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Synthesis and crystal structure of dimeric dialkylaluminium μ-dialkylamido compounds*

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Dialkylaluminium μ-dialkylamido compounds of formula $(R^1{}_2AlNR^2{}_2)_2$ (R^1 = Me, Et, Pr^i, Bu^i or Bu^t; R^2 = Me, Et, Pr^i, Bu^i or Ph) were synthesized by alkane or arene elimination from the corresponding adduct of formula $R^1{}_3Al{\cdot}NHR^2{}_2$. The crystal structures of the following dimeric compounds were determined: $(Me_2AlNEt_2)_2$, $(Me_2AlNBu^i{}_2)_2$, $(Et_2AlNPr^i{}_2)_2$, $(Pr^i{}_2AlNMe_2)_2$, $(Pr^i{}_2AlNEt_2)_2$, $(Bu^i{}_2AlNMe_2)_2$, $(Bu^i{}_2AlNEt_2)_2$ and also the mononuclear compound $Et_2Al(OEt_2)NPh_2$. The general trends identified in these structures suggest that the environments around aluminium and nitrogen are affected primarily by their closest alkyl groups, *i.e.* R^1 and R^2 respectively, but that loss of a centre of symmetry is dependent only on R^2. Infrared data can also show the presence of a molecular centre of symmetry. Mass spectroscopic data suggest that dimers are present in the gas phase but they are partially dissociated into monomers which in turn fragment into the more stable species $[R^1AlNR^2{}_2]^+$. The NMR data show that aromatic solvents shield the R^2 protons causing downfield chemical shifts. Low-pressure (10^{-2} Torr) thermal decomposition (500–600 °C) to produce films of aluminium nitride was studied.

Several reviews on metal amides have been published in recent years.[1–5] The chemistry of molecules containing Al–N bonds has been receiving special attention due to their potential use as single-source precursors for the deposition of AlN thin films. Compounds such as hexakis(dimethylamido)dialuminium, $Al_2(NMe_2)_6$,[6–8] azides of formula $(R_2AlN_3)_3$ (R = Me or Et)[9–12] and amides of formula $(R^1{}_2AlNR^2{}_2)_n$ (R^1 = Me; R^2 = H, Me or Pr^i; $n = 2$ or 3)[13–20] have been used to deposit polycrystalline AlN films, although an atmosphere of ammonia is required to obtain good-quality material.

We now report the results of a systematic study of the synthesis and characterization of a range of dialkylaluminium dialkylamides $(R^1{}_2AlNR^2{}_2)_2$.

Results and Discussion

The dialkylaluminium dialkylamides whose formulae are written in Table 1 were synthesized or an attempt was made to synthesize them by using the thermal elimination of alkane from the corresponding adducts of formula $R^1{}_3Al{\cdot}NHR^2{}_2$ [equation (1)]. Some of these amides (also indicated in Table 1)

$$2R^1{}_3Al{\cdot}NHR^2{}_2 \longrightarrow (R^1{}_2AlNR^2{}_2)_2 + 2R^1H \qquad (1)$$

were pyrolysed to investigate the role that R^1 and R^2 alkyl groups play in giving aluminium nitride or aluminium metal films in the light of previous work.[18,19] Based on the behaviour of these adducts at room temperature, 110 °C (b.p. of toluene) and above 110 °C, the following order of thermal stability, as R^2 varies, was found: phenyl < alkyl < tmpip ≈ $SiMe_3$.

The ready elimination of alkane when R^2 = phenyl is well known[22] and has been attributed to the greater acidity of the amino proton in the $R^1{}_3Al{\cdot}NHPh_2$ adducts. Its greater acidity arises from the electron-withdrawing effect of the phenyl groups compared with the more electron-donating alkyl groups. On first inspection, the difficulty in eliminating alkane when R^2 = tmpip or $SiMe_3$ could be explained in terms of steric hindrance which prevents the amino proton from reacting with the R^1 group. However, bulkier alkyl(mono- and bis-trialkylsilylamino)aluminium compounds of general formula $R^1{}_xAlN(SiR^3{}_3)_{3-x}$ (R^1 = Et or Me; R^3 = Me, Et or Ph; x = 1 or 2) have been obtained by the alkane-elimination method at temperatures as low as 40 °C.[23]

The alkane-elimination method did not work for adducts such as $Pr^i{}_3Al{\cdot}NHPr^i{}_2$ and $Bu^t{}_3Al{\cdot}NHR^2{}_2$ (R^2 = Me, Et, Bu^i or Pr^i), where the aluminium atom is attached to the bulky Pr^i or Bu^i groups. Yellow, highly viscous liquids were isolated after these adducts were heated in boiling toluene. The same happened when neat $Pr^i{}_3Al{\cdot}NHPr^i{}_2$ was heated in an oil-bath at 40, 60 and 80 °C. These yellow, viscous products were not characterized. These results suggest that bulky groups attached to the aluminium atoms preclude alkane elimination, whatever the temperature. Interestingly, when $Bu^t{}_3Al{\cdot}NHPh_2$ was heated at 60 °C dissociation into the starting materials, *i.e.* $AlBu^t{}_3$ and $NHPh_2$, occurred. The bulky Bu^t group evidently destabilizes the Al←N bond and alkane elimination is prevented.

All of the dialkylaluminium dialkylamides have a common framework in which alkyl groups are attached to a four-membered $(AlN)_2$ ring. The framework undergoes distortion according to the steric and electronic effects of R^1 and R^2 groups. To identify possible trends associated with these effects, spectroscopic and structural values were tabulated in increasing order and associated with their respective R^1 and R^2 alkyl groups. The resulting tables are presented and discussed as follows.

Infrared spectra (Table 2)

Most of the compounds did not show well resolved spectra in which the ν_{asym}(Al–C), and ν(Al–N) frequencies could be unambiguously assigned. The difficulties for assignment are: (*a*) partial (*i.e.* appearance of shoulders) or complete overlap of the ν_{asym}(Al–C), ν_{sym}(Al–C) and unassigned frequencies; (*b*) variation in intensities of the ν(Al–N) frequencies from strong to weak, sometimes with disappearance of peaks as evidenced in Fig. 1. In another work involving similar amides the infrared peaks were not assigned, possibly due to these difficulties.[24] Despite these difficulties, 'assignments' based on the literature values[25,26] are given in Table 2. The approximate nature of the assignments must be stressed, however, because the force constants and reduced masses that characterize each bond will be very similar, producing a degree of coupling between Al–C and Al–N vibrations and hence a range of molecular vibrations.

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* *Non-SI unit employed:* Torr ≈ 133 Pa.

Table 1 Numbering scheme for dialkylaluminium dialkylamides synthesized or attempted to be synthesized[a]

	$AlMe_3$	$AlEt_3$	$AlBu^i_3$	$AlPr^i_3$	$AlBu^t_3$
$NHMe_2$	$(Me_2AlNMe_2)_2$ **1**[b]	$(Et_2AlNMe_2)_2$ **2** (liquid)[b]	$(Bu^i_2AlNMe_2)_2$ **3**[b]	$(Pr^i_2AlNMe_2)_2$ **4**[c]	$(Bu^t_2AlNMe_2)_2$ **5**[c,d]
$NHEt_2$	$(Me_2AlNEt_2)_2$ **6**[b]	$(Et_2AlNEt_2)_2$ **7** (liquid)[b]	$(Bu^i_2AlNEt_2)_2$ **8**[b]	$(Pr^i_2AlNEt_2)_2$ **9**[b,c]	**10**
$NHBu^i_2$	$(Me_2AlNBu^i_2)_2$ **11**[b,c]	$(Et_2AlNBu^i_2)_2$ **12**[b,c]	$(Bu^i_2AlNBu^i_2)_2$ **13**[b,c]	$(Pr^i_2AlNBu^i_2)_2$ **14**[c]	**15**
$NHPr^i_2$	$(Me_2AlNPr^i_2)_2$ **16**[b]	$(Et_2AlNPr^i_2)_2$ **17**[b]	**18**	$(Pr^i_2AlNPr^i_2)_2$ **19**	**20**
hmds	$Me_2AlN(SiMe_3)_2$ **21**[e]	**22**	**23**	**24**	**25**
$NHPh_2$	$(Me_2AlNPh_2)_2$ **26**	$(Et_2AlNPh_2)_2$ **27**	$(Bu^i_2AlNPh_2)_2$ **28**	$(Pr^i_2AlNPh_2)_2$ **29**[e,f]	$(Bu^t_2AlNPh_2)_2$ **30**[e]
Htmpip	$[Me_2Al(tmpip)]_2$ **31**[e]	$[Et_2Al(tmpip)]_2$ **32**[e]	$[Bu^i_2Al(tmpip)]_2$ **33**[e]	**34**	**35**

Htmpip = 2,2,6,6-Tetramethylpiperidine. Hmds = hexamethyldisilazane. [a] The experimental work refers to all amides whose molecular formulae are shown. [b] Used in pyrolysis experiments. [c] New compound. [d] Obtained by salt-elimination route.[21] [e] Attempted synthesis. [f] The monomer $Pr^i_2Al(OEt_2)NPh_2$ was obtained using a salt-elimination route.

Table 2 Assignments of infrared bands (cm^{-1}) $(R^1_2AlNR^2_2)_2$ compounds

R^1	R^2	Compound	Molecular symmetry	ν_{asym}(Al–C)	ν_{sym}(Al–C)	(?)[a]	ν(Al–N)
Me	Me	**1**	C_i	697s (br)	586s	—	510s
	Et	**6**	C_2	689vs	610s	567w	—
	Bu^i	**11**	C_1	689vs	666s (sh)	595s	—
	Pr^i	**16**	?	682vs (br)	645s (sh)	569m	—
Et	Me	**2**	D_{2h}[b]	658vs (br)	—	564vs (sh)	525s
	Et	7	D_{2h}[b]	633s (br)	612s (sh)	—	520w
	Bu^i	**12**	?	644vs (br)	623s (sh)	581vs (sh)	511w
	Pr^i	**17**	C_2	644vs	595s	555m (sh)	523w
Bu^i	Me	**3**	C_i	682vs	595s	—	530vs
	Et	**8**	C_1	699s	601s	572s	—
	Bu^i	**13**	?	672vs	586m	567m	—
Pr^i	Me	**4**	C_i	624s	550vs	—	498s
	Et	**9**	C_2	—	604vs	—	508w
Bu^t	Me	**5**	C_i	572 (sh) s	—	555s	514m

[a] Unassigned peak; see discussion. [b] Based on averaged intramolecular motion in the liquid.

The infrared activity of these normal modes of vibration will be dependent on the symmetry: the centre of symmetry in molecules of point group C_i should render the a_g modes IR inactive.

Assuming intramolecular motion in liquids will produce an apparent centre of symmetry in compounds **2** and **7** (and an ultimate symmetry D_{2h}) then these, along with crystallographically centrosymmetric compounds **1**, **3**, **4** and **5** (of point group C_i) should have no IR-active a_g (for D_{2h}) or a′ (for C_i) modes. All these compounds are missing either the second or third peak in Table 2. The only other compound with such an absence is **9**, which has such an intense peak at 604 cm^{-1} it is likely to have obscured any other peaks near it. [Indeed, the ν_{asym}(Al–C) is also apparently absent.] Those compounds found with this absence match predictions from crystallographic data (see below), *viz.* a molecular centre of symmetry will be present in solids only when R^2 is small. All those compounds known to be non-centrosymmetric (**6**, **8**, **9**, **11** and **17**) show three peaks between 700 and 550 cm^{-1}, as do all compounds with R^2 larger than an ethyl group. The infrared data therefore indicates that no molecular centre of symmetry exists for any of these compounds. A two-fold axis will not have such an effect on the IR activity, so distinguishing C_2 from C_1 molecular symmetry is not possible by peak absences in infrared spectra; the absence of data for the nominal ν(Al–N) in Table 2 must be because the intensity is too low.

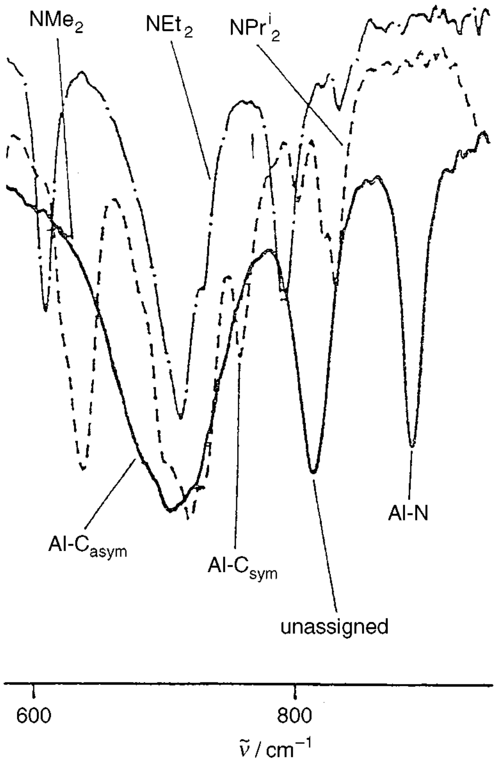

Fig. 1

^{1}H NMR (Table 3)

The α- and β-protons of the R^2 group become more deshielded as R^1 becomes bulkier. This could be attributed to the collision complex effect[27] which is explained as follows: due to the donation of the lone pair from nitrogen to aluminium to form the $(AlN)_2$ four-membered ring, the R^2 protons acquire a partial positive charge which interacts with the ring current of the aromatic solvent molecules ([$^2H_6$]benzene). Increasing steric hindrance of the R^1 groups minimizes this R^2 proton–solvent interaction, leading to increasing deshielding of the R^2 protons. Similarly, deshielding of the R^2 α-protons as R^2 becomes bulkier and R^1 is kept constant is also supposed to be due to steric hindrance in precluding the formation of the solvent collision complex. Concerning the β-protons of the R^2 group, the deshielding trend appeared (except for an anomaly in the $R^2 = Bu^i$ series) as R^1 becomes bulkier. Although significant changes in chemical shift were observed for the R^1 protons when R^2 was varied, no trend was found.

Table 3 The α- and β-proton chemical shifts (C_6D_6, 250 MHz) of R^2 as R^1 becomes bulkier

	R^2			
R^1	Me	Et	Bu^i	Pr^i
(*a*) α-Protons				
Me	2.130	2.720	2.865	3.685
Et	2.180	2.740	2.910	3.620
Bu^i	2.120	2.820	3.050	
Pr^i	2.320	2.905		
(*b*) β-Protons				
Me		0.820	2.080	1.250
Et		0.850	2.050	1.255
Bu^i		0.900	2.215	
Pr^i		0.995		

Table 4 Intensity and *m*/*z* values of the $[M^+ - R^1]$ species

		m/*z*	
Compound	Intensity	Found	Calc.
1 $(Me_2AlNMe_2)_2$	100	187.1335	187.1335
2 $(Et_2AlNMe_2)_2$	100	229.1810	229.1806
3 $(Bu^i{}_2AlNMe_2)_2$	96	313.2745	313.2744
4 $(Pr^i{}_2AlNMe_2)_2$	95.7	271.2280	271.2274
7 $(Et_2AlNEt_2)_2$	100	285.2457	285.2430
8 $(Bu^i{}_2AlNEt_2)_2$	100	369.3380	369.3370
9 $(Pr^i{}_2AlNEt_2)_2$	100	327.2900	327.2900
11 $(Me_2AlNBu^i{}_2)_2$	92	327.2942[a]	327.2900
12 $(Et_2AlNBu^i{}_2)_2$	100	397.3688	397.3643
13 $(Bu^i{}_2AlNBu^i{}_2)_2$	50.6	481.4678	481.4622
16 $(Me_2AlNPr^i{}_2)_2$	37.4	299.2594	299.2587
17 $(Et_2AlNPr^i{}_2)_2$	100	341.3051	341.3057

[a] $P^+ - Pr$.

Mass spectra

The main feature of the mass spectra (Table 4) is the existence of the $[\text{dimer} - R^1]^+$ species as the most intense Al-containing species. This showed that the dimeric species retained their integrity in the vapour phase, although the lower intensities for compounds **13** and **16** suggest significant dissociation to monomers. Significant peaks were also present for $[\text{monomer} - R^1]^+$ species for several compounds together with other fragment ions (see Experimental section).

Physical appearance (Table 1)

These compounds are either colourless liquids [$(Et_2AlNMe_2)_2$ and $(Et_2AlNEt_2)_2$] or white solids (all of the others). According to the literature[24] compounds of formula $(Me_2AlNR^2{}_2)_2$ (where R^2 = Et, Pr^n, Pr^i or Bu^i) are colourless liquids.

Crystallization into large, cubic, colourless crystals in light petroleum was a common feature of the $(R^1{}_2AlNPh_2)_2$ compounds. Additionally they start to decompose (becoming green) under a nitrogen flow or, more precisely, by residual moisture or oxygen contaminants in the nitrogen. Further decomposition leads to darkening and destruction of the crystalline structure. Such decomposition observed for $(Me_2AlNPh_2)_2$ was attributed to light sensitivity of this compound.[24] However we observed that decomposition occurred even in the dark after being exposed to a flow of nitrogen or even in the glove-box nitrogen atmosphere. This suggests that the decomposition process, once started, continues in the absence of the factor which triggered it. Further studies must be made to check if a trigger effect, in fact, occurs.

The markedly greater sensitivity of the arylamides compared with the alkylamides may then indicate that the aluminium is much more open to chemical attack. Also, diethylaluminium diphenylamide can form an adduct with diethyl ether (**29**) which is probably typical of all these arylamides (but certainly not of the alkylamides, which are stable dimers in ether). This suggests that their energy of dimerization is small. This shows that the weak Lewis basicity of arylamines persists into the aluminium amide compounds.

Crystal structures (Fig. 2)

The Al–C and N–C bonds lie above and below the plane which contains all the four atoms of the planar $(AlN)_2$ ring but the aluminium and nitrogen atoms undergo significant distortions from the ideal tetrahedral geometry. Ring angles at aluminium range from 86.5(2) to 89.1(2)° and at nitrogen from 87.6(2) to 93.5(2)°. The focus of the analysis is to assess in which degree steric and electronic contributions affect the bond angles, planarity, non-bonding distances and bond lengths. In these analyses the experimental data (Table 5) are compared with the literature data (Table 6) which are mostly related to compounds of formula $(R^1{}_2AlNHR^2)_2$ where both R^1 and R^2 groups are alkyls.

Mean values of bond distances (Table 7) and angles (Table 8) are arranged in increasing order and associated with their respective R^1 and R^2 groups. Trends which show how these crystallographic parameters vary by changing R^1 and R^2 groups are clearest when considered over the whole range of values rather than between adjacent values which are usually comparable within the experimental error. Additionally, the fact that some rings are planar while others are non-planar complicates comparisons. Bearing in mind such difficulties, we identify the following six trends.

(1) The Al–C [Table 7(*c*)] and N–C [Table 7(*d*)] bond lengths increase as R^1 and R^2 become bulkier respectively. The lengthening of the Al–C bonds as R^1 becomes bulkier could be due to either or both of the following two factors: (*a*) increasing steric repulsion among the R^1 groups and (*b*) reduction of the ionic contribution of the $Al^{\delta+}\rightarrow C^{\delta-}$ bond by increased electron donation of bulkier R^1 groups to the carbon atom whose electronegativity is consequently diminished. Conversely, the increased electron donation of bulkier R^2 groups increases the ionic character of the $N^{\delta-}\leftarrow C^{\delta+}$ bond by reducing the carbon electronegativity and should then shorten the bond. As a result, only the steric effect can account for the increase in the N–C bond length as R^2 becomes bulkier.

(2) The Al–N bond lengths undergo little variation with R^1 and R^2 bulkiness presumably due to the high rigidity of the ring. This ring rigidity is underlined in Table 9: Δ_{Al-N} is smaller than Δ_{Al-C}. The symbol Δ defines the maximum variation of a certain crystallographic parameter in a range of compounds. Then Δ_{Al-N}, Δ_{Al-C}, $\Delta_{Al\cdots Al}$, $\Delta_{N\cdots N}$, $\Delta_{Al-N-Al}$, Δ_{N-Al-N} mean the maximum variation undergone by the Al–N and Al–C bond distances, Al···Al and N···N non-bonded distances and Al–N–Al and N–Al–N endocyclic angles, respectively; Δ^i accounts for the variation within a compound.

(3) The Al···Al [Table 7(*a*)] and N···N [Table 7(*e*)] non-bonded distances increase as R^1 and R^2 becomes bulkier, respectively. This is mostly due to the repulsion between the R^1 groups along the Al···Al line and, similarly, between R^2 groups along the N···N line. The repulsion is more severe along the Al···Al vector: $\Delta_{Al\cdots Al}$ is *ca.* 70% greater than $\Delta_{N\cdots N}$. The larger size of the aluminium atom could account for this situation. Non-bonded distance variations in the Al_2N_2 rings could be useful in spectroscopic studies involving spatial electronic interaction between atoms of groups attached to these atoms.

(4) Ring distortions occur with decreases in the N–Al–N [Table 8(*c*)] and Al–N–Al [Table 8(*a*)] angles as R^1 and R^2 increases respectively. Relief of this tension could be achieved by substituting alkyl groups by hydrogen, which could then lead to the formation of the trimeric six-membered ring with the

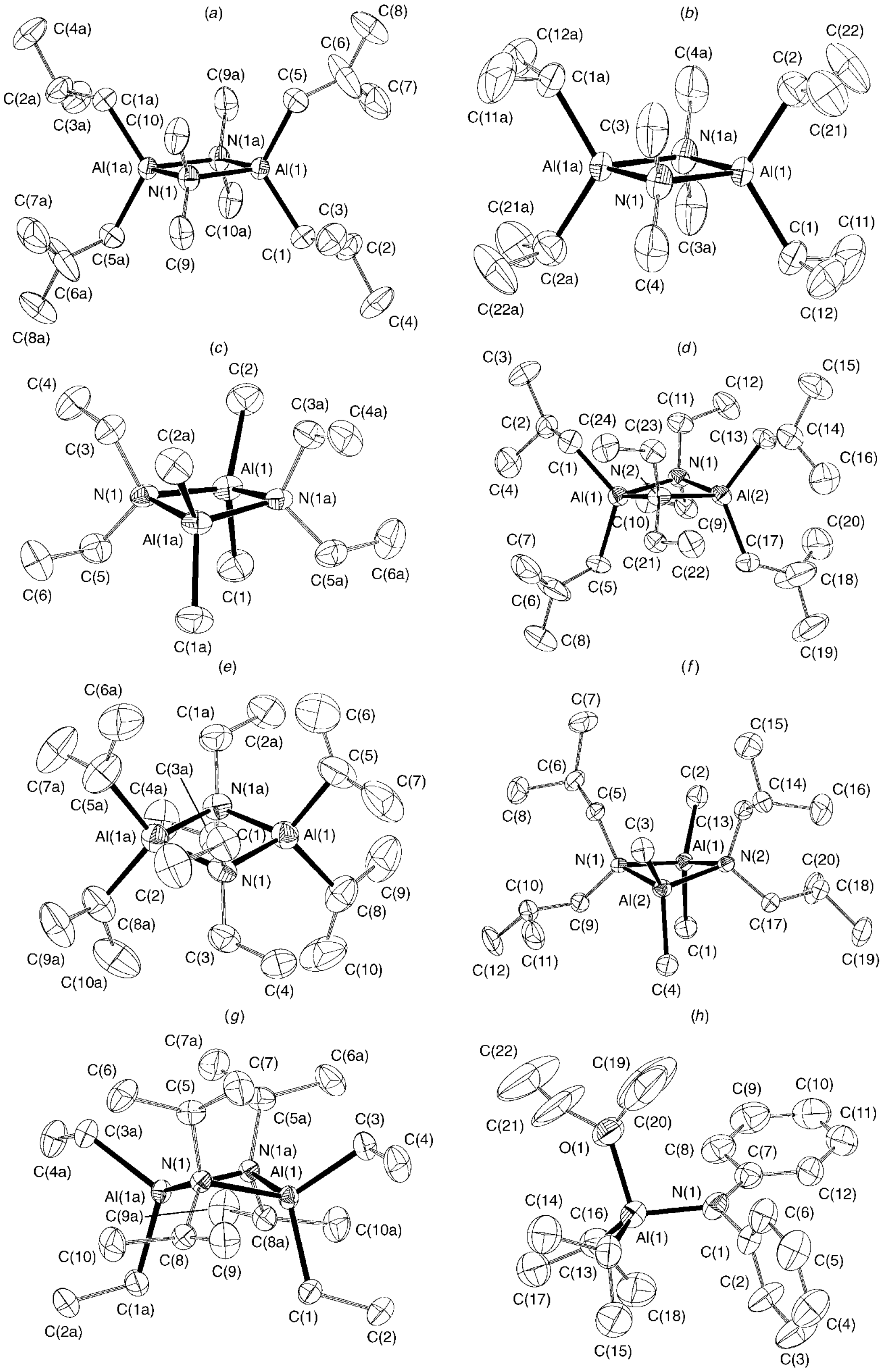

Fig. 2

N–Al–N and Al–N–Al angles larger than 100 and 115° respectively.[38]

(5) The C–N–C angle increases as R^2 becomes bulkier [Table 8(*b*)]. This is probably due to repulsion between R^2 electron clouds, with intraamido repulsion being greater than the interamido repulsions across the Al_2N_2 ring.

(6) The separation (*S*) of the midpoints of the N ⋯ N and Al ⋯ Al vectors [Table 7(*f*)] increases as R^2 becomes bulkier (Table 10) but does not show a trend associated with increasing bulkiness of R^1. This shows that the planarity of the ring is more sensitive to the bulkiness of R^2 than R^1 which reflects the smaller size of the nitrogen atom with less room than the aluminium atom to accommodate bulky groups. A similar conclusion was drawn in comparing the organo amides of formula $[(Me_3CCH_2)_6AlNHR]_2$ [R = adamantyl, Bu^t or C_6H_3-Pr^i_2-2,6].[35]

These six trends can be summarised as follows: as the bulk of R^1 increases the Al–C bonds extend and the two aluminium

Table 5 Experimental mean crystallographic values of the $(R^1_2AlNR^2_2)_2$ compounds

			Distance/Å		Angle/°	
Compound	Molecular symmetry	Planarity of $(AlN)_2$	Al–N	Al···Al	Al–N–Al	N–Al–N
3	C_i	Yes	1.962(5)	2.833(5)	92.4(1)	87.6(1)
4	C_i	Yes	1.953(6)	2.831(4)	97.7(1)	87.3(1)
5[21]	C_i	Yes	1.994(4)	2.903(3)	93.5(2)	86.5(2)
6	C_2	No	1.962(5)	2.793(5)	90.8(3)	88.5(3)
8	C_1	No	1.987(10)	2.835(7)	91.1(4)	87.4(4)
9	C_2	No	1.976(5)	2.841(5)	91.9(7)	88.0(3)
11	C_1	No	1.984(5)	2.774(5)	88.6(2)	89.1(2)
17	C_2	No	2.009(4)	2.781(1)	87.6(1)	88.4(1)

Table 6 Literature mean crystallographic values of $(R^1_2AlNR^2_2)_2$ compounds

				Distance/Å		Angles/°		
Compound*	Isomer	Symmetry	Planarity of Al_2N_2	Al–N	Al···Al	Al–N–Al	N–Al–N	Ref.
$[(Me_3Si)_2AlNH_2]_2$		C_i	Yes	1.955(2)	2.838(1)	93.1(1)	86.9(1)	28
$[Me_2AlN(H)C_6H_4Me\text{-}o]_2$	*trans*	C_i	Yes	1.957(7)	—	93.2(3)	86.3(3)	29
$[Me_2AlN(H)C_6H_3Me_2\text{-}2,6]_2$	*trans*	—	—	—	—	—	—	29
$[Me_2AlN(H)C_6H_3Pr^i_2\text{-}2,6]_2$	*trans*	C_1	No	1.987(12)	2.894(10)	94.7(5)	82.6(4)	30
		C_1	No	*2.025(11)*	*2.998(8)*	*94.2(4)*	*83.6(4)*	
$[Me_2AlN(H)R^1]_2$	*trans*	C_i	Yes	1.963(2)	2.859(1)	93.5(1)	86.5(1)	30
		C_i	Yes	*2.0245(3)*	*2.977(1)*	*94.7(1)*	*85.3(1)*	31
$[Me_2AlN(H)R^2]_2$	*trans*	C_1	No	1.978(4)	—	93.2(2)	86.2(1)	32
$[Me_2AlN(H)SiEt_3]_2$	*trans*	C_i	Yes	1.967(3)	2.802(3)	90.8(1)	89.2(1)	33
$[Me_2AlN(H)SiPh_3]_2$	*trans*	C_i	Yes	1.971(3)	2.832(2)	91.8(1)	88.2(1)	33
$[Me_2AlN(H)Pr^i_2]_2$	*trans*	C_{2h}	Yes	1.959(5)	2.789(4)	90.8(2)	89.2(2)	34
$[Me_2AlN(H)Pr^i_2]_2$	*cis*	C_{2v}	No	1.949(4)	2.800(3)	91.5(2)	87.4(2)	34
$[Bu^i_2AlN(H)R^2]_2$	*cis*	C_1	Yes	1.975(8)	—	94.0(4)	85.8(4)	32
$[(Me_3CCH_2)_2AlN(H)R^1]_2$	*cis*	C_2	No	1.966(12)	2.877(9)	94.2(6)	81.6(6)	35
$[(Me_3CCH_2)_2AlN(H)Bu^t]_2$	*cis*	C_2	No	1.987(7)	2.870(5)	93.1(3)	83.5(3)	35
$[(Me_3CCH_2)_2AlN(H)C_6H_3Pr^i_2\text{-}2,6]_2$	*cis*	C_1	Yes	2.015(5)	2.954(3)	94.5(2)	85.4(2)	35
$[(Me_3CCH_2)_2AlN(H)R^2]_2$	*cis*	C_1	Yes	1.989(3)	2.881(2)	92.9(1)	87.1(1)	35
$[Me_2AlN(R^3)]_2$	—	C_i	Yes	2.005(–)	2.790(1)	89.5(3)	90.5(2)	36
$[Me_2AlN(SiMe_3)_2]_2$	—	C_1	Yes	1.992(2)	2.813(1)	89.8(1)	90.2(1)	36
$[Me_2AlNMe_2]_2$	—	C_i	Yes	1.963(3)	2.815(3)	91.6(3)	88.4(3)	37

—, Data not available. * R^1 = Adamantan-1-yl; R^2 = biphenyl-2-yl; $HN(R^3)$ = 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane. Italics refer to gallium analogues.[30,31]

atoms in a molecule move further apart (with concomitant effects on both the Al···Al distance and N–Al–N angle). The lack of a trend within the C–Al–C angles shows that geminal alkyl repulsion is balanced by repulsion between the metal alkyls and the amide groups. As the bulk of R^2 increases, however, not only do the N–C bonds stretch and the nitrogen atoms move apart, but the C–N–C angles increase. This shows that the repulsion between alkyl groups on the same nitrogen atom is greater than the repulsions between these and the metal alkyls and hence also greater than the repulsions between geminal metal alkyls. This reflects the shortness of the N–C bond compared to the Al–N bond.

Another effect of bulky R^2 groups is to distort the $(AlN)_2$ ring out of a planar configuration. Increasing R^2 bulk gives increasing distortion. Neither R^1 nor R^2 has a clear effect on the Al–N bond, which changes least of all these parameters, so it is by distorting the $(AlN)_2$ ring that steric compressions between amides across the ring is relieved. Compression between the aluminium alkyls across the ring is far less, in part because Al–C bonds are longer and in part because the Al···Al distance is longer than the N···N distance (Al–N–Al angles are not, within experimental error, acute), both placing these alkyls further apart.

Distortion of a planar $(AlN)_2$ ring results in a change of molecular symmetry (Table 5). This change (from C_i) is in the form of a loss of a centre of symmetry; sometimes a two-fold axis is gained (to give C_2), sometimes no new symmetry element occurs (so the molecular symmetry is C_1). In the latter case, however, equivalent angles and bond lengths within the molecule remain the same within experimental error (Table 10). Loss of a centre of symmetry also affects the number of normal molecular vibrations which can be detected by infrared spectroscopy. The loss of a centre of symmetry when the R^2 group is large is predicted from the crystallography results and is in perfect agreement with the trend found in the infrared spectra (see above).

In the structure of $Et_2Al(Et_2O)(NPh_2)$ **29** [Fig. 2(*h*)] the aluminium atom is co-ordinated by the Et_2O oxygen, and the Al–N bond length is within the range of the Al–N bond lengths found for monomeric amides (1.78–1.88 Å).[40,41] This is significantly shorter than the Al–N bond lengths found in the nitrogen-bridging dimeric amides (1.95–2.02 Å). The weakness of the Al–O bond is suggested by the long Al–O bond length [1.938(7) Å]. The angles around the four-co-ordinate aluminium of this etherate complex range from 101.3(3) to 117.8(4)° in a distorted tetrahedral environment. On the other hand, the angles around the three-co-ordinate nitrogen atom add up to 359.6 ± 0.5° which shows that the N is trigonal planar.

Pyrolysis experiments

The films and powders produced by low-pressure metal-organic vapour chemical deposition (MOCVD) were analysed by infrared spectroscopy and showed up to four major bands (Fig. 3) which have been assigned to O–H, Al–H, N–C and Al–X vibrations (X = N or C), based on literature values.[42,43] Most of the films and powders (the latter were analysed as Nujol mulls), irrespective of deposition temperature and nature of the precursor, exhibited the Al–H band which hydrolyses in the air giving the O–H band. In some cases, hydrolysis led to partial or

Table 7 Mean values of the atom separations (Å) in the $(R^1{}_2AlNR^2{}_2)_2$ compounds

(*a*)

Al···Al	R^1	R^2
2.774(5)^a	Me	Bu^i

2.781(1)^a	Et	Pr^i
2.793(5)^a	Me	Et
2.815(7)	Me	Me
2.827(6)	Pr^i	Me
2.831(4)^a	Bu^i	Et
2.833(5)	Bu^i	Me
2.841(5)^a	Pr^i	Et
2.903(5)	Bu^t	Me
2.954	CH_2CMe_3	*(H)Bu^t*

(*b*)

Al–N	R^1	R^2
1.953(5)^a	Me	Bu^i

1.958(5)^a	Me	Et

1.963(3)	Me	Me
1.960(6)	Pr^i	Me
1.968(5)	Bu^i	Me
1.980(5)^a	Pr^i	Et
1.984(5)^a	Bu^i	Et
1.994(4)	Bu^t	Me

2.009(2)^a	Et	Pr^i
2.015(5)	CH_2CMe_3	$C_6H_3Pr^i{}_2$-2.6

(*c*)

Al–C	R^1	R^2

1.956(7)^a	Me	Et
1.965(7)	Me	Me
1.964(7)^a	Me	Bu^i
1.965(6)	Bu^i	Me
1.970(8)	Pr^i	Me
1.979(7)^a	Bu^i	Et
1.981(2)^a	Et	Pr^i
1.989(7)^a	Pr^i	Et
2.044(5)	Bu^t	Me

(*d*)

N–C	R^1	R^2

1.436(4)	*Bu^i*	Biphenyl-2-yl
1.475(8)	Pr^i	Me
1.479(6)	Bu^i	Me
1.482(4)	Bu^t	Me
1.493(7)	Me	Me
1.494(6)^a	Pr^i	Et
1.496(7)^a	Bu^i	Et
1.498(6)^c	Me	Bu^i
1.501(7)^a	Me	Et
1.512(2)^a	Et	Pr^i

(*e*)

N···N	R^1	R^2
2.961	*Me*	*(H)R^c*

2.697	Pr^i	Me
2.717	Bu^i	Me
2.733	Bu^t	Me
2.737	Me	Me
2.737^a	Me	Et
2.742^c	Bu^i	Et
2.745	Pr^i	Et
2.786^c	Me	Bu^i
2.800^c	Et	Pr^i

(*f*)

S^b	R^1	R^2

0	Bu^t	Me
0	Bu^i	Me
0	Pr^i	Me
0	Me	Me
0.044(4)	Pr^i	Et
0.161(3)	Me	Et
0.238(5)	Bu^i	Et
0.278(4)	Me	Bu^i
0.376(2)	Et	Pr^i

Literature values (in italics) (see refs. in Table 6) are given when they are less or greater than the experimental values in order to assess the maximum variation of the crystallographic parameters. The dashed lines confine the range where trends were identified. ^{a} Non-centrosymmetric. ^{b} The separation of the midpoints of the N···N and Al···Al vectors. ^{c} R = Adamantan-1-yl.

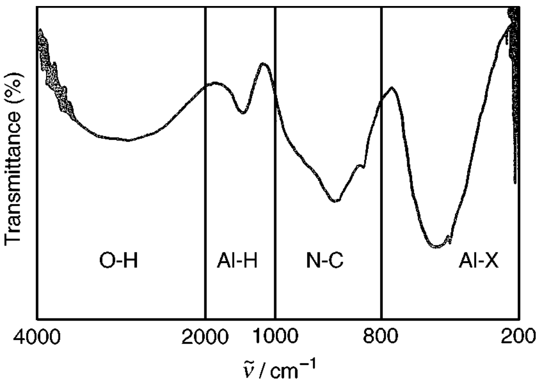

Fig. 3

Table 8 The Al–N–Al, C–N–C, N–Al–N and C–Al–C angles (°) in compounds of formula $(R^1{}_2AlNR^2{}_2)_2$

(*a*)

Al–N–Al	R^1	R^2

87.6(1)^a	Et	Pr^i
88.6(2)^a	Me	Bu^t
90.8(3)^a	Me	Et
91.1(2)^a	Bu^i	Et
91.6(3)	Me	Me
91.9(3)^a	Pr^i	Et
92.36(3)	Bu^i	Me
92.7(5)	Pr^i	Me
93.5(2)	Bu^t	Me

94.7(5)	*Me*	$C_6H_3Pr^i{}_2$-2,6

(*b*)

C–N–C	R^1	R^2

104.4(3)	Bu^t	Me
106.9(5)	Bu^t	Me
107.1(6)	Pr^i	Me
108.1(4)	Me	Me
110.0(4)	Pr^{ia}	Et
110.5(4)	Me^a	Et
111.2(5)	Bu^{ia}	Et
111.4(4)	Me^a	Bu^i
117.1(1)	Et^a	Pr^i

(*c*)

N–Al–N	R^1	R^2
81.6(6)	*Me*	(*H*)$C_6H_3Pr^i{}_2$-2,6

86.5(2)	Bu^t	Me
87.3(4)	Pr^i	Me
87.4(2)^a	Bu^i	Et
87.6(3)	Bu^i	Me
88.0(3)^a	Pr^i	Et
88.4(1)^a	Et	Pr^i
88.4(3)	Me	Me
88.5(3)^a	Me	Et
89.1(2)^a	Me	Bu^i
90.5(2)	*Me*	*b*

(*d*)

C–Al–C	R^1	R^2
106.4(4)^a	Pr^i	Et
109.4(1)^a	Et	Pr^i
113.1(2)	Bu^t	Me
115.7(4)^a	Me	Et
115.9(4)	Me	Me
116.4(4)^a	Me	Bu^i
116.9(4)	Pr^i	Me
119.0(3)	Bu^i	Me
120.6(3)^a	Bu^i	Et
126.5(3)	CH_2CMe_3	$C_6H_3Pr^i{}_2$-2,6

Literature values (in italics) (see refs. in Table 6) are given when they are less or greater than the experimental values in order to assess the maximum variation of the crystallographic parameters. The dashed lines confine the range where trends were identified. ^{a} Non-centrosymmetric. ^{b} $HN(R^2)$ = 2,2,5,5-Tetramethyl-1-aza-2,5-disilacyclopentane.

Table 9 Maximum variation (Δ) in endocyclic angles and bonded and non-bonded distances in the full range of experimental compounds

$\Delta_{\mathbf{Al}\cdots \mathrm{Al}}$	0.18 Å	$\Delta_{\mathbf{Al}\text{–C}}$	0.088(6) Å
$\Delta_{\mathbf{N}\cdots \mathrm{N}}$	0.109 Å	$\Delta_{\mathbf{Al}\text{–N–Al}}$	7.1°
$\Delta_{\mathbf{Al}\text{–N}}$	0.062(5) Å	$\Delta_{\mathbf{N}\text{–Al–N}}$	8.9°
$\Delta_{\mathbf{N}\text{–C}}$	0.076(14) Å		

Table 10 Bond distances (Å) and angles (°) of the compounds with C_1 symmetry

	8 $(Bu^i{}_2AlNEt_2)_2$	**11** $(Me_2AlNBu^i{}_2)_2$
Ring's outer angles		
C–Al(1)–C	120.7(3)	116.3(4)
C–Al(2)–C	120.6(3)	116.5(4)
C–N(1)–C	109.9(5)	111.5(4)
C–N(2)–C	110.6(5)	111.4(4)
Ring's inner angles		
N–Al(1)–N	87.4(2)	89.2(2)
N–Al(2)–N	87.1(2)	89.0(2)
Al–N(1)–Al	91.1(2)	88.6(2)
Al–N(2)–Al	91.1(2)	88.7(2)
Distance variation		
$\Delta^i{}_{\mathbf{Al}\text{–N}}$	0.010(7)	0.025(5)
$\Delta^i{}_{\mathbf{Al}\text{–N}}$	0.025(10)	0.010(8)
$\Delta^i{}_{\mathbf{Al}\text{–C}}$	0.026(11)	0.020(7)

total disintegration of the layer. The Al–H band survived at temperatures as high as 700 °C. Interestingly, compounds containing Al–H bonds such as alanes and their derivatives have been used as aluminium precursors in the deposition of $Al_xGa_{1-x}As$[44–54] materials by MOCVD, despite the great strength of the Al–H bonds. In fact, the Al–H bond is stronger than Al–C[55] which has been considered the main source of residual carbon contamination of the aluminium-containing materials.[44–54] The incorporation and elimination of hydrogen contaminants from aluminium-containing films could be, as is carbon contamination, an interesting subject for further studies. A common feature of the infrared spectra of the gaseous and liquid by-products of pyrolysis is the presence of N−H vibrations at 3320–3330 cm^{-1} which could be due to β elimination of alkene involving the dialkylamido group. Additionally the dialkylamido group could capture a hydrogen attached to the aluminium atom and eliminate an amine by breaking the Al−N bond.

Rough electrical measurements showed that adherent conductive and insulating films were deposited onto two different substrates in the same deposition experiment or even in different regions of the same substrate. This may be due to temperature gradients inside the reactor which favoured different modes of amide decomposition and, in turn, variation in the electrical conductivity of films. In general the conductive films are dark and the insulators are yellow or blue.

Conclusion

Dialkylaluminium μ-dialkylamido and dialkylaluminium μ-diarylamido compounds of formula $(R^1_2AlNR^2_2)_2$ were synthesized by alkane elimination from the corresponding adducts of formula $R^1_3Al{\cdot}NHR^2_2$. The ease of alkane elimination varies with R^2 in the order: phenyl < alkyl < tmpip < $SiMe_3$. The steric hindrance in $Pr^i_3Al{\cdot}NHPr^i_2$ and adducts where $R^1 = Bu^t$ led to decomposition without alkane elimination giving, as a result, an undesirable, yellow, highly viscous liquid.

The dialkylamido compounds are dimers and present a central rigid $(AlN)_2$ ring which becomes more folded along the N···N line as the R^2 group becomes bulkier. This has been shown qualitatively by infrared spectroscopy in all the compounds synthesized and quantitatively in those analysed by X-ray crystallography. The angles and bond lengths around the aluminium and nitrogen atoms are primarily affected by R^1 and R^2 groups respectively. The elongation of the Al−C bond as R^1 becomes bulkier could be attributed to either (or both) steric and electronic effects of the R^1 group. On the other hand the lengthening of the N−C bond as R^2 becomes bulkier was attributed solely to the steric effect of the R^2 group. Decreasing bulkiness of R^1 and R^2 alleviates the tension in the ring by increasing the Al−N−Al and N−Al−N angles respectively. The distortions of all remaining crystallographic parameters could be explained in terms of steric effects.

The crystal structure of $Et_2Al(Et_2O)(NPh_2)$, as far as we know, is the first of this class of compounds where the aluminium atom of a monomeric dialkylaluminium diphenylamide is co-ordinated with a Lewis base.

Depending on deposition temperature, conducting or insulating materials can be obtained from the same dialkylamido compound. The films all exhibited Al−H infrared bands irrespective of the deposition conditions.

Experimental

All compounds were manipulated under dry nitrogen using vacuum-line, glove-box and Schlenk-style apparatus. Proton NMR spectra were obtained at room temperature using a Bruker EM 250FT spectrometer with dried deuteriobenzene as solvent, infrared spectra (neat and Nujol mulls placed between CsI plates) in the 4000–200 cm^{-1} range using a Perkin-Elmer FT 1720X spectrophotometer and mass spectra using a Kratos MS 50 TC spectrometer operating at 70 eV (*ca.* 1.12×10^{-17} J). The analyses (C, H and N) were obtained from the Microanalytical Service of University College London. For structure determination, under a nitrogen atmosphere, a suitable single crystal was selected, attached to a glass fibre by using silicon grease and then mounted inside a 0.7 mm diameter glass capillary which was flamed sealed.

Table 11 gives the elemental analysis data for the amides. The remaining data, *i.e.* those obtained from infrared, ^1H NMR and mass spectra, are given below. In the mass spectral data the symbols P^+ and $P^+/2$ correspond to the dimer and monomer species respectively. In the IR data presentation the following abbreviations were used: s, strong; m, medium; w, weak; br, broad; sh, shoulder; v, very.

Table 11 Analytical data for $(R^1_2AlNR^2_2)_2$ compounds (calculated values in parentheses)

Compound	C	H	N
1	48.0 (47.5)	12.1 (12.0)	14.2 (13.9)
2	55.4 (55.8)	12.4 (12.5)	10.2 (10.8)
3	64.2 (64.9)	12.9 (13.0)	7.2 (7.6)
4	60.7 (61.1)	12.9 (12.8)	8.5 (8.9)
6	56.3 (55.8)	12.5 (12.5)	11.0 (10.8)
7	61.0 (61.1)	12.4 (12.8)	8.4 (8.9)
8	67.3 (67.6)	12.9 (13.1)	6.4 (6.6)
9	64.2 (64.9)	12.8 (13.0)	7.3 (7.6)
11	64.7 (64.9)	13.3 (13.0)	7.8 (7.6)
12	67.3 (67.6)	13.3 (13.1)	6.6 (6.6)
13	71.1 (71.3)	13.7 (13.5)	5.4 (5.2)
16	61.1 (61.1)	13.0 (12.9)	8.6 (8.9)
17	63.3 (64.9)	12.8 (13.0)	7.2 (7.6)
26	73.1 (74.6)	6.6 (7.2)	6.8 (6.2)
27	74.6 (75.8)	7.8 (8.0)	5.8 (5.5)
28	77.1 (77.6)	9.3 (9.1)	5.1 (4.5)
29	72.1 (74.1)	9.7 (9.6)	4.0 (3.9)

Dialkylaluminium μ-dialkylamido compounds of formula $(R^1_2AlNR^2_2)_2$ (where R^1, R^2 = Me, Et, Pr^i or Bu^i) were obtained by heating the corresponding adduct in boiling toluene for at least 2 h, allowing to cool to room temperature and removing the solvent in vacuum. Residues were then sublimed or distilled at 10^{-2} Torr and the resulting liquids were distilled. All compounds were either white solids or colourless liquids. Crystals for X-ray diffraction analysis were grown from light petroleum at −25 °C. In Table 12 the experimental conditions used for obtaining each compound are given together with the respective yield, physical appearance and melting point.

Dialkylaluminium μ-diarylamido compounds of formula $(R^1_2AlNPh^2_2)_2$ (R^1 = Me, Et, Pr^i, Bi^i or Bu^t) were obtained (or a synthesis was attempted) by adding the stoichiometric amount of diphenylamine to a light petroleum (b.p. 35–60 °C) solution of the trialkylaluminium at room temperature. After 1 h of reaction the mixture was left at −25 °C whereupon colourless crystals were deposited. The experimental conditions for synthesis and purification of dialkylaluminium μ-diphenylamido compounds are summarized in Table 6(*b*). These compounds are very air sensitive, decomposing partially even under a nitrogen atmosphere, turning green and in severe cases becoming an amorphous black solid. They decomposed when mixed with Nujol, giving a black mull, so no IR spectra were recorded for them.

Attempted syntheses

Most of the syntheses of alkyl- and aryl-amides were performed as above. In those cases, namely compounds **29**, **31**, **32** and **33**, where a different synthesis procedure was used this is given together with the characterization data below.

Pyrolysis

The compounds were pyrolysed as thin films onto silicon substrates using a horizontal, hot-wall quartz reactor operating at low pressure (10^{-2} Torr) in the 500–600 °C temperature range. The silicon substrates were mirror polished on both sides and, before each deposition experiment, they were degreased with trichloroethylene (Aldrich, spectrophotometric grade) at 60 °C for 30 min followed by absolute ethanol at 40 °C for 30 min. Then they were rinsed with doubly distilled water and finally dried in a stream of nitrogen. The films were analysed by infra-

Table 12 Experimental conditions for synthesis and purification

(*a*) $(R^1{}_2AlNR^2{}_2)_2$ compounds

Compound	Adduct amount		Heating time/h	Purification	Yield		Physical appearance	Melting point/°C
	g	mmol			g	%		
1	5.0	43.0	2	s, 40	4.1	95	w.s.	136–138
2	5.0	31.0	6	d, 90	3.5	87	c.l.	
3	4.0	16.0	6	d, 100 ^{a}	2.5	85	w.s.	44–46
4	2.5	12.5	6	s, 140	1.6	82	w.s.	129–131
6	5.0	34.0	6	d, 58 ^{a}	4.1	93	w.s.	40–42
7	4.5	24.0	3	d, 150 ^{a}	4.0	90	c.l.	
8	3.3	12.3	15	d, 110 ^{a}	2.3	89	w.s.	69–71
9	7.1	30.8	26	s, 110	5.3	93	w.s.	185–186
11	7.5	37.1	12	s, 110	6.1	89	w.s.	65–67
12	7.3	30.0	15	d, 120 ^{a}	5.4	84	w.s.	82–84
13	5.9	18.1	15	s, 120	4.5	92	w.s.	134–136
16	12.3	71.0	6	s, 110	9.0	80	w.s.	154 (decomp.)
17	5.0	23.2	15	100	3.5	70	w.s.	117 (decomp.)

(*b*) $(R^1{}_2AlNPh_2)_2$ compounds

Compound	$AlR^1{}_3$ mmol	$NHPh_2$/mmol	*t*/h	Physical appearance	Yield (%)
26	105.0	105.0	2	c.c.c. ^{c}	90
27	60.4	60.4	1	c.c.c	85
28	33.5	33.5	1	c.c.c	83
29 ^{d}	17.4	17.2	1	n.c.c. ^{e}	93
30 ^{f}	35.5	35.5	1	c.c.c	95

s = Sublimation. d = distillation, decomp. = decomposes, w.s. = white solid, c.l. = colourless liquid. ^{a} Solid melts before vaporization at 10^{-2} Torr. ^{b} The reactions occurred at room temperature and the products were isolated and purified by recrystallization from light petroleum at −25 °C. ^{c} Cubic-shaped, colourless crystals. ^{d} The compound obtained was $Pr^i{}_2Al(OEt_2)NPh_2$ because $R^1{}_3Al{\cdot}OEt_2$ was used as a reagent. ^{e} Needle-shaped colourless crystals. ^{f} In fact the corresponding adduct was obtained.

red spectroscopy using a FT-1720X model Perkin-Elmer spectrometer. Gaseous and liquid by-products of pyrolysis were analysed by Fourier-transform IR spectroscopy using KBr windows for both gas cells and plates respectively. The conductive nature of the films (conducting or insulating) was established with an ordinary ammeter (RS Avo 1000). The morphology of the films is described in terms of colour and adherence. Non-adherent films were considered to be those which could be easily removed or scratched from the substrate with tweezers.

Characterization data

Compound 1. IR, $\tilde{\nu}_{max}$/cm^{-1} (Nujol, CsI): 2922 (br)vs, 1461vs, 1378m, 1233s, 1198vs, 1118vs, 1041vs, 983w, 902vs, 697s (br), 586s, 510s and 348m. $\delta_H(C_6D_6$, 250 MHz), 0.530 (12 H, s, $AlCH_3$) and 2.130 (12 H, s, NCH_3). Mass spectrum: *m*/*z* 187 (100, $P^+ - Me$), 144 (14, Me_5HAlN^+), 100 [16, $(P^+/2) - H$], 86 [13, $(P^+/2) - Me$] and 57 (8%, Me_2Al^+).

Compound 2. IR, $\tilde{\nu}_{max}$/cm^{-1} (neat, CsI): 2911vs, 2863vs (br), 1461vs, 1408s, 1374w, 1233vs, 1192s, 1164m, 1121vs, 1043vs, 982vs, 953vs, 903vs, 659 (br) vs, 564 (sh) vs, 525 (sh) s, 496 (sh) and 368. $\delta_H(C_6D_6$ 250 MHz) 0.150 (8 H, q, $J = 7.5$, $AlCH_2$), 1.30 (12 H, t, $J = 7.5$ Hz, $AlCH_3$) and 2.180 (12 H, s, NCH_3). Mass spectrum: *m*/*z* 257 (6, $P^+ - H$), (20, $P^+ - C_2H_4$), 229 (100, $P^+ - Et$), 202, 201 (39%, $P^+ - Et - C_2H_4$), 86 [6, $(P^+/2) - Me - C_2H_4$] and 72 (21%, $HAlNMe_2{}^+$).

Compound 3. IR, $\tilde{\nu}_{max}$/cm^{-1} (neat, CsI): 2943vs, 1466s, 1401w, 1383s, 1361s, 1321m, 1231s, 1182s, 1160s, 1119vs, 1065vs, 1042vs, 1014m, 942w, 910vs, 819m, 682vs, 595s, 530vs and 432w. $\delta_H(C_6D_6$, 250 MHz) 0.175 (18 H, d, $J = 7$ Hz, $AlCH_2CH$), 1.120 (24 H, d, $J = 7$, CH_2CHCH_3), 2.050 (4 H, spt, $J = 7$ Hz, $AlCH_2CH$) and 2.210 (12 H, s, NCH_3). Mass spectrum: *m*/*z* 313 (96, $P^+ - Bu^i$), 257 (19, $P^+ - C_4H_8 - Bu^i$), 145 (11, $P^+ - 3C_4H_8 - Bu^i$), 128 [9, $(P^+/2) - Bu^i$] and 100 (12%, $P^+ - Bu^i - C_3H_6$).

Compound 4. IR, $\tilde{\nu}_{max}$/cm^{-1} (Nujol mull, CsI): 2895vs, 1450vs, 1383s, 1231s, 1209m, 1162m, 1117s, 1040s, 965s, 899s, 867s, 723w, 624s, 550vs, 498s and 327w. $\delta_H(C_6D_6$, 250 MHz) 0.540 (4 H, spt, $J = 7.5$, AlCH), 1.360 (24 H, d, $J = 7.5$ Hz, $ACHCH_3$) and 2.320 (12 H, s, NCH_3). Mass spectrum: *m*/*z* 271 (96, $P^+ - Pr^i$), 229 (100, $P^+ - Pr^i - C_3H_6$), 187 (9, $P^+ - Pr^i - 2C_3H_6$) and 114 [4%, $(P^+/2) - Pr^i$].

Compound 6. IR, $\tilde{\nu}_{max}$/cm^{-1} (Nujol mull, CsI): 2935s, 1462m, 1383s, 1292w, 1198s, 1178 (sh) m, 1132s, 1114s, 1045m, 1004m, 903m, 854m, 791s, 689vs, 610vs, 567w and 353m. $\delta_H(C_6D_6$, 250 MHz) −0.44 (12 H, s, $AlCH_2$), 0.820 (12 H, t, $J = 6$, NCH_2CH_3) and 2.720 (8 H, q, $J = 7$ Hz, NCH_2CH_3). Mass spectrum not available.

Compound 7. IR, $\tilde{\nu}_{max}$/cm^{-1} (neat, CsI): 2938 (br) vs, 1456m, 1411m, 1382s, 1292w, 1195m, 1177m, 1132s, 1113s, 1044m, 1004m, 981m, 956m, 920w, 901w, 854m, 791s, 633s (br) and 520w. $\delta_H(C_6D_6$, 250 MHz) 0.195 (8 H, q, $J = 8.8$, CH_2Al), 0.850 (12 H, t, $J = 7.5$, NCH_2CH_3), 1.145 (12 H, t, $J = 8.8$, $AlCH_2CH_3$) and 2.740 (8 H, q, $J = 7.5$ Hz, NCH_2CH_3). Mass spectrum: *m*/*z* 285 (100, $P^+ - Et$), 156 [10, $(P^+/2) - H$], 128 [17, $(P^+/2) - Et$], 100 (26, $HAlNEt_2{}^+$) and 98 [6%, $(P^+/2) - 2Et$].

Compound 8. IR, $\tilde{\nu}_{max}$/cm^{-1} (Nujol mull, CsI): 2935vs, 1403m, 1360s, 1316s, 1290w, 1210m, 1185s, 1159s, 1130s, 1110s, 1066s, 1043s, 1002s, 955 (sh) w, 942w, 901m, 853s, 819m, 790s, 722w, 669s (br), 601s, 572s, 420m, 400w, 383w and 359m. $\delta_H(C_6D_6$, 250 MHz) 0.31 (8 H, d, $J = 7.5$, $AlCH_2$), 0.90 (12 H, t, $J = 7.5$, NCH_2CH_3), 1.25 (24 H, d, $J = 6.3$, $AlCH_2CHCH_3$), 2.11 (4 H, m, $J = 7.5$, $AlCH_2CHCH_3$) and 2.82 (8 H, q, $J = 7.5$ Hz, NCH_2CH_3). Mass spectrum: *m*/*z* 369 (100, $P^+ - Bu^i$), 313 (45, $P^+ - Bu^i - C_4H_8$), 156 [7, $(P^+/2) - Bu^i$] and 128 [16%, $(P^+/2) - C_4H_8 - Et$].

Compound 9. IR, $\tilde{\nu}_{max}$/cm^{-1} (Nujol mull, CsI): 2922vs, 2852vs, 1456s, 1379s, 1290w, 1260w, 1212w, 1175w, 1130m, 1111m, 1042m, 1002m, 960m, 899w, 870m, 794m, 722w, 604s and 509w.

δ_H(C_6D_6, 250 MHz) 0.620 (4 H, s, $J = 7.5$, AlCH), 0.995 (12 H, t, $J = 7.5$, NCH_2CH_3), 1.375 (24 H, d, $J = 7.5$, $AlCHCH_3$), 2.905 (8 H, q, $J = 7.5$, $AlCHCH_3$) and 2.905 (8 H, q, $J = 7.5$ Hz, NCH_2CH_3). Mass spectrum: m/z 327 (100, $P^+ - Pr^i$), 285 (30, $P^+ - Pr^i - C_3H_6$), 214 (6, $P^+ - 2C_3H_6 - NEt_2$), 184 [6, $(P^+/2) - H$] and 142 [16%, $(P^+/2) - Pr^i$].

Compound 11. IR, $\tilde{\nu}_{max}$/cm^{-1} (Nujol mull, CsI): 2926vs, 1463vs, 1392s, 1298w, 1271w, 1199s, 1132w, 1060s, 977s, 955m, 926w, 896w, 863m, 829m, 808m, 689vs (br), 666 (sh) s, 595s, 456w, 399w (br), 326w and 305w. δ_H(C_6D_6, 250 MHz) 0.215 (12 H, s, CH_3Al), 0.920 (24 H, d, $J = 6.3$, $NCHCH_3$) 2.080 (4 H, spt, $J = 6.3$, NCH_2CHCH_3), 2.865 (8 H, d, $J = 6.3$ Hz, NCH_2). Mass spectrum: m/z 355 (92, $P^+ - Me$), 327 (21, $P^+ - Pr^i$), 297 (11, $P^+ - Bu^i - MeH$), 283 (6, $P^+ - Pr^i - HPr^i$), 242 (100, $P^+ - NBu^i_2$), 226 (6, $P^+ - NBu^i_2 - MeH$), 184 [39, $(P^+/2) - H$], 170 [47, $(P^+/2) - Me$], 168 [25, $(P^+/2) - 2MeH$], 154 [6, $(P^+/2) - Me - MeH$], 142 [66, $(P^+/2) - Pr^i$], 126 [9, $(P^+/2) - Pr^i - MeH$], 112 [11, $(P^+/2) - Bu^i - CH_4$], 86 (17, $NHBu^{i+}$) and 84 (6%, $HNBu^{i+} - H_2$).

Compound 12. IR, $\tilde{\nu}_{max}$/cm^{-1} (Nujol, CsI): 2922vs, 1417m, 1299w, 1274w, 1238w, 1205w, 1163w, 1131w, 1059s, 978s, 957 (sh) m, 924m, 892w, 863, 829m, 807w, 723w, 644vs, 581s, 511w, 462w, 420w, 398w and 339w. δ_H(C_6D_6, 250 MHz) 0.415 (8 H, q, $J = 7.5$, CH_3CH_2Al), 0.960 (24 H, d, $J = 7.5$, $CHCH_3$), 1.460 (12 H, t, $J = 7.5$, CH_3CH_2), 2.050 (4 H, spt, $J = 7.5$, $CHCH_3$) and 2.910 (8 H, d, $J = 6.3$ Hz, NCH_2). Mass spectrum: m/z 425 (7, $P^+ - H$), 397 (100, $P^+ - Et$), 311 (14, $P^+ - Et_2Al - EtH$), 212 [18, $(P^+/2) - H$], 184 [23, $(P^+/2) - Et$], 182 [7, $(P^+/2) - Et - H_2$], 156 [12, $(P^+/2) - Bu^i$], 154 [13, $(P^+/2) - Bu^i - H_2$], 112 [27, $(P^+/2) - Bu^i - H_2 - C_3H_6$] and 86 (18%, $NHBu^{i+}$).

Compound 13. IR, $\tilde{\nu}_{max}$/cm^{-1} (Nujol, CsI): 2927vs, 1465vs, 1391m, 1360m, 1323w, 1272w, 1209w, 1186m, 1159m, 1130w, 1066 (sh) s, 1054s, 1020m, 978m, 943w, 925w, 863m, 832m, 811m, 672vs, 586m, 567m, 470m, 434w and 333w. δ_H(C_6D_6, 250 MHz) 0.505 (8 H, d, $J = 6.3$, $AlCH_2$), 1020 (24 H, d, $J = 7.5$, NCH_2CHCH_3), 1.295 (24 H, d, $J = 6.3$, $AlCH_2CHCH_3$), 2.215 (8 H, m, $J = 7.5$, NCH_2CHCH_3 and $AlCH_2CHCH_3$) and 3.050 (8 H, d, $J = 6.3$ Hz, NCH_2CHCH_3). Mass spectrum: m/z 481 (51, $P^+ - Bu^i$), 426 (20, $P^+ - 2C_4H_8$), 370 (11, $P^+ - 3C_4H_8$), 298 (6, $P^+ - 2C_4H_8 - NBu^i_2$), 269 [10, $(P^+/2)$], 226 [64, $(P^+/2) - Pr^i$], 212 [19, $(P^+/2) - Bu^i$], 170 [45, $(P^+/2) - C_4H_8 - Pr^i$], 156 [40, $(P^+/2) - 2C_4H_8 - H$, 154 [22, $(P^+/2) - Bu^i - H$], 141 (13, $Bu^i_2Al - H$) and 129 (11%, $HNBu^i_2$).

Compound 16. IR, $\tilde{\nu}_{max}$/cm^{-1} (Nujol, CsI): 2943vs, 1466vs, 1403s, 1303w, 1199s, 1161vs, 1134vs, 955s, 917m, 835m, 763s, 682vs, 645s (sh), 599w, 569m, 443w, 376w and 339w. δ_H(C_6D_6, 250 MHz) −0.200 (12 H, s, CH_3Al), 1.250 (24 H, d, $J = 6.3$, $NCHCH_3$) and 3.685 (4 H, spt, $J = 7.5$ Hz, $NCHCH_3$). Mass spectrum: m/z 299 (37, $P^+ - Me$), 214 ($P^+ - NPr^i_2$), 157 [7, $(P^+/2)$], 156 [10, $(P^+/2) - H$], 142 [100, $(P^+/2) - Pr^i$], 126 [6, $(P^+/2) - HPr^i - HMe$], 86 (6, $NHPr^i_2 - Me$) and 57 (7%, Me_2Al^+).

Compound 17. IR, $\tilde{\nu}_{max}$/cm^{-1} (Nujol, CsI): 2924vs, 1464vs, 1308w, 1236w, 1161s, 1129vs, 981s, 956s, 916m, 833m, 756vs, 644vs, 595s, 555m, 523m, 446m, 378 (sh) w and 349m. δ_H(C_6D_6, 250 MHz) 0.395 (8 H, q, $J = 6.3$, $AlCH_2$), 1.255 (24 H, d, $J = 6.25$, $CHCH_3$), 1.430 (12 H, t, $J = 7.5$, CH_3CH_2Al) and 3.62 (4 H, spt, $J = 7.5$ Hz, $NCHCH_3$). Mass spectrum: m/z 341 (100, $P^+ - Et$), 270 (7, $P^+ - NPr^i - HNPr^i$), 184 [6, $(P^+/2) - H$], 170 [5, $(P^+/2) - Me$], 156 [32 $(P^+/2) - Et$], 128 [11, $(P^+/2) - Et - C_2H_4$] and 126 (6%, $P^+ - Et - C_2H_4 - H_2$).

Compound 21: attempted synthesis. The adduct trimethylaluminium–1,1,1,3,3,3-hexamethyldisilazane (3 g, 12.8 mmol) was heated under reflux in toluene overnight. The mixture was allowed to cool to room temperature and the solvent was removed in vacuum, leaving a white solid whose ^{1}H NMR spectrum revealed it to be the starting material. The same procedure was repeated in p-xylene (b.p. 135 °C) and in mesitylene (b.p. 162–164 °C) and again a white solid was obtained after the removal of the solvent in both cases. Only in the latter case the ^{1}H NMR spectrum indicated the presence of a trace of the amide (two additional singlets to those found in the adduct). We did not attempt to isolate the amide.

Compound 26. This is a very air-sensitive compound which decomposes partially even under a nitrogen atmosphere turning green and, in severe cases, becoming an amorphous black solid. It decomposed when mixed with Nujol giving, as a result, a black mull δ_H($C_6D_5CD_3$, 250 MHz) −0.305 (12 H, s, MeAl) and 6.710–7.310 (20 H, m, Ph).

Compound 27. This is also a very air-sensitive compound which decomposes partially even under a nitrogen atmosphere turning green and, in severe cases, becoming an amorphous black solid. It decomposed when mixed with Nujol giving, as a result, a black mull. δ_H(C_6D_6, 260 MHz) 0.250 (4 H, $J = 7.5$, CH_2Al), 1.195 (6 H, $J = 7.5$ Hz, CH_2CH_3) and 6.750–7.310 (10 H, Ph).

Compound 28. This is a white crystalline solid which is very air sensitive. It decomposes partially under a nitrogen atmosphere becoming green, and, in severe cases, becoming an amorphous black solid. It decomposes when mixed with Nujol giving a black mull. δ_H(C_6D_6, 250 MHz) 0.330 (4 H, d, $J = 7.5$, $AlCH_2$), 1.020 (12 H, d, $J = 7.5$, CH_3CH), 1.980 (2 H, d, $J = 6.3$ Hz, $CHCH_3$) and 6.76–7.310 (m, Ph). Mass spectrum: m/z 309 [10, $(P^+/2)$], 197 [11, $(P^+/2) - 2C_4H_8$], 196 [10, $(P^+/2) - Bu^i - C_4H_8$], 169 (32, $HNPh_2^+$), 168 (11, NPh_2^+), 167 (6, $NPh_2 - H$), 141 (100, $Bu^i_2Al^+$) and 99 (13%, $Bu^i_2Al - C_3H_6$).

Compound 29. This is the only case in the R^2 series where a trialkylaluminium etherate was used as a reagent instead of trialkylaluminium. Diphenylamine (17.2 g) was added to neat triisopropylaluminium–diethyl ether (17.4 g) at room temperature in a glove-box, giving a pink solution. The mixture was left to react for 4 d yielding a pink solid impregnated with liquid. Light petroleum was added giving a pink solution and a white solid. After 4 d the solution was filtered and the filtrate was left at room temperature, under nitrogen. Large needle-shaped crystals of $Pr^i_2Al(OEt_2)NPh_2$ formed. IR, $\tilde{\nu}_{max}$/cm^{-1} (Nujol, KBr): 1597m, 1587m, 1484vs, 1332w, 1278vs, 1214m, 1193w, 1181w, 1150w, 1089w, 1067w, 1023s, 993m, 961m, 934m, 908w, 892m, 880m, 869s, 833w, 772m, 760m, 750vs, 703m, 694m, 675w, 615m, 578w, 534m, 464w, 447m and 434m. δ_H(C_6D_6, 250 MHz) 0.52 (2 H, spt, $J = 7.5$, $CHCH_3$), 0.75 (6 H, badly resolved, CH_2CH_3), 1.28 (12 H, d, $J = 7.5$ Hz, CH_3CH), 3.57 (4 H, badly resolved q, CH_2CH_3) and 7.10 (10 H, Ph). Mass spectrum: m/z 169 (100, $NHPh_2^+$), 168 (35, NPh^+), 77 (7, Ph^+), 74 (17, OEt_2^+) and 59 (23%, $OEt_2 - Me$).

Compound 30: attempted synthesis. This produced an extremely air-sensitive compound which smokes even under nitrogen flow. The presence of the NH bands in the infrared (3383 cm^{-1}) and ^{1}H NMR spectrum indicate that the $Bu^t_3Al-NHPh_2$ adduct, a yellowish white solid, did not decompose at room temperature (unlike the other compounds of the $R^2 = Ph$ series) to give the corresponding amide. This was confirmed by the generation of the starting material ($HNPh_2$) when the product was heated at 60 °C. IR, $\tilde{\nu}_{max}$/cm^{-1} (Nujol, CsI): 383m, 1595vs, 1510vs, 1494vs, 1417m, 1311vs, 1258s, 1245s, 1200 (sh) m, 1174s, 1084w, 1028w, 1001w, 934m, 878s, 810s, 747vs, 691vs, 635s, 571w, 521w, 479w and 421m. δ_H($C_6D_5CD_3$, 250 MHz) 1.015 (not assigned), 1.10 (27 H, s, CH_3), 5.02 (1 H, s, NH) and 6.74–7.13 (20 H, m, Ph).

Table 13 Summary of data collection and structure refinement

	3	**4**	**6**	**8**	**9**	**11**	**17**	**29**
Formula	$C_{20}H_{48}Al_2N_2$	$C_{16}H_{40}Al_2N_2$	$C_{12}H_{32}Al_2N_2$	$C_{24}H_{56}Al_2N_2$	$C_{20}H_{48}Al_2N_2$	$C_{20}H_{48}Al_2N_2$	$C_{20}H_{48}Al_2N_2$	$C_{22}H_{34}AlNO$
M	370.578	314.47	258.36	426.68	370.578	370.578	370.56	367.511
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_2/c$	$I2/a$	$C2/c$	$P2_1/n$	$C2/c$	$P2_1/c$	$I2/a$	$C2/c$
a/Å	8.740(8)	17.176(3)	8.356(5)	16.173(2)	9.174(1)	13.015(4)	18.145(5)	18.378(2)
b/Å	9.440(6)	8.785(1)	13.428(7)	16.641(2)	16.181(2)	12.696(8)	7.514(4)	8.530(1)
c/Å	15.436(10)	13.964(2)	15.546(2)	11.508(1)	17.141(3)	15.380(8)	19.084(8)	29.602(2)
β/°	92.12(6)	91.67(2)	93.58(4)	106.58(1)	102.70(2)	94.40(4)	115.19(4)	104.69(2)
U/Å^3	1272.68(1.6)	2106.15(0.53)	1741(2)	2968.4(6)	2482.24(6)	2533.88(2)	2355(2)	4488.85(94)
Z	2	4	4	4	4	4	4	8
D_c/g cm^{-3}	0.967	0.992	0.986	0.955	0.991	0.971	1.045	1.087
F(000)	416	704	576	960	832	832	832	1600
μ/cm^{-1}	1.15	1.29	0.151	1.05	1.179	1.155	1.29	0.965
$\theta_{min/max}$/°	1.5, 25	1.5, 25	1.5, 25	1.5, 25	1.5, 25	1.5, 25	2.36, 24.9	1.5, 25
Total no. reflections	3454	2144	1624	5208	3004	5004	4297	4823
No. unique reflections	3071	1861	1526	5199	2170	4439	2067	3124
No. observed reflections [$F_o > 3\sigma(F_o)$]	1384	901	929	1575	977	2485	1750	1467
No. refined parameters	139	123	137	281	143	397	125	232
g in $w = 1/[\sigma^2(F) + gF^2]$	0.000 231	0.000 32	0.000 021	*a*	0.000 121	0.000 021	*b*	0.000 121
Final R	0.0697	0.0640	0.0557	0.0976	0.0629	0.0649	0.039	0.0714
Final R_G	0.0638	0.0596	0.0357	$wR2 = 0.2013$	0.0494	0.0588	$wR2 = 0.113$	0.0680

[a] Refinement on F^2, $w = 1/[\sigma^2(F_o^2) + (0.1001P)^2]$ where $P = [F_o^2 + 2F_c^2]/3$. [b] Refinement on F^2, $w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 1.24P]$ where $P = [F_o^2 + 2F_c^2]/3$.

Compounds 31–33: attempted syntheses. The corresponding adducts (3 g) were heated under reflux in toluene for 2 d, the solvent removed in vacuum and the residue analysed by ^{1}H NMR spectroscopy. In all cases the spectra were similar to that of a mixture of the starting materials, revealing that no reaction had occurred.

Crystallography

The intensity data were collected on a CAD4 diffractometer and Mo-Kα radiation (λ 0.710 69 Å) using ω–2θ scans at 290 K. The unit-cell parameters were determined by a least-squares refinement on diffractometer angles 10 ⩽ θ ⩽ 13° for 25 automatically centred reflections. All data were corrected for absorption by empirical methods (ψ scan).[56] The structures were solved by direct methods using the SHELXS 86[57] program and refined anisotropically by full-matrix least squares on F, using the SHELX 80[58] program. Compounds **8** and **17** were refined on F^2 using the SHELXL 93[59] program. The H atoms were calculated geometrically and refined with a riding model. The program PLATON 96[60] was used for drawing the molecules. The data collection and structure refinement is summarized in Table 13.

CCDC reference number 186/594.

Acknowledgements

We are grateful to the National Research Council of Brazil (CNPq) and the Centre of Research and Development (CPqD) of Brazilian Telecom (Telebrás) for financial support. We thank Greg Coumbarides for obtaining the NMR spectra and Peter Cook for the mass spectra. We wish to thank Dr R. Alan Howie of the Department of Chemistry of the University of Aberdeen for his effort and constructive suggestions during the writing of this manuscript.

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Received 30*th May* 1997; *Paper* 7/03771F