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Carbene complexes of Group 13 trihydrides: synthesis and characterisation of $[\mathrm{MH_3\{\overline{CN(Pr^i)C_2Me_2N}(Pr^i)\}}]$, M = Al, Ga or In

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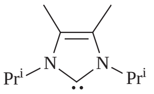
The reaction of $\mathrm{LiInH_4}$ with $\mathrm{NMe_3{\cdot}HCl}$ yielded $[\mathrm{InH_3(NMe_3)}]$ which could not be isolated in the solid state. Treatment of $[\mathrm{MH_3(NMe_3)}]$ with either 1 or 2 equivalents of the stable carbene $:\mathrm{\overline{CN(Pr^i)C_2Me_2N}(Pr^i)}$ afforded the carbene–metal trihydride complexes $[\mathrm{MH_3\{\overline{CN(Pr^i)C_2Me_2N}(Pr^i)\}}]$, M = Al, Ga or In. The aluminium and indium complexes could also be prepared by treating either $\mathrm{LiAlH_4}$ or $\mathrm{LiInH_4}$ with 1 or 2 equivalents of $:\mathrm{\overline{CN(Pr^i)C_2Me_2N}(Pr^i)}$. Variable temperature ^{1}H NMR studies of the carbene–$\mathrm{MH_3}$ complexes revealed them to be fluxional in solution at room temperature. The crystal structures of the monomeric aluminium and gallium hydride complexes showed them to contain partially delocalised carbene ligands.

Introduction

In recent years complexes of N-, P- or O-donor Lewis bases with aluminium and gallium trihydrides have been extensively studied.[1] This interest stems largely from the many applications such complexes have found in a variety of areas which include organic synthesis[2] and chemical vapour deposition technology.[3] Not long after the preparation of the first imidazol-2-ylidene carbene in 1991,[4] *viz.* $:\mathrm{\overline{CN(Mes)C_2H_2N}(Mes)}$, Mes = $\mathrm{C_6H_2Me_3}$-2,4,6, it was realised that these highly nucleophilic species could be used as ligands in the formation of both transition and main group metal complexes.[5] In each the singlet carbene generally acts as a two electron donor in a similar fashion to the co-ordinating behaviour of tertiary phosphines and ethers. Prior to our work in this area, carbene complexes of Group 13 trihydrides could be restricted to a series of borane complexes, **1**,[6] and one $\mathrm{AlH_3}$ complex, **2**.[7] Additionally, the trimethyl-aluminium and -gallium complexes, **3** and **4**, had been reported.[8]

Our interest in carbene–Group 13 hydride chemistry arose from the remarkable thermal stability of complex **2** (mp 246 °C) which is presumably due to the highly nucleophilic nature of the carbene ligand. From this the possibility of using similar carbenes to form stable $\mathrm{InH_3}$ complexes, which were unknown, became apparent. It is noteworthy that other indium hydride complexes are extremely rare and can be confined to a handful of cases, *viz.* $[\mathrm{Li(thf)_2}][\mathrm{In_2H_5\{C(SiMe_3)_3\}_2}]$,[9] $\mathrm{K[H\{In(CH_2CMe_3)_3\}_2]}$,[10] $\mathrm{K_3[K(Me_2SiO)_7][InH(CH_2CMe_3)_3]_4}$,[11] $[\mathrm{InH(2\text{-}Me_2NCH_2C_6H_4)_2}]$,[1,2] $[\mathrm{Me_2InB_3H_8}]$[13] and $[\mathrm{Li(tmen)_2}][\mathrm{H(InMe_3)_2}]$.[14] Our initial attempts to prepare carbene–$\mathrm{InH_3}$ complexes centred on the treatment of the carbene–indium halide complexes **5**–**7**[15] with various hydride sources. Although this proved fruitless a successful strategy was devised, whereby treatment of $[\mathrm{InH_3(NMe_3)}]$ or $\mathrm{LiInH_4}$ with the carbene $:\mathrm{\overline{CN(Pr^i)C_2Me_2N}(Pr^i)}$ **I** yielded the first structurally characterised indium trihydride complex, **8**. We have described some aspects of this work in a preliminary communication.[16] Herein, we report full synthetic details for both $[\mathrm{InH_3(NMe_3)}]$ and **8**. In addition the synthesis and structural characterisation of the aluminium and gallium analogues of **8** are described.



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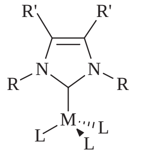
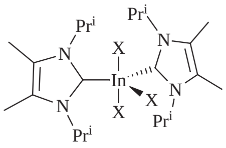


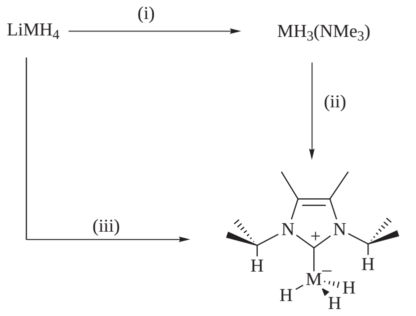
1 M = B, L = H, R = Me, Et, Pr^i, R' = Me
2 M = Al, L = H, R = mesityl, R' = H
3 M = Al, L = Me, R = Pr^i, R' = Me
4 M = Ga, L = Me, R = Pr^i, R' = Me
5 M = In, L = Br, R = Pr^i, R' = Me



X = Cl **6**
X = Br **7**

Results and discussion

At the outset of this work it was believed it would be necessary to prepare $[\mathrm{InH_3(NMe_3)}]$ for use as a precursor in the ligand displacement reaction that affords **8** (Scheme 1). This was achieved by a variation of the preparation of $[\mathrm{MH_3(NMe_3)}]$, M = Al[17] or Ga.[18] A diethyl ether solution of $\mathrm{LiInH_4}$ was treated with 1 equivalent of solid $\mathrm{NMe_3{\cdot}HCl}$ at −30 °C and the resulting suspension was stirred until all the $\mathrm{NMe_3{\cdot}HCl}$ had been



M = Al **9**, Ga **10**, In **8**

Scheme 1 (i) M = In, $\mathrm{NMe_3{\cdot}HCl}$, −30 °C, 2 h, −LiCl, $-\tfrac{1}{2}\,\mathrm{H_2}$; (ii) **I**, 2 h, $-\mathrm{NMe_3}$; (iii) M = Al or Ga, **I**, 5 h.

consumed (*ca.* 2 h), as evidenced by the cessation of gas evolution and the formation of a colourless solution. The *in-situ* generated complex, $[\mathrm{InH_3(NMe_3)}]$, was assumed to have been formed quantitatively and was used in further experiments without work-up due to its extreme thermal instability. In ether solutions of *ca.* 0.1 M it decomposes above −25 °C (*cf.* 0 °C for $\mathrm{LiInH_4}$[19]) to yield indium metal and hydrogen gas. Moreover, concentrating these solutions to greater than 0.1 M leads to decomposition, even at −30 °C, and therefore $[\mathrm{InH_3(NMe_3)}]$ could not be obtained in the solid state. Owing to this instability all attempts to obtain solution state spectroscopic data met with failure. It does, however, seem reasonable to assume that $[\mathrm{InH_3(NMe_3)}]$ is formed in the reaction of $\mathrm{LiInH_4}$ with $\mathrm{NMe_3{\cdot}HCl}$ because (i) all the $\mathrm{NMe_3{\cdot}HCl}$ is consumed in the reaction and $\mathrm{H_2}$ gas is evolved, (ii) its further reaction with the carbene, **I**, affords the $\mathrm{InH_3}$ complex, **8**, in moderate yield (see below) and (iii) thermal decomposition of solutions of $[\mathrm{InH_3(NMe_3)}]$ yield the expected amounts of indium metal.

Treatment of ethereal solutions of $[\mathrm{MH_3(NMe_3)}]$ with 1 equivalent of compound **I** led to the formation of $[\mathrm{MH_3\{\overline{CN(Pr^i)C_2Me_2N}(Pr^i)\}}]$ in moderate yields [M = Al **9** (64), Ga **10** (40) or In **8** (42%)] after recrystallisation from diethyl ether (Scheme 1). When similar reactions were carried out with 2 equivalents of **I** only the 1 : 1 complexes, **8**–**10**, were formed. In the case of **8** this is interesting because 2 : 1 complexes of the carbene with indium halides, **6** and **7**, are readily formed.[15] This can be rationalised if it is assumed that the $\mathrm{InH_3}$ unit is less Lewis acidic than $\mathrm{InX_3}$ (X = Cl or Br) and therefore more easily electronically satisfied. Such an assumption seems feasible on electronegativity grounds (Cl and Br are more electronegative than H) and if a comparison is drawn with $\mathrm{AlH_3}$ which has quantitatively been shown to be less Lewis acidic than $\mathrm{AlCl_3}$.[20]

Compound **8** was also prepared in moderate yield (38%) by treating ether solutions of $\mathrm{LiInH_4}$ with either 1 or 2 equivalents of **I** (Scheme 1). In these reactions an insoluble by-product was formed which proved to be too thermally unstable to characterise. It seems likely that this is a complex indium hydride species if a comparison is drawn with the related reactions of $\mathrm{LiAlH_4}$ with tertiary amines which can yield alane adducts, $[\mathrm{AlH_3(NR_3)}]$, and $\mathrm{Li_3AlH_6}$.[21] To test this hypothesis the analogous reaction of $\mathrm{LiAlH_4}$ with 1 equivalent of **I** was carried out and, indeed, this led to the formation of **9** (30%) and a highly air sensitive by-product which is insoluble in all common organic solvents. This precipitate was isolated, washed with thf and dried *in vacuo*. It is, however, believed not to be crystalline $\mathrm{Li_3AlH_6}$ (or LiH) for a number of reasons. Attempts to obtain an X-ray powder diffraction pattern on the material failed, which suggests it is an amorphous solid. It exhibits a broad Al–H absorbance centred at 1700 $\mathrm{cm^{-1}}$ (*cf.* 1720 $\mathrm{cm^{-1}}$ for $\mathrm{Li_3AlH_6}$[22]) in its infrared spectrum, in addition to other absorbances which suggest the presence of some organic components. The material shows no decomposition to aluminium metal up to temperatures of 300 °C ($\mathrm{Li_3AlH_6}$ decomposes to LiH, Al and $\mathrm{H_2}$ at 210 °C[23]). The powder was decomposed in 0.1 M HCl and an ICP MS analysis of the resulting solution yielded an Li : Al ratio of 4.1 : 1 (*cf.* 3 : 1 in $\mathrm{Li_3AlH_6}$). Finally, CHN analysis of the precipitate showed the presence of a significant amount of carbon (12.05%) but no nitrogen. Therefore, it is difficult to say what this by-product is but it is most likely a mixture of complex aluminium hydride species (and perhaps LiH) that are partially solvated with diethyl ether (or thf).

The complexes **8**–**10** are all extremely moisture sensitive, colourless materials, the thermal stability of which decreases in the order **9** > **10** > **8**. The alane complex, **9**, melts at 160 °C with slow gas evolution but does not completely decompose until *ca.* 250 °C without aluminium deposition. The gallane complex, **10**, melts with decomposition at 180 °C *via* a mechanism that involves some gallium deposition and gas evolution. The indane complex, **8**, is unstable in solution above −20 °C and decomposes in the solid state above −5 °C, depositing indium metal and generating a gas. The decomposition temperatures of **9** and **10** are much higher than is normally seen for Lewis base adducts {*e.g.* $[\mathrm{AlH_3(NMe_3)}]$ *ca.* 100 °C,[17] $[\mathrm{GaH_3(NMe_3)}]$ *ca.* 70 °C[18]} which generally decompose cleanly to the metal, hydrogen and the ligand. The greater thermal stability of **9** and **10** can probably be attributed to the high nucleophilicity of the carbene ligand, relative to normal Lewis bases, as the primary process in the thermal decomposition of most alane and gallane complexes is thought to be dissociation of the non-hydride ligand.[1] It is interesting that **9** does not deposit aluminium metal during its decomposition. Moreover, although some deposition of Ga and In is seen in the decomposition of **10** and **8**, analysis of the other decomposition products revealed a complex mixture of compounds (not including the free carbene, **I**) that test positive for the metal involved. Therefore it seems that in all cases the mechanism of decomposition is more complicated than is typical for Lewis base adducts of the metal trihydrides.

The IR spectra (Nujol mulls) of complexes **8**–**10** all display strong, broad absorbances [**9** 1730 (*cf.* **2** 1743),[7] **10** 1775, **8** 1640 $\mathrm{cm^{-1}}$] which have been attributed to their M–H stretching modes. These values follow the same pattern as seen for the matrix isolated, unco-ordinated, monomeric species [$\mathrm{MH_3}$, M = Al (1882.9), Ga (1923.2) or In (1754.5 $\mathrm{cm^{-1}}$)],[24] though all are at significantly lower wavenumbers. Interestingly, the values for **9** and **10** are at lower wavenumbers than are normally seen for adducts of alane and gallane, *e.g.* $[\mathrm{MH_3(NMe_3)}]$ M = Al 1792, Ga 1853 $\mathrm{cm^{-1}}$,[25] which presumably reflects the greater donor strength of the carbene, **I**, relative to standard Lewis bases. Finally, the fact that the M–H stretching frequency in **10** is higher than in **9** relates to the anomalous electronegativity of Ga (1.8) relative to Al (1.5) which results in a less polar, more covalent bond with hydrogen (2.1). An identical argument has been used to explain the positions of the M–H stretching frequencies for $[\mathrm{MH_3(NMe_3)}]$, M = Al or Ga.[25]

The solution NMR data for complexes **8**–**10** support their proposed structures. Their ^{1}H NMR spectra are similar and display very broad hydride resonances at δ 4.63 **9**, 4.48 **10** and 5.58 **8** which integrate for 3 hydrogens each. The broadness of these peaks is due to the quadrupolar nature of the metals involved. It is interesting that the value for **9** is at higher field than that for **10** since hydride resonances for $\mathrm{GaH_3}$ complexes are normally at lower field than those for their $\mathrm{AlH_3}$ analogues.[26] Moreover, the value for the $\mathrm{InH_3}$ complex, **8**, is at significantly lower field than the values for both **9** and **10**, though whether this is unusual or not is difficult to say as there are no other NMR data for $\mathrm{InH_3}$ complexes that can be compared.

It was observed that the isopropyl methine septet resonances were broadened in the room temperature ^{1}H NMR spectra of complexes **9** and **10**. Obviously the spectrum of **8** could not be obtained at room temperature, but at −30 °C the same resonance appeared as a broad unresolved peak. It was, therefore, thought that some fluxional process might be occurring in solution and consequently variable temperature ^{1}H NMR studies were carried out on **8**–**10**. The results were similar for all complexes and those for **10** are reproduced in Fig. 1. It can be seen that the resonances arising from the isopropyl methine and methyl protons, and the ring methyl substituent protons, all broaden as the solution of **10** is cooled. It seems feasible that this results from the rotation of both the isopropyl groups and the $\mathrm{GaH_3}$ unit in the complex. This rotation slows at lower temperatures but it is clear from Fig. 1 that the solution of **10** could not be cooled sufficiently to halt the dynamic process and hence resolve the spectrum. Evidence for the steric viability of the proposed dynamic processes in **8**–**10** comes from their crystal structures (see below). In all, at least one isopropyl group is disordered, having its methyl groups directed either toward or away from the metal centre. Therefore at least two conformations of each molecule are possible in the solid state. Interestingly, the crystal structure of the closely related indium

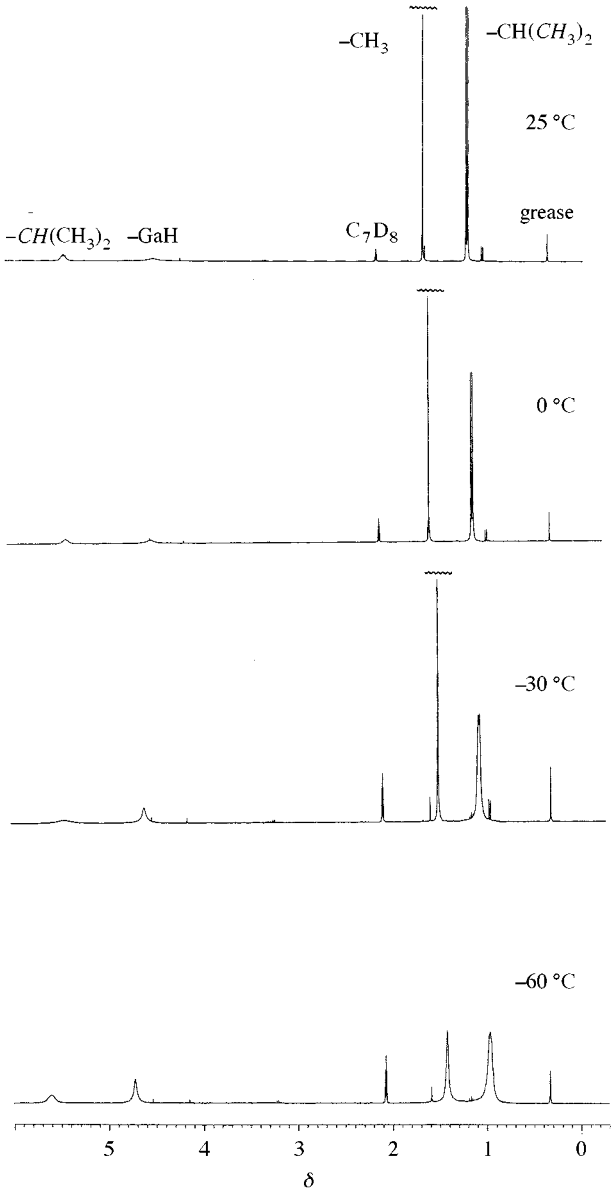


Fig. 1 Variable temperature ^{1}H NMR spectra of complex **10**.

bromide complex, **5**, shows no such disorder and the signals in its ^{1}H NMR spectrum remain sharp and unchanged over a range of temperatures.[15] It seems, therefore, that in the case of **5** the rotation of its isopropyl groups is not sterically viable, perhaps because the bulk of the bromide ligands is preventing this.

The ^{13}C NMR spectra of complexes **8**–**10** are all similar but in the case of **9** and **8** the signal for the metal co-ordinated carbene centre was not observed, doubtless because of the high quadrupole moment of aluminium and indium respectively. Although gallium is also quadrupolar, it is less so than Al or In and hence the carbene resonance of **10** could be seen as a broad peak at δ 173.4 (*cf.* 176.8 for **4**[8]). Interestingly, this lies between the value for the free carbene **I** (δ 205.9)[27] and its fully delocalised imidazolium cation counterpart, $[\mathrm{H\overline{CN(Pr^i)C_2Me_2N}(Pr^i)}]^+$ (δ 131.8),[15] which suggests an intermediate degree of delocalisation within the heterocyclic ligand of **10**. Further evidence for this is to be found in its crystal structure (see below). No peak was observed in the ^{115}In NMR spectrum of **8**, again because of the quadrupolar nature of indium and the lack of spherical symmetry about the metal centre. In contrast, a very broad signal was detected in the ^{27}Al NMR spectrum of **9** at δ 106 (*cf.* 107 for **2**[7]) in the region typical of four-co-ordinate aluminium complexes.

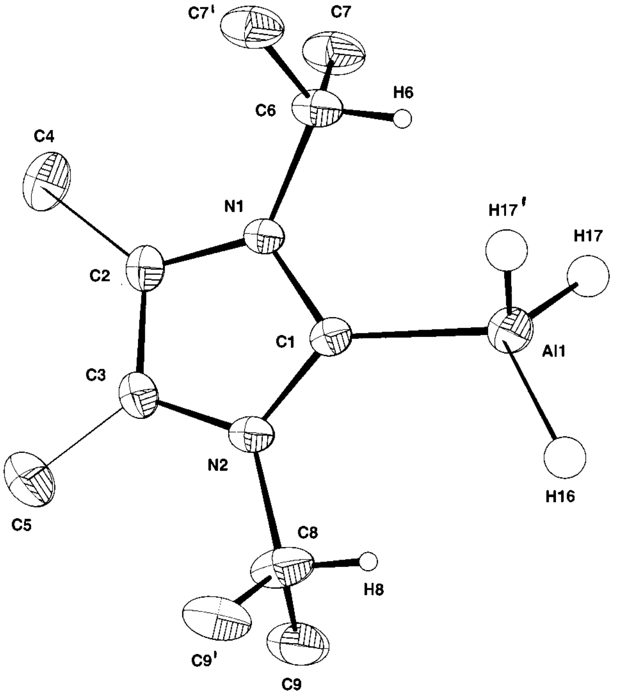


Fig. 2 Molecular structure of compound **9**.

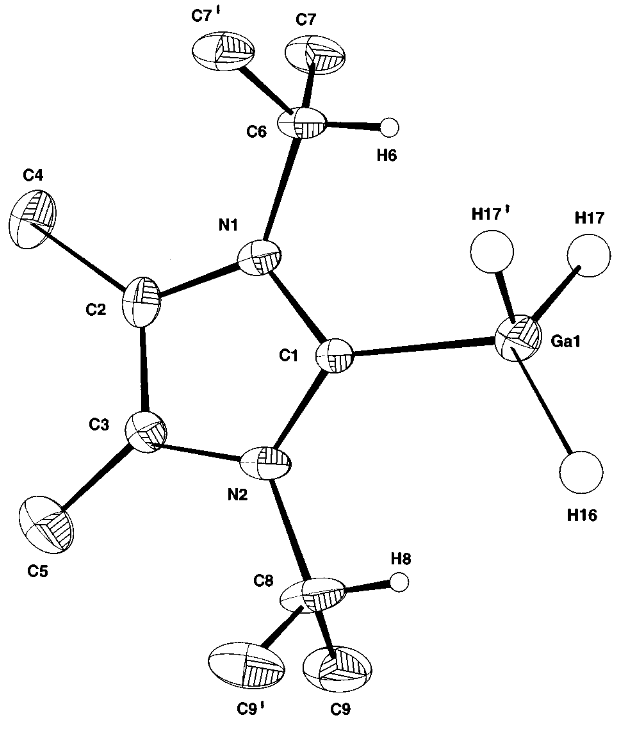


Fig. 3 Molecular structure of compound **10**.

The molecular structures of complexes **9** and **10** are depicted in Figs. 2 and 3 respectively (see also Tables 1–3), while the crystal structure of **8** has been described in a preliminary communication.[16] Compounds **9** and **10** are isomorphous with the asymmetric unit of each containing two crystallographically independent half molecules. One of the complete molecules lies on a mirror plane which contains the carbene heterocycle; the other lies on a two-fold axis which is coincident with the M–C axis and bisects the heterocycle. No intermolecular interactions were observed in either crystal structure. In addition, there are no significant intra-ring geometric differences between both full molecules in either structure and, therefore, only one molecule of each is shown in Figs. 2 and 3. In both these molecules the hydride ligands were located from difference maps and their

Table 1 Selected intramolecular distances (Å) and angles (°) for compound **9** with estimated standard deviations (e.s.d.s) in parentheses

Al(1)–H(16)	1.53(4)	Al(1)–H(17)	1.51(3)
Al(1)–C(1)	2.046(5)	N(1)–C(1)	1.355(5)
N(1)–C(2)	1.385(5)	N(1)–C(6)	1.489(5)
N(2)–C(1)	1.363(5)	N(2)–C(3)	1.372(6)
N(2)–C(8)	1.496(5)	C(2)–C(3)	1.368(6)
C(2)–C(4)	1.489(6)	C(3)–C(5)	1.505(6)
C(1)–Al(1)–H(16)	114(2)	C(1)–Al(1)–H(17)	106(1)
H(16)–Al(1)–H(17)	108(1)	H(17)–Al(1)–H(17′)	114(2)
C(1)–N(1)–C(2)	112.1(3)	C(1)–N(1)–C(6)	121.4(4)
C(2)–N(1)–C(6)	126.5(3)	C(1)–N(2)–C(3)	111.5(3)
C(1)–N(2)–C(8)	124.7(4)	C(3)–N(2)–C(8)	123.8(4)
N(1)–C(1)–N(2)	103.8(4)	N(1)–C(1)–Al(1)	124.7(3)
N(2)–C(1)–Al(1)	131.5(3)	C(3)–C(2)–N(1)	105.4(4)
N(1)–C(2)–C(4)	126.2(4)	C(2)–C(3)–N(2)	107.1(4)
N(2)–C(3)–C(5)	124.8(4)		

Table 2 Selected intramolecular distances (Å) and angles (°) for compound **10** with e.s.d.s in parentheses

Ga(1)–H(17)	1.62(3)	Ga(1)–H(16)	1.58(5)
Ga(1)–C(1)	2.071(5)	N(1)–C(1)	1.333(6)
N(1)–C(2)	1.400(6)	N(1)–C(6)	1.488(6)
N(2)–C(1)	1.368(6)	N(2)–C(3)	1.384(7)
N(2)–C(8)	1.484(7)	C(2)–C(3)	1.359(8)
C(2)–C(4)	1.495(8)	C(3)–C(5)	1.471(9)
C(1)–Ga(1)–H(17)	102(2)	C(1)–Ga(1)–H(16)	112(2)
H(17)–Ga(1)–H(17′)	111(2)	H(16)–Ga(1)–H(17)	114(2)
C(1)–N(1)–C(2)	110.7(4)	C(1)–N(1)–C(6)	121.4(4)
C(2)–N(1)–C(6)	127.9(4)	C(1)–N(2)–C(3)	110.7(4)
C(1)–N(2)–C(8)	124.1(5)	C(3)–N(2)–C(8)	125.2(5)
N(1)–C(1)–N(2)	105.6(4)	N(1)–C(1)–Ga(1)	124.8(4)
N(2)–C(1)–Ga(1)	129.6(4)	C(3)–C(2)–N(1)	106.8(4)
C(3)–C(2)–C(4)	127.7(5)	N(1)–C(2)–C(4)	125.5(5)
C(2)–C(3)–N(2)	106.3(5)	C(2)–C(3)–C(5)	128.7(6)
N(2)–C(3)–C(5)	125.0(6)		

Table 3 Crystal data for $[MH_3\{\overline{CN(Pr^i)C_2Me_2N}(Pr^i)\}]$, M = Al **9** or Ga **10***

	9	**10**
Chemical formula	$C_{11}H_{23}AlN_2$	$C_{11}H_{23}GaN_2$
M	210.29	253.03
a/Å	9.492(9)	9.4140(9)
b/Å	15.051(11)	15.0910(9)
c/Å	19.059(7)	19.0760(9)
U/Å^3	2723(3)	2710.1(3)
D_c/g cm^{-3}	1.026	1.240
μ(Mo-Kα)/cm^{-1}	1.20	20.01
DIFABS absorption correction T_{max}, T_{min}	1.11, 0.88	1.22, 0.82
F(000)	928	1072
Reflections collected	9041	10171
No. unique reflections	2192	2245
Crystal size/mm	0.25 × 0.20 × 0.25	0.40 × 0.25 × 0.20
θ range/°	2.14–25.06	2.14–25.14
R (all data)	0.1065	0.0828
$[I > 2\sigma(I)]$	0.0553	0.0463
R′ (all data)	0.1661	0.1140
$[I > 2\sigma(I)]$	0.1496	0.1070

* Details in common: orthorhombic, space group *Pbcm*; $Z = 8$; T 150(2) K; $R = \Sigma(\Delta F)/\Sigma(F_o)$; $R' = [\Sigma w(\Delta F^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ where $P = [\max(F_o^2) + 2(F_c^2)]/3$ and $a = 0.090$ for complex **9** and 0.049 for **10**.

positional parameters refined. It was found that in each of these molecules the methyl groups attached to C(8) are disordered over two sites, *viz.* C(9) [**9** (50), **10** (65%)] pointing away from the metal centre and C(9a) [**9** (50), **10** (35%)] pointing toward the metal centre [only one disordered set, C(9), is depicted in Figs. 2 and 3]. A similar disorder was observed in the structure of **8**.[16] It is noteworthy that while the reported crystal structure of **8** is not isomorphous to those of **9** and **10**, a previous, poor quality structural determination of **8** revealed that it can crystallise in the isomorphic form.[28]

The metal centres in complexes **9** and **10** have distorted tetrahedral environments with the Al–H and Ga–H bond lengths lying in the normal range.[1] The Al–C distances in **9** [*e.g.* Al(1)–C(1) 2.046(5) Å] are close to that in **2** [2.034(3) Å][7] but longer than the terminal Al–C distances in $[(AlPh_3)_2]$ (1.958 Å).[29] Similarly, the Ga–C distances in **10** [*e.g.* Ga(1)–C(1) 2.071(5) Å] are shorter than the Ga–C (carbene) bond length in the closely related complex, **4** [2.13(2) Å],[8] but longer than the Ga–C distances in $GaPh_3$, 1.961 Å (average).[30] The geometries of the co-ordinated carbene heterocycles in **9** and **10** are close to each other and, likewise, close to those in all other complexes between a Group 13 metal fragment and this carbene, **3**–**8**. These geometries reveal that, upon co-ordination, the carbene ligand exhibits a degree of delocalisation somewhere between that of the free carbene, **I**, and the fully delocalised imidazolium cation, $[H\overline{CN(Pr^i)C_2Me_2N}(Pr^i)]^+$, as predicted from NMR studies (see above). The N–C–N angles in **9** and **10** [*e.g.* 103.8(4) and 105.6(4)° respectively] exemplify this point as they lie between the normal values for free imidazol-2-ylidene carbenes (*ca.* 102°) and imidazolium cations (*ca.* 108°).[7]

Conclusion

A series of carbene–Group 13 trihydride complexes, **8**–**10**, have been reported. Two distinct synthetic routes to these complexes have been devised. It has been shown that the highly nucleophilic carbene ligand utilised in this study has imparted greater thermal stability to these complexes than is normally seen for their Lewis base adduct analogues. In solution **8**–**10** all display fluxional behaviour which has been studied by variable temperature ^1H NMR. The crystal structures of **8**–**10** have been determined and are consistent with partial delocalisation within the co-ordinated carbene heterocycles of each complex. We are currently exploring the further chemistry of these complexes.

Experimental

General remarks

All manipulations were carried out using standard Schlenk and glove-box techniques under an atmosphere of high purity argon or dinitrogen. The solvents tetrahydrofuran (thf), diethyl ether and hexane were distilled over Na/K alloy then freeze–thaw degassed prior to use. The ^1H, ^{13}C and ^{27}Al NMR spectra were recorded on either a Bruker WM-250 or AM 400 spectrometer in $C_6D_5CD_3$ and were referenced to the residual ^1H resonances of the solvent used (^1H NMR), the ^{13}C resonance of the deuteriated solvent (^{13}C NMR) or to an external 1 M $[Al(H_2O)_6]^{3+}$ solution (^{27}Al NMR) respectively. Mass spectra were recorded using a VG-autospec/Cs$^+$ ions/25 kV/Nujol matrix (FAB) instrument and conditions. A Perkin-Elmer Elan 5000 instrument was used to carry out the ICP MS analysis. The powder diffraction study was carried out using an Enraf-Nonius FR571 X-ray generator and an INEL PDS120 detector at the EPSRC Crystallography Service, University of Wales, Cardiff. Microanalyses were obtained from the University of Wales, Cardiff Microanalytical Service or the Warwick Analytical Service. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. The starting materials, $:\overline{CN(Pr^i)C_2Me_2N}(Pr^i)$,[27] $[AlH_3(NMe_3)]$[17] and $[GaH_3(NMe_3)]$[18] were prepared by published procedures, $LiInH_4$ by a variation on the published procedure.[19] All other reagents were used as received.

Syntheses

$[InH_3(NMe_3)]$. The compound $NMe_3{\cdot}HCl$ (0.27 g, 2.83

mmol) was added as a powder to a solution of $\mathrm{LiInH_4}$ (2.83 mmol) in $\mathrm{Et_2O}$ (40 $\mathrm{cm^3}$) at −78 °C. The resulting suspension was warmed to −30 °C and stirred until gas evolution had ceased (*ca.* 2 h) to yield a clear colourless solution of $[\mathrm{InH_3(NMe_3)}]$. The solution could be stored at −30 °C for 24 h without visible decomposition.

$[\mathrm{InH_3}\{\overline{\mathrm{CN(Pr^i)C_2Me_2N}}\mathrm{(Pr^i)}\}]$ 8. (i) The compound $:\overline{\mathrm{CN(Pr^i)C_2Me_2N}}\mathrm{(Pr^i)}$ (0.51 g, 2.83 mmol) in thf (20 $\mathrm{cm^3}$) was added to a solution of $[\mathrm{InH_3(NMe_3)}]$ (2.83 mmol) in $\mathrm{Et_2O}$ (40 $\mathrm{cm^3}$) at −78 °C over 5 min. The resulting solution was warmed to −30 °C and stirred for 2 h whereupon volatiles were removed *in vacuo* to yield a white oily solid. This was washed with cold hexane (20 $\mathrm{cm^3}$) and extracted with cold (−25 °C) $\mathrm{Et_2O}$ (25 $\mathrm{cm^3}$), filtered and the filtrate placed at −35 °C overnight to yield complex **8** as colourless crystals (0.35 g, 42%), decomp. −5 °C.

(ii) The compound $:\overline{\mathrm{CN(Pr^i)C_2Me_2N}}\mathrm{(Pr^i)}$ (0.49 g, 2.7 mmol) in thf (20 $\mathrm{cm^3}$) was added to a solution of $\mathrm{LiInH_4}$ (2.6 mmol) in $\mathrm{Et_2O}$ (30 $\mathrm{cm^3}$) at −78 °C over 5 min. The resulting suspension was warmed to −30 °C and stirred for 5 h whereupon volatiles were removed *in vacuo* to yield a white solid. This was washed with cold hexane (20 $\mathrm{cm^3}$) and extracted with cold (−25 °C) $\mathrm{Et_2O}$ (25 $\mathrm{cm^3}$), filtered and the filtrate placed at −35 °C overnight to yield complex **8** as colourless crystals (0.29 g, 38%), decomp. −5 °C. ^{1}H NMR (250 MHz, $\mathrm{C_6D_5CD_3}$, 243 K): δ 1.04 [d, 12 H, $\mathrm{CH(C}H_3)_2$, $^3J_{\mathrm{HH}} = 6$ Hz], 1.54 (s, 6 H, Me), 5.05 [br, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$] and 5.58 (br s, 3 H, In–H). ^{13}C NMR (100.6 MHz, $\mathrm{C_6D_5CD_3}$, 243 K): δ 10.0 (Me), 20.7 [$\mathrm{CH(}C\mathrm{H_3)_2}$], 46.3 [$C\mathrm{H(CH_3)_2}$] and 121.0 (C=C). IR: 1640s (br) $\mathrm{cm^{-1}}$ (In–H str.).

$[\mathrm{AlH_3}\{\overline{\mathrm{CN(Pr^i)C_2Me_2N}}\mathrm{(Pr^i)}\}]$ 9. (i) The compound $:\overline{\mathrm{CN(Pr^i)C_2Me_2N}}\mathrm{(Pr^i)}$ (0.81 g, 4.5 mmol) in $\mathrm{Et_2O}$ (20 $\mathrm{cm^3}$) was added to a solution of $[\mathrm{AlH_3(NMe_3)}]$ (0.37 g, 4.1 mmol) in $\mathrm{Et_2O}$ (20 $\mathrm{cm^3}$) at 0 °C over 5 min. The resulting solution was warmed to room temperature and stirred for 2 h whereupon volatiles were removed *in vacuo* to yield a white solid. This was washed with hexane (20 $\mathrm{cm^3}$) and extracted with $\mathrm{Et_2O}$ (40 $\mathrm{cm^3}$), filtered and the filtrate placed at −35 °C overnight to yield complex **9** as colourless crystals (0.55 g, 64%), mp 160 °C.

(ii) The compound $:\overline{\mathrm{CN(Pr^i)C_2Me_2N}}\mathrm{(Pr^i)}$ (1.10 g, 6.1 mmol) in $\mathrm{Et_2O}$ (20 $\mathrm{cm^3}$) was added to a solution of $\mathrm{LiAlH_4}$ (0.20 g, 5.3 mmol) in $\mathrm{Et_2O}$ (30 $\mathrm{cm^3}$) at 0 °C over 5 min. The resulting suspension was warmed to room temperature and stirred for 5 h whereupon volatiles were removed *in vacuo* to yield a white solid. This was washed with hexane (20 $\mathrm{cm^3}$) and extracted with $\mathrm{Et_2O}$ (40 $\mathrm{cm^3}$), filtered and the filtrate placed at −35 °C overnight to yield complex **9** as colourless crystals (0.33 g, 30%), mp 160 °C. ^{1}H NMR (250 MHz, $\mathrm{C_6D_5CD_3}$, 298 K): δ 1.22 [d, 12 H, $\mathrm{CH(C}H_3)_2$, $^3J_{\mathrm{HH}}$ 6], 1.65 (s, 6 H, Me), 4.63 (br s, 3 H, Al–H) and 5.40 [spt, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$, $^3J_{\mathrm{HH}}$ 6 Hz]. ^{13}C-{^{1}H} NMR (100.6 MHz, $\mathrm{C_6D_5CD_3}$, 298 K): δ 9.5 (Me), 21.3 [$\mathrm{CH(}C\mathrm{H_3)_2}$], 51.9 [$C\mathrm{H(CH_3)_2}$] and 125.4 (C=C). ^{27}Al NMR (65 MHz, $\mathrm{C_6D_5CD_3}$, 298 K): δ 106 (width at half peak height 1170 Hz). MS (FAB, Nujol matrix): *m*/*z* 181 ($\mathrm{MH^+} - \mathrm{AlH_3}$, 100%). IR 1730s (br) $\mathrm{cm^{-1}}$ (Al–H str.) (Found: C, 61.79; H, 10.96; N, 13.39. Calc. for $\mathrm{C_{11}H_{23}AlN_2}$: C, 62.82; H, 11.02; N, 13.32%).

$[\mathrm{GaH_3}\{\overline{\mathrm{CN(Pr^i)C_2Me_2N}}\mathrm{(Pr^i)}\}]$ 10. The compound $:\overline{\mathrm{CN(Pr^i)C_2Me_2N}}\mathrm{(Pr^i)}$ (0.55 g, 3.1 mmol) in $\mathrm{Et_2O}$ (20 $\mathrm{cm^3}$) was added to a solution of $[\mathrm{GaH_3(NMe_3)}]$ (0.45 g, 3.4 mmol) in $\mathrm{Et_2O}$ (20 $\mathrm{cm^3}$) at −78 °C over 5 min. The resulting solution was warmed to room temperature and stirred for 3 h whereupon volatiles were removed *in vacuo* to yield a white solid. This was extracted with $\mathrm{Et_2O}$ (40 $\mathrm{cm^3}$), filtered and the filtrate placed at −35 °C overnight to yield complex **10** as colourless crystals (0.31 g, 40%), mp 180 °C (decomp.). ^{1}H NMR (250 MHz, $\mathrm{C_6D_5CD_3}$, 298 K): δ 1.16 [d, 12 H, $\mathrm{CH(C}H_3)_2$, $^3J_{\mathrm{HH}}$ 7], 1.60 (s, 6 H, Me), 4.48 (br s, 3 H, Ga–H) and 5.44 [spt, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$, $^3J_{\mathrm{HH}}$ 7 Hz]. ^{13}C-{^{1}H} NMR (100.6 MHz, $\mathrm{C_6D_5CD_3}$, 298 K): δ 10.2 (Me), 21.7 [$\mathrm{CH(}C\mathrm{H_3)_2}$], 52.7 [$C\mathrm{H(CH_3)_2}$], 125.9 (C=C) and 173.4 (NCN). MS (FAB, Nujol matrix): *m*/*z* 181 ($\mathrm{MH^+} - \mathrm{GaH_3}$, 100%). IR 1775s (br) $\mathrm{cm^{-1}}$ (Ga–H str.) (Found: C, 52.11; H, 9.88; N, 11.36. Calc. for $\mathrm{C_{11}H_{23}GaN_2}$: C, 52.21; H, 9.16; N, 11.07%).

Structure determinations

Crystals of complexes **9** and **10** were grown from ether solutions of the relevant compound and mounted in silicone oil. Intensity data were measured on a FAST[31] area detector diffractometer using Mo-Kα radiation (λ 0.71069 Å). The structure of **9** was solved by direct methods, heavy atom methods for **10** (SHELXS 86[32]). Refinement of both structures was by full matrix least squares on F^2 using all unique data (SHELXL 93[33]). Neutral-atom complex scattering factors were employed.[34] Empirical absorption corrections were carried out by the DIFABS method.[35] Crystal data, details of data collections and refinement are given in Table 3. Anisotropic thermal parameters were refined for all non-hydrogen atoms in both structures. The hydrogen atoms were included in calculated positions (riding model) with the exception of H(16) and H(17) which were located from difference maps and their positional parameters refined. The hydride ligands in the molecules with two-fold rotational symmetry could not be located, presumably because they are necessarily disordered. This fact also explains the higher thermal parameters of the metal atom of this molecule in both structures. In addition it was found that the methyl groups attached to C(8) were disordered over two sites, *viz.* C(9) [**9** (50), **10** (65%)] and C(9a) [**9** (50), **10** (35%)]. The disorder was successfully modelled.

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