Neutral and Cationic Aluminum Complexes Supported by Sterically Bulky Amidinate Ligands

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Aluminum complexes supported by sterically bulky amidinate ligands containing terphenyl substituents on the backbone carbon atoms are described. Three amidinate ligands featuring differing substituents at the ortho positions of the 2,6-phenyl rings have been employed: [2,6-(2,4,6-$Me_3Ph)_2Ph$]C(NH-*i*-Pr)N-*i*-Pr (**$L_{Me}H$**), [2,6-(2,4,6-*i*-$Pr_3Ph)_2Ph$]C(NH-*i*-Pr)N-*i*-Pr (**$L_{Pr}H$**), and [2,6-(4-*t*-$BuPh)_2Ph$]C(NH-*i*-Pr)N-*i*-Pr (**$L_{Bu}H$**)]. Monoamidinate dialkyl complexes were generated (L_RAlMe_2), and their reactions with methide abstraction reagents to yield cationic aluminum alkyl species were studied. Additionally, an amidinate aluminum dichloride was synthesized ($L_{Me}AlCl_2$), with concomitant formation of an unexpected amidinium salt, [$L_{Me}H_2$][$EtAlCl_3$]. The crystal structures of representative dimethyl and dichloro species, as well as the latter salt, are presented.

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Introduction

Neutral aluminum complexes of the form AlX_3 (X = alkyl, alkoxide, or halide) have long been known to function as useful Lewis acid catalysts, with applications as mediators in Friedel−Crafts and Diels−Alder reactions, as alkylation reagents, and as initiators for cationic polymerizations. Aluminum species also function as cocatalysts in Ziegler−Natta olefin polymerizations. Recently, there has been increased interest in cationic aluminum systems for use in olefin polymerization due to the enhanced electrophilicity in these systems versus their neutral analogues.[1] It has been postulated that the cationic charge of these complexes may lead to enhanced olefin coordination and greater activities in these ionic systems.[2−6]

Various mono- and bisamidinate aluminum species have been reported.[7−16] A wide array of amidinate ligands have been employed to form monoamidinate complexes (Figure 1). By examination of the metrical parameters from the crystal structures of a series of dimethyl and dichloro monoamidinate complexes, Jordan has noted various structural effects caused by variance of the steric bulk of the amidinate ligands employed.[13,14] Specifically, the bite angle (N−Al−N) decreases (and the C−N−R angle increases) as the steric bulk of the ligand is increased, due to steric interactions between the three substituents on the amidinate backbone.

For polymerization applications, monoamidinate complexes have been of great interest because cationic species formed from these precursors retain an alkyl group that can undergo useful reactivity. A thorough investigation of the structure and reactivity of cationic aluminum amidinate species was published recently.[10] A number of cationic aluminum complexes were reported, and the molecular structures of these materials were shown to be strongly influenced by the steric properties of the amidinate ligand (Figure 2). In general, smaller amidinates seem to favor multinuclear aluminum cations (**A**, **B**), while more sterically bulky amidinates provide mononuclear aluminum cations (**C**). The latter have shown moderate activity for ethylene polymerization catalysis.

We have previously reported the use of *m*-terphenyl groups as substituents at the carbon atom of the amidinate backbone in the formation of sterically bulky amidinate ligands.[17] In our initial report, it was noted that terphenyl moieties provide steric shielding above and below the plane of the amidinate ligand, creating a bowl-shaped ligand. Investigation of the reactivity of these ligands led to the formation of a unique lithium amidinate species in which the amidinate coordinates

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(1) Atwood, D. A. *Coord. Chem. Rev.* **1998**, *176*, 407−430.

(2) Emig, N.; Nguyen, H.; Krautscheid, H.; Reau, R.; Cazaux, J. B.; Bertrand, G. *Organometallics* **1998**, *17*, 3599−3608.

(3) Jegier, J. A.; Atwood, D. A. *Inorg. Chem.* **1997**, *36*, 2034−2039.

(4) Bochmann, M.; Dawson, D. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2226−2228.

(5) Hayashi, Y.; Rohde, J. J.; Corey, E. J. *J. Am. Chem. Soc.* **1996**, *118*, 5502−5503.

(6) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *J. Am. Chem. Soc.* **1995**, *117*, 6779−6780.

(7) Ergezinger, C.; Weller, F.; Dehnicke, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1988**, *43*, 1621−1627.

(8) Lechler, R.; Hausen, H. D.; Weidlein, J. *J. Organomet. Chem.* **1989**, *359*, 1−12.

(9) Doyle, D.; Gun'ko, Y. K.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **2000**, 4093−4097.

(10) Dagorne, S.; Guzei, I. A.; Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **2000**, *122*, 274−289.

(11) Kottmairmaieron, D.; Lechler, R.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1991**, *593*, 111−123.

(12) Dehnicke, K.; Ergezinger, C.; Hartmann, E.; Zinn, A.; Hosler, K. *J. Organomet. Chem.* **1988**, *352*, C1−C4.

(13) Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G. *Organometallics* **1997**, *16*, 5183−5194.

(14) Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G. *Organometallics* **1998**, *17*, 4042−4048.

(15) Aeilts, S. L.; Coles, M. P.; Swenson, D. G.; Jordan, R. F.; Young, V. G. *Organometallics* **1998**, *17*, 3265−3270.

(16) Chang, C. C.; Hsiung, C. S.; Su, H. L.; Srinivas, B.; Chiang, M. Y.; Lee, G. H.; Wang, Y. *Organometallics* **1998**, *17*, 1595−1601.

(17) Schmidt, J. A. R.; Arnold, J. *J. Chem. Soc., Chem. Commun.* **1999**, 2149−2150.

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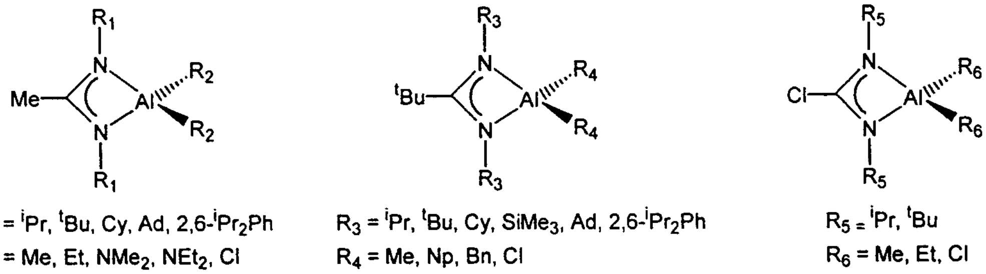

Figure 1. Amidinate ligands have been employed to form a wide variety of monoamidinate aluminum complexes.

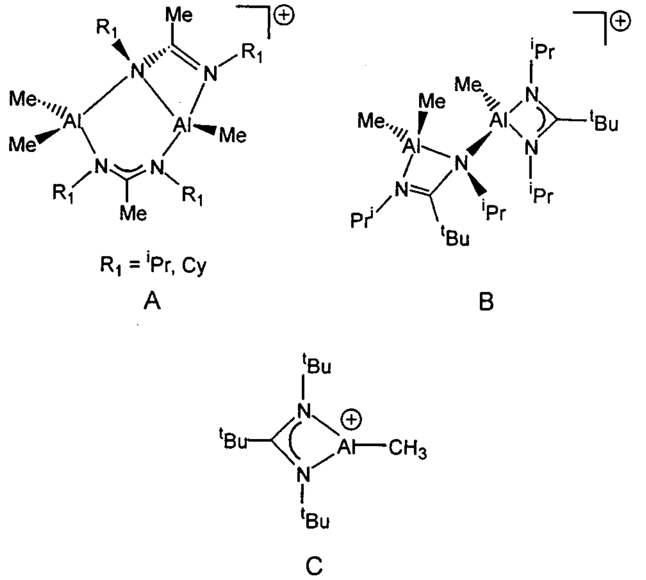

Figure 2. Amidinate aluminum cations show a wide variety of structural motifs.

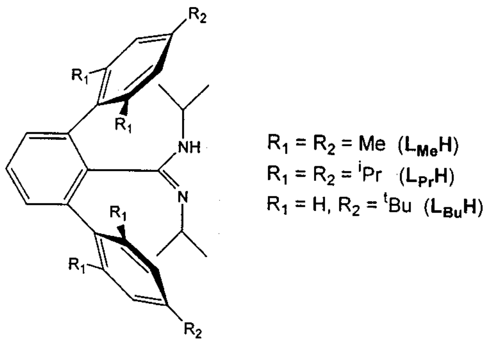

Figure 3. Sterically bulky amidines employed in this study.

to lithium in a monodentate fashion. Additionally, a group of monoamidinate yttrium species was demonstrated, in contrast to the bisamidinate complexes observed when using less sterically hindered ligands.[17] Recently, we have reported the synthesis of a series of amidinate ligands incorporating terphenyl substituents bound to the amidinate carbon atom (Figure 3).[18]

The three ligands shown differ by virtue of the alkyl groups attached to the external phenyl groups of the terphenyl moiety. We investigated the free-base and lithium salts of these amidines and described the structural differences owing to the different terphenyl moieties employed.[18] In short, it was found that the functional groups located at the ortho position of the external phenyl groups (R_1, Figure 3) played a strong role in the steric effect of these substituents. This position is proximate to the metal center, and groups attached here interact sterically with other metal-bound ligands. Additionally, it was shown that ligands having only hydrogen atoms at this position had little effect on the structural parameters of these species, while those with methyl or isopropyl groups caused substantial changes in structure and bonding.[18]

Here, the application of these sterically bulky amidinate ligands toward the synthesis of aluminum amidinates is reported, including the synthesis of a series of dialkyl- and dichloroaluminum species. Cationic aluminum complexes generated by methide abstraction from the amidinate dimethylaluminum complexes are presented, and the attempted use of these cationic compounds in olefin polymerization is described.

Experimental Section

General Considerations. Standard Schlenk-line and glovebox techniques were used throughout. Pentane, hexanes, diethyl ether, and methylene chloride were passed through a column of activated alumina and degassed with argon. Trimethylaluminum (2.0 M in heptane), $EtAlCl_2$ (1.8 M in toluene), and $HBF_4{\cdot}Et_2O$ (85% in diethyl ether) were purchased from Aldrich and used as received. Neat $AlEt_3$ (Aldrich) was dissolved in benzene to give a 2.2 M solution. The ligands (**$L_{Me}H$**, **$L_{Pr}H$**, **$L_{Bu}H$**) were synthesized as detailed previously.[17,18] C_6D_6 and C_7D_8 were vacuum transferred from sodium/benzophenone ketyl. $CDCl_3$ and C_6D_5Cl were vacuum transferred from CaH_2. Melting points were determined in sealed capillary tubes under nitrogen and are uncorrected. Unless otherwise specified, ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded in C_6D_6 at ambient temperature on a Bruker DRX-500 spectrometer. ^1H NMR chemical shifts are given relative to C_6D_5H (δ 7.16), $C_6D_5CD_2H$ (δ 2.09), C_6D_4HCl (δ 7.14), and $CHCl_3$ (δ 7.26). ^{13}C NMR chemical shifts are relative to C_6D_6 (δ 128.39), C_7D_8 (δ 20.4), C_6D_5Cl (δ 126.0), and $CDCl_3$ (δ 77.16). ^{11}B and ^{19}F NMR chemical shifts were referenced to external standards $BF_3{\cdot}Et_2O$ (0.1 M) and $CFCl_3$, respectively. IR samples were prepared as Nujol mulls and taken between KBr plates. Elemental analyses were determined by the Microanalytical Laboratory of the College of Chemistry, University of California, Berkeley. Mass spectra are from the Mass Spectrometry Laboratory of the College of Chemistry, University of California, Berkeley, and in all cases employed electron impact conditions. Single-crystal X-ray structure determinations were performed at CHEXRAY, University of California, Berkeley.

[*N*,*N*′-Diisopropyl-(2,6-bismesityl)benzamidinato]dimethylaluminum(III), (L_{Me})$AlMe_2$ (1). A solution of $AlMe_3$ (5 mL, 2.0 M in heptane, 10 mmol) was added to a solution of **$L_{Me}H$** (4.0 g, 9.1 mmol) in pentane (125 mL). The mixture immediately turned slightly yellow, and the evolution of gas was noted. After being stirred for 14 h, the solution remained slightly cloudy; after filtration, it was concentrated in vacuo

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(18) Schmidt, J. A. R.; Arnold, J. *Dalton Trans.* **2002**, submitted.

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to a volume of 20 mL. Cooling to −40 °C overnight resulted in the formation of colorless crystalline needles (3.17 g, 70%); mp 165−167 °C; ^{1}H NMR δ 7.03 (t, 1H, 7.5 Hz), 6.92 (d, 2H, 7.5 Hz), 6.84 (s, 4H), 3.23 (sept, 2H, 5 Hz), 2.17 (s, 12H), 2.13 (s, 6H), 0.67 (d, 12H, 5 Hz), −0.39 (s, 6H); ^{13}C NMR δ 169.3 (C), 141.6 (C), 138.6 (C), 137.2 (C), 136.7 (C), 132.8 (CH), 130.9 (C), 129.0 (CH), 128.6 (CH), 45.5 (CH), 26.1 (CH$_3$), 22.3 (CH$_3$), 20.9 (CH$_3$), −9.4 (CH$_3$); IR 1613 (m), 1573 (m), 1414 (s), 1337 (s), 1299 (w), 1262 (m), 1179 (m), 1151 (m), 1109 (m), 1018 (m), 920 (w), 851 (m), 817 (w), 782 (s), 761 (m), 703 (s), 681 (w), 668 (m), 592 (w). Anal. Calcd for $C_{33}H_{45}N_2Al$: C, 79.80; H, 9.13; N, 5.37. Found: C, 79.37; H, 9.32; N, 5.37.

{*N,N'*-Diisopropyl-[2,6-bis(2,4,6-triisopropylphenyl)]-benzamidinato}dimethylaluminum(III), (L$_{Pr}$)AlMe$_2$ (2). A solution of AlMe$_3$ (1.4 mL, 2.0 M in heptane, 2.8 mmol) was added to a flask charged with **L$_{Pr}$H** (1.12 g, 1.84 mmol) and pentane (50 mL), to give a pale yellow solution. After being stirred for 14 h, the solution was filtered and concentrated to 10 mL under vacuum. Cooling to −40 °C overnight resulted in the formation of colorless crystals, which were isolated by filtration and dried under vacuum (604 mg, 49%); mp 162 °C (dec); ^{1}H NMR δ 7.28 (d, 2H, 6 Hz), 7.20 (s, 4H), 7.11 (t, 1H, 6 Hz), 3.24 (sept, 2H, 6 Hz), 3.00 (sept, 4H, 6 Hz), 2.83 (sept, 2H, 6 Hz), 1.33 (d, 12H, 6 Hz), 1.25 (d, 12H, 6 Hz), 1.08 (d, 12H, 6 Hz), 0.60 (d, 12H, 6 Hz), −0.37 (s, 6H); ^{13}C NMR δ 169.5 (C), 149.5 (C), 147.3 (C), 141.2 (C), 138.9 (C), 135.0 (CH), 130.8 (C), 127.4 (CH), 122.1 (CH), 46.2 (CH), 35.1 (CH), 31.2 (CH), 26.8 (CH$_3$), 25.9 (CH$_3$), 24.6 (CH$_3$), 23.2 (CH$_3$), −4.34 (CH$_3$); MS *m*/*z* 664 (M$^+$); IR 1653 (s), 1606 (m), 1567 (w), 1488 (s), 1361 (s), 1317 (m), 1260 (s), 1183 (w), 1167 (w), 1119 (w), 1100 (w), 1070 (w), 1052 (w), 941 (w), 874 (m), 805 (s), 796 (m), 778 (m), 765 (s), 706 (w), 649 (w). Anal. Calcd for $C_{45}H_{69}N_2Al$: C, 81.27; H, 10.46; N, 4.21. Found: C, 81.12; H, 10.09; N, 4.19.

{*N,N'*-Diisopropyl-[2,6-bis(4-tertbutylphenyl)]benzamidinato}dimethylaluminum(III), (L$_{Bu}$)AlMe$_2$ (3). A solution of AlMe$_3$ (1.2 mL, 2.0 M in heptane, 2.4 mmol) was added via syringe to a suspension of **L$_{Bu}$H** (1.00 g, 2.13 mmol) in pentane (40 mL), and the mixture was stirred overnight. The volatile materials were removed under vacuum from the cloudy solution, and the resulting white solid was extracted with diethyl ether (60 mL). After filtration, the solution was concentrated to 25 mL while heating gently. Cooling to −40 °C resulted in the formation of colorless crystals in two crops (736 mg combined, 68%); mp 229−231 °C; ^{1}H NMR δ 7.645 (d, 4H, 8.5 Hz), 7.454 (d, 4H, 8.5 Hz), 7.393 (d, 2H, 7.5 Hz), 7.229 (t, 1H, 7.5 Hz), 3.124 (sept, 2H, 6 Hz), 1.273 (s, 18H), 0.647 (d, 12H, 6 Hz), 0.257 (s, 6H); ^{13}C NMR δ 171.1, 151.1, 141.3, 137.7, 130.1, 129.5, 129.3, 127.0, 125.8, 45.8, 34.5, 31.3, 25.0; IR 1613 (w), 1588 (w), 1576 (w), 1559 (w), 1512 (w), 1490 (w), 1363 (s), 1346 (s), 1312 (w), 1267 (s), 1199 (w), 1182 (m), 1169 (w), 1154 (m), 1123 (w), 1100 (m), 1026 (m), 844 (m), 834 (w), 803 (s), 772 (s), 747 (w), 728 (m), 712 (w), 688 (m), 674 (m), 666 (w). Anal. Calcd for $C_{35}H_{49}N_2Al$: C, 80.11; H, 9.41; N, 5.34. Found: C, 79.88; H, 9.22; N, 5.09.

[*N,N'*-Diisopropyl-(2,6-bismesityl)benzamidinato]diethylaluminum(III), (L$_{Me}$)AlEt$_2$ (4). A solution of AlEt$_3$ (0.65 mL, 2.2 M in benzene, 1.43 mmol) was added to a reaction flask charged with **L$_{Me}$H** (500 mg, 1.13 mmol) and hexanes (50 mL). After stirring for 3 h, the reaction mixture was pumped down to a white solid in vacuo. Extraction into pentane (20 mL) yielded a clear solution. This solution was concentrated under vacuum and cooled to −30 °C, resulting in the formation of a small crop of clear, colorless crystals. The crystals were isolated by filtration and dried under vacuum (143 mg, 24%); mp 93−94 °C; ^{1}H NMR (C$_7$D$_8$) δ 7.073 (t, 1H, 7.5 Hz), 6.898 (d, 2H, 7.5 Hz), 6.794 (s, 4H), 3.218 (sept, 2H, 6 Hz), 2.141 (s, 6H), 2.134 (s, 12H), 1.211 (t, 6H, 8.1 Hz), 0.685 (d, 12H, 6 Hz), 0.137 (q, 4H, 8.1 Hz); ^{13}C NMR (C$_7$D$_8$) δ 169.8 (C), 141.8 (C), 138.6 (C), 137.2 (C), 136.6 (C), 132.6 (CH), 129.2 (CH), 128.3 (C), 128.1 (CH), 45.3 (CH), 26.3 (CH$_3$), 22.3 (CH$_3$), 21.4 (CH$_3$), 20.9 (CH$_3$), 9.6 (CH$_2$); MS *m*/*z* 524 (M$^+$); IR 1612 (w), 1572 (w), 1415 (s), 1334 (s), 1264 (m), 1151 (m), 1109 (m), 1034 (s), 995 (w), 945 (w), 854 (m), 814 (w), 779 (s), 758 (w), 697 (w), 654 (s), 634 (w), 607 (w), 469 (w). Anal. Calcd for $C_{35}H_{49}N_2Al$: C, 80.11; H, 9.41; N, 5.34. Found: C, 80.00; H, 9.76; N, 5.28.

[*N,N'*-Diisopropyl-(2,6-bismesityl)benzamidinato]-(methyl)(perfluorophenyl) aluminum(III), (L$_{Me}$)AlMe-(C$_6$F$_5$) (5). A solution of **1** (250 mg, 0.503 mmol) dissolved in toluene (30 mL) was added to a flask charged with B(C$_6$F$_5$)$_3$ (258 mg, 0.504 mmol) and toluene (30 mL), immediately forming a clear and colorless solution. After stirring for 1 h at ambient temperature, the reaction mixture was pumped down to a cloudy white oil, which slowly solidified on standing for 14 h. The solid was extracted with pentane (40 mL) to give a cloudy solution. Filtration afforded a clear solution, which was pumped down in vacuo to yield a clear oil; this solidified to a colorless mass over the course of 2 days (211 mg, 42%); ^{1}H NMR δ 7.045 (t, 1H, 7.5 Hz, *p*-Ar*H*), 6.894 (dd, 1H, ^3J = 5 Hz, ^4J = 1.5 Hz, *m*-Ar*H*), 6.878 (dd, 1H, ^3J = 5 Hz, ^4J = 1.5 Hz, *m*-Ar*H*), 6.834 (s, 4H, *m*-mes*H*), 3.302 (sept, 2H, 6 Hz, Me$_2$C*H*), 2.157 (s, 3H, *p*-mes-C*H*$_3$), 2.149 (s, 3H, *p*-mes-C*H*$_3$), 2.119 (s, 6H, *o*-mes-C*H*$_3$), 2.111 (s, 6H, *o*-mes-C*H*$_3$) 0.703 (d, 6H, 6 Hz, *Me*$_2$CH), 0.660 (d, 6H, 6 Hz, *Me*$_2$CH), −0.256 (mult, 3H, Al-C*H*$_3$); ^{13}C NMR δ^{19} 172.6 (N*C*N), 150.1 (d, CF, ^1J = 237 Hz), 142.1 (C), 141.7 (C), 141.5 (d, CF, ^1J = 252 Hz), 138.1 (C), 137.8 (C), 137.6 (C), 137.5 (C), 137.5 (d, CF, ^1J = 242 Hz), 136.6 (C), 136.5 (C), 132.6 (*m*-Ar-*C*H), 132.4 (*m*-Ar-*C*H), 130.2 (C), 129.3 (*p*-Ar-*C*H), 129.1 (mes-*C*H), 129.0 (mes-*C*H), 45.9 (Me$_2$*C*H), 25.9 (*Me*$_2$CH), 25.8 (*Me*$_2$CH), 22.1 (*o*-mes-*C*H$_3$), 22.0 (*o*-mes-*C*H$_3$), 20.9 (*p*-mes-*C*H$_3$), 20.8 (*p*-mes-*C*H$_3$) −8.9 (Al-*C*H$_3$); ^{19}F NMR δ −120 (2F), −155 (1F), −163 (2F); IR 1645 (m), 1613 (w), 1572 (w), 1519 (s), 1507 (s), 1411 (s), 1335 (s), 1316 (m), 1268 (m), 1183 (w), 1165 (m), 1111 (w), 1073 (s), 1035 (w), 1021 (w), 977 (s), 958 (s), 879 (w), 847 (w), 816 (w), 781 (w), 761 (w), 699 (w), 680 (m), 653 (m), 630 (w).

Observation of {[*N,N'*-Diisopropyl-(2,6-bismesityl)benzamidinato]methylaluminum(III)}[tetrakis(pentafluorophenyl)boron], [(L$_{Me}$)AlMe]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (6). A solution of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (22 mg, 0.024 mmol) in C$_6$D$_5$Cl (0.5 mL) was added to a vial containing **1** (12 mg, 0.024 mmol). The red-orange solution was transferred to an NMR tube, and after 15 min, the NMR spectra were consistent with quantitative conversion to a 1:1 mixture of **5** and Ph$_3$CCH$_3$. Spectroscopic characterization of **5**: ^{1}H NMR (C$_6$D$_5$Cl) δ 7.674 (t, 1H, 7.5 Hz, *p*-Ar*H*), 6.974 (d, 2H, 7.5 Hz, *m*-Ar*H*), 6.816 (s, 4H, *m*-mes*H*), 3.171 (sept, 2H, 6 Hz, Me$_2$C*H*), 2.170 (s, 6H, *p*-mes-C*H*$_3$), 2.027 (s, 12H, *o*-mes-C*H*$_3$), 0.502 (d, 12H, 6 Hz, *Me*$_2$CH), −0.52 (br, 3H, Al-C*H*$_3$); ^{11}B NMR (C$_6$D$_5$Cl) δ −16.8; ^{13}C NMR (C$_6$D$_5$Cl) δ^{20} 149.3 (*p*-Ar-*C*H), 148.9 (d, CF, ^1J = 242 Hz), 143.2 (C), 142.2 (*m*-Ar-*C*H), 139.5 (C), 138.8 (d, CF, ^1J = 244 Hz), 136.7 (d, CF, ^1J = 243 Hz), 136.4 (C), 133.9 (C), 130.5 (C), 130.2 (mes-*C*H), 45.6 (Me$_2$*C*H), 26.2 (*Me*$_2$CH), 21.8 (*o*-mes-*C*H$_3$), 20.9 (*p*-mes-*C*H$_3$); ^{19}F NMR (C$_6$D$_5$Cl) δ −132.6 (8F), −162.9 (4F), −166.5 (8F).

Synthesis of [*N,N'*-Diisopropyl-(2,6-bismesityl)benzamidinium] [ethyltrichloroaluminate], [L$_{Me}$H$_2$][EtAlCl$_3$] (7), and [*N,N'*-Diisopropyl-(2,6-bismesityl)benzamidinato]dichloroaluminum(III), (L$_{Me}$)AlCl$_2$ (8). A reaction flask charged with **L$_{Me}$H** (1.5 g, 3.4 mmol) and hexanes (100 mL) was cooled to −78 °C in a dry ice bath. A solution of EtAlCl$_2$ (2.0 mL, 1.8 M in tol, 3.6 mmol) was added via syringe, resulting in the formation of a substantial amount of precipitate. After warming to room temperature, the reaction mixture was evaporated, removing residual solvent and yielding a white solid. The solid was washed with pentane (50 mL), and the remaining solid was extracted with methylene chloride (40 mL). This yellow solution was concentrated under vacuum to ∼5 mL, and pentane (30 mL) was layered above this solution. The solutions diffused together over a period of 1 week, resulting in the formation of clear colorless crystals at room temperature. The crystals were isolated by filtration and dried

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Table 1. Crystal Data and Collection Parameters

	1	**7**·CH_2Cl_2	**8**
formula	$C_{33}H_{45}AlN_2$	$C_{34}H_{48}AlCl_5N_2$	$C_{31}H_{39}AlCl_2N_2$
fw	496.71	687.00	537.55
space group	$P\bar{1}$ (#2)	$P2_1/c$ (#14)	$P2_1/n$ (#14)
temperature (°C)	−161	−119	−148
a (Å)	11.0521(8)	10.201(1)	10.784(1)
b (Å)	11.7282(8)	18.618(1)	13.377(1)
c (Å)	12.5994(9)	19.975(1)	20.745(1)
α (deg)	87.263(2)	90	90
β (deg)	80.941(1)	97.958(2)	94.399(1)
γ (deg)	67.894(1)	90	90
V (Å^3)	1494.1(2)	3757.1(3)	2983.7(2)
Z	2	4	4
density$_{calc}$ (g/cm^3)	1.104	1.214	1.197
diffractometer	Siemens SMART	Siemens SMART	Siemens SMART
radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
monochromator	graphite	graphite	graphite
detector	CCD area detector	CCD area detector	CCD area detector
scan type, width	ω, 0.3°	ω, 0.3°	ω, 0.3°
scan speed (s/frame)	30.0	10.0	10.0
no. of reflns measd	hemisphere	hemisphere	hemisphere
2θ range (deg)	3−46.5	3−52.1	3−52.4
μ (cm^{-1})	0.90	4.34	2.68
T_{max}, T_{min}	0.988, 0.844	0.930, 0.756	0.955, 0.859
cryst dimens (mm)	0.30 × 0.20 × 0.10	0.34 × 0.33 × 0.24	0.33 × 0.28 × 0.17
no. of reflns measd	7230	18 166	14 458
no. of unique reflns	4197	6858	5560
no. of obsns	2275	2142	3332
no. of params	325	396	325
R, R_w, R_{all}	0.043, 0.045, 0.104	0.071, 0.080, 0.122	0.036, 0.043, 0.049
GOF	1.33	2.57	1.41

under vacuum to yield the salt (**7**) (375 mg, 18%); mp 114 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.694 (t, 1H, 8 Hz), 7.324 (d, 2H, 8 Hz), 6.980 (s, 4H), 5.427 (br, 1H), 4.003 (br, 1H), 3.819 (br, 1H), 3.378 (br, 1H), 2.333 (s, 6H), 2.067 (s, 6H), 2.029 (s, 6H), 0.982 (t, 3H, 8 Hz), 0.955 (d, 12H, 6 Hz), 0.013 (q, 2H, 8 Hz); ^{13}C NMR ($CDCl_3$) δ 159.6 (C), 141.7 (C), 139.4 (C), 135.7 (C), 134.6 (C), 134.1 (C), 131.9 (CH), 129.6 (CH), 129.3 (CH), 49.9 (CH), 46.0 (CH), 23.3 (CH_3), 22.4 (CH_3), 21.6 (CH_3), 21.2 (CH_3), 20.8 (CH_3), 9.0 (CH_2); IR: 3424 (s), 3319 (s), 3292 (s), 3220 (m), 2730 (w), 1622 (s), 1554 (m), 1301 (w), 1263 (w), 1184 (m), 1161 (m), 1125 (m), 1026 (m), 973 (w), 938 (w), 879 (w), 860 (m), 851 (m), 816 (m), 771 (w), 739 (w), 723 (w), 666 (w), 619 (m), 574 (m), 528 (w), 498 (s), 482 (s), 465 (s), 441 (s). Anal. Calcd for $C_{33}H_{46}N_2AlCl_3 \cdot 0.58\ CH_2Cl_2$: C, 63.57; H, 7.28; N, 4.29. Found: C, 63.56; H, 7.59; N, 4.16. The supernatant was evaporated under vacuum to yield a white solid. After extraction with diethyl ether (30 mL), the solution was concentrated in vacuo to a final volume of 3 mL. This was cooled to −30 °C, resulting in the formation of clear and colorless crystals, which were isolated by filtration and dried under vacuum to yield **8** (60 mg, 3%); mp 249−252 °C; ^{1}H NMR δ 6.971 (t, 1H, 8 Hz), 6.856 (d, 2H, 8 Hz), 6.810 (s, 4H), 3.189 (sept, 2H, 6 Hz), 2.103 (s, 12 H), 2.096 (s, 6H), 0.673 (d, 12 H, 6 Hz); ^{13}C NMR δ 174.6, 141.6, 137.8, 137.7, 136.4, 133.2, 129.6, 129.3, 128.8, 46.1, 25.4, 22.1, 20.8; MS m/z 536 (M$^+$); IR 1612 (w), 1574 (w), 1451 (s), 1401 (s), 1385 (s), 1336 (s), 1281 (m), 1262 (m), 1150 (w), 1114 (w), 1024 (m), 924 (w), 866 (w), 852 (w), 818 (w), 798 (w), 781 (m), 766 (w), 699 (m), 655 (m), 601 (w). Anal. Calcd for $C_{31}H_{39}N_2AlCl_2$: C, 69.27; H, 7.31; N, 5.21. Found: C, 69.11; H, 7.54; N, 4.90.

[*N*,*N*′-Diisopropyl-(2,6-bismesityl)benzamidinium]tetrafluoroborate, [$L_{Me}H_2$][BF_4] (9). A flask was charged with **L_{Me}H** (300 mg, 0.68 mmol), and diethyl ether (40 mL) was added, giving a clear solution. Via syringe, a solution of $HBF_4 \cdot Et_2O$ (0.15 mL, 85% in diethyl ether, 0.86 mmol) was added, causing a large amount of precipitate to form. The mixture was stirred for 45 min, and then the solid was allowed to settle out upon standing. The solid was isolated by filtration and was washed with diethyl ether (40 mL). Drying under vacuum yielded the pure product (200 mg, 56%); mp 201−203 °C; ^{1}H NMR ($CDCl_3$) δ 7.688 (t, 1H, 8 Hz), 7.481 (d, 1H, 10 Hz), 7.301 (d, 2H, 8 Hz), 6.966 (s, 2H), 6.948 (s, 2H), 5.353 (d, 1H, 8 Hz), 3.844 (dsept, 1H, ^3J = 10 Hz, ^3J = 7 Hz), 3.343 (dsept, 1H, ^3J = 8 Hz, ^3J = 7 Hz), 2.328 (s, 6H), 2.061 (s, 6H), 2.016 (s, 6H), 0.945 (d, 6H, 7 Hz), 0.931 (d, 6H, 7 Hz); ^{13}C NMR ($CDCl_3$) δ 159.6 (C), 140.9 (C), 138.5 (C), 135.2 (C), 133.9 (C), 133.7 (C), 131.6 (CH), 131.1 (CH), 128.9 (CH), 128.4 (CH), 126.8 (C), 49.1 (CH), 44.9 (CH), 22.0 (CH_3), 20.9 (CH_3), 20.6 (CH_3), 20.5 (CH_3), 20.2 (CH_3); ^{19}F NMR ($CDCl_3$) δ −151.1; IR 3336 (m), 3307 (s), 3229 (w), 2731 (w), 1626 (s), 1557 (m), 1396 (m), 1340 (w), 1323 (w), 1306 (w), 1277 (w), 1184 (w), 1166 (m), 1142 (m), 1123 (m), 1103 (s), 1052 (s), 994 (s), 945 (w), 853 (m), 814 (m), 768 (m), 739 (w), 673 (w), 653 (w), 604 (w), 573 (w), 517 (w). Anal. Calcd for $C_{31}H_{41}N_2BF_4$: C, 70.45; H, 7.82; N, 5.30. Found: C, 70.49; H, 7.84; N, 5.30.

X-ray Crystallography. A summary of crystal data and collection parameters for the crystal structures of **1**, **7**, and **8** is given in Table 1. Details of individual data collection and solution are given below, while complete tables of structural data can be found in the Supporting Information. ORTEP diagrams were created using the ORTEP-3 software package.[21] For each sample, a crystal was mounted on a glass capillary using Paratone-N hydrocarbon oil. The crystal was transferred to a Siemens SMART[22] diffractometer/CCD area detector, centered in the X-ray beam, and cooled using a nitrogen-flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. A least-squares refinement on data from 60 sample frames allowed determination of cell constants and the orientation matrix. An arbitrary hemisphere of data was collected using 0.3° ω-scans, and the data were integrated by the program SAINT.[23] The final unit cell parameters were determined by least-squares analysis of the reflections with $I > 10\sigma$-

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(19) The ipso-C resonances for the perfluorophenyl groups were not observed.

(20) The ipso-C resonances for the perfluorophenyl groups, the amidinate backbone, and the methyl bound to aluminum were not observed.

(21) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(22) *SMART: Area-Detector Software Package*; Siemens Industrial Automation, Inc.: Madison, WI, 1995.

(23) *SAINT: SAX Area-Detector Integration Program, V4.024*; Siemens Industrial Automation, Inc.: Madison, WI, 1995.

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(I). Data analysis using Siemens XPREP[24] determined the space group. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. Equivalent reflections were averaged, and the structure was solved by direct methods[25] and expanded using Fourier techniques,[26] all within the teXsan[27] software package. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included as fixed atoms but not refined. The weighting schemes were based on counting statistics and included a factor ($p = 0.030$) to reduce the weight of intense reflections. The analytical forms of the scattering factor tables for the neutral atoms were used,[28] and all scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[29]

Compound 1. X-ray quality crystals were grown from a saturated pentane solution that was cooled to −40 °C. The final cycle of full-matrix least squares refinement (minimizing the quantity $\sum w(|F_o| - |F_c|)^2$, where w is the weight of a given observation) was based on 2275 observed reflections [$I > 3.00\sigma(I)$] and 355 variable parameters and converged yielding final residuals:[30] $R = 0.043$, $R_w = 0.045$, and GOF = 1.33.

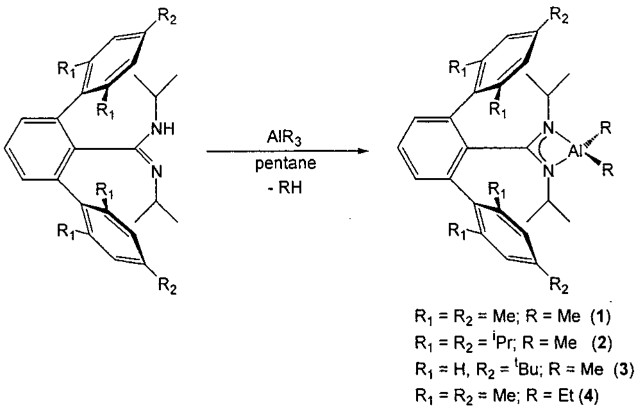
Compound 7. X-ray quality crystals were grown by slow diffusion of pentane into a saturated methylene chloride solution. Disorder was present in two portions of the crystal structure. A molecule of methylene chloride solvate was disordered over four chloride positions and was modeled such that the total occupancy of these positions was two. Additionally, the methyl of the ethyl group on the anion was rotationally disordered over two positions and was modeled such that the total occupancy of this methyl group was one. In the ordered regions of the structure, non-hydrogen atoms were refined anisotropically, while disordered atoms were refined isotropically. In the ordered portion of the structure, hydrogen atoms were included as fixed atoms but not refined. The final cycle of full-matrix least squares refinement (minimizing the quantity $\sum w(|F_o| - |F_c|)^2$, where w is the weight of a given observation) was based on 2142 observed reflections [$I > 3.00\sigma(I)$] and 396 variable parameters and converged yielding final residuals:[30] $R = 0.071$, $R_w = 0.080$, and GOF = 2.57.

Compound 8. X-ray quality crystals were grown by slow cooling of a saturated diethyl ether solution. The final cycle of full-matrix least squares refinement (minimizing the quantity $\sum w(|F_o| - |F_c|)^2$, where w is the weight of a given observation) was based on 3332 observed reflections [$I > 3.00\sigma(I)$] and 325 variable parameters and converged yielding final residuals:[30] $R = 0.036$, $R_w = 0.043$, and GOF = 1.41.

Results and Discussion

The sterically hindered amidine ligands shown in Figure 3 were used to prepare a series of aluminum complexes. Our investigations focused on the mesityl-substituted amidine ligand ($\mathbf{L_{Me}H}$) because of its preferable steric properties and convenient solubility. In addition, some related compounds employing two other sterically hindered amidinates ($\mathbf{L_{Pr}H}$ and $\mathbf{L_{Bu}H}$) were also investigated.

Scheme 1



All three amidine ligands ($\mathbf{L_{Me}H}$, $\mathbf{L_{Pr}H}$, and $\mathbf{L_{Bu}H}$) react readily with 1 equiv of trimethylaluminum, forming monoamidinate species of the form $(L_R)AlMe_2$, with concomitant elimination of methane (Scheme 1).[31] These reactions proceeded readily in pentane at room temperature, resulting in nearly quantitative conversion to the dimethyl species (**1**, **2**, and **3**, respectively). The first two were quite soluble in pentane and could be readily crystallized from this solvent, whereas **3** precipitated from pentane; a pure, crystalline sample of this compound was obtained by crystallization from diethyl ether. The ^{1}H NMR spectrum of each compound was indicative of a highly symmetric species in solution, with the terphenyl group of the amidinate ligand exhibiting C_{2v} symmetry on the NMR time scale. Also, the two amidinate isopropyl groups were equivalent, as well as the two Al-bound methyl groups. On the basis of these results, a pseudo-tetrahedral aluminum center was postulated for each of the three species (**1**−**3**). The same molecular symmetry was maintained in the ^{13}C NMR spectra of the compounds.

X-ray quality crystals of **1** were grown from saturated pentane; the structure of this compound confirmed the tetrahedral assignment of these complexes, showing a bidentate amidinate ligand bound to an aluminum dimethyl moiety (Figure 4). Although the compound does not reside on any crystallographic symmetry element, the observed Al−N bond lengths are identical, as are the Al−C bond lengths (1.953(4) and 1.951(4) Å). This is in complete agreement with the symmetry observed spectroscopically in solution. Both sets of bond lengths fall near the middle of the ranges observed in previously characterized (amidinate)$AlMe_2$ species (Al−N: 1.912−1.939 Å, Al−C: 1.940−1.968 Å).[8,13,14] Similarly, the observed bond angles in this compound for the amidinate backbone (N−C−N = 108.2(3)°) and the bite angle (N−Al−N = 68.9(1)°) also parallel those observed previously.[8,13,14] Finally, the torsion angle between NCNAl and phenyl planes is 119.69°. On the basis of these metrical parameters, it seems that the incorpora-

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[24] *XPREP: Part of the SHELXTL Crystal Structure Determination Package, V5.03*; Siemens Industrial Automation, Inc.: Madison, WI, 1995.

[25] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343−350.

[26] Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF Program System, Technical Report of the Crystallography Laboratory*; University of Nijmegen: The Netherlands, 1992.

[27] *teXsan: Crystal Structure Analysis Package*; Molecular Structure Corporation: 1992.

[28] Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

[29] Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781−782.

[30] $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$, GOF $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where N_o = number of observations and N_v = number of variables, and the weight $w = 4F_o^2/\sigma^2(F_o)^2 = [\sigma^2(F_o) + (pF_o/2)^2]^{-1}$ and p is the factor used to lower the weight of intense reflections.

[31] While the manuscript was in preparation, the synthesis of a related bulky amidinate aluminum dimethyl species was reported: Abeysekera, D.; Robertson, K. N.; Cameron, T. S.; Clyburne, J. A. C. *Organometallics* **2001**, *20*, 5532−5536.

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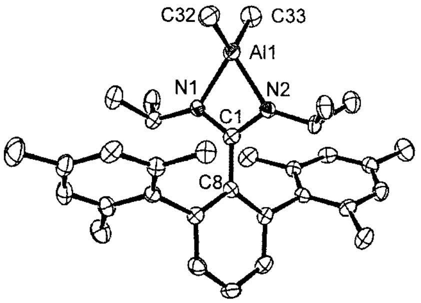

Figure 4. ORTEP view of $(L_{Me})AlMe_2$ (**1**) with 50% thermal ellipsoids. Selected bond lengths (Å): Al1−N1 = 1.922(3), Al1−N2 = 1.924(3), Al1−C32 = 1.953(4), Al1−C33 = 1.951(4), N1−C1 = 1.347(4), N2−Cl = 1.342(4), C1−C8 = 1.502(5). Bond angles (deg): N1−Al1−N2 = 68.9(1), N1−Al1−C32 = 114.7(2), N1−Al1−C33 = 114.1(2), N2−Al1−C32 = 112.6(1), N2−Al1−C33 = 117.4(2), C32−Al1−C33 = 119.1(2), N1−C1−N2 = 108.2(3).

tion of the sterically bulky amidinate ligand in these aluminum dimethyl complexes has an insignificant steric effect, as there appears to be very little interaction with the rather small methyl substituents.

Diethyl aluminum species were formed in a fashion similar to that of the methyl analogues. The mesityl-substituted amidine (**L_{Me}H**) was reacted with 1 equiv of $AlEt_3$ in hexanes, forming $(L_{Me})AlEt_2$ (**4**) with the loss of 1 equiv of ethane (Scheme 1). Crystals of **4** were readily obtained by crystallization from saturated pentane. As in the methyl analogue (**1**), NMR spectra for this compound showed high symmetry, in agreement with the expected tetrahedral coordination of the aluminum atom. Compound **4** has a substantially lower melting point than that observed for its methyl analogue, but was otherwise similar in its physical properties. Spectroscopically, the ethyl groups did not appear to cause any rotational hindrance to the terphenyl moiety, further supporting the assertion that these bulky amidinates have little interaction with the alkyl groups in species of the form $(L_R)AlR_2$.

Cationic aluminum species were generated from the dimethyl complexes (**1**−**3**) by reaction with methide abstraction reagents. The reaction between equimolar amounts of **1** and $B(C_6F_5)_3$ led to the formation of a cationic aluminum complex, which immediately decomposed by transfer of a $C_6F_5^-$ group from boron to aluminum, yielding $(L_{Me})AlMe(C_6F_5)$ (**5**) and $MeB(C_6F_5)_2$ (Scheme 2). The ^{1}H NMR spectrum of **5** showed a substantial reduction in symmetry from its precursor. The two halves of the terphenyl group became inequivalent, as did the isopropyl methyls, consistent with C_s symmetry. The 1:1 mixture of **5** and $MeB(C_6F_5)_2$ was isolated as a colorless oil that slowly solidified. Several crystallization attempts were unsuccessful, and heating the mixture under vacuum to remove $MeB(C_6F_5)_2$ by sublimation resulted in substantial decomposition of **5**. Transfer of a $C_6F_5^-$ group from $MeB(C_6F_5)_3^-$ to a cationic aluminum center has been reported previously for an amidinate species (*i*-PrNC-*t*-BuN-*i*-Pr)$AlMe^+$ and for diketiminato complexes.[10,32]

As shown in Scheme 2, reaction of **1** with 1 equiv of $[Ph_3C][B(C_6F_5)_4]$ in chlorobenzene proceeds instantaneously and quantitatively to yield the orange aluminum methyl cation **6** and Ph_3CCH_3, as observed by ^{1}H NMR spectroscopy. The NMR spectra of **6** showed it to be highly symmetrical. Notably, the terphenyl group exhibits C_{2v} symmetry and the two isopropyl groups of the ligand backbone are equivalent. Although when generated in chlorobenzene, **6** was found to be stable in solution for more than 12 h, the compound rapidly decomposed upon removal of solvent under vacuum, preventing isolation of pure samples. This is perhaps due to the loss of weakly coordinated chlorobenzene, as noted in previous reports of aminotroponiminate-supported aluminum cations.[33] Jordan has reported the synthesis of [(*t*-BuNC-*t*-BuN-*t*-Bu)Al-Me]$[B(C_6F_5)_4]$ using an analogous route, and this compound suffers from similar decomposition problems.[10]

Cationic aluminum complexes are known to catalyze the polymerization of olefins.[34−36] In the present study, three aluminum cations were investigated for activity in olefin polymerization catalysis, employing 1-hexene and ethylene as monomers. The cations were generated in situ by mixing equimolar amounts of the aluminum dimethyl species (**1**−**3**) with $[Ph_3C][B(C_6F_5)_3]$ in chlorobenzene. After 5 min, the monomer was introduced and allowed to interact for 30 or 60 min for ethylene and 1-hexene, respectively. In all cases, the cations showed negligible activity, as determined by formation of insignificant amounts of polymer. This contrasts with a previous report that the related cationic aluminum compound, [(*i*-PrNC-*t*-BuN-*i*-Pr)Al-Me]$[B(C_6F_5)_4]$, synthesized analogously, generates polyethylene at a rate of 2708 g mol^{-1} h^{-1} atm^{-1}.[10] Interestingly, a recent theoretical study suggests that β-hydride elimination is favored over olefin insertion for all known cationic amidinate-supported aluminum complexes.[37] These authors rule out all of the methyl species formulated above as the active components of ethylene polymerization, proposing instead that impurities in the reaction mixtures are responsible for the observed activity, most likely due to contamination by traces of transition metals or the formation of multinuclear aluminum clusters. At present, however, the reason that the cationic aluminum species generated from **1**−**3** are catalytically inactive remains unknown.

Additionally, we sought to prepare the dichloride $(L_R)AlCl_2$, which might allow access to alternate routes for the formation of cationic aluminum species. Two methods were explored: reaction of the lithium amidinate **L_{Me}Li(TMEDA)** with $AlCl_3$ and reaction of the amidine **L_{Me}H** with $EtAlCl_2$. Unfortunately, neither of these methods was found to be efficient. The reaction of **L_{Me}Li(TMEDA)** with $AlCl_3$ resulted in the formation of a highly insoluble, intractable material. Reaction of the amidine **L_{Me}H** with $EtAlCl_2$ was marginally successful, and low yields of $(L_{Me})AlCl_2$ (**8**) were isolated from the reaction mixture. The primary product of this

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[32] Qian, B. X.; Ward, D. L.; Smith, M. R. *Organometallics* **1998**, *17*, 3070−3076.

[33] Korolev, A. V.; Ihara, E.; Guzei, I. A.; Young, V. G.; Jordan, R. F. *J. Am. Chem. Soc.* **2001**, *123*, 8291−8309.

[34] Bruce, M.; Gibson, V. C.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1998**, 2523−2524.

[35] Ihara, E.; Young, V. G.; Jordan, R. F. *J. Am. Chem. Soc.* **1998**, *120*, 8277−8278.

[36] Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1997**, *119*, 8125−8126.

[37] Talarico, G.; Busico, V.; Budzelaar, P. H. M. *Organometallics* **2001**, *20*, 4721−4726.

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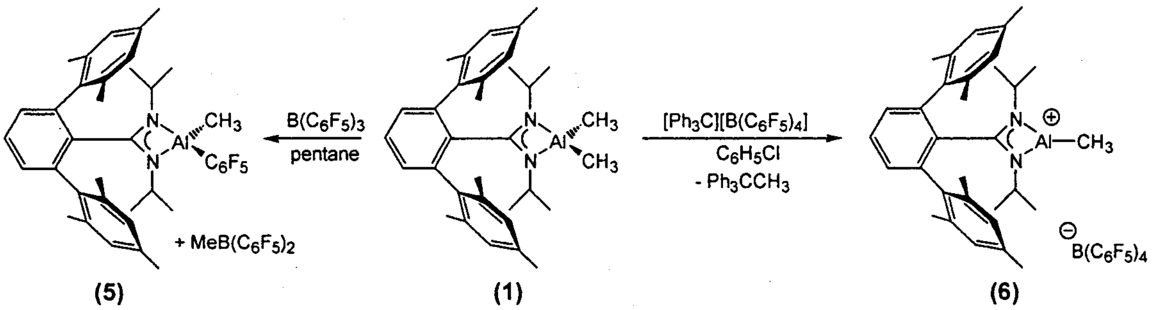
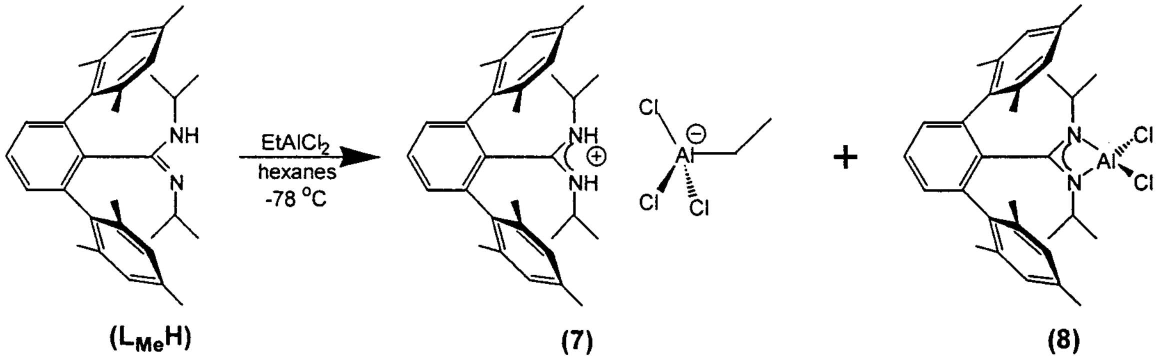
Scheme 2



Scheme 3



reaction was an unexpected and surprisingly stable salt: $[L_{Me}H_2][EtAlCl_3]$ (**7**, Scheme 3). This was isolated in relatively low yield by dissolving the product mixture in methylene chloride and allowing pentane to slowly diffuse into this solution. The ^1H NMR spectrum of **7** showed a set of amidine resonances in which the terphenyl group was freely rotating, equilibrating its phenyl groups. The amidine isopropyl groups were inequivalent and there were four broad resonances between 6 and 3 ppm, attributable to methine and N-H protons. Additionally, signals representative of an ethyl group were observed. On the basis of these data, formation of an amidinium ion seemed reasonable, with an ethyltrichloroaluminate anion being the counterion. It was surprising that an ethyl aluminum bond was stable in the presence of the relatively acidic amidinium ion, but no decomposition of **7** was observed in solution at room temperature over several weeks. The crystalline solid was stable to 114 °C, at which point it decomposed with gas evolution. While we have not investigated the mechanism of formation of **7**, the fact that it is formed in nontrivial amounts would tend to argue against adventitious hydrolysis; nonetheless, this pathway has not been definitively ruled out.

To confirm the identity of **7**, the amidinium cation was synthesized independently. Reaction of $\mathbf{L_{Me}H}$ with HBF_4 in diethyl ether resulted in the rapid formation of a white precipitate. After filtration and thorough washing with ether, $[L_{Me}H_2][BF_4]$ (**9**) was isolated as a white solid. The ^1H NMR spectrum of this material was very similar to that observed for **7**, again showing C_{2v} symmetry, supporting the presence of the amidinium cation in **7**. This salt was much more thermally robust than **7**, melting reversibly at 202 °C.

For final confirmation of the composition of **7**, X-ray quality crystals were grown, and the solid-state structure was obtained. As expected, the crystallographic model shows an amidinium cation and an ethyltrichloroaluminate anion (Figure 5). Additionally, 1 equiv of methylene chloride was incorporated as solvent of crystallization. The ethyltrichloroaluminate anion has been observed previously,[38-40] but in no case was a Brønsted acid also present. Examination of the metrical

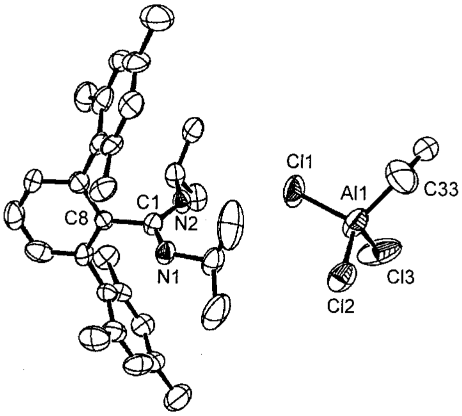


Figure 5. ORTEP view of $[L_{Me}H_2)[EtAlCl_3]$ (**7**) with 50% thermal ellipsoids. One of the two methyl positions for the disordered ethyl group and the incorporated methylene chloride have been omitted for clarity. Selected bond lengths (Å): Al1−Cl1 = 2.140(4), Al1−Cl2 = 2.159(4), Al1−Cl3 = 2.126(5), Al1−C33 = 2.06(2), N1−C1 = 1.33(1), N2−Cl = 1.31(1), C1−C8 = 1.51(1). Bond angles (deg): Cl1−Al1−Cl2 = 107.4(2), Cl1−Al1−Cl3 = 108.1(2), Cl1−Al1−C33 = 111.6(5), Cl2−Al1−C13 = 108.5(2), Cl2−Al1−C33 = 110.1(6), Cl3−Al1−C33 = 111.1(7), N1−C1−N2 = 120.9(8).

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[38] Atwood, J. L.; Elgamal, H.; Robinson, G. H.; Bott, S. G.; Weeks, J. A.; Hunter, W. E. *J. Inclusion Phenom. Macrocyclic Chem.* **1984**, *2*, 367−376.

[39] Sobota, P.; Utko, J.; Brusilovets, A. I.; Jerzykiewicz, L. B. *J. Organomet. Chem.* **1998**, *553*, 379−385.

[40] Self, M. F.; Pennington, W. T.; Laske, J. A.; Robinson, G. H. *Organometallics* **1991**, *10*, 36−38.

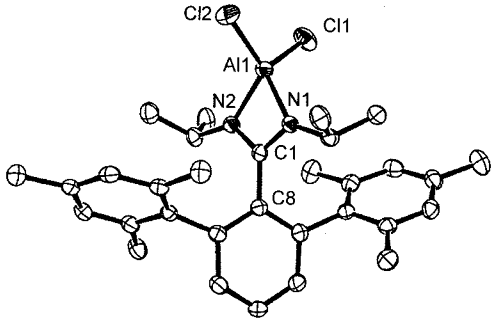

Figure 6. ORTEP view of $(L_{Me})AlCl_2$ (**8**) with 50% thermal ellipsoids. Selected bond lengths (Å): Al1−Cl1 = 2.110(1), Al1−Cl2 = 2.111(1), Al1−N1 = 1.874(2), Al1−N2 = 1.873(2), N1−C1 = 1.347(3), N2−Cl = 1.339(3), C1−C8 = 1.513(3). Bond angles (deg): Cl1−Al1−Cl2 = 112.29(5), Cl1−Al1−N1 = 116.56(8), Cl1−Al1−N2 = 115.05(8), Cl2−Al1−N1 = 117.84(8), Cl2−Al1−N2 = 118.33(8), N1−Al1−N2 = 71.13(9), N1−Al1−N2 = 71.13(9), N1−C1−N2 = 108.4(2).

parameters associated with the amidinium cation (Figure 5) shows that the two N−C bonds comprising the backbone of this material are of the same length, within experimental error. This indicates a delocalized system, as drawn in Scheme 3. The bond lengths in the ethyltrichloroaluminate anion are consistent with those observed previously for these anions.

Crystals of the dichloride $(L_{Me})AlCl_2$ (**8**) were isolated in poor yield by crystallization from diethyl ether (Scheme 3). This thermally robust material exhibited C_{2v} symmetry in solution by ^1H NMR spectroscopy. The mass spectrum showed a molecular ion peak consistent with the $(L_{Me})AlCl_2$ formulation, which was further borne out by the elemental analysis.

Crystals of **8** proved to be suitable for X-ray diffraction (Figure 6). The structure shows a rather unremarkable tetrahedral aluminum species coordinated by the two nitrogen atoms of a bidentate amidinate ligand and two chlorines. Again, delocalization of the amidinate double bond was observed by nearly equal C−N bond lengths in the ligand backbone (Figure 6). The Al−Cl bond lengths observed in this species (2.110(1) and 2.111(1) Å) and the N−Al bond lengths are well within the ranges observed for previously characterized amidinate aluminum dichloride complexes.[7,13,15,16] Additionally, the bond angle for the amidinate core (N−C−N) and the ligand bite angle (N−Al−N) are similar to those found in these related species. Last, the torsional angle between NCNAl and phenyl planes is 120.05°. From these crystallographic details, it can be concluded that the sterically bulky ligands used for these aluminum complexes seem to have little effect on the bonding of the chloride to the aluminum, and perhaps only influence the overall coordination geometry of the aluminum slightly.

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Supporting Information Available: Tables of atomic coordinates, anisotropic displacement parameters, bond lengths, and angles for **1**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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