Complexes of Organoaluminium Compounds. Part 13.[1] Preparation and Nuclear Magnetic Resonance Spectra of the Arylamido-compounds $AlMe_2(NHR')$ (R' = Ph, C_6H_4Me-o, C_6H_4Me-p, $C_6H_3Me_2$-2,6) and the Imido-compounds AlMe(NR'). Crystal and Molecular Structures of [{$AlMe_2(NHC_6H_4Me$-o)}$_2$] and [{AlMe(NPh)}$_6$]†
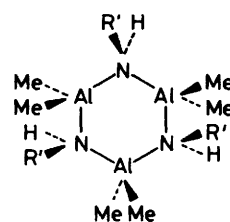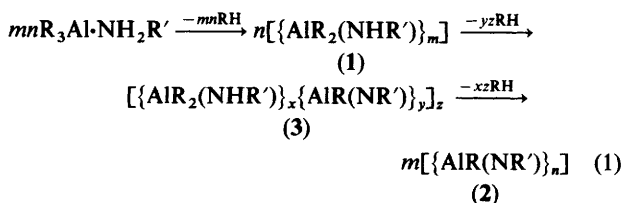
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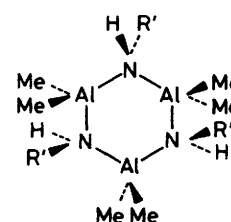
The compounds [{$AlMe_2(NHR')$}$_m$] (1) [R' = Ph (1a), C_6H_4Me-o (1b), C_6H_4Me-p (1c), $C_6H_3Me_2$-2,6 (1d)] have been isolated. An X-ray study has shown that compound (1b) crystallises as centrosymmetrical *trans* dimers with the aromatic rings almost perpendicular to the $(AlN)_2$ plane. The solid compound (1d) is also obtained as a *trans* dimer but full structural details have not been determined. In solution, however, all four compounds appear to exist as mixtures of two isomers which are probably *trans* dimers and *trans* trimers. On heating the amido-compounds (1) give methane and the imido-compounds [{AlMe(NR')}$_n$] (2a)—(2d); there is no evidence for formation of mixed amido–imido-compounds. The compound [{AlMe(NPh)}$_6$] (2a) has been shown by an X-ray study to have a cage structure with S_6 symmetry in the solid state, and the hexameric structure in the gas phase is confirmed by mass spectrometry. The o-tolyl derivative (2b) seems to give tetrameric molecules [{AlMe(NC_6H_4Me-2)}$_4$] and there is evidence that the p-tolyl compound may form a mixture of tetramers and hexamers. The compound [{$AlMe_2(NHPr^n)$}$_3$] appears from n.m.r. spectra to have the *cis* configuration in benzene, and [{$AlMe_2(NHBu^t)$}$_2$] the *trans* configuration. There is no evidence for mixtures of isomers. The thermal decomposition of [{$AlMe_2(NHPr^i)$}$_2$] appears to be catalysed by amines.

Amido- and imido-compounds of aluminium are formed from amine adducts by condensation reactions [equation (1), $z(x + y) = mn$]. The stoicheiometry of this reaction sequence has been established for 40 years,[2] but there are still unanswered questions about the factors determining the molecular complexities and structures of the products (1)—(3). For R = H, attention has been focused on the imido-compounds (iminoalanes) (2) which have been isolated with n = 4,[3] 6,[4–6] or 8,[6] depending on the group R'. For R = Ph, the amido-compounds are mainly dimeric or mixtures of dimers and trimers[7] and the products (2) are tetramers.[8] For R = Me, several compounds (1)—(3) have been characterised by X-ray diffraction. With R' = Me, both *cis* and *trans* trimers (4a), (4b) may be isolated,[9] as well as imido-compounds with n = 7 and 8[10] and compounds (3) with $x = 2$, $y = 6$.[11] For R' = Pr^i or CH_2Ph,[12] *cis* and *trans* dimeric amido-compounds (5a), (5b) have been characterised. For R' = Pr^i both tetrameric (6)[3] and hexameric (7)[4] [{AlMe(NPr^i)}$_n$] have been isolated.

We have now prepared a series of amido-compounds

$$mnR_3Al\cdot NH_2R' \xrightarrow{-mnRH} n[\{AlR_2(NHR')\}_m] \xrightarrow{-yzRH}$$

(1)

$$[\{AlR_2(NHR')\}_x\{AlR(NR')\}_y]_z \xrightarrow{-xzRH}$$

(3)

$$m[\{AlR(NR')\}_n] \quad (1)$$

(2)

(4a) *cis*

(4b) *trans*

(5a) *cis*

(5b) *trans*
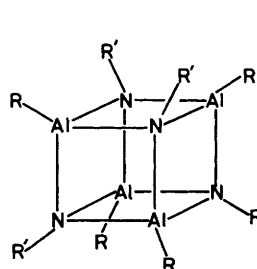
(6)

(7)

$[\{AlMe_2(NHR')\}_m]$ [R' = Ph (1a), C_6H_4Me-o (1b), C_6H_4Me-p (1c), or $C_6H_3Me_2$-2,6 (1d)] and converted them into the corresponding imido-compounds $[\{AlMe(NR')\}_n]$ (2a)—(2d). As for the series of compounds where R' = Me and Pr^i, we have found that compounds (1) and (2) show a variety of molecular complexities. We have also made the n-propyl and t-bu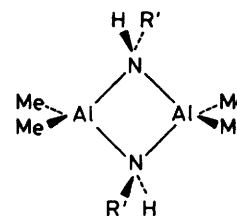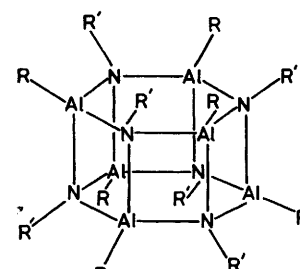tyl compounds $[\{AlMe_2(NHPr)\}_3]$ and $[\{AlMe_2(NHBu^t)\}_2]$; in contrast, these show simple n.m.r. spectra, indicating that in each case almost all the species in solution have the same stereochemical configuration.

Experimental

Air and moisture were as far as possible excluded from all reactions. Solvents were dried over sodium wire and distilled from calcium hydride. Liquid amines were stored over KOH and freshly distilled before use. Trimethylaluminium was distilled into reaction vessels under vacuum.

N.m.r. spectra of samples in C_6D_6 or $C_6D_5CD_3$ were recorded at 90 or 360 MHz. For ^1H spectra, small amounts of cyclohexane were added as reference [$\delta(H)$ taken as 1.38 p.p.m.]. Chemical shifts for ^1H and ^{13}C spectra are given relative to $SiMe_4$. All attempts to obtain ^{27}Al spectra were unsuccessful, presumably because of severe quadrupole broadening.

The Reaction between Trimethylaluminium and Aniline.—Trimethylaluminium (0.608 g, 8.43 mmol) was dissolved in degassed toluene (3 cm^3) and aniline (0.775 g, 8.43 mmol) in toluene (3 cm^3) was added at -78 °C. The reaction vessel was agitated gently and allowed to warm. Gas evolution began as the temperature reached 15 °C and was completed after *ca.* 15 min at 35 °C. Methane (8.24 mmol, identified by its i.r. spectrum) was collected in a Sprengle pump. The solution was concentrated, giving white crystals of *anilinodimethylaluminium* (1a), 1.19 g (86%), m.p. 125 °C (decomp.) (from toluene–heptane) (Found: C, 62.4; H, 7.9; N, 9.2. $C_8H_{12}AlN$ requires C, 64.4; H, 8.0; N, 9.4%). $\delta(H)$ ($C_6D_5CD_3$): -0.91, -0.79, -0.55, -0.38, -0.21 (6 H, AlMe see Discussion section), 3.1 (br), 3.8 (br) (1 H, NH, assignment confirmed by deuteriation), and 6.6—7.3 (5 H, m, Ph). $\delta(C)$: -10.0 (br, AlMe), 121.1, 122.2, 122.4, 123.7, 129.2, 129.5, 142.0, and 143.4 p.p.m. The ^{13}C n.m.r. spectrum showed the presence of at least two distinct phenyl groups but the full spectrum was partly obscured by residual solvent peaks. The mass spectrum (sample at 130 °C) showed dimers (D) and monomers (M): m/z (relative intensities in parentheses) 298 (14, D^+), 283 (100, $[D - Me]^+$), 267 (62, $[D - Me - CH_4]^+$), 252 (8), 226 (7), 190 (26), 149 (60, M^+), 134 (41, $[M - Me]^+$), 119 (8, $[M - Me - CH_4]^+$), and 93 (71%, $PhNH_2^+$). The mass spectrum of a sample made from $PhND_2$ and held at 100 °C gave weak peaks corresponding to trimer (T), *i.e.* m/z 435 ($T - Me)^+$, 418 ($T - Me - CH_3D$), and 401.

Compounds (1b)—(1d) were made similarly.

Dimethyl(o-tolylamido)aluminium (1b). Methane evolution 97% (Found: C, 63.3; H, 8.6; N, 7.4. $C_9H_{14}AlN$ requires C, 66.2; H, 8.6; N, 7.7%). $\delta(H)$ (C_6D_6): -0.93, -0.79, -0.42, -0.28, -0.06 (6 H, AlMe), 1.89, 2.11, 2.27 (3 H, CMe), 3.5 (br), 3.7 (br), 4.1 (br) (1 H, NH), and 6.7—7.2 [4 H, m, CH (aryl)]. The intensities of the peaks at 2.27 and 2.11 were in the ratio 1:2, as were the intensities of those at -0.06 and -0.28 (see Discussion section). Mass spectrum: m/z 326 (14, D^+), 311 (48, $[D - Me]^+$), 295 (10, $[D - Me - CH_4]^+$), 204 (3, $[D - Me - o-MeC_6H_4NH_2]$), 163 (45, M^+), 148 (22, $[M - Me]^+$), 107 (100, o-$MeC_6H_4NH_2^+$), and 106 (95%, o-$MeC_6H_4NH^+$).

Dimethyl(p-tolylamido)aluminium (1c). Methane evolution 95%, m.p. 135 °C (from toluene) (Found: C, 63.5; H, 8.7; N, 7.6. $C_9H_{14}AlN$ requires C, 66.2; H, 8.6; N, 7.7%). $\delta(H)$ (C_6D_6): -0.90, -0.76, -0.52, -0.35, -0.17 (6 H, AlMe), 1.93, 1.95 (3

H, CMe), 3.1 (br), 3.7 (br) (1 H, NH), and 6.5—7.3 (5 H, m, Ph). Mass spectrum: m/z 326 (7), 311 (41), 295 (17), 254 (7), 204 (7), 163 (52), 148 (20), 107 (82), and 106 (100%). For assignments see above.

(2,6-Dimethylphenylamido)dimethylaluminium (1d). M.p. 118—120 °C (from toluene–heptane) (Found: C, 67.6; H, 9.3; N, 8.0%. $C_{10}H_{16}AlN$ requires C, 67.8; H, 9.0; N, 7.9%). $\delta(H)$ ($C_6D_5CD_3$): -0.45 (6 H, AlMe), 2.29 (6 H, CMe), 4.13 (1 H, NH), and 6.8—7.3 [3 H, CH(aryl)].

Hexakis(methyl-μ_3-phenylimido-aluminium) (2a).—Anilino-dimethylaluminium (1.03 g, 6.9 mmol) in toluene (5 cm^3) was heated in a sealed ampoule for 24 h at 180 °C. The colourless *crystals* (0.54 g, 78%) which formed as the ampoule cooled were filtered off and washed with cold toluene, m.p. > 320 °C (Found: C, 62.2; H, 5.9; N, 10.2%; M^+ 798. $C_{42}H_{48}Al_6N_6$ requires C, 63.1; H, 6.0; N, 10.5%; M^+ 798). $\delta(H)$ ($C_6D_5CD_3$): -0.73 (3 H, s, Me) and 6.7—7.2 (5 H, m, Ph). $\delta(C)$ (C_6D_6): -10.3 (1 C, s, vbr, Me), 123.1 (1 C, s, C^4), 126.3 (2 C, s, C^2), 130.0 (2 C, s, C^3), and 148.0 p.p.m. (1 C, s, C^1).

Thermal Decomposition of $AlMe_2(NHC_6H_4Me$-$o)$ *and* $AlMe_2(NHC_6H_4Me$-$p)$.—Small samples of the amido-compounds in C_6D_6 were heated in n.m.r. tubes until no further change was observed in the spectra. The peaks assigned to $AlMe_2(NHC_6H_4Me$-$o)$ had disappeared after 3 h at 150 °C and were replaced by signals at 0.16 (CH$_4$), -0.26 (3 H, s, AlMe), 2.22 (3 H, s, CMe), and 6.8—7.5 (4 H, m, CH). A mass spectrum of the residue showed that it gave tetrameric species in the gas phase (Found: M^+ 588. $C_{32}H_{40}Al_4N_4$ requires M^+ 588). No peaks attributable to species other than the starting amido-compound and product imido-compound were observed.

In a similar experiment, the peaks due to the *p*-tolyl derivative (1c) disappeared after 3 h at 150 °C and were replaced by signals at 0.16 (CH$_4$) and 2.11 (A), 2.04 (B), -0.17 (C), and -0.53 (D). Peak (A) had the same intensity as that of (C) and peak (B) the same intensity as that of (D). The ratio of the intensity of peak (C) to that of peak (D) was *ca.* 0.6. By comparison with the spectra of the hexamer (2a) and the tetramer (2b) it is reasonable to assign peaks (A) and (C) to $[\{AlMe(NC_6H_4Me$-$p)\}_4]$ and (B) and (D) to $[\{AlMe(NC_6H_4Me$-$p)\}_6]$. Again no species were detected by n.m.r. spectroscopy other than the starting amido- and product imido-compounds. When compound (1c) was heated for 1 h at 200 °C the ratio of tetramer to hexamer was *ca.* 1.5:1.

The high stability of the $(AlN)_4$ and $(AlN)_6$ frameworks under electron impact is shown by the almost complete absence in the mass spectra of peaks other than those from parent ions, from parent ions minus methyl, and peaks at m/z *ca.* 100 from amine fragments.

Tris(dimethyl-μ-propylamido-aluminium).—Trimethyl-aluminium (22.3 mmol) and NH_2Pr^n (22.3 mmol) were warmed without solvent to 75 °C, and the methane evolved (19.9 mmol) was collected in the Sprengle pump and identified by its i.r. spectrum. The liquid product was distilled, b.p. 62—63 °C (10^{-2} mmHg, *ca.* 1.33 Pa) [Found: Me (by hydrolysis), 18.1; Al, 21.5%; M (cryoscopic in C_6H_6) 345. $C_{15}H_{42}Al_3N_3$ requires Me, 18.1, Al, 22.6%; M, 345]. The mass spectrum showed prominent peaks corresponding to loss of Me, and CH$_4$ from trimer, dimer, and monomer. $\delta(H)$ (C_6H_6): -0.52 (6 H, s, AlMe), 0.73 (3 H, t), 1.23 (2 H, tq), and 2.47 (2 H, dt) (Pr). Spectra obtained from samples in $C_6D_5CD_3$ at lower temperatures showed no significant change.

Bis(dimethyl-μ-t-butylamido-aluminium).—A mixture of $AlMe_3$ (29.3 mmol) and NH_2Bu^t (29.3 mmol) in toluene (10 cm^3) was heated to 70 °C for 10 h. When the solution was

concentrated white crystals were obtained [Found: C, 54.8; H, 13.3; N, 11.5%; M 243 $(M - \text{Me})^+$. $C_{12}H_{32}Al_2N_2$ requires C, 55.3; H, 13.2; N, 10.8%; M 243 $(M - \text{Me})^+$]. $\delta(\text{H})$ (C_6H_6): -0.27 (6 H, s, AlMe), 0.97 (9 H, s, Bu^t), and 1.47 (1 H, br, NH). No change was observed in the n.m.r. spectrum when solutions of the compound were heated for prolonged periods at 190 °C.

Crystal Structure Determinations.—(*a*) [{AlMe$_2$(NHC$_6$H$_4$-Me-*o*)}$_2$] (**1b**). Crystals were sealed in Lindemann glass capillaries under argon.

Crystal data. $C_{18}H_{28}Al_2N_2$, $M = 326.4$, monoclinic, $a = 9.365(10)$, $b = 6.948(14)$, $c = 14.893(11)$ Å, $\beta = 94.93(8)°$, $U = 965.5$ Å^3, $Z = 2$, $D_c = 1.12$ g cm^{-3}, $F(000) = 352$, monochromated Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 1.5$ cm^{-1}, space group $P2_1/n$ from systematic absences of $0k0$ for k odd and $h0l$ for $h + l$ odd.

Data collection and processing. With a crystal *ca.* 0.3 × 0.2 × 0.2 mm, preliminary cell dimensions were found using the SEARCH and INDEX routines of the Enraf–Nonius CAD4 diffractometer and final values were calculated from the setting angles for 25 reflections with θ *ca.* 10°. Intensities for $h \pm k \pm l$ reflections with $2 < \theta < 18°$ were measured by a θ–2θ scan with a scan width of $\Delta\theta = (1.2 + 0.35 \tan \theta)°$. The scan rate for each reflection was determined by a rapid pre-scan at 10° min^{-1} in θ at which point any reflection with $I < \sigma(I)$ was coded as unobserved. The remaining reflections were re-scanned at such a speed as to give a minimum value of $\sigma(I)/I$ of 0.05 subject to a maximum scan time of 60 s. Two standard reflections monitored every hour showed no significant variation. Data were corrected for Lorentz polarisation effects but not for absorption, and after averaging any equivalent reflections 441 reflections with $|F| >$

$\sigma(F^2)$ were used in the structure refinement. The values of $\sigma(F^2)$ were taken as $[\sigma^2(I) + (0.02I)^2]^{\frac{1}{2}}/\text{Lp}$.

Structure analysis and refinement. The structure was solved by direct methods using the MULTAN[13] program. Refinement of non-hydrogen atoms with anisotropic thermal parameters was by full-matrix least squares. A difference map showed H-atom peaks for all atoms except C(7), and H atoms were included at calculated positions (C–H 1.08 Å), with six half atoms for those on C(7), and held fixed with a common isotropic thermal parameter of $B = 6.0$ Å^2. Refinement converged at $R = 0.087$, $R' = 0.085$, when the maximum shift/error was 0.01 and the weighting scheme was $w = 1/\sigma^2(F)$. A final difference map was everywhere featureless.

The structure solution and refinement were done on a PDP 11/34 computer using the Enraf–Nonius structure determination package. Scattering factors for neutral atoms were taken from ref. 14. Final atom co-ordinates are listed in Table 1 and bond lengths and angles within the dimeric molecules (**5b**) (Figure 1) are listed in Table 2.

(*b*) [{AlMe(NPh)}$_6$]. *Crystal data.* $C_{42}H_{48}Al_6N_6$, $M = 798.8$, rhombohedral, $a = 12.476(4)$ Å, $\alpha = 62.35(3)°$, $U = 1\,445.1$ Å^3, $Z = 2$, $D_c = 1.84$ g cm^{-3}, $F(000) = 840$, monochromated Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 2.9$ cm^{-1}, space group $R\bar{3}$.

Data collection and structure analysis. The crystal was an irregular lump 0.5 × 0.5 × 0.5 mm. The procedure for data collection and processing was the same as that for compound

Table 1. Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for compound (**1b**)

Atom	x	y	z
Al	776(5)	792(7)	776(3)
N	$-1\,229(10)$	589(15)	316(6)
C(1)	$-2\,313(13)$	$-81(19)$	867(8)
C(2)	$-3\,538(14)$	961(19)	910(7)
C(3)	$-4\,607(16)$	378(21)	1 459(9)
C(4)	$-4\,487(14)$	$-1\,342(22)$	1 895(9)
C(5)	$-3\,282(16)$	$-2\,446(20)$	1 862(8)
C(6)	$-2\,197(15)$	$-1\,906(19)$	1 317(9)
C(7)	$-3\,814(17)$	2 916(20)	480(10)
C(8)	1 331(15)	$-734(22)$	1 852(8)
C(9)	1 338(15)	3 529(18)	758(8)

Table 2. Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for compound (**1b**)*

Al–N	1.949(7)	Al–N′	1.965(7)
Al–C(8)	1.954(9)	Al–C(9)	1.974(9)
N–C(1)	1.436(11)	C(1)–C(2)	1.363(12)
C(1)–C(6)	1.434(14)	C(2)–C(3)	1.406(14)
C(2)–C(7)	1.514(14)	C(3)–C(4)	1.360(14)
C(4)–C(5)	1.369(13)	C(5)–C(6)	1.405(13)
N–Al–N′	86.8(3)	N–Al–C(8)	115.4(4)
N–Al–C(9)	108.4(4)	N′–Al–C(8)	110.7(3)
N′–Al–C(9)	112.5(3)	C(8)–Al–C(9)	118.8(4)
Al–N–Al′	93.2(3)	Al–N–C(1)	122.0(6)
Al′–N–C(1)	121.9(6)	N–C(1)–C(2)	120(1)
N–C(1)–C(6)	122(1)	C(1)–C(2)–C(6)	119(1)
C(1)–C(2)–C(3)	121(1)	C(1)–C(2)–C(7)	125(1)
C(3)–C(2)–C(7)	114(1)	C(2)–C(3)–C(4)	120(1)
C(3)–C(4)–C(5)	121(1)	C(4)–C(5)–C(6)	121(1)
C(1)–C(6)–C(5)	118(1)		

* Primed atoms are related by the symmetry element $\bar{x}, \bar{y}, \bar{z}$.

Table 3. Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses for compound (**2a**)

Atom	x	y	z
Al	325(4)	1 828(4)	$-1\,218(4)$
N	$-335(10)$	1 092(9)	$-1\,770(9)$
C(1)	$-671(14)$	1 525(13)	$-2\,881(12)$
C(2)	$-1\,021(14)$	799(15)	$-3\,099(13)$
C(3)	$-1\,373(16)$	1 215(18)	$-4\,265(14)$
C(4)	$-1\,392(23)$	2 363(26)	$-5\,015(17)$
C(5)	-580	2 970	$-5\,080$
C(6)	$-676(25)$	2 717(21)	$-3\,679(20)$
C(7)	660(17)	3 479(13)	$-2\,228(16)$
C(8)	2 270	2 770	2 770^a
C(9)	3 590	3 590	3 590^a
C(10)	3 320	3 594	2 773^b

^{a} Occupancy 0.17. ^{b} Occupancy 0.25, from unidentified solvent.

Table 4. Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for compound (**2a**)*

Al–N	1.951(6)	Al–N′	1.902(5)
Al–N″	1.922(5)	Al–C(7)	1.977(7)
N–C(1)	1.423(8)	C(1)–C(2)	1.339(10)
C(1)–C(6)	1.351(12)	C(2)–C(3)	1.503(11)
C(3)–C(4)	1.294(14)	C(4)–C(5)	1.48
C(5)–C(6)	1.58		
N–Al–N′	90.7(2)	N–Al–N″	90.2(2)
N–Al–C(7)	123.1(3)	N′–Al–N″	113.7(2)
N′–Al–C(7)	116.9(3)	N″–Al–C(7)	117.1(3)
Al–N–Al′	88.9(2)	Al–N–Al″	89.5(2)
Al–N–C(1)	132.0(5)	Al′–N–Al″	126.0(2)
Al′–N–C(1)	110.3(4)	Al″–N–C(1)	110.2(4)
N–C(1)–C(2)	121.2(6)	N–C(1)–C(6)	117.4(9)
C(2)–C(1)–C(6)	121.3(8)	C(1)–C(2)–C(3)	122.9(8)
C(2)–C(3)–C(4)	115(1)	C(3)–C(4)–C(5)	121
C(4)–C(5)–C(6)	109	C(1)–C(6)–C(5)	115

* Primed atoms are related by the symmetry elements $\bar{z}, \bar{x}, \bar{y}$, doubly primed ones by $\bar{y}, \bar{z}, \bar{x}$.
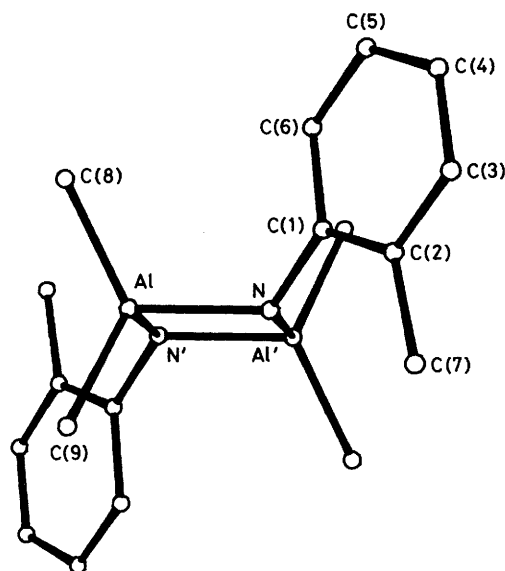
Figure 1. The structure of [{AlMe$_2$(NHC$_6$H$_4$Me-o)}$_2$] (**1b**)

(**1b**) above. Seventeen reflections with θ *ca.* 15° were used for the determination of preliminary cell dimensions and 629 reflections with $|F^2| > \sigma(F^2)$ for the structure refinement.

The structure was solved by routine heavy-atom methods in space group $R\bar{3}$, but the phenyl C atoms were not very clear and refined to a rather distorted geometry. The space-group symmetry was relaxed to $R3$ and the structure refinement continued. However the least-squares matrix was ill conditioned and the resulting phenyl-group geometries even less likely. It was therefore decided to return to space group $R\bar{3}$, and in order to get a reasonable geometry the atom C(5) had to be held fixed. A difference map showed three diffuse peaks near the three-fold rotation axis which were presumed to be part of a disordered solvent molecule and included in the structure-factor calculation with partial occupancy and with thermal parameters of $B = 9.0$ Å^2, but not refined. All other atoms were refined by full-matrix least squares with anisotropic thermal parameters. Refinement converged at $R = 0.158$, $R' = 0.216$ with a weighting scheme of $w = 1/\sigma^2(F)$.

Final atom co-ordinates are given in Table 3 and bond lengths and angles in Table 4. The hexameric molecules are shown in Figure 2.

(*c*) AlMe$_2$(NHC$_6$H$_3$Me$_2$-2,6) (**1d**). In an *X*-ray study of this compound the crystal decomposed before data collection was complete. An analysis based on the incomplete data set showed unequivocally that the molecules consisted of *trans* dimers (**5b**) like those of compound (**1b**), but the molecular parameters were not considered accurate enough to merit publication.

Results and Discussion

The compound AlMe$_2$(NHC$_6$H$_4$Me-o) (**1b**) crystallises in centrosymmetrical *trans* dimers (Figure 1). Unlike [{AlMe$_2$-(NHPr^i)}$_2$],[1] the *cis* and *trans* dimers do not crystallise together. The mean Al–N and Al–C bond lengths [1.957(7) and 1.964(9) Å respectively] are similar to those in *trans*-[{AlMe$_2$(NHPr^i)}$_2$] [1.958(4) and 1.964(9) Å], in [{AlMe$_2$-(NMe$_2$)}$_2$],[9,15] and in other compounds having four-membered (AlN)$_2$ rings. The (NHC$_6$H$_4$Me-2) fragment lies in a plane which makes an angle of 84° with the (AlN)$_2$ plane. As in *trans*-[{AlMe$_2$(NHPr^i)}$_2$], however, the AlMe$_2$ groups are twisted slightly away from the perpendicular to the (AlN)$_2$ ring. There are no intermolecular contacts shorter than the sum of the van der Waals radii.

Table 5. Proportion (%) of the amido-compound [{AlMe$_2$(NHR′)}$_m$] as dimer in C$_6$D$_5$CD$_3$ at different temperatures (K) in parentheses

R′	
Ph	34 (333), 31 (310), 25 (273), 14 (253)
C$_6$H$_4$Me-o	58 (293), 40 (213)
C$_6$H$_4$Me-p	31 (293), 25 (213)
C$_6$H$_3$Me$_2$-2,6	83 (278), 76 (268), 68 (248), 62 (238)

The *X*-ray diffraction studies establish the structures of the amido-compounds (**1b**) and (**1d**) in the solid state. If these structures persisted in solution the ¹H n.m.r. spectra would show two signals in the methyl region, one corresponding to protons of methyl groups attached to aluminium and the other to protons of methyl substituents in the aromatic rings. The ¹H n.m.r. spectra of the amido-compounds (**1a**)—(**1d**) are, however, more complicated. All four compounds show a pattern of five resonances in the AlMe region. The four outer peaks have intensities which are consistently in the ratio 1:2:2:1. It is clear that crystals of the amido-compounds, which at least for (**1b**) and (**1d**) are known to consist only of *trans* dimers (**5b**), give other species on dissolution. If there were *cis* dimers, as well as *trans*, three rather than five signals would be expected in the AlMe region. It seems likely, however, that the oligomers found in solutions should not be lower than those in the gas phase. Since trimers have been detected by mass spectroscopy, at least for (**1a**), it is reasonable to postulate that the extra peaks in the n.m.r. spectra of solutions result from trimers (**4a**) or (**4b**) as found for [{AlMe$_2$(NHMe)}$_3$];[9] *cis* trimers (**4a**) would give two peaks of equal intensity corresponding to axial and equatorial AlMe groups, and *trans* trimers would give four in ratio 1:1:2:2.

The similarity in the spectra of compounds (**1a**)—(**1d**) suggests that similar species are found in solutions of each of the four compounds. The spectra are those expected for *trans* dimers (**5b**) and *trans* trimers (**4b**), not those for the *cis* isomers. For large groups R′ the preponderance of (**5b**) compared with (**5a**) is easily understood. Steric interactions in (**4b**) compared with (**4a**) are less equally seen, but molecular models indicate unfavourable contacts in the *cis* isomer between the methyl groups on aluminium and the substituents (H or Me) at the *ortho*-positions of the rings attached to nitrogen. This is perhaps why the *trans* conformation is preferred. The spectral evidence does not distinguish between chair and boat forms of the (AlN)$_3$ ring. Models suggest that the substituents are best accommodated by a twist-boat conformation, but we have been unable to confirm this since trimers have not been isolated in the solid state.

As expected for a dimer–trimer equilibrium, the central peak in the n.m.r. spectrum becomes stronger relative to the outer peaks at higher temperatures (Table 5). In spectra recorded at a given temperature, this peak becomes stronger as the number of *ortho*-substituents increases, consistent with the fact, noted in 1965,[16] that steric interactions between substituents are greater in trimers than in dimers. In principle, the proportion of dimers and trimers could be found by cryoscopic molecular-weight determinations, but it has not been possible to obtain sufficiently accurate values in the present case because of the low solubility and high molecular weight of the compounds.

The observations on the arylamido-compounds (**1a**)—(**1d**) provide further evidence that the amounts of various isomers in a particular solution are determined by thermodynamic rather than kinetic factors. The isomers are distinct on an n.m.r. time-scale but interconvert in a few minutes. Dissolution of a crystal containing a particular oligomer gives a solution containing several species. Conversely, a mixture of isomers or oligomers in solution may be converted on crystallisation into the species which has the lowest solubility.

The n-propylamido-derivative $[\{AlMe_2(NHPr)\}_3]$ shows only one peak in the AlMe region of the n.m.r. spectrum. Cryoscopic measurements show that the compound is trimeric so the predominant isomer appears to be *cis* (**4a**). With increased steric hindrance at nitrogen, mixtures of dimers and trimers are obtained as in the arylamido-compounds (**1a**)—(**1d**), or mixtures of *cis* and *trans* dimers (**5a**), (**5b**), as in $[\{AlMe_2(NHPr^i)\}_2]$,[1] $[\{AlMe_2(NMePh)\}_2]$,[17,18] or $[\{AlMe_2(NHCH_2Ph)\}_2]$.[12] With even more hindered groups attached to nitrogen only *trans* dimers (**5b**) are observed, as in $[\{AlMe_2(NHBu^t)\}_2]$.

On heating, the amido-compounds (**1**) give methane quantitatively and imido-compounds (**2**), and a number of attempts have been made to study the kinetics of the reaction (1) by n.m.r. spectroscopy. Most of these have involved the isopropyl compounds $[\{AlMe_2(NHPr^i)\}_2]$, since the structures of the species in solution appear to be well defined[1] and the peaks from the product $[\{AlMe(NPr^i)\}_4]$ at $\delta(H) -0.07$ (AlMe) and 1.3 (d, CMe_2) are well separated from those of the starting amido-compound $[\delta -0.35$ to -0.45 and 1.1 (d)].

In experiments where the temperature was raised slowly the onset of thermal decomposition was sharp and the reaction was complete over a range of 5—10 °C. Similar observations were made concerning the decomposition of adducts of *N*-methyl-aniline, dibutylamine, and n-octylamine with isobutyldimethyl- and dimethylpropynyl-aluminium.[19] At a particular temperature, e.g. 150 ± 5 °C, the decomposition of $[\{AlMe_2(NHPr^i)\}_2]$ to $[\{AlMe(NPr^i)\}_4]$ showed induction periods of variable length. Since these could indicate that the thermal decomposition was catalysed by traces of moisture desorbed from the surface of the n.m.r. tubes, we investigated the effect of adding small quantities of both primary and tertiary amines (ca. 0.1 mol %) as catalysts. These caused a marked acceleration of the rate as noticed earlier[20] and decreased the induction period. With 10 mol % triethylamine as catalyst at 190 °C plots of the logarithm of the fraction of $[\{AlMe_2(NHPr^i)\}_2]$ left *versus* time were linear to more than 75% completion of reaction but it was still not easy to get completely reproducible kinetic results. Our data could not be well described by zero-order plots, as observed for the thermal decomposition of $AlEt_2Cl$–$NHMe_2$.[21]

We have also attempted, with compounds having a range of substituents R', to detect species (**3**) similar to $[\{AlMe_2(NHMe)\}_2\{AlMe(NMe)\}_6]$[11] or $[\{AlH_2(NHPr^i)\}_3\{AlH(NPr^i)\}_2]$[22] by keeping the temperature for decomposition as low as possible. No success has been achieved. It is possible that the amido–imido-compounds (**3**) which have been isolated represent low-energy 'dead ends' in the normal condensation process in much the same way as the adducts $R_3Al\cdot NHR'_2$ appear not to be intermediates in the formation of the amido-compounds $[\{AlR_2(NHR')\}_m]$ themselves.[23]

Compound (**2a**) appears to be the first hexameric alkyl-aluminium imide to be characterised by X-ray diffraction, though preparations of others have been described,[4] and the structures of two hydrido-species $[\{AlH(NPr^i)\}_6]$[5] and $[\{AlH(NPr^n)\}_6]$[6] have been determined. The quality of the data from (**2a**) is low because of the inclusion of solvent in the crystal, but the molecular structure is clear. The $(AlN)_6$ cage (**7**) with crystallographically required symmetry $S_6(R\bar{3})$ consists of almost planar four- and six-membered rings. Bond lengths and angles within the cage are very similar to those in the two compounds previously studied; Al–N bonds in the six-membered rings [1.912(6) Å] are significantly shorter than the transverse bonds [1.951(6) Å] joining these rings. The methyl substituents on aluminium are similarly oriented to the hydride substituents in $[\{AlH(NR')\}_6]$ (R = Pr^n or Pr^i), but the phenyl groups on nitrogen, which are almost perpendicular to the $(AlN)_3$ rings, are bent towards the S_3 axis, making Al–N–C(1) large. There are no unusual intermolecular contacts and the
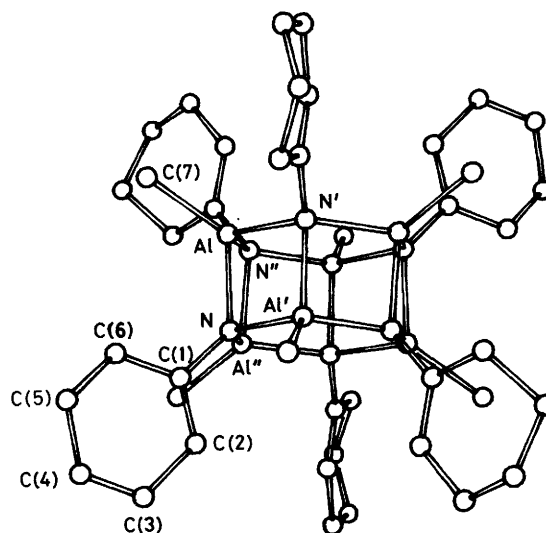

Figure 2. The structure of $[\{AlMe(NPh)\}_6]$ (**2a**)

variation in orientations within the organic groups outside the cages, which complicates the structure of the $[\{AlH(NR')\}_6]$, is absent in (**2a**).

N.m.r. (see Experimental section) and mass spectra suggest that compound (**2b**) forms tetramers and (**2c**) a mixture of tetramers and hexamers. From the series $[\{AlMe(NMe)\}_n]$ ($n = 7$ or 8), $[\{AlMe(NPh)\}_6]$, $[\{AlMe(NPr^i)\}_n]$ ($n = 4$ or 6) and $[\{AlPh(NPh)\}_4]$ it seems that the oligomer size is determined at least in part by the size of the groups attached to the aluminium–nitrogen cage. What determines the relative amounts when mixtures are formed is less clear. The compounds $[\{AlMe(NMe)\}_7]$ and $[\{AlMe(NMe)\}_8]$ appeared not to interconvert, even on prolonged heating at 200 °C.[11] The present work suggests that the amount of each oligomer depends both on the temperature of the initial reaction and on the length of the heating period. For (**2c**), although more hexamer was formed at 150 than at 200 °C, there was also a slow transformation of tetramer to hexamer on prolonged heating at 200 °C. However, more work is required on this point.

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