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Reactivity of Me_3M (M = Al, Ga, In) with benzylamine to form the dimers, $[Me_2MN(H)CH_2Ph]_2$, and the hexamers, $[MeAlNCH_2Ph]_6$ and $[MeGaNCH_2Ph]_6$: molecular structures of *trans*-$[Me_2MN(H)CH_2Ph]_2$ and $[MeAlNCH_2Ph]_6$

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Abstract

1:1 Equimolar mixtures of Me_3Al, Me_3Ga, or Me_3In and benzylamine, when heated to 90–120 °C in toluene solution, undergo methane elimination to yield the respective dimers, $[Me_2MN(H)CH_2Ph]_2$, where M = Al, Ga, or In. These dimers exist as 1:1 mixtures of *cis* and *trans* isomers in toluene-d_8 solution, over the temperature range 30–90 °C, consistent with the results of Beachley [1] for the aluminum derivative. However, single-crystal X-ray data indicate the dimers each crystallize in the *trans* form. The structure of each dimer exhibits a center of symmetry and each M_2N_2 core has a slightly distorted square planar geometry. The ^1H- and ^{13}C-NMR chemical shift assignments were made for the *cis* and *trans* isomers of the three compounds using a combination of 1D- and 2D-NMR techniques. Thermolysis of the 1:1 mixtures at higher temperatures (120–180 °C) generates the more condensed hexameric species, $[MeAlNCH_2Ph]_6$ and $[MeGaNCH_2Ph]_6$. $[MeAlNCH_2Ph]_6$ crystallizes in a rhombohedral structure where the Al–N cage consists of two six-membered $(AlN)_3$ rings linked together by six transverse Al–N bonds. The results of these thermolyses involving benzylamine are compared with the results of analogous reactions employing dibenzylamine, where an orthometalated product, $[MeMN(CH_2Ph)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$, (M = Al, Ga), is obtained. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Trimethylaluminum; Trimethylgallium; Trimethylindium; Thermolysis; Benzylamine; Dibenzylamine

1. Introduction

The chemical reactivity of organoaluminum, -gallium, and -indium compounds toward amines has been investigated extensively over the past sixty years [1–13]. Our research group has reported the synthesis and characterization of four series of $R_3M\cdot$secondary amine adducts (M = Al, Ga, In; R = Me, Et) [14–16] and three series of aminoalane and aminogallane dimers [8,14,16]. Thermolysis of 1:1 mixtures of Me_3Al with each of thirteen secondary amines, R′H, proceeds smoothly to yield the corresponding aminoalane dimers, $[Me_2AlR']_2$, via methane elimination [14]. Similar reactions with Me_3Ga lead to the synthesis and characterization of ten aminogallanes [8]. However, when the secondary amines contain the more sterically demanding groups R′ = N^iPr_2, N^sBu_2, and $N(CH_2Ph)_2$, the corresponding aminogallanes could not be synthesized by thermolysis, but were obtained by the reaction of Me_2GaCl with the appropriate lithium amide. Careful monitoring of the thermolysis of a 1:1 Me_3Ga/$HN(CH_2Ph)_2$ mixture at 120 °C by ^1H-NMR indicates that partial conversion of the initial product $[Me_2GaN(CH_2Ph)]_2$ to a more condensed Ga–N species occurs before adduct consumption is complete. Subsequent thermolysis of the Me_3Ga/$HN(CH_2Ph)_2$ mixture at 150 °C yields the orthometalated dimer

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$[Me_2GaN(CH_2Ph)\text{-}\mu\text{-}(CH_2C_6H_4)]_2$ [17]. Thermolysis of mixtures of Me_3Al with diphenylamine and of Me_3Al with dibenzylamine have also been reported to produce Al_2N_2-containing orthometalated dimers [18,19]. Although $[Me_2InNMe_2]_2$ was synthesized initially by thermolysis of Me_3In with $HNMe_2$ [2c], other aminoindane dimers, with more sterically demanding secondary amine functions, have been synthesized primarily by other methods [5]. Several attempts at the preparation of $[Me_2InN(CH_2Ph)]_2$ in our laboratory by thermolysis of $Me_3In/HN(CH_2Ph)_2$ mixtures led to poor product yield. However, thermolysis of mixtures of Me_3M ($M = Al$, Ga, In) with the sterically hindered primary amine 2-aminobiphenyl, NH_2Bp, gives quantitative yields of the respective dimers, $[Me_2MN(H)Bp]_2$ [20,21]. Because the synthesis of $[Me_2AlN(H)CH_2Ph]_2$ results from the thermolysis of a mixture of Me_3Al and H_2NCH_2Ph [1], we wanted to determine whether the corresponding gallium- and indium-containing dimers could be synthesized by thermolysis using benzylamine instead of dibenzylamine. Also, a comparison of the structural and spectroscopic properties for the $[Me_2MN(CH_2Ph)_2]_2$ series, ($M = Al$, Ga, In) [8,14,19,22], with those of the $[Me_2MN(H)CH_2Ph]_2$ series could be relevant in terms of understanding the steric requirements of the benzyl group.

Thermolysis of mixtures of Me_3M ($M = Al$, Ga, In) with a variety of primary amines (H_2NR'') yields initially the species $[Me_2MN(H)R'']_n$ ($n = 2$, 3) via methane elimination. Thermolysis at higher temperatures may result in additional methane elimination with the formation of more condensed species such as $[MeMNR'']_n$ ($n = 3$, 4, 6–8) [3,4,6,7,10–12,19,23–26,28–32] or alternately, cyclometalated dimers [7,11,20,27,28]. The results of these studies suggest that the nature and the degree of aggregation of the product obtained are dependent on the steric nature of the alkyl or aromatic group attached to the amine nitrogen and the metal present. Therefore, we investigated the thermolysis of the three Me_3M/benzylamine systems at temperatures above those required for dimer formation to determine whether a more condensed species, $[MeMNCH_2Ph]_n$, or possibly an orthometalated dimer, as in the reactions of Me_3Al and Me_3Ga with dibenzylamine, would be obtained.

2. Results and discussion

2.1. Synthesis and characterization of $[Me_2AlN(H)CH_2Ph]_2$ (**1**), $[Me_2GaN(H)CH_2Ph]_2$ (**2**), and $[Me_2InN(H)CH_2Ph]_2$ (**3**)

Thermolysis of 1:1 mol ratio mixtures of Me_3M, $M = Al$, Ga, and In, and benyzlamine in toluene proceed smoothly to produce the respective dimers $[Me_2AlN(H)CH_2Ph]_2$ (**1**), $[Me_2GaN(H)CH_2Ph]_2$ (**2**), and $[Me_2InN(H)CH_2Ph]_2$ (**3**) in excellent yields. The synthesis data for **1** are in agreement with those of Beachley [1]. The dimeric nature of **1**, **2**, and **3** has been confirmed by NMR, mass spectral, and single crystal X-ray data. In comparison, the corresponding thermolysis reactions of Me_3M with dibenzylamine, where there is the substitution of a second benzyl group for the amine hydrogen, led to an acceptable yield of isolated dimer product for $[Me_2AlN(CH_2Ph)_2]_2$ only [8,14,22].

The ^1H- and ^{13}C-NMR spectra for the three dimers each suggest the presence of both *cis* and *trans* isomers with respect to the four-membered M_2N_2 ring in solution. For example, the RT-^1H-NMR methyl group resonance for each dimer consists of three singlets in a 1:2:1 ratio. The two resonances of equal intensity are assigned to the two non-equivalent methyl groups on the two sides of the M_2N_2 ring in the *cis* isomer and the third methyl resonance arises from the two symmetry equivalent methyl groups in the *trans* isomer. The ^1H-NMR spectral assignments for the individual *cis* and *trans* isomers were made from the 1D- and 2D-H,H-COSY- and H,H-NOESY-NMR spectra. The two ^1H-NMR *cis* isomer methyl resonances can be separated by H,H-NOESY experiments into those on the NH side of the M_2N_2 ring and to those on the NCH_2Ph side of the ring. The *cis* methyl resonances for **1**–**3** which show NOESY crosspeaks to the amine NH group occur at slightly higher magnetic fields. Each of the three dimers exists as a 1:1 mixture of *cis*–*trans* geometrical isomers from 30–90° in toluene-d_8 solution. These unusual 1:1 non-temperature dependent isomer ratios suggest that the dimer complexes are not sterically hindered in terms of the benzyl group and that the benzyl group only minimally affects transition state energies and entropies for isomer interconversion [1,12,13,31b,34,35]. The ^1H- and ^{13}C-NMR chemical shifts of the methyl groups in **1**–**3** are dependent on the metal present (higher to lower magnetic field: ^1H, $Al > Ga > In$; ^{13}C, $Al > In > Ga$), consistent with our previous observations on $Me_3M\cdot$secondary amine adducts [15] and the $[Me_2MN(CH_2Ph)_2]_2$ series [8,14,22]. The ^{13}C-NMR chemical shift assignments were made from the ^1H-NMR assignments; 1D- and DEPT-NMR experiments; and the 2D-C,H-COSY- and H,C-HMBC-NMR experiments. The ^{13}C-NMR *cis* isomer methyl resonance which arises from the methyl group on the same side of the ring as the amine hydrogen occurs at slightly lower magnetic fields, in contrast to the respective ^1H-NMR resonances. Slight differences in the *ipso* and *ortho* aromatic ^{13}C-NMR resonances for the *cis* and *trans* isomers allowed the assignment of their individual ^{13}C-NMR chemical shifts from H,C-HMBC-NMR experiment correlations with the methylene protons of the benzyl group. The ^1H- and ^{13}C-NMR chemical shifts for the methyl and methylene groups in **1**–**3** are consistent with, but to higher magnetic field than the corresponding resonances for the $[Me_2MN(CH_2Ph)_2]_2$ series [8,14,22].

The expected molecular ion peaks $[M^+]$ for **1**–**3** are not present in the electron impact mass spectral (EI-MS) data. Instead, $[M^+ - Me]$ peaks are observed, which is consistent with reported data on other series of aminoalane and aminogallane dimers [8,9,14,36,37]. Ion peaks related to the benzylamino moiety are a significant feature of the three mass spectra. The ion peak at $m/z = 106$, arising from $C_6H_5CH_2NH^+$ [38], is the base peak for **1** and **2**. Characteristic ion peaks for alkylbenzenes, such as $C_7H_7^+$ at $m/z = 91$, are also observed. Interestingly, significant concentrations of the monomer species, $[M^+/2 - Me]$, are observed for **2** and **3**, but not for **1**. This observation is consistent with the reported EI-MS data for aminoindane dimers which show significant concentrations of both monomer and dimer species, with an increasing ratio of monomer as the steric bulk of the amide ligand is increased [5], and with the relative enthalpies of dative bond formation for $Me_3M{\cdot}NMe_3$ (Al–N > Ga–N ≈ In–N) [2h]. The EI-MS for $[Me_2AlN(CH_2Ph)_2]_2$, obtained under the same experimental conditions, shows significant formation of $[M^+/2 - Me]$ and related ion peaks, which suggests that there is significantly more steric strain in $[Me_2AlN(CH_2Ph)_2]_2$ than in **1**.

*2.2. Synthesis and characterization of $[MeAlNCH_2Ph]_6$ (**4**) and $[MeGaNCH_2Ph]_6$ (**5**)*

Equimolar mixtures of Me_3M and benzylamine in toluene were heated from 120 to 180 °C and monitored by ^1H-NMR to establish experimental conditions for methane elimination and product formation of a highly condensed species. Thermolysis of the mixtures led to the formation of $[MeAlNCH_2Ph]_6$ (**4**) at 135 °C and $[MeGaNCH_2Ph]_6$ (**5**) at 175 °C. All attempts at obtaining a higher condensed indium-nitrogen containing compound were unsuccessful. The ^1H-NMR spectra were simple, consisting of one single resonance (area = 3) for the methyl group, a single resonance for the CH_2 group (area = 2), and a spectral pattern characteristic of a monosubstituted aromatic group. These data and the accompanying ^{13}C-NMR data suggest the formation of an imidoalane and an imidogallane and not an orthometalated species, as in the higher-temperature thermolysis reactions of Me_3Al and Me_3Ga mixtures with dibenzylamine. Recent work in our laboratory has shown that the rate of the orthometalation reaction for $HN(^tBu)CH_2Ph$ with Me_3Al at 120 °C is much faster than the corresponding reaction of dibenzylamine with Me_3Al at 150 °C due to the incorporation of the sterically bulky ^tBu group [39]. Therefore, substitution of the less sterically demanding hydrogen for a benzyl group would arguably make orthometalation a noncompetitive process in these systems.

The mass spectral data for **4** and **5** and the single crystal X-ray data for **4**, as discussed below, are consistent with hexamer formation ($x = 6$). The major features of the mass spectrum of $[MeAlNCH_2Ph]_6$ are an $[M^+ - Me]$ ion peak at $m/z = 867$, similar to the mass spectra for **1**–**3**, as discussed above; a small ion peak at $m/z = 426$, assignable to $[M^+ - 2Me]/2$, or trimer formation; and the ion peaks associated with $C_6H_5CH_2NH^+$ ($m/z = 106$) and its decomposition. The EI-MS of $[MeGaNCH_2Ph]_6$ is rich in spectral features showing an envelope of ion peaks representing $[M^+]$, starting at $m/z = 1134$. The isotopically derived spectrum, based on $C_{48}H_{60}N_6Ga_6$, is in excellent agreement with the experimental spectrum. The $[MeGaNCH_2Ph]_6$ parent ion fragments more readily than that for $[MeAlNCH_2Ph]_6$. There is a series of ion peak clusters representing the sequential loss of a monomer unit leading from pentamer down to monomer. Within each cluster is an additional series of ion peaks resulting from the loss of methyl and benzylamino groups. Me_2Ga^+ peaks at $m/z = 99$ and 101 are prominent in the spectrum, as in the mass spectrum of **2**.

Imidoalanes, $[MeAlNR'']_n$, derived from the reaction of Me_3Al with primary amines (H_2NR'') are oligomeric, where $n = 3$, 4, 6, 7, and 8 [3,4,6,7,10–12,23–26,28,29,30b,c,32b]. The degree of aggregation, n, depends strongly on the nature of the R'' group attached to nitrogen. For arylamines, $n = 6$ for R'' = phenyl [25], but by adding more sterically demanding groups to the aromatic ring, imidoalanes with $n = 4$ (R'' = 1,3,5-trimethylphenyl) and $n = 3$ (R'' = 2,6-di-*iso*propylphenyl) have been synthesized [28]. Likewise, values of $n = 4$, 6, and 8 have been reported for imidogallanes, $[MeGaNR'']_n$ [24,30a,c,31,32], where the sterically demanding groups R'' = *i*-propyl, ^tBu, and trimethylsilyl display an oligimerization of $n = 4$; the groups R'' = 4-fluorophenyl, ^iBu, and *n*-propyl require $n = 6$; and $n = 8$ for R'' = methyl. Therefore, hexamer formation, $[MeMNCH_2Ph]_6$, for R'' = benzyl is in agreement with the literature values for n.

*2.3. Crystal Structures for **1a**, **2a**, **3a**, and **4***

The X-ray crystal data for **1a**, **2a**, and **3a** are given in Table 1. The ORTEP drawing of the molecular structure and the atom labeling scheme for *trans*-$[Me_2InN(H)CH_2Ph]_2$ (**3a**), are shown in Fig. 1. Selected bond lengths (Å) and angles (°) from the X-ray data are summarized in Table 2 for **1a**, **2a**, and **3a** and are comparable with literature values for structurally similar aminoalane [3,4,6,7,9,16,18–21,25,28,36,40], aminogallane [3,8,11,13,18,28,31b,41–43], and aminoindane dimers [3,5,20,34,35]. The three dimers each crystallize in the *trans* conformation with a planar, almost square, M_2N_2 core. The M(1)–N(1) and M(1)–N(1A) bond distances forming the four-membered ring are slightly different for each of the three dimers. The N–M–N and M–N–M bond angles deviate from 90°, with the deviations being greatest for **3a** and least for **1a**. The N–M–N bond angles are less than 90° and the M–N–M bond angles are greater than 90°; therefore, the M_2N_2 cores are slightly elongated along the M···M axis. These data are in agreement with structural data reported for aminoalanes and aminogallanes with the general formula $[Me_2MN(H)R'']_2$ [7,8,13,20,21,25,28,31b,42,43a]. Significant structural changes occur when the amine hydrogen is replaced by the more sterically demanding benzyl group to form $[Me_2MN(CH_2Ph)_2]_2$ [8,19,22]. On the average: the M–N bonds lengthen 0.028(6) Å (Al), 0.029(6) Å (Ga), and 0.034(8) Å (In); the N–M–N angles increase 3.1(3)° (Al), 2.9(3)° (Ga), and 3.4(3)° (In) with a corresponding decrease in the M–N–M angles; and the external C–M–C angles decrease 3.6(4)° (Al), 3.8(5)° (Ga), and 2.3(6)° (In). Another effect of the substitution of the benzyl group is to distort the M_2N_2 ring so that it is no longer planar, but folded along the N···N axis by 4.0° (Al), 2.7° (Ga), and 4.6° (In). Therefore, in these three series increasing the steric bulk of the amido group is accommodated by small increases in the M–N distances, changes in the internal angles, significant decreases in the external C–M–C angles, and folding of the M_2N_2 rings along the N···N

Table 1
Crystal data and structure refinement parameters for **1a**, **2a**, **3a**, and **4**

Empirical formula	$C_{18}H_{28}Al_2N_2$	$C_{18}H_{28}Ga_2N_2$	$C_{18}H_{28}In_2N_2$	$C_{48}H_{60}Al_6N_6$
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Rhombohedral
Space group	*Pbca*	*Pbca*	$P\bar{1}$	$R\bar{3}$
Unit cell dimensions				
a (Å)	10.7484(12)	10.7231(15)	9.2085(11)	16.7118(20)
b (Å)	8.3002(12)	8.3057(15)	10.4239(11)	
c (Å)	22.1151(28)	22.0896(38)	12.8026(19)	14.9796(30)
α (°)			70.743(10)	
β (°)			85.474(11)	
γ (°)			63.568(9)	
V (Å^3)	1973.0(10)	1967.4(10)	1035.5(5)	3623(2)
Z	2	4	1	3
Crystal size (mm)	0.30 × 0.10 × 0.05	0.45 × 0.35 × 0.30	0.30 × 0.30 × 0.30	0.40 × 0.30 × 0.30
Absorption coefficent (mm^{-1})	0.146	2.737	2.226	0.172
Radiation (Mo–K$_\alpha$), λ (Å)	0.71073	0.71073	0.71073	0.71073
2θ range (°)	2.0–45.0	2.0–45.0	2.0–45.0	1.0–45.0
Scan type	ω	ω	ω–2θ	ω–2θ
Index ranges	$0 \leq h \leq 11$, $0 \leq k \leq 8$, $-23 \leq l \leq 23$	$0 \leq h \leq 11$, $0 \leq k \leq 8$, $-23 \leq l \leq 23$	$-9 \leq h \leq 9$, $-11 \leq k \leq 11$, $-13 \leq l \leq 13$	$-17 \leq h \leq 17$, $-17 \leq k \leq 17$, $-16 \leq l \leq 16$
Reflections collected	2530	2539	5381	6270
Independent reflections	1286 ($R_{int} = 5.68\%$)	1285 ($R_{int} = 4.57\%$)	2691 ($R_{int} = 3.69\%$)	1049 ($R_{int} = 2.82\%$)
Observed reflections	666 ($F > 3.0\sigma(F)$)	829 ($F > 6.0\sigma(F)$)	2187 ($F > 6.0\sigma(F)$)	711 ($F > 6.0\sigma(F)$)
Final *R* indices (observed data)	$R = 8.75\%$, $R_w = 9.11\%$	$R = 3.62\%$, $R_w = 4.14\%$	$R = 4.34\%$, $R_w = 4.72\%$	$R = 4.02\%$, $R_w = 4.21\%$
R indices (all data)		$R = 6.72\%$, $R_w = 7.46\%$	$R = 5.26\%$, $R_w = 7.43\%$	$R = 7.56\%$, $R_w = 5.64\%$
Largest differential peak and hole (e Å^{-3})	0.51 and −0.40	0.52 and −0.38	1.19 and −1.22	0.27 and −0.24

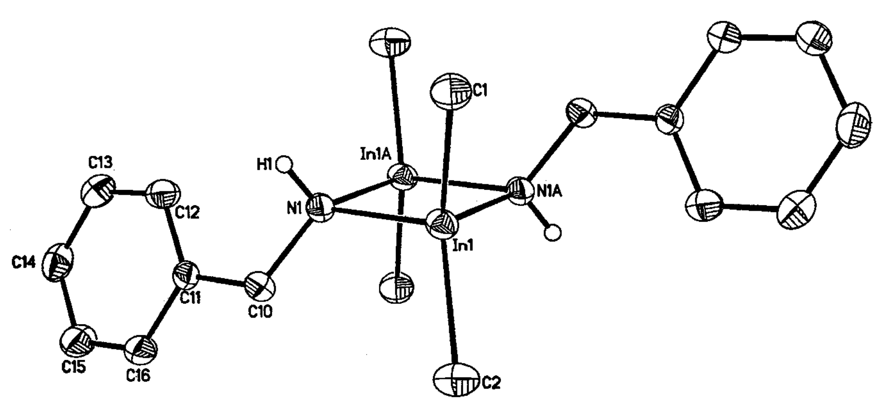

Fig. 1. Molecular structure of **3a**.

Table 2
Selected bond lengths (Å) and bond angles (°) for **1a**, **2a**, and **3a** (M = Al, Ga, In)

	$[Me_2AlN(H)CH_2Ph]_2$	$[Me_2GaN(H)CH_2Ph]_2$	$[Me_2InN(H)CH_2Ph]_2$
Bond lengths			
M(1)–N(1)	1.949(8)	2.005(6)	2.205(9)
M(1)–C(1)	1.931(12)	1.960(8)	2.161(7)
M(1)–C(2)	1.955(10)	1.951(7)	2.144(7)
M(1)···M(1A)	2.817(5)	2.924(1)	3.292(1)
M(1)–N(1A)	1.961(7)	2.024(5)	2.222(6)
N(1)–C(10)	1.422(11)	1.479(8)	1.455(9)
Bond angles			
N(1)–M(1)–C(1)	111.5(4)	110.9(3)	108.4(4)
N(1)–M(1)–C(2)	111.8(4)	106.5(3)	107.1(3)
C(1)–M(1)–C(2)	121.6(4)	125.4(3)	131.4(4)
N(1)–M(1)–N(1A)	87.8(3)	87.0(2)	84.0(3)
C(1)–M(1)–N(1A)	109.6(4)	108.2(3)	106.4(3)
C(2)–M(1)–N(1A)	109.3(4)	112.1(3)	109.3(3)
M(1)–N(1)–C(10)	121.9(6)	118.3(4)	116.9(5)
M(1)–N(1)–M(1A)	92.2(3)	93.0(2)	96.0(3)
C(10)–N(1)–M(1A)	120.1(6)	117.4(4)	115.3(5)
N(1)–C(10)–C(11)	117.2(8)	116.7(5)	117.5(6)

axes. These observations are in agreement with reported correlations of the steric properties of functional groups attached to the amine nitrogen with the corresponding dimer geometries [5,7–9,25,28,35,36, 40,41,43b].

The ORTEP drawing of the molecular structure and the atom labeling scheme for $[MeAlNCH_2Ph]_6$ (**4**), is shown in Fig. 2 and selected bond lengths (Å) and angles (°) are summarized in Table 3. $[MeAlNCH_2Ph]_6$ crystallizes in a rhombohedral structure where the $(AlN)_6$ cage consists of two six-membered $(AlN)_3$ rings linked by six transverse Al–N bonds. The Al–N bonds in the two six-membered rings (1.890(7) Å, average) are shorter than the transverse bonds (1.985(3) Å, average) consistent with the structural data for other imidoalane hexamers of the form $[MeAlNR]_6$, where R = *i*-propyl [23], phenyl [25], 4-fluorophenyl [30c], and $C_2H_4NMe_2$ [12]. The N–Al–N bond angles in the two six-membered rings are significantly smaller (114.2(2)°) than the Al–N–Al bond angles (125.3(1)°), whereas the trend is opposite for the bond angles in the four-membered rings.

3. Experimental details

3.1. General experimental conditions

Standard inert-atmosphere techniques were used for the synthesis, solution preparation, and manipulation of all compounds. Trimethylaluminum, Texas Alkyls, was used as obtained; trimethylgallium, Morton Advanced Materials, was distilled under vacuum prior to use; and trimethylindium, Morton Advanced Materials, was sublimed prior to use. Benzylamine, benzene-d_6, and toluene-d_8, Aldrich, were stored over molecular sieves. ^{1}H- and ^{13}C-NMR spectra were obtained on a Bruker DRX-400 NMR spectrometer, using benzene-d_6 as solvent and internal reference for the room temperature (r.t.) studies. Toluene-d_8 was used as the solvent for the variable-temperature studies. The ^{1}H- and ^{13}C-NMR chemical shift assignments were made based on normal 1D- and ^{13}C-DEPT- and 2D-H,H-COSY-, H,H-NOESY-, C,H-COSY-, and H,C-HMBC-NMR

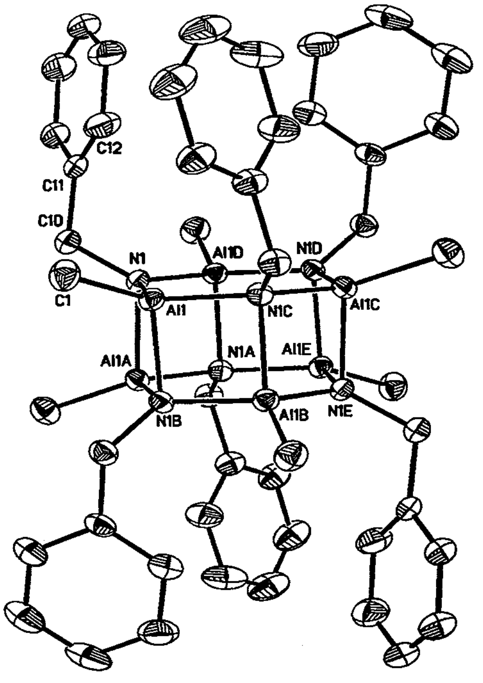

Fig. 2. Molecular structure of **4**.

Table 3
Selected bond lengths (Å) and bond angles (°) for $[MeAlNCH_2Ph]_6$ (**4**)

Bond lengths			
Al(1)–N(1)	1.893(4)	Al(1)–C(1)	1.935(3)
Al(1)···Al(1A)	2.703(2)	Al(1)···Al(1B)	2.703(1)
Al(1)–N(1C)	1.888(3)	Al(1)–N(1B)	1.985(3)
N(1)–C(10)	1.508(5)	N(1)–Al(1A)	1.985(3)
Bond angles			
N(1)–Al(1)–C(1)	118.8(2)	N(1)–Al(1)–N(1C)	114.2(2)
C(1)–Al(1)–N(1C)	119.7(2)	C(1)–Al(1)–N(1B)	113.5(1)
N(1C)–Al(1)–N(1B)	91.4(1)	Al(1)–N(1)–C(10)	115.5(2)
Al(1)–N(1)–Al(1A)	88.3(1)	C(10)–N(1)–Al(1A)	117.1(2)
Al(1)–N(1)–Al(1D)	125.3(1)	C(10)–N(1)–Al(1D)	114.3(2)
Al(1A)–N(1)–Al(1D)	88.5(1)	N(1)–C(10)–C(11)	115.6(3)

experiments. IR spectra were obtained using split mull samples in Nujol and Kel-F (halocarbon) on KBr plates. EI-MS data were obtained on a Finnigan MAT95Q mass spectrometer with an electron energy of 70 eV. The samples were introduced using a direct-insertion probe under inert-atmosphere conditions. Elemental analyses were performed by E&R Microanalytical Laboratory, Inc., Parsippany, NJ. Melting points were obtained in capillaries under nitrogen and are uncorrected.

3.2. Synthesis of $[Me_2AlN(H)CH_2Ph]_2$ (1), $[Me_2GaN(H)CH_2Ph]_2$ (2), and $[Me_2InN(H)CH_2Ph]_2$ (3)

Compounds **1** [1], **2**, and **3** were synthesized by thermolysis of 1:1 equimolar mixtures of the respective Me_3M (M = Al, Ga, In) with benzylamine dissolved in 15 ml of toluene. Each mixture was put into a high-pressure tube which was placed in an oil bath at a selected temperature. The progress of each reaction was monitored by ^{1}H-NMR. The reaction conditions were: compound **1**, 0.673 g Me_3Al with 1.000 g benzylamine at 90 °C for 1.5 days (1.47 g, 96% yield); **2**, 1.072 g Me_3Ga with 1.000 g benzylamine at 120 °C for 3.0 days (1.89 g, 98% yield); and **3**, 1.492 g Me_3In with 1.000 g benzylamine at 90 °C for 2.0 d (2.03 g, 87% yield). In solution, each of the dimers exists as a 1:1 mixture of *trans* (**a**) and *cis* (**b**) isomers. Crystals were obtained from each of the reaction mixtures upon standing at r.t. The crystals were dried under vacuum and recrystallized from toluene at −15 °C. In each case, only solid *trans* (**a**) isomer was obtained as evidenced by single crystal X-ray structural analysis.

3.3. Synthesis of $[MeAlNCH_2Ph]_6$ (4) and $[MeGaNCH_2Ph]_6$ (5)

The aluminum and gallium hexamers were synthesized and crystals obtained in a manner similar to the dimers above, except that greater thermolysis temperatures were required. The reaction conditions were: compound **4**, 0.673 g Me_3Al with 1.000 g benzylamine at 135 °C for 2.0 days (1.14 g, 83% yield); and **5**, 1.060 g Me_3Ga with 1.000 g benzylamine at 175 °C for 3.0 days (0.85 g, 48% yield). X-ray quality crystals were obtained for **4** only. We were unsuccessful in synthesizing the corresponding indium hexamer from either the thermolysis of 1:1 Me_3In/benzylamine mixtures or thermolysis of **3**.

3.4. Characterization data

3.4.1. $[Me_2AlN(H)CH_2Ph]_2$ (1) [1]

M.p.: 87–89 °C (65–68 °C) [1]. ^{1}H-NMR (**1a**): δ −0.53 (s, 12H, $AlCH_3$), 0.99 (t, 2H, NH), 3.66 (d, 4H, NCH_2), 6.96 (m, 4H, H12, H16), 7.09 (m, 4H, H13, H15), 7.02 (m, 2H, H14); ^{1}H-NMR (**1b**): δ −0.58 (s, 6H, $AlCH_3$), −0.48 (s, 6H, $AlCH_3$), 0.90 (t, 2H, NH), 3.68 (d, 4H, NCH_2), 6.96 (m, 4H, H12, H16), 7.09 (m, 4H, H13, H15), 7.02 (m, 2H, H14). ^{13}C-NMR (**1a**): δ −10.44 ($AlCH_3$), 47.10 (NCH_2), 141.57 (C11), 127.02 (C12, C16), 128.83 (C13, C15), 127.35 (C14); ^{13}C-NMR (**1b**): δ −12.34 ($AlCH_3$), −8.54 ($AlCH_3$), 47.19 (NCH_2), 141.55 (C11), 126.92 (C12, C16), 128.83 (C13, C15), 127.33 (C14). MS; m/z: 311 [$M^+ - 15$].

3.4.2. $[Me_2GaN(H)CH_2Ph]_2$ (2)

M.p.: 82–86 °C. ^{1}H-NMR (**2a**): δ −0.19 (s, 12H, $GaCH_3$), 1.04 (t, 2H, NH), 3.71 (d, 4H, NCH_2), 6.96 (m, 4H, H12, H16), 7.10 (m, 4H, H13, H15), 7.03 (m, 2H, H14); ^{1}H-NMR (**2b**): δ −0.21 (s, 6H, $GaCH_3$), −0.17 (s, 6H, $GaCH_3$), 0.995 (t, 2H, NH), 3.72 (d, 4H, NCH_2), 6.96 (m, 4H, H12, H16), 7.10 (m, 4H, H13, H15), 7.03 (m, 2H, H14). ^{13}C-NMR (**2a**): δ −8.01 ($GaCH_3$), 48.87 (NCH_2), 142.54 (C11), 126.90 (C12, C16), 128.72 (C13, C15), 127.07 (C14); ^{13}C-NMR (**2b**): δ −10.77 ($GaCH_3$), −5.32 ($GaCH_3$), 49.00 (NCH_2), 142.51 (C11), 126.89 (C12, C16), 128.72 (C13, C15), 127.07 (C14). IR (cm^{-1}): 3307 (w), 3028 (w), 2944 (w), 2884 (m), 2823 (w), 1950 (w), 1661 (w), 1199 (s), 1156 (m), 1078 (m), 1039 (s), 1023 (s), 961 (m), 848 (s), 734 (vs), 694 (s), 620 (m), 578 (s). MS; m/z: 395, 397, 399 [$M^+ - 15$]. Anal. Calc. for $C_{18}H_{28}Ga_2N_2$: C, 52.49; H, 6.85; N, 6.80. Found: C, 52.63; H, 6.90; N 6.80%.

3.4.3. $[Me_2InN(H)CH_2Ph]_2$ (3)

M.p.: 80–82 °C. ^{1}H-NMR (**3a**): δ −0.15 (s, 12H, $InCH_3$), 0.91 (t, 2H, NH), 3.79 (d, 4H, NCH_2), 6.95 (m, 4H, H12, H16), 7.11 (m, 4H, H13, H15), 7.02 (m, 2H, H14); ^{1}H-NMR (**3b**): δ −0.16 (s, 6H, $InCH_3$), −0.13 (s, 6H, $InCH_3$), 0.87 (t, 2H, NH), 3.81 (d, 4H, NCH_2), 6.95 (m, 4H, H12, H16), 7.11 (m, 4H, H13, H15), 7.02 (m, 2H, H14). ^{13}C-NMR (**3a**): δ −9.30 ($InCH_3$), 50.60 (NCH_2), 144.62 (C11), 126.72 (C12, C16), 128.79 (C13, C15), 126.98 (C14); ^{13}C-NMR (**3b**): δ −11.26 ($InCH_3$),

−7.34 ($InCH_3$), 50.72 (NCH_2), 144.57 (C11), 126.69 (C12, C16), 128.79 (C13, C15), 126.98 (C14). IR (cm^{-1}): 3297 (m), 3061 (w), 3023 (w), 2963 (m), 2911 (m), 2852 (w), 1943 (w), 1802 (w), 1599 (m), 1294 (m), 1189 (s), 1158 (m), 1145 (s), 1077 (m), 1043 (s), 1025 (vs), 968 (s), 810 (s), 728 (s), 692 (vs), 508 (s). MS; m/z: 487 [$M^+ - 15$]. Anal. Calc. for $C_{18}H_{28}In_2N_2$: C, 43.06; H, 5.62; N, 5.58. Found: C, 43.39; H, 5.92; N 5.69%.

3.4.4. *[$MeAlNCH_2Ph]_6$* (**4**)

M.p. (dec.): 328 °C. ^1H-NMR (**4**): δ −0.44 (s, 18H, $AlCH_3$), 4.22 (s, 12H, NCH_2), 7.13 (m, 12H, H12, H16), 7.20 (m, 12H, H13, H15), 7.16 (m, 6H, H14). ^{13}C-NMR (**4**): δ −13.52 ($AlCH_3$), 49.95 (NCH_2), 143.72 (C11), 127.4 (C12, C16), 128.9 (C13, C15), 126.9 (C14). IR (cm^{-1}): 3083 (vw), 3058 (w), 3026 (w), 2927 (w), 2884 (w), 2853 (w), 1946 (w), 1869 (w), 1802 (w), 1661 (w), 1310 (m), 1246 (m), 1198 (m), 1180 (m), 1005 (s), 992 (s), 976 (s), 905 (m), 746 (s), 734 (s), 691 (s), 531 (s). MS; m/z: 867 [$M^+ - 15$]. Anal. Calc. for $C_{48}H_{60}Al_6N_6$: C, 65.29; H, 6.85; N, 9.52. Found: C, 65.19; H, 6.88; N, 9.39%.

3.4.5. *[$MeGaNCH_2Ph]_6$* (**5**)

M.p. (dec.): 290 °C. ^1H-NMR (**4**): δ −0.28 (s, 18H, $GaCH_3$), 4.28 (s, 12H, NCH_2), 7.16 (m, 12H, H12, H16), 7.25 (m, 12H, H13, H15), 7.16 (m, 6H, H14). ^{13}C-NMR (**4**): δ −12.69 ($GaCH_3$), 53.13 (NCH_2), 144.50 (C11), 126.83 (C12, C16), 128.71 (C13, C15), 126.71 (C14). IR (cm^{-1}): 3081 (vw), 3057 (w), 3026 (w), 2914 (w), 2869 (w), 2840 (w), 1661 (m), 1307 (m), 1241 (m), 1196 (m), 1178 (m), 1030 (m), 1015 (s), 1007 (s), 982 (m), 904 (m), 742 (m), 698 (m), 620 (m), 569 (m). MS; m/z: 1134–1144 [M^+]. Anal. Calc. for $C_{48}H_{60}Ga_6N_6$: C, 50.60; H, 5.31; N, 7.38. Found: C, 50.42; H, 5.31; N, 6.43%.

3.5. *Crystallographic data*

X-ray quality single crystals of **1**–**4** were sealed in thin-walled capillaries under nitrogen. Molecular structure data were acquired using an Enraf–Nonius CAD4 diffractometer with κ-geometry at 298 K using Mo–K_α radiation ($\lambda = 0.71073$ Å). Refinement procedures were conducted using the SHELXTL-PC program package [33]. Each structure was solved by direct methods with full-matrix least-squares refinement. Positional and anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions with the appropriate staggered geometry. The U_{eq} of each hydrogen atom was set equal to that of the carbon atom to which it was bound. Refinement continued until convergence was reached with the mean $\Delta/\sigma < 0.01$. Upon convergence, no chemically significant residuals were observed in the final difference-Fourier synthesis. Further details of the data collection and refinement processes are provided in Table 1.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 132624, 132625, 132626, and 132627 for *trans*-[$Me_2AlN(H)CH_2Ph]_2$, *trans*-[$Me_2GaN(H)CH_2Ph]_2$, *trans*-[$Me_2InN(H)CH_2Ph]_2$, and [$MeAlNCH_2Ph]_6$, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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