

**BULKY METAL ARYLOXIDES, ARYLAMIDES AND
SULPHUR AND PHOSPHORUS ANALOGUES—III.* ALUMINIUM
COMPOUNDS DERIVED FROM 2,4,6-TRI-*t*-BUTYLANILINE;
X-RAY STRUCTURE OF
[AlMe₂{μ-NHC₆H₂Bu^{*t*}_{3-2,4,6}-C(Me)₂CH₂-2}]₂**

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Abstract—Treatment of AlMe₃ with ArNH₂ (Ar = C₆H₂Bu^{*t*}_{3-2,4,6}) in C₆H₁₄ at 60°C afforded [AlMe₂(μ-NHAr)]₂ (**1**). Heating the amide **1** either at 200°C for 3 h or (NMR) in C₆D₆ at 80°C for 3 weeks in a sealed tube led to methane elimination and formation of the cyclometallated compound [AlMe{μ-NHC₆H₂Bu^{*t*}_{3-2,4,6}-C(Me)₂CH₂-2}]₂ (**2**); unexpectedly, the hydrogen atom abstracted from the \bar{N} HAr ligand of **1** originated from the 2-*t*-butyl group rather than the NH. Deuterolysis of **2** yielded D₂NC₆H₂Bu^{*t*}_{3-2,4,6}-C(Me)₂CH₂D-2. AlCl₃ and ArNH₂ gave the 1:1 adduct AlCl₃(NH₂Ar) (**3**), which upon heating either at 150°C and 10⁻⁴ torr or (NMR) in C₆D₆ at 80°C for 24 h gave isobutene and the retro-Friedel Crafts product AlCl₃(NH₂C₆H₃Bu^{*t*}_{3-2,4}) (**4**). An excess of LiNHAr did not react with AlMe₃, but with AlCl₃ furnished Al(NHAr)₂Cl (**5**). The X-ray structure of the cyclometallated compound **2** showed it to be a pentacyclic centrosymmetric dimer, containing a central (AlN)₂ square [⟨Al—N⟩ 1.965(6) Å], with the adjacent six-membered unsaturated alumino-heterocycles in a twisted boat conformation, one below and the other above the (AlN)₂ plane and the two anilido ligands in a *transoid* arrangement. The preparation of the metal anilides M(NHAr) [M = Li (**6**), SiMe₃ (**7**) or SnMe₃ (**8**)] is described.

We have introduced the sterically demanding aryl-amido ligand \bar{N} HAr (Ar = C₆H₂Bu^{*t*}_{3-2,4,6}) into coordination chemistry in the context of complexes of Li,^{1,2} B,³ Sn^{II},¹ P^{III},^{4,5} As^{III},^{4,5} P^{III}/Li,⁵ P^{III}/Al⁵ and Ni^{II}.¹

Secondary amido-metal complexes L_nM—NHR are much less well known than tertiary analogues (L_nM—NRR'), because of their frequently encountered intermolecular amine elimination to form the bis(metallo)amine L_nM—N(R)—ML_n;⁶ a bulky group R, such as R = Ar, is expected to hinder such an associative decomposition pathway. Alternatively, the amide L_nM—NHR, by virtue of its NH proton, may participate in alkane elimination, as in the conversion of an alkylaminoalane into an alkyliminoalkane [e.g.⁷ *cis*- or *trans*-{AlMe₂(μ-NHPr^{*t*})₂}₂ → *trans*-{AlMe(μ-NPr^{*t*})₄ or ₇}].

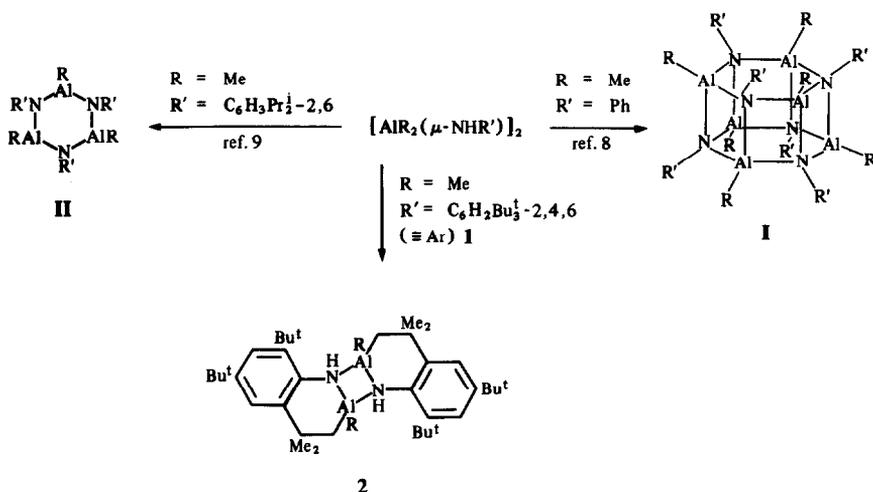
The \bar{N} HAr ligand is of further interest because of its potential for geometrical isomerism; for

example, [Li(μ-NHAr)(OEt₂)₂]₂ has the two aryl groups arranged in a *transoid* fashion.¹ Another feature, directly attributable to its substantial steric requirements, is the capacity of the ligand \bar{N} HAr to stabilize unusual partners; e.g. the compounds B(NHAr)X₂ (X = F, Cl, or NH₂) were found to be unexpectedly thermally stable with respect to HX elimination.³

The reaction between trimethylaluminium and a series of anilines was first investigated by Smith and co-workers.⁸ They observed that the reaction between AlMe₃ and the aniline R'NH₂ afforded [AlMe₂(NHR')]_m (*m* = 2 for R' = 2-MeC₆H₄; X-ray), which on heating, yielded [AlMe(NR')]_n [*n* = 6 for R' = Ph (**I**) (see Scheme 1); X-ray] [R' = R' 2- or 4-MeC₆H₄, or 2,6-Me₂C₆H₃]. Using the more sterically hindered 2,6-di(isopropyl)aniline Ar''NH₂, Power and co-workers found that the ambient temperature product [AlMe₂(μ-NHAr'')]₂ upon heating at 170°C afforded the iminoalane [AlMe(μ-NAr'')]₃ (**II**) (Scheme 1); this was of special interest, because it

* For Part II, see ref. 13.

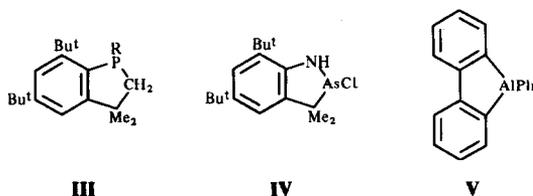
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Scheme 1. Thermolysis products of three arylamino(dimethyl)alanes; in each case methane was the co-product.

provided the first example of an Al—N compound having both Al and N in a three-coordinate environment, an AlN borazine analogue.⁹ Curiously we have found¹⁰ that for the even more sterically crowded 2,4,6-tri-*t*-butylaniline system, an iminoalane was not observed but instead **1** afforded the cyclometallated product (**2**) (Scheme 1); these results are now presented in full.

Cyclometallation in the context of a 2,4,6-tri-*t*-butylphenyl derivative of P^{III} (**III**) [R = CH(SiMe₃)₂]¹¹ or As^{III} (**IV**)⁵ had previously been noted; and the topic has been reviewed in the context of 2,6-di-*t*-butylphenoxometal complexes.¹² However, the complexes [AlMe₂(μ-OC₆H₃Bu₂-2,4)]₂ were thermally stable.¹³ A rare example of a cyclometallation in aluminium chemistry is the formation of **V** by thermolysis of 2-phenyl-1-(diphenylaluminum)benzene.¹⁴



The chemistry¹⁵ and spectroscopy¹⁶ of base adducts of AlCl₃ is well documented. The crystalline pyridine adduct of AlCl₃ has the structure [AlCl₂(py)₄][AlCl₄].¹⁷

Numerous chloro(amino)alanes and chloro(imino)alanes are known,⁶ such as the dimeric AlCl₂(NMe₂)₂¹⁸ and the tetrameric AlCl(NPr)₄.¹⁹

EXPERIMENTAL

Materials, measurements and techniques

2,4,6-Tri-*t*-butylaniline, ArNH₂ (from ArH, via ArNO₂),²⁰ and [Li(μ-NHAr)(OEt₂)₂]¹ were prepared by published methods. Manipulative procedures for the air-sensitive aluminium compounds and their precursors were described in Part II;¹³ IR, NMR and EI mass spectra were obtained using Perkin-Elmer FT1700, Bruker WP80 or WM360 and Kratos MS80RF, respectively.

Synthesis of Li(NHAr) (**6**)

LiBuⁿ in hexane (20 cm³, 1.5 mol dm⁻³, 30 mmol) was syringed into a solution containing the freshly sublimed ArNH₂ (6.00 g, 22.98 mmol) in hexane (100 cm³) at ca 25°C. A white precipitate was immediately formed. The reaction mixture was refluxed for 3 h, cooled and filtered. The insoluble 2,4,6-tri-*t*-butylanilidolithium (**6**) (5.6 g, 92%), m.p. ca 300°C (decomp.), was washed with hexane (20 cm³) to remove any residual *n*-butyl-lithium and then pumped dry. In repeat experiments, the yield was in the range 85–95%. Compound **6** was not sublimable at 250°C and 10⁻⁴ torr without complete decomposition.

Synthesis of Me₃Si(NHAr) (**7**)

Freshly distilled chloro(trimethyl)silane (1.05 cm³, 0.90 g, 8.37 mmol) was added to a solution of **6** (2.2 g, 8.24 mmol) and triethylamine (5 cm³) in

diethyl ether (150 cm³). The reaction mixture was refluxed for 3 days and the precipitated LiCl was filtered off. Volatiles were removed from the filtrate *in vacuo*. The residue comprised 2,4,6-tri-*t*-butylanilino(trimethyl)silane (**7**) (2.39 g, 87%), m.p. 88°C (Found: C, 75.8; H, 11.5; N, 4.3. Calc. for C₂₁H₃₉NSi: C, 75.6; H, 11.8; N, 4.1%); it was purified by sublimation at 130°C and 10⁻³ torr.

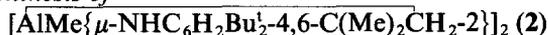
Synthesis of Me₃Sn(NHAr) (**8**)

The procedure was that used for the preparation of the anilinosilane (**7**), using **6** (1.00 g, 3.74 mmol), triethylamine (5 cm³) and chloro(trimethyl)tin (1.00 g, 5.02 mmol). The 2,4,6-tri-*t*-butylanilido(trimethyl)tin (**8**) (1.16 g, 73%), m.p. 66–67°C, was crystallized from hexane at -30°C, but with difficulty, due to its high solubility; it sublimed at 250°C and 10⁻⁴ torr, but there was extensive decomposition.

Synthesis of **1**

A trimethylaluminium solution in hexane (10 cm³, 2 mol dm⁻³, 20 mmol) was added (10 min) to a hexane solution (100 cm³) of ArNH₂ (4.00 g, 15.3 mmol). A white precipitate gradually (30 min) formed. The reaction mixture was heated with stirring at 60°C for 48 h and filtered whilst warm. Cooling the filtrate yielded colourless crystals of 2,4,6-tri-*t*-butylanilino(dimethyl)alane (**1**) (3.40 g, 89%), m.p. 241–244°C. ¹H NMR (C₆D₆): -0.38 (s, 6H, AlMe₂), 1.37 (s, 18H, 2-, 4- and 6-Bu^t), 3.8 (br, 1H, NH), 7.37 (s, 2H, 3- and 5-H).

Synthesis of



The anilinoalane **1** (4.00 g, 12.6 mmol) was slowly heated for *ca* 4 h at 210°C, using a Wood's alloy bath. Some foaming was observed. The cooled residue was crystallized from hexane (50 cm³, -78°C) to furnish colourless crystals of the cyclometallated aminoalane **2** (2.5 g, 66%), m.p. 240–243°C [Found: *M* (Signer method in Et₂O), 294. C₁₈H₂₉AlN requires *M*, 301]. IR (Nujol): ν(N—H) 3349(vs) cm⁻¹. ¹H and ¹³C{¹H} NMR data are summarized in Figs 1 and 2, respectively.

In a separate experiment, the anilinoalane **1** was heated at 80°C in a sealed NMR tube. After 3 weeks, the cyclometallation to produce **2** was 75% complete. After a further 1 week, no trace of **1** was detectable.

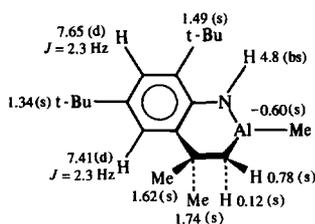


Fig. 1. Assignments of the ¹H NMR signals of **2**; spectrum at 360 MHz and 305 K.

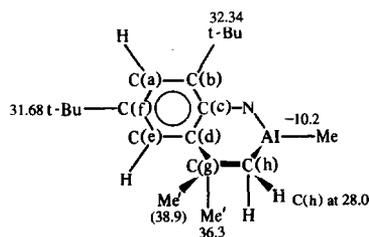


Fig. 2. Assignments of the ¹³C{¹H} NMR signals of **2**; spectrum at 90.67 MHz and 305 K; chemical shifts only for the methyl groups of the Bu^t groups are shown.

Deuterolysis of the cyclometallated aminoalane **2**

Deuterium oxide (1 cm³) was added dropwise to a solution of compound **2** (0.4 g, 1.33 mmol) in diethyl ether (30 cm³). An immediate white precipitate was formed. After stirring for 3 days, the ether was removed *in vacuo* and the residue extracted into hexane (30 cm³). The extract was concentrated and cooled to give colourless crystals of D₂NC₆H₂Bu₂-4,6-C(Me)₂CH₂D-2, m.p. 139°C (m.p. 137°C for the deuterium-free aniline). IR (Nujol) (trideuterated amine): ν(N—D) at 2620(m) and 2520(m) cm⁻¹ [cf. for the deuterium-free amine, ν(N—H) at 3510(m) and 3440(m) cm⁻¹]. MS for the deuterium-free amine gave (*m/z*, *e* = 1): *P*⁺ at 261.2457 (C₁₈H₃₁N requires 261.2456) and (*P*—Me)⁺ at 246.2221 [(*P*—Me)⁺ requires 246.2222]; the trideuterated amine gave (*P*—Me)⁺ at 249.2410 [C₁₇H₂₅D₃N requires (*P*—Me)⁺ at 249.2387].

Synthesis of AlCl₃(NH₂Ar) (**3**)

Aluminium trichloride (1.3 g, 9.74 mmol) (sublimed twice prior to use) was added to freshly sublimed ArNH₂ (2.2 g, 8.43 mmol) in toluene (100 cm³). The reaction mixture was stirred for 48 h and filtered. The filtrate upon concentration (to *ca* 20 cm³) yielded colourless needles of **3** (2.6 g, 74%), m.p. 140°C (Found: C, 53.9; H, 8.3; N, 3.2. Calc. for C₁₈H₃₁AlCl₃N: C, 54.7; H, 7.9; N, 3.5%). IR (Nujol): ν(N—H) 3380(s) and 3150(br) cm⁻¹,

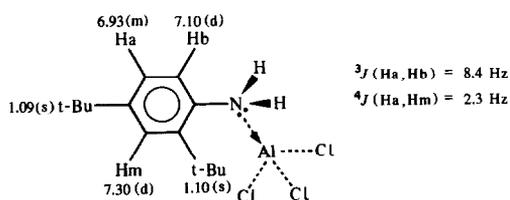


Fig. 3. Assignments of the ^1H NMR signals of **4**; spectrum at 80 MHz and 305 K.

$\nu(\text{AlCl}_3)$ 570(s) cm^{-1} . ^1H NMR data are summarized in Fig. 3.

Thermolysis of **3**, a retro-Friedel Crafts reaction

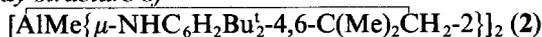
The adduct **3** (0.5 g, 1.26 mmol) was slowly heated for 3 h *in vacuo* at 150°C at 10^{-4} torr in a sublimation apparatus. This yielded white crystals of the sublimate $\text{AlCl}_3(\text{H}_2\text{NC}_6\text{H}_3\text{Bu}_2-2,4)$ (**4**) (0.2 g, 47%), m.p. 110–115°C (Found: C, 48.5; H, 6.5; N, 4.2. Calc. for $\text{C}_{14}\text{H}_{23}\text{AlCl}_3\text{N}$: C, 49.6; H, 6.8; N, 4.1%). IR (Nujol): $\nu(\text{N—H})$ 3315(s), $\nu(\text{AlCl}_3)$ 570(s) and 290(s) cm^{-1} . MS (m/z , $e = 1$; assignments in parentheses): 337 and 339 (P^+), 281 and 283 ($P-\text{Bu}^+$), 148 [$\text{C}_6\text{H}_4(\text{t-Bu})\text{NH}_2$] $^+$ and 133 [$\{\text{C}_6\text{H}_4(\text{t-Bu})\text{NH}_2\}-\text{Me}\}^+$].

In another experiment, a solution of **3** in C_6D_6 was heated at 80°C in a sealed NMR tube. After 24 h no trace of **3** was detected; complete conversion into **4** and 2-methylpropene had been effected.

Synthesis of $\text{Al}(\text{NHAr})_2\text{Cl}$ (**5**)

LiNHAr (2.29 g, 8.57 mmol) was added to freshly sublimed AlCl_3 (0.4 g, 2.99 mmol) in toluene (100 cm^3) and diethyl ether (20 cm^3). The reaction mixture was stirred for 6 days, whereafter volatiles were removed *in vacuo*. The residue was extracted into hexane (50 cm^3). The extract was concentrated and cooled (to ca 30 cm^3 at 5°C) to afford colourless crystals of the di(anilido)aluminium chloride **5** (1.8 g, 36%), m.p. 199–201°C (Found: C, 74.6; H, 10.2; N, 4.3. Calc. for $\text{C}_{36}\text{H}_{60}\text{AlClN}_2$: C, 74.1; H, 10.3; N, 4.8%). IR (Nujol): $\nu(\text{N—H})$ 3430(s) cm^{-1} .

X-ray structure of



X-ray quality crystals of the cyclometallated anilide **2** were crystallized from *n*-hexane at -30°C . A crystal of dimensions ca 0.20 \times 0.30 \times 0.15 mm was mounted and sealed under argon in a Lindemann capillary. Intensities of $+h \pm k \pm l$ reflections with $2 < \theta < 55^\circ$ were measured in the $\theta/2\theta$ mode with a scan width of $\Delta\theta = (0.8 + 0.14 \tan \theta)$ and a maximum scan time of 1 min.

Two standard reflections monitored every hour showed no significant variation. Data were corrected for Lp effects but not for absorption and, after averaging any equivalent reflections, 2711 reflections with $|F^2| > \sigma(F^2)$ were used in the structure refinement. The values of $\sigma(F^2)$ were taken as $[\sigma^2(I) + (0.02I)^2]^{1/2}/Lp$.

Crystal data. $\text{C}_{38}\text{H}_{64}\text{Al}_2\text{N}_2$, $M = 602.95$, triclinic, $a = 9.309(2)$, $b = 9.860(1)$, $c = 22.132(4)$ Å, $\alpha = 80.03(2)$, $\beta = 81.43(2)$, $\gamma = 73.84(1)^\circ$, $U = 1910.7$ Å 3 , $Z = 2$, $D_c = 1.044$ g cm^{-3} , $F(000) = 664$, Cu- K_α radiation (Ni filter), $\lambda = 1.5418$ Å, $\mu = 8.4$ cm^{-1} . Space group $P\bar{1}$.

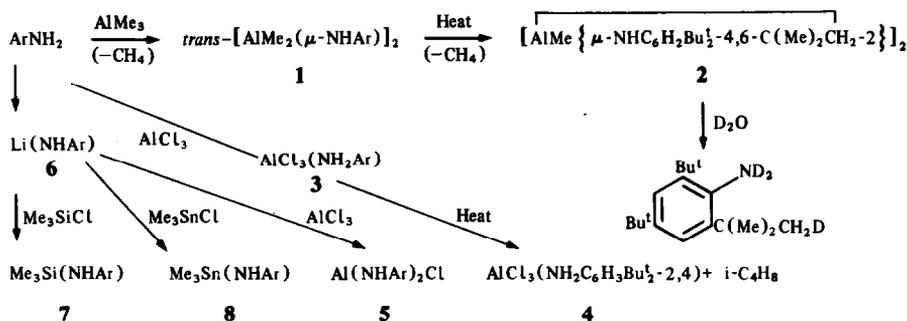
The structure was solved by direct methods using the MULTAN program.²¹ The Al, N and C atoms were refined with anisotropic temperature factors by full-matrix least-squares. The H atoms were placed at calculated positions ($\text{C—H} = 1.08$ Å) and held fixed with a common isotropic temperature of $B = 8.0$ Å 2 . Refinement converged at $R = 0.083$, $R' = 0.095$ when the maximum shift/error was 6.9 and the weighting scheme was $w = 1/\sigma^2(F)$. A final difference map was everywhere < 0.44 e Å $^{-3}$. The structure solution and refinement were carried out using a PDP 11/34 computer and the Enraf–Nonius Structure Determination Package. Scattering factors were taken from ref. 22. Tables of atom coordinates, thermal parameters and remaining bond lengths and angles are available from the Cambridge Crystallographic Data Centre. A list of final structure factors is available from one of the authors (P.B.H.).

RESULTS AND DISCUSSION

The reactions leading to the new compounds **1–8** are summarized in Scheme 2.

The formation of *trans*- $[\text{AlMe}_2(\mu\text{-NHAr})_2]$ (**1**) by aminolysis of trimethylaluminium with an equivalent portion of 2,4,6-tri-*t*-butylaniline (ArNH_2) is unexceptional. The structure of **1** has not been unambiguously elucidated. It is based on analogy with data from the literature^{6–9} and on the ^1H NMR spectrum, which showed that the following pairs were magnetically equivalent: (i) the methyls on Al, (ii) the 2- and 6- Bu^t groups of Ar and (iii) the 3- and 5-hydrogens of Ar. In diethyl ether, compound **1** appeared to be the monomer $\text{AlMe}_2(\text{N-HAr})(\text{OEt}_2)_n$.

The thermolysis of the aminoalane **1** afforded the cyclometallated aminoalane **2**. This is surprising, as an iminoalane was expected: cf. the formation of the crystallographically characterized compounds **I** and **II**, from apparently analogous reactions of $[\text{AlMe}_2(\mu\text{-NHPh})_2]$ and $[\text{AlMe}_2(\mu\text{-NHC}_6\text{H}_3\text{Pr}_2-2,6)]_2$, respectively (Scheme 1).



Scheme 2. Reactions of 2,4,6-tri-*t*-butylaniline (ArNH_2) leading to the aluminium derivatives 1–5, and some related reactions.

The formation of **2** from **1** demonstrates an unusual cyclization in aluminium chemistry, involving unprecedented aliphatic C—H bond cleavage. It is remarkable that the methane elimination from **1** results from capture of a *CH* rather than the *NH* hydrogen by an aluminium-bound methyl group. This is attributed to a steric, rather than an electronic, effect. As for the latter, it is well known that Al—Me bonds are readily cleaved by protic reagents; the NH proton of **1** is in all probability acidic (cf. the two related reactions in Scheme 1), as is the case in $\text{P}(\text{NHAr})(\text{:NAr})$ which is readily N-deprotonated by treatment with LiBu^n or AlMe_3 .⁵

The evidence for the structure of the cyclometallated anilinoalane (**2**) rests ultimately on single crystal X-ray diffraction data, *vide infra*. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are readily assigned, Figs 1 and 2, respectively. The fact that the pair of C-methyl substituents in the AlNC_4 ring are diastereotopic is consistent with this ring being non-planar (boat-shaped in the crystal). The presence of the NH protons is inferred both from the ^1H NMR and the IR spectra, $\nu(\text{NH})$ 3349 cm^{-1} .

Confirmation of the cyclometallation was further demonstrated by the deuteration of **2** (Scheme 2). It is interesting that the *N,N*-dideuteration of ArNH_2 was slow, the half-life of ArNHD in C_6D_6 in the presence of D_2O being > 1 day at 300 K. This is attributed to the steric protection afforded by the 2- and 6- Bu^t groups.

The chlorobis(anilino)alane $\text{AlCl}(\text{NHAr})_2$ (**5**) was obtained from $\text{AlCl}_3 + 2\text{Li}(\text{NHAr})$, but was not accessible from $\text{AlCl}_3(\text{NH}_2\text{Ar})$ (**3**). Thermolysis of **3**, did not cause the expected dehydrochlorination, but instead the retro-Friedel Crafts product, **4**, was obtained in quantitative yield.

Compound **4** was identified *inter alia* by its ^1H NMR spectrum; for assignments, see Fig. 3. The formation of **4** was shown to be accompanied by 2-methylpropene elimination, derived site-selectively from the 2- Bu^t group of **3**. When the thermolysis of

3 was carried out in C_6D_6 , no $\text{C}_6\text{D}_5\text{Bu}^t$ was formed. This retro-Friedel Crafts reaction for a Group 13 metal halide-arylamine complex appears to be unprecedented. A dealkylation has been observed in a Fries rearrangement.²³

The X-ray structure of **2** reveals two independent dimers, each lying on a crystallographic inversion centre, the mid-point of the almost square AlNAlN ring. The molecular geometry and atom numbering scheme for one of the dimers is illustrated in Fig. 4; they have the same basic features, hence the following discussion will refer to only one of the dimers. Selected geometric parameters are in Table 1.

The dimensions of the planar AlNAlN ring are very similar to those in $[\text{AlMe}_2(\mu\text{-NMe}_2)]_2$ [AlN : $1.948(7)$ and $1.967(7)$ Å, $\text{Al}\cdots\text{Al}$ 2.823 and $\text{N}\cdots\text{N}$ 2.735 Å],²⁴ or $[\text{AlMe}_2(\mu\text{-NHC}_6\text{H}_4\text{Me-2})]_2$ [AlN : $1.949(7)$ and $1.965(7)$ Å].⁸ The tetrahedral coord-

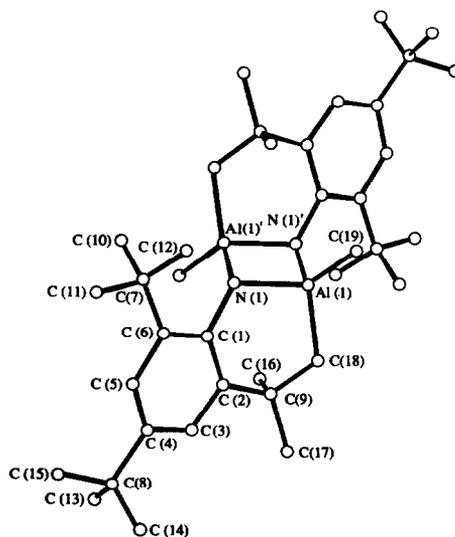


Fig. 4. The molecular structure and atom numbering scheme for crystalline **2**. Only one of the two independent molecules is shown.

Table 1. Selected intramolecular distances (Å) and angles (°) for **2** with ESDs in parentheses

(a) Bonds			
Al(1)—N(1)	1.957(6)	Al(1)—N(1')	1.973(6)
Al(1)—C(18)	1.933(8)	Al(1)—C(19)	1.966(11)
N(1)—C(1)	1.497(9)	C(1)—C(2)	1.418(9)
C(1)—C(6)	1.398(8)	C(2)—C(3)	1.419(10)
C(2)—C(9)	1.527(9)	C(3)—C(4)	1.368(9)
C(4)—C(5)	1.375(10)	C(4)—C(8)	1.581(11)
C(5)—C(6)	1.423(10)	C(9)—C(18)	1.572(13)
Al(2)—N(2)	1.973(6)	Al(2)—C(35)	1.945(8)
Al(2)—C(38)	1.944(9)	N(2)—C(20)	1.465(10)
C(20)—C(21)	1.436(11)	C(20)—C(25)	1.412(9)
C(21)—C(22)	1.389(12)	C(21)—C(28)	1.564(10)
C(22)—C(23)	1.390(10)	C(23)—C(24)	1.391(12)
C(23)—C(27)	1.549(13)	C(24)—C(25)	1.391(12)
C(25)—C(26)	1.567(12)	C(26)—C(35)	1.542(12)
Al(2)—N(2'')	1.956(7)		
(b) Angles			
N(1)—Al(1)—N(1')	88.1(3)	N(1)—Al(1)—C(18)	99.8(3)
N(1)—Al(1)—C(19)	120.9(3)	N(1')—Al(1)—C(18)	113.9(3)
N(1')—Al(1)—C(19)	115.1(3)	C(18)—Al(1)—C(19)	115.5(4)
Al(1)—N(1)—Al(1')	91.9(2)	Al(1)—N(1)—C(1)	118.8(4)
Al(1)—N(1')—C(1')	124.2(5)	N(1)—C(1)—C(2)	120.3(5)
N(1)—C(1)—C(6)	117.2(6)	C(2)—C(1)—C(6)	122.4(6)
C(1)—C(2)—C(3)	115.5(6)	C(1)—C(2)—C(9)	128.4(6)
C(3)—C(2)—C(9)	116.1(6)	C(2)—C(3)—C(4)	123.7(7)
C(3)—C(4)—C(5)	118.7(7)	C(3)—C(4)—C(8)	120.7(6)
C(5)—C(4)—C(8)	120.5(6)	C(4)—C(5)—C(6)	122.0(6)
C(1)—C(6)—C(5)	117.4(6)	C(1)—C(6)—C(7)	125.4(6)
C(5)—C(6)—C(7)	117.1(5)	N(2)—Al(2)—N(2'')	87.8(3)
N(2)—Al(2)—C(35)	98.6(3)	N(2)—Al(2)—C(38)	121.3(3)
N(2'')—Al(2)—C(35)	116.5(3)	N(2'')—Al(2)—C(38)	112.9(3)
C(35)—Al(2)—C(38)	116.2(3)	Al(2)—N(2)—Al(2'')	92.2(3)
Al(2)—N(2)—C(20)	120.2(4)	Al(2)—N(2'')—C(20'')	120.8(4)
N(2)—C(20)—C(21)	118.1(6)	N(2)—C(20)—C(25)	122.5(7)
C(21)—C(20)—C(25)	119.3(7)	C(20)—C(21)—C(22)	118.0(6)
C(20)—C(21)—C(28)	123.3(7)	C(22)—C(21)—C(28)	118.7(7)
C(21)—C(22)—C(23)	123.2(8)	C(22)—C(23)—C(24)	117.4(8)
C(22)—C(23)—C(27)	120.0(8)	C(24)—C(23)—C(27)	122.5(7)
C(23)—C(24)—C(25)	122.6(7)	C(20)—C(25)—C(24)	119.1(7)
C(20)—C(25)—C(26)	126.2(7)	C(24)—C(25)—C(26)	114.7(6)

Symmetry element ' is $\bar{x}, 1-y, 1-z$.Symmetry element '' is $1-x, 1-y, z$.

dination environment at Al is extremely irregular: N(1)AlN(1') 88.1(3), N(1)AlC(18) 99.8(3), N(1)Al(1)C(19) 120.9(3) and C(18)Al(1)C(19) 115.5(4)°; likewise the nitrogen environment is also distorted tetrahedral.

The anilido ligands are mutually *transoid* and there is disorder in the Me moieties of the 4-Bu^t groups of dimer (a) only. Each of the two six-membered rings NAlC(18)C(9)C(2)C(1) containing the Al atoms is in a twisted boat conformation, one being below and the other above the (AlN)₂ plane;

C(1) and C(18) are *ca* 0.98 and 1.74 Å above the (AlN)₂ plane. The methyl group bonded to Al is 1.48 Å out of the (AlN)₂ plane in a direction opposite to that of the six-membered ring. The C(1)—C(6) plane forms an angle of 105.7° with respect to the (AlN)₂ plane in dimer (a), while in dimer (b) this angle is 103.2°.

The endocyclic angles at the substituted carbons of the aromatic ring are smaller than the others, presumably because of steric effects. The central carbon atoms of the *o*-Bu^t group, C(7), lies in the

aromatic plane; while C(9), the central carbon of the CMe₂ moiety, is *ca* 0.11 Å above the plane and the N atom is *ca* 0.17 Å below the plane.

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