Synthesis and properties of some gallium amidine complexes [GaX$_y$L$_{3-y}$] [X = Me, Et or Cl; L = RNCR′NR (R, R′ = H, alkyl or aryl); y = 0–2]. Crystal structures of [GaMe$_2$(PhNCPhNPh)] and [GaMe-(PhNCPhNPh)$_2$]*

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The amidinato compounds [GaMe$_2$L] [L = RNCR′NR (R, R′ = H, alkyl or aryl)], [GaMe(PhNCPhNPh)$_2$], [GaEt(PhNCMeNPh)$_2$] and [Ga(PhNCRNPh)$_3$] (R = Me or Ph) have been isolated from the reaction of the appropriate gallium trialkyl with 1, 2 and 3 mol of amidine RNCR′N(H)R, respectively. The chloro derivatives [GaCl$_3${RNCR′N(H)R}] (R = Ph or p-ClC$_6$H$_4$; R′ = Me) and [GaCl$_2$(p-ClC$_6$H$_4$NCMeNC$_6$H$_4$Cl-p)] have also been prepared. The compounds have been fully characterised, and mass spectrometric data indicate that the volatile dimethylgallium derivatives exist as either monomers or dimers in the gas phase. X-Ray crystallographic studies on [GaMe$_2$(PhNCPhNPh)] and [GaMe(PhNCPhNPh)$_2$] revealed monomeric structures and the presence of chelating amidinate ligands, with distorted tetrahedral and trigonal-bipyramidal co-ordination respectively at the metal centres. Cleavage of the Ga–Me bond occurs on photolysis in the presence of a spin-trapping agent, and thermal decomposition of the solids leads to the formation of gallium nitride.

The co-ordination chemistry of the amidines, either in the neutral form RNCR′N(H)R or more usually as the amidinate [RNCR′NR]$^-$ (R, R′ = H, alkyl, aryl, SiMe$_3$, *etc*.), is well established, especially for the transition metals.[1,2] The amidinato group is isoelectronic with a number of other species such as the carboxylate [O$_2$CR]$^-$ and triazenido [RN=N–NR]$^-$ ions, and the allyl radical, and as with these a number of modes of co-ordination are possible. For the transition metals the most common are the bridging (**A**) and chelating (**B**) forms, although for the latter considerable steric strain occurs in the four-membered M(NCN) ring. In contrast much less is known about the complexes involving the main-group elements. For the Group 13 elements in particular there are four definitive structures reported, the monomeric aluminium [AlCl$_2$(Me$_3$SiNCPhNSiMe$_3$)][3] and ionic thallium species [PhC(NHSiMe$_3$)$_2$]$^+$[TlCl$_3${PhC(NSiMe$_3$)$_2$}]$^{-4}$ contain a chelating, type **B**, amidinato group, while the aluminium (and gallium) derivatives [MMe$_2$(MeNCMeNMe)] (M = Al or Ga) **1** adopt a dimeric form with a puckered eight-membered ring and bridging amidinate ligands **C**.[5] In view of the current interest in the potential use of compounds of the Group 13 elements as volatile precursors for the synthesis of Group 13–15 materials, we have initiated a study of their amidine complexes. We report here the synthesis of some organometallic (and halogeno) derivatives of gallium with amidinate ligands together with some thermogravimetric analysis (TGA) of their thermal decomposition reactions, and other studies on the photoactivation of the gallium–alkyl bonds. In addition to **1** only three other gallium–amidine complexes are known, namely [GaMe$_2$(RNCMeNR)] (R = SiMe$_3$ or Pr^i)[6] and [GaCl$_2$(Me$_3$SiNCPhNSiMe$_3$)].[4,7]

Results and Discussion

The reaction of equimolar quantities of trimethylgallium with a series of amidines RNCR′N(H)R (R, R′ = H, alkyl or aryl; see Experimental section) leads to the evolution of 1 mol of methane. The reactions proceed easily in toluene or hexane

A   B   C
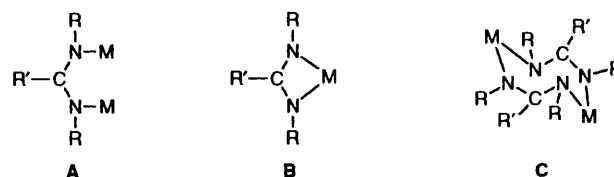
solution with gas evolution commencing at about −50 °C, and being complete by the time the solution has warmed to room temperature. We have also confirmed that an identical reaction occurs between triethylgallium and diphenylbenzamidine PhNCPhN(H)Ph [equation (1)].

$$\text{GaMe}_3 + \text{RNCR′N(H)R} \xrightarrow[25\,°C]{\text{hexane}}$$
$$\text{[GaMe}_2\text{(RNCR′NR)]} + \text{CH}_4 \quad (1)$$
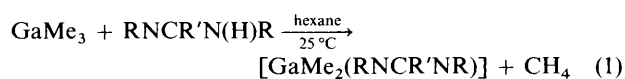
The colourless or pale yellow solid products are all volatile, and can be purified either by sublimation *in vacuo*, or by recrystallisation from toluene–hexane mixtures. The former method is preferable due to the air sensitivity of the products, especially in solution when free amidine can be detected after exposure to air for a few minutes. All the products have been fully characterised by elemental analysis, NMR, mass spectroscopy (see Experimental section), and in one case by a crystal structure. The IR spectral data vary according to the ligand used, and predictions of the type of ligand binding cannot be made with confidence, although observed bands near 1630 and 1550 cm^{-1} have been suggested to be characteristic of a chelating amidinate ligand.[8] The ^{1}H NMR and mass spectroscopic data are however particularly useful, since the former confirm that up to 60 °C these derivatives, *e.g.* [GaMe$_2$(PhNCPhNPh)], are stable to disproportionation, and that no rapid alkyl exchange occurs between [GaMe$_2$(PhNC-

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* *Non-SI units employed:* G = 10^{-4} T, eV ≈ 1.60 × 10^{-19} J.

PhNPh)] and [GaMe(PhNCPhNPh)$_2$] since two methyl resonances are observed corresponding to those in the two compounds. In all cases the resonances from both the ligand and the GaMe$_2$ group are well defined, and also the singlet near δ −0.1 from the metal alkyl protons shows some splitting if any hydrolysis of the sample has occurred. One point of interest is to determine how variation in the R groups of the amidine affects the degree of association of the complexes, especially in view of the dimeric nature of **1**. In this study the electron impact–chemical ionisation (EI–CI) mass spectra of the dialkylgallium compounds show that the nature of the R groups on the amidine nitrogen atoms does play a significant part in determining the degree of association. In those cases where the amidine ligand contains NPh (or substituted phenyl) groups only ions corresponding to monomeric species are observed, whereas when NH groups are present in the amidinate ligand (*e.g.* NHCPhNH) there is clear evidence for the existence of dimeric species similar to **1**. Although we have not investigated any amidines with NMe groups in this study, in the light of other results it would appear that dimeric species of the type **1** may be expected for NH, and probably NMe, containing amidines.[5] The present data do not exclude the presence of weakly bound dimers for the 'NPh' class of amidines, but the mass spectra are in accord with the X-ray data presented below.

With GaCl$_3$ a slightly different reaction occurs in that the initial product is the 1:1 colourless solid adduct [GaCl$_3$·RN-CR′N(H)R] (R = Ph or p-ClC$_6$H$_4$, R′ = Me). Heating to 140 °C in the absence of solvent liberates 1 mol of HCl and affords [GaCl$_2$·RNCR′NR]. It is noteworthy that even when a mixture of GaCl$_3$ with **2**, or **3**, mol equivalents of amidine is heated up to 180 °C the reaction does not proceed beyond the GaCl$_2$ derivative, and excess of amidine can be recovered.

The molecular structure of the diphenylbenzamidine derivative [GaMe$_2$(PhNCPhNPh)] **2** has been determined by X-ray crystallography, and confirms the monomeric form as shown in Fig. 1. Selected bond lengths and angles are given in Table 1. The existence of a monomer in this case compared with the dimer found for **1** clearly demonstrates the effect of the substituents on the amidine framework as mentioned above. The four-membered GaNCN ring leads to a severe distortion of the tetrahedral arrangement around the metal, with the C–Ga–C and N–Ga–N angles being 123 and 65°, respectively. In comparison the arrangement around the gallium centre in the dimeric **1** shows much less distortion with angles varying from 105 to 114°.[5] The small 'bite angle' of 65° is significantly less than that of 73° found in [AlCl$_2$(SiMe$_3$NCPhNSiMe$_3$)],[3] but is close to that of 63–65° observed for the 1,3-diphenyltriazenide ligand [PhN=N-NPh]$^-$ in complexes with aluminium such as [Al(PhNNNPh)$_3$],[9] indicating a structural similarity between these ligands and the amidines. The Ga–N distances in **2** lengthen to 2.04 Å (*cf.* 1.98 Å in **1**), but are still relatively short when compared with other Ga–N donor bonds (*cf.* 2.20 Å in Me$_3$Ga·NMe$_3$),[10] while the Ga–C bonds shorten significantly to 1.94 Å (*cf.* 2.0 Å in **1**, and 1.97 Å in GaMe$_3$[11]). The latter are amongst the shortest reported for a dimethylgallium compound,[12,13] and presumably arise as a consequence of the electronic effects arising from the co-ordination of the amidinate ligand. In both **1** and **2** extensive delocalisation occurs over the NCN amidine fragment, as indicated by the two C–N distances being essentially equal at 1.33 Å in both compounds. In the parent *N,N′*-diphenylbenzamidine the N–C–NH unit is asymmetric with the C–N bonds being clearly differentiated into amine (1.36 Å) and imine (1.30 Å), with an N–C–N angle of 121.6°,[14] compared with that of 110.6° in **2** and 117.4° in **1**.

The reaction of GaMe$_3$ with 2 molar equivalents of PhNCPhN(H)Ph in hexane at room temperature leads to the evolution of 1 mol of methane but no further reaction, and an excess of amidine remains in solution. Heating to 100 °C in a
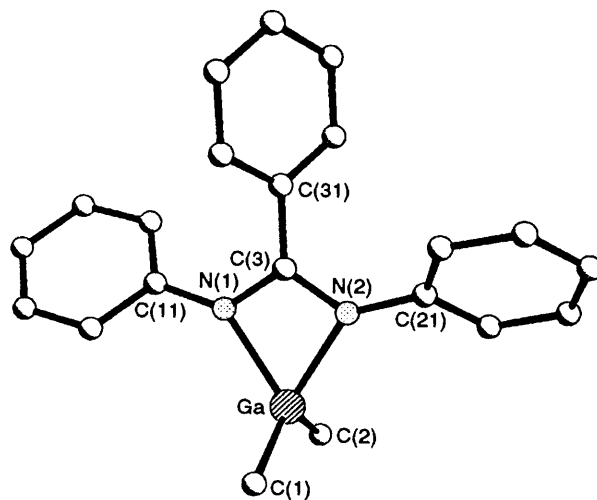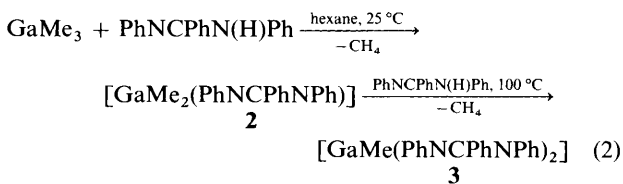

Fig. 1 Molecular structure of compound **2**, showing the labelling scheme. All hydrogen atoms have been omitted for clarity

Table 1 Selected bond lengths (Å) and angles (°) for [GaMe$_2$(PhNCPh-NPh)] **2**

Ga–N(1)	2.047(6)	N(2)–C(3)	1.319(9)
Ga–N(2)	2.031(6)	N(1)–C(11)	1.388(9)
Ga–C(1)	1.955(10)	N(2)–C(21)	1.417(10)
Ga–C(2)	1.944(9)	C(3)–C(31)	1.485(10)
N(1)–C(3)	1.336(9)		
N(1)–Ga–N(2)	64.7(2)	N(2)–C(3)–C(31)	124.9(7)
C(1)–Ga–N(2)	113.6(4)	C(3)–N(1)–Ga	91.7(4)
C(1)–Ga–N(1)	111.1(3)	C(3)–N(2)–Ga	92.9(5)
C(2)–Ga–N(1)	116.8(3)	C(11)–N(1)–Ga	138.6(5)
C(2)–Ga–N(2)	113.2(3)	C(21)–N(2)–Ga	137.9(5)
C(1)–Ga–C(2)	123.2(4)	C(3)–N(1)–C(11)	129.0(6)
N(2)–C(3)–N(1)	110.6(7)	C(3)–N(2)–C(21)	128.6(7)
N(1)–C(3)–C(31)	124.3(6)		

sealed tube, or in toluene under reflux, leads to a further mol of methane being released, and the bis(amidinato) product [GaMe(PhNCPhNPh)$_2$] **3** deposits on cooling as a pale yellow solid [equation (2)]. The product can also be sublimed *in vacuo*

$$GaMe_3 + PhNCPhN(H)Ph \xrightarrow[-CH_4]{\text{hexane, 25 °C}}$$

$$\underset{\mathbf{2}}{[GaMe_2(PhNCPhNPh)]} \xrightarrow[-CH_4]{\text{PhNCPhN(H)Ph, 100 °C}}$$

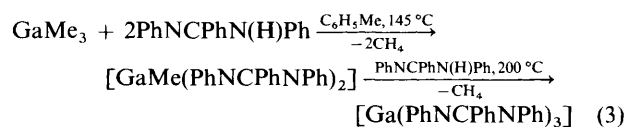$$\underset{\mathbf{3}}{[GaMe(PhNCPhNPh)_2]} \quad (2)$$

but is less air-sensitive than **2**, and elemental analysis and other spectroscopic data confirm the formulation of **3**. In the ^{1}H NMR spectrum the GaMe resonance is shifted slightly downfield to δ 0.28 compared with the dimethylgallium compound **2** (δ 0.01). These compounds are also stable towards disproportionation unlike the [AlR(PhNNNPh)$_2$] (R = Me or Bu^i) triazenido compounds which decompose rapidly in solution.[9,15] Ligand-exchange reactions in both the amidinato and triazenido complexes will necessarily involve opening of the chelate ring, and the probable formation of a bridging intermediate. The present results may be rationalised in terms of the greater inherent strain in the smaller metal–triazenido ring, which would facilitate the ring-opening reaction and thus promote exchange reactions in these compounds. If a solution (CDCl$_3$) of **3** is left open to the air the GaMe resonance decreases by about 50% over 2 h due to slow hydrolysis, forming free PhNCPhN(H)Ph and unknown

gallium species. Small resonances from GaMe fragments occur at δ 1.28 and −0.36 in the hydrolysed solution.

The crystal and molecular structure of compound **3** has been determined by X-ray diffraction and is shown in Fig. 2. Selected bond lengths and angles are given in Table 2. The central structural unit features a monomeric five-co-ordinate gallium(III) atom, which adopts a highly distorted trigonal-bipyramidal geometry, with two amidine ligands acting in a bidentate chelating fashion. The pseudo-axial sites are occupied by N(1), N(4) and the equatorial plane is defined by N(2), N(3) and C(1), from which the gallium atom deviates only slightly [0.026(2) Å]. The axial and equatorial valency angles [N(1)–Ga–N(4) 150.05(9), N(2)–Ga–N(3) 97.94(10)°] deviate considerably from the ideal values, the distortions arising from the intramolecular interactions between the ligands and the steric constraints imposed by the rigidity of the chelating amidinate ligands.

The two Ga–N bond distances within each chelate ring differ significantly as expected since the nitrogen atoms occupy an equatorial and axial site. Several studies on five-co-ordinate gallium complexes have shown that Ga–N$_{ax}$ > Ga–N$_{eq}$, with the two distances varying over 1.94–2.78 and 1.92–2.48 Å, respectively.[13,16,17] In **3** Ga–N$_{ax}$ (average 2.127 Å) and Ga–N$_{eq}$ (average 2.002 Å) fall well within these ranges. The Ga–C distance (1.940 Å, cf. 1.98 Å calculated as the sum of the covalent radii[18]) is similar to that in **2** and also lies within the range 1.924–2.080 Å reported for other five-co-ordinate organogallium compounds.[12] The bond lengths and bite angles (≈63–65°) of the amidinate ligand in **2** and **3** are essentially identical despite the asymmetry of the ligation of the amidinato group in **3**, indicating that the principal bonding modes within the ligand are only little affected by changes in the metal co-ordination number and geometry. However, the angles around the nitrogen atoms in **2** and **3** differ as expected due to both the steric factors and the inequality of the Ga–N distances in **3**.

The sequential substitution of the alkyl groups in GaMe$_3$ can be continued with PhNCPhN(H)Ph, but much more extreme conditions are required. Thus when GaMe$_3$ (1 mol) and the benzamidine (3 mol) in toluene solution are heated in a sealed tube to 145 °C for 12 h only 2 mol of methane are evolved with the formation of **3**. Removal of the solvent and further heating of the melt at 200 °C for 0.5 h leads to the tris-substituted product [Ga(PhNCPhNPh)$_3$] **4** [equation (3)]. The product

$$\text{GaMe}_3 + 2\text{PhNCPhN(H)Ph} \xrightarrow[-2\text{CH}_4]{C_6H_5Me,\,145\,°C}$$

$$[\text{GaMe(PhNCPhNPh)}_2] \xrightarrow[-\text{CH}_4]{\text{PhNCPhN(H)Ph},\,200\,°C}$$

$$[\text{Ga(PhNCPhNPh)}_3] \quad (3)$$

4 is a pale yellow solid which is soluble in toluene, tetrahydrofuran and chloroform. In contrast to **2** and **3** this solid is only hydrolysed very slowly in air. The ¹H NMR spectrum shows the equivalence of both the three CPh and the six NPh groups, consistent with the presence of a six-co-ordinate gallium atom with chelating amidine ligands, similar to that found for [Al(PhNNNPh)$_3$].[9] However, in this case there are some notable differences in the reactions involving the triazines and amidines. With the former the [M(PhNNNPh)$_3$] (M = Al, Ga or In) compounds are obtained at room temperature, and with the aluminium compound this is the only product even when an excess of AlMe$_3$ is used,[9] although the intermediates [AlR$_2$(PhNNNPh)] and [AlR(PhNNNPh)$_2$] can be obtained for the bulky R = Bu^i group.[15] There has been an earlier report of [GaMe$_2$(PhNNNPh)] being formed when 1 mol of the triazine is added to slightly more than 1 mol of GaMe$_3$,[19] but this type of intermediate product has not been reported in the later work. With the amidines, controlled sequential substitution reactions occur in the formation of
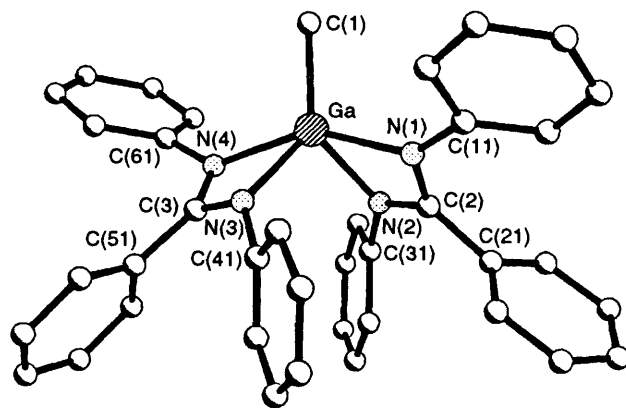

Fig. 2 Molecular structure of compound **3**, showing the labelling scheme. All hydrogen atoms have been omitted for clarity

Table 2 Selected bond lengths (Å) and angles (°) for [GaMe(PhNCPh-NPh)$_2$] **3**

Ga–N(1)	2.112(2)	N(4)–C(3)	1.319(3)
Ga–N(2)	1.995(2)	N(1)–C(11)	1.399(3)
Ga–N(3)	2.009(2)	N(2)–C(31)	1.409(3)
Ga–N(4)	2.141(2)	N(3)–C(41)	1.410(3)
Ga–C(1)	1.940(3)	N(4)–C(61)	1.409(3)
N(1)–C(2)	1.326(3)	C(2)–C(21)	1.481(4)
N(2)–C(2)	1.335(3)	C(3)–C(51)	1.479(4)
N(3)–C(3)	1.338(3)		
N(1)–Ga–C(1)	106.97(13)	N(3)–C(3)–C(51)	124.1(2)
N(1)–Ga–N(2)	63.98(9)	N(4)–C(3)–C(51)	125.5(2)
N(1)–Ga–N(3)	94.58(9)	Ga–N(1)–C(2)	90.2(2)
N(4)–Ga–C(1)	102.96(13)	Ga–N(2)–C(2)	95.2(2)
N(4)–Ga–N(2)	97.46(10)	Ga–N(3)–C(3)	95.4(2)
N(4)–Ga–N(3)	63.43(9)	Ga–N(4)–C(3)	90.1(2)
N(2)–Ga–C(1)	129.10(13)	Ga–N(1)–C(11)	140.3(2)
N(2)–Ga–N(3)	97.94(10)	Ga–N(2)–C(31)	133.4(2)
N(3)–Ga–C(1)	132.90(13)	Ga–N(3)–C(41)	131.6(2)
N(1)–Ga–N(4)	150.05(9)	Ga–N(4)–C(61)	138.4(2)
N(1)–C(2)–N(2)	109.9(2)	C(2)–N(1)–C(11)	128.3(2)
N(3)–C(3)–N(4)	110.6(2)	C(2)–N(2)–C(31)	127.8(2)
N(1)–C(2)–C(21)	124.1(2)	C(3)–N(3)–C(41)	125.9(2)
N(2)–C(2)–C(21)	125.9(2)	C(3)–N(4)–C(61)	124.8(2)

aluminium[20] and gallium compounds. Similar reaction conditions also lead to [Ga(PhNCMeNPh)$_3$].

Two further properties of the above compounds are worthy of mention. First, the alkylgallium products [GaR$_x$L$_{3-x}$] (R = Me or Et, L = PhNCPhNPh, x = 1 or 2) are photoactive. For example, irradiation of [GaEt$_2$(PhNCPhNPh)] in degassed benzene solution with visible light (λ > 435 nm) in the presence of a ten-fold excess of 2,4,6-tri-*tert*-butylnitrosobenzene as a spin trap yields the EPR spectrum shown in Fig. 3. The spectrum results from the overlapping signals due to the aminyl oxide RN(Ȯ)Et and RṄOGaL (R = 2,4,6-Bu$^t_3$C$_6$H$_2$, L = PhNCPhNPh) radicals. The former radical gives a triplet of triplets, from coupling of the electron with the nitrogen atom and the CH$_2$ protons of the Et group, with hyperfine splitting constants of a^N = 13.5, a^H(CH$_2$) = 18.0 G and a g value of 2.0060. Extra fine splitting is also seen from the two protons on the aryl ring [a^H(*meta*) = 0.83 G]. The gallium-containing radical produces a complicated pattern due to the presence of two gallium isotopes (⁶⁹Ga, 60.5%; ⁷¹Ga, 39.5%; both $I = \frac{3}{2}$) which give two different hyperfine splitting constants. However, there is little doubt as to the presence of the ethyl-based radical, and the simulated spectrum[21] shows excellent agreement with that observed for this radical. The EPR spectrum obtained prior to any irradiation showed only a weak signal, mainly from the ethyl radical indicating that dissociation
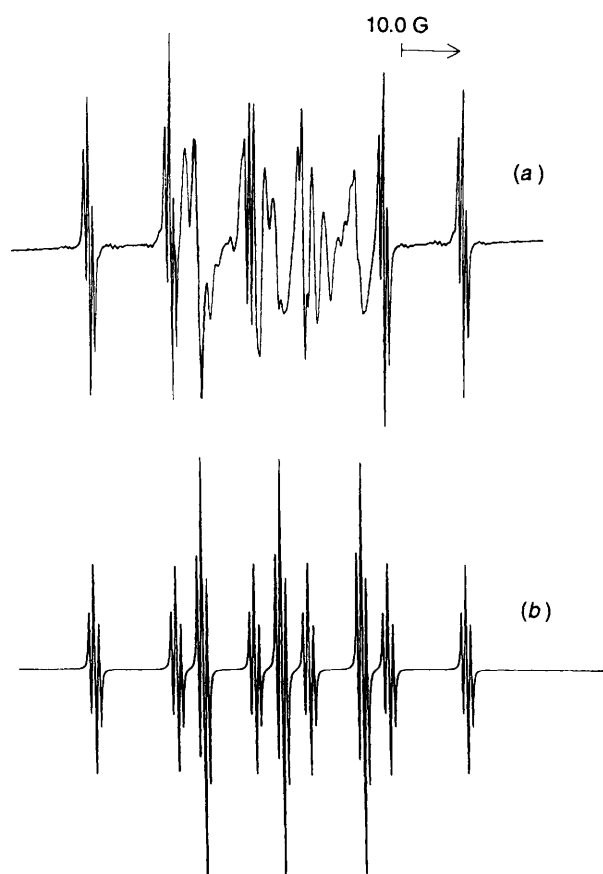
Fig. 3 The EPR spectrum of a benzene solution of [GaEt₂(PhNCPh-NPh)] with 2,4,6-tri-*tert*-butylnitrosobenzene upon light irradiation (a), together with the simulated spectrum for RN(Ȯ)Et (R = 2,4,6-Bu$^t_3$C₆H₂) (b)

also proceeds thermally, albeit slowly, at room temperature. The gallium methyl compounds behave similarly, with the methyl radicals giving a triplet of quartets. Thus although the above results indicate that homolytic cleavage of the Ga–R bonds can be achieved by visible light, in the absence of the nitrosobenzene no EPR spectrum is observed presumably due to the rapid recombination of the radicals produced. These results are related to those observed previously for the ethyl-aluminium tetraazamacrocycle complex [Al(C₂₂H₂₂N₄)Et],[22] and while the co-ordination geometry around the metal is different in the two cases there is the similarity that in each the metal centre is bonded to four nitrogen atoms. Activation of the metal–alkyl bond is of interest in view of the known ability of porphyrin–alkylaluminium derivatives to catalyse under photolysis the polymerisation of a range of functional unsaturated compounds.[23]

The second property of the above compounds which is of current interest relates to their thermal decomposition. The use of volatile precursors to produce semiconductors is well established, but the search continues for suitable single compounds.[24] For the Group 13–15 semiconductors attention has been focused mainly on the phosphide and arsenide derivatives. There is an increasing need for the nitrides, especially gallium nitride (GaN) in view of its wide band gap of 3.39 eV, which leads to its use as blue emitter in LED (light-emitting diode) devices. The above compounds, notably [GaMe$_x$(PhNCPhNPh)$_{3-x}$] (x = 1 or 2), start to decompose at about 250 °C as determined from TGA data, and when heated to 500–600 °C under a nitrogen atmosphere produce grey powders. These powders are essentially unaffected by strong mineral acids and were identified as being predominantly gallium nitride by X-ray powder diffraction data, EDX (energy-dispersive X-ray) measurements and electron microscopy (see

Experimental section). In addition to the gallium nitride varying quantities of carbon (also identified by EDX data) are produced, and unless rigorous precautions are taken to exclude oxygen some gallium oxide contaminates the nitride. We have not yet optimised the decomposition process for the whole range of compounds reported herein, or identified the nature of any gases released, and studies using different atmospheres and various flow systems are continuing.

In summary, a series of volatile complexes involving the Group 13 elements and amidine ligands have been prepared, and the degree of association has been shown to be dependent on the nature of the substituents (H, alkyl, aryl) involved in the amidine. Further studies are clearly required to explore more fully the photolytic and thermal properties of this type of complex.

Experimental

Infrared spectra were recorded from either Nujol or hexachlorobutadiene mulls using CsI plates and a Perkin-Elmer 580B spectrophotometer, ¹H and ¹³C NMR spectra using Bruker Associates AC200, ACF250 or WH400 instruments and CDCl₃ as solvent unless otherwise specified. Chemical shifts are quoted relative to SiMe₄ (δ 0) with upfield shifts being assigned negative values. Analytical data were obtained using a Perkin-Elmer 2400, and TGA measurements made using a Stanton Redcroft STA 1000 instrument. Mass spectra were run on a Kratos MS80 or a Finnegan-MATT ITD instrument under EI, or where specified CI (NH₃). The air-reactive compounds were handled using a conventional Schlenk or high-vacuum line, and in a dry nitrogen-filled glove-box. Gallium trichloride was prepared by the action of chlorine on gallium metal, trimethylgallium was obtained from Strem, and the amidines from Aldrich, or known synthetic methods, except for N,N'-dicyclohexylacetamidine which was prepared from the action of methyl lithium on dicyclohexylcarbodiimide, and the colourless solid product (yield 72%) was purified by sublimation at 100 °C *in vacuo*.[2,25]

Syntheses

Dimethylgallium amidinato compounds. [GaMe₂(PhNCPh-NPh)] 2. N,N'-Diphenylbenzamidine (0.93 g, 3.4 mmol) was dissolved in dry degassed toluene (30 cm³) and GaMe₃ (0.40 g, 3.5 mmol) was distilled in under vacuum. The stirred mixture was allowed to warm to room temperature over 2 h, over which time methane (78 cm³ at normal temperature and pressure, 3.5 mmol) was evolved. After distilling all the volatiles from the flask under vacuum, the pale yellow solid residue was purified by sublimation at 110 °C. Yield 1.1 g (79%) (Found: C, 67.85; H, 5.70; N, 7.45. C₂₁H₂₁GaN₂ requires C, 67.95; H, 5.70; N, 7.55%). IR (Nujol, major bands): 1625, 1588, 1540, 1490, 1028, 701 and 530 cm⁻¹. NMR: ¹H, δ 7.36 (1 H, t, J 7, p-H of CPh), 7.31–7.23 (4 H, m, o-, m-H of CPh), 7.10 (4 H, d, J 8, m-H of NPh), 6.93 (2 H, t, J 7, p-H of NPh), 6.67 (4 H, d, J 8 Hz, o-H of NPh) and 0.01 (6 H, s, GaMe₂); ¹³C, δ 167.24 (NCN), 144.10 (NPh), 129.85 (CPh), 129.21 (o-C of Ph), 128.54 (m-C of CPh), 128.48 (m-C of NPh), 123.23 (o-C of NPh) and 122.48 (p-C of NPh). Electron impact mass spectrum: m/z 370 (M⁺, 20), 355 ([M − Me]⁺, 100), 271 ([M − GaMe₂]⁺, 11.5), 180 ([M − GaMe₂NPh]⁺, 96.5) and 161 ([PhNHGa]⁺, 37.2%).

The remaining [GaMe₂(RNCR'NR)] were prepared in a similar way; details given below show the solvent used, yield, elemental analysis, IR, NMR and mass spectral data (EI unless specified) for the different amidinato groups used. In the mass spectra the molecular ion quoted is based on the ⁶⁹Ga (60.5%) isotope, and use is made of the fragmentation patterns of the free amidines.[26]

Di-p-*chlorophenylbenzamidine*, p-ClC₆H₄NCPhNC₆H₄Cl-p. Hexane, 78% (Found: C, 57.65; H, 4.65; N, 6.05. C₂₁H₁₉-

Cl_2GaN_2 requires C, 57.35; H, 4.35; N, 6.35%). δ 7.38 (1 H, t, J 7), 7.29 (2 H, t, J 7), 7.19 (2 H, d, J 8), 7.03 (4 H, d, J 7), 6.54 (4 H, d, J 8 Hz) and −0.01 (6 H, s). m/z 438 (M^+, 1.6), 423 ([M − Me]$^+$, 6.4), 339 ([M − GaMe$_2$]$^+$, 3.5) and 214 ([M − GaMe$_2$NC$_6$H$_4$Cl]$^+$, 100%).

p-MeC$_6$H$_4$NCPhNC$_6$H$_4$Me-p. Hexane, 74% (Found: C, 69.85; H, 6.30; N, 7.05. C$_{23}$H$_{25}$GaN$_2$ requires C, 69.20; H, 6.30; N, 7.00%). δ 7.35 (5 H, m), 6.95 (4 H, d), 6.60 (4 H, d) and 0.00 (6 H, s). m/z 398 (M^+, 26), 383 ([M − Me]$^+$, 70), 299 ([M − GaMe$_2$]$^+$, 16) and 194 ([M − GaMe$_2$NC$_6$H$_4$Me]$^+$, 100%).

PhNCMeNPh. Hexane, 71% (Found: C, 62.55; H, 6.05; N, 8.90. C$_{16}$H$_{19}$GaN$_2$ requires C, 62.20; H, 6.20; N, 9.05%). IR: 1635, 1588, 800, 705, 580 and 530 cm^{-1}. δ 7.35 (4 H, t, J 8), 7.10 (2 H, t, J 7), 7.01 (4 H, d, J 8 Hz), 2.20 (3 H, s) and 0.03 (6 H, s). m/z 308 (M^+, 6), 293 ([M − Me]$^+$, 49) and 118 ([M − GaMe$_2$NPh]$^+$, 100%).

p-FC$_6$H$_4$NCMeNC$_6$H$_4$F-p. Hexane, 89% (Found: C, 55.75; H, 4.85; N, 7.95. C$_{16}$H$_{17}$F$_2$GaN$_2$ requires C, 55.70; H, 4.95; N, 8.10%). δ 7.10–6.90 (8 H, m), 2.07 (3 H, s) and −0.04 (6 H, s). m/z 344 (M^+, 34), 329 ([M − Me]$^+$, 100), 245 ([M − GaMe$_2$]$^+$, 15), 136 ([M − GaMe$_2$NC$_6$H$_4$F]$^+$, 94) and 95 ([M − GaMe$_2$NC$_6$H$_4$FCMe]$^+$, 80%).

p-ClC$_6$H$_4$NCMeNC$_6$H$_4$Cl-p. Toluene, 63% (Found: C, 50.75; H, 4.40; N, 7.30. C$_{16}$H$_{17}$Cl$_2$GaN$_2$ requires C, 50.85; H, 4.50; N, 7.40%). IR: 1625, 1587, 1540, 1015, 820, 580 and 525 cm^{-1}. δ (C$_6$D$_5$CD$_3$) 7.12 (4 H, d), 6.61 (4 H, d), 1.42 (3 H, s) and −0.11 (6 H, s). m/z 378 (M^+, 72), 363 ([M − Me]$^+$, 100) and 152 ([M − GaMe$_2$NC$_6$H$_4$Cl]$^+$, 67%).

p-MeC$_6$H$_4$NCMeNC$_6$H$_4$Me-p. Hexane, 88% (Found: C, 65.45; H, 6.80; N, 8.85. C$_{18}$H$_{23}$GaN$_2$ requires C, 64.15; H, 6.8; N, 8.30%). δ 7.15 (4 H, d), 6.93 (4 H, d), 2.33 (6 H, s), 2.10 (3 H, s) and −0.08 (6 H, s). m/z 336 (M^+, 17), 321 ([M − Me]$^+$, 99), 237 ([M − GaMe$_2$]$^+$, 12) and 132 ([M − GaMe$_2$NC$_6$H$_4$Me]$^+$, 100%).

C$_6$H$_{11}$NCMeNC$_6$H$_{11}$. No solvent, 72% (Found: C, 61.35; H, 9.65; N, 8.95. C$_{16}$H$_{31}$GaN$_2$ requires C, 59.85; H, 9.75; N, 8.75%). δ 3.25–3.05 (2 H, m), 1.87 (3 H, s), 1.80–0.95 (20 H, m) and −0.31 (6 H, s). m/z 320 (M^+, 2.9), 305 ([M − Me]$^+$, 100) and 124 ([M − GaMe$_2$NC$_6$H$_{11}$]$^+$, 8.6%).

HNCMeNH. Hexane, 57% (Found: C, 31.55; H, 7.35; N, 16.25. C$_4$H$_{11}$GaN$_2$ requires C, 30.65; H, 7.05; N, 17.85%). The reaction product is very sensitive to moisture, and good analytical and spectroscopic data were difficult to obtain. δ 7.34 (2 H, s, NH), 1.99 (3 H, s) and −0.46 (6 H, s).

HNCPhNH. No solvent, 58% (Found: C, 49.65; H, 6.00; N, 12.10. C$_9$H$_{13}$GaN$_2$ requires C, 49.35; H, 6.00; N, 12.80%). IR: 1590, 1555, 1200, 700, 565 and 532 cm^{-1}. δ 7.35 (3 H, m), 7.10 (3 H, m), 4.63 (2 H, br s, NH) and −0.276 (6 H, s). m/z (CI, NH$_3$) 437 ([dimer + H]$^+$, 9.0), 219 ([M + H]$^+$, 49) and 203 ([M − Me]$^+$, 72.9%). Only a weak molecular ion and no dimeric species were observed in the EI spectrum.

PhNCHNPh. Hexane, 75% (Found: C, 59.25; H, 5.85; N, 9.25. C$_{15}$H$_{17}$GaN$_2$ requires C, 61.05; H 5.80; N, 9.50%). IR: 1660, 1605, 1588, 1562, 1210, 760, 575 and 530 cm^{-1}. δ 8.75 (1 H, s, CH), 7.30 (4 H, t, J 8 Hz), 7.07–6.96 (6 H, m) and 0.15 (6 H, s). m/z 294 (M^+, 13), 279 ([M − Me]$^+$, 40), 195 ([M − GaMe$_2$]$^+$, 19), 99 ([M − PhNCHNPh]$^+$, 19) and 77 ([M − GaMe$_2$NCHNPh]$^+$, 100%).

3,4-Cl$_2$C$_6$H$_3$NCHNC$_6$H$_3$Cl$_2$-3,4. Toluene, 74% (Found: C, 41.80; H, 3.20; N, 6.15. C$_{15}$H$_{13}$Cl$_4$GaN$_2$ requires C, 41.65; H, 3.05; N, 6.45%). δ 8.60 (1 H, s, CH), 7.32 (2 H, d, J 8), 7.05 (2 H, d, J 2.5), 6.80 (2 H, d, J 9, 2.5 Hz) and 0.034 (6 H, s, GaMe$_2$).

p-O$_2$NC$_6$H$_4$NCPhC$_6$H$_4$NO$_2$-p. Hexane, 85% (Found: C, 54.80; H, 4.05; N, 12.00. C$_{21}$H$_{19}$GaN$_4$O$_4$ requires C, 54.70; H, 4.15; N, 12.15%). δ 7.98 (4 H, d, J 9), 7.47 (1 H, t, J 6), 7.39 (2 H, m, J 6), 7.23 (4 H, d, J 8), 6.65 (2 H, d, J 9 Hz) and 0.07 (6 H, s). m/z 460 (M^+, 6.7), 445 ([M − Me]$^+$, 90.3), 361 ([M − GaMe$_2$]$^+$, 3.3) and 225 ([M − GaMe$_2$NC$_6$H$_4$NO$_2$]$^+$, 100%).

HNCBu^{t}NH. No solvent, 70% (Found: C, 42.0; H, 8.5; N,

13.7. C$_7$H$_{17}$GaN$_2$ requires C, 42.3; H, 8.6; N, 14.1%). δ$_H$(C$_6$D$_6$) 4.73 (2 H, br s, NH), 0.79 (9 H, s, Bu^t) and 0.08 (6 H, s, GaMe$_2$). δ$_C$ 184.2 (CN$_2$), 38.4 (CBu^t), 27.6 (Bu^t) and −7.74 (GaMe$_2$). m/z (CI) 397.13724 ([dimer + H]$^+$, calc. 397.13734), 381 ([dimer − Me]$^+$, 4.3), 267 ([dimer − Ga − 4Me]$^+$, 2.5), 198 (M^+, 5.0), 183 ([M − Me]$^+$, 100),168 ([M − 2Me]$^+$, 12), 99 ([GaMe$_2$]$^+$, 27) and 69 (Ga$^+$, 25%).

[GaEt$_2$(PhNCPhNPh)]. Toluene, 68% (Found: C, 69.40; H, 6.45; N, 7.00. C$_{23}$H$_{25}$GaN$_2$ requires C, 69.20; H, 6.30; N, 7.00%). δ 7.40–7.25 (5 H, m, Ph), 7.12 (4 H, t, Ph, J 7), 6.93 (2 H, t, Ph, J 7) and 6.67 (4 H, d, Ph, J 7 Hz). m/z 398 (M^+, 1.0), 369 ([M − Et]$^+$, 9.0), 271 ([M − GaEt$_2$]$^+$, 9.0) and 180 ([M − GaEt$_2$NC$_6$H$_5$]$^+$, 100%).

Gallium chloride amidine compounds. [GaCl$_3$·L] [L = p-ClC$_6$H$_4$NCMeN(H)C$_6$H$_4$Cl-p or PhNCMeN(H)Ph]. Both compounds were prepared by a similar method, e.g. solutions of GaCl$_3$ (1.02 g, 5.79 mmol, in 30 cm^3 toluene) and p-ClC$_6$H$_4$NC(Me)N(H)C$_6$H$_4$Cl-p (0.67 g, 5.98 mmol, in 30 cm^3 toluene) were mixed and warmed to 40 °C when a colourless precipitate was formed. This dissolved on further heating, but reappeared on cooling. After filtering and washing with toluene (50 cm^3) the solid was dried by pumping under vacuum. Yield 2.1 g (80%) (Found: C, 36.7; H, 2.6; Cl, 38.8; N, 5.8. C$_{14}$H$_{12}$Cl$_5$GaN$_2$ requires C, 36.9; H, 2.6; Cl, 38.9; N, 6.1%). IR: 3290, 1635, 1598, 1570, 1090, 495, 375 and 350 cm^{-1}. NMR (CD$_3$COCD$_3$): ^{1}H, δ 10.36 (1 H, br s, NH), 7.52 (8 H, m, Ph) and 2.42 (3 H, s, Me); ^{13}C, δ 164.4 (NCN), 136.5 (CN), 133.7 (CCl), 130.7 (CH), 127.9 (CH) and 18.95 (CH$_3$).

[GaCl$_3$·PhNCMeN(H)Ph]: Yield 91% (Found: C, 42.7; H, 3.4; Cl, 27.3; N, 7.3. C$_{14}$H$_{14}$Cl$_3$GaN$_2$ requires C, 43.5; H, 3.6; Cl, 27.5; N, 7.3%). NMR: ^{1}H, δ 10.3 (1 H, br s, NH), 7.48–7.35 (10 H, m, Ph) and 2.39 (3 H, s, Me); ^{13}C, δ 163.5 (NCN), 138.0 (CN), 130.5 (CH), 128.3 (p-CH), 125.8 (CH) and 18.8 (Me).

[GaCl$_2$·p-ClC$_6$H$_4$NCMeNC$_6$H$_4$Cl-p]. A mixture of GaCl$_3$ (0.92 g, 5.2 mmol) and p-ClC$_6$H$_4$NCMeN(H)C$_6$H$_4$Cl-p (4.4 g, 15.6 mmol) was heated to 140 °C in the melt for 2 h. On cooling the reaction mixture set to a colourless solid, and the excess of amidine was removed by washing with toluene. Using a 1:1.5 molar ratio (Ga:amidine) only very little of the amidine was recovered. Yield 0.6 g (27%) (Found: C, 40.0; H, 2.4; N, 6.1. C$_{14}$H$_{11}$Cl$_4$GaN$_2$ requires C, 40.1; H, 2.6; N, 6.7%). m/z (EI) 418 (M^+, 2.6), 278 ([M − GaCl$_2$]$^+$, 9.5), 152 ([p-ClC$_6$H$_4$NCMe]$^+$, 100) and 111 ([p-ClC$_6$H$_4$]$^+$, 32.7%).

Monomethyl gallium bis(amidinato) compounds. [GaMe(PhNCPhNPh)$_2$] 3. N,N'-Diphenylbenzamidine (2.28 g, 8.4 mmol) was dissolved in dry degassed toluene (40 cm^3), and GaMe$_3$ (0.49 g, 4.25 mmol) was distilled in under vacuum. The stirred solution was allowed to warm to room temperature, over which time methane (95 cm^3, 4.24 mmol) was evolved. The solution was heated to 100 °C for 12 h, evolving further methane (95 cm^3), allowed to cool to room temperature and reduced in volume to ca. 20 cm^3 under vacuum. Hexane (30 cm^3) was added and the pale yellow precipitate was filtered off. Yield 1.8 g (68%) (Found: C, 74.60; H, 5.35; N, 8.95. C$_{39}$H$_{33}$GaN$_4$ requires C, 74.65; H, 5.30; N, 8.95%). NMR: ^{1}H, δ 7.19 (t, 2 H, J 6, p-H of CPh), 7.14 (d, 8 H, J 4, o-, m-H of CPh), 6.95 (t, 8 H, J 8, m-H of NPh), 6.83 (t, 4 H, J 7, p-H of NPh), 6.57 (d, 8 H, J 8 Hz, o-H of NPh) and 0.28 (s, 3 H, GaCH$_3$); ^{13}C, δ 167.96 (NCN), 144.90 (NPh), 130.70 (CPh), 129.82 (p-C of CPh), 129.31 (o-C of CPh), 128.05 (m-C of CPh), 127.96 (m-C of NPh), 124.96 (o-C of NPh) and 122.22 (p-C of NPh). m/z (EI) 626 (M^+, 7.8), 611 ([M − Me]$^+$, 43.4), 355 ([M − PhNCPhNPh]$^+$, 13.5) and 180 ([PhNCPh]$^+$, 100%).

[GaEt(PhNCMeNPh)$_2$]. A similar method to that above was used. Yield 65% (Found: C, 69.4; H, 6.00; N, 10.8. C$_{30}$H$_{31}$GaN$_4$ requires C, 69.6; H, 6.05; N, 10.8%). NMR: ^{1}H, δ 7.17 (t, 8 H, J 8, m-H of Ph), 7.00 (t, 4 H, J 7, p-H of Ph), 6.82 (d, 8 H, J 8, o-H of Ph), 2.08 (s, 6 H, CH$_3$C), 1.42 (t, 3 H, J

Table 3 Crystal data and structure refinement for compounds **2** and **3**

	2	**3**
Formula	$C_{21}H_{21}GaN_2$	$C_{39}H_{33}GaN_4$
M	371.12	627.41
Crystal system	Orthorhombic	Triclinic
Space group	$P2_1cn$ (non-standard setting of $Pna2_1$)	$P\bar{1}$
a/Å	9.385(4)	10.206(5)
b/Å	10.280(10)	10.511(6)
c/Å	19.58(2)	14.799(9)
α/°		96.89(5)
β/°		94.28(4)
γ/°		90.58(4)
U/Å³	1889(3)	1571(2)
T/K	290(2)	293(2)
Systematic absences	$hk0, h + k = 2n + 1; h0l, l = 2n + 1$	None
Z	4	2
D_c/g cm⁻³	1.305	1.326
Colour	Colourless block	Yellow
Crystal size/mm	0.53 × 0.40 × 0.34	0.48 × 0.46 × 0.34
μ/mm⁻¹	1.46	0.910
$F(000)$	768	652
$\theta_{min}, \theta_{max}$/°	1.5, 25	2.0, 22.1
hkl ranges	0–11, 0–12, 0–23	0–10, −11 to 11, −15 to 15
Number of data collected	1950	4152
Independent reflections	1785	3884 ($R_{int} = 0.02$)
Maximum, minimum transmission	0.65, 0.58	0.75, 0.66
Weighting parameters: a, b	0.074, 0.2652	0.034, 0.861
$R(F) [I > 2\sigma(I)]$	0.0477	0.0297
$wR(F^2)$ (all data)	0.133	0.072
Goodness of fit on F^2	1.049	1.085
Largest difference peak and hole/e Å⁻³	±0.5	±0.2
Data, restraints, parameters	1784, 0, 218	3883, 46, 399
Extinction coefficient	—	0.0234(9)

8, EtGa) and 1.13 (q, 2 H, J 8 Hz, EtGa); ^{13}C, δ 167.2 (NCN), 145.3 (NPh), 128.4 (m-C of NPh), 124.5 (o-C of NPh), 122.6 (p-C of NPh), 14.1 (CH_3C), 10.3 (CH_3CH_2Ga) and 4.5 (CH_3CH_2Ga). m/z (EI) 517 (M^+, 1.9), 488 ([M − Et]⁺, 65.7) and 118 ([PhNCMe]⁺, 100%).

Gallium tris(amidinato) compounds. [Ga(PhNCPhNPh)₃] **4**. N,N'-Diphenylbenzamidine (0.95 g, 3.5 mmol) and [GaMe(PhNCPhNPh)₂] (2.19 g, 3.5 mmol) were placed in a sealed tube and heated to 200 °C for 30 min over which time methane (78 cm³, 3.5 mmol) was evolved. The pale yellow solid was dissolved in chloroform (15 cm³), and the solution cooled to − 35 °C, producing pale yellow crystals. These were filtered off, washed with hexane (2 × 10 cm³), and dried in vacuum. Yield 2.0 g (65%) (Found: C, 77.1; H, 5.25; N, 9.4. $C_{57}H_{45}GaN_4$ requires C, 77.5; H, 5.15; N, 9.5%). NMR: ^1H, δ 7.21 (t, 1 H, J 7, p-H of CPh), 7.13 (t, 2 H, J 8, m-H of CPh), 7.03 (t, 4 H, J 8, m-H of NPh), 6.94 (d, 2 H, J 7, o-H of CPh), 6.87 (t, 2 H, J 7, p-H of NPh) and 6.68 (d, 4 H, J 1 Hz, o-H of NPh); ^{13}C, δ 166.70 (NCN), 144.60 (NPh), 130.97 (CPh), 129.50 (o-C of CPh), 129.23 (p-C of CPh), 128.27 (m-C of CPh), 127.83 (m-C of NPh), 124.71 (o-C of NPh) and 121.78 (p-C of NPh). m/z (EI) 882 (M^+,7.0), 611 ([M − PhNCPhNPh]⁺, 26.4) and 77 (Ph⁺, 100%).

[Ga(PhNCMeNPh)₃]. Similar method to that above, colourless solid, yield 65% (Found: C, 72.0; H, 5.60; N, 11.8. $C_{42}H_{39}GaN_6$ requires C, 72.3; H, 5.65; N, 12.1%). NMR: ^1H, δ 7.00 (t, 4 H, J 7.5, m-H of Ph), 6.85 (t, 2 H, J 7, p-H of Ph), 6.63 (d, 4 H, J 7.5 Hz, o-H of Ph) and 1.95 (s, 3 H, CH_3); ^{13}C, δ 166.5 (NCN), 146.2 (NPh), 128.5 (m-C), 124.8 (o-C), 122.4 (p-C) and 14.73 (CH_3).

Thermal decomposition

Samples were heated to 600 °C under a nitrogen atmosphere in a silica tube contained in a thermostatically controlled furnace. The optimum decomposition temperature was determined from the TGA data which were also obtained under a nitrogen atmosphere. The residual grey powder was stored under nitrogen. Electron microscopy revealed domains of GaN, many of which were on the surface of background carbon particles. X-Ray powder diffraction data showed lines at d (Å) 2.79, 2.58, 2.43, 1.59, 1.46 and 1.38 characteristic of GaN. Energy-dispersive X-ray (EDX) spectroscopy, obtained using a 5 keV electron beam with a Cambridge S250 instrument and a link to an analytical X-ray system using an LZ5 windowless detector, showed X-ray emissions corresponding to the L and K shell of gallium and nitrogen respectively, together with smaller emissions corresponding to carbon and oxygen.

Crystallography

Data were collected using a Siemens P3R3 four-circle diffractometer, ω–2θ mode. Scan speed 3–29° min⁻¹, depending upon the intensity of the 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. Three standard reflections were monitored every 200, and showed a slight decrease during data collection; the data were rescaled to correct for this. Reflections were corrected for absorption effects by the analytical method using ABSPSI.[27] Specific parameters are given in Table 3.

Structure analysis and refinement. For compound **3** space group $P\bar{1}$ was assumed; for **2**, the systematic absences combined with the probable value of Z suggested $P2_1cn$; the phenyl groups do not conform to the mirror plane that would be required in $Pmcn$. Both space groups were shown to be correct by successful refinement. The structures were solved by direct methods using SHELXTL PLUS.[28] Hydrogen atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; the H atoms were given isotropic displacement parameters equal to $U = 0.08$ Å². For **2** the absolute structure of the individual crystal chosen was checked by refinement of a df''

multiplier, and the x coordinate of the Ga atom was fixed to define the origin. Absolute structure parameter $x = 0.02(3)$. The phenyl groups in **3** were restrained to be flat with C_{2v} symmetry. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Refinement on F^2 was made using SHELXL 93.[29]

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Acknowledgements

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