Synthesis and Characterization of the Monomeric Aluminum Monoamides $(t\text{-Bu})_2AlN(R)R'$ (R and R′ = Bulky Aryl, Alkyl, or Silyl Groups)

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The synthesis and characterization of the compounds $(t\text{-Bu})_2AlNR_2$ (R = Mes, **1**, and $SiPh_3$, **2**) and $(t\text{-Bu})_2AlN(R')SiPh_3$ (R′ = 2,6-*i*-$Pr_2C_6H_3$ (Dipp), **3**, and 1-adamantyl (1-Ad), **4**) are described. They were characterized by X-ray crystallography and ^1H NMR and IR spectroscopy. In the crystal phase, the structures of **1–4** are monomeric with essentially trigonal planar coordinations at aluminum and nitrogen and Al–N bond lengths that range from 1.82 to 1.89 Å. The variation in the Al–N bond lengths are a consequence of the steric interactions between the large groups at aluminum and nitrogen, different change separations across the Al–N bond, and, in some instances, weak Al–N π-bonding. The structural data together with VT ^1H NMR studies of these and related compounds indicate that a decrease in the size of these groups affords considerably shorter Al–N distances and, in some cases, barriers to rotation around the Al–N bond that have a maximum value of ca. 9–10 kcal mol^{-1}. The synthesis and characterization of $[(t\text{-Bu})_2Al\{N(H)CPh_3\}_2(Li)]$, **5**, are also described. Crystal data with Mo Kα (λ = 0.710 69 Å) at 130 K: **1**, $C_{26}H_{40}AlN$, $a = 9.965(3)$ Å, $b = 13.746(5)$ Å, $c = 17.700(6)$ Å, orthorhombic, space group $Pca2_1$, $Z = 4$, $R = 0.069$; **2**, $C_{44}H_{48}AlNSi_2$, $a = 12.623(4)$ Å, $b = 16.880(3)$ Å, $c = 18.600(2)$ Å, $\alpha = 93.45(1)°$, $\beta = 100.25(2)°$, $\gamma = 99.46(2)°$, triclinic, space group $P\bar{1}$, $Z = 4$, $R = 0.051$; **3**, $C_{38}H_{50}AlNSi$, $a = 10.413(4)$ Å, $b = 10.585(6)$ Å, $c = 18.281(6)$ Å, $\alpha = 97.75(4)°$, $\beta = 96.41(3)°$, $\gamma = 118.97(2)°$, triclinic, space group $P\bar{1}$, $Z = 2$, $R = 0.050$; **4**, $C_{36}H_{48}AlNSi$, $a = 10.372(3)$ Å, $b = 17.957(8)$ Å, $c = 19.184(8)$ Å, $\alpha = 113.87(3)°$, $\beta = 99.23(3)°$, $\gamma = 96.71(3)°$, triclinic, space group $P\bar{1}$, $Z = 4$, $R = 0.045$; **5**, $C_{46}H_{50}AlLiN_2$, $a = 37.78(2)$ Å, $b = 10.635(4)$ Å, $c = 19.237(7)$ Å, $\beta = 98.19(3)°$, monoclinic, space group $C2/c$, $Z = 8$, $R = 0.056$.

Introduction

In recent years there has been widespread interest in the synthesis and characterization of compounds which have multiple bonds involving the heavier main group elements.[1] These studies have been mostly concerned with compounds of the phosphorus[2] and silicon[3] groups. For the main group 3 elements the existence of p–p π-bonding in compounds such as $R_2BE(R')R''$ (E = N, P, or As) or R_2BER' (E = O and S), have been firmly established.[4–8] In these species the primary structural indicators of multiple bonding have been shortening of the B–E bond and low twist angles between the planes at boron and the group 5 or 6 element. In addition, activation barriers as high as 25 kcal mol^{-1} have been observed for rotation around B–E bonds.[4–8]

Heavier main group 3 elements such as aluminum or gallium are, in principle, capable of similar multiple bonding to the main group 5 and 6 elements. In contrast to boron, however, recent studies of dialkylaluminum aryloxides have shown than an Al–O p–p π-interaction probably accounts for less than 5% of the overall Al–O bond strength.[9] This conclusion was based on solution ^1H NMR studies which indicated rapid rotation around the Al–O bond at temperatures as low as −100 °C. Moreover, the short M–O bond lengths observed in these compounds could be largely accounted for in terms of the low coordination numbers at aluminum and oxygen and a strong ionic contribution to the bond strength. It was, however, proposed[9] that there was a greater likelihood of detecting an aluminum–nitrogen π-interaction in the related aluminum amides owing to the smaller differences in size[10] and electronegativity[10] in the Al–N pair. There is little evidence for Al–N π-bonding in the literature. For example, only two structures of unassociated aluminum amides, $Al[N(SiMe_3)_2]_3$[11] and $[\{MeAlN(2,6\text{-}i\text{-}Pr_2C_6H_3)\}_3]$[12] have been reported. In these compounds the π-bond order in each Al–N bond is reduced since there is competition by either two or three nitrogen lone pair orbitals for each empty aluminum 3p orbital. It is therefore desirable to have compounds involving only a single Al–N p–p π-interaction in which the effects of π-bonding could be expected to be maximized. This paper describes the synthesis of some monomeric aluminum monoamides and the study of the Al–N bonding by X-ray crystallography, VT ^1H NMR and IR spectroscopy.

Experimental Section

General Procedures. All experiments were performed either by using modified Schlenk techniques or a Vacuum Atmospheres HE 43-2 drybox under nitrogen. Solvents were freshly distilled from sodium–potassium alloy and degassed twice prior to use. ^1H NMR spectra were recorded in C_6D_6 or C_7D_8 solutions by using a General Electric QE-300 spectrometer. Infrared spectra were recorded as a Nujol mull between CsI plates by using a Perkin-Elmer PE-1430 spectrometer. The reagents $HNMes_2$,[13] $HN(SiPh_3)_2$,[14] and $(t\text{-Bu})_2AlCl$[15] were prepared by literature

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Table I. Selected Crystallographic Data and Structural Parameters for **1–5**

	compd				
	1[a]	**2**[b]	**3**[a]	**4**[a]	**5**[a]
formula	$C_{26}H_{40}AlN$	$C_{44}H_{48}AlNSi_2$	$C_{38}H_{50}AlNSi$	$C_{36}H_{48}AlNSi$	$C_{46}H_{50}AlLiN_2$
fw	393.6	674	575.9	549.8	664.8
color and habit	colorless needles	colorless needles	colorless plates	colorless plates	colorless plates
temp, K	130	130	130	130	130
cryst system	orthorhombic	triclinic	triclinic	triclinic	monoclinic
a, Å	9.965(3)	12.623(4)	10.413(4)	10.372(3)	37.78(2)
b, Å	13.746(5)	16.880(3)	10.585(6)	17.957(8)	10.635(4)
c, Å	17.700(6)	18.600(2)	18.281(6)	19.184(8)	19.237(7)
α, deg		93.45(1)	97.75(4)	113.87(3)	
β, deg		100.25(2)	96.41(3)	99.23(3)	98.19(3)
γ, deg		99.46(2)	118.97(2)	96.71(3)	
V, Å^3	2424.7(13)	3830.7(15)	1709.8(10)	3159(2)	7651(5)
space group	$Pca2_1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
Z	4	4	2	4	8
cryst dims, mm	0.17 × 0.15 × 0.30	0.18 × 0.28 × 0.04	0.02 × 0.28 × 0.38	0.96 × 0.70 × 0.20	0.63 × 0.42 × 0.75
D_{calc}, g cm^{-3}	1.078	1.169	1.118	1.156	1.154
μ, mm^{-1}	0.094	1.286	0.120	0.127	0.087
ranges of transm coefs	0.93, 0.99	0.97, 0.98	0.96, 0.99	0.81, 0.93	0.97, 0.98
diffractometer	Syntex $P2_1$	Siemens P4/RA	Siemens R3m	Siemens R3m	Syntex $P2_1$
scan method	ω, 1.00° range	2θ–θ, 1.80° range	ω, 1.00° range	ω, 0.90° range	ω, 1.00° range
scan speed, deg min^{-1}	29.30 in ω	58.59 in ω	8.08 in ω	14.65 in ω	29.30 in ω
2θ range, deg	0–55	1–108	0–50	0–55	0–50
octants collcd	$\pm h,-k,-l$	$\pm h,\pm k,+l$	$+h,\pm k,\pm l$	$\pm h,\pm k,+l$	$\pm h,-k,-l$
no. of data collcd	13235	10322	4214	16344	13235
no. of obsd reflcns	1749, $I > 2\sigma(I)$	6533, $I > 2\sigma(I)$	3250, $I > 2\sigma(I)$	10 122, $I > 2.5\sigma(I)$	4477, $I > 2\sigma(I)$
no. of variables	254	865	370	704	458
R, R_w	0.069, 0.062	0.051, 0.059	0.050, 0.050	0.045, 0.045	0.056, 0.053

[a] Data were collected with Mo Kα radiation (λ = 0.710 69 Å). [b] Data were collected with Cu Kα radiation (λ = 1.541 84 Å, 50 kV/250 mA).

methods. H_2NCPh_3, H_2NDipp, H_2N(1-Ad) and Ph_3SiCl (Dipp = 2,6-*i*-$Pr_2C_6H_3$, 1-Ad = 1-adamantyl) were purchased from Aldrich or Strem and were purified by recrystallization or distillation.

Synthesis. (*t*-Bu)$_2$AlNMes$_2$ (1). The synthesis of compounds **1**, **3** and **4** may be illustrated by the procedure for **1** which is described here. A slurry of $LiNMes_2$ (2 mmol) in hexane (30 mL) prepared from $HNMes_2$ (0.51 g, 2 mmol) and *n*-BuLi (1.25 mL, 2 mmol) was added via cannula at ambient temperature to a hexane (20 mL) solution of (*t*-Bu)$_2$AlCl (0.35 g, 2 mmol). After stirring for 12 h, the solution was filtered and concentrated to incipient crystallization. Colorless crystals of **1** appeared after cooling overnight in a -20 °C freezer (yield: 0.65 g, 83%). M.p. 171–174 °C; ^{1}H NMR (C_7D_8) δ = 1.00 (s, Al(C(CH$_3$)$_3$)$_2$), 2.11 (s, *o*-CH$_3$), 2.13 (s, *p*-CH$_3$), 2.49 (s, *o*-CH$_3$), 6.65 (s, *m*-H), 6.74 (s, *m*-H); IR 2910 (bs), 2730 (w), 1450 (s), 1300 (m), 1247 (s), 1207 (m), 1162 (w), 1147 (w), 1065 (bw), 1015 (w), 1002 (w), 958 (w), 945 (w), 935 (sh), 895 (m), 852 (m), 835 (w), 808 (m), 730 (m), 611 (w), 587 (sh), 572 (m), 558 (sh), 505 (w), 418 (m), 410 (sh), 385 (w), 298 (w), 292 cm^{-1} (w).

(*t*-Bu)$_2$AlN(SiPh$_3$)$_2$ (2). The synthesis of compounds **2** and **5** may be illustrated by the procedure for **2** which is described here. A toluene (20 mL) solution of HN(SiPh$_3$)$_2$ (1.07 g, 2 mmol) was treated with *n*-BuLi (1.25 mL, 2 mmol), warmed to 50 °C for 30 min., and stirred for 3 h. The slurry was then added dropwise to (*t*-Bu)$_2$AlCl (0.35 g, 2 mmol) in toluene (20 mL). After stirring for 12 h, all volatile materials were removed and the residue taken up in warm hexane (45 mL). Filtration and cooling in a -20 °C freezer gave the product as colorless crystals (yield: 0.52 g, 39%). M.p. >180 °C (dec.); ^{1}H NMR (C_6D_6) δ = 1.09 (s, Al(C(CH$_3$)$_3$)$_2$), 7.19 (m, *m*-H), 7.66 (m, *o* and *p*-H); IR 2910 (bs), 1583 (w), 1563 (w), 1452 (s), 1425 (m), 1302 (bw), 1258 (w), 1180 (bw), 1153 (w), 1103 (bs), 1061 (sh), 1025 (w), 993 (w), 975 (sh), 930 (bs), 860 (vw), 850 (vw), 788 (bm), 735 (s), 706 (sh), 695 (s), 647 (sh), 615 (vw), 575 (vw), 512 (s), 483 (s), 457 (sh), 400 (vw), 362 (w), 345 (w), 244 cm^{-1} (vw).

(*t*-Bu)$_2$AlN(Dipp)SiPh$_3$ (3). By using hexane as solvent, the asymmetric amine, HN(Dipp)SiPh$_3$ was prepared in situ by treatment of H_2-NDipp with one equivalent of 1.6 M *n*-BuLi followed by the addition of Ph_3SiCl. Yield: 0.92 g, 80%; m.p. >150 °C (dec.); ^{1}H NMR (C_7D_8) δ = 0.60 (d, *o*-CH(C*H*$_3$)$_2$), 0.93 (s, Al(C(CH$_3$)$_3$)$_2$), 1.39 (d, *o*-CH(C*H*$_3$)$_2$), 3.86 (m, *o*-C*H*(CH$_3$)$_2$), 7.07 (m, *m*-H for Ph, Dipp), 7.55 (m, *o* and *p*-H for Ph, Dipp); IR 3025 (w), 2905 (bs), 2718 (w), 1955 (w), 1882 (w), 1822 (w), 1767 (w), 1583 (w), 1563 (w), 1460 (bs), 1425 (s), 1373 (s), 1361 (sh), 1327 (w), 1307 (w), 1267 (w), 1260 (sh), 1227 (w), 1185 (w), 1168 (m), 1100 (s), 1046 (w), 1037 (w), 1025 (w), 993 (w), 970 (w), 960 (w), 929 (w), 889 (s), 842 (s), 795 (s), 740 (m), 735 (sh), 707 (s), 698 (s), 672 (w), 602 (m), 596 (w), 568 (w), 549 (w), 531 (w), 503 (s), 457 (m), 433 (bm), 390 (vw), 372 (vw), 340 (m), 317 cm^{-1} (vw).

(*t*-Bu)$_2$AlN(1-Ad)SiPh$_3$ (4). The amine, HN(1-Ad)SiPh$_3$ was prepared in situ by the treatment of H_2N(1-Ad) with one equivalent of *n*-BuLi followed by the addition of Ph_3SiCl. Yield: 0.38 g, 34%; m.p. 182–185 °C (dec.); ^{1}H NMR (C_7D_8) δ = 1.10 (s, Al(C(CH$_3$)$_3$)$_2$), 1.43, 1.86, 2.04 (br s's, intensity ratio 2:1:2, 1-Ad), 7.2 (m, *m*-H for Ph), 7.93 (m, *o* and *p*-H for Ph); IR 3125 (w), 3063 (sh), 3043 (sh), 3023 (sh), 2890 (bs), 2695 (w), 1975 (sh), 1958 (w), 1898 (w), 1835 (w), 1672 (w), 1583 (m), 1562 (w), 1425 (s), 1378 (s), 1362 (sh), 1352 (s), 1340 (sh), 1310 (sh), 1298 (s), 1283 (sh), 1260 (m), 1181 (m), 1153 (w), 1090 (bs), 1038 (w), 1026 (w), 993 (s), 960 (s), 938 (s), 868 (bs), 806 (s), 780 (m), 730 (bs), 700 (bs), 680 (sh), 658 (m), 638 (w), 617 (w), 572 (s), 500 (bs), 460 (m), 425 (sh), 398 (bs), 365 (sh), 328 (sh), 304 cm^{-1} (bs).

(*t*-Bu)$_2$Al{N(H)CPh$_3$}$_2$(Li) (5). Yield: 0.26 g, 20% (based on Al); m.p. >159 °C (dec.); ^{1}H NMR (C_7D_8) δ = 1.14 (s, AlC(CH$_3$)$_3$), 7.04 (m, Ph), 7.25 (m, Ph).

X-ray Data Collection and the Solution and Refinement of the Structures. Crystals of **1–5** were coated with a layer of hydrocarbon oil upon removal from the Schlenk tube. A suitable crystal was selected, attached to a glass fiber by using silicon grease and immediately placed in the low temperature N_2 stream.[16] X-ray data were collected with a Syntex $P2_1$ (**1** and **5**), Siemens R3 m/V (**3** and **4**) or a P4/RA/V (**5**) diffractometer equipped with a graphite monochromator and a locally modified Enraf-Nonius LT apparatus. Calculations were carried out on a Microvax 3200 computer using the SHELXTL PLUS program system. Neutral atom scattering factors and the correction for anomalous dispersion were from ref 17. The structures of all molecules were solved by direct methods. The hydrogen atoms attached to N(1) and N(2) of **5** were located from a difference map and the coordinates and isotropic thermal parameters of each were allowed to refine freely. Details of data collection and refinement and important atom coordinates are provided in Tables I and II, respectively.

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Table II. Selected Atom Coordinates ($\times 10^4$) for **1–5**

	x	*y*	*z*		*x*	*y*	*z*
1							
Al(1)	2071(2)	7513(2)	8887	C(5)	1016(6)	7171(4)	9809(4)
N(1)	3890(4)	7388(3)	8928(4)	C(9)	4589(6)	6909(4)	8337(4)
C(1)	1229(6)	7981(4)	7942(4)	C(18)	4647(6)	7822(4)	9529(4)
2							
Al(1)	2822(1)	–380(1)	2277(1)	Al(2)	7302(1)	6378(1)	2453(1)
N(1)	2233(3)	485(2)	2632(2)	N(2)	8056(3)	5515(2)	2380(2)
Si(1)	1684(1)	1093(1)	2006(1)	Si(3)	7973(1)	5079(1)	1501(1)
Si(2)	2352(1)	627(1)	3582(1)	Si(4)	8761(1)	5238(1)	3190(1)
C(1)	4424(4)	–442(3)	2544(3)	C(45)	5660(4)	6223(3)	2161(3)
C(5)	1846(4)	–1288(3)	1583(3)	C(49)	8097(4)	7482(3)	2899(3)
C(9)	152(3)	1001(3)	1831(2)	C(53)	7424(3)	5822(3)	889(2)
C(15)	2149(4)	834(3)	1127(2)	C(59)	7059(3)	4063(3)	1277(3)
C(21)	2191(3)	2206(3)	2247(2)	C(65)	9308(3)	4928(3)	1247(2)
C(27)	1064(3)	763(3)	3918(2)	C(71)	8527(3)	4122(3)	3284(2)
C(33)	3440(3)	1501(3)	4034(2)	C(77)	10286(3)	5550(3)	3346(2)
C(39)	2682(3)	–341(3)	3944(2)	C(83)	8212(4)	5704(3)	3955(2)
3							
Al	125(1)	2319(1)	1861(1)	C(19)	4351(4)	3592(4)	3210(2)
N	1863(4)	3969(3)	2396(2)	C(25)	1774(4)	3373(4)	3933(2)
Si	2994(1)	4286(1)	3267(1)	C(31)	–590(5)	280(5)	2059(2)
C(1)	2483(4)	5197(4)	2013(2)	C(35)	–1118(5)	2392(5)	951(2)
C(13)	4208(4)	6315(4)	3732(2)				
4							
Al(1)	1735(1)	3111(1)	3606(1)	Al(2)	2438(1)	8062(1)	3323(1)
N(1)	1423(2)	2237(1)	2620(1)	N(2)	2238(2)	7157(1)	2375(1)
Si(1)	–60(1)	1962(1)	1947(1)	Si(2)	3621(1)	7015(1)	1992(1)
C(1)	2526(2)	4256(1)	3771(1)	C(37)	1818(2)	9095(1)	3366(1)
C(5)	1653(2)	2931(1)	4574(1)	C(41)	3042(2)	7998(1)	4342(1)
C(9)	132(2)	1945(1)	979(1)	C(45)	5014(2)	7843(1)	2784(1)
C(15)	–1141(2)	954(1)	1765(1)	C(51)	3707(2)	7289(1)	1146(1)
C(21)	–990(2)	2801(1)	2425(1)	C(57)	4038(2)	5955(1)	1723(1)
C(27)	2595(2)	1856(1)	2401(1)	C(63)	912(2)	6575(1)	2037(1)
5							
Al(1)	1250(1)	1558(1)	5250(1)	C(16)	261(1)	2329(3)	6159(2)
N(1)	850(1)	1984(3)	5728(1)	C(22)	538(1)	217(3)	6299(2)
N(2)	1622(1)	2533(2)	5805(1)	C(28)	1831(1)	3729(3)	5903(2)
Li(1)	1218(2)	3027(6)	6340(3)	C(29)	1938(1)	4254(3)	5216(2)
C(1)	1470(1)	–185(3)	5331(2)	C(35)	2177(1)	3504(3)	6429(2)
C(5)	1054(1)	2053(3)	4250(2)	C(41)	1597(1)	4711(3)	6222(2)
C(9)	628(1)	1626(3)	6285(2)	H(1A)	707(7)	2235(30)	5400(14)
C(10)	847(1)	2074(3)	6986(2)	H(2A)	1777(7)	2000(27)	5897(17)

Table III. Selected Bond Distances (Å) and Angles (deg) for **1–6**

	1	**2a**	**2b**	**3**	**4a**	**4b**	**5**	**6**
Al–N	1.823(4)	1.880(4)	1.878(4)	1.834(3)	1.853(2)	1.845(2)	1.938(3) 1.933(3)	1.784(3)
Al–C	1.997(7) 1.979(7)	2.026(4) 2.016(6)	2.018(4) 2.015(5)	2.025(5) 2.015(5)	2.022(3) 2.000(2)	2.009(3) 2.008(3)	2.030(3) 2.028(3)	1.960(4) 1.959(3)
N–C	1.434(9) 1.417(9)			1.459(5)	1.500(3)	1.494(2)	1.499(4) 1.496(4)	1.431(4)
N–Si		1.744(4) 1.727(4)	1.740(4) 1.730(4)	1.757(4)	1.716(2)	1.712(2)		
R–N–R′ [a]	118.8(4)	125.7(2)	126.9(2)	113.7(2)	121.3(1)	125.6(1)		106.6(2)
Al–N–R	120.8(4)	118.0(2)	117.4(2)	115.1(2)	116.2(1)	117.1(1)		137.1(2)
Al–N–R′	120.3(5)	116.3(2)	115.7(2)	131.0(2)	121.9(1)	117.2(1)		115.0(1)
C–Al–C′	123.0(3)	117.3(2)	117.3(2)	114.7(2)	117.0(1)	117.6(1)	113.5(1)	127.8(2)
angle between planes at Al and N	49.5	62.3	66.2	16.1	87.7	84.9		5.5

[a] R, R′ = Mes, Mes, **1**; $SiPh_3$, $SiPh_3$, **2**; Dipp, $SiPh_3$, **3**; 1-Ad, $SiPh_3$, **4**; Dipp, H, **6**.

Results

Structural Descriptions. Selected structural parameters for **1–5** and other related compounds are summarized in Table III. The structural descriptions of **1** and **2**, and, **3** and **4** are considered together here owing to their formulae.

$(t\text{-}Bu)_2AlNR_2$ [R = Mes (1), $SiPh_3$ (2)]. The structure of **1** which is depicted in Figure 1 consists of well separated $(t\text{-}Bu)_2AlNMes_2$ monomers. The structure of **2** has two chemically equivalent, but crystallographically independent, molecules of the monomer in the asymmetric unit, one of which is shown in Figure 2. The Al–N bond lengths for **1** and **2** are 1.823(4) Å and 1.88 (av.) Å, respectively. The angles at nitrogen in **1** are within 1.2° of idealized trigonal values. The coordination at the nitrogen center in **2** is distorted trigonal planar with the widest angle, 126.3° (av.) between the silyl groups. The coordination at aluminum in both **1** and **2** is trigonal planar with relatively minor (≤3°) angular deviations from 120°. It is noteworthy, however, that the C–Al–C angle is 123.0(3)° in **1** whereas it is 117.3(2)° in **2**. The angle between the perpendiculars to the planes at aluminum and nitrogen in **1** and **2** are 49.5° and 64.2° (av.). In addition, the average Al–C bond lengths in **1** (1.988 Å) are ~0.03

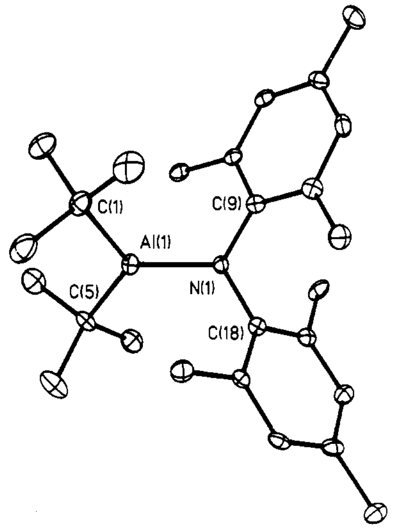

Figure 1. Computer-generated thermal ellipsoid (30%) plot of **1**. Hydrogen atoms are omitted for clarity.

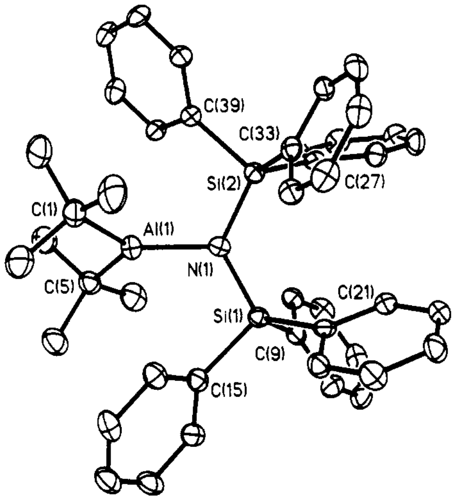

Figure 2. Computer-generated thermal ellipsoid (30%) plot of **2**. Hydrogen atoms are omitted for clarity.

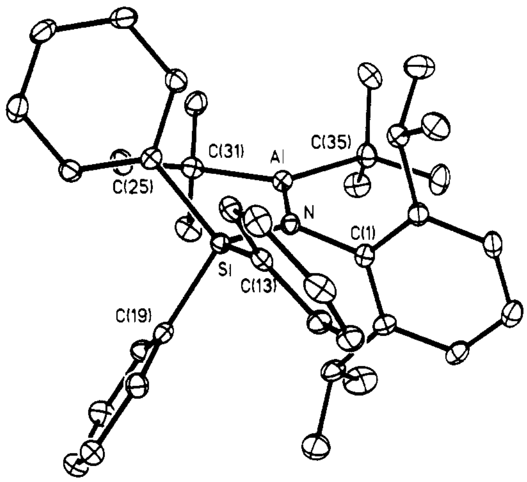

Figure 3. Computer-generated thermal ellipsoid (30%) plot of **3**. Hydrogen atoms are omitted for clarity.

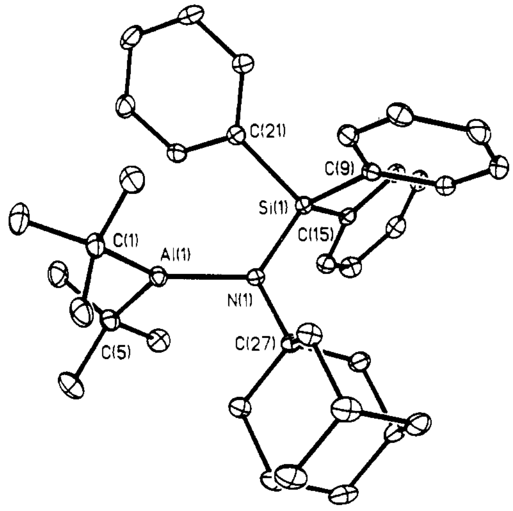

Figure 4. Computer-generated thermal ellipsoid (30%) plot of **4**. Hydrogen atoms are omitted for clarity.

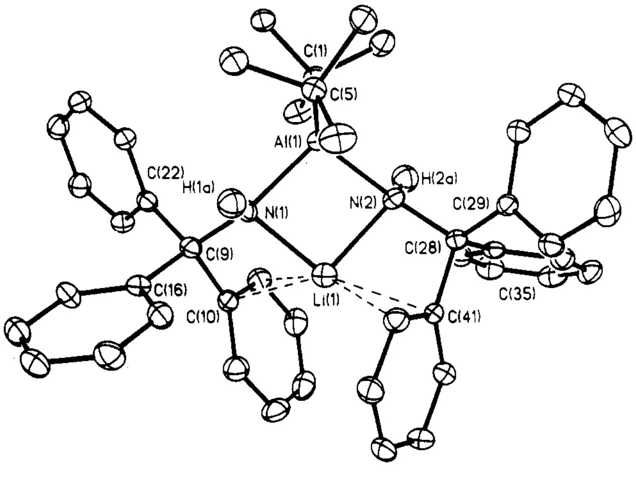

Figure 5. Computer-generated thermal ellipsoid (30%) plot of **5**. Hydrogen atoms are omitted for clarity.

Å longer than those found in **2** (2.019 Å). The average N–C and N–Si bonds lengths in **1** and **2** are 1.424 Å and 1.735 Å, respectively.

(t-Bu)$_2$AlN(R′)SiPh$_3$[R′ = Dipp (3), 1-Ad (4)]. The structure of **3** which has no crystallographically imposed symmetry is presented in Figure 3. The structure of **4** features two independent molecules in the asymmetric unit, one of which is shown in Figure 4. The nitrogen center in **3** has severely distorted trigonal planar coordination with interligand angles of 113.7(2)°, 115.1(2)° and 131.0(2)°. The corresponding angles in **4** show less distortion, but, there are significant differences in the values of the C–N–Si and Al–N–Si angles between the two molecules in the asymmetric unit. The angles for one molecule are 121.3(1)° and 125.6(1)°, whereas for the other they are 121.9(1)° and 117.2(1)°. The C–Al–C angle for **3** and **4** are 114.7(2)° and 117.3° (av.). The Al–N bond lengths are 1.834(3) Å (**3**) and 1.849 Å (av.) (**4**), and the angles between the perpendiculars to the planes at the aluminum and nitrogen are 16.1° in the case of **3** and 86.3° (av.), for **4**. The N–Si bond lengths (1.714 Å (av.)) in **4** are ~0.04 Å shorter than in **3**, 1.757(4) Å. The Al–C and N–C distances in **3** and **4** are within normal ranges.

[(t-Bu)$_2$Al{N(H)CPh$_3$}$_2$(Li)] (5). The structure of **5** is illustrated in Figure 5. It consists of well separated molecules which have no crystallographically imposed symmetry. The coordination at aluminum is distorted tetrahedral with angles that span the range, 99.7(1)° to 121.4(2)°. The smallest angle, which is N(1)–Al(1)–N(2), is due to nitrogen coordination of the Li$^+$ ion. The environment at the four coordinate nitrogen atoms is extremely distorted with angles that vary from 83.4(2)° to 146.6(2)° in the case of N(1) and from 83.0(2)° to 148.5(2)°, for N(2). The Al(1)–N(1) and Al(1)–N(2) bond lengths are 1.933(3) Å and 1.938(3) Å. The average Al–C and N–C bond distances are 2.029 Å and 1.497 Å. The Li$^+$ ion is coordinated by two nitrogen donors with Li–N distances of ~2.025 Å. There are also short

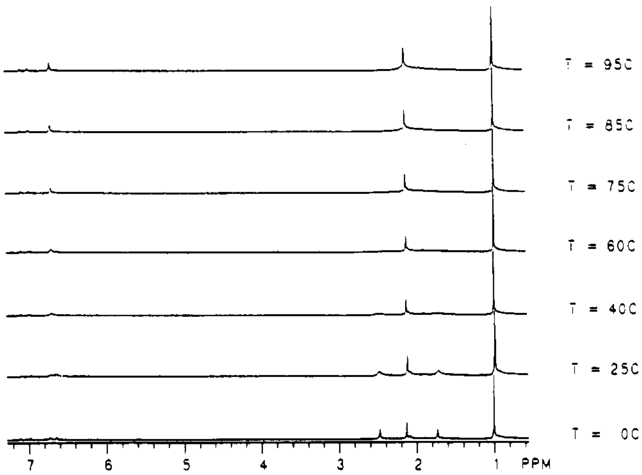

Figure 6. Variable temperature ^1H NMR study (0–95 °C) of $(t\text{-Bu})_2AlNMes_2$, **1**.

Li–C distances (2.244(7) Å to 2.570(7) Å) to the phenyl ring carbons C(10), C(11), C(41) and C(46).

Infrared Studies. Assignments of the Al–N stretching frequency in the IR spectra of **1**–**4** are not obvious owing to the complexity of the spectra and the lack of comparable data. In general, metal–nitrogen stretching frequencies are difficult to assign owing to coupling between the M–N, C–N and Si–N stretches. In the case of $Al[N(SiMe_3)_2]_3$,[18] however, several Al–N stretches were assigned which included a symmetric Al–N band at 840 cm^{-1}. In addition, aluminum nitride (AlN) gives an IR absorption at 750 cm^{-1}.[19] Similarly, the spectra of **1**–**4** all display a strong absorption within 10 cm^{-1} of 800 cm^{-1} which may be due to the Al–N stretching vibration.

Variable Temperature ^1H NMR Studies. The temperature dependence of the ^1H NMR spectra of **1**, **3** and **4**, between +100 °C and −100 °C, were investigated in C_7D_8 solution. For **1** (Figure 6), at $T = 0$ °C, well resolved, broadened doublets were observed for the *m*-H and *o*-Me resonances. Increasing the temperature results in further broadening and coalescence of both sets of peaks. The coalescence temperature, T_c for the *m*-H resonances was obvious while T_c for the *o*-Me group less apparent due to overlap with the *p*-Me singlet. Insertion of these temperatures ($T_c = 35$ °C, *m*-H and ≥65 °C, *o*-Me) together with the maximum peak separations (at 0 °C, 26.1 Hz and 223 Hz for *m*-H and *o*-Me) into an approximate formula[20] affords a consistent barrier (ΔG^*) of about 15.6 kcal mol^{-1} for the dynamic process. Splitting of the $Al(t\text{-Bu})_2$ and *p*-Me singlets was not observed as low as −100 °C. In the case of **3** (Figure 7), at $T = -20$ °C, two doublets representing inequivalent $o\text{-CH}(CH_3)_2$ groups are observed and a singlet for the *t*-butyl ligands of aluminum. Minor peaks are also present representing impurities (H_2NDipp, 0.95 δ and possibly $(t\text{-Bu})_2AlCl$, 1.11 δ). As the temperature is increased, the $o\text{-CH}(CH_3)_2$ doublets broaden and coalesce at ca. 85 °C. The T_c taken along with a maximum peak separation at −20 °C of 245 Hz gives a barrier of ~16.6 kcal mol^{-1} for the dynamic process. Upon cooling, the $Al(t\text{-Bu})_2$ singlet splits at ~(−75 °C) with a maximum peak separation of 21.6 Hz at −90 °C. This corresponds to a barrier of 9.9 kcal mol^{-1} for the dynamic process. In marked contrast, the VT ^1H NMR of **4** lacked any dynamic behavior, in particular, splitting of the $Al(t\text{-Bu})_2$ singlet was not observed as low as −100 °C.

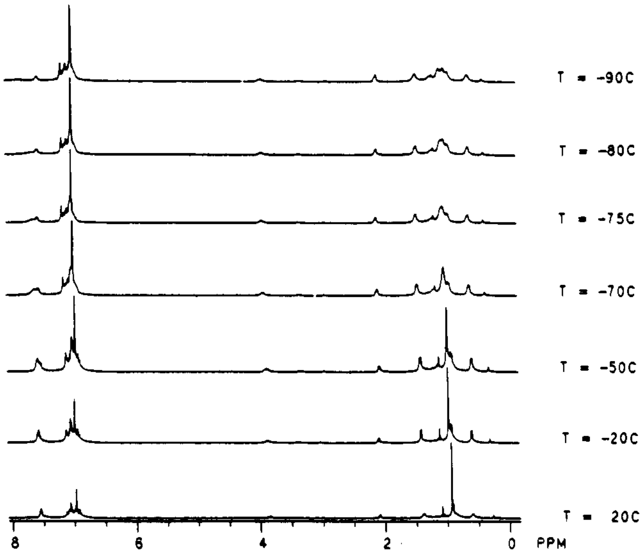

Figure 7. Variable temperature ^1H NMR study (20 to −90 °C) of $(t\text{-Bu})_2AlN(Dipp)SiPh_3$, **3**.

Discussion

The synthesis of **1**–**4** in Et_2O proceeded in good yield with LiCl elimination. However, reactions involving $(t\text{-Bu})_2AlCl$ and $LiN(R')R$ (R = Mes, Dipp, R′ = $SiMe_3$, where Dipp = $2,6\text{-}i\text{-}Pr_2C_6H_3$) gave impure oils which did not crystallize. The asymmetric amines, HN(R′)R used in the synthesis of **3** and **4** were prepared in situ by the addition of Ph_3SiCl to the lithiated primary amide, LiN(H)R (R = Dipp and 1-Ad). The formation of **5** was the unexpected result of the reaction of $(t\text{-Bu})_2AlCl$ with one equivalent of $LiN(H)CPh_3$ in toluene. All the products, **1**–**5**, were crystallized from pentane or hexane.

Structures. The series **1**–**4** represent the first well characterized examples of unassociated aluminum monoamides. In these compounds there is a bond between one three-coordinate aluminum and one nitrogen center. In this respect these species resemble the borylamides $R_2BNR'_2$ which, in most cases, have a moderately strong B–N π-bond owing to overlap of the boron and nitrogen 2p orbitals. This overlap is reflected in short B–N bond lengths and low angles between the planes at boron and nitrogen. In addition, the barriers to rotation around B–N bonds are generally in the range 5 to 25 kcal mol^{-1}.[8] Thus, the compounds **1**–**4** allow a structural comparison of the boryl and aluminum amides to be made for the first time. The primary focus of this work is the study of a possible π-interaction between aluminum and nitrogen.

The major conclusion to be drawn from Table III (which includes data for the diarylaluminum, $Trip_2AlN(H)Dipp$, **6** (Trip = $2,4,6\text{-}i\text{-}Pr_3C_6H_2$))[21] is that there is substantial variation of structure in the aluminum-nitrogen compounds **1**–**4** and **6**. For example, the Al–N bond lengths span the range 1.78 to 1.89 Å. These bond lengths are short in comparison to the sum of the aluminum (1.3 Å)[10] and nitrogen (0.70 Å)[22] covalent radii, i.e. 2.0 Å, which suggests the presence of a considerable degree of Al–N p–p π-bonding. If, however, the predicted Al–N bond length is modified to include an ionic correction for the differences in electronegativity between aluminum and nitrogen a considerably shorter bond is to be expected on the basis of calculations that use either the Schomaker–Stevenson[23] (Al–N = 1.85 Å) or

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(18) Burger, H.; Cichon, J.; Goetze, U.; Wannagat, U.; Wismar, H. J. *J. Organomet. Chem.* **1971**, *33*, 1.

(19) Brame, E. G.; Margrave, J. L.; Maloch, V. M. *Inorg. Nucl. Chem.* **1957**, *5*, 48.

(20) Kost, D.; Carlson, E. H.; Raban, M. *J. Chem. Soc., Chem. Commun.* **1971**, 656.

(21) Wehmschulte, R. J.; Ruhlandt-Senge, K.; Power, P. P. Unpublished work. These results, in addition to a corresponding study on its gallium analogue, will be reported subsequently.

(22) A slightly smaller value (0.7 Å) for the radius of sp^2 hybridized nitrogen, which takes into account its planar coordination, is used. For more information see the following reference: Pestana, D. C.; Power, P. P. *Inorg. Chem.* **1991**, *30*, 528.

(23) Schomaker, V.; Stevenson, D. P. *J. Am. Chem. Soc.* **1941**, *63*, 37.

the Blom and Haaland[24] (Al–N = 1.79 Å) formula. The 1.79 Å value is of course in good agreement with the Al–N distance in **6** and also the Al–N distances in Al[N(SiMe$_3$)$_2$]$_3$,[11] **7**, (MeAlNDipp)$_3$,[12] **8**, and Al[N(*i*-Pr)$_2$]$_3$,[25] **9** (vide infra). In sharp contrast, considerably longer Al–N bonds are observed in **1–4**. In three of these compounds (**1**, **3**, and **4**) the Al–N distances are in close agreement with the value predicted by the original Schomaker–Stevenson formula.[23] The longer Al–N bonds in **1**, **3** and **4** may be a consequence of increased steric congestion at the nitrogen center and, perhaps, different change separations across the Al–N bond.. Although there is some correlation between Al–N bond lengths and smaller angles between the planes at Al and N, it is not a strong one. For example **1**, which has a relatively short Al–N bond of 1.823(4) Å has a large (twist) angle of 49.5° between the planes at aluminum and nitrogen. On the other hand the Al–N bond in **3** is 1.834(3) Å, whereas the twist angle is only 16.1°. The Al–N bond length (1.784(3) Å) in **6** does indeed correspond to the smallest twist angle (5.5°), however, it is notable that the Al–N bond distances in **7–9** are very similar and the twist angles in these compounds quite different, 50°, 0° and 48.1° (av.). For compounds **2** and **4** the nitrogen ligands (–N(SiPh$_3$)$_2$ and –N(1-Ad)SiPh$_3$) are quite bulky in three dimensions and they impose long Al–N distances and twist angles of almost 90°. This structural phenomenon was also observed in the gallium–nitrogen compound, (*t*-Bu)$_2$GaN(*t*-Bu)SiPh$_3$.[26] In the case of **3** and **6**, the orientation of the approximately two dimensional Dipp ligand perpendicular to the nitrogen plane minimizes steric interaction with the aluminum *t*-butyl groups. However, the long N–C and N–Si bonds and narrow C–Al–C′ and C–N–Si angles in **3** reflect considerably greater steric strain than that seen in **6**. In the latter species the two dimensional Trip and Dipp substituents are oriented so as to minimize steric interactions. The presence of a hydrogen substituent also contributes greatly to relieve the steric crowding. The gallium–nitrogen analogue of **6** has a very similar structure.

It is notable that the aryloxide analogues (*t*-Bu)$_2$MOR (M = Al or Ga, R = 2,4,6-*t*-Bu$_3$C$_6$H$_2$, 2,6-*t*-Bu$_2$-4-MeC$_6$H$_2$) also feature nearly planar C$_2$MOC cores.[9] In this case the planar conformation was, in part, attributed to close approach of one of the *t*-butyl hydrogens to the electron deficient Al centers rather than any substantial Al–O π-bonding. There are, however, no short Al···H contacts in **3** and **6**. It is probable that the steric requirements of the Dipp and SiPh$_3$ groups in **3** and **6** permit a conformation in which p–p π-bonding may occur. In **1**, **2** and **4** the energy gained by aluminum–nitrogen π-bonding is apparently insufficient to overcome the steric repulsion between the large substituents at aluminum and nitrogen in the planar conformation. This phenomenon has been observed in the aminoborane Ph$_2$BN(*t*-Bu)SiMe$_3$ which possesses a relatively long B–N bond (1.433 Å) and a nonplanar C$_2$BNCSi {interplanar angle (C$_2$B/NCSi) 45°} core.[27] Thus, steric repulsion by large groups on boron and nitrogen effectively prevent a strong B–N π-interaction. A comparison of the structural data for **1–4** and **6** to those of the bis and tris amidoaluminum compounds Al[N(SiMe$_3$)$_2$]$_3$,[11] **7** (Al–N = 1.78(2) Å), (MeAlNDipp)$_3$,[12] **8** (Al–N = 1.782(4) Å), Al{N(*i*-Pr)$_2$}$_3$,[25] **9** (Al–N 1.795(5) Å av.) and MesAl{N(SiMe$_3$)}$_2$,[25] **10** (Al–N 1.807(3) Å) reveals that the bond lengths of the monomers are some 0.02 to 0.08 Å longer except in the case of **6** where the Al–N distance is similar. These data are not consistent with the presence of strong Al–N π-bonding. This is because in **7–10** the empty p-orbital on aluminum is shared between two or three nitrogens, making for a weaker Al–N multiple interaction (and longer Al–N bonds) to each nitrogen. By this criterion the bis and trisamides **7–10** ought to have longer Al–N bonds than the monoamides **1–4**. It should be noted that longer B–N bonds are observed for bis and tris aminoboranes, consistent with significant weakening of the boron–nitrogen π-bonding.[11,12,25]

VT ^{1}H NMR Studies. In order to examine restricted rotation around the Al–N bonds, variable temperature ^{1}H NMR studies of **3** and **4** were undertaken. In the case of **3** two different barriers ($\Delta G^{\ddagger}$) were observed which correspond to separate dynamic processes. The higher barrier of 16.6 kcal mol^{-1}, involving coalescence of two *o*-isopropyl doublets of the Dipp group, can be attributed to an aryl ring flip. In this regard a similar VT ^{1}H NMR analysis of **1** gives two identical barriers of 15.6 kcal mol^{-1} which are assigned to a mesityl ring flip process. Similar ring flip barriers have been observed for alkoxydiarylboranes and triarylboranes which range from 10 to 16 kcal mol^{-1}.[7,28] The second process observed in **3**, involving the Al(*t*-Bu) signal, is associated with the lower barrier, 9.9 kcal mol^{-1} and most probably is due to restricted rotation around the Al–N bond. The two factors which may result in hindered rotation are steric repulsion and/or Al–N π-bonding. On the one hand, it may be that at low temperatures the Al(*t*-Bu)$_2$ group is held in position (similar to that observed in the crystal structure) by the –N(Dipp)SiPh$_3$ group on nitrogen. Rotation of the aluminum and nitrogen ligand sets past each other may then be induced by increasing the temperature. Alternatively, the barrier may be due to an Al–N π-overlap which has a maximum value of about 10 kcal mol^{-1} in this compound. In **4**, no splitting of the signal was observed at temperatures as low as –100 °C which might suggest facile Al–N bond rotation. The structure of **4**, however, if retained in solution, with the planes at aluminum and nitrogen "locked" in a roughly orthogonal orientation also gives magnetically equivalent *t*-butyl groups. Quite possibly, a planar conformation of **4** which maximizes Al–N π-bonding is prohibited due to steric repulsion of greater energy between the large Al and N groups.

Preliminary experiments on the solution behavior of **6**, which has a less sterically demanding set of ligands on nitrogen, also does not support the presence of strong Al–N π-bonding.[21] As the temperature was decreased, broadening of the *o*-isopropyl and *p*-isopropyl doublets of Trip were observed while the *o*-isopropyl resonances of Dipp remained sharp. At ~ –85 °C the *o*-isopropyl peak splits into two broad peaks with maximum separation of ~20.1 Hz at –100 °C. Splitting of the *p*-isopropyl peak was not observed as low as –100 °C, however, the signal broadened considerably upon cooling. For compound **6**, two dynamic processes may occur; aromatic ring flip or rotation about the Al–N bond. The extent of broadening of the *p*-isopropyl resonance compared to the resolution of other peaks in the spectrum suggests a T_c below –100 °C. This observation is inconsistent with an aromatic ring flip mechanism. This uncertainty notwithstanding, it is possible to say that the upper limit of the strength of π-bonding in **6** based on the dynamic behavior of the *o*-isopropyl peak is ca. 9–10 kcal mol^{-1}. This estimate is consistent with the observed upper limits, 8–9 kcal mol^{-1} for Al–O or Ga–O π-bonds.[9] Obviously aluminum amides that have smaller groups at Al and N must be prepared in order to fully assess the maximum possible strength of Al–N π-bonding. Work directed along these lines is continuing.

Compound 5. The lithium salt (*t*-Bu)$_2$Al{N(H)CPh$_3$}$_2$(Li), **5** was isolated rather than the expected species (*t*-Bu)$_2$AlN(H)CPh$_3$, from the reaction of LiN(H)CPh$_3$ with (*t*-Bu)$_2$AlCl in a 1:1 ratio. The structure of **5** may be viewed as the monomer

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(24) Blom, R.; Haaland, A. *J. Mol. Struct.* **1985**, *129*, 21. In this paper the bond length for the pair A–B is calculated by using the empirical expression $r_A + r_B - c|EN_A - EN_B|^n$, where $c = 0.085$ and $n = 1.4$ and r_A and r_B are equal to the radii of r_A and r_B. The authors use radii of 1.18 Å for Al and 0.73 Å for N.

(25) Olmstead, M. M.; Power, P. P. Unpublished work.

(26) This compound and related Ga–N species will be discussed in a separate paper: Waggoner, K. M.; Ruhlandt-Senge, K.; Wehmschulte, R. J.; He, X.; Olmstead, M. M.; Power, P. P. *Inorg. Chem.*, in press.

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(28) Blount, J. F.; Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 7019.

(t-Bu)$_2$AlN(H)CPh$_3$ reacted with LiN(H)CPh$_3$. A comparison of the structures of **5** and **6** suggests that, although the –CPh$_3$ group is quite bulky, the t-butyl ligands at Al are not as efficient as Trip in stabilizing three coordination at aluminum. A notable feature of **5** is the coordination of the Li$^+$ ion. In addition to bonding to two amide nitrogen the coordination sphere of Li$^+$ has further close contacts to two of the phenyl rings, Li–C distances in the range, 2.244(7) Å to 2.570(7) Å. The structure resembles that of the imido species, Li(t-Bu$_2$C=N)$_2$Al{N=C(t-Bu)$_2$}$_2$[29] most closely although an unsolvated Li$^+$ ion is also present in the polymeric structure of [LiAl(H)(NEt$_2$)$_3$]$_n$.[30] The long (due to four coordination at Al, N, and Li) Li–N and Al–N distances in **5** of 2.03 Å and 1.93 Å, respectively, are within the range observed in the above compounds.

Conclusions

The main conclusions that may be drawn from these structural and spectroscopic studies of aluminum monoamides are that (i) Al–N bonds are shorter than the sum of atomic radii of Al and N (ca. 2.0 Å) primarily because of an ionic (or resonance) contribution to the Al–N bond strength, (ii) variation in the Al–N bond lengths is observed owing to the different sizes and electronic properties of the Al substituents, and (iii) there is evidence for weak (<10 kcal mol^{-1}) Al–N p–p π-bonding when substituent groups allow approximately parallel orientation of the Al and N p-orbitals.

Acknowledgment. We thank the National Science Foundation for financial support.

Supplementary Material Available: Full tables of data collection parameters, atom coordinates, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters (52 pages). Ordering information is given on any current masthead page.

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(30) Linti, G.; Nöth, H.; Rahm, P. *Z. Naturforsch.* **1988**, *43b*, 1101.