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Journal of Organometallic Chemistry 586 (1999) 138–144

# *N*,*N*′-Unsubstituted amidinato metallacycle complexes of Group 13 metal alkyls: the crystal structure of trimeric [{$Me_2Al(\mu\text{-}HNCPhNH)$}$_3$]

James Barker [a], Damian R. Aris [b], Nicholas C. Blacker [b], William Errington [b], Paul R. Phillips [b], Malcolm G.H. Wallbridge [b,]*

[a] *Associated Octel Co. Ltd., Ellesmere Port, South Wirral L65 3HF, UK*
[b] *Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK*

Received 26 February 1999; received in revised form 20 April 1999

**Abstract**

The amidinato complexes [$Me_2ML$] (L = HNCPhNH, M = Al, Ga, In; L = HNCBu$^t$NH, M = Ga) result from the reaction of the trialkylmetal with an equimolar amount of the amidine. MS data indicate that the complexes exist as dimers or trimers in the gas phase. X-ray crystallographic studies on [{$Me_2Al(\mu\text{-}HNCPhNH)$}$_3$] (**1**) reveal a novel trimeric structure in the solid state, with bridging benzamidinato ligands, and a 12-membered metallacycle. Reaction of $InMe_3$ with two moles of benzamidine yields a cyclic imidoylamidinato derivative with a six-membered [InNCNCN] ring. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Group 13; Amidinato; Structure; Trimer; Metallacycle

## 1. Introduction

The recent interest in the use of Group 13 metal nitrides (AlN, GaN, etc.) as blue lasers and light-emitting diodes, has led to a renewed interest in the chemistry of Group 13/15 molecular species which might serve as precursors to such materials [1]. As part of our study of the amidinato complexes of Group 13 metals, we have reported some *N*,*N*′-diarylbenzamidinato derivatives of trialkylgallium, e.g. [$Me_2Ga(PhNCPhNPh)$], and have shown that they do exist as monomers, and act as precursors to gallium nitride [2]. However, there is still a need to minimise both the carbon content of the ligand group while still retaining the desirable properties of the derivatives, such as volatility, and to use amidines which are readily available and easily handled. In addition to those mentioned above, similar compounds involving other *N*,*N*′-substituted ligands have been reported, as typified by [$Me_2Al(R'NCRNR')$] [R = Me, R′ = $SiMe_3$ [3]; R = Me, R′ = Pr$^i$, Cy (cyclohexyl) [4]; R = Bu$^t$, R′ = Pr$^i$, Bu$^t$, Cy [4]; R = Cl, R′ = Bu$^t$ [5]], [$R''_2Al(R'NCRNR')$] (R″ = $CH_2Ph$, R = Bu$^t$, R′ = Pr$^i$, Cy; R″ = $CH_2CMe_3$, R = Bu$^t$, R′ = Pr$^i$, Cy) [4], [$Cl_2Al(R'NCRNR')$] (R = Ph, R′ = $SiMe_3$ [6]; R = Me, R′ = Pr$^i$ [4]; R = Bu$^t$, R′ = Pr$^i$, Cy, $NSiMe_3$ [4]; R = $NPr^i_2$, R′ = Pr$^i$ [5]). X-ray studies on these types of compounds show that they also adopt a monomeric structure with the amidinato ligand bonding in the chelating bidentate form (**A**).

Both the substituents on the *N*,*N*′-atoms of the amidinato ligand, and the size of the central metal atom, are important in determining the degree of association of the metal complex. This is clearly demonstrated by the fact that in contrast to the above series the compounds [$Me_2M(MeNCMeNMe)$] (M = Al, Ga, In) [7] are dimeric in the solid state. Also, while the bis-amidinato aluminium derivatives [$ClAl(R'NCRNR')_2$] (R = Me, R′ = Pr$^i$; R = Bu$^t$, R′ = Pr$^i$, Cy) are monomeric [4] the

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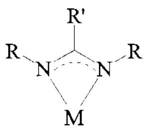
* Corresponding author. Fax: + 44-1203-524112.

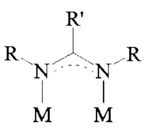
*E-mail address:* msihh@snow.csv.warwick.ac.uk (M.G.H. Wallbridge)

PII: S0022-328X(99)00253-3

indium compounds [XIn(CyNCHNCy)$_2$] (X = Cl, Me) are dimeric with amidinato ligands in the bridging mode (**B**) [8].



**A**



**B**

Various types of bonding, in the amidinato–metal system, are well established for the transition metals [9,10]. Nevertheless, there remains a need to rationalise the bonding patterns adopted by variously substituted amidine ligands, such as those with smaller substituents on the nitrogen atoms, with a wider range of metals, and especially the post-transition elements. We now report a series of compounds derived from the *N*,*N*′-unsubstituted amidinato ligands [HNCRNH]$^-$ (R = $Bu^t$, Ph) and the metal methyls of aluminium, gallium and indium.

## 2. Experimental

Manipulations were carried out using standard Schlenk techniques and in a dinitrogen-filled glove box. Solvents were dried over $CaH_2$, $P_2O_5$ or benzophenone ketyl as appropriate and distilled under dinitrogen prior to use. The trimethylmetal compounds were purchased from Strem, and the amidine salts from Aldrich. Microanalytical data were obtained using a Leeman Labs Inc. CE440 elemental (C, H, N) analyser. NMR spectra were recorded using a Bruker Associates ACF 250 instrument, and mass spectra were run using a Kratos MS80, or were recorded by the EPSRC service at the University of Swansea. Benzamidine was prepared by the action of sodium methoxide on benzamidine hydrochloride in methanol, followed by the removal of the solvent, and sublimation of the residue in vacuo at 80°C. The *t*-butylamidine [$H_2NCBu^tNH$] was prepared by the action of LiBu on the hydrochloride salt of the amidine, followed by sublimation under vacuum at 100°C.

### 2.1. Preparation of [{$Me_2Al(\mu$-HNCPhNH)}$_3$] (**1**)

Trimethylaluminium (1.40 cm$^3$ of 2 mol dm$^{-3}$ $Me_3Al$ in hexane; 2.8 mmol) was added to a suspension of benzamidine (0.31 g, 2.6 mmol) in hexane (40 cm$^3$) at −78°C. The reaction mixture was allowed to warm to room temperature (r.t.), and stirred for 1 h. After concentrating the solution, the colourless solid product was filtered off and dried under vacuum (yield 0.33 g, 72%). Anal. Calc. for $C_{27}H_{39}N_6Al_3$: C, 61.3; H, 7.44; N, 15.9. Found: C, 61.01; H, 6.94; N, 16.1%. NMR ($CDCl_3$) $\delta_H$: 7.53–7.42 (m, 5H, $C_6H_5$), 5.74 (br, s, 1H, NH), 4.90 (br, s, 1H, NH) and −0.97 (s, 6H, Al–$CH_3$). NMR ($CDCl_3$) $\delta_C$: 176.16 (N$\underline{C}$N), 137.40 (NC($\underline{C}$)N), 131.14, 128.57, 127.12 ($C_6H_5$) and −9.48 (Al-$\underline{C}H_3$). Crystals of **1** were obtained from the reaction filtrate by removal of some of the solvent, and storage of the concentrated solution under argon at −20°C for 4 weeks.

### 2.2. Preparation of [{$Me_2Ga(\mu$-HNCPhNH)}$_3$] (**2**)

Trimethylgallium (0.45 g, 3.92 mmol) was condensed on to benzamidine (0.47 g, 3.92 mmol) under vacuum at −196°C in the absence of solvent to give a foamy mass which could be broken down to give a colourless solid. Anal. Calc. for $C_{27}H_{39}N_6Ga_3$: C, 49.4; H, 5.98. Found: C, 49.6; H, 6.00%. NMR ($CDCl_3$) $\delta_H$: 7.35 (m, 2H, $C_6H_5$), 7.10 (m, 3H, $C_6H_5$), 5.88 (br, s, 1H, NH), 4.63 (br, s, 1H, NH) and −0.27 (s, 6H, Ga–$C\underline{H}_3$).

### 2.3. Preparation of [{$Me_2In(\mu$-HNCPhNH)}$_3$] (**3**)

Benzamidine (0.65 g, 5.42 mmol) was added to a suspension of trimethylindium (0.96 g, 6.0 mmol) in hexane (50 cm$^3$) at −78°C. After stirring for 1.5 h at r.t., an insoluble colourless product had formed, and this was isolated by filtration. Anal. Calc. for $C_{27}H_{39}N_6In_3$: C, 40.9; H, 4.96; N, 10.6. Found: C, 40.7; H, 5.13; N, 10.2%. NMR ($CDCl_3$) $\delta_H$: 7.54–7.37 (m, 5H, $C_6H_5$), 5.35 (br, s, 1H, NH), 4.67 (br, s, 1H, NH) and −0.48 (s, 6H, In–$CH_3$). NMR ($CDCl_3$) $\delta_C$: 176.04 (N$\underline{C}$N), 139.95 (NC($\underline{C}$)N), 129.82, 128.38, 126.54 ($C_6H_5$) and 8.90 (In–$\underline{C}H_3$).

### 2.4. Preparation of [$Me_2Ga(\mu$-$HNCBu^tNH$)] (**4**)

Trimethylgallium (0.44 g, 3.83 mmol) was condensed on to the *t*-butyl substituted amidine [$H_2NCBu^tNH$] (0.38 g, 3.83 mmol) under vacuum at −196°C in the absence of solvent to give a colourless solid. This residue sublimed at 80°C under a static vacuum onto a water-cooled cold finger. Anal. Calc. for $C_7H_{17}N_2Ga$: C, 42.3; H, 8.6; N, 14.1. Found: C, 41.9; H, 8.5; N, 13.7%. NMR ($C_6D_6$) $\delta_H$: 4.73 (s, br, 2H, NH), 0.79 (s, 9H, C($CH_3$)$_3$), 0.08 (s, 6H, Ga–$CH_3$). NMR ($C_6D_6$) $\delta_C$: 184.19 (N$\underline{C}$N), 38.38 ($\underline{C}$($CH_3$)$_3$), 27.61 (C($\underline{C}H_3$)$_3$) and −7.74 (Ga–$\underline{C}H_3$). IR (Nujol) 3409(m), 3016(m), 1562(s), 1536(m), 1514(s), 1503(m), 1372(m), 1297(w), 1066(w), 1033(m), 799(s), 722(s), 699(s), 608(s), 574(s), 531(s), 409(w–m) cm$^{-1}$.

### 2.5. Preparation of [$Me_2In$(HNCPhNCPhNH)]

Trimethyl indium (0.45 g, 2.8 mmol) was suspended in hexane (ca. 50 cm$^3$) and benzamidine (0.61 g, 5.1 mmol) was added slowly with stirring at −80°C. After the initial reaction had diminished the mixture was heated to 55°C for 6 h. The product was isolated by filtration as a colourless solid (0.68 g, 73%), and identified from its spectroscopic data, which was not only extremely clean but also very closely parallels that observed for the corresponding aluminium and gallium compounds. NMR ($CDCl_3$) $\delta_H$: 7.57–7.42 (m, 10H, $C_6H_5$), $-0.50$ (s, 6H, In–$CH_3$). NMR ($CDCl_3$) $\delta_C$: 176.1 (C ring), 137.4, 131.2, 128.6, 127.1 (Ph group), $-9.4$ (In–$CH_3$), MS (FAB, 3-nitrobenzyl alcohol) $m/z = 368$ (M + 1), 367 (M, where $M = C_{16}H_{18}N_3In$, based on $^{115}In$), 352 ($M - CH_3$), 351 ($M - CH_4$), 222 ($M - InMe_2$), 145 ($M - C_{14}H_{12}N_3$), and 115 (from $^{115}In$, 100%). IR (Nujol) 3363(m), 1585(s), 1290(m), 1270(m), 1194(m), 788(s), 633(s) 457(m) $cm^{-1}$.

### 2.6. X-ray crystallography

Crystals of **1** were placed under Nujol and mounted into Lindemann tubes under argon. The tubes were then sealed using a small flame.

#### 2.6.1. Crystal data

$C_{27}H_{39}Al_3N_6$, $M_r = 528.58$, monoclinic, $a = 10.235(2)$, $b = 14.541(2)$, $c = 10.8190(12)$ Å, $\beta = 103.940(14)°$, $V = 1562.7(4)$ Å$^3$ (by least-squares refinement on 250 reflections), $T = 150(2)$ K, $\lambda = 0.71073$ Å, space group $P2_1$, $Z = 2$, colourless crystal dimensions 0.28 × 0.14 × 0.11 mm.

#### 2.6.2. Data collection and processing

Data were collected using a Delft Instruments FAST TV area-detector diffractometer. The *hkl* ranges were $-11/11$, $-16/15$, $-7/12$; 7062 ($R_{int} = 0.09$) reflections measured, 4387 unique, $\theta$ max. = 25°. No absorption correction was applied.

#### 2.6.3. Structure analysis and refinement

The structure was solved by direct methods using SHELXTL [11]. Full-matrix least-squares refinement on $F^2$ for all data using SHELXL-93 [12]. Hydrogen atoms were added at calculated positions and refined using a riding model. Anisotropic temperature factors were used for all non-H atoms; H-atoms were given isotropic temperature factors equal to 1.2 (or 1.5 for methyl hydrogens) times the equivalent isotropic displacement parameter of the atom to which the H-atom is attached. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0664P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. Goodness-of-fit on $F^2$ was 0.982, $R_1$ for $[I > 2\sigma(I)] = 0.0619$, $wR_2 = 0.1625$ (see Table 1).

## 3. Results and discussion

The reaction of equimolar quantities of the trimethylmetal compounds with *N*,*N*′-unsubstituted amidines [$H_2NCRNH$] leads to the evolution of one mole of methane (Eq. (1)). The reactions of benzamidine (R = Ph) with the trimethyl derivatives of aluminium and indium proceed cleanly in hexane, with methane being evolved at $-50$°C, to produce [$Me_2M(HNCPhNH)$] [M = Al (**1**); In (**3**)] as colourless solids which are slightly air-reactive. The reactions involving trimethylgallium were most successfully achieved in the absence of solvent, by condensing the reagent onto the appropriate amidine in vacuo. In this way, trimethylgallium has been reacted with benzamidine and the *t*-butylamidine (R = Bu$^t$) to give [$Me_2Ga(HNCRNH)$] (R = Ph (**2**); Bu$^t$ (**4**)). Yields from these type of reaction are generally good (ca. 75%), with little in the way of side reactions. The products can be purified by recrystallisation from hexane, or in the case of **4**, by sublimation under vacuum.

$$Me_3M + [H_2NCRNH] \rightarrow [Me_2M(HNCRNH)] + CH_4\uparrow \quad (1)$$

(R = Ph, M = Al, Ga, In; R = Bu$^t$, M = Ga)

The compounds have been characterised by NMR, elemental analyses, IR, and MS and the structure of **1** has been determined by a single-crystal X-ray diffraction study. The $^1$H-NMR ($CDCl_3$) spectra for each of the compounds **1**–**3** show two broad resonances at 6–4.5 ppm, each corresponding to a single hydrogen. These have been assigned to the NH groups on the

Table 1
Selected bond lengths (Å) and bond angles (°) for compound **1**

| | | | |
|---|---|---|---|
| Al(1)–N(1) | 1.910(5) | Al(2)–N(2) | 1.912(4) |
| Al(2)–N(3) | 1.905(4) | Al(3)–N(4) | 1.900(4) |
| Al(3)–N(5) | 1.915(5) | Al(1)–N(6) | 1.922(4) |
| Al(1)–C(26) | 1.961(6) | Al(1)–C(27) | 1.965(6) |
| Al(2)–C(8) | 1.950(5) | Al(2)–C(9) | 1.976(6) |
| Al(3)–C(17) | 1.962(6) | Al(3)–C(18) | 1.971(5) |
| N(1)–C(1) | 1.328(7) | N(2)–C(1) | 1.325(6) |
| N(3)–C(10) | 1.322(6) | N(4)–C(10) | 1.316(6) |
| N(5)–C(19) | 1.351(6) | N(6)–C(19) | 1.312(6) |
| C(1)–C(2) | 1.480(8) | C(10)–C(11) | 1.491(7) |
| C(19)–C(20) | 1.473(7) | | |
| N(1)–Al(1)–N(6) | 98.5(2) | N(2)–Al(2)–N(3) | 102.6(2) |
| N(4)–Al(3)–N(5) | 96.6(2) | N(1)–Al(1)–C(26) | 105.1(2) |
| N(1)–Al(1)–C(27) | 109.3(2) | N(2)–Al(2)–C(9) | 99.5(2) |
| N(2)–Al(2)–C(8) | 118.8(2) | N(3)–Al(2)–C(8) | 105.9(2) |
| N(3)–Al(2)–C(9) | 112.9(2) | N(4)–Al(3)–C(17) | 111.3(2) |
| N(4)–Al(3)–C(18) | 113.4(2) | N(5)–Al(3)–C(17) | 111.6(2) |
| N(5)–Al(3)–C(18) | 104.1(2) | N(6)–Al(1)–C(26) | 111.9(2) |
| N(6)–Al(1)–C(27) | 109.2(2) | C(8)–Al(2)–C(9) | 116.5(3) |
| C(17)–Al(3)–C(18) | 117.5(2) | C(26)–Al(1)–C(27) | 120.5(3) |
| N(1)–C(1)–N(2) | 122.0(5) | N(3)–C(10)–N(4) | 122.6(4) |
| N(5)–C(19)–N(6) | 123.2(5) | C(1)–N(1)–Al(1) | 129.8(4) |
| C(1)–N(2)–Al(2) | 136.7(4) | C(10)–N(3)–Al(2) | 129.9(4) |
| C(10)–N(4)–Al(3) | 137.1(4) | C(19)–N(5)–Al(3) | 131.5(4) |
| C(19)–N(6)–Al(1) | 132.9(4) | N(1)–C(1)–C(2) | 119.9(5) |
| N(2)–C(1)–C(2) | 118.1(5) | N(3)–C(10)–C(11) | 119.9(5) |
| N(4)–C(10)–C(11) | 117.5(4) | N(5)–C(19)–C(20) | 118.4(4) |
| N(6)–C(19)–C(20) | 118.4(4) | | |

benzamidinato ligands. The source of the difference between these two NH groups is uncertain, and variable temperature $^1$H-NMR of compound **1** in $C_6D_5CD_3$ showed no significant change in either the intensity or the position of these resonances. However, the crystal structure of **1** does show that there are two sets of NH protons (with three protons in each set) around the 12-membered ring which could explain the two different resonances, assuming that the same orientation of the two sets of NH groups persists in solution. This point is discussed further below in the section concerned with details of the structure. The aromatic region of these spectra is generally not well defined, but the sharp singlets near $\delta$ −0.5 from the methyl metal protons give a good indication of purity. The $^1$H-NMR spectrum ($C_6D_6$) of compound **4** shows one NH resonance at 4.73 ppm, which corresponds to two hydrogen atoms. The $^{13}$C-NMR data are useful in that they indicate that the benzamidinato ligands adopt a bridging bonding mode, as **1**, **3** and **4** show shifts for the central carbon in the amidinato back bone of ca. 176–184 ppm which differ considerably from the typical shifts for chelating benzamidinato ligands of 156–167 ppm.

Chemical ionisation (CI) MS using ammonia reveals a molecular ion for compound **1** (RMM 528) at $m/z = 529$ (7.4%) that corresponds to the trimeric state seen in the crystal structure. The highest mass peak seen in the EI spectrum of **1** occurs at $m/z = 498$ (1.0%) corresponding to the loss of two methyl groups and the ion $[C_{25}H_{33}N_6Al_3]^+$. Although compounds **2** and **3** do not show molecular ions, the spectra provide important evidence that these complexes are isostructural with compound **1**. The isotope distribution (based on $^{69}$Ga, 60.5%; $^{71}$Ga, 39.5%), was consistent with the presence of three gallium atoms in the ion with $m/z = 527$ corresponding to $[Me_5Ga_3(C_{14}H_{14}N_4)]H^+$, and the loss of a benzamidinato ligand ($C_7H_7N_2$) in the higher regions of the CI spectrum of compound **2**. FAB MS for compound **3** (RMM = 792) with 3-nitrobenzyl alcohol as the matrix, shows fragments such as $[C_{20}H_{31}N_6In_3]^+$ ($m/z$ 700, 1.5%) and $[C_{19}H_{27}N_6In_3]^+$ ($m/z$ 684, 2.5%), which arise from the loss of phenyl plus methyl groups, and then methane with the proposed trimer ring left intact. EI MS for this complex shows the loss of $Me_2In(NH)_2$ from the ring, mirroring the similar pathway seen for compound **1**, to give $[C_{25}H_{31}N_4In_2]^+$ ($m/z$ 617, 0.4%). Accurate mass measurement using CI for compound **4** reveals both $MH^+$ and $DH^+$ (M, monomer; D, dimer) peaks with $m/z$ values of 199.0726 and 397.1373 mass units, based on $^{69}$Ga, compared to the calculated values of 199.07258 and 397.13733, respectively. No peaks corresponding to any trimeric fragment are seen in this case.

The molecular structure of $[Me_2Al(HNCPhNH)]$ (**1**) was determined by a single-crystal X-ray diffraction study, and is illustrated in Fig. 1.

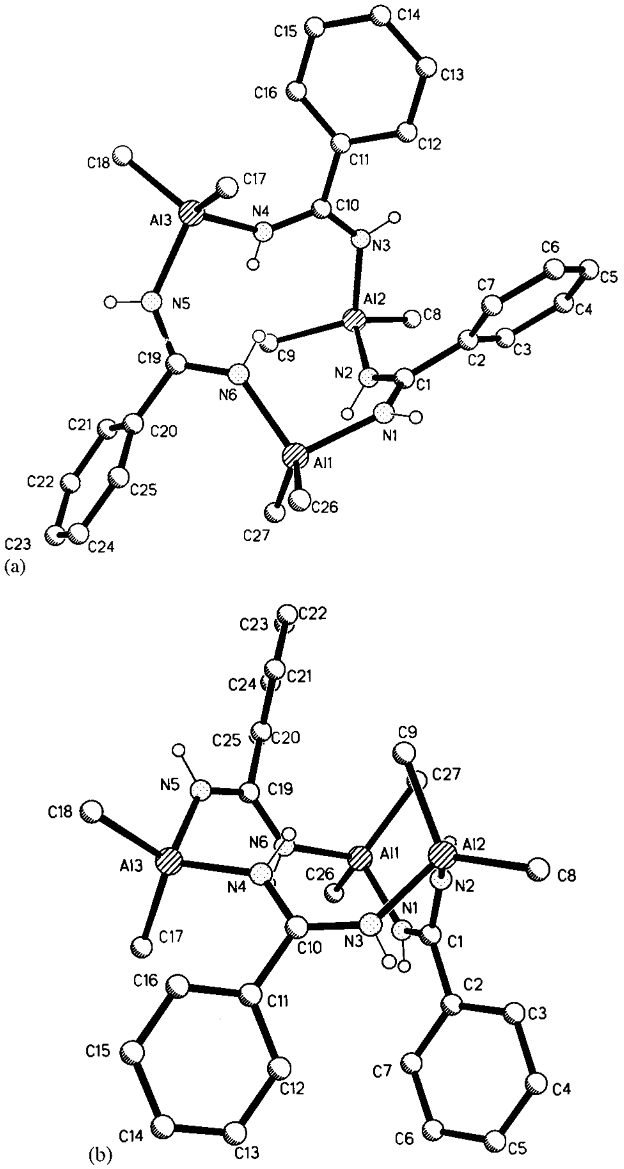


Fig. 1. Two views of the molecular structure of compound **1**, showing the labelling scheme, and the puckering of the twelve-membered ring with respect to the three planar aluminium centres. In both figures the methyl and phenyl hydrogen atoms have been omitted for clarity.

The 12-membered ring system is puckered, such that two amidinato ligands are above a plane constructed through the three metal centres, and one below. The NC(C)–N unit of the amidinato ligand is planar in each case. The N–C–N angles ranging from 122.0(5) to 123.2(5)° are larger, as expected, than for other chelating monomeric amidinato systems where the angles are 114.8(4)° for $[Cl_2Al\{PhC(NSiMe_3)_2\}]$ [6] and 113.0(2)° for $[Me_2Al\{MeC(NSiMe_3)_2\}]$ [3] and they are also larger than the corresponding angles in the dimeric $[\{Me_2M(MeNCMeNMe)\}_2]$ (M = Al, Ga), which are 118.5(1) and 117.4(4)°, respectively [7]. The N–C–N angle, however, is comparable with the corresponding angles found in the complexes $[Rh_2(Am)_4]$ and

$[Rh_2(Am)_4CH_3CN]$ at 123.7(5) and 122.9(2)°, respectively (Am = *N*,*N*′-diphenylformamidinato) [13], and 121.5(4)° for the bridging acetamidinato ligand in the binuclear Co(III) complex $Na[(NH_3)_3Co\{\mu\text{-}OH,\mu\text{-}NH_2,\mu\text{-}CH_3C(NH)_2\}Co(NH_3)_3](S_2O_6)_2\cdot H_2O$ [14].

The average C–N bond length found for the benzamidinato complex of 1.326(7) Å is close to the mean of the two different N–C bond lengths in the parent amidine of 1.294(3) and 1.344(3) Å [15]. The N–C bonds are all of similar length, indicating delocalisation along the N–C–N unit. This delocalisation, however, does not extend to the phenyl ring of the benzamidinato complex, with the mean C–C bond length of 1.481(8) Å well within the range for a $sp^2C\text{–}sp^2C$ bond length, and comparable to the 1.489(3) Å found in the parent amidine [15], 1.471(8) Å found in the benzamidine hydrochloride monohydrate [16] and 1.50(1) Å for the same parameter in the complex $[PPh_4][\{H_2NCPhNH\}PdCl_3]\cdot CH_3CN$ [17]. This is also evident from the fact that the phenyl ring does not lie flat in the plane of the N–C–N unit, but is twisted out of the plane by varying degrees. In benzamidine hydrochloride monohydrate the angle between the ring and the backbone is 36.6(8)° [16], and for benzamidinium hexachlorostannate the corresponding angle is 35.8(4)° [18]. In the aluminium benzamidinato complex the corresponding angles vary from 34.48 to 52.36°.

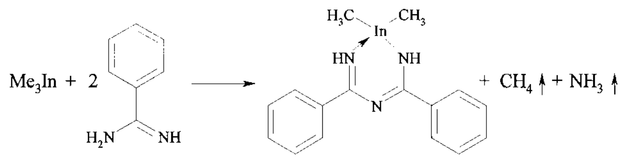
The three metal centres in **1** exhibit similar but distorted tetrahedral geometries, with an average N–Al–N bond angle of 99.2(2)° and average C–Al–C angle of 118.5(3)°. Such an arrangement differs appreciably from the dimeric $[\{Me_2Al(\mu\text{-}MeNCMeNMe)\}_2]$ system, where the metal centre displays a more regular tetrahedral geometry, with an average N–Al–N angle of 111.6(1)°, and an average C–Al–C angle of 112.5(1)° [7]. The mean Al–N distance of 1.911(5) Å is slightly shorter than the 1.925(1) Å for the acetamidine compound [7], and the 1.927(2) Å for $[Me_2Al\{RNCMeNR\}]$ ($R = SiMe_3$) [3]. The average Al–C bond length of 1.964(6) Å is consistent with other similar dimethylaluminium complexes such as $[\{Me_2Al\}_2C_2(NMe)_4]$ [19], $[\{Me_2Al(MeNCMeNMe)\}_2]$ [7], and $[Me_2Al\{(NSiMe_3)_2CMe\}]$ [3], where the bond lengths are in the range 1.942(4)–1.977(6) Å. Two differing orientations for the NH groups within the ring are observed in the solid state structure, with the hydrogen atoms on the two nitrogen atoms of an amidinato ligand (e.g. those on N1, N2, as shown in Fig. 1) being approximately *cis* and *trans*, respectively, with respect to the aromatic ring. Thus the respective torsion angles for the three pairs of hydrogen atoms are (H–N1–C1–C2, −11.4°, H–N2–C1–C2, 148.5°), (H–N3–C10–C11, −7.5°, H–N4–C10–C11, 166.9°), and (H–N5–C19–C20, 3.2°, H–N6–C19–C20, −168.2°). These NH orientations may be the origin of the two NH resonances seen in the $^1H$-NMR spectra for both this compound, and for **2** and **3**. Variable temperature $^1H$-NMR spectra obtained for **1** in $C_6D_5CD_3$ over a range of 50°C showed no significant change in either the position or relative intensities of these NH resonances, indicating the absence of any facile fluxional process leading to equivalence of the NH protons on the NMR time-scale.

The trimeric structure of **1** may now be compared to other structures adopted by compounds of the type $[Me_2Al(RNCR'NR)]$. The substituents on the nitrogen atoms appear to play a dominant role, since as they vary from aryl → alkyl → H there is a corresponding change in the degree of association of the compounds from monomer → dimer → trimer, respectively. This is reflected in the X-ray structures of the compounds $[Me_2Al(PhNCPhNPh)]$ [20], $[\{Me_2Al(MeNCMeNMe)\}_2]$ [7] and the present $[\{Me_2Al(HNCPhNH)\}_3]$. The steric effects of the substituent on the central carbon in the dimeric and trimeric arrangements are minimal, compared to those arising from the substituents on the nitrogen atoms. In the dimeric $[\{Me_2Al(MeNCMeNMe)\}_2]$ the eight-membered $(AlNCN)_2$ ring is puckered and this minimises the interactions between the methyl groups on the aluminium and nitrogen atoms. The planarity of the NCN amidinato unit is maintained but a degree of twist is introduced, and the three methyl groups of the amidinato ligand are not aligned. If this molecule were to adopt a trimeric arrangement similar to **1**, there would then be considerable strain with the Al–Me groups if the N–H protons in the *cis* positions were replaced by methyl groups.

In the monomeric $[Me_2M(PhNCPhNPh)]$ (M = Al, Ga, In) the four-membered (MNCN) ring is highly strained [2,20], and it might be expected that such systems would be more stable as dimers. However, in the monomer there is a considerable separation of all the amidinato substituents within the (MNCN) ring, both from each other and from the metal methyl groups. For example in the aluminium derivative the increase in the N–C–N angle from ca. 100° in the monomer to ca. 120° in a dimer would result in a greater steric effect between the amidinato substituents, and this is consistent with the *N*,*N*′-diaryl compounds showing a preference for the monomeric form.

We have also studied the reactions between $InMe_3$ and benzamidine using a 1:2 molar ratio of reactants. Heating the reactants in hexane solution at 55°C for 6 h results in the formation of a colourless solid (yield ca. 70%), and no residue of either unreacted metal alkyl or benzamidine could be detected in the filtrate. The product was identified from spectroscopic data by comparison with data from the previously characterised products involving aluminium and gallium, which contain for example a dimethyl gallium fragment bonded into the imidoylamidinate ligand [HNCPhNCPhNH] to give a near-planar [Ga–N–C–N–C–N] ring [21]. Thus the molecular ion was observed at $m/z = 367$

$[C_{16}H_{18}N_3In]^+$ (based on $^{115}In$) and, as with the aluminium and gallium compounds fragmentation leads to ions at 352, 351 and 222 corresponding to the loss of $CH_3$, $CH_4$, and $In(CH_3)_2$ fragments respectively. Both the $^1H$- and $^{13}C$-NMR spectra are clean and simple (see Section 2), reflecting both the purity and relatively high symmetry of the product, and are also very similar to those observed for the other Group 13 (Al, Ga) derivatives [21]. Although the two NH protons were detected as a broad resonance with the aluminium compound, they were not observed in the present case, probably due to extensive broadening induced by the indium nucleus (for $^{115}In$, $I = 9/2$). However, they are clearly visible in the IR spectrum appearing as a sharp absorption near 3350 $cm^{-1}$. The overall reaction can therefore be represented as shown in the scheme below.



The reaction pathway leading to the formation of the benzimidoylbenzamidinato group remains obscure. It is not unreasonable to suggest that it probably arises from the nucleophilic attack of the second molecule of benzamidine on the carbon atom centre of a coordinated amidinato ligand in the initially formed complex $[Me_2In(HNCPhNH)]$. However, it should be pointed out that the formation of the cyclic system is not always the reaction which occurs, since we and others have shown that for many amidine ligands the action of two moles of amidine on a Group 13 metal alkyl can lead directly to the bis-substituted product, e.g. $[MeGa(PhNCPhNPh)_2]$ [2,8].

## 4. Conclusions

The results reported here are relevant to the possible use of this type of compound as precursors to metal nitride materials in MOCVD processes, and we are currently examining the thermal properties of the further substituted compounds $[R_xM(amidinato)_{3-x}]$ (M = Al, Ga, In; R = alkyl; $x = 0$, 1) to determine their pathways of decomposition. The results also show that both the type of substituent on the nitrogen atoms of the amidine, and the size of the metal atom involved, exercise a significant influence on the properties of the metal–amidinato complex. The trend appears to be that only for substituents with low steric bulk, such as hydrogen and methyl, in conjunction with a smaller Group 13 metal, such as aluminium, may to some degree of association into dimers or trimers might be expected. With the larger metals, e.g. indium as in $[\{Me_2In(CyNCHNCy)\}_2]$, it is apparent that even large and bulky groups, such as cyclohexyl, can be tolerated in a dimeric structure. However, it is clearly desirable to have results on a broader range of compounds to substantiate these tentative predictions.

## 5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CSD-118475 for compound **1**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

## Acknowledgements

We thank the EPSRC and the Associated Octel Co. Ltd. for grants in support of this work, and both the EPSRC X-ray crystallography service at the University of Cardiff and the MS service at the University of Swansea for recording the mass spectra.

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