0.7 (t, $^1J_{CH}$ = 115), −1.7 (t, $^1J_{CH}$ = 115), −3.5 (t, $^1J_{CH}$ = 114) ($AlCH_2CH_3$ terminal and bridging of both). ^{13}C, ^{11}B, and ^{19}F NMR spectra in CD_2Cl_2 confirmed that the $B(C_6F_5)_4^-$ anion is free.

At −3 °C, NMR spectra contain only one set of broad resonances for the (^{i}Pr$_2$-ATI)$^-$ ligand and the Al-Et group, which is indicative of fast exchange between **15** and **16**. ^{1}H NMR (CD_2Cl_2, 26 °C) δ 7.86 (br s, 2H, H4 and H6), 7.62 (br s, 3H, H3 and H7, H5), 4.10 (br s, 2H, Me_2CHN), 1.49 (br d, $^3J_{HH}$ = 5.5, 12H, Me_2CHN), 1.04 (br s, 12H, $AlCH_2CH_3$), 0.33 (br s, 8H, $AlCH_2CH_3$). ^{13}C NMR (CD_2Cl_2, 26 °C) δ

(72) Straub, T.; Haskel, A.; Eisen, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 6365.

Table 3. Summary of X-ray Diffraction Data for Aluminum Aminotroponiminate Complexes

	2b	**3**	**4c**(ClPh)·0.5PhCl	**8c**	**10**·2CH_2Cl_2	**13**·5PhCl	**15**
formula	$C_{53}H_{47}Al_2BF_{20}N_4$	$C_{31}H_{21}AlBF_{15}N_2$	$C_{48}H_{31.5}AlBCl_{1.5}F_{20}N_2$	$C_{41}H_{27}AlBF_{20}N_3$	$C_{82}H_{56}Al_2B_2Cl_4F_{40}N_4O_2$	$C_{116}H_{81}Al_2B_2Cl_5F_{40}N_4$	$C_{45}H_{39}Al_2BF_{20}N_2$
fw	1184.72	744.29	1107.22	979.45	2106.68	2543.68	1052.55
cryst system	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
color	yellow	yellow	yellow	yellow	yellow	yellow	colorless
a, Å	10.4815(2)	10.0419(3)	14.2338(9)	11.1053(6)	13.4003(7)	12.5421(6)	10.9714(6)
b, Å	14.0422(3)	10.0407(3)	20.026(1)	28.576(2)	14.4792(8)	27.494(1)	12.3277(6)
c, Å	18.7747(4)	15.9755(4)	16.546(1)	13.7262(7)	22.604(1)	16.7627(8)	17.3766(9)
α, deg	104.450(1)	105.921(1)					80.783(1)
β, deg	94.848(1)	96.061(1)	98.450(1)	106.606(1)	91.756(1)	103.906(1)	79.894(1)
γ, deg	96.639(1)	95.456(1)					88.790(1)
V, Å^3	2639.44(9)	1527.31(8)	4665.1(5)	4174.2(4)	4383.7(4)	5610.8(5)	2283.8(2)
temp, K	173(2)	173(2)	173(2)	163(2)	173(2)	163(2)	173(2)
Z	2	2	4	4	2	2	2
*R*1, *wR*2 ($I>2\sigma(I)$)	0.0447, 0.0891	0.0446, 0.0951	0.0879, 0.1855	0.0320, 0.0851	0.0688, 0.2079	0.0430, 0.1171	0.0391, 0.1108
GOF on F^2	0.980	0.997	1.017	1.037	1.008	1.003	1.066

148.9 (C4 and C6), 138.9 (C5), 137.0 (C3 and C7), 50.3 (Me_2CHN), 22.9 (Me_2CHN), 8.5 ($AlCH_2CH_3$), 2.2 ($AlCH_2CH_3$). The C1 and C2 resonance was not observed.

Reaction of [(^{i}Pr$_2$-ATI)Al^{i}Bu][B(C$_6$F$_5$)$_4$] with Ethylene. An NMR tube was charged with [(^{i}Pr$_2$-ATI)Al^{i}Bu][B(C_6F_5)$_4$] (52 mg, 54 μmol), and C_6D_5Cl (ca. 0.5 mL) and ethylene (ca. 160 μmol) were added by vacuum transfer at −196 °C. The tube was sealed and warmed to 25 °C. NMR spectra taken immediately contained signals corresponding to [(^{i}Pr$_2$-ATI)Al^{i}Bu][B(C_6F_5)$_4$] and [(^{i}Pr$_2$-ATI)AlEt][B(C_6F_5)$_4$] as well as C_2H_4. After 12 h at 25 °C, a colorless precipitate had formed, and NMR spectra contained only signals corresponding to [(^{i}Pr$_2$-ATI)AlEt][B(C_6F_5)$_4$] as well as C_2H_4, polyethylene, and polyisobutylene. In a similar experiment, the reaction of [(^{i}Pr$_2$-ATI)Al^{i}Bu][B(C_6F_5)$_4$] and ethylene-d_4 resulted in complete conversion to [(^{i}Pr$_2$-ATI)$AlCD_2CD_2H$][B(C_6F_5)$_4$] after 8 h at 25 °C. Data for [(^{i}Pr$_2$-ATI)$AlCD_2CD_2H$][B(C_6F_5)$_4$]: ^{1}H NMR (C_6D_5Cl) δ 7.16 (t, $^3J_{HH}$ = 10.5, 2H, H4 and H6), 6.78 (t, $^3J_{HH}$ = 10, 1H, H5), 6.74 (d, $^3J_{HH}$ = 11, 2H, H3 and H7), 3.51 (sept, $^3J_{HH}$ = 6.5, 2H, Me_2CHN), 1.09 (d, $^3J_{HH}$ = 6.5, 12H, Me_2CHN); the $AlCD_2CD_2H$ resonance was obscured by polyisobutylene signals. ^{13}C{H} NMR (C_6D_5Cl) δ 159.9 (s, C1 and C2), 139.0 (C4 and C6), 128.7 (C5), 119.7 (C3 and C7), 47.3 (Me_2CHN), 22.8 (Me_2CHN), 6.9 (quint, $^1J_{CD}$ = 20, $AlCD_2CD_2H$); the $AlCD_2CD_2H$ resonance was not observed.

Ethylene Polymerization at 1 atm. Toluene (ca. 15 mL) was added to a mixture of (^{i}Pr$_2$-ATI)Al^{i}Bu$_2$ (22 mg, 64 μmol) and [Ph_3C][B(C_6F_5)$_4$] (66 mg, 72 μmol) in a round-bottom flask by a pipet in a glovebox. The flask was moved to a high vacuum line, the mixture was stirred at 23 °C for 30 min, and phase separation occurred. The mixture was degassed three times by the freeze/pump/thaw method. The mixture was heated to 80 °C, 1 atm of ethylene was introduced, and the reaction mixture was stirred for 1 h at 80 °C. MeOH was added to the mixture and the resulting solid was collected by filtration, washed with MeOH and acetone, and dried under vacuum for 5 h affording 58 mg of polyethylene. Activity: 908 g PE/mol·h·atm.

Ethylene polymerization by (^{i}Pr$_2$-ATI)AlEt$_2$ (15 mg, 52 μmol) and [Ph_3C][B(C_6F_5)$_4$] (48 mg, 52 μmol) was performed using the same procedure. Yield of polyethylene: 136 mg. Activity: 2615 g PE/mol·h·atm.

X-ray Crystallography. The structures of **2b** and **3** were determined by V. G. Young, Jr. (University of Minnesota) and the structures of **4c**, **8c**, **10**, **13**, and **15** were determined by I. A. Guzei (Iowa State University). X-ray data are summarized in Table 3. Full details of the crystallographic analyses of **2b**, **10**, and **13** can be found in Supporting Information of the preliminary communications.[22] Full details of the analyses for **3**, **4c**, **8c**, and **15** are given in the Supporting Information. Thermal ellipsoids in Figures 1−7 are drawn at the 30% probability level.

Acknowledgment. This work was supported by Eastman Chemical Company and DOE grant DE-FG02-00ER15036.

Supporting Information Available: Additional experimental details and characterization data for new compounds and crystal data, data collection, solution and refinement details, tables of atomic coordinates, isotropic displacement parameters, anisotropic displacement parameters, and bond distances and bond angles for **3**, **4c**, **8c**, and **15** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA010242E