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1,3-Diphenylamidine and methylaminopyridine compounds of gallium†

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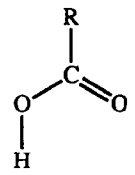
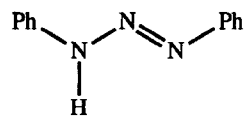
Abstract—Reaction of $Ga(^tBu)_3$ with the 1,3-diphenylamidine [PhN(H)C(H)=NPh, H-dpam] yields monomeric $(^tBu)_2Ga(dpam)$ (**1**). The partial hydrolysis of **1** results in the isolation of $(^tBu)_2Ga(\mu\text{-dpam})(\mu\text{-OH})Ga(^tBu)_2$ (**2**), whose structure consists of a gallium dimer in which the amidine and hydroxide ligands bridge two $Ga(^tBu)_2$ moieties. Reaction of $[Me_2Ga(\mu\text{-Cl})]_2$ with H-dpam results in the complex $[H_2\text{-dpam}][Me_2GaCl_2]$ (**3**). The solid state structure of **3** indicates the presence of a hydrogen bonded cation–anion complex, in which the core has a twisted eight-membered ring configuration. The versatility of amidines as both chelating and bridging ligands to gallium is discussed with respect to the predominance of bridging and chelating modes of coordination of carboxylates and triazenides, respectively. Reaction of 2-(methylamino)pyridine (H-map) with $Ga(^tBu)_3$ allows for the isolation of $(^tBu)_2Ga(map)$ (**4**). In contrast, reaction with $[(^tBu)_2Ga(\mu\text{-Cl})]_2$ and $[Me_2Ga(\mu\text{-Cl})]_2$ yields the Lewis acid base adducts, $(^tBu)_2GaCl(H\text{-map})$ (**5**) and $Me_2GaCl(H\text{-map})$ (**6**), respectively. Reaction of compound **6** with $^nPrNH_2$ does not result in the deprotonation of the H-map ligand, but ligand metathesis and the formation of $(^tBu)_2GaCl(NH_2{}^nPr)$ (**7**). The structures of **2, 3, 6,** and **7** have been determined by X-ray crystallography.

Keywords: amidine; aminopyridine; hydrogen bonding; hydrolysis; gallium.

We have become interested in the structural relationships between potentially isolobal [1] (and isoelectronic) ligands as they pertain to their coordination to the Group 13 metals: aluminum, gallium and indium. Our initial studies in this area involved a comparison of carboxylates (**I**) [2] and their isolobal analogs, 1,3-diphenyl triazenide ligands (**II**) [3,4,5,6]. We have demonstrated that despite the clear isolobal relationship between the parent ligands [7], the propensity of triazenides to act as a chelating rather than bridging ligand (as is observed for carboxylates) to aluminum, gallium or indium, suggests that they are better considered equivalent to acetylacetenoates. While we originally ascribed the differences in coordination of carboxylates and triazenides to the greater steric strain that would be imposed on a chelating carboxylate than is observed for the triazenide [8], it is possible that the presence of aryl (or alkyl) substituents on the 1,3 positions of the triazenide may add a steric component to the difference in observed coordination. In order to determine if it is steric rather than ring strain factors controlling the preferred coordination mode for carboxylates and triazenides it would be desirable to study a hybrid class of ligand, such as a dialkylamidines (**III**) [9]. A particular advantage of the amidines is that the steric bulk at both carbon (*R'*) and nitrogen (*R*) may be tuned as desired. Dialkylamidine complexes of transition metals have been well studied; however, compared to the extensive chemistry of carboxylate compounds a limited number of compounds



(**I**)



(**II**)

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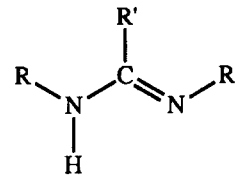
† Dedicated to Professor D. C. Bradley, FRS for his seminal contributions to the chemistry of alkoxide and amide compounds of the main group and transition metals.



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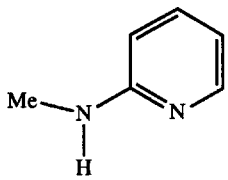

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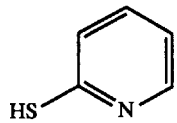


(V)

of the Group 13 metals have been reported for amidines [10,11]. The dialkylamidine compounds of gallium were shown by X-ray crystallography to be both chelating and bridging, suggesting that amidines are potentially more flexible ligands for the Group 13 metals than either carboxylates or triazenides. Our studies involve the reactions of 1,3-diphenylamidine (H-dpam, **III**, R = Ph, R' = H).

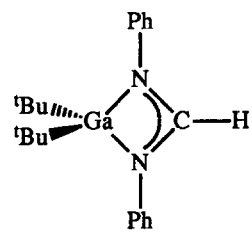
Alternative isolobal (and isoelectronic) analogs of an amidine are 2-(methylamino)pyridine (H-map, **IV**) and 2-mercaptopyridine ligand (H-Spy, **V**). The latter has previously been demonstrated to form both bridging and chelating complexes with aluminum, gallium and indium [12,13].

In order to determine the relative coordination modes for these isolobal ligands we have investigated the reactions of 1,3-diphenylamidine (H-dpam) and 2-(methylamino)pyridine (H-map) with gallium trialkyls and di-alkyl chlorides. The initial results of this study are presented herein.

RESULTS AND DISCUSSION

Amidine compounds

Reaction of $Ga(^tBu)_3$ with one equivalent of H-dpam yields $(^tBu)_2Ga(dpam)$ (**1**), with the con-



(1)

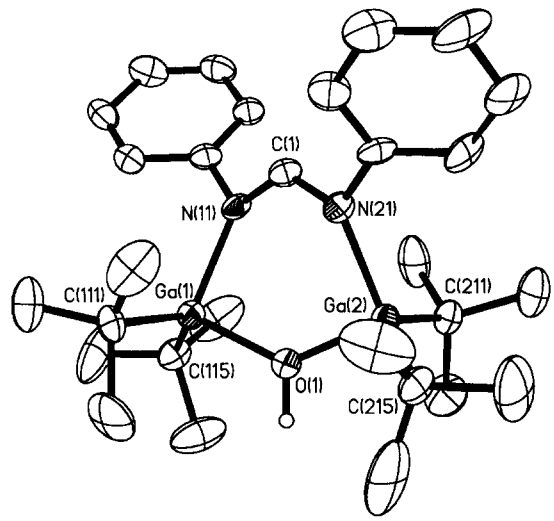


Fig. 1. The molecular structure of one of the crystallographically independent molecules of $(^tBu)_2Ga(\mu$-dpam$)(\mu$-OH$)Ga(^tBu)_2$ (**2**). Thermal ellipsoids are shown at the 30% level and organic hydrogen atoms are omitted for clarity.

comitant liberation of iso-butane. Based upon mass spectrometry (M^+ = 378) compound **1** appears to be isostructural to the 1,2,3-triphenylamidine compound $Me_2Ga(PhNCPhNPh)$ [11].

Compound **1** undergoes partial hydrolysis to liberate dpam-H and the dimeric hydroxide compound, $(^tBu)_2Ga(\mu$-dpam$)(\mu$-OH$)Ga(^tBu)_2$ (**2**), whose molecular structure is shown in Fig. 1; selected bond lengths and angles are given in Table 1. Two independent molecules are present in the asymmetric unit; however, all bond lengths and angles are close to or within experimental error between the two molecules (see Table 1). The Ga_2ON_2C cycle occupies a twist boat conformation (see Fig. 2) as a consequence of the steric interaction between the *tert*-butyl and phenyl groups [2]. The coordination around each gallium is distorted tetrahedral, with the smallest angles being

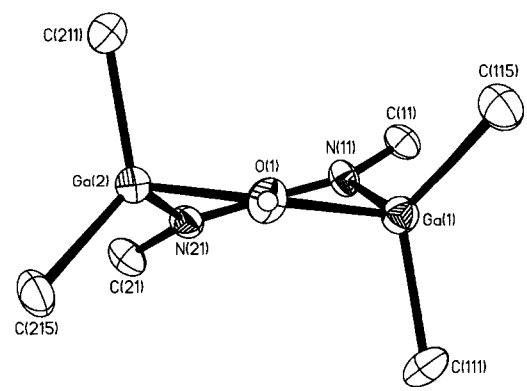


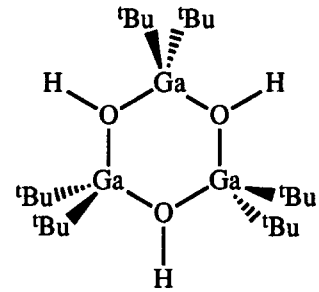
Fig. 2. Partial coordination of $(^tBu)_2Ga(\mu$-dpam$)(\mu$-OH$)Ga(^tBu)_2$ (**2**) viewed along the O(1)···C(1) vector demonstrating the twist boat conformation of the Ga_2ON_2C cycle.

Table 1. Selected bond lengths (Å) and angles (°) for ('Bu)$_2$Ga(μ-dpam)(μ-OH)Ga('Bu)$_2$ (**2**)

Molecule 1		Molecule 2	
Ga(1)—O(1)	1.933(6)	Ga(3)—O(2)	1.938(5)
Ga(1)—N(11)	2.028(7)	Ga(3)—N(31)	2.020(7)
Ga(1)—C(111)	2.038(9)	Ga(3)—C(311)	1.99(1)
Ga(1)—C(115)	2.010(8)	Ga(3)—C(315)	2.00(1)
Ga(2)—O(1)	1.938(6)	Ga(4)—O(2)	1.945(6)
Ga(2)—N(21)	2.032(6)	Ga(4)—N(41)	2.020(6)
Ga(2)—C(211)	2.001(9)	Ga(4)—C(411)	1.999(9)
Ga(2)—C(215)	2.01(1)	Ga(4)—C(415)	1.999(8)
N(11)—C(1)	1.30(1)	N(31)—C(2)	1.33(1)
N(11)—C(11)	1.42(1)	N(31)—C(31)	1.414(9)
N(21)—C(1)	1.34(1)	N(41)—C(2)	1.331(9)
N(21)—C(21)	1.42(1)	N(41)—C(41)	1.43(1)
O(1)—Ga(1)—N(11)	93.8(3)	O(2)—Ga(3)—N(31)	93.4(2)
O(1)—Ga(1)—C(111)	104.4(3)	O(2)—Ga(3)—C(311)	105.3(3)
O(1)—Ga(1)—C(115)	106.7(3)	O(2)—Ga(3)—C(315)	105.4(3)
N(11)—Ga(1)—C(111)	108.3(3)	N(31)—Ga(3)—C(311)	110.5(4)
N(11)—Ga—(1)—C(115)	113.3(4)	N(31)—Ga(3)—C(315)	113.6(3)
C(111)—Ga(1)—C(115)	125.2(4)	C(311)—Ga(3)—C(315)	123.5(4)
O(1)—Ga(2)—N(21)	94.4(2)	O(2)—Ga(4)—N(41)	94.3(3)
O(1)—Ga(2)—C(211)	103.9(3)	O(2)—Ga(4)—C(411)	104.4(3)
O(1)—Ga(2)—C(215)	105.4(3)	O(2)—Ga(4)—C(415)	105.4(3)
N(21)—Ga(1)—C(211)	110.5(3)	N(41)—Ga(4)—C(411)	110.4(3)
N(21)—Ga(1)—C(215)	112.9(3)	N(41)—Ga(4)—C(415)	112.7(3)
C(211)—Ga(2)—C(215)	124.6(4)	C(411)—Ga(4)—C(415)	124.5(3)
Ga(1)—O(1)—Ga(2)	132.0(3)	Ga(3)—O(2)—Ga(4)	132.4(3)
Ga(1)—N(11)—C(1)	127.9(6)	Ga(3)—N(31)—C(2)	127.7(5)
Ga(1)—N(11)—C(11)	118.2(5)	Ga(3)—N(31)—C(31)	118.1(6)
C(1)—N(11)—C(11)	112.9(7)	C(2)—N(31)—C(31)	113.5(6)
Ga(2)—N(21)—C(1)	125.6(5)	Ga(4)—N(41)—C(2)	126.2(6)
Ga(2)—N(21)—C(21)	119.1(5)	Ga(4)—N(41)—C(41)	118.5(4)
C(1)—N(21)—C(21)	114.2(6)	C(2)—N(41)—C(41)	113.6(7)
N(11)—C(1)—N(21)	128.1(8)	N(31)—C(2)—N(41)	128.0(8)

intra-ring, i.e., N—Ga—O [93.4(2)–94.4(2)°]. The Ga—N bond lengths [2.020(7)–2.032(6) Å] are within the range reported for chelating amidine compounds of gallium [2.009(2)–2.141(2) Å] [10,11]. As is typical for amidine ligands the N—C bond distances within the amidine core [1.30(1)–1.34(1) Å] are intermediate between those of isolated N—C single (*ca* 1.45 Å) and N=C double bond (*ca* 1.28 Å) lengths, consistent with delocalization of the N···C···N π-bond. The Ga—O—Ga angle [132.0(3), 132.4(3) Å] is smaller than that reported for [('Bu)$_2$Ga(μ-OH)]$_3$ (**VI**) [143.0(2) Å] [14].

Whereas Barker *et al.* have previously reported that the reaction of 1,2,3-triphenylamidine with $GaMe_3$ yields Me_2Ga(PhNCPhNPh) [11], the reaction of H-dpam with [$Me_2Ga(\mu$-Cl)]$_2$ does not result in alkane elimination but the formation of the salt, [H_2-dpam][Me_2GaCl_2] (**3**) (see Experimental), whose formation presumably occurs *via* the series of reactions shown in Eqs 1–3. We note that while Me_2Ga(PhNCPhNPh) [11] and Me_2Ga(PhNCMeNPh) [10] have been previously reported, we were unable to isolate Me_2Ga(dpam) under the present reaction conditions.



(VI)

$$Me_2GaCl + H\text{-dpam} \rightarrow Me_2Ga(dpam) + HCl \quad (1)$$

$$H\text{-dpam} + HCl \rightarrow [H_2\text{-dpam}]Cl \quad (2)$$

$$Me_2GaCl + [H_2\text{-dpam}]Cl \rightarrow [H_2\text{-dpam}][Me_2GaCl_2] \quad (3)$$

The structure of [H_2-dpam][Me_2GaCl_2] (**3**) is shown in Fig. 3; selected bond lengths and angles are given in Table 2. The coordination environment about

Table 2. Selected bond lengths (Å) and angles (°) for $[H_2$-dpam$][Me_2GaCl_2]$ (**3**)

Ga(1)—Cl(1)	2.307(4)	Ga(1)—C(11)	1.95(2)
N(2)—C(2)	1.31(1)	N(2)—C(3)	1.40(2)
Cl(1)—Ga(1)—Cl(1a)	97.4(1)	Cl(1)—Ga(1)—C(11)	106.3(6)
C(11)—Ga(1)—C(11a)	130.3(5)	C(1)—N(2)—C(3)	127(1)
N(2)—C(2)—N(2a)	125(1)		

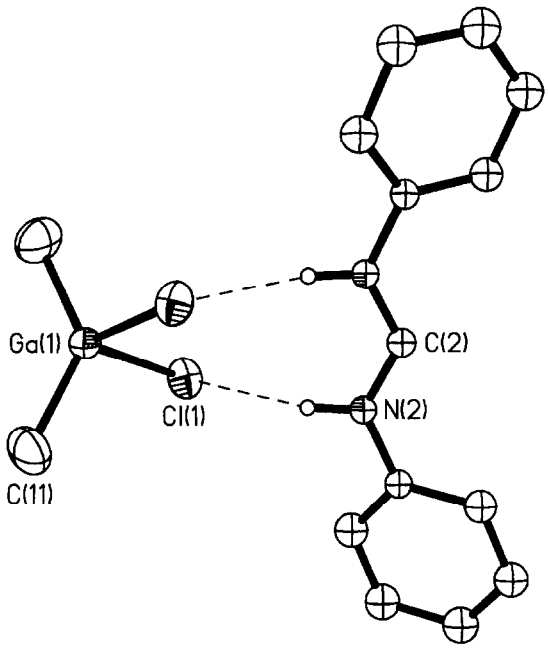


Fig. 3. The structure of $[H_2$-dpam$][Me_2GaCl_2]$ (**3**). Thermal ellipsoids are shown at the 30% level and organic hydrogen atoms are omitted for clarity.

Ga(1) is similar to previously characterized anion in $[Me_4As][Me_2GaCl_2]$ [15]. The Ga(1)—Cl(1) bond distance [2.307(4) Å] is slightly longer than non-hydrogen bonded terminal analogs [2.276(4), 2.277(4) Å] consistent with the hydrogen bonding interaction. Similarly, the Cl(1)—Ga(1)—Cl(1a) bond angle in **3** [97.4(1)°] is smaller than that in $[Me_4As][Me_2GaCl_2]$ [99.7(1)°], presumably due to the constraints of the two N—H···Cl hydrogen bonds. The hydrogen bonded anion–cation complex forms an unusual twisted 8-membered ring (see Fig. 4). The N—H···Cl hydrogen bonding distances [2.13(4) Å] is slightly shorter than recently observed for $[H_2N^iPr_2][MeGaCl_3]$, 2.43(7), 2.60(7) Å [16].

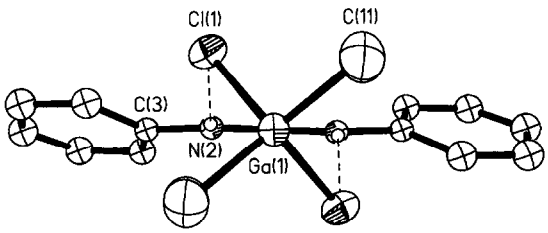
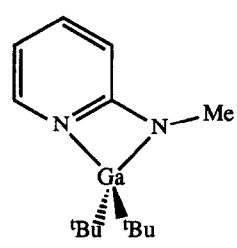


Fig. 4. $[H_2$-dpam$][Me_2GaCl_2]$ (**3**) viewed along the Ga(1)···C(1) vector demonstrating the conformation of the $GaCl_2H_2N_2C$ cycle.

Amidines: intermediaries between carboxylates and triazenides

We have previously suggested that the propensity of carboxylate ligands to act as bridging rather than chelating ligands to the Group 13 metals is due to the topotactic nature of the reaction [2], since no reorganization of the O—C—O framework is required in going from the 'free' carboxylic acid to the bridging carboxylate ligand. In particular the O—C—O angle in the free ligand (*ca* 123°) is similar to the range we have reported for bridging complexes (122–125°), and distinct to that observed and calculated for chelating carboxylates [2,17]. This is represented graphically in Fig. 5. In contrast, the N—N—N angle in bridging triazenide complexes is significantly larger than that for free and chelating triazenides (see Fig. 5) in accord with the observed preference of the latter mode of coordination.

The observations herein, and previously [10,11], that amidines exist as both bridging and chelating ligands suggests that they are more flexible ligands to Group 13 metals than either triazenides or carboxylates. This effect may be expected based on the rationale used for the triazenide and carboxylate preferential binding [2,8]. Thus, from Fig. 5 it is seen that the N—C—N angle in 'free' amidines occurs in between the values observed for chelating and bridging coordination. Furthermore, in both carboxylates and triazenides the intra-ligand angle is essentially invariant; however, the N—C—N angle in amidines may be



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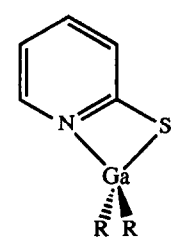

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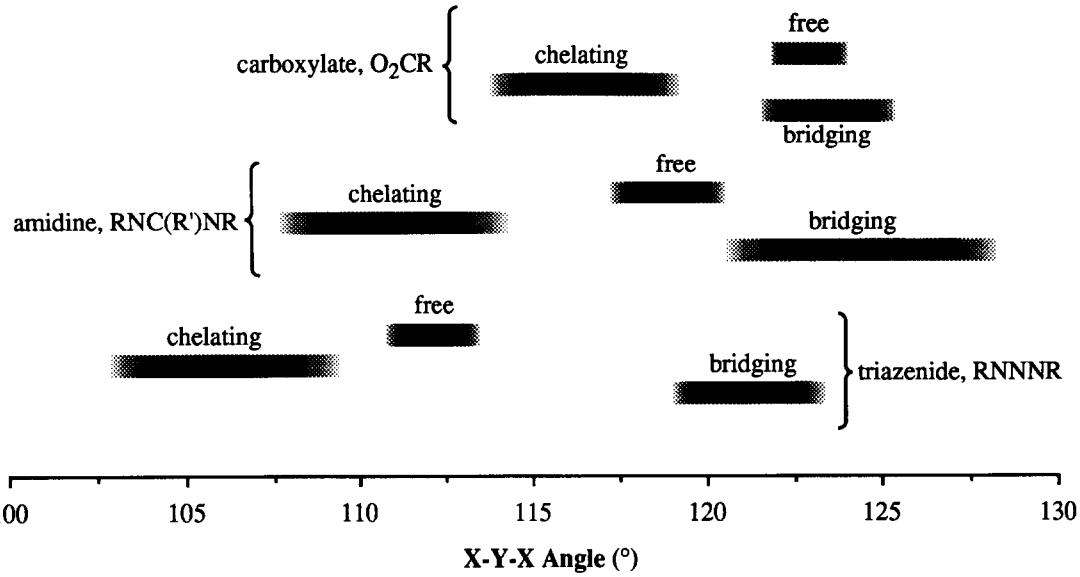


Fig. 5. Graphical representation of the X—Y—X bond angle (°) for triazenides, amidines, and carboxylates in chelating and bridging complexes as well as the 'free' ligand.

increased through the use of sterically demanding groups at either or both C and N. Thus, amidine ligands offer an entry into a diverse range of Group 13 metal complexes. Our studies in this regard are continuing.

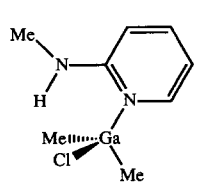
2-(Methylamino)pyridine compounds

Reaction of $Ga(^tBu)_3$ with 2-(methylamino)pyridine (H-map) yields $(^tBu)_2Ga$(2-map) (**4**). Mass spectra of compound **4** indicate it to be monomeric in the gas phase (see Experimental), and thus analogous to $(R)_2Ga$(Spy) (**VII**, R = Me,^{t}Bu).

As was observed for H-dpam (*vide supra*), the reaction of H-map with $[R_2Ga(\mu\text{-Cl})]_2$ (R = Me,^{t}Bu) does not result in alkane elimination, but yields the Lewis acid–base complexes, Me_2GaCl(2-map) (**5**) and $(^tBu)_2$GaCl(2-map) (**6**). The molecular structure of Me_2GaCl(2-map) (**6**) has been determined by X-ray crystallography and is shown in Fig. 6; selected bond lengths and angles are given in Table 3.

The 2-(methylamino)pyridine ligand in compound **6** coordinates *via* the pyridine nitrogen, consistent with the greater Lewis basicity of pyridine over a secondary amine. It is interesting to note that the configuration of the Me_2GaCl moiety in the solid state (**VIII**) with respect to the 2-(methylamino)pyridine ligand precludes N—H···Cl hydrogen bonding (i.e. **IX**). In addition to the lack of intra-molecular N—H···Cl hydrogen bonding, there is no evidence for inter-molecular hydrogen bonding from the crystal packing. The ν(N—H) stretch in the IR spectra of compound **6** is unchanged between solution (3327 cm^{-1}, CH_2Cl_2) and the solid state (3329 cm^{-1}, KBr disk), suggesting that no N—H···Cl hydrogen bonding occurs to the methyl amine of the H-map ligand. Similarly the change observed for compound **5** (3346 cm^{-1}, CH_2Cl_2 versus 3354 cm^{-1}, KBr disk) is consistent with no hydrogen bonding.

Reaction of compound **6** with ^{n}PrNH$_2$ does not result in the deprotonation of the H-map ligand, but ligand metathesis and the formation of $(^tBu)_2$



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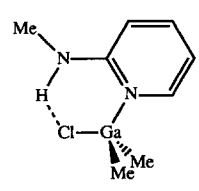

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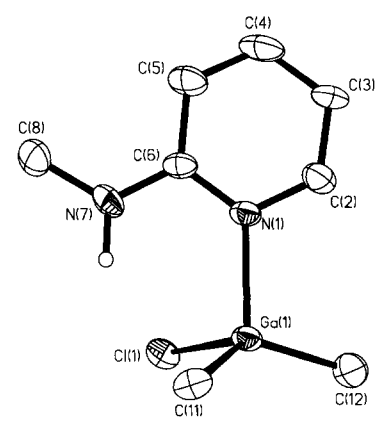

Fig. 6. The molecular structure of Me_2GaCl(H-map) (**6**). Thermal ellipsoids are shown at the 30% level and organic hydrogen atoms are omitted for clarity.

Table 3. Selected bond lengths (Å) and angles (°) for Me_2GaCl[H-map] (**6**)

Ga(1)—Cl(1)	2.276(1)	Ga(1)—N(1)	2.066(3)
Ga(1)—Cl(11)	1.945(5)	Ga(1)—C(12)	1.958(4)
Cl(1)—Ga(1)—N(1)	99.18(9)	Cl(1)—Ga(1)—C(11)	106.8(1)
Cl(1)—Ga(1)—C(21)	107.5(1)	N(1)—Ga(1)—C(11)	108.0(2)
N(1)—Ga(1)—C(21)	106.8(2)	C(11)—Ga(1)—C(21)	125.5(2)

Table 4. Selected bond lengths (Å) and angles (°) for $(^tBu)_2GaCl(NH_2{}^n Pr)$ (**7**)

Ga(1)—Cl(1)	2.285(2)	Ga(1)—N(1)	2.067(4)
Ga(1)—C(11)	1.979(7)	Ga(1)—C(21)	1.987(6)
Cl(1)—Ga(1)—N(1)	94.1(1)	Cl(1)—Ga(1)—C(11)	107.9(2)
Cl(1)—Ga(1)—C(21)	109.3(2)	N(1)—Ga(1)—C(11)	105.7(2)
N(1)—Ga(1)—C(21)	111.0(2)	C(11)—Ga(1)—C(21)	124.5(2)

$GaCl(NH_2{}^n Pr)$ (**7**), whose structure has been confirmed by X-ray crystallography. The molecular structure of compound **7** is shown in Fig. 7; selected bond lengths and angles are given in Table 4. The Ga(1)—N(1) distance [2.067(4) Å] is similar to that observed for the pyridine donor in compound **6** (*vide supra*). In addition the Ga(1)—Cl(1) bond [2.285(2) Å] is essentially the same as that observed for compound **6**; however, while there is no evidence for intramolecular hydrogen bonding in **7**, the crystal packing (Fig. 8) shows strong inter-molecular N—H···Cl hydrogen bonding.

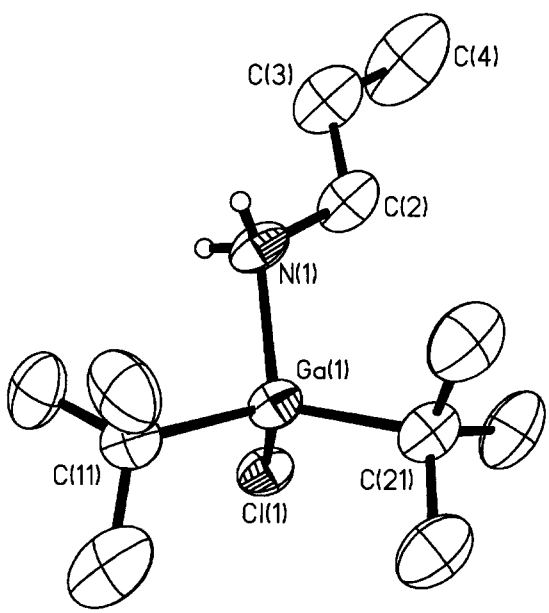

Fig. 7. The molecular structure of $(^tBu)_2GaCl(NH_2{}^n Pr)$ (**7**). Thermal ellipsoids are shown at the 30% level and hydrogen atoms are omitted for clarity.

EXPERIMENTAL

All operations were carried out using Schlenk techniques or in an argon atmospheric VAC glovebox. The synthesis of $Ga(^tBu)_3$ [18,19] $[(^tBu)_2Ga(\mu\text{-}Cl)]_2$ [20], and $[Me_2Ga(\mu\text{-}Cl)]_2$ [21] are reported elsewhere. ^1H and ^{13}C NMR analysis was carried out on a Bruker WM-250 MHz spectrometer. Mass spectra analysis was obtained on a Finnegan MAT95 mass spectrometer with an electron beam energy of 70 eV for EI mass spectra. IR analysis was carried out on a Perkin–Elmer 1600 Series FT-IR spectrometer using Nujol mulls.

$(^tBu)_2Ga(dpam)$ (**1**)

H-dpam (1.82 g, 8.31 mmol) was dissolved in degassed toluene (50 cm^3) and the solution was cooled to −78°C. $Ga(^tBu)_3$ (2.0 cm^3, 8.31 mmols) was then added slowly and the mixture was left to stir overnight while warming to room temperature. The solution was filtered, concentrated *in vacuo*, and cooled (−22°C). Several crops of pale yellow crystals were collected by filtration and subsequent recooling of the filtrate. MS (EI, %): *m/z* 378 (M^+, 7), 321 (M^+—^{t}Bu, 98), 265 (M^+—2^{t}Bu, 80), 196 (dpam, 7), 57 (^{t}Bu, 27). IR (cm^{-1}): 2961 (m), 2924 (m), 2338 (m), 1265 (s), 1084

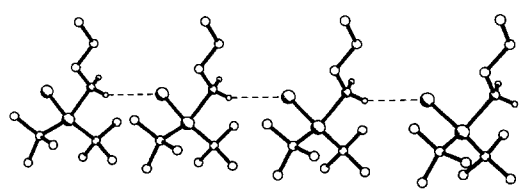

Fig. 8. A view of the inter-molecular hydrogen bonding observed in the solid state for $Me_2GaCl(NH_2{}^n Pr)$ (**7**).

(s), 1011 (s), 794 (s). ^{1}H NMR (C_6D_6): δ 8.32 [1H, s, C*H*N], 7.12 [2H, dd, J(H—H) = 7.8 Hz, *m*-C*H*], 6.87 [1H, t, J(H—H) = 7.8 Hz, *p*-C*H*], 6.82 [2H, d, J(H—H) = 7.8 Hz, *o*-C*H*], 1.29 [18H, s, C(CH_3)$_3$]. ^{13}C NMR (C_6D_6): δ 155.56 (N*C*N), 144.98 (N*C*), 130.11 (*o*-*C*H), 124.78 (*p*-*C*H), 119.06 (*m*-*C*H), 30.53 [C(*C*H$_3$)$_3$].

(^{t}Bu)$_2$Ga(μ-dpam)(μ-OH)Ga(^{t}Bu)$_2$ (**2**)

To a hexane (50 cm^3) suspension of H-dpam (1.0 g, 5.1 mmol) was added Ga(^{t}Bu)$_3$ (1.2 g, 5.0 mmol) dropwise to provide a clear solution. The solution was allowed to stir at ambient temperature for 1 h. The solvents and volatiles were removed *in vacuo* to yield the colorless solids. The product was re-dissolved in wet CH_2Cl_2 and recrystallized at -24°C. Yield: 69%. MS (EI, %): *m*/*z* 523 [M$^+$—^{t}Bu, 100], 321. IR (cm^{-1}): 2928 (m), 2839 (m), 1650 (vs), 1589 (s), 1532 (m), 1489 (m), 1308 (w), 1292 (w), 1201 (m), 1025 (w). ^{1}H NMR: δ 7.33 [2H, dd, J(H—H) = 7.8 Hz, *m*-C*H*], 7.09 [1H, t, J(H—H) = 7.8 Hz, *p*-C*H*], 7.08 [2H, d, J(H—H) = 7.8 Hz, *o*-C*H*], 2.36 (1H, s, O*H*), 1.28 [1H, s, NC(*H*)N], 1.04 [36H, s, C(CH_3)$_3$]. ^{13}C NMR: δ 129.8 (*m*-*C*H), 126.0 (*p*-*C*H), 124.8 (*o*-*C*H), 31.7 [C(*C*H$_3$)$_3$], 24.1 (N*C*N).

[H$_2$-dpam][Me$_2$GaCl$_2$] (**3**)

To a CH_2Cl_2 solution (2.0 cm^3) of H-dpam (0.42 g, 2.2 mmol) was added dropwise an Et_2O solution (2.0 cm^3) of [Me$_2$Ga(μ-Cl)]$_2$ (0.29 g, 2.2 mmol) at -78°C. The solution mixture was stirred overnight and allowed to rise to anambient temperature. The solvents and volatiles were removed under vacuum to yield a yellow oily residue. The residue was sublimed at *ca* 140°C to obtain pale yellow crystals. Yield: 49%. MS (EI, %): *m*/*z* 294 (M$^+$—2 Cl, 38), 279 [(M$^+$—2 Cl—Me, 100]. IR (cm^{-1}): 3398 (w), 1650 (vs), 1590 (s), 1495 (w). 1307 (w), 1201 (w). ^{1}H NMR: δ 7.2 (2H, br s, N—*H*), 7.2–6.8 (10H, m, C_6H_5), 2.11 [1H, s, NC(*H*)N], 0.30 [6H, s, Ga—CH_3]. ^{13}C NMR (δ): 129.8 (*o*-*C*H), 123.9 (*p*-*C*H), 120.0 (*m*-*C*H), 1.76 (Ga—*C*H$_3$).

(^{t}Bu)$_2$Ga(map) (**4**)

To H-map (0.9 g, 8.31 mmol) in hexane (50 cm^3) was added Ga(^{t}Bu)$_3$ (2.0 g, 8.31 mmol) at -78°C. After warming to room temperature and stirring overnight, the mixture was filtered, and after removal of all volatiles yielded a yellow oil. MS (EI, %): *m*/*z* 233 (M$^+$—^{t}Bu, 18), 177 (M$^+$—2^{t}Bu, 20), 107 (map, 82), 57 (^{t}Bu, 12). R(cm^{-1}): 2960 (s), 2837 (s), 1608 (s), 1501 (m), 1419 (m), 1296 (m), 1086 (s), 1009 (s), 799 (s), 656 (m). ^{1}H NMR (C_6D_6): δ 7.02 [1H, d, J(H—H) = 7.5, 6-C*H*], 6.92 [1H, dd, J(H—H) = 7.5, 4-C*H*], 5.81 [1H, dd, J(H—H) = 7.5, 5-C*H*], 5.77 [1H, d, J(H—H) = 6.8 Hz, 3-C*H*], 2.67 (3H, s, NCH_3), 1.22 [18H, s, C(CH_3)$_3$]. ^{13}C NMR (C_6D_6): δ 144.3 (6-*C*H), 140.2 (4-*C*H), 107.1 (5-*C*H), 103.8 (3-*C*H), 30.6 [C(*C*H$_3$)$_3$], 24.1 (N*C*H$_3$).

(^{t}Bu)$_2$GaCl(H-map) (**5**)

To neat H-map (0.40 g, 3.9 mmol) was added [(^{t}Bu)$_2$Ga(μ-Cl)]$_2$ (0.86 g, 3.9 mmol) at ambient temperature. The resulting colorless oily product was agitated for 1 h. Hexane (2 cm^3) was added and stirred additional 1 h. The solvent and volatiles were removed *in vacuo* to yield a colorless solid. The material was recrystallized from CH_2Cl_2 at -24°C. Yield: 79%. MS (EI, %): *m*/*z* 269 (M$^+$—^{t}Bu, 36), 233 (M$^+$—^{t}Bu—Cl, 18), 183 [(^{t}Bu)$_2$GaCl, 75]. IR (cm^{-1}): 3309 (s, br), 2952 (s), 2939 (s), 2839 (s), 1711 (w), 1661 (s), 1625 (vs), 1581 (vs), 1540 (s), 1474 (s), 1423 (m), 1362 (w), 1350 (w), 1172 (s), 1078 (w), 997 (w), 814 (m), 508 (w). ^{1}H NMR: δ 7.65 [1H, d, J(H—H) = 7.5, 6-C*H*], 6.73 [1H, dd, J(H—H) = 7.5, 4-C*H*], 5.92 [1H, dd, J(H—H) = 7.5, 5-C*H*], 5.61 [1H, d, J(H—H) = 6.8 Hz, 3-C*H*], 1.99 [3H, d, J(H—H) = 5.0 Hz, NCH_3], 1.36 [18H, s, C(CH_3)$_3$]. ^{13}C NMR: δ 144.8 (6-*C*H), 140.7 (4-*C*H), 111.4 (5-*C*H), 108.1 (3-*C*H), 30.9 [C(*C*H$_3$)$_3$], 28.5 [N*C*H$_3$].

Me$_2$GaCl(H-map) (**6**)

To neat H-map (0.20 g, 1.9 mmol) was added [Me$_2$Ga(μ-Cl)]$_2$ (0.25 g, 1.9 mmol) at ambient temperature. The resulting colorless oily product was agitated for 30 min and then set in a freezer (-24°C) overnight to obtain crystalline solids. Yield: 93%. MS (EI, %): *m*/*z* 227 [M$^+$—Me, 15], 207 (M$^+$—Cl, 10), 191 (M$^+$—Cl—CH_4, 15), 121 (MeGaCl, 21), 108 (map-H, 100), 99 (GaMe$_2$, 41). IR (cm^{-1}): 3682 (w), 3331 (m, br), 1663 (s), 1626 (s), 1579 (s), 1537 (m), 1472 (m), 1170 (m), 1007 (w). ^{1}H NMR: δ 7.49 [1H, d, J(H—H) = 7.5, 6-C*H*], 7.40 (1H, br, N—*H*), 6.70 [1H, dd, J(H—H) = 7.5, 4-C*H*], 5.86 [1H, dd, J(H—H) = 7.5, 5-C*H*], 5.58 [1H, d, J(H—H) = 6.8 Hz, 3-C*H*], 1.97 [3H, d, J(H—H) = 5.0 Hz, NCH_3], 0.26 (6H, s, Ga—CH_3). ^{13}C NMR: δ 158.8 (6-*C*H), 143.8 (6-*C*H), 141.4 (4-*C*H), 112.7 (5-*C*H), 108.3 (3-*C*H), 29.0 (N*C*H$_3$), -2.9 (Ga—*C*H$_3$).

(^{t}Bu)$_2$GaCl(NH$_2$^{n}Pr) (**7**)

To (^{t}Bu)$_2$GaCl(H-map) (1.1 g, 4.1 mmol) was added NH$_2$^{n}Pr (0.25 g, 4.2 mmol) and the mixture stirred for 1 h. As this slightly exothermic reaction cooled down to ambient temperature, needle like crystals were formed. Yield: 96%. MS (EI, %): *m*/*z* 220 (M$^+$—^{t}Bu, 37). ^{1}H NMR: δ 2.21 (1H, br, NH$_a$), 1.86 (1H, br, NH$_b$), 1.24 [18H, s, C(CH$_3$)$_3$], 1.07 [2H, t, J(H—H) = 7.2 Hz, NH$_2$CH_2], 0.68 [2H, qt,

Table 5. Summary of X-ray diffraction data

Compound	(^{t}Bu)$_2$Ga(μ-dpam)(μ-OH)Ga(^{t}Bu)$_2$ (**2**)	[H$_2$-dpam][Me$_2$GaCl$_2$] (**3**)	Me$_2$GaCl(H-map) (**6**)	(^{t}Bu)$_2$GaCl(NH$_2$^{n}Pr) (**7**)
Formula	$C_{29}H_{48}Ga_2N_2O$	$C_{15}H_{19}Cl_2GaN_2$	$C_8H_{14}ClGaN_2$	$C_{11}H_{27}ClGaN$
Cryst size (mm)	$0.21 \times 0.24 \times 0.26$	$0.09 \times 0.10 \times 0.28$	$0.18 \times 0.21 \times 0.24$	$0.10 \times 0.12 \times 0.45$
Cryst system	triclinic	orthorhombic	monoclinic	triclinic
Space group	$P\bar{1}$	*Pbcn*	$P2_1/n$	$P\bar{1}$
a (Å)	11.592(1)	18.648(2)	8.945(2)	6.3492(7)
b (Å)	16.712(2)	11.135(1)	11.305(2)	10.907(1)
c (Å)	17.009(2)	8.543(1)	11.273(2)	12.510(1)
α (°)	79.146(8)			109.412(8)
β (°)	89.238(8)		106.50(1)	97.407(8)
γ (°)	73.688(8)			97.010(9)
V (Å^3)	3103.1(6)	1773.9(4)	1093.0(3)	787.6(1)
Z	4	4	4	2
D (calcd) (g/cm^3)	1.242	1.378	1.479	1.160
μ (cm^{-1})	17.51	18.41	27.09	18.62
T (K)	298	298	298	298
2θ range (°)	3.0–44.0	3.0–44.0	3.0–55.0	3.0–50.0
No. collected	7576	1292	2787	2808
No. ind	7576	1292	2639	2808
No. obsd	4429 ($\|F_0\| > 6.0\sigma\|F_0\|$)	449 ($\|F_0\| > 6.0\sigma\|F_0\|$)	1739 ($\|F_0\| > 6.0\sigma\|F_0\|$)	2294 ($\|F_0\| > 6.0\sigma\|F_0\|$)
Weighting scheme	$w^{-1} = 0.04\ (\|F_0\|)^2 + \sigma(\|F_0\|)^2$	$w^{-1} = 0.04\ (\|F_0\|)^2 + \sigma(\|F_0\|)^2$	$w^{-1} = 0.04\ (\|F_0\|)^2 + \sigma(\|F_0\|)^2$	$w^{-1} = 0.04\ (\|F_0\|)^2 + \sigma(\|F_0\|)^2$
R	0.0413	0.0482	0.0324	0.0517
R_w	0.0502	0.0585	0.0335	0.0556
Largest diff peak (eÅ^{-3})	0.37	0.38	0.45	0.83

J(H—H) = 7.2 Hz, $NH_2CH_2CH_2$], 0.35 [3H, t, J(H—H) = 7.2 Hz, $NH_2CH_2CH_2CH_3$].

Crystallographic studies

Crystals of compounds **2, 3, 6,** and **7** were sealed in a glass capillary under argon and mounted on the goniometer of an Enraf–Nonius CAD-4 automated diffractometer. Data collection and cell determinations were performed in a manner previously described [22], using the $\theta/2\theta$ scan technique. Pertinent details are given in Table 3. The structures were solved by Patterson or direct Fourier methods, and the model refined using full-matrix least squares techniques. All non-hydrogen atoms were refined anisotropically, except for compound **3** in which Ga(1), Cl(1), and C(11) were the only atoms refined anisotropically. Except for the hydroxide and amine hydrogens, all hydrogen atoms were calculated and constrained to 'ride' upon the appropriate atoms [d(C—H) = 0.95 Å, U(H) = $1.3B_{eq}$(C)]. The hydroxide and amine hydrogens were located in the difference map, and their isotropic thermal parameter was allowed to 'ride' upon the heavy atom [U(H) = $1.3B_{eq}$(O) or $1.3B_{eq}$(N)]. All computations were performed using MolEN [23] or SHELX86 [24]. A summary of cell parameters, data collection, and structure solution is given in Table 5. Scattering factors were taken from ref. [25].

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