Aluminum pentafluorophenyl–amide complexes

Carsten Cornelissen, Gigi Chan, Jason D. Masuda, and Douglas W. Stephan

Abstract: The pentafluoroaryl amine $(C_6F_5)_2NH$ (**1**) reacts with $AlH_3{\cdot}NEtMe_2$ to give $[(C_6F_5)_2N]AlH_2{\cdot}NEtMe_2$ (**2**) and $[(C_6F_5)_2N]_2AlH{\cdot}NEtMe_2$ (**3**). The related fluorinated-aryl amine $(C_6F_5)(n\text{-}C_4H_9)NH$ (**4**) also reacts with $AlH_3{\cdot}NEtMe_2$ to give $[(C_6F_5)(n\text{-}C_4H_9)N]_3Al{\cdot}NEtMe_2$ (**5**). This latter compound undergoes ligand exchange with PMe_3 or *N*-methylimidazole to form $[(C_6F_5)(n\text{-}C_4H_9)N]_3Al{\cdot}PMe_3$ (**6**) and $[(C_6F_5)(n\text{-}C_4H_9)N]_3Al{\cdot}$(Me-imid) (**7**), respectively. The latter amine also reacts with $AlMe_3$, affording $[Me_2AlN(C_6F_5)(n\text{-}C_4H_9)]_2$ (**8**).

Key words: almunium, amides, pentafluorophenylamine.

Résumé : L'amine pentafluorée $(C_6F_5)_2NH$ (**1**) réagit avec le complexe $AlH_3{\cdot}NEtMe_2$ pour conduire à la formation du $[(C_6F_5)_2N]AlH_2{\cdot}NEtMe_2$ (**2**) et du $[(C_6F_5)_2N]_2AlH{\cdot}NEtMe_2$ (**3**). L'amine aromatique fluorée apparentée $(C_6F_5)(n\text{-}C_4H_9)NH$ (**4**) réagit aussi avec le complexe $AlH_3{\cdot}NEtMe_2$ pour conduire à la formation du $[(C_6F_5)(n\text{-}C_4H_9)N]_3Al{\cdot}NEtMe_2$ (**5**). Ce dernier produit subit une réaction d'échange de ligand avec le PMe_3 ou le *N*-méthylimidazole pour conduire à la formation du $[(C_6F_5)(n\text{-}C_4H_9)N]_3Al{\cdot}PMe_3$ (**6**) et du $[(C_6F_5)(n\text{-}C_4H_9)N]_3Al{\cdot}$(Me-imid) (**7**) respectivement. Cette dernière amine réagit aussi avec le $AlMe_3$ avec formation du $[Me_2AlN(C_6F_5)(n\text{-}C_4H_9)]_2$ (**8**).

Mots-clés : aluminium, amides, pentafluorophénylamine.

[Traduit par la Rédaction]

Introduction

Lewis acids play dominant roles as co-catalysts in olefin polymerization and as catalysts in a variety of reactions in organic chemistry. The borane $B(C_6F_5)_3$ has been studied in such applications (1, 2), and a number of studies have targeted structural modifications. For example, Marks and coworkers (3–9), as well as Piers and co-workers (1, 10–13), have developed elegant syntheses to both elaborate the substituents on B or to access *bis*-borane compounds. Related alanes have also been prepared and evaluated for a variety of applications in catalysis (14–16). Generally, fluoroarylalanes have been effective in these applications (17–23), although they have proved to be dangerous, as species such as $Al(C_6F_5)_3$ are known to be heat and shock sensitive. In an effort to develop new Al-based Lewis acids, we began an exploration of the Al–amide derivatives, incorporating pentafluoroaryl substitutents. In this paper, we describe the synthesis and structure of several such compounds. An initial attempt to apply these species to the activation of early metal-catalyst precursors is also briefly described.

Experimental section

General data

All preparations were done under an atmosphere of dry, O_2-free N_2, employing both Schlenk line techniques and an MBraun or Vacuum Atmospheres inert-atmosphere glovebox. Solvents were purified, employing a Grubbs-type solvent purification system, manufactured by Innovative Technologies. All organic reagents were purified by conventional methods. ^1H, $^{31}P\{^1H\}$, ^{19}F, and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance-300 and -500 spectrometers. All spectra were recorded at 25 °C. Trace amounts of protonated solvents were used as a reference for ^1H NMR spectra, while the solvent was used as a reference for $^{13}C\{^1H\}$ spectra, and chemical shifts for ^1H and $^{13}C\{^1H\}$ spectra were reported relative to $SiMe_4$. $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% H_3PO_4. IR spectra were recorded on a Bruker FTIR spectrometer. Combustion analyses were done in-house, employing a PerkinElmer CHN Analyzer. $(C_6F_5)_2NH$ (**1**) was purchased from Aldrich Chemical Co. $(C_6F_5)(n\text{-}C_4H_9)NH$ **(4)** was prepared following a literature procedure (24).

Synthesis of $[(C_6F_5)_2N]AlH_2{\cdot}EtMe_2$ (2)

A solution of $(C_6F_5)_2NH$ (0.524 g, 1.5 mmol) in toluene (10 mL) was added dropwise to a solution of $AlH_3{\cdot}NEtMe_2$ (3.0 mL, 1.5 mmol, 0.5 mol/L in toluene) at 25 °C. The reaction mixture was stirred overnight, and the solvent was removed in vacuo to yield 0.653 g (1.45 mmol, 97%) of a light yellow oil. ^1H NMR (CD_2Cl_2): 2.85 (q, $^3J_{HH}$ = 7 Hz, 2H, NCH_2Me), 2.48 (s, 6H, NMe_2), 1.18 (t, $^3J_{HH}$ = 7.3 Hz, 3H, NCH_2Me). ^1H NMR (CD_2Cl_2, –80 °C): 3.39 (br s, 2H, Al*H*), the resonance for Al*H* was not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 144.9 (dm, $^1J_{FC}$ = 239 Hz, *o*-C_6F_5), 138.4 (dm, $^1J_{FC}$ = 246 Hz, *m*-C_6F_5), 138.0 (dm, $^1J_{FC}$ = 250 Hz, *m*-C_6F_5), 126.2 (m, C_6F_5), 54.4 (s, NCH_2Me), 44.5 (s, NMe_2), 8.6 (s, NCH_2Me). ^{19}F NMR (CD_2Cl_2): –149.2 (d, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), –164.7 (t, $^3J_{FF}$ = 23 Hz, *p*-C_6F_5), –165.5 (m, *m*-C_6F_5). Anal. calcd. for $C_{16}H_{13}AlF_{10}N_2$: C 42.68, H 2.91, N 6.22; found: C 42.46, H 2.56, N 6.13.

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Synthesis of $[(C_6F_5)_2N]_2AlH{\cdot}NEtMe_2$ (3)

$AlH_3{\cdot}NEtMe_2$ (5 mL, 2.5 mmol, 0.5 mol/L in toluene) was added dropwise to a vigorously stirring solution of $(C_6F_5)_2NH$ (2.618 g, 7.5 mmol) in toluene (5 mL) at 25 °C. After stirring overnight, the white product was collected on a frit, washed three times with pentane, and dried in vacuo. For a second fraction, the solvent was removed in vacuo, and the crude product **3** was recrystallized from pentane to yield 1.94 g (overall, 1.7 mmol, 68%) of a white solid. ^1H NMR (CD_2Cl_2): 2.98 (q, $^3J_{HH}$ = 7 Hz, 2H, NCH_2Me), 2.52 (s, 6H, NMe_2), 1.14 (t, $^3J_{HH}$ = 7 Hz, 3H, NCH_2Me), the resonance for Al*H* was not observed. ^1H NMR (CD_2Cl_2, –80 °C): 3.21 (br s, 1H, Al*H*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 145.6 (dm, $^1J_{FC}$ = 246 Hz, *o*-C_6F_5), 139.0 (dt, $^1J_{FC}$ = 251 Hz, $^3J_{FC}$ = 13 Hz, *p*-C_6F_5), 138.0 (dm, $^1J_{FC}$ = 255 Hz, *m*-C_6F_5), 124.3 (m, *i*-C_6F_5), 53.0 (s, NCH_2Me), 43.0 (s, NMe_2), 6.7 (s, NCH_2Me). ^{19}F NMR (CD_2Cl_2): –147.6 (d, $^3J_{FF}$ = 20 Hz, *o*-C_6F_5), –161.7 (t, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), –164.7 (m, *m*-C_6F_5). Anal. calcd. for $C_{28}H_{12}AlF_{20}N_3$: C 42.18, H 1.52, N 5.27; found: C 41.66, H 1.56, N 5.73. Single crystals suitable for X-ray diffraction experiments were obtained by cooling a saturated pentane solution to –30 °C overnight.

Synthesis of $[(C_6F_5)(n\text{-}C_4H_9)N]_3Al{\cdot}NEtMe_2$ (5)

$AlH_3{\cdot}NEtMe_2$ (5 mL, 2.5 mmol, 0.5 mol/L in toluene) was added dropwise to a vigorously stirring solution of $(C_6F_5)(n\text{-}C_4H_9)NH$ (**4**) (1.794 g, 7.5 mmol) in toluene (5 mL) at 25 °C. After stirring overnight, the solvent was removed in vacuo. The crude product was recrystallized from pentane to yield 1.466 g (1.8 mmol, 72%) of a white solid. ^1H NMR (CD_2Cl_2): 3.18 (q, $^3J_{HH}$ = 7 Hz, 2H, NCH_2Me), 2.92 (m, 6H, NCH_2CH_2), 2.62 (s, 6H, NMe_2), 1.17 (t, $^3J_{HH}$ = 7 Hz, 3H, NCH_2Me), 1.04 (m, 6H, NCH_2CH_2), 0.92 (m, 6H, CH_2CH_2Me), 0.76 (m, 9H, CH_2CH_2Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 147.4 (dm, $^1J_{FC}$ = 235 Hz, *o*-C_6F_5), 138.2 (dm, $^1J_{FC}$ = 250 Hz, *m*-C_6F_5), 127.6 (m, *ipso*-C_6F_5), 52.1 (s, NCH_2Me), 51.5 (s, NMe_2), 43.4 (s, NCH_2CH_2), 32.9 (s, NCH_2CH_2), 20.5 (s, CH_2CH_2Me), 14.0 (s, CH_2CH_2Me), 5.3 (s, NCH_2Me), the resonances for *p*-C_6F_5 were masked by the *m*-C_6F_5 signal. ^{19}F NMR (CD_2Cl_2): –147.2 (d, $^3J_{FF}$ = 20 Hz, *o*-C_6F_5), –165.1 (t, $^3J_{FF}$ = 21 Hz, *p*-C_6F_5), –166.6 (m, *m*-C_6F_5). Anal. calcd. for $C_{34}H_{38}AlF_{15}N_4$: C 50.13, H 4.70, N 6.88; found: C 50.01, H 4.55, N 6.54. Single crystals suitable for X-ray diffraction experiments were grown from pentane.

Synthesis of $[(C_6F_5)(n\text{-}C_4H_9)N]_3Al{\cdot}PMe_3$ (6) and $[(C_6F_5)(n\text{-}C_4H_9)N]_3Al{\cdot}$(Me-imid) (7)

These compounds were prepared in a similar fashion, using the appropriate reagent; thus, only one preparation is detailed. PMe_3 (0.17 mL, 1.67 mmol) was added to a solution of **5** (545 mg, 0.67 mmol) in toluene (5 mL) and stirred overnight at 25 °C. The solvent was removed in vacuo, and the crude product was recrystallized from pentane to yield 145 mg (0.18 mmol, 27%) of a white microcrystalline solid **6**. ^1H NMR (C_7D_8): 3.05 (m, 6H, NCH_2), 1.06 (m, 12H, CH_2CH_2Me), 0.78, (t, $^3J_{HH}$ = 7 Hz, 9H, CH_2Me), 0.71 (d, $^2J_{PH}$ = 8 Hz, 9H, PMe_3). $^{13}C\{^1H\}$ NMR (C_7D_8): 146.0 (dm, $^1J_{FC}$ = 240 Hz, *o*-C_6F_5), 137.9 (dm, $^1J_{FC}$ = 252 Hz, *m*-C_6F_5), 136.8 (dm, $^1J_{FC}$ = 253 Hz, *p*-C_6F_5), 136.2 (m, *ipso*-C_6F_5), 49.7 (s, NCH_2), 33.3 (s, NCH_2CH_2), 20.2 (s, CH_2Me), 13.7 (s, CH_2Me), 10.7 (d, $^1J_{PC}$ = 23.2 Hz, PMe_3), *ipso*-C_6F_5 resonances was not detected. ^{19}F NMR (C_7D_8): –149.4 (d, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), –165.2 (m, *m*-C_6F_5, *p*-C_6F_5). $^{31}P\{^1H\}$ NMR (C_7D_8): –50.3 (s, PMe_3). Anal. calcd for $C_{33}H_{36}AlF_{15}N_3P$: C 48.48, H 4.44, N 5.14; found: C 48.22, H 4.21, N 5.01. Compound **7**: 162 mg, white solid (0.2 mmol, 100%). ^1H NMR (CD_2Cl_2): 8.00 (s, 1H, NC*H*N), 7.03 (s, 1H, NC*H*CHN), 7.00 (s, 1H, NCHC*H*N), 3.82 (s, 3H, N*Me*), 3.09 (m, 6H, NCH_2), 1.10 (m, 12H, CH_2CH_2Me), 0.76 (t, $^1J_{HH}$ = 7 Hz, 9H, CH_2Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 146.2 (d, $^1J_{CF}$ = 234 Hz, *o*-C_6F_5), 139.6 (s, N*C*HN), 138.0 (m, *m*-C_6F_5), 127,1 (s, NCH*C*HN), 122.4 (s, MeN*C*H), 49.6 (s, NCH_2), 35.6 (s, N*Me*), 33.7 (s, NCH_2CH_2), 20.5 (s, CH_2Me), 14.1 (s, CH_2Me), resonances for *p*-C_6F_5 and *ipso*-C_6F_5 were not detected. ^{19}F NMR (CD_2Cl_2): –150.4 (d, $^3J_{FF}$ = 20 Hz, *o*-C_6F_5), –167.5 (m, *m*-C_6F_5), –168.7 (m, *p*-C_6F_5). Anal. calcd. for $C_{34}H_{33}AlF_{15}N_5$: C 49.58, H 4.04, N 8.50; found: C 49.21, H 4.13, N 8.67.

Synthesis of $[Me_2AlN(C_6F_5)(n\text{-}C_4H_9)]_2$ (8)

A solution of $(C_6F_5)(n\text{-}C_4H_9)NH$ (1.436 g, 6 mmol) in toluene (6 mL) was added slowly to a solution of $AlMe_3$ (95 µL, 2 mmol) in toluene (3 mL) at –30 °C. The solution was allowed to warm to 25 °C overnight. After the solvent was reduced in vacuo to half of its volume, the solution was stored at –30 °C overnight to yield colourless crystals. The product was collected on a frit in dried in vacuo to yield 862 mg (1.5 mmol, 73%). ^1H NMR (C_6D_6): 3.18 (m, 4H, NCH_2), 1.23 (m, 4H, NCH_2CH_2), 0.97 (m, 4H, CH_2Me), 0.73 (t, $^3J_{HH}$ = 7 Hz, 6H, CH_2Me), –0.04 (m, 6H, $AlMe_2$), –0.73 (m, 6H, $AlMe_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): 145.3 (dm, $^1J_{FC}$ = 244 Hz, *o*-C_6F_5), 139.6 (dm, $^1J_{FC}$ = 255 Hz, *p*-C_6F_5), 138.0 (dm, $^1J_{FC}$ = 257 Hz, *m*-C_6F_5), 122.9 (m, *ipso*-C_6F_5), 55.9 (s, NCH_2), 29.6 (s, NCH_2CH_2), 20.3 (s, CH_2Me), 13.7 (s, CH_2Me), –9.6 (br, $AlMe_2$), –10.5 (br, $AlMe_2$). ^{19}F NMR (C_6D_6): –140.3 (d, $^3J_{FF}$ = 23 Hz, *o*-C_6F_5), –155.2 (t, $^3J_{FF}$ = 23 Hz, *p*-C_6F_5), –161.9 (dd, $^3J_{FF}$ = 23 Hz, $^3J_{FF}$ = 23 Hz, *m*-C_6F_5). Anal. calcd for $C_{24}H_{30}Al_2F_{10}N_2$: C 48.82, H 5.12, N 4.74; found: C 48.61, H 5.11, N 4.65. Single crystals suitable for X-ray diffraction experiments were obtained by storing a concentrated pentane solution at –30 °C overnight.

X-ray data collection and reduction

Crystals were manipulated and mounted in capillaries in a glovebox, thus, maintaining a dry, O_2-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data were collected in a hemisphere of data in 1329 frames with 10 s exposure times. The observed extinctions were consistent with the space groups in each case. The data sets were collected ($4.5° < 2\theta < 45–50.0°$). A measure of decay was obtained by recollecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP processing packages. An empirical absorption correction, based on redundant data, was applied to each data set. Subsequent solution and refinement was performed, using the SHELXTL solution package.

Structure solution and refinement

Non-hydrogen atomic-scattering factors were taken from

Table 1. Crystallographic data.

Crystal	**1**	**2**·C_6H_5Me	**4**	**8**
Empirical formula	$C_{12}HF_{10}N$	$C_{35}H_{20}AlF_{20}N_3$	$C_{34}H_{38}AlF_{15}N_4$	$C_{24}H_{30}Al_2F_{10}N_2$
Formula weight	349.14	889.52	814.66	590.46
Crystal system	Monoclinic	Triclinic	Monoclinic	Monolcinic
a (Å)	21.383(5)	12.3959(19)	23.36(3)	14.713(3)
b (Å)	5.9810(14)	12.7928(19)	8.902(10)	12.980(2)
c (Å)	4.5176(11)	13.306(2)	19.97(2)	15.085(3)
α (°)		104.584(2)		
β (°)	100.344(3)	106.602(2)	112.660(15)	98.488(2)
γ (°)		108.169(2)		
Volume (Å^3)	568.4(2)	1781.5(5)	3833(8)	2849.3(9)
Space group	$C2$	$P1$	$P2_1/c$	$P2_1/n$
$D_{\text{calcd.}}$ (g cm^{-3})	1.02	1.658	1.412	1.376
Z	1	2	4	4
Absorption coefficient (μ) (mm^{-1})	0.118	0.195	0.156	0.183
Reflections collected	2325	17357	35570	26972
Data $F_o^2 > 3\sigma(F_o^2)$	811	6274	6754	5013
Parameters	107	536	487	349
$R_1{}^a$	0.0291	0.0539	0.0577	0.0557
$wR_2{}^b$	0.0727	0.1112	0.1063	0.1272
Goodness-of-fit	0.729	0.997	0.998	1.019

[a] Data collected at 20 °C with Mo Kα radiation (λ = 0.71069 Å), $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma(wF_c)^2]^{1/2}$.

the literature tabulations (25). The heavy-atom positions were determined, using direct methods, employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function $w(|F_o| - |F_c|)^2$, where the weight w is defined as $4F_o{}^2/2\sigma(F_o{}^2)$, and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases, atoms were treated isotropically. H-atom positions were calculated and allowed to ride on the carbon to which they are bonded, assuming a C–H bond length of 0.95 Å. Hydrogen-atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C atom to which they are bonded. The H-atom contributions were calculated but not refined. The locations of the largest peaks in the final difference Fourier map calculation, as well as the magnitude of the residual electron densities in each case, were of no chemical significance. Additional details are provided in the supplementary data.[2] Crystallographic data for **1**, **2**, **4**, and **8** are given in Table 1.

Results and discussion

The pentafluoroaryl amine $(C_6F_5)_2NH$ (**1**) has not been frequently used as a ligand in main-group or tranisition-metal chemistry. In initiating work with this species, we were able to obtain X-ray quality crystals of **1** (Fig. 1). The reaction of this amine with $AlH_3 \cdot NEtMe_2$ in a 1:1 ratio affords a light-yellow oil **2** in 97% isolated yield. The ^{1}H NMR data were consistent with the presence of coordinated $NEtMe_2$, although resonances attributable to Al–H fragments were not observed at 25 °C. At –80 °C, a resonance appeared at 3.39 ppm, and it was attributed to two protons on Al. The ^{19}F NMR spectrum of **2** showed the resonances expected for the amide substituents. Based on these data and elemental analyses, compound **2** was formulated as $[(C_6F_5)_2N]AlH_2 \cdot NEtMe_2$ (Scheme 1).

Using 1:3 stoichiometry, the reaction of $AlH_3 \cdot NEtMe_2$ with $(C_6F_5)_2NH$ proceeds upon stirring at 25 °C for 12 h to afford the product **3** (Scheme 1). The product was recrystallized from pentane to yield a white crystalline material in 83% yield. For compound **3**, the ^{1}H NMR spectrum showed resonance attributable to coordinated $NEtMe_2$, although no resonances attributable to AlH were observed. Nonetheless, similar to **2**, cooling to –80 °C resulted in the observation of a ^{1}H NMR resonance at 3.21 ppm attributable to the single Al–H atom. The $^{13}C\{^1H\}$ NMR spectrum revealed the corresponding ^{13}C resonances, as well as signals arising from C_6F_5 rings. Similarly, the ^{19}F NMR data are consistent with the presence of the $(C_6F_5)_2N$ fragments. Suitable crystals were obtained from a pentane solution at

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[2] Supplementary data for this article are available on the journal Web site (http://canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 5132. For more information on obtaining material, refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 633717 and 633720 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Scheme 1.

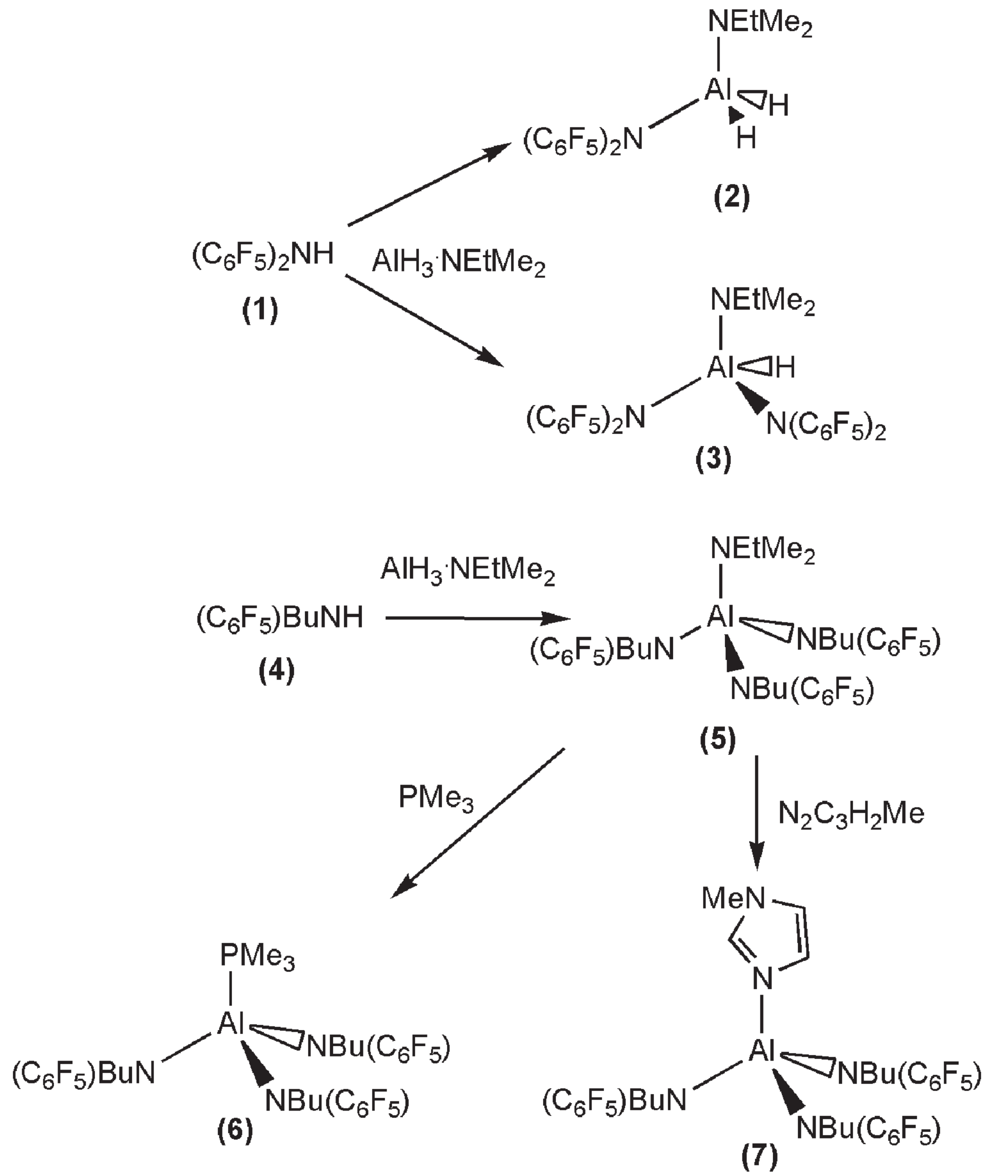
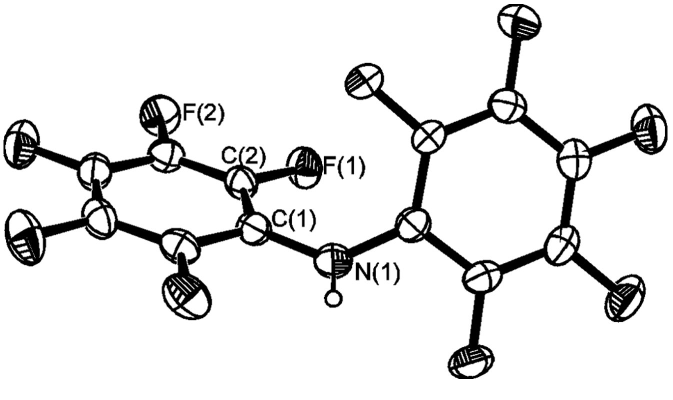


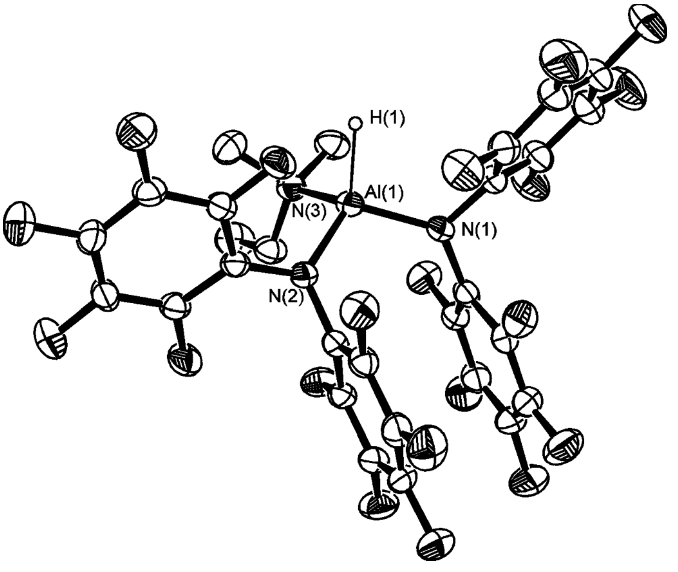
Fig. 1. ORTEP drawing of **1** (30% thermal ellipsoids are shown). Selected distances (Å) and angles (°): N(1)—C(1), 1.389(3); C(1)–N(1)–C(1), 127.7(3).



–30 °C, allowing the unambiguous determination of the nature of **3**, as $[(C_6F_5)_2N]_2AlH{\cdot}NEtMe_2$, by a single-crystal X-ray diffraction study (Fig. 2). The geometry about Al is pseudo-tetrahedral, with the amide Al—N distances averaging 1.855(3) Å. The coordinated tertiary amine gives rise to an Al—N distance of 2.006(3) Å. The resulting N–Al–N angles range from 105.48(12)° to 113.78(13)°. The Al-bound H atom was located and refined, giving rise to an Al–H distance of 1.62 Å. Similar Al—H distances have been reported for $(i\text{-}Pr_2C_6H_3N)C(Me)CHPPh_2(NC_6H_3\text{-}i\text{-}Pr_2)AlH_2$ (26). Adjacent arene rings on the two amide ligands are oriented in an approximately parallel offset π-stacking arrangement. The distance between these rings is 3.284 Å, while the angle between the planes is 2°.

The related fluorinated-aryl amine $(C_6F_5)(n\text{-}C_4H_9)NH$ (**4**) was prepared via a known method (24). Reactions of this less bulky and more basic amine with $AlH_3{\cdot}NEtMe_2$ in 1:1 and 2:1 ratios afforded unresolved mixtures of products.

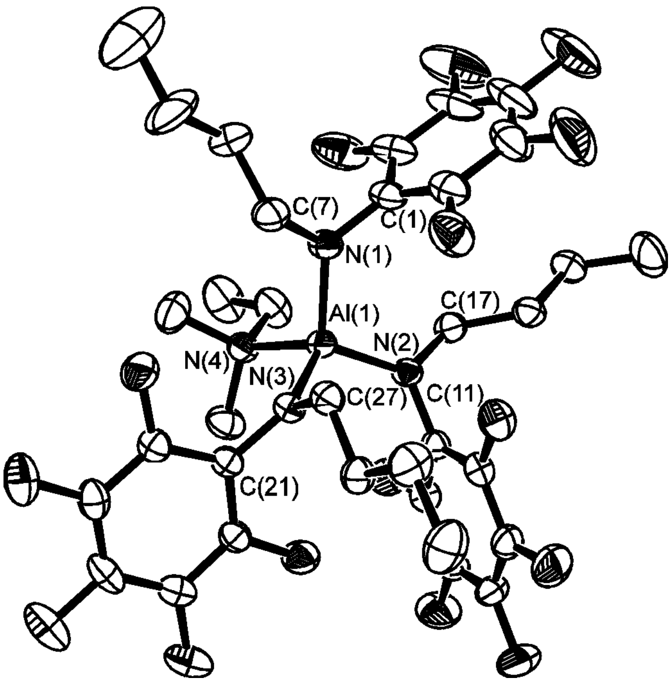
Fig. 2. ORTEP drawing of **2** (30% thermal ellipsoids are shown). All hydrogen atoms except the AlH are omitted for clarity. Selected distances (Å) and angles (°): Al(1)—N(1), 1.855(3); Al(1)—N(2), 1.856(3); Al(1)—N(3), 2.006(3); N(1)–Al(1)–N(2), 111.44(13); N(1)–Al(1)–N(3), 113.78(13); N(2)–Al(1)–N(3), 105.48(12).



However, the reaction of **4** in a 3:1 ratio with $AlH_3·NEtMe_2$ proceeded to give a white solid **5** in 72% isolated yield. ^1H NMR data were consistent with a ratio of amide to coordinated $NEtMe_2$ of 3:1. $^{13}C\{^1H\}$ and ^{19}F NMR data also supported the formulation of **5** as $[(C_6F_5)(n\text{-}C_4H_9)N]_3Al·NEtMe_2$ (Scheme 1). This view was subsequently confirmed via X-ray crystallography (Fig. 3). The Al center in **5** has a pseudo-tetrahedral geometry with Al—N distances for the amide ligands ranging from 1.827(3) Å to 1.838(4) Å. These distances are slightly shorter than those reported earlier for **3**, consistent with the increased basicity of the amide derived from **4**. The coordinated amine $NEtMe_2$ gave rise to an Al—N distance of 2.043(4) Å. Interestingly, this distance is significantly shorter than that seen in **4**, suggesting that although the Al in **5** has three amide ligands, the Al center is more accessible to the donor, presumably because of the lesser steric demands of the amide substituents.

Compound **5** reacts with other donors to afford the replacement of the coordinated amine. For example, the reaction with PMe_3 results in the formation of the white microcrystalline product **6**, albeit in a relatively low isolated yield of 27%. ^1H NMR confirms the displacement of the coordinated $NEtMe_2$ by PMe_3. In addition, the observation of a $^{31}P\{^1H\}$ NMR signal at –50.3 ppm is consistent with coordination to Al, and thus, the formulation of **6** as $[(C_6F_5)(n\text{-}C_4H_9)N]_3Al·PMe_3$ (Scheme 1). In a similar fashion, the reaction of **5** with *N*-methylimidazole $MeN_2C_3H_3$ results in the displacement of the amine, affording the product $[(C_6F_5)(n\text{-}C_4H_9)N]_3Al·(Me\text{-}imid)$ (**7**) in quantitative yields (Scheme 1). NMR data supported this formulation, although repeated attempts to isolate X-ray quality crystals of **7** were unsuccessful. The dramatically higher yields of **7** than **6** are consistent with hard–soft donor considerations, as well as the lesser steric congestion provided by the imidazole N-atom donor.

Fig. 3. ORTEP drawing of **4** (30% thermal ellipsoids are shown). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Al(1)—N(1), 1.838(4); Al(1)—N(2), 1.833(3); Al(1)—N(3), 1.827(3); Al(1)—N(4), 2.043(4); N(3)–Al(1)–N(2), 114.55(15); N(3)–Al(1)–N(1), 111.01(16); N(2)–Al(1)–N(1), 112.25(14); N(3)–Al(1)–N(4), 106.37(14); N(2)–Al(1)–N(4), 105.66(15); N(1)–Al(1)–N(4), 106.34(14).



In contrast to the reactions with $AlH_3·NEtMe_2$, the amine **4** reacts with $AlMe_3$ in a 1:1 ratio to form the colorless crystalline product **8** in 73% isolated yield. The ^1H NMR spectrum of **8** is consistent with replacement of one methyl group by an amide ligand. However, this spectrum also shows two resonances at –0.04 and –0.73 ppm, attributable to Al-bound methyl groups. This suggests molecular dissymmetry and the formulation of **8** as $[Me_2AlN(C_6F_5)(n\text{-}C_4H_9)]_2$ (Fig 4, Scheme 2). The $^{13}C\{^1H\}$ and ^{19}F NMR and elemental analysis data were also consistent with this formulation. Single crystals of **8**, suitable for X-ray diffraction experiments, were grown from a concentrated pentane solution at –30 °C. The X-ray data confirmed the dimeric formulation of **8**, in which the amido-N atoms bridge the two Al centers. The substituents on N are oriented such that the C_6F_5 rings are on *cis*. It is this feature that accounts for the inequivalent methyl groups on the Al atoms. The Al—N distances were found to range from 1.993(3) Å to 2.031(3) Å, significantly longer than the terminal Al–amide distances described earlier. The geometry and metric parameters are similar to those recently reported for a series of Al-dimers $[Me_2AlN(C_6F_nH_{5-n})H]_2$($n$ = 1, 2, 4, and 5) (27). The Al—C distances range from 1.947(4) to 1.959(3) Å, similar to those seen in the previously mentioned Al-dimers and in $[Me_2Al(NPt\text{-}Bu_3)]_2$ (28). The Al-centers are pseudo-tetrahedral, with C–Al–C′ and N–Al–N′ angles averaging 122.4(2)° and 86.8(1)°, respectively. In addition, the Al_2N_2

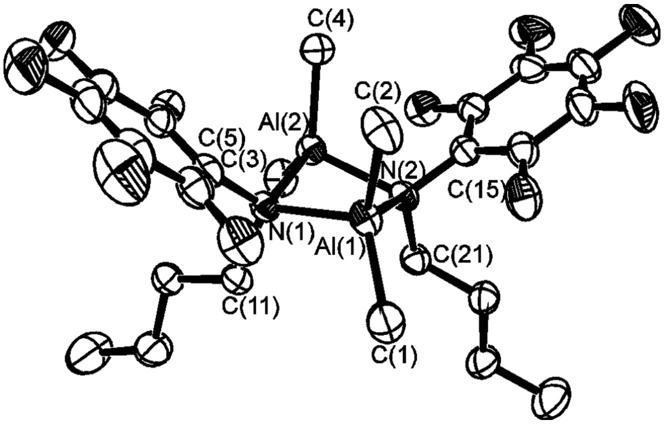
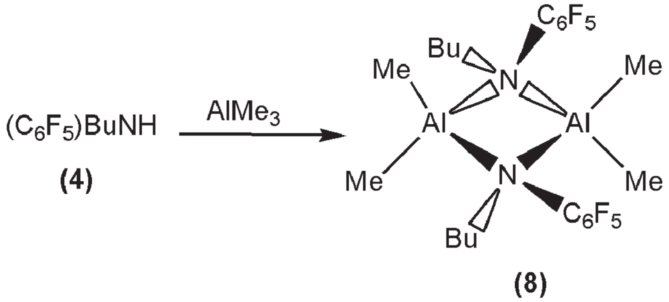


Fig. 4. ORTEP drawing of **8** (30% thermal ellipsoids are shown). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (°): Al(1)—C(1), 1.947(4); Al(1)—C(2), 1.956(4); Al(1)—N(2), 1.993(3); Al(1)—N(1), 2.031(3); Al(1)—Al(2), 2.8280(14); Al(2)—C(4), 1.958(3); Al(2)—C(3), 1.959(3); Al(2)—N(1), 2.002(3); Al(2)—N(2), 2.030(3); C(1)–Al(1)–C(2), 123.70(18); C(1)–Al(1)–N(2), 112.08(15); C(2)–Al(1)–N(2), 109.36(14); C(1)–Al(1)–N(1), 111.89(14); C(2)–Al(1)–N(1), 106.70(15); N(2)–Al(1)–N(1), 86.87(10); C(4)–Al(2)–C(3), 121.04(18); C(4)–Al(2)–N(1), 110.78(14); C(3)–Al(2)–N(1), 113.11(14); C(4)–Al(2)–N(2), 107.39(14); C(3)–Al(2)–N(2), 112.50(14); N(1)–Al(2)–N(2), 86.65(10); Al(2)–N(1)–Al(1), 89.02(10); Al(1)–N(2)–Al(2), 89.33(10).

Scheme 2.



core is essentially planar, and thus, this results in an Al—Al′ separation of 2.8280(14) Å.

Summary

Several Al compounds incorporating hexafluorophenylamido-ligands have been prepared and characterized. The amides derived from the amines $(C_6F_5)_2NH$ and $(C_6F_5)(n\text{-}C_4H_9)NH$ react with $AlH_3.NEtMe_2$ to give the momeric Al products **2**, **3**, and **5**, with varying numbers of amido-substituents. The degree of substitution appears to be dominated by the steric demands of the amide subsitutents. Donor exchange is facile for **5**, readily affording **6** and **7**. The amine $(C_6F_5)(n\text{-}C_4H_9)NH$ also reacts with $AlMe_3$ to give the dimeric product **8**. These Al–amido species proved to be generally difficult to handle and demonstrated poor reactivity. We will continue to develop new main-group chemistry that will result in new activators for applications in olefin polymerization catalysts.

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References

1. W.E. Piers and T. Chivers. Chem. Soc. Rev. **26**, 345, (1997).
2. G. Erker. Dalton Trans.1883, (2005).
3. Y.-X. Chen, M.V. Metz, L. Li, C.L. Stern, and T.J. Marks. J. Am. Chem. Soc. **120**, 6287, (1998).
4. Y.-X. Chen, C.L. Stern, S. Yang, and T.J. Marks. J. Am. Chem. Soc. **118**, 12451, (1996).
5. L. Li, C.L. Stern, and T.J. Marks. Organometallics, **19**, 3332, (2000).
6. T.J. Marks and Y.-X. Chen. US Patent 6-087-460, 2000.
7. T.J. Marks and Y.-X. Chen. US Patent 6-130-302, 2000.
8. T.J. Marks, L. Li, Y.-X. Chen, M.H. McAdon, and P.N. Nickias. PCT Int. Appl. WO 9906412, 1999.
9. M.V. Metz, D.J. Schwartz, C.L. Stern, T.J. Marks, and P.N. Nickias. Organometallics, **21**, 4159, (2002).
10. D.J.H. Emslie, W.E. Piers, and M. Parvez. Angew. Chem., Int. Ed. Engl. **42**, 1252, (2003).
11. I. Ghesner, W.E. Piers, M. Parvez, and R. McDonald. Organometallics, **23**, 3085, (2004).
12. R. Roesler, W.E. Piers, and M. Parvez. J. Organomet. Chem. **680**, 218, (2003).
13. P.E. Romero, W.E. Piers, S.A. Decker, D. Chau, T.K. Woo, and M. Parvez. Organometallics, **22**, 1266, (2003).
14. T. Ooi, and K. Maruoka. Sci. Synth. **7**, 225, (2004).
15. A.W. Langer, Jr. US Patent 4-096-092, 20 June 1978.
16. G.B. Smith, D.H. McDaniel, E. Biehl, and C.A. Hollingsworth. J. Am. Chem. Soc. **82**, 3560, (1960).
17. T. Belgardt, J. Storre, H.W. Roesky, M. Noltemeyer, and H.-G. Schmidt. Inorg. Chem. **34**, 3821, (1995).
18. J.S. Kim, L.M. Wojcinski, II, S. Liu, J.C. Sworen, and A. Sen. J. Am. Chem. Soc. **122**, 5668, (2000).
19. W.R. Mariott, L.O. Gustafson, and E.Y.-X. Chen. Organometallics, **25**, 3721, (2006).
20. D. Chakraborty, and E.Y.X. Chen. Inorg. Chem. Commun. **5**, 698, (2002).
21. A. Rodriguez-Delgado, and E.Y.-X. Chen. Inorg. Chim. Acta, **357**, 3911, (2004).
22. J. Klosin, G.R. Roof, E.Y.-X. Chen, and K.A. Abboud. Organometallics, **19**, 4684, (2000).
23. W.R. Mariott, L.M. Hayden, and E.Y.-X. Chen. ACS Symp. Ser. **857**, 101, (2003).
24. V.E. Platonov, A. Haas, M. Schelvis, M. Lieb, K.V. Dvornikova, O.I. Osina, T.V. Rybalova, and Y.V. Gatilov. J. Fluorine Chem. **114**, 55, (2002).
25. D.T. Cromer, and J.T. Waber. Int. Tables X-ray Crystallogr. **4**, 71, (1974).
26. J.D. Masuda, D.M. Walsh, P. Wei, and D.W. Stephan. Organometallics, **23**, 1819, (2004).
27. P. Shukla, A.H. Cowley, J.N. Jones, J.C. Gordon, and B.L. Scott. Dalton Trans.1019, (2005).
28. C.M. Ong, P. McKarns, and D.W. Stephan. Organometallics, **18**, 4197, (1999).