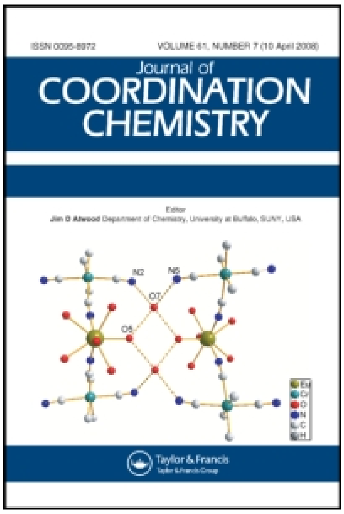

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GROUP 13 AMIDES. SYNTHESES AND MOLECULAR STRUCTURES OF $[(i\text{-Bu})_2\text{Al-N(H)Mes}]_2$, $[(i\text{-Bu})\text{Al-N(H)Ph}(t\text{-Bu})_2\text{-}\mu\text{-}(\text{CMe}_2\text{CH}_2)]_2$, $[\text{Me}_2\text{In-N(H)Ph}']_2$, AND $[(i\text{-Bu})_2\text{Al-N(H)Ada}]_2$

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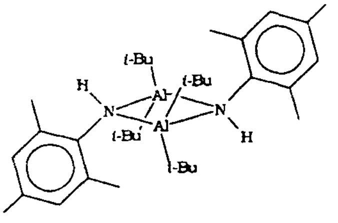
The sterically demanding Group 13 amide dimers $[(i\text{-Bu})_2\text{Al-N(H)Mes}]_2$ (**I**), $[(i\text{-Bu})\text{Al-N(H)Ph}(t\text{-Bu})_2\text{-}\mu\text{-}(\text{CMe}_2\text{CH}_2)]_2$ (**II**), $[\text{Me}_2\text{In-N(H)Ph}']_2$ (**III**), and $[(i\text{-Bu})_2\text{Al-N(H)Ada}]_2$ (**IV**) (Ada = adamantyl; Bu = butyl; Mes = Ph(Me)_3; Ph = phenyl; Ph′ = 2-biphenyl) have been prepared by reaction of $(i\text{-Bu})_2\text{AlH}$ or Me_3In with the respective primary amine and characterized by ^{1}H NMR, elemental analyses, and single crystal X-ray diffraction. **I** crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 9.272(1)$, $b = 9.718(2)$, $c = 11.585(2)$Å, $\alpha = 101.76(1)°$, $\beta = 106.69(1)°$, $\gamma = 109.70(1)°$, $V = 887.5(2)$Å^3, and $D_{calc} = 1.03\ \text{g cm}^{-3}$ for $Z = 1$. Least-squares refinement based on 1644 observed reflections with intensities $I > 3\sigma(I)$ in the range $3.5 < 2\theta < 45.0°$ converged at $R = 0.043$ and $R_w = 0.054$. **II** crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters $a = 11.292(5)$, $b = 17.544(9)$, $c = 11.532(5)$Å, $\beta = 107.99(4)°$, $V = 2173(2)$Å^3, and $D_{calc} = 1.05\ \text{g cm}^{-3}$ for $Z = 2$. Least-squares refinement based on 1819 observed reflections with intensities $I > 3\sigma(I)$ in the range $3.5 < 2\theta < 45.0°$ converged at $R = 0.066$ and $R_w = 0.088$. **III** crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 9.710(1)$, $b = 17.755(1)$, $c = 9.109(2)$Å, $\alpha = 102.27(1)°$, $\beta = 117.46(2)°$, $\gamma = 88.38(1)°$, $V = 1357(2)$Å^3, and $D_{calc} = 1.53\ \text{g cm}^{-3}$ for $Z = 2$. Least-squares refinement based on 2569 observed reflections with intensities $I > 3\sigma(I)$ in the range $4.0 < 2\theta < 50.0°$ converged at $R = 0.035$ and $R_w = 0.049$. These compounds reside in *trans* conformations about M_2N_2 (M = Al or In) four-membered rings. **II** is an interesting metallated product. The ^{1}H NMR spectrum of **IV** suggests the presence of both *trans* and *cis* isomers (in approximately a 2:1 ratio).

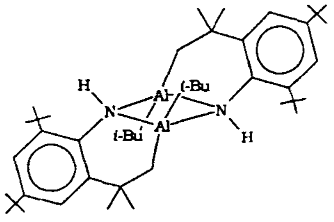
KEY WORDS: Aluminium alkyl, amine, *cis*, indium alkyl, *trans*, X-ray structure.

INTRODUCTION

The literature reveals a voluminous body of work concerning reactions of organoaluminium compounds with amines.[1,2,3] Notably, the interaction of organoindium moieties with amines has been investigated to a considerably lesser extent. Recently, this laboratory initiated investigations concerning sterically demanding amines with Group 13 metal alkyls.[4,5] Herein, we report the syntheses and molecular structures of [(i-Bu)$_2$Al-N(H)Mes]$_2$ (**I**), [(i-Bu)Al-N(H)Ph(t-Bu)$_2$-μ-(CMe$_2$CH$_2$)] (**II**), [(Me)$_2$In-N(H)Ph$'$]$_2$ (**III**), and [(i-Bu)$_2$-Al-N(H)Ada]$_2$ (**IV**), isolated from the reaction of (i-Bu)$_2$AlH or Me$_3$In with 2,4,6-trimethylaniline (H$_2$N-Mes; Mes = Ph(Me)$_3$; Ph = C$_6$H$_2$), 2,4,6-tri-t-butylaniline (H$_2$N-Ph(t-Bu)$_3$), 2-aminobiphenyl (H$_2$N-Ph$'$; Ph$'$ = 2-biphenyl), and adamantanamine (H$_2$N-Ada; Ada = C$_{10}$H$_{15}$), respectively.



(I)



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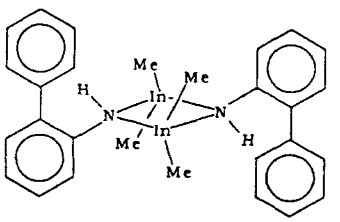

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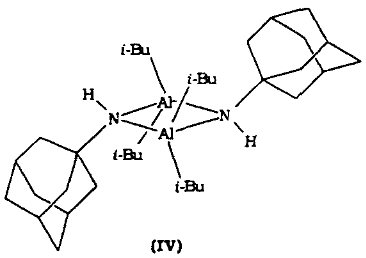


(IV)

EXPERIMENTAL

General

Due to the extreme air and water sensitivity of reactants and products, care was taken to exclude oxygen and moisture by employing standard Schlenk techniques and an inert atmosphere dry box (Vacuum Atmospheres HE-43 Dri-Lab). The sterically demanding amines and diisobutylaluminium hydride, purchased from Aldrich Chemical Co., were used without further purification. Trimethylindium was purchased from Strem Chemical Co. Toluene and hexane were distilled under an atmosphere of dried nitrogen over sodium/benzophenone and calcium hydride, respectively, prior to use. Elemental analyses were performed by E + R Microanalytical Laboratories, Corona, NY. ^{1}H NMR data were recorded on a Bruker AC300 FT-NMR spectrometer. Single crystal X-ray diffraction studies for **I** and **II** were performed on a Nicolet R3mV diffractometer; calculations, structure solution, and refinement were performed using the SHELXTL[6] package of computer programs. Single crystal X-ray diffraction data for **III** were collected on an Enraf Nonius CAD-4 diffractometer.

Synthesis of $[(i\text{-}Bu_2Al\text{-}N(H)Mes]_2$ (I)

In the dry box, $(i\text{-}Bu)_2AlH$ (1.78 cm^3, 10 mmol) was added *via* syringe to a reaction tube containing a solution of toluene (20 cm^3) and H_2N-Mes (0.70 cm^3, 5.0 mmol). The reaction tube was sealed and placed in an oil bath at 120°C for 12 hours. After cooling to room temperature, the reaction solution was transferred to a 100 cm^3 Schlenk flask and evaporated to half volume. Upon cooling at 0°C for 24 hours, crystals of **I** formed on the walls of the flask in 50% yield (based on the amine). ^1H NMR (C_6D_6): δ0.79 (d, 8H, Al-CH_2), 0.94 (d, 24H, $AlCH_2CH(CH_3)_2$), 1.94 (sept. 4H, $AlCH_2CH$), 2.06 (s, 6H, Mes-*p*-CH_3), 2.43 (s, 12H, Mes-*o*-CH_3), 6.68 (s, 4H, C_6H_2). m.p.: 153–155°C. Anal: found (calcd) for $C_{34}H_{60}N_2Al_2$: C, 71.76 (74.14); H, 10.86 (10.98)% (the carbon analysis for this compound has consistently proved a little low while that for hydrogen was satisfactory).

Synthesis of $[(i\text{-}Bu)Al\text{-}N(H)Ph(t\text{-}Bu)_2\text{-}\mu\text{-}(CMe_2CH_2)]_2$ (II)

A reaction vessel was charged with $H_2N\text{-}Ph(t\text{-}Bu)_3$ (0.65 g, 2.5 mmol), toluene (20 cm^3), and $(i\text{-}Bu)_2AlH$ (0.89 cm^3, 5.0 mmol) inside the drybox. A vigorous reaction ensued. The reaction mixture was transferred to a 100 cm^3 Schlenk flask and evaporated to half volume in vacuo. After chilling in the freezer at −20°C overnight, crystals of **II** formed on the walls of the flask in quantitative yield (based on the amine). ^1H NMR (C_6D_6): δ0.16 (t, 4H, $AlCH_2$), 0.81 (t, 4H, $AlCH_2$ of metallated *t*-Bu), 0.82 (sept., 2H, $AlCH_2CH$), 0.86 (s, 12H, *o*-*t*-Bu-CH_3 (non-metallated CH_3's on metallated *t*-Bu)), 1.36 (d, 12H, $AlCH_2CH(CH_3)_2$), 1.34 (s, 18H, *p*-*t*-Bu-CH_3), 1.52 (s, 18H, *o*-*t*-Bu-CH_3 (non-metallated)), 7.66 (s, 4H, C_6H_2). m.p.: 203–205°C. Anal: found (calcd) for $C_{44}H_{76}N_2Al_2$: C, 75.51 (76.92); H, 11.42 (11.15)%.

Synthesis of $[(Me_2In\text{-}N(H)Ph']_2$ (III)

In the dry box, Me_3In (0.25 g, 1.56 mmol), H_2N-Ph' (0.26 g, 1.56 mmol), and toluene (15 cm^3) were combined in a reaction tube. The reaction tube was then heated to 100°C overnight in an oil bath, and then cooled to −20°C in the freezer for another 12 hours. Long, colourless, rectangular, crystals were isolated in quantitative yield (based on the amine). ^1H NMR (C_6D_6): $\delta-0.12$ (d, 12H, $InCH_3$), 3.12 (bs, 2H, N*H*), 6.41–7.37 (m, 18H, Ph'-*H*). m.p.: 335°C (dec). Anal: found (calcd) for $C_{28}H_{32}N_2In_2$: C, 52.58 (53,70); H, 5.27 (5.15)%.

Synthesis of $[(i\text{-}Bu)_2\text{-}Al\text{-}N(H)Ada]_2$ (IV)

Inside the dry box a reaction vessel was charged with H_2N-Ada (0.76 gm 5.02 mmol) toluene (20 cm^3), and $(i\text{-}Bu)_2AlH$ (0.90 cm^3, 5.0 mmol). Reaction was immediate and vigorous. Heating the mixture in an oil bath (100°C, 24 hr) resulted in a clear, homogeneous solution. Cooling to room temperature afforded a multitude of colourless crystals. **IV** was obtained in quantitative yield (based on the amine). ^1H NMR (C_6D_6): δ0.28–0.53 (m, 8H, $AlCH_2$), 0.92(s, 2H, N*H*, *trans* isomer), 0.95 (s, 2H, N*H*, *cis* isomer, 1.22 (d, 12H, $AlCH_2CH(CH_3)_2$, *cis* isomer), 1.25 (d, 24H, $AlCH_2CH(CH_3)_2$, *trans* isomer), 1.26 (d, 12H, $AlCH_2CH(CH_3)_2$, *cis* isomer), 1.47 (dd, 12H, Ada-CH_2), 1.83 (s, 12H, Ada-CH_2, *trans* isomer), 1.88 (s, 12H, Ada-CH_2, cis isomer), 1.91 (bs, 6H, Ada-C*H*), 2.03–2.25 (m, 4H, $AlCH_2CH$). m.p. = 181–183°C (dec). Anal: found (calcd) for $C_{36}H_{68}Al_2N_2$: C, 74.36; (74.18) H, 11.24. (11.76).

X-ray Structural Solution and Refinement for $[(i\text{-}Bu)_2Al\text{-}N(H)Mes]_2$ (**I**), $[(i\text{-}Bu)Al\text{-}N(H)Ph(t\text{-}Bu)_2\text{-}\mu\text{-}(CMe_2CH_2)]_2$ (**II**), *and* $[(Me)_2In\text{-}N(H)Ph']_2$ (**III**)

Single crystals of **I**, **II**, and **III** were mounted in thin-walled glass capillaries under an inert atmosphere of argon. Cell parameters and an orientation matrix for data collection were obtained from a least-squares fitting of several carefully centred high-order reflections. Structures were solved by direct methods and refined by full matrix least-squares. For **I** and **II**, the asymmetric unit consists of one monomer which is situated about a centre of inversion that generates the other half of the molecule. Except where indicated otherwise, hydrogen atoms for **I**, **II**, and **III** were located by standard difference Fourier techniques and placed in idealized positions ($d_{C\text{-}H} = 0.96\text{Å}$) and were allowed to ride on the atoms to which they were bonded. Isotropic group thermal parameters were refined for the hydrogen atoms on **I** and **II** ($U_{iso} = 0.103(3)\text{Å}^2$ for **I**; $0.098(4)\text{Å}^2$ for **II**) except where indicated otherwise. Hydrogen atoms for **III** were not refined ($B_{iso} = 5.2\text{Å}^2$ for **III**). For **I**, the mesityl methyl hydrogen atoms were found to be disordered over two equally occupied sites; two sets of half-hydrogen atoms were included to model this phenomenon. For compound **II**, the methane carbon atom of the *iso*-butyl group (atom C(20)) was found to be disordered over two possible positions with multiplicities of 0.67 for C(20) and 0.33 for C(20A). The multiplicities of these two atoms were determined by refinement of the occupancy (m) of the major component atom; the occupancy of the minor component atoms was set equal to (1-m). The parameter m was allowed to vary in the early stages of refinement, but was constrained in the final stages. The non-hydrogen atoms, other than the minor component atoms (C(20A)), were refined using anisotropic thermal parameters. Hydrogen atoms of the disordered isobutyl group were not included. Relevant crystallographic data are given in Table 1 while selected bond distances and angles are given in Table 2. Final fractional atomic coordinates for **I**, **II**, and **III** are given in Tables 3, 4, and 5, respectively. Although X-ray quality crystals of **IV** were obtained and examined, severe crystallographic disorder associated with one of the adamantyl units precluded successful refinement. However, preliminary data confirmed that **IV**, structurally similar to **I**, **II**, and **III**, resides in a *trans* conformation. The molecular structure of **I**, **II**, and **III** are given in Figures 1, 2, and 3, respectively.

RESULTS AND DISCUSSION

The formation of M_2N_2 four-membered rings and concomitant dimer formation are ubiquitous in Group 13 amide chemistry. Indeed, the formation of discrete dimeric units is mandatory along the reaction coordinate to higher Group 13 amines (i.e., trimers and tetramers) and metallated products.[7]

The mean Al-N bond distance in **I** of 1.981Å compares to 1.956Å for **II**. Clearly, this variation is a consequence of the steric demands of $Ph(Me)_3$ compared to $Ph(t\text{-}Bu)_3$. Compounds **I** and **II** reside about crystallographic centres of symmetry. As demanded by symmetry, the Al_2N_2 cores of both compounds are planar. In contrast, the core of **III** is decidedly non-planar, displaying a significant In_2N fold angle of 19.0°. Moreover, **III** is readily compared to its aluminium analogue, $[Me_2Al\text{-}N(H)Ph']_2$, where the M_2N fold angle is observed to be 19.1°.[4] It is interesting that planar cores are observed in both cases where the organic substituent on the metal is the bulkier *iso*-butyl group (**I** and **II**) and the non-planar fragment is observed

Table 1 Crystal data for $[(i\text{-Bu})_2\text{Al-N(H)Mes}]_2$ (**I**), $[(i\text{-Bu})\text{Al-N(H)Ph}(t\text{-Bu})_2\text{-}\mu\text{-}(\text{CMe}_2\text{CH}_2)]_2$ (**II**), and $[(\text{Me})_2\text{In-N(H)Ph}']_2$ (**III**)

	I	II	III
Chemical formula	$C_{34}H_{60}N_2Al_2$	$C_{44}H_{76}N_2Al_2$	$C_{28}H_{32}N_2In_2$
Mol wt	550.82	687.06	691.09
Size, mm	0.26 × 0.29 × 0.33	0.17 × 0.28 × 0.31	0.30 × 0.30 × 0.20
Colour; habit	colourless; parallelepiped	colourless; parallelepiped	colourless; parallelepiped
Space group	$P\bar{1}$ (No. 2) Triclinic	$P2_1/c$ (No. 14) Monoclinic	$P\bar{1}$ (No. 2) Triclinic
a, Å	9.272(1)	11.292(4)	9.710(1)
b, Å	9.718(2)	17.544(9)	17.755(1)
c, Å	11.585(2)	11.532(5)	9.109(2)
α, deg	101.76(1)		102.27(1)
β, deg	106.69(1)	107.99(4)	117.46(2)
γ, deg	109.70(1)		88.38(1)
Volume, Å^3	887.5(2)	2173(2)	1357(2)
Z	1	2	3
D_{calc}, g cm^{-3}	1.03	1.05	1.53
Temperature, °C	21	21	21
Reflect, collected	2493	3108	3364
Reflect. unique	2323	2824	3322
Reflect. obsd	1644 ($I > 3\sigma(I)$)	1819 ($I > 3\sigma(I)$)	2569 ($I > 3\sigma(I)$)
2θ range, deg	3.5–45.0	3.5–45.0	4.0–50.0
R	0.043	0.066	0.035
R_w	0.054	0.088	0.049

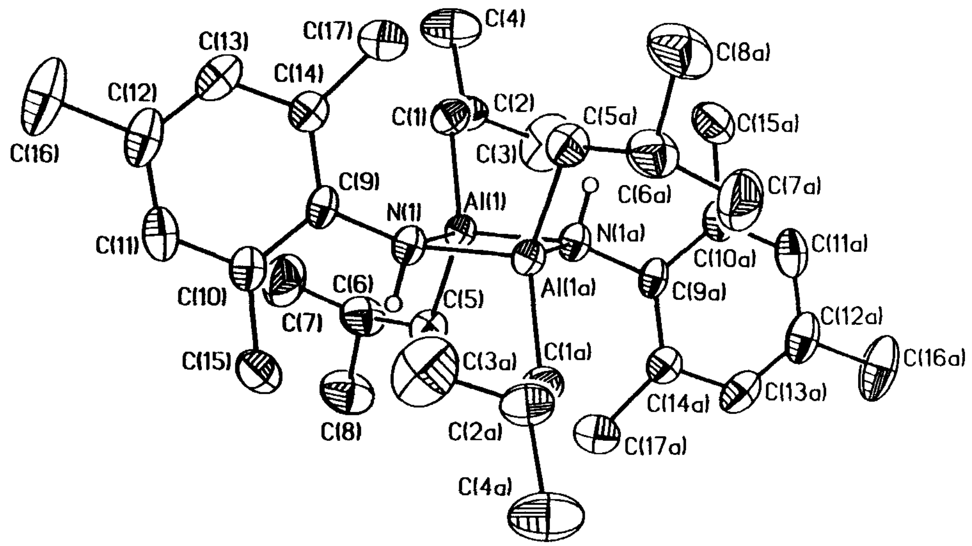


Figure 1 A thermal ellipsoid plot of $[(i\text{-Bu})_2\text{Al-N(H)Mes}]_2$, **I**, showing the atom-labelling scheme. Thermal ellipsoids show 35% probability levels. Hydrogen atoms, except those bound to nitrogen, have been omitted.

Table 2 Selected bond lengths (Å) and angles (°)

$[(i\text{-Bu})_2\text{Al-N(H)Mes}]_2$ (**I**)			
Al(1)-Al(1a)	2.952(2)	Al(1)-N(1)	1.982(3)
Al(1)-N(1a)	1.980(3)	Al(1)-C(1)	1.973(4)
Al(1)-C(5)	1.980(4)	N(1)-C(9)	1.459(3)
C(1)-C(2)	1.532(6)	C(5)-C(6)	1.498(5)
Al(1)-N(1)-Al(1a)	96.3(1)	N(1)-Al(1)-N(1a)	83.7(1)
N(1)-Al(1)-C(1)	115.8(1)	N(1)-Al(1)-C(5)	109.3(2)
C(1)-Al(1)-C(5)	118.3(2)	Al(1)-N(1)-C(9)	128.2(2)
Al(1a)-N(1)-C(9)	127.2(2)	Al(1)-C(1)-C(2)	117.6(2)
Al(1)-C(5)-C(6)	119.2(2)	N(1)-C(9)-C(14)	122.6(3)
$[(i\text{-Bu})\text{Al-N(H)Ph}(t\text{-Bu})_2\text{-}\mu\text{-}(\text{CMe}_2\text{CH}_2)]_2$ (**II**)			
Al(1)-Al(1a)	2.843(4)	Al(1)-N(1)	1.956(5)
Al(1)-N(1a)	1.994(5)	Al(1)-C(19)	1.978(6)
Al(1)-C(8)	1.945(5)	N(1)-C(1)	1.470(5)
C(1)-C(2)	1.404(6)	C(2)-C(7)	1.559(7)
C(7)-C(8)	1.535(8)	C(19)-C(20)	1.545(13)
Al(1)-N(1)-Al(1a)	92.1(2)	N(1)-Al(1)-N(1a)	87.9(2)
N(1)-Al(1)-C(8)	97.7(2)	N(1)-Al(1)-C(19)	124.2(2)
C(8)-Al(1)-C(19)	116.3(3)	Al(1)-N(1)-C(1)	120.3(3)
Al(1a)-N(1)-C(1)	124.0(3)	Al(1)-C(8)-C(7)	119.3(4)
Al(1)-C(19)-C(20)	116.1(4)	N(1)-C(1)-C(2)	121.2(4)
N(1)-C(1)-C(6)	118.8(4)	C(1)-C(2)-C(7)	126.2(4)
C(2)-C(7)-C(8)	112.0(4)		
$[(\text{Me})_2\text{In-N(H)Ph}']_2$ (**III**)			
In(1)-In(2)	3.3275(9)	In(1)-N(1)	2.242(7)
In(1)-N(2)	2.236(5)	In(2)-N(1)	2.238(4)
In(2)-N(2)	2.255(7)	In(1)-C(25)	2.135(9)
In(1)-C(26)	2.144(8)	In(2)-C(27)	2.144(7)
In(2)-C(28)	2.117(9)	N(1)-C(1)	1.413(8)
N(2)-C(13)	1.387(9)		
In(1)-N(1)-In(2)	95.9(2)	In(1)-N(2)-In(2)	95.6(2)
N(1)-In(1)-N(2)	82.6(2)	N(1)-In(2)-N(2)	82.3(2)
C(25)-In(1)-C(26)	131.4(4)	C(27)-In(2)-C(28)	131.7(4)
In(1)-N(1)-C(1)	119.7(5)	In(2)-N(1)-C(1)	123.0(4)
In(1)-N(2)-C(13)	120.9(4)	In(2)-N(2)-C(13)	121.0(5)
N(1)-C(1)-C(2)	123.9(6)	N(1)-C(1)-C(6)	120.3(5)
N(2)-C(13)-C(14)	121.0(6)	N(2)-C(13)-C(18)	121.1(6)
N(1)-In(1)-C(25)	107.6(3)	N(1)-In(1)-C(26)	110.9(3)
N(1)-In(2)-C(27)	111.7(3)	N(1)-In(2)-C(28)	107.7(2)
N(2)-In(1)-C(25)	111.8(3)	N(2)-In(1)-C(26)	101.6(2)
N(2)-In(2)-C(27)	101.5(3)	N(2)-In(2)-C(28)	110.5(3)

where the smaller methyl substituent is present (**III**). The non-planarity observed in **III** appears to be the result of the better ability of the Me_2M (M = Al, In) unit to accommodate such distortion, presumably due to intermolecular packing interactions, than the sterically more demanding i-Bu_2M group. The ligands on the associated metals appear to play a role in determining the *cis-trans* dominance only if they are sterically more demanding than *iso*-butyl. Indeed, neopentyl-based aminoalanes have

Table 3 Atomic coordinates and equivalent isotropic thermal paramaters (Å^2 × 10^3) for [(*i*-Bu)$_2$Al-N(H)Mes]$_2$ (**I**)

	x/a	*y/b*	*z/c*	*U*(eq)*
Al(1)	0,4303(1)	0.5762(1)	0.4155(1)	38(1)
N(1)	0.4612(3)	0.3820(3)	0.3390(2)	44(1)
C(1)	0.1997(4)	0.5529(3)	0.3736(3)	50(2)
C(2)	0.1631(4)	0.6901(4)	0.3520(4)	58(2)
C(3)	0.2638(6)	0.8334(5)	0.4661(5)	105(3)
C(4)	−0.0202(5)	0.6520(5)	0.3130(5)	94(3)
C(5)	0.5675(4)	0.7053(3)	0.3412(3)	51(2)
C(6)	0.4852(5)	0.7119(5)	0.2119(3)	69(2)
C(7)	0.3774(6)	0.5563(6)	0.1128(4)	103(3)
C(8)	0.6094(6)	0.8106(5)	0.1679(4)	92(3)
C(9)	0.3578(4)	0.2309(3)	0.2995(3)	40(1)
C(10)	0.4248(4)	0.1776(3)	0.2147(3)	49(2)
C(11)	0.3296(5)	0.0353(4)	0.1196(3)	61(2)
C(12)	0.1708(5)	−0.0567(4)	0.1036(3)	64(2)
C(13)	0.1080(4)	−0.0024(4)	0.1867(3)	59(2)
C(14)	0.1985(4)	0.1403(3)	0.2860(3)	46(2)
C(15)	0.5974(5)	0.2705(4)	0.2241(4)	70(2)
C(16)	0.0690(6)	−0.2123(4)	−0.0011(4)	103(3)
C(17)	0.1164(4)	0.1870(4)	0.3721(3)	65(2)

*Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4 Atomic coordinates and equivalent isotropic thermal parameters (Å^2 × 10^3) for [(*i*-Bu)Al-N(H)Ph(*t*-Bu)$_2$-*μ*-(CMe$_2$CH$_2$)]$_2$ (**II**)

	x/a	*y/b*	*z/c*	*U*(eq)*
Al(1)	0.4404(1)	0.4908(1)	0.0911(1)	42(1)
N(1)	0.5311(3)	0.5729(2)	0.0409(3)	37(2)
C(1)	0.6301(4)	0.6145(3)	0.1323(4)	35(2)
C(2)	0.7110(4)	0.5769(3)	0.2334(4)	37(2)
C(3)	0.8158(5)	0.6177(3)	0.3044(5)	40(2)
C(4)	0.8393(4)	0.6926(3)	0.2857(4)	38(2)
C(5)	0.7439(4)	0.7294(3)	0.1926(5)	39(2)
C(6)	0.6450(4)	0.6937(3)	0.1152(4)	35(2)
C(7)	0.6960(5)	0.4940(3)	0.2755(5)	43(2)
C(8)	0.5587(5)	0.4725(3)	0.2516(5)	51(2)
C(9)	0.7575(6)	0.4375(3)	0.2109(6)	70(3)
C(10)	0.7592(6)	0.4855(3)	0.4132(5)	72(3)
C(11)	0.9545(5)	0.7356(3)	0.3664(5)	46(2)
C(12)	0.9117(6)	0.7966(4)	0.4378(7)	84(3)
C(13)	1.0246(7)	0.7717(5)	0.2887(7)	100(4)
C(14)	1.0451(6)	0.6835(4)	0.4578(6)	78(3)
C(15)	0.5499(5)	0.7434(3)	0.0167(5)	41(2)
C(16)	0.5877(6)	0.8286(3)	0.0306(6)	69(3)
C(17)	0.4189(5)	0.7403(3)	0.0319(6)	59(2)
C(18)	0.5463(6)	0.7200(3)	−0.1123(5)	59(2)
C(19)	0.2631(5)	0.4968(4)	0.0828(6)	66(3)
C(20)	0.2367(8)	0.5223(6)	0.2008(9)	58(4)
C(20A)	0.2124(20)	0.5561(13)	0.1365(20)	65(6)
C(21)	0.0965(6)	0.5192(5)	0.1842(8)	103(4)
C(22)	0.2869(7)	0.6014(4)	0.2432(7)	90(3)

*Atoms C(20) and C(20A) represent alternative sites for this disordered atom (occupancies = 0.667/0.333).

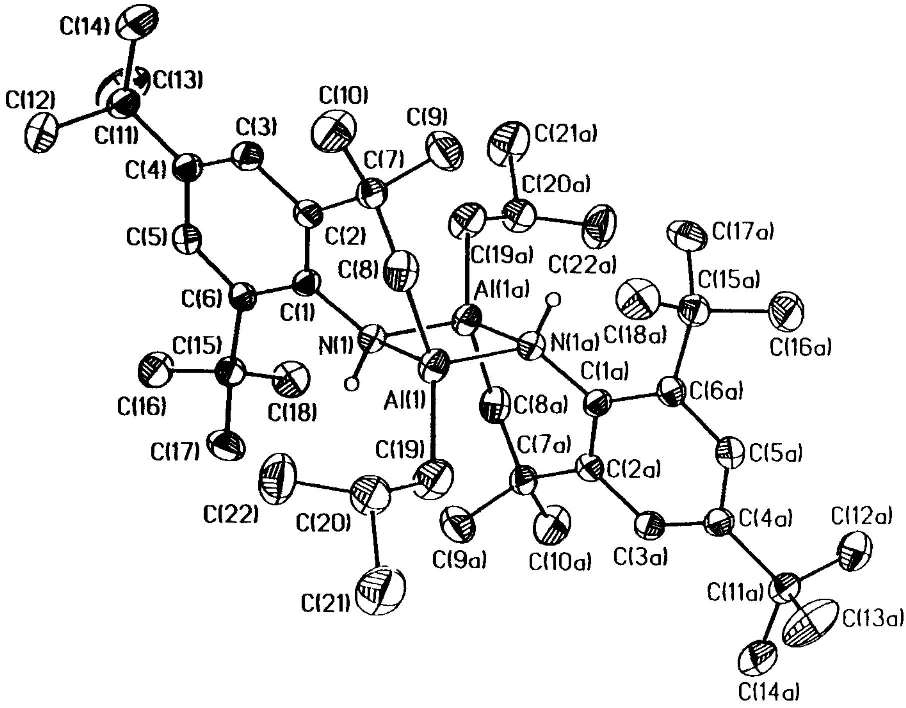


Figure 2 A thermal ellipsoid plot of $[(i\text{-Bu})\text{Al-N(H)Ph}(t\text{-Bu})_2\text{-}\mu\text{-}(\text{CMe}_2\text{CH}_2)]_2$, **II**, showing the atom-labelling scheme. Thermal ellipsoids show 35% probability levels. Hydrogen atoms, except those bound to nitrogen, have been omitted.

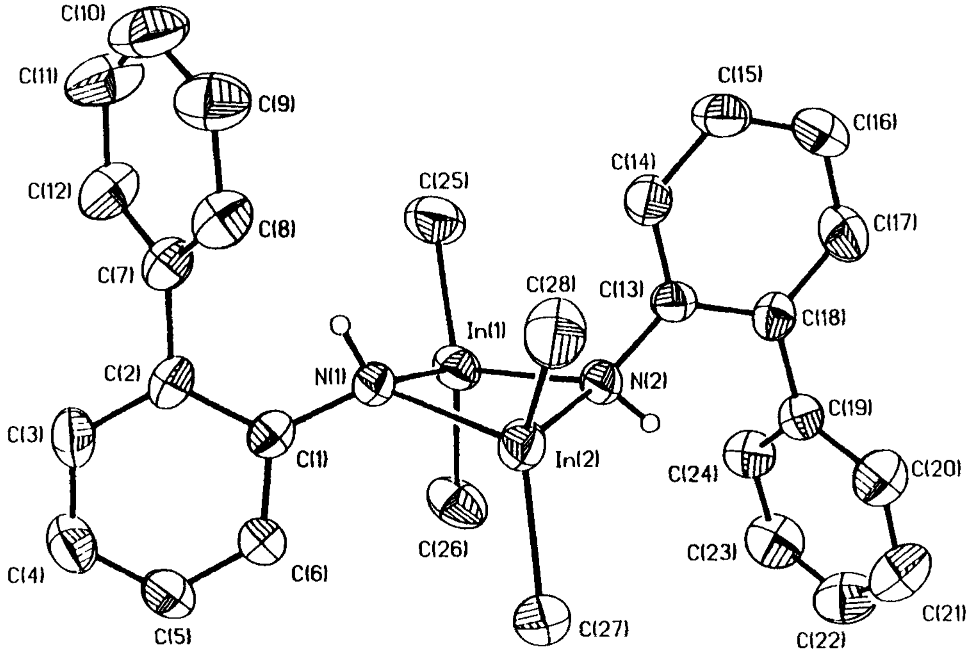


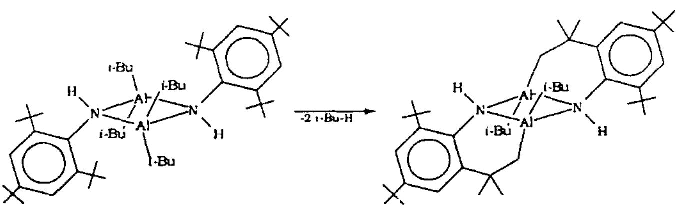
Figure 3 A thermal ellipsoid plot of $[(\text{Me})_2\text{In-N(H)Ph}']_2$, **III**, showing the atom-labelling scheme. Thermal ellipsoids show 35% probability levels. Hydrogen atoms, except those bound to nitrogen, have been omitted.

Table 5 Atomic coordinates and equivalent isotropic thermal parameters for $[(Me)_2In\text{-}N(H)Ph']_2$ (**III**)

	x/a	y/b	z/c	B(eq)
In(1)	0.79645(6)	0.25686(3)	0.44658(6)	4.73(1)
In(2)	1.12254(5)	0.29567(3)	0.43187(6)	4.51(1)
N(1)	0.8710(6)	0.2612(3)	0.2492(6)	4.1(1)
N(2)	1.0531(6)	0.2596(3)	0.6129(6)	4.5(2)
C(1)	0.7825(7)	0.2991(4)	0.1172(7)	3.9(2)
C(2)	0.7031(7)	0.2616(4)	−0.0542(7)	4.2(2)
C(3)	0.6121(8)	0.3022(5)	−0.1734(8)	5.2(2)
C(4)	0.6003(8)	0.3807(5)	−0.1287(8)	5.7(2)
C(5)	0.6806(8)	0.4185(4)	0.0373(8)	5.4(2)
C(6)	0.7666(7)	0.3793(4)	0.1546(8)	4.5(2)
C(7)	0.7107(7)	0.1769(4)	−0.1119(7)	4.3(2)
C(8)	0.8525(8)	0.1449(5)	−0.0813(9)	5.6(2)
C(9)	0.858(1)	0.0680(5)	−0.143(1)	7.0(3)
C(10)	0.719(1)	0.0206(5)	−0.233(1)	8.2(3)
C(11)	0.587(1)	0.0512(5)	−0.256(1)	8.2(3)
C(12)	0.576(1)	0.1285(5)	−0.2033(9)	6.7(3)
C(13)	1.1180(7)	0.1983(4)	0.6878(7)	4.0(2)
C(14)	1.1041(8)	0.1253(4)	0.5903(9)	5.2(2)
C(15)	1.1677(8)	0.0633(4)	0.6653(9)	5.9(2)
C(16)	1.2505(9)	0.0733(4)	0.8391(9)	5.9(2)
C(17)	1.2651(8)	0.1463(5)	0.9364(9)	5.6(2)
C(18)	1.2002(7)	0.2089(4)	0.8671(7)	4.2(2)
C(19)	1.2190(7)	0.2869(4)	0.9769(7)	4.1(2)
C(20)	1.3637(8)	0.3267(5)	1.0749(9)	5.9(2)
C(21)	1.378(1)	0.4011(6)	1.171(1)	7.4(3)
C(22)	1.2511(9)	0.4328(5)	1.1724(9)	7.0(3)
C(23)	1.1105(9)	0.3956(5)	1.0789(9)	6.3(2)
C(24)	1.0916(8)	0.3235(4)	0.9785(8)	5.2(2)
C(25)	0.683(1)	0.1448(5)	0.384(1)	7.6(3)
C(26)	0.7461(9)	0.3692(5)	0.5442(9)	6.8(2)
C(27)	1.1651(1)	0.4184(4)	0.529(1)	6.5(3)
C(28)	1.2552(8)	0.2121(5)	0.3639(9)	6.7(2)

been shown to consistently afford *cis* dimers.[8] The ^1H solution NMR spectrum of **IV** suggests the presence of both *cis* and *trans* isomers (in approximately a 2:1 ratio).

The metallation which occurred in **II** is particularly noteworthy. Although not isolated, it is instructive to consider the formation of the $[(i\text{-Bu})_2\text{-Al-N(H)Ph}(t\text{-Bu})]_2$ dimer as a precursor to **II** (below).



An increase in temperature coupled with the relative proximity of the *iso*-butyl and *t*-butyl groups make the observed condensation (and elimination of isobutane) quite reasonable. The proximity of the *ortho*-*t*-butyl groups of the amine to the *iso*-butyl groups on the aluminium atoms serves to make the observed metallation more favourable than formation of a higher amide (i.e., trimer or tetramer). Although similar metallations have been reported involving Me_3Al and Me_3Ga with H_2N-Ph(Me_3),[7] it is interesting that **I** did not undergo metallation. The Al(1)-C(8) bond distance of 1.945(5) compares well with *regular* Al-C distances.

The study of Group 13 amines remains a popular area of study. Forthcoming studies will address other aspects of these compounds.

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Supplementary Material Available

Summary of data collection and refinement, plots of molecules, tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters (36 pages), and a listing of observed and calculated structure factors (39 pages) are available from G.H.R.

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