DALTON

Monomeric, N-functionalised amido complexes of aluminium: Synthesis of $[AlCl\{NR(8\text{-}C_9H_6N)\}_2]$ (R = H or $SiMe_3$) and $[Al\{N(2\text{-}C_5H_4N)(2\text{-}C_5H_4N)\}_3]$†

Lutz M. Engelhardt,[a] **Michael G. Gardiner,**[b] **Cameron Jones,**[c] **Peter C. Junk,**[b] **Colin L. Raston** *,[b] **and Allan H. White**[a]

[a] *Department of Chemistry, University of Western Australia, Nedlands, W.A., 6907, Australia*
[b] *Department of Chemistry, Monash University, Clayton, Victoria, 3168, Australia*
[c] *Department of Chemistry, University of Wales, Swansea, Singleton Park, Swansea SA2 8PP, UK*

Routes have been devised to a series of aluminium(III) amide complexes containing either of the bulky, N-functionalised amides $NR(8\text{-}C_9H_6N)^-$ (R = H or $SiMe_3$) or $N(2\text{-}C_5H_4N)_2{}^-$. Reaction of the lithium amides $[\{Li(OEt_2)[NR(8\text{-}C_9H_6N)]\}_2]$ (R = H or $SiMe_3$) with $AlCl_3$ afforded $[AlCl\{NR(8\text{-}C_9H_6N)\}_2]$ (R = H or $SiMe_3$) respectively. The crystal structure of five-co-ordinate $[AlCl\{NH(8\text{-}C_9H_6N)\}_2]$ shows it to be monomeric in the solid state with intramolecular dative interactions between the aluminium centre and both aromatic nitrogen atoms. Treatment of $NH(2\text{-}C_5H_4N)_2$ with $[AlH_3(NMe_3)]$ yielded the six-co-ordinate complex $[Al\{N(2\text{-}C_5H_4N)(2\text{-}C_5H_4N)\}_3]$, the crystal structure of which confirms it to be monomeric with intramolecular Al–N (aromatic) dative bonds from one pyridyl functionality of each amide ligand. In solution this complex exhibits fluxional behaviour which has been investigated by variable-temperature ^1H NMR spectroscopy.

The study of aluminium amides is a rapidly expanding area of chemistry that derives its current importance from the potential utility such compounds have as precursors for the chemical vapour deposition of the refractory, wide-band semiconducting material aluminium nitride.[1] Throughout this work aluminium amides have been shown to possess a wide variety of structural motifs that normally involve oligomerisation through bridging amido nitrogen centres.[2] Such association can be blocked with the use of sterically bulky ligands as in the monomeric species $[Al\{N(SiMe_3)_2\}_3]$ [3] and $[AlH_2\{N(CMe_2CH_2)_2CH_2\}(NMe_3)]$.[4] Additionally, functional groups can be incorporated into the bulky amide ligand which can further stabilise monomeric amides through chelation and an increased electronic saturation of the metal centre, *e.g.* $[AlCl(H)\{N(Bu^t)CH_2CH_2NH(Bu^t)\}]$ [5] and $[Al\{N(C_6H_4OMe\text{-}p)NN(C_6H_4OMe\text{-}p)\}_3]$.[6]

We have become interested in the latter tactic through an examination of the co-ordination chemistry of a series of bulky, N-functionalised amide ligands. This interest stems from a systematic study we have carried out aimed at the stabilisation of novel bonding modes *via* the use of N-functionalised alkyl ligands, *e.g.* $[Al\{C(SiMe_3)_2(2\text{-}C_5H_4N)\}_2]^+[AlCl_4]^-$.[7] Particular success has been achieved with the 8-quinolylamide ligand $NH(8\text{-}C_9H_6N)^-$ and its bulkier 8-quinolyl(trimethysilyl)-amido counterpart $N(SiMe_3)(8\text{-}C_9H_6N)^-$ which have been employed in the synthesis of a range of monomeric complexes, *viz.* $[Al\{N(SiMe_3)(8\text{-}C_9H_6N)\}Cl_2]$ **1**,[8] $[M\{N(SiMe_3)(8\text{-}C_9H_6N)\}_2]$ (M = Zn **2** or Mg **3**)[9] and $[Sb\{NH(8\text{-}C_9H_6N)\}Cl_2]$ **4**,[10] all of which display intramolecular electron donation to the metal from the aromatic ring nitrogen. It is noteworthy that a related oligomeric aluminium amide, $[Al_4\{\mu_3\text{-}N(8\text{-}C_9H_6N)\}_2Me_8]$,[11] has been prepared by double deprotonation of 8-aminoquinoline with a two-fold excess of trimethylaluminium.

We were keen to extend our investigations into $N(SiMe_3)(8\text{-}C_9H_6N)^-$ and $NH(8\text{-}C_9H_6N)^-$ and their use in the formation of aluminium complexes. In addition we desired to initiate a study to explore the co-ordination chemistry of the closely related di-2-pyridylamide $N(2\text{-}C_5H_4N)_2{}^-$ which, to the best of our knowledge, has not previously been employed in main-group metal complex formation. The results of these investigations are reported herein.

Results and Discussion

Compounds **5** and **6** were prepared in high yields by metathetical exchange reactions involving lithium amide intermediates and $AlCl_3$ as outlined in Scheme 1. These lithium amides, one of which (R = $SiMe_3$) we have previously structurally characterised,[12] have proved to be efficient transfer reagents in a range of related compounds, **1** and **4**. In addition, the preparation of **5** and **6** was also attempted by reaction of 8-[bis(trimethylsilyl)amino]quinoline and 8-(trimethylsilylamino)quinoline respectively, with $AlCl_3$ in an attempt to effect chlorotrimethylsilane-elimination reactions, but to no avail. We have previously observed similar elimination and boron amide formation in the reaction of BCl_3 with $N(SiMe_3)_2(8\text{-}C_9H_6N)$.[8] However, in the present study chlorotrimethylsilane eliminations did not occur, presumably because they are thermodynamically unfavourable. Both **5** and **6** possess a high degree of thermal stability which allowed their purification by sublimation at 250 and 290 °C (0.1 mmHg), respectively.

It seems likely that this thermal stability is derived, at least in part, from intramolecular electron donation from the aromatic ring nitrogens of the ligands to the aluminium centres in compounds **5** and **6**. This has been confirmed by X-ray crystallography in the case of **5** [Fig. 1(*a*)], and can be inferred in **6** considering that all known structurally characterised complexes employing the $N(SiMe_3)(8\text{-}C_9H_6N)^-$ ligand exhibit similar chelate formation.[8,9,12] A survey of the Cambridge Structural Database suggests that **5** is only the second example of a monomeric chlorodiamidoaluminium(III) species, the other being chloro(phthalacyaninato)aluminium(III).[13] Interestingly,

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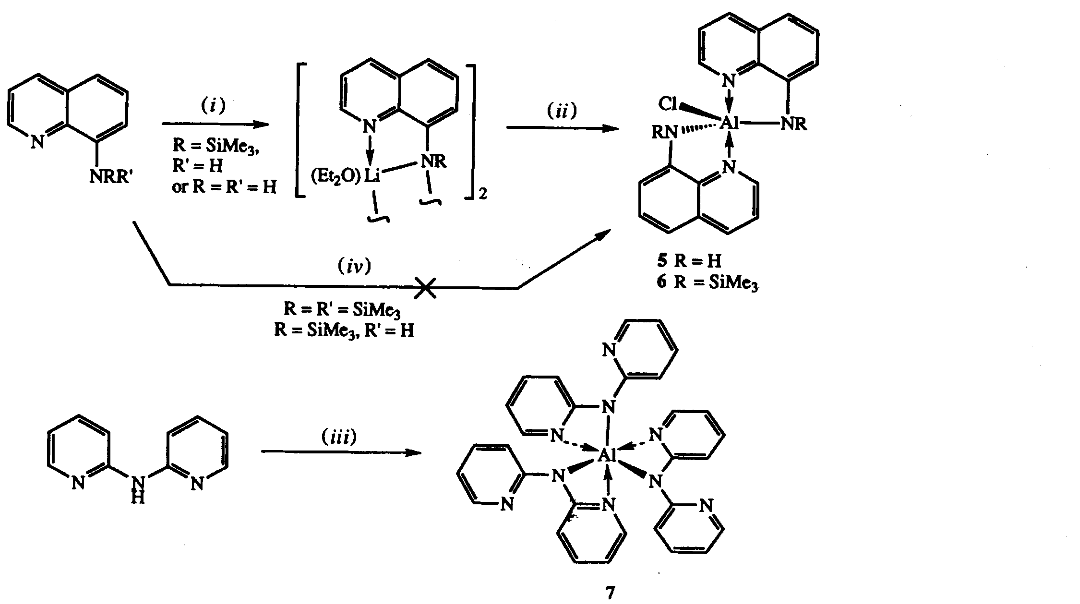
† *Non-SI unit employed:* mmHg ≈ 133 Pa.



Scheme 1 (*i*) LiBu^n, Et$_2$O, $-$Bu^{n}H, 0 °C; (*ii*) AlCl$_3$, Et$_2$O, $-$LiCl; (*iii*) [AlH$_3$(NMe$_3$)], Et$_2$O, $-$H$_2$, $-$NMe$_3$, $-$40 °C; (*iv*) excess of AlCl$_3$, Et$_2$O, 20 °C

in this case the aluminium centre possesses a distorted square-pyramidal co-ordination sphere, whereas in **5** the aluminium atom has a distorted trigonal-bipyramidal environment with the nitrogen (aromatic) centres in the apical positions. The Al–Cl distance [2.184(4) Å] compares well with those in other complexes containing terminal Al–Cl bonds, *e.g.* [AlCl$_3$(NHMe$_2$)$_2$] [2.18 Å (mean)],[14] but is shorter than expected for bridging chlorides, *e.g.* [{Al(C$_5$Me$_5$)Me(Cl)}$_2$] [2.380 Å (mean)].[15] It is noteworthy that the Al–Cl distance in five-co-ordinate **5** is significantly longer than in the related four-co-ordinate complex **1** [2.116 Å (mean)],[8] an observation consistent with the larger co-ordination sphere in **5**. By a similar argument, the Al–N (amide) distances in **5** [1.842 Å (mean)] are longer than in **1** [1.816(8) Å] and in the three-co-ordinate complex [Al{N(SiMe$_3$)$_2$}$_3$] [1.78(2) Å],[3] but shorter than observed for bridging amides, *e.g.* [{AlCl$_2$(NMe$_2$)}$_2$] [1.910(4) Å].[16] The Al–N (aromatic) distances in **5** [2.064 Å (mean)] are considerably longer than its Al–N (amide) interactions; they are also longer than the Al–N (aromatic) distance in **1** [1.935(8) Å],[8] but close to the dative Al–N distances seen in other five-co-ordinate complexes, *e.g.* [AlCl$_3${NMe(CH$_2$CH$_2$)$_2$NMe}] [2.037 Å (mean)].[17] Finally, the unit-cell contents, Fig. 1(*b*), reveal that ligands 'A' from adjacent centrosymmetrically related molecules are coplanar and π-stacked at the van der Waals limit, 3.43(1)–3.52(1) Å.

Unfortunately compound **5** proved to be only sparingly soluble in organic solvents and therefore no meaningful NMR data were obtained. Its mass spectrum gave a molecular ion of m/z 349, consistent with **5** being monomeric in the gas phase; predominant peaks at m/z 314 ($M^+ -$ Cl) and 143 (parent amine). The infrared spectrum displayed characteristic absorbances at 3400 (N–H stretch) and 550 cm^{-1} (Al–Cl stretch). Compound **6** has considerably greater solubility and, as expected, exhibited a single SiMe$_3$ resonance close to δ 0 in both its ^{1}H and ^{13}C NMR spectra. Its mass spectrum gave the molecular ion required for it being monomeric in the gas phase (m/z 493, M^+) and its infrared spectrum was almost identical to that of **5** except for the absence of any N–H stretches and the presence of trimethylsilyl C–H deformation (1260 cm^{-1}) and Si–C stretch (830 cm^{-1}) absorbances.

Compound **7** was synthesised in high yield *via* the treatment of 3 mole equivalents of di-2-pyridylamine, with [AlH$_3$(NMe$_3$)] and subsequently purified by recrystallisation from diethyl ether. As with **5** and **6**, it possesses considerable thermal stability which again can be attributed to the likely presence of intramolecular Al–N (aromatic) electron donation. This was confirmed by its molecular structure (Fig. 2) which shows it to crystallise as a racemic mixture of the Λ and Δ optical isomers (Fig. 2 depicts the Λ isomer). Moreover, co-ordination compounds in which the central atom is bound to three unsymmetrical bidentate ligands may exist as two geometric isomeric forms, facial (*cis*) or meridional (*trans*).[18] Surprisingly, **7** appears to exist only as the sterically less favourable *cis* isomer, in the solid state at least.

During the course of refinement the structure of compound **7** was found to contain a disorder which involved the site of the aluminium centre and the orientation of the 2-pyridyl substituents (Fig. 3). The aluminium atoms reside in two alternative sites with refined populations of 85 [Al(1), anisotropic] and 15% [Al(2), isotropic] (Fig. 2). The position of the pyridyl nitrogens was not apparent in Fourier-difference maps, but can be implied as a result of steric interactions which make a *cis* conformation for the ligand unfeasible due to steric interactions between protons *ortho* to the amido centres (Fig. 3). The disorder in the pyridyl ligands was not modelled, instead the orientation of the substituents governed by the position of the major site of the aluminium atom was given 100% population.

The aluminium centre in compound **7** possesses a highly distorted octahedral environment [intraligand N–Al(1)–N angles 66.0° (mean)] in which the three ligands are planar. The Al(1)–N (amide) distances [1.973 Å (mean)] are significantly longer than in **5** and even than in bridging amides, *e.g.* [{AlCl$_2$(NMe$_2$)}$_2$] [1.910(4) Å].[16] This is most likely a result of an even higher six-fold co-ordination of the metal centre. All the Al(1)–N (aromatic) distances [2.03 Å (mean)] compare well to those in **5**. The metal environment is similar to those in the closely related compounds [Al{N(C$_6$H$_4$R)NN(C$_6$H$_4$R)}$_3$] (R = 2-Me, 4-Cl or 4-OMe) where the Al(1)–N distances range from 1.968(4) to 2.003(9) Å.[6]

In solution compound **7** is fluxional. The room-temperature ^{1}H NMR spectrum exhibits four resonances for the aromatic protons of the metallated bis(2-pyridyl)amide ligand at δ 6.14, 7.04, 7.74 and 7.96. The two low-field resonances appear as broad singlets while the high-field resonances are narrow, showing multiplet structure. Heating the sample to 60 °C results in narrowing of the broad low-field resonances which also exhibit multiplet structure at this temperature, the high-field

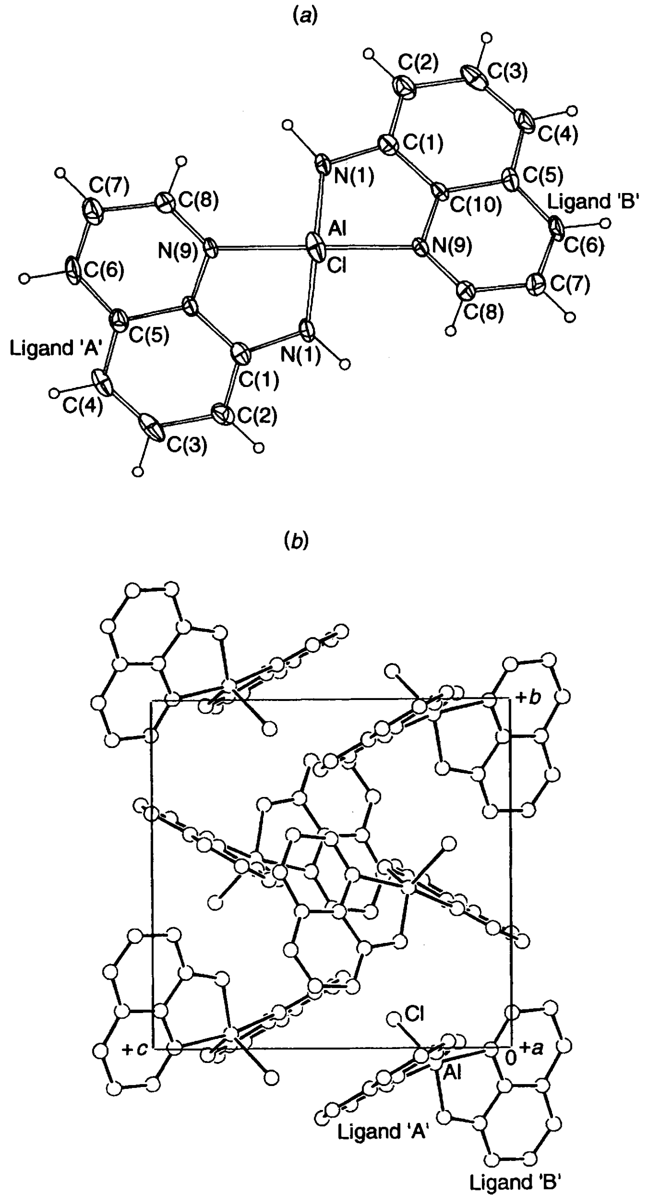


Fig. 1 (*a*) Molecular structure of $[\overline{\mathrm{AlCl\{NH(8\text{-}C_9H_6N}})\}_2]$ **5**, showing 20% probability ellipsoids. Selected bond distances (Å) and angles (°): Al–Cl 2.184(4), Al–N(A1) 1.844(7), Al–N(A9) 2.059(6), Al–N(B1) 1.840(7) and Al–N(B9) 2.069(6); Cl–Al–N(A1) 117.9(3), Cl–Al–N(A9) 96.1(2), Cl–Al–N(B1) 116.6(2), Cl–Al–N(B9) 94.5(2), N(A1)–Al–N(A9) 82.7(3), N(A1)–Al–N(B1) 125.5(3), N(A1)–Al–N(B9) 92.9(3), N(A9)–Al–N(B1) 92.7(3), N(A9)–Al–N(B9) 169.4(3) and N(B1)–Al–N(B9) 82.1(3). (*b*) Unit-cell contents projected down *a*

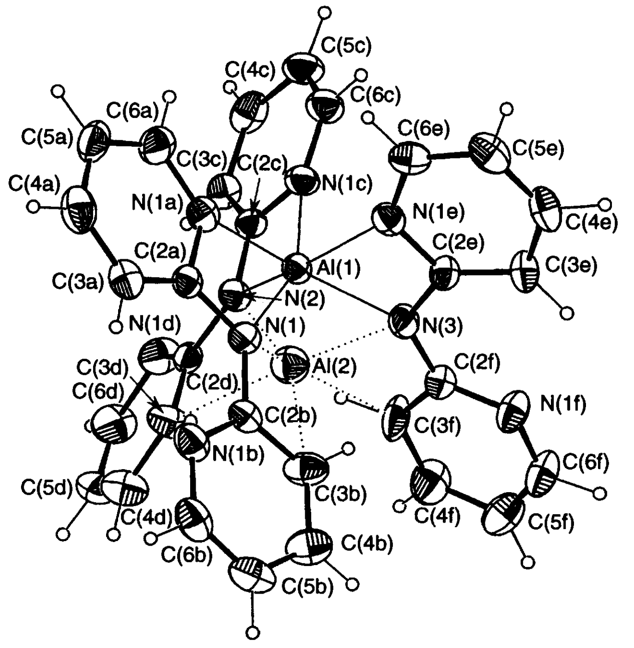


Fig. 2 Molecular structure of $[\overline{\mathrm{Al\{N(2\text{-}C_5H_4N}})(2\text{-}\mathrm{C_5H_4N})\}_3]$ **7**, showing 20% probability ellipsoids and crystallographic disorder. Selected bond distances (Å) and angles (°) for the highest aluminium population site: Al(1) • • • Al(2) 1.60(3), Al(1)–N(1) 1.999(9), Al(1)–N(2) 1.964(8), Al(1)–N(3) 1.968(9), Al(1)–N(1a) 2.12(1), Al(1)–N(1c) 2.018(9) and Al(1)–N(1e) 2.062(9); N(1)–Al(1)–N(1a) 65.7(4), N(1)–Al(1)–N(2) 104.1(4), N(1)–Al(1)–N(1c) 156.5(4), N(1)–Al(1)–N(3) 102.2(4), N(1)–Al(1)–N(1e) 97.7(3), N(2)–Al(1)–N(1c) 66.1(3), N(2)–Al(1)–N(3) 104.7(4), N(2)–Al(1)–N(1e) 157.8(4), N(3)–Al(1)–N(1e) 66.2(4), N(1a)–Al(1)–N(2) 96.9(4), N(1a)–Al(1)–N(1c) 93.5(4), N(1a)–Al(1)–N(3) 157.6(4), N(1a)–Al(1)–N(1e) 95.7(4), N(1c)–Al(1)–N(3) 101.0(4) and N(1c)–Al(1)–N(1e) 95.0(4)

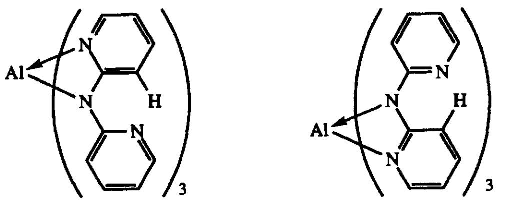


Fig. 3 Schematic representation of the crystallographic disorder in $[\overline{\mathrm{Al\{N(2\text{-}C_5H_4N}})(2\text{-}\mathrm{C_5H_4N})\}_3]$ **7**

signals show no marked difference from their appearance at room temperature. At low temperature the low-field resonances at δ 7.74 and 7.96 broaden further still and split at *ca.* −10 °C into four distinct resonances exhibiting fine structure below −60 °C. Similarly the high-field signals at δ 6.14 and 7.04 split at *ca.* −15 and −50 °C, respectively, each giving two resonances showing fine structure below −60 °C.

The fluxional behaviour in tris(bidentate chelate) complexes of aluminium involving unsymmetrical ligands is well established.[19] Previous reports have identified many processes for the Λ–Δ racemisation and *cis–trans* isomerisation of these complexes. In the case of **7** the variable-temperature NMR studies are consistent with it only existing as the two possible *cis* isomers (Λ and Δ) in solution, as in the solid state. Therefore its fluxionality can be limited to one of three possible mechanisms. The first involves decomplexation of each pyridyl nitrogen atom, followed by a 180° rotation along the N (amide) bond of the ligand with subsequent complexation of the aluminium centre by the other pyridyl nitrogen atom. This would presumably involve a three-co-ordinate trigonal triamide species without involvement of the pyridyl nitrogen atoms with the aluminium centre. Such a process would not lead to Λ–Δ racemisation but cannot be ruled out as **7** is most likely formed as a racemic mixture during its synthesis. The second possible mechanism also involves bond rupture, but only of one Al–N (pyridyl) bond, which would lead to *cis*-Λ–*cis*-Δ racemisation *via* a bis(chelate) square-pyramidal intermediate with one pendant ligand. The final process, a 'trigonal twist', also involves a racemisation, but not bond rupture, in which the molecule twists through a trigonal-prismatic intermediate to its enantiomeric partner. What mechanism is in operation for **7** cannot be determined from the data presented.

Experimental

All manipulations were carried out using standard Schlenk and glove-box techniques under an atmosphere of high-purity argon or nitrogen. Solvents were dried then freeze–thaw degassed prior to use. 8-Aminoquinoline and di-2-pyridylamine

Table 1 Crystal data for [AlCl{NH(8-C_9H_6N)}$_2$] **5** and [Al{N(2-C_5H_4N)(2-C_5H_4N)}$_3$] **7** at 298 K (λ = 0.7103 Å)

	5	**7**
Formula	$C_{18}H_{14}AlClN_4$	$C_{30}H_{24}AlN_9$
M	348.7	537.56
Crystal symmetry	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	13.51(1)	10.45(2)
b/Å	10.800(9)	17.82(1)
c/Å	11.105(10)	14.66(2)
β/°	95.10(7)	91.95(9)
U/Å^3	1614(2)	2727(7)
Z	4	4
D_c/g cm^{-3}	1.435	1.309
μ(Mo-Kα)/cm^{-1} (no correction)	3.0	1.1
F(000)	720	1120
Crystal dimensions	0.3 × 0.3 × 0.25	0.35 × 0.35 × 0.25
No. unique reflections	2114	4794
No. observed reflections	1272	1945
$2\theta_{max}$/°	45	50
R^a	0.074	0.083
R'	0.067^c	0.083^d

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$. [c] Weights $w = [\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. [d] Unit weights.

were obtained from Aldrich and used without further purification. 8-(Trimethylsilylamino)quinoline,[12] and [$AlH_3(NMe_3)$][20] were prepared according to the literature procedures. Proton NMR spectra were recorded on Bruker WM-250 and Varian Gemini-200 spectrometers in deuteriated benzene or toluene and referenced to the residual ^{1}H resonances of the solvent (δ 7.15 and 6.98 respectively), ^{13}C NMR spectra in deuteriated benzene on the same spectrometers using broadband proton decoupling and referenced to the ^{13}C resonances of the deuteriated solvent (δ 128.00). Elemental analyses were performed by Canadian Micro Analytical Services Ltd., Vancouver, and Micro Analytical Services Pty. Ltd., Melbourne. Melting points were determined in sealed glass capillaries under argon and are uncorrected.

Syntheses

[AlCl{NH(8-C_9H_6N)}$_2$] 5. *n*-Butyllithium (4.11 cm^3, 1.7 mol dm^{-3}, 7.0 mmol) was added over 30 min to a solution of 8-aminoquinoline (1.0 g, 7.0 mmol) in diethyl ether (30 cm^3) at 0 °C. The resulting dark red-orange solution was stirred for 1 h whereupon $AlCl_3$ (0.47 g, 3.5 mmol) in diethyl ether (10 cm^3) was added over 15 min yielding an orange solution and precipitate. Volatiles were removed under vacuum and the residue sublimed (0.1 mmHg, 250 °C) to yield orange diamond-shaped crystals of compound **5** (1.9 g, 78% yield). M.p. 286 °C (Found: C, 62.05; H, 4.15; N, 16.3. $C_{18}H_{14}AlClN_4$ requires C, 62.0; H, 4.05; N, 16.05%).

[AlCl{N($SiMe_3$)(8-C_9H_6N)}$_2$] 6. *n*-Butyllithium (6.6 cm^3, 1.6 mol dm^{-3}, 10.2 mmol) was added over 30 min to a solution of 8-(trimethylsilylamino)quinoline (2.2 g, 10.2 mmol) in diethyl ether (20 cm^3) at 0 °C and the resulting mixture stirred for 1 h. Trichloroaluminium (0.7 g, 5.25 mmol) in diethyl ether (10 cm^3) was then added over 15 min to yield a brown solution and a yellow precipitate. The suspension was stirred for 2 h, volatiles were removed under vacuum and the residue was sublimed (0.1 mmHg, 290 °C) to yield large yellow rectangular crystals of compound **6** (4.0 g, 79%). M.p. >290 °C (decomp.) ^{1}H NMR (250 MHz, C_6D_6, 298 K): ^{1}H, δ 0.15 (9 H, s, $SiMe_3$) and 6.63–8.74 (6 H, m, aromatics); ^{13}C, δ 2.32 ($SiMe_3$), 113.8, 117.2, 121.4, 129.6, 139.5, 144.3 (aromatic CH), 129.2, 140.4 and 151.1 (aromatic quaternary): IR: 1260 (C–H deformation), 830 (Si–C str.) and 550 cm^{-1} (Al–Cl str.) (Found: C, 59.15; H, 6.15; N, 11.45. $C_{24}H_{30}AlClN_4Si_2$ requires C, 58.45; H, 6.15; N, 11.35%).

[Al{N(2-C_5H_4N)(2-C_5H_4N)}$_3$] 7. To a stirred solution of di-2-pyridylamine (1.44 g, 8.41 mmol) in diethyl ether (30 cm^3) at −40 °C was added a solution of [$AlH_3(NMe_3)$] (0.25 g, 2.81 mmol) in diethyl ether (20 cm^3) over 5 min with immediate gas evolution. The pale yellow solution was warmed to room temperature and left to stand for 4 h, after which time gas evolution had ceased and pale yellow crystals of compound **7** deposited. The mother-liquor yielded further product upon concentration under vacuum and cooling to −30 °C (1.32 g, 87% yield). M.p. 232–234 °C. NMR (C_6D_6, 298 K): δ ^{1}H (200 MHz), 6.14 (2 H, m, CH), 7.04 (2 H, m, CH), 7.74 (2 H, br, CH) and 7.96 (2 H, br, CH); ^{13}C (50 MHz), δ: 113.6, 114.4, 139.1, 144.4 (CH) and 160.8 (C) (Found: C, 66.85; H, 4.55; N, 23.75. $C_{30}H_{24}AlN_9$ requires C, 67.05; H, 4.50; N, 23.45%).

Crystallography

Crystals suitable for structure determination were grown by sublimation (compound **5**) or crystallisation from diethyl ether (**7**) and were mounted in capillaries under an argon atmosphere. Unique data sets were measured using Enraf-Nonius CAD4 diffractometers. Reflections with $I > 2\sigma(I)$, **5**, and $I > 2.5\sigma(I)$ **7**, were considered observed and used in full-matrix least-squares refinements, minimising $\Sigma w\Delta^2$ after solution of the structures by direct methods. Conventional residuals on F at convergence are quoted. No extensive, significant extinction effects were found. Neutral-atom complex scattering factors were employed.[21] Computation used the XTAL program systems.[22] Crystal data are given in Table 1. In **7** the aluminium is disordered unequally over two sites (see text). Anisotropic thermal parameters were refined for all non-hydrogen atoms in the structure determination of **5**, and all but Al(2) in that of **7**. All hydrogen atoms in both structures are in calculated positions.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/113.

Acknowledgements

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