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Metallacycles of the imidoylamidinato compounds HNC(R)NC(R)NH and Group 13 elements. Crystal structure of the complex $[GaMe_2\{HNC(CF_3)NC(CF_3)NH\}]$

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Reaction of trimethylgallium with trifluoroacetamidine $[H_2NC(CF_3)NH]$ resulted in an unusual elimination reaction, and yielded the air-stable volatile metallacycle $[GaMe_2\{HNC(CF_3)NC(CF_3)NH\}]$ which shows a planar six-membered (GaNCNCN) ring; a related aluminium system $[AlMe_2\{HNC(Ph)NC(Ph)NH\}]$ was formed using benzamidine $[H_2NC(Ph)NH]$.

Amidines $[R_2NC(R')=NR]$ (R, R′ = H, alkyl, aryl, *etc.*) are versatile ligands in that they co-ordinate to metals in a variety of ways, in either the neutral form, or more usually as the amidinato group $[RNCR'NR]^-$. In their anionic form, they are isoelectronic with the carboxylate and triazenide ions and they can act as both chelating and bridging systems, where the two (or more) metal atoms involved in the bridging mode may be the same or different.[1,2] While complexes involving transition metals are well known, less attention has been paid to species involving main-group elements. Treatment of amidines with Group 13 metal alkyls leads to substitution reactions, and products of the type $[MMe_x(RNCRNR)_{3-x}]$ (R = alkyl or aryl; M = Al, Ga or In; $x = 0$–2) are obtained.[3] We have now observed an unusual elimination reaction which occurs in this type of reaction, and report here the formation of aluminium and gallium heterocycles derived from the imidoylamidinate HNC(R)NC(R)NH (R = CF_3 or Ph). These are the first examples of such systems containing a main-group element.

When $GaMe_3$ (1 mol) is condensed onto $H_2NC(CF_3)NH$ (1 mol) *in vacuo* at −196 °C, and the reaction mixture allowed to warm to −78 °C evolution of methane (1 mol) occurs. The residue consists of a colourless viscous liquid together with some colourless solid material. Warming the reaction tube to 70 °C *in vacuo* results in the sublimation of colourless cube-shaped crystals (yield 35%) onto the colder parts of the tube, and a viscous liquid remains at the bottom of the vessel. The yield of the crystalline product increases to 40% (based on the weight of $GaMe_3$ used) when 2 mol of the amidine are used in the reaction, but still only 1 mol of methane is evolved.*

The crystal structure of the sublimate† shows the presence of a planar six-membered metallacycle with a dimethylgallium fragment co-ordinated symmetrically by the N,N′-chelating ligand $HNC(CF_3)NC(CF_3)NH$ (Fig. 1). All six atoms of the ring are coplanar within 0.010(7) Å, although the arrangement around the metal atom is distorted from the ideal tetrahedral geometry due to the small bite angle of 86.7(4)° in the N(1)–Ga(1)–N(3) fragment. The two CF_3 groups are symmetrically orientated with the carbon and one of the fluorine atoms from each group [F(11) and F(41)] lying approximately in the ring plane. While the NH hydrogen atoms were not clearly detected in the difference map the orientation of the CF_3 groups suggests that some interaction occurs between the in-plane fluorine atoms and these hydrogen atoms. When the latter are placed in calculated positions on N(1) and N(3), the H–F separations are 2.217 [N(1)–F(11)] and 2.231 Å [H(3)–F(41)], compared with the sum of their van der Waals radii of 2.67 Å.

The carbon–nitrogen distances in the ring indicate extensive delocalisation throughout the NCNCN π-skeletal system. The

* The compound $[GaMe_2\{HNC(CF_3)NC(CF_3)NH\}]$ was prepared by treating $GaMe_3$ (0.5 g, 4.4 mmol) with trifluoroacetamidine (0.98 g, 8.7 mmol) at 60 °C, and then subliming the product at 70 °C under vacuum. Yield 40% [Found (required for $C_6H_8F_6GaN_3$): C, 23.1 (23.6); H, 2.60 (2.60); N, 13.35 (13.75%)]. ^{1}H NMR ($CDCl_3$, 250 MHz, 295 K), δ 7.37 (br, 2 H, NH), −0.27 (s, 6 H, $GaMe_2$); ^{13}C (400 MHz), δ 162.0 (q, *J* 141.6, NCN), 117.2 (q, *J* 1114.6 Hz, CF_3), −4.70 (s, $GaMe_2$); ^{19}F (400 MHz), δ −76.2 (CF_3). Mass spectrum (EI): *m*/*z* 305 (M^+, based on ^{69}Ga, 2.0), 290 [$(M - Me)^+$, 100], 205 [$(M - GaMe_2)^+$, 3.8%].

The aluminium compound was prepared in a similar manner, except that the reaction was carried out in hexane at 55 °C, and the colourless solid product was filtered off. Yield 35%. ^{1}H NMR ($CDCl_3$, 250 MHz, 295 K), δ 8.8 (br, 2 H, NH), 7.55–7.42 (m, 10 H, Ph), −0.96 (s, 6 H, $AlMe_2$); ^{13}C (250 MHz), δ 176.0 (NCN), 137.4 [NC*C*(Ph)N], 131.1 (*o*-C of Ph), 128.5 (*p*-C of Ph), 127.1 (*m*-C of Ph), −9.5 ($AlMe_2$). Mass spectrum (EI): *m*/*z* 279 (M^+, 4.0), 249 [$(M - 2Me)^+$, 12.1], 222 [$(M - AlMe_2)^+$, 1.2], 176 [$(M - PhCN)^+$, 2.4], 171 [$(M - 2Me - Ph - H)^+$, 3.9%].

† Crystal data: $C_6H_8F_6GaN_3$, $M = 305.9$, tetragonal, space group $P\bar{4}2_1c$, (no. 114), $a = 15.356(5)$, $c = 9.681(5)$ Å, $U = 2282.9$ Å^3, $Z = 8$, $D_c = 1.78$ g cm^{-3}, Mo-Kα radiation, $\lambda = 0.710\,69$ Å, μ(Mo-Kα) = 2.47 mm^{-1}, $T = 240$ K, $R = 0.056$ for 761 unique observed [$I/\sigma(I) \geqslant 2.0$] reflections. Crystal character: colourless blocks, mounted in a Lindemann tube. Data were collected with a Siemens R3m four-circle diffractometer in ω–2θ mode. The crystal was held at 240 K with an Oxford Cryosystems Cryostream Cooler.[4] Maximum 2θ 50°. Three standard reflections were monitored every 200 and showed a significant decrease during data collection (12%). The data were rescaled to correct for this. 1984 Reflections were processed using profile analysis to give 964 unique reflections ($R_{int} = 0.106$), of which 706 were considered observed [$I/\sigma(I) \geqslant 2.0$]. These were corrected for Lorentz and polarisation but not absorption effects. The almost spherical crystal had approximate dimensions 0.35 × 0.34 × 0.33 mm. Systematic reflection conditions: *hhl*, $l = 2n$, *h*00, $h = 2n$ indicate space group $P4_12_1c$. The methyl groups were treated as rigid CH_3 units, with their initial orientation based on a staggered configuration. The NH hydrogen atoms were not clearly visible on Fourier-difference maps, and were not included in the refinement (though they are shown in calculated positions in Fig. 1). The absolute structure of the individual crystal chosen was checked by refinement of a $\delta f''$ multiplier. Final $R = 0.056$, $R' = 0.068$, $S = 0.87$; R for all reflections = 0.081. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/434.

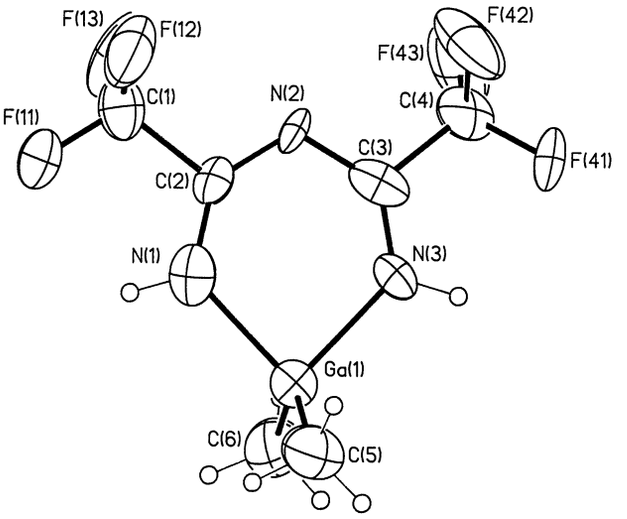

Fig. 1 Molecular structure of $[GaMe_2\{HNC(CF_3)NC(CF_3)NH\}]$. Selected bond lengths (Å) and angles (°): Ga(1)–C(5) 1.900(12), Ga(1)–N(1) 1.992(9), Ga(1)–N(3) 2.012(9), N(1)–C(2) 1.315(14), N(2)–C(2) 1.294(14), N(2)–C(3) 1.354(14), N(3)–C(3) 1.274(13); C(5)–Ga(1)–C(6) 125.5(7), N(1)–Ga(1)–N(3) 86.7(4), C(2)–N(1)–Ga(1) 125.2(7), C(2)–N(2)–C(3) 118.7(10), C(3)–N(3)–Ga(1) 127.2(8), N(2)–C(2)–N(1) 132.4(10), N(2)–C(3)–C(4) 111.2(10)

mean distance of 1.309(14) Å is slightly shorter than the corresponding average distance of 1.333(11) Å found in the strained four-membered GaNCN ring in $[GaMe_2(NPhCPhNPh)]$ where the geometry around the metal atom is also distorted from the ideal tetrahedral structure.[3]

A similar reaction involving trimethylaluminium and benzamidine $[H_2NC(Ph)NH]$, using a 1:2 mol ratio, also liberates methane and appears to form a similar cyclic product $[AlMe_2\{NHC(Ph)NC(Ph)NH\}]$. We have so far been unable to obtain suitable crystals for an X-ray crystallographic determination, but its analytical and spectroscopic (^{1}H and ^{13}C NMR) data, are closely similar to those obtained for the gallium compound. Thus the ^{1}H NMR spectrum shows a sharp singlet at δ −0.96 ($AlMe_2$, relative intensity 6), a multiplet centred at δ 7.42 (Ph, relative intensity 10) and a broad resonance at δ 8.8 (N–H, approximate relative intensity 2). A molecular ion (*M* 279) is observed in the electron impact (EI) mass spectrum, and peaks also occur at $m/z = 249$ and 171, corresponding to $(M - 2Me)^+$ and the ring fragment $[AlN(H)C(Ph)NCN]^+$ respectively. There is also a strong similarity between the IR spectra of the two compounds with major bands at 3361, 3324 (corresponding bands for the gallium compound ocur at 3331, 3307), 1592 (1628), 1564 (1561), 1291 (1295), 1193 (1199), 798 (804) and 667 (675) cm^{-1}.

It is interesting to compare the above reactions with those involving Group 8 transition-metal compounds. Various types of metallacycles, including those with ring systems of the type discussed here, are formed in reactions between trifluoroacetonitrile, CF_3CN, and Group 8 complexes, namely $[M\{HNC(CF_3)NC(CF_3)NH\}]$ $[M = Ir(CO)(PPh_3)_2$,[5] $Ru(PPh_3)(C_5H_5)$ or $Ru\{P(OMe)_3\}(C_5H_5)]$.[6] Lithiobenzamidine reacts with $[PtCl_2(PhCN)_2]$ to form $[Pt\{HNC(Ph)NC(Ph)NH\}_2]$,[7] and more recently some ruthenium and osmium complexes, *e.g.* $[RuH(CO)(PPh_3)_2\{HNC(CF_3)NC(CF_3)NH\}]$, have been obtained by the action of trifluoroacetamidine on species such as $[RuH(CO)(PPh_3)_3]$.[8] All these products show general delocalisation over the NCNCN fragment of the ring although with considerable variation in the bond lengths. The reaction pathways involved are far from clear. In the present case we have confirmed the absence of trifluoroacetonitrile impurity in the starting amidine, so the imidoylamidinato ligand could not have arisen by nucleophilic attack of free CF_3CN upon a co-ordinated amidinate. It is relevant here that the formation of similar compounds involving boron have been claimed, *e.g.* $[(C_3H_7)_2B\{HNC(Ph)NC(Ph)NH\}]$, by heating a mixture of tri-*n*-propylborane, benzonitrile and benzamidine to 100–120 °C;[9] but these have not been characterised structurally. However, in the present work we have been unable to obtain the corresponding aluminium derivative either by the action of various amidines on the adducts $Me_3Al{\cdot}NCR$ (R = Ph or C_6F_5) or by the action of RCN (R = Ph or C_6F_5) on $[AlMe_2(HNCPhNH)]$. Since the existence of the $[MMe_2(RNCRNR)]$ species is well established,[3] it is possible that the cyclic products reported here arise from nucleophilic attack on the co-ordinated amidine by the excess free amidine. However, such a pathway must be characteristic of the trifluoroacetamidine and benzamidine ligands, since a variety of other ligands simply react to produce the bis(amidinato) product, *e.g.* $[GaMe(RNCRNR)_2]$.[3] Clearly the elimination of ammonia is required in the reaction, but we have been unable to detect any ammonia in the gases evolved. We assume that the, as yet, unidentified liquid obtained as a by-product of the reactions arises from the trapping of a dimethylgallium (or -aluminium) amidinato intermediate reacting with the ammonia evolved. The ^{1}H NMR spectra of these by-products shows a complex series of resonances in the region δ 0.0 to −1.0 indicating the presence of a number of species containing metal–methyl fragments. In other work we have found that amidinato complexes such as $[GaMe_2(NPhCPhNPh)]$ act as Lewis acids,[10] and will co-ordinate with bases such as 4-*tert*-butylpyridine forming 1:1 adducts, consistent with the retention of the ammonia within the reaction mixture.

In conclusion, it is now apparent that the imidoylamidinato group is a versatile species which can co-ordinate to a wide range of metal species. Since it is isoelectronic with the β-diketonate anion, $[OC(R)C(H)OC(R)]^-$ (acac), which is well known to form a large number of complexes of academic and industrial interest, including for example $[M(acac)_3]$ (M = Al or Ga),[11] further studies on the use of the imidoylamidinate group, and the properties of the metal complexes formed, would be timely.

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