N-heterocyclic carbene coordinated gallanes and chlorogallanes

Marcus L. Cole [a],*, Samantha K. Furfari [a], Marc Kloth [b]

[a] School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia
[b] School of Chemistry and Physics, University of Adelaide, Adelaide, South Australia 5005, Australia

ABSTRACT

The preparation of the *N*-heterocyclic carbene coordinated gallium complexes [GaH$_3$(IXy)] (**1**), [GaH$_3$(IDipp)] (**2**), [GaClH$_2$(IMes)] (**3**) and [GaCl$_2$H(IMes)] (**4**), where IXy = 1,3-bis(2,6-dimethylphenyl)imidazol-2-ylidene, IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene and IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, are reported. All four complexes have been characterised by ^{1}H, ^{13}C NMR and IR spectroscopy and, for complexes **2**, **3** and **4**, single crystal X-ray structure determination. These compounds represent some of the most thermally stable molecular gallium hydrides known, with **4** being the most thermally stable gallium hydride reported (dec. 274 °C). These remarkable thermal stabilities translate to significant aerobic stability such that all four compounds may be handled in dry air without significant decomposition. Compounds **2**, **3** and **4** exist as distorted tetrahedra in the solid state with gallium to carbene C-donor bonds that shorten with increasing Lewis acidity of the gallium centre. Compound **2** co-crystallizes with 1 equiv. of 2,6-diisopropylphenylaniline and exhibits several weak intermolecular bonding interactions in the solid-state.

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1. Introduction

The synthetic and materials utility of group 13 hydrides is well established [1] and, despite the increased frailty of the gallium to hydrogen bond relative to those of boron and aluminium, gallohydrides have found broad application [2]. We are interested in the development of methods for the stabilisation of heavy group 13 hydride bonds [3], such as gallo- and indohydrides [4], such that these species may be studied and their synthetic and materials applications potential explored. Further to simply coordinating strong Lewis bases to group 13 trihydrides, one means of accomplishing this goal is to substitute one or two hydrides about the group 13 element with halides to inductively strengthen the remaining M–H bond(s) by halide σ-electron withdrawal [5]. This strategy has been very successful for aluminohydrides [3a,6].

Amongst Lewis base donors, bulky 1,3-bis(aryl)imidazol-2-ylidene *N*-heterocyclic carbenes (NHCs) (Fig. 1) are without peer for the stabilisation of group 13 hydrides [1c,4d,7]. For instance, the NHC IMes; 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, generates the most stable complexes of alane (AlH$_3$) [7a], gallane (GaH$_3$) [4d] and indane (InH$_3$) [4d] reported to date. This stability is borne out of the donor characteristics of the NHC [8], which satisfy the trihydride electronically, and the steric protection afforded by the mesityl (2,4,6-trimethylphenyl) nitrogen substituents. These spatially shield the MH$_3$ unit and impede M–H–M interac-

tions that are believed to provide a low energy path to decomposition by reductive dehydrogenation [9], a mode of decomposition that becomes increasingly favourable as group 13 is descended [9]. The significant temperature stability of the IMes supported trihydride complexes depicted in Fig. 1 translates to considerable air stability. For instance, all three compounds may be manipulated in air for brief periods without significant decomposition.

Considering the stability of [GaH$_3$(IMes)] (dec. 214 °C) [4d] over-and-above simple group 15 coordinated complexes like [GaH$_3$-(Quin)] (dec. 100 °C) [10a] or [GaH$_3$(PCy)$_3$] (dec. 130 °C) [10b], it is somewhat surprising that only three NHC coordinated gallanes ([GaH$_3$(NHC)]) have been reported; the aforementioned [GaH$_3$(IMes)] [4d] [GaH$_3$(I^{i}PrMe)] (I^{i}PrMe = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) (dec. 180 °C) [7b] and [GaH$_2$I(IMes)] (dec. 177–181 °C) [11]. It is noteworthy that the decomposition temperature of [GaH$_2$I(IMes)] [11], which is some 40 °C below that of its gallane congener, is far lower than that expected on the basis of NHC coordinated haloalanes, e.g. [AlCl$_2$H(IMes)] dec. 320 °C [3a] vs. [AlH$_3$(IMes)] [7a] dec. 256 °C [12]. Indeed, one would expect the decomposition temperature of this complex to be greater than that of [GaH$_3$(IMes)] [4d], perhaps suggesting a different mode of decomposition for this species [5].

Lewis base adducts of chlorogallanes, in-particular dichlorogallanes, have been studied in some depth by Schmidbaur [13], Raston [14] and Gladfelter [15] and there are several methods for their high yield preparation (Scheme 1). These include (i) the stoichiometric reaction of gallium trichloride with organosilanes [13] and (ii) the stoichiometric redistribution of gallium trihydrides and

* Corresponding author. Tel.: +61 2 93854678; fax: +61 2 93856141.
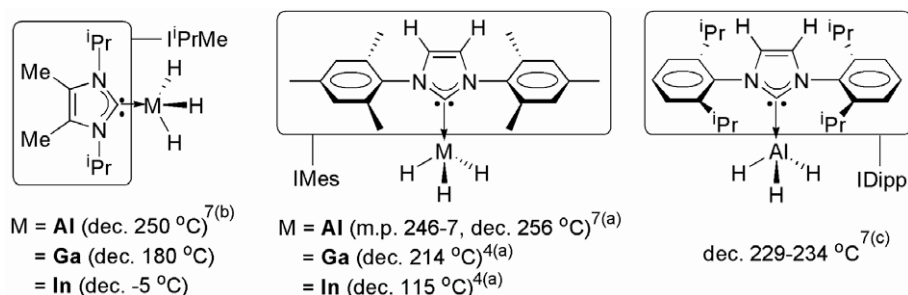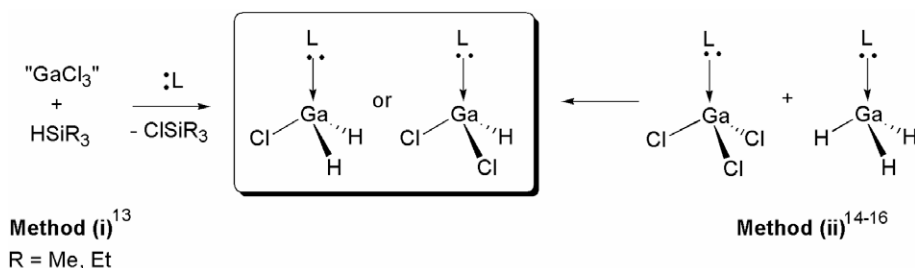*E-mail address:* m.cole@unsw.edu.au (M.L. Cole).

Fig. 1. Reported NHC complexes of group 13 trihydrides and their solid-state decomposition temperatures.

Scheme 1. High yielding methods for the preparation of mono- and dichlorogallane complexes.

trichlorides [14–16]. Herein we report the application of method (ii) to the preparation of the monochloro and dichlorogallane complexes [GaClH$_2$(IMes)] (**3**) and [GaCl$_2$H(IMes)] (**4**), which complete the series [GaCl$_n$H$_{3-n}$(IMes)] (n = 0–3) in which n = 0 [4d] and 3 [17] are known, and extend the family of gallane (GaH$_3$) NHC complexes to [GaH$_3$(IXy)] (**1**) and [GaH$_3$(IDipp)] (**2**) (IXy = 1, 3-bis(2,6-dimethylphenyl)imidazol-2-ylidene, IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene). We also report the spectroscopic characterisation of [GaClH$_2$(IXy)] (**3^{Xy}**) formed as a co-product during some preparations of **1**.

2. Results and discussion

2.1. Synthesis and spectroscopy

2.1.1. NHC complexes of gallium trihydride

The treatment of ethereal solutions of *in situ* prepared lithium tetrahydridogallate with single equivalents of IXy or IDipp [18] affords the NHC complexes [GaH$_3$(IXy)] (**1**) and [GaH$_3$(IDipp)] (**2**) by lithium hydride substitution (Scheme 2), as evidenced by the infrared spectra of both crude products after removal of reaction volatiles under reduced pressure. These spectra (Table 1) exhibit strong infrared Ga–H stretching absorptions at 1789 and 1801 cm^{-1}, respectively, which may be compared to the analogous absorptions of [GaH$_3$(IMes)] (1780 cm^{-1}) [4d] and [GaH$_3$(I^{i}PrMe)] (1775 cm^{-1})

[7b]. These data indicate that the IDipp of **2** does not coordinate to gallane as strongly as the less bulky NHCs of **1** and the aforementioned literature compounds (Table 1). This most likely results from the increase in bulk at the *N*-substituents of IDipp vs. IXy/IMes/I^{i}PrMe. Curiously, the opposing trend in metal-hydride stretching frequencies is observed in the Al–H stretching absorptions of the aluminium counterparts of **2** and [AlH$_3$(IMes)] (v 1729 and 1743 cm^{-1}, respectively) [7a,7c].

During some preparations of [GaH$_3$(IXy)] (**1**) an additional strong Ga–H absorption was observed at 1855 cm^{-1}. Based on our studies of chloroalanes supported by IMes [3a,6], this absorption is likely to be that of the monochlorogallane [GaClH$_2$(IXy)] (**3^{Xy}**), resulting from incomplete conversion of gallium trichloride to [LiGaH$_4$], i.e. formation of [LiGaClH$_4$], during *in situ* preparation of this precursor by reaction of gallium trichloride with lithium hydride at low temperature (*cf* dec. [LiGaH$_4$] *ca* 0 °C). A similar unintended preparation of [LiGaClH$_3$], and its subsequent reactivity, has been reported by Himmel and co-workers during their studies of 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidate (hppH) yielding the chlorogallane dimer [{GaClH(hpp)}$_2$] [19]. The shift of Ga–H stretching absorption to higher wavenumber for **3^{Xy}** relative to that of **1** is consistent with inductive strengthening of the gallium to hydrogen bond by halide electron withdrawal [5]. Pure samples of **1** were acquired by extending the preparation time used to prepare [LiGaH$_4$], prior to reaction with the NHC IXy.
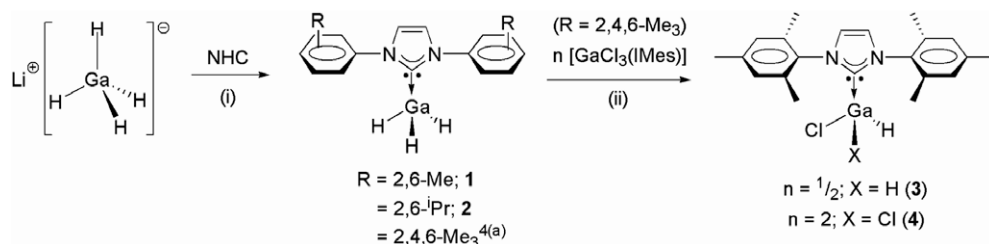
Scheme 2. The preparations of NHC coordinated gallane and chlorogallanes reported in this article. *Reaction conditions*: (i) NHC = IXy (**1**), IDipp (**2**), or IMes (see (ii)), Et$_2$O, −40 °C to RT overnight, − LiH; (ii) toluene, 50 °C, 6 h (**3**) or 14 h (**4**).

Table 1
Selected solid-state physical and spectroscopic data for complexes reported in this article and relevant literature compounds

Compound	dec. (°C)[a]	IR v M–H (cm^{-1})[b]	Ga–H ^{1}H NMR (ppm)[c]	C$_2H_2$ ^{1}H NMR (ppm)
[GaH$_3$(I^{i}PrMe)] [7b]	180	1775	4.48	–
[GaH$_3$(IXy)] (**1**)	186	1789	3.90	6.16
[GaH$_3$(IDipp)] (**2**)	166	1801	3.81	6.54
[GaH$_3$(IMes)] [4d]	214	1780	3.96	6.16
[GaClH$_2$(IMes)] (**3**)	263	1870	4.72	5.95
[GaClH$_2$(IXy)] (**3^{Xy}**)	–	1855	–	6.08
[GaCl$_2$H(IMes)] (**4**)	274	1917	–	5.84
[GaCl$_3$(IMes)][17]	–	–	–	5.78 (in CDCl$_3$)
[GaH$_2$I(IMes)][11]	177–181	1863	4.12	5.89

[a] Melting points and decomposition temperatures conducted using capillary sealed samples under UHP argon
[b] All IR spectroscopy conducted as a Nujol mull with sodium chloride plates.
[c] ^{1}H NMR spectroscopy conducted in C$_6$D$_6$ unless otherwise stated.

The ^{1}H NMR spectra (C$_6$D$_6$) of **1** and **2**, the former with monochlorogallane impurity **3^{Xy}**, display the expected resonances, including distinct resonances for the diastereotopic isopropyl methyls of coordinated IDipp [18] in [GaH$_3$(IDipp)] (**2**) and the GaH$_3$ moieties (Table 1) of **1** and **2** (**1** 3.90 ppm, **2** 3.81 ppm, no hydride resonance observed for **3^{Xy}**), cf [GaH$_3$(IMes)] ^{1}H NMR, C$_6$D$_6$, GaH_3 br s 3.96 ppm [4d]. It is interesting to note that the 4,5-C$_2H_2$ ^{1}H NMR singlet resonances of [GaH$_3$(IXy)] (**1**) (6.16 ppm) and [GaClH$_2$(IXy)] (**3^{Xy}**) (6.08 ppm) may be used to estimate the proportions of each complex in preparations of **1**, with all remaining "IXy" resonances of **3^{Xy}** coincident with those of **1**. The upfield shift of the 4,5-C$_2H_2$ singlet resonance of **3^{Xy}** relative to that of **1** is consistent with the trend observed for the series of aluminium complexes [AlCl$_n$H$_{3-n}$(IMes)], n = 0–3 [3a,6,7a], in which the upfield shift of the 4,5-C$_2H_2$ singlet increases with chloride content; n = 0 6.01 ppm, n = 1 5.93 ppm, n = 2 5.86 ppm, n = 3 5.78 ppm. Several solvent systems were used in attempts to separate **1** from **3^{Xy}** by extraction or recrystallisation, however all efforts afforded samples characterising as per crude reaction mixtures for **1/3^{Xy}**.

The solid-state decomposition points of **1** and **2**, the former without a **3^{Xy}** impurity, were recorded using capillary sealed samples under ultra high purity argon (**1** dec. 186, **2** dec. 166 °C). Compound **1** is more thermally robust than **2**, but neither compound exceeds the thermal stability of [GaH$_3$(IMes)] (214 °C) [4d] (Table 1). The greater thermal stability of [GaH$_3$(IMes)] and **1** relative to **2** may be attributed to the lessened proximity of gallane to the methyls of these species relative to the isopropyl methyls of **2**. Thus, while it is true that the Dipp group may be used to kinetically and sterically stabilise transient or frail chemical functions [4e] the 'reach' of the alkyl groups of **2** most likely accelerates decomposition, perhaps by C–H activation, at high temperature. A rationale for the contrasting decomposition temperatures of **1** and [GaH$_3$(IMes)] [4d] is less obvious (Table 1), although it could be that the spatial imposition of the 4-methyls of the latter serve to distance the gallane units of [GaH$_3$(IMes)] in the solid-state, thereby decreasing the likelihood of decomposition by Ga–H–Ga bridging at high temperature. Both **1** and **2** may be handled in dry air (e.g. a dessicator) without any decomposition. However, as per aluminium counterparts [6], the exposure of solutions of **1** or **2** to air results in rapid decomposition to afford 2-dihydroimidazoles [4d,20].

2.1.2. IMes complexes of mono- and dichlorogallane

The preparation of Lewis base complexes of mono- and dichlorogallane may be accomplished by the redistribution of stoichiometric quantities of gallium trichloride and gallium trihydride complexes (Fig. 1). This method was introduced by Greenwood in 1965 [16] and utilised by the groups of Raston and Gladfelter to prepare tricyclohexylphosphine [14] and mono/bis(quinuclidine) adducts of mono- and dichlorogallane [15a], respectively. One benefit of this method relative to the silane route of Schmid-

baur and co-workers (cf method (i) Fig. 1) [13] is the absence of co-products.

Toluene solutions of [GaH$_3$(IMes)] [4d] and [GaCl$_3$(IMes)] [17] were combined in either a 2:1 (**3**) or 1:2 (**4**) stoichiometric ratio at room temperature, and stirred at 50 °C for 6 (**3**) or 14 (**4**) hours (Scheme 2), followed by filtration and gradual cooling to ambient temperature. Over this time colourless crystals of **3** and **4** deposited in moderate yield (33% and 37%, respectively). These were isolated by decanting of the mother liquor and characterised by IR, ^{1}H and ^{13}C NMR spectroscopies (Table 1). The IR Ga–H stretch absorptions of both compounds are consistent with gradual strengthening of the Ga–H bond(s) of **3** and **4** relative to [GaH$_3$(IMes)] [4d]. For instance, there is a +90 cm^{-1} shift for monochlorogallane **3** relative to its trihydride counterpart (cf **3^{Xy}**; +66 cm^{-1} viz **1**), and a 47 cm^{-1} increase in the Ga–H infrared stretching absorption of dichlorogallane **4** relative to that of **3**. These shifts are comparable to those observed for mono-, dichloro- and bromoalanes, wherein mean shifts of +55 and +45 cm^{-1} are observed upon substitution of hydrides with a chloride or bromide about tertiary amine stabilised alanes (AlH$_3$) [6], and a +134 cm^{-1} shift is observed on dihalogenation (Cl or Br) of [AlH$_3$(IMes)] [3a,6].

Close comparison of the ^{1}H NMR data of **3** and **4** with that of the gallane [4d] and gallium trichloride [17], indicates a shift in 4,5-C$_2H_2$ resonance for the complexes [GaCl$_n$H$_{3-n}$(IMes)] (n = 0–3) consistent with that described for aluminium [3a,6,7a]. This comprises an upfield shift with increasing chloride content (Table 1) and is consistent with the increased Lewis acidity of the gallium centre due to chloride electron withdrawal [5].

The solid-state decomposition temperatures of **3** and **4**, acquired as per **1** and **2**, are significantly higher than those of the trihydride [GaH$_3$(IMes)] [4d] (dec. 214, **3** dec. 263, **4** dec. 274 °C) making **3** and **4** the most stable molecular gallium hydrides reported at this time. Like complexes **1** and **2**, both compounds may be handled in dry air, e.g. a dessicator, without decomposition.

2.2. Crystallographic studies

2.2.1. [GaH$_3$(IDipp)]·NH$_2$Dipp

Recrystallisation of reaction mixtures for **2** lead to the deposition of microcrystalline powders unsuitable for single crystal X-ray structure determination. Small colourless blocks were isolated on one occasion and their structure determined by X-ray methods (Fig. 2). Table 2 contains selected bonding parameters for the complexes characterised by X-ray diffraction methods herein as-well-as relevant literature compounds. Table 3 provides a summary of crystallographic data for the compounds reported in this article.

Compound **2** (Fig. 2) is the second structurally authenticated NHC complex of gallium trihydride and may be compared to its I^{i}PrMe counterpart [7b]. During the refinement of X-ray diffraction data for **2** it was noted that [GaH$_3$(IDipp)] (**2**) had co-crystallised
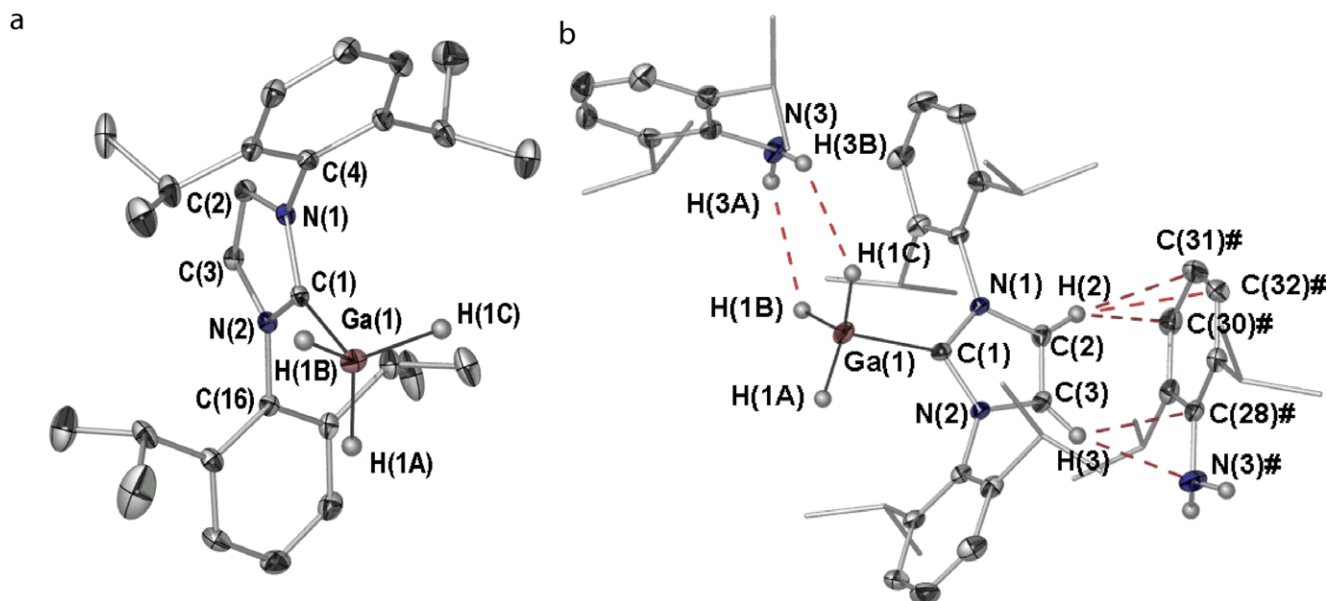
Fig. 2. Molecular structure of [GaH₃(IDipp)]·NH₂Dipp (**2**·NH₂Dipp): (a) **2** without NH₂Dipp, 50% thermal ellipsoids, all hydrogen atoms except hydrides H(1A), H(1B) and H(1C) omitted for clarity; (b) **2**·NH₂Dipp, 50% thermal ellipsoids, all hydrogens except those involved in intermolecular interactions omitted for clarity. Isopropyl groups depicted as wire frames. Symmetry transformation used to generate '#' atoms: ½ + x, ½ − y, ½ + z. Selected contact distances for intermolecular interactions (Å): H(1B)···H(3A) 2.540(32), H(1C)···H(3B) 2.497(32), H(2)···C(30)# 2.84, H(2)···C(31)# 2.76, H(2)···C(32)# 2.75, H(3)···C(28)# 2.70, H(3)···N(3)# 2.59 (see Table 2 for further bonding parameters).

Table 2
Selected bond lengths (Å) and angles (°) for complexes reported in this article and relevant literature compounds.

Compound	Ga–C (Å)	Ga–H (Å)	H–Ga–H/Cl–Ga–Cl (°)	C–Ga–H (°)	C–Ga–Cl/I (°)	N–C–N (°)
[GaH₃(IʲPrMe)] [7b]	2.071(5)	1.58(5), 1.62(3)	114(2), 111(2)	112(2), 102(2)	–	105.6(4)
[GaH₃(IDipp)] (**2**)	2.0545(14)	1.46(2), 1.47(2), 1.54(2)	115.8(11), 112.7(12),111.6(12)	104.8(9), 104.5(8), 106.3(8)	–	104.15(12)
[GaClH₂(IMes)]ᵃ (**3**)	2.030(3)	1.85(3), 1.51(4)	117.6(19)	107.2(10), 107.0(16)	105.07(10)	104.2(3)
[GaCl₂H(IMes)]ᵃ (**4**)	2.005(6)	2.00(5)	110.99(10)	112.3(13)	106.24(18), 108.3(18)	105.6(5)
[GaCl₃(IMes)] [17]	1.954(4)	–	107.86(4)	–	113.26(8)	102.9(3)
[GaH₂I(IMes)] [11]	2.022(4)	1.52(4),1.59(5)	120(2)	111.4(18), 109.5(19)	105.23(12)	104.4(4)

ᵃ Two unique molecules are present in the asymmetric unit. Only bonding parameters for the lowest numbered unit reported here.

Table 3
Summary of crystallographic data for compounds characterised by single crystal X-ray structure determination.

	2·NH₂Dipp	**3**	**4**ᵃ
Mol. formula	C₃₉H₅₈GaN₃	C₄₂H₅₂Cl₂Ga₂N₄	C₄₂H₅₀Cl₄Ga₂N₄
Mol. weight	638.60	823.22	892.10
Space group	P2₁/n	Pca2₁	Pca2₁
a (Å)	12.8389(4)	16.142(3)	17.1580(6)
b (Å)	18.1264(6)	14.413(3)	16.4134(6)
c (Å)	15.9583(5)	17.646(4)	15.6186(5)
β (°)	93.761(2)	90	90
V (Å³)	3705.9(2)	4105.4(14)	4398.5(3)
Z	4	4	4
D_calc, g cm⁻³	1.145	1.332	1.347
μ (mm⁻¹)	0.771	1.476	1.501
Reflections collected	74 716	49 982	46 495
Unique reflections	10 747	10 994	11 889
Parameters varied	420	479	489
R(int)	0.0726	0.0870	0.0864
R₁	0.0382	0.0467	0.0702
wR₂ (all data)	0.0972	0.0976	0.2183

ᵃ Isostructural with aluminium counterpart [6].

its subsequent inclusion in the small number of crystals isolated, presumably results from concentration of toluene samples of **2**. Thus, although this impurity was not evident in the bulk sample, subsequent IR, ¹H NMR and C, H, N microanalytical data collected on these crystals confirms that NH₂Dipp is included. The IR spectrum of a crystal of **2**·NH₂Dipp exhibits a broad stretch at 3368 cm⁻¹ (N–H) in addition to the characteristic Ga–H single stretch of **2** at 1801 cm⁻¹, and a ¹H NMR spectrum (C₆D₆) of a crystal from the same batch exhibits broad resonances at 3.81 and 3.28 ppm, in a 3:2 integration ratio. These correspond to the GaH₃ and the NH₂ hydrogens, respectively. This co-crystallisation clearly indicates that **2** does not react with NH₂Dipp in toluene solution.

The N–C–N angle of **2** (Fig. 2a) is 104.15(12)°, which is typical for coordinated NHCs ([AlH₃(IMes)]: 104.2(2)°) [7a]. The Ga(1)–C(1) bond length of 2.0545(14) Å is considerably longer than that of [GaCl₃(IMes)] (1.954(4) Å) [17] and longer than that of [GaCl₃(IDipp)] (2.016(2) Å) [17] indicating the increased Lewis acidity of gallium trichloride relative to gallane, and the increased steric bulk of IDipp vs. IMes. The gallium–hydrogen contacts of 1.46(2), 1.47(2) and 1.54(2) Å compare well with those of [GaH₃(IʲPrMe)] (1.58(5) and 1.62(3) Å) [7b] and are consistent with gallium hydride bonds of group 15 Lewis base adducts of gallane [10]. In terms of intermolecular contacts, the 4,5-C₂H₂ of the IDipp of **2** (H(2) and H(3)) act as C–H acceptors to arene π-donation from

with residual 2,6-diisopropylaniline (NH₂Dipp). This was carried forward as a minor impurity in samples of IDipp·HCl used to prepare IDipp [18]. The high boiling point of NH₂Dipp (257 °C), and

the lattice NH$_2$Dipp (C(28)–C(33)) (Fig. 2b). Furthermore, two of the Ga–H bonds (H(1B) and H(1C)) interact with the hydrogens of the NH$_2$ functionality of the lattice aniline (Fig. 2b). These weak intermolecular forces hold the NH$_2$Dipp in a defined position in the crystal lattice (see graphical abstract illustration) but are not evident in solution (*cf* ^{1}H NMR and IR data for **2** vs. **2**·NH$_2$Dipp). All of the intermolecular interactions described are within accepted bonding parameters for atom–atom or C–H···π-arene contacts of this type (see Fig. 2b caption) [21].

2.2.2. IMes complexes of mono- and dichlorogallane

Chlorogallane complexes **3** and **4** were also characterised by single crystal x-ray diffraction and their molecular structures are depicted in Figs. 3 and 4, respectively. In both cases the hydride ligands were located from difference maps and refined isotropically. Selected bond lengths (Å) and angles (°) are provided in Table 2 with relevant bond distances and angles for salient literature compounds. Table 3 contains a summary of crystal measurement and refinement data for the molecular structures reported in this article.

The four-coordinate IMes complexes **3** and **4** crystallise with two molecular units in the asymmetric unit. The two distinct units exhibit comparable bonding parameters. Accordingly, only one molecule is discussed here. The "Ga(IMes)" subunits of **3** and **4** are similar to those of their iodogallane counterpart [GaH$_2$I(IMes)] [11] prepared by the reaction of [GaH$_3$(IMes)] with monovalent gallium iodide, from Baker and Jones, and the molecular structure of [GaCl$_3$(IMes)] [17]. Unfortunately, the solid-state structure of [GaH$_3$(IMes)] is not available for comparison.

The Ga–C bonding contacts and N–C–N angles of **3** (2.030(3) Å and 104.2(3)°) and **4** (2.005(6) Å, 105.6(5)°) compare well with those of [GaH$_2$I(IMes)] (2.022(4) Å and 104.4(4))°) [11] but differ markedly to those of [GaCl$_3$(IMes)] (1.954(4) Å and 102.9(3)°) [17] wherein the higher Lewis acidity of gallium trichloride decreases the Ga–C bond length.

The Ga–H contacts of **3** and **4** are of length 1.85(3), 1.51(4) (**3**) and 2.00(5) Å (**4**) (Table 2). For **3**, the shorter contact lies coplanar with the "Ga-NHC" plane. Overall these contacts are significantly longer than those observed in **2**·NH$_2$Dipp, but this increase in bond length is consistent with similar increases observed for the chloroalane counterparts of **3** and **4** relative to [AlH$_3$(IMes)] [6,7a]. However, it is interesting to note that, despite the questionable reliability of M–H bond determination by x-ray methods, the extension of these bonds is contrary to expectation based on trends in ν Ga–H IR data [6].

The relative pyramidalisation of the gallium centres of **3**, **4**, [GaCl$_3$(IMes)] [17]. and [GaH$_2$I(IMes)] [11] (Table 2) is consistent with trends in gallium 'hybridisation' expected according to Bent's rule [22]. For instance, the Cl–Ga–Cl angle of **4** is greater than that of [GaCl$_3$(IMes)] (Table 2), and the H–Ga–H angle of **3** approaches the ideal angle for *sp^2*-hybridisation with a Cl–Ga–C angle that is

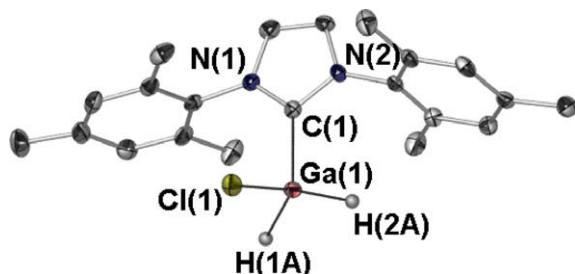**Fig. 4.** Molecular structure of lowest numbered unique molecule of [GaCl$_2$H(IMes)] (**3**) (50% thermal ellipsoids POV-RAY illustration). All hydrogen atoms excepting H(1A) omitted for clarity. See Table 2 for selected bonding parameters.

lower than that of **4**. This trend is also observed for quinuclidine adducts of mono- and dichlorogallane [15a] and the aluminium congeners of **3** and **4** [6].

3. Conclusion

In summary, we have extended the family of gallohydride NHC species with the addition of four fully characterised complexes that exhibit spectroscopic and structural trends consistent with the relative Lewis acidities of the gallohydrides and the sterics of the NHCs used. The structures of the compounds studied by X-ray methods exhibit intermolecular bonding interactions owing to inclusion of co-crystallised aniline (**2**), or trends consistent with Bent's rule (**3** and **4**) [22]. The co-crystallisation of NH$_2$Dipp with **2** suggests either that the pK_b of **2** may be too high for deprotonation of this aniline, or there is a steric impediment to reaction. From thermal decomposition data, it is clear that IMes is a superior ligand for the stabilisation of gallane relative to IDipp and IXy, and that chloride substitution of hydrides leads to increased gallohydride stability culminating in **4**, which is the most stable molecular gallium hydride reported. The stabilities of the compounds reported herein make them ideal candidates for 'bottleable' hydrogallation reagents in organic synthesis.

The preparation and reactivity of Lewis base adducts of group 13 halohydrides is ongoing in our laboratory and will form the basis of forthcoming publications.

4. Experimental

Diethyl ether was dried over sodium and freshly distilled from sodium diphenylketyl before freeze–thaw degassing prior to use. Toluene was dried over sodium and freshly distilled from potassium before freeze–thaw degassing prior to use. Lithium tetrahydridogallate was prepared and used *in situ* by reaction of gallium trichloride with excess lithium hydride (*ca* 30 equiv.) at −30 °C in diethyl ether. [GaH$_3$(IMes)] [4d], [GaCl$_3$(IMes)] [17] IXy and

Fig. 3. Molecular structure of lowest numbered unique molecule of [GaClH$_2$(IMes)] (**3**) (50% thermal ellipsoids POV-RAY illustration). All hydrogen atoms excepting hydrides H(1A) and H(2A) omitted for clarity. See Table 2 for selected bonding parameters.
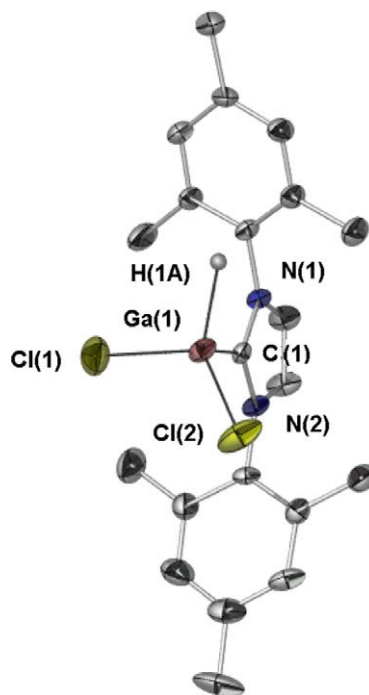
IDipp [18] were prepared by literature procedures. All manipulations were performed using conventional Schlenk or glovebox techniques under an atmosphere of ultra high purity argon in flame-dried glassware. Infrared spectra were recorded as Nujol mulls using sodium chloride plates on a Nicolet Nexus FTIR spectrophotometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded using Bruker spectrometers (see below for MHz) with chemical shifts referenced to the residual ^{1}H resonances of the *deutero*-benzene solvent (δ 7.16 and 128.39 ppm, respectively). Melting points were determined in sealed glass capillaries under argon and are uncorrected. All microanalyses were conducted by the Campbell Microanalytical Laboratory, Chemistry Department, University of Otago, P.O. Box 56, Dunedin, New Zealand. Single crystal X-ray data collections were undertaken at Monash University or UNSW on Bruker Apex II (**2**·NH$_2$Dipp), Enraf-Nonius Kappa (**3**) or Bruker X8 Apex (**4**) instruments. Further details are listed in a separate section below.

4.1. [GaH₃(IXy)] (1) (and [GaClH₂(IXy)] (3^{Xy}))

A cooled ($-40\,^\circ$C) solution of IXy (0.60 g, 2.17 mmol) in diethyl ether (50 cm^3) was added to a stirred slurry of LiGaH$_4$ (2.32 mmol) also in diethyl ether (70 cm^3). The resulting grey/brown reaction mixture was stirred below 0 $^\circ$C for 2 h and gradually warmed to room temperature overnight. The brown solution was filtered and the solvent removed *in vacuo* to afford **1** as an off-white powder that was recrystallised from the minimum volume of toluene (430 mg, 72%), m.p. 186 $^\circ$C (dec.). Samples of **1** repeatedly gave microanalyses low in carbon and nitrogen. This presumably results from incomplete combustion. Example analysis: Anal. Calc. for C$_{19}$H$_{23}$GaN$_2$: C, 65.36; H, 6.64; N, 8.02; Found: C, 55.68; H, 7.37, N, 5.21%; ^{1}H NMR (400.13 MHz, C$_6$D$_6$, 300 K); δ 2.12 [s, 12H, C*H*$_3$], 3.90 [br s, 3H, Ga–*H*], 6.16 [s, 2H, C$_2$*H*$_2$], 6.72 [s, 6H, C$_6$*H*$_3$]; ^{13}C NMR (100.62 MHz, C$_6$D$_6$, 300 K); δ 17.2 (*C*H$_3$), 121.6 (*C*$_2$H$_2$), 121.8 (*p*-C$_6$H$_3$), 129.0 (*o*-C$_6$H$_3$), 134.6 (*m*-C$_6$H$_3$), 135.0 (*ipso*-C$_6$H$_3$), 138.9 (NCN); IR (Nujol) v/cm^{-1}: 1789 (br s, Ga–H str). Additional data for **3^{Xy}**: ^{1}H NMR; δ 2.12 [s, 12H, C*H*$_3$], 6.08 [s, 2H, NC*H*], 6.72 [s, 6H, C$_6$*H*$_3$]; IR (Nujol) v/cm^{-1}; 1855 (br, s, Ga–H str).

4.2. [GaH₃(IDipp)] (2) and [GaH₃(IDipp)]·NH₂Dipp (2·NH₂Dipp)

A cooled ($-40\,^\circ$C) solution of IDipp (1.12 g, 2.88 mmol) in diethyl ether (20 cm^3) was added to a stirred slurry of LiGaH$_4$ (2.84 mmol) also in diethyl ether (100 cm^3). The grey/brown reaction mixture stirred below 0 $^\circ$C for 2 h and gradually warmed to room temperature overnight. Filtration and removal of volatiles *in vacuo* afforded crude **2** as a beige powder (993 mg, 76%), m.p. 166 $^\circ$C (dec.). During one preparation, recrystallisation from toluene afforded a small number of colourless blocks that characterised as **2**·NH$_2$Dipp, m.p. 136 $^\circ$C. Anal. Calc. for C$_{39}$H$_{58}$GaN$_3$ (**2**·NH$_2$Dipp): C, 73.23; H, 9.30; N, 6.57; Found: C, 72.71; H, 9.28, N, 6.45%; ^{1}H NMR (NH$_2$Dipp free sample) (300.13 MHz, C$_6$D$_6$, 300 K); δ 1.15 [d, *J* = 6.3 Hz, 12H, CH(C*H*$_3$)$_2$], 1.53 [d, *J* = 6.3 Hz, 12H, CH(C*H*$_3$)$_2$], 2.76 [sept, *J* = 6.3 Hz, 4H, C*H*(CH$_3$)$_2$], 3.81 [br s, 3H, Ga–*H*], 6.54 [s, 2H, C$_2$*H*$_2$], 7.19 [d, *J* = 6.9 Hz, 4H, *m*-C$_6$*H*$_3$], 7.36 [t, *J* = 6.9 Hz, 2H, *p*-C$_6$*H*$_3$]; ^{13}C NMR (100.62 MHz, C$_6$D$_6$); δ 23.0 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 28.6 (*C*H(CH$_3$)$_2$), 118.5 (*C*$_2$H$_2$), 123.2 (*p*-C$_6$H$_3$), 123.8 (*o*-C$_6$H$_3$), 130.2 (*m*-C$_6$H$_3$), 134.8 (*ipso*-C$_6$H$_3$), 145.2 (NCN); IR (Nujol) v/cm^{-1}; 1801 (br, s, Ga–H str).

4.3. [GaClH₂(IMes)] (3)

[GaCl$_3$(IMes)] (0.19 g, 0.40 mmol) in toluene (10 cm^3) was added dropwise to a solution of [GaH$_3$(IMes)] (0.30 g, 0.80 mmol) in toluene (10 cm^3) at ambient temperature. The resulting light yellow solution was warmed to 50 $^\circ$C and stirred for 6 h. Filtration

at 50 $^\circ$C and slow cooling to ambient temperature yielded **3** as colourless blocks (0.18 g, 33%), m.p. 263 $^\circ$C (dec.). Anal. Calc. for C$_{21}$H$_{26}$ClGaN$_2$: C, 61.28; H, 6.37; N, 6.81; Found: C, 60.30; H, 6.39; N, 6.58%; ^{1}H NMR (300 MHz, C$_6$D$_6$, 300 K): δ 2.03 [s, 12H, *o*-C*H*$_3$], 2.05 [s, 6H, *p*-C*H*$_3$], 4.72 [br s, 2H, Ga–*H*], 5.95 [s, 2H, C$_2$*H*$_2$], 6.71 [s, 4H, *m*-*H*]; ^{13}C NMR (75.5 MHz, C$_6$D$_6$, 300 K): δ 18.0 [s, *o*-CH$_3$], 21.4 [s, *p*-CH$_3$], 123.0 [s, C$_2$H$_2$], 129.9 [s, *m*-CH], 135.1 [s, *p*-CCH$_3$], 135.4 [s, *o*-CCH$_3$], 140.2 [s, *ipso*-C], 172.5 [s, NCN]; IR (Nujol) v/cm^{-1}: 1870 (sharp s, Ga–H str).

4.4. [GaCl₂H(IMes)] (4)

[GaCl$_3$(IMes)] (0.1 g, 0.26 mmol) in toluene (10 cm^3) was added dropwise to a solution of [GaH$_3$(IMes)] (0.25 g, 0.52 mmol) in toluene (10 cm^3) at ambient temperature. The resulting light yellow solution was warmed to 50 $^\circ$C and stirred for 14 h. Filtration at 50 $^\circ$C and slow cooling to ambient temperature yielded **4** as thin plates (0.26 g, 37%), m.p. 274 $^\circ$C (dec.). Anal. Calc. for C$_{21}$H$_{25}$Cl$_2$GaN$_2$: C, 56.54; H, 5.65; N, 6.28; Found: C, 56.39; H, 5.75; N, 6.27%; ^{1}H NMR (300 MHz, C$_6$D$_6$, 300 K): δ 2.02 [s, 12H, *o*-C*H*$_3$], 2.04 [s, 6H, *p*-C*H*$_3$], 5.84 [s, 2H, C$_2$*H*$_2$], 6.69 [s, 4H, *m*-*H*]; ^{13}C NMR (75.5 MHz, C$_6$D$_6$, 300 K): δ 17.6 [s, *o*-CH$_3$], 20.9 [s, *p*-CH$_3$], 123.2 [s, C$_2$H$_2$], 129.5 [s, *m*-CH], 133.0 [s, *p*-CCH$_3$], 135.0 [s, *o*-CCH$_3$], 140.3 [s, *ipso*-C]; IR (Nujol) v/cm^{-1}: 1917 (br s, Ga–H str).

4.5. X-ray structure determination

Crystalline samples of **2**·NH$_2$Dipp, **3** and **4** were mounted on glass fibres in silicone oil at $-150(2)\,^\circ$C (123(2) K). A summary of crystallographic data can be found in Table 3 and salient bond lengths and angles and listed in Table 2. Hydrogen atoms were refined in calculated positions (riding model) with the exception of hydride ligands and the aniline NH$_2$ hydrogens of **2**·NH$_2$Dipp, which were located and refined isotropically in all cases. Data were collected using graphite monochromated Mo Kα X-ray radiation (λ = 0.71073 Å) on a Bruker Apex II (**2**·NH$_2$Dipp), Enraf-Nonius Kappa (**3**), or Bruker X8 Apex (**4**) CCD diffractometer, and data were corrected for absorption by empirical methods using SADABS. Structural solution and refinement was carried out using the SHELX suite of programs [23]. Flack tests for compounds **3** and **4** are supportive of the correct structure and space group refinement. For compound **4**, a peak of electron density >1.5 e Å^{-3} is placed 0.01 Å from H(1A). This hydride is associated with an unusually long Ga to H contact.

Acknowledgements

Appendix A. Supplementary material

CCDC 714187, 714188 and 714189 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.04.030.

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