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Recent advances in the chemistry of the Group 13 metals: hydride derivatives and compounds involving multiply bonded Group 13 metal atoms

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> ‘But facts are facts and flinch not’
> Robert Browning, The Ring and the Book, book ii

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Abstract

Two aspects of Group 13 metal chemistry are surveyed in the light of recent research, particularly that reported in the period 1992–1998. The first concerns compounds containing M–H bonds (M = Al, Ga or In) and including binary as well as mixed derivatives in either the base-free or complexed conditions. The second concerns compounds offering the opportunity for the metal atom to engage in multiple bonding. Seemingly unrelated, the two types of molecular compound have several features in common. Both typically contain highly reactive functional groups that are unusually susceptible to oxidation, hydrolysis or aggregation; as a result, developments in both areas have depended on similar strategies. The account focuses (i) on the reactions giving access to the relevant compounds; (ii) on the methodologies of trapping or shielding needed for the preservation of reactive M–H fragments or putative multiple bonds to M atoms; (iii) on the characteristics of the compounds, with particular reference to the structures they assume, and to their response to thermal, photolytic and chemical stimuli; and (iv) on the interplay between experimental and theoretical methods. Some of the hydrides show promise as synthetic reagents or as sources of the metal or metal compounds with extended structures of predefined morphology. On the evidence to hand, π-type interactions play only a minor role in the chemistry of the Group 13 metals, their contribution being obscured by the effects of low coordination number and non-covalent forces.

Keywords: Group 13; Metal atom; Multiple bonding; Reaction; π-type metals

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1. Introduction

1.1. Preamble

Long overshadowed by boron, the Group 13 metals are now acknowledged to have rich and distinctive chemical lives of their own, often far removed from boron's image. The change has come about not just through the commercial importance of aluminium and alumina-based solids [1,2], but through the explosion of activity within the past two decades involving solid materials or devices chemically and physically tailored to have specific electronic, optical, thermal or other properties. From being chemical curios, compounds like gallium arsenide and indium phosphide have thus come to touch our lives daily through light-emitting diodes (LEDs) and detectors, lasers, high-speed and microwave integrated circuits, and other contemporary gadgetry [1,3]. To the range of microporous and layered solids afforded by the familiar zeolites and clays there have been added both aluminophosphate ($AlPO_4$) [4] and gallophosphate ($GaPO_4$) [5] materials having potential applications as catalysts, catalyst supports and sorbents. Typically based on mixtures of aluminium chloride and a salt like *N*-butylpyridinium chloride, ionic liquids [6] and polymers [7] have also gained prominence as reaction media and as convenient electrolytes for aluminium-plating or in advanced batteries, e.g. for electric vehicles. Nor has there been any want of incident on the biological front, with lively controversy continuing to shroud the role of aluminium in a number of human diseases—most notably Alzheimer's disease [8]; elsewhere the hunt has been on for gallium and indium complexes that lend themselves to detection methods in nuclear medicine [1,9].

1993 saw the publication of two books, one devoted to the coordination chemistry of aluminium [2], the other to the chemistries of all four of the Group 13 metals [1]. These provide a convenient baseline on which to build the present review. On the basis of research activity in the intervening years, the survey will focus on two topics, namely:

1. hydride derivatives
2. multiple bonding involving the Group 13 metal atoms

In concentrating mainly on discrete molecular, rather than macromolecular, derivatives, the treatment is necessarily arbitrary and selective; it will also touch on other areas where major advances have occurred, for example, metal–metal bonded systems and derivatives of the metals in low formal oxidation states. The main protagonists have been aluminium, gallium and indium. Thallium has seen very little of the recent action; of the Group 13 elements (M) it is the least suited to engaging in M–H, M–M or multiple bonds, and its stock is further devalued nowadays by its toxicity [1]. Otherwise the purpose of this review is not only to bring out some of the highlights of recent research in the areas selected, but also to place the results in a wider context.

1.2. Common themes

There are certain motifs common to many of the recent advances that have been made.

1.2.1. Experimental and theoretical methods

In the first place, the acidity and oxophilicity that characterise in varying degrees Group 13 metal centres cause units like M–H, M–M or M=Se to be susceptible to oxidation or hydrolysis. In addition, some of the new compounds are thermally labile into the bargain. Rigorous exclusion of air and moisture has tended therefore to be a minimum, but by no means always a sufficient requirement. Some of the hydride derivatives have proved particularly demanding, their manipulation and characterisation requiring, for example, the use of an all-glass apparatus and special procedures [10,11].

The principal methods used to identify, monitor and characterise the compounds are listed in Table 1. The structural scene is dominated, as usual, by X-ray diffraction studies of single crystals. These have their limitations when it comes to fixing the dimensions of metal hydride units, the metal–hydrogen distances being usually rather poorly defined and significantly different in any case from the distances determined by neutron or electron diffraction or by spectroscopic methods. The most obvious remedy in these circumstances is to turn to neutron diffraction but, whether for reasons of convenience, expense or technical difficulty, this has seldom been done. M–H distances and interbond angles remain, therefore, to be quantified accurately for all but the gaseous monohydrides [12,13]. With neutron-diffraction measurements, as well as the improved capacity of modern X-ray facilities, moreover, it cannot be long before electron densities are being mapped, with an eye to resolving some of the contentious questions about multiple and secondary bonding [14]. The structures of some gaseous molecules have been determined by electron diffraction but here, too, hydrogen atoms are hard to pin down exactly, and without information from other independent sources it is rarely possible to extract good estimates of all the structural and vibrational parameters that determine the molecular scattering. The best way of dealing with this problem is to carry out a combined analysis incorporating the geometric and vibrational information carried not only by the electron-diffraction pattern, but also by the rotational constants and an appropriate force field. A further improvement has been made with the development of the so-called SARACEN method whereby parameters, which cannot be refined freely, are made subject to restraints derived from an array of ab initio calculations [15]. Both here and elsewhere, such calculations now make a significant input, with program suites such as GAUSSIAN [16] putting quite sophisticated treatments within the reach of many researchers. Where comparisons can be made, the calculations typically yield dimensions, energies, vibrational wavenumbers and intensity patterns, and chemical shifts that reproduce well, experimental findings, and in some cases *improve upon* those findings. Accordingly we can now place trust in the results of the calculations to anticipate the equilibrium structures and dimensions and spectroscopic properties of a wide range of molecules, including ones whose existence has yet to be authenticated. In this way, for example, the identities and structures of molecules like MH_2 [17], MH_3 [18], and Me_2AlNH_2 [19] ($M = Al$, Ga or In) have been established with some conviction with the aid of their measured infrared spectra, and ^{27}Al- and ^{71}Ga-NMR studies can be made to shed light on the forms assumed by aluminium(I) and gallium(I) compounds in solution [20].

1.2.2. Environmental control

Progress has also depended upon *trapping* or *protection* of reactive fragments. This may be achieved *physically*, for example by matrix isolation [21]. Here reactive vapour species, like metal atoms or AlCl, may be quenched with an excess of a suitable inert diluent and trapped in the resulting solid matrix; alternatively, photolysis of appropriate precursors may give access to the desired product, as exemplified by reactions (1) and (2). This approach has been highly successful as a

Table 1
Physical techniques used for identification and characterisations of hydride, low-valent, multiply bonded and other reactive derivatives of the Group 13 metals

Technique	Parameters	Uses	Examples
Vibrational spectroscopy	Vibrational wavenumbers and intensities; isotopic effects	Identification of new molecules and deduction of likely structures; of particular use in the study of hydrides and in support of matrix-isolation studies; quantum chemical simulation often important	MH_2 and MH_3 (M = Al, Ga or In) [17,18]; Ga_2H_6 [10,11]; Me_2AlNH_2 [19]; Mx, M_2X_2 (M = Al or Ga; X = F, Cl or Br) [20]
High-resolution electronic emission or absorption, IR diode laser, and microwave spectroscopies	Vibrational and rotational constants of molecules in their electronic ground and excited states	Detailed characterisation of diatomic and other simple molecules	MH (M = Al, Ga, In or Tl) [12,13]; $M(C_5H_5)$ (M = In or Tl) [40]
NMR spectroscopy	Chemical shifts, multiplet patterns, *J* values, linewidths and intensities; quantum chemical simulation	Mainly for solution studies; ^{27}Al and ^{71}Ga chemical shifts used as an index to the coordination shell of the metal. ^{27}Al measurements particularly important in fixing the Al environment in extended solid structures, e.g. zeolites and aluminophosphates; quantum chemical simulation also useful [20]	AlX (X = Cl, Br or I) [20]; $M(C_5Me_5)$ (M = Al or Ga) [20]; barriers to rotation about Al–X and Ga–X bonds (X = Group 15 or Group 16 element) with the potential for multiple bonding [41]
EPR spectroscopy	*g*- and *A*-values, multiplet patterns	Identification and characterisation of M(0) M(II) and other paramagnetic species, e.g. in cryogenic experiments	MH_2 (M = Al [42] or Ga [43]); $Al(NH_3)_n$ ($n = 2$ or 4) and $HAlNH_2$ [44]; $Al(PF_3)_2$ [45]; $[R_2MMR_2]^-$ (M = Al or Ga; R = $CH(SiMe_3)_2$ or 2,4,6-$Pr^i_3C_6H_2$) [41]
Colligative measurements	Molecular masses	Identification of state of aggregation in solution	$[Ga\{C(SiMe_3)_3\}]_n$; $[Ga(CH_2CMe_3)]_n$ [20]

Table 1 (Continued)

Technique	Parameters	Uses	Examples
X-ray diffraction of single crystals	Crystal and molecular structures; molecular dimensions and intermolecular contacts	Principal method of structural characterisation in the solid state; MH_n units seldom well defined and M–H distances differ from those determined by neutron diffraction or spectroscopic methods	$[GaBH_6]_n$ [37]; $[Ga(C_5Me_5)]_6$ [47]; $[L{\cdot}MH_3]_n$ (M = Al or Ga; L = N or P base) [48]; $H_3M{\cdot}\overline{CN(Pr^i)C_2Me_2N}Pr^i$ (M = Al, Ga or In) [23]; $Tp^{Bu_2}ME$ (M = Ga or In; E = Se or Te) [28]; $Na_2\{Ar^*GaGaAr^*]$ $[Ar^* = 2,6\text{-}(2,4,6\text{-}Pr^i_3C_6H_2)\text{–}C_6H_3]$ [31]; $[(Me_3Se)_3Si]_2TlTl[Si(SeMe_3)_3]_2$ [41]; $M(EMes^*)_3$ (M = Al, Ga or In; E = S or Se; $Mes^* = 2,4,6\text{-}Bu^t_3C_6H_2$) [39]; $[H_2GaNH_2]_3$ [49]; $[Al_{77}\{N(SiMe_3)_2\}_{20}]^{2-}$ [50]; $[H_2ME(SiMe_3)_2]_3$ (M = Al or Ga; E = P or As) [51,52]; $[(C_5Me_5)Al]_6P_4$ [20]; $[(C_5Me_5)Al]_3Al_2$ [53]
Neutron diffraction	Crystal and molecular structures; molecular dimensions and intermolecular contacts	Applicable to single crystal and powder samples; means of defining MH_n units accurately but little exploited to date	AlD_3 [1]; $[D_2GaND_2]_3$ [49]
Electron diffraction of vapour samples	Vibrationally averaged molecular structure; molecular dimensions and vibrational amplitudes; geometric and vibrational problem commonly underdetermined	Most reliable structure usually determined by combined analysis of electron diffraction, vibrational and other spectroscopic data, and the results of quantum chemical calculations; MH_n units not well defined on the basis of electron-diffraction results alone	Ga_2H_6 [11]; $GaBH_6$ [37]; $H_2GaB_3H_8$ [54]; $HGa(BH_4)_2$ [55] $Me_3N{\cdot}GaH_3$ [38]; $M(C_5Me_5)$ (M = Al or Ga) [20]; $[Bu^tGaS]_4$ [46]
Quantum chemical calculations	Equilibrium molecular structures and dimensions, vibrational properties, chemical shifts, and energies	Exploration of species still to be authenticated experimentally; validation of inferences drawn from vibrational and NMR spectra and from diffraction measurements	MH_2 [17], MH_3 [18,56,57], M_2H_6 [56,57] (M = Al, Ga, In or Tl); $H_2GaB_3H_8$ [54]; $Me_3N{\cdot}GaH_3$ [38]; Me_2AlNH_2 [19]; $[M(C_5H_5)]_n$ [20]; $[RGaGaR]^{2-}$, $Na_2[MeGaGaMe]$ (R = H or Me) [58–60]; $[H_2MNH_2]_3$ (M = B, Al or Ga) [49]

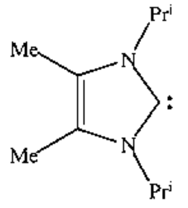
means of reconnaissance and of tracking down molecules like MH_2 and MH_3 (M = Al, Ga or In) that are short-lived under normal conditions [17,18].

$$GaCl + HX \xrightarrow{\text{Ar matrix, hv}} ClGaHX \text{ (X = H or Cl [22])} \tag{1}$$

$$Me_3Al{\cdot}NH_3 \xrightarrow{\text{Ar matrix, } hv} Me_2AlNH_2 + CH_4 \quad [19] \tag{2}$$

Trapping or protection of vulnerable units may also be achieved by chemical means. For example, highly reactive species like alane or gallane may be intercepted by a suitable donor and preserved in the form of known, thermally more robust adducts, as represented by Eq. (3) (M = Al or Ga; $m = 1$ or 2). In the same spirit, it has been possible to preserve aluminium(I) and gallium(I) halides in solution at relatively high temperatures by an appropriate choice of solvent, thereby opening the way to the synthesis of other low-valent derivatives of these metals [20]. Chemical stabilisation can be achieved by electronic or steric means or by a combination of these stratagems. Electronic factors are plainly uppermost in the stabilisation of MH_3 (including M = In) through coordination by the highly nucleophilic imidazol-2-ylidene carbene **1** [23]. By contrast, steric factors are probably the dominant principle governing the stabilities and structures of compounds containing (i) very bulky aryl ligands, e.g. $[Mes^*MH_2]_n$ ($Mes^* = 2,4,6\text{-}Bu^t_3C_6H_2$: M = Al, $n = 2$ [24]; M = Ga, $n = 1$ [25]) and Mes^*_2MH (M = Al [26] or Ga [27]); or (ii) substituted tris(pyrazolyl)borate ligands like $Tp^{Bu^t}2$, **2** [28]. With ligands of the second type it has proved possible to control the coordination environment of the metal centre so effectively as to permit the stabilisation of not only M(I) but also multiple M=E bonds, where M = Ga or In and E = Se or Te.

$$1/n[MH_3]_n + m NMe_3 \xrightarrow{178\ \text{K}} H_3M(NMe_3)_m \quad [10, 11] \tag{3}$$



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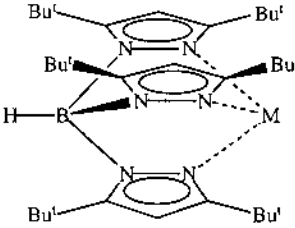

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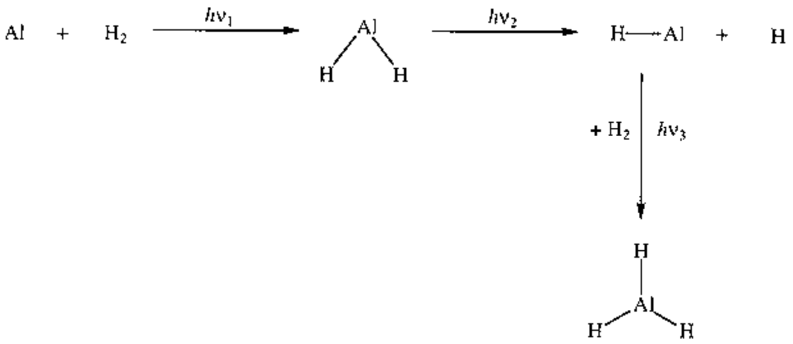
1.2.3. Chemical reactions

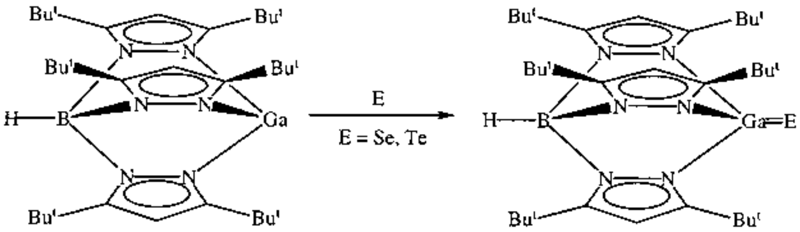
The principal chemical reactions encompassing the synthesis or disposal of new compounds are also confined to quite a narrow range, extending from addition (with or without oxidation), through metathesis and displacement, to elimination, and including aggregation as a recurrent principle.

1.2.3.1. Addition. Ranging from metal vapour synthesis and oxidation to simple complexation, addition is exemplified by reactions (1) and (3), by the sequence (4) initiated by photoexcitation of aluminium atoms in the presence of dihydrogen

[17,18], and by the addition of elemental selenium or tellurium to the gallium(I) precursor, $(Tp^{Bu^t}2)Ga$, as in Eq. (5) [28].



(4)



(5)

1.2.3.2. Reduction. Access to the lower oxidation states, and particularly to systems with homonuclear metal–metal bonds can be gained by reduction, typically at the hands of a powerful reducing agent such as an alkali metal and with the support of bulky substituents, as illustrated by reactions (6) and (7):

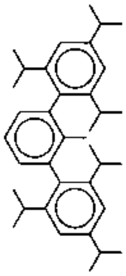
$$2R_2AlX + 2K \overset{\text{hexane}}{\rightarrow} R_2AlAlR_2 + 2KX \qquad (6)$$

$\{R = (Me_3Si)_2CH,\ X = Cl$ [29];

$R = 2,4,6,\text{-}Pr^i_3C_6H_2,\ X = Br\}$ [30]

$$2Ar^*GaCl_2 + 6Na \overset{Et_2O}{\rightarrow} Na_2[Ar^*GaGaAr^*] + 4NaCl \qquad (7)$$

where Ar* is the highly encumbered aryl group **3** [31].



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1.2.3.3. Elimination. This is the principal pathway open to the decomposition of mononuclear species, as in reaction (2), and leading normally to oligomeric cyclic or cluster compounds and, ultimately, to extended structures, sometimes of the metal, more often of heteronuclear assemblies. Examples include reactions (8)–(10).

$$[H_2GaNH_2]_3 \rightarrow GaN + 6H_2 \text{ [32]} \tag{8}$$

$$1/n[H_2GaN_3]_n \rightarrow GaN + H_2 + N_2 \text{ [33]} \tag{9}$$

$$1/2[Bu^t_2Ga(\mu\text{-}SH)]_2 \rightarrow 1/4[Bu^tGa(\mu_3\text{-}S)]_4 + Bu^tH \text{ [34]} \tag{10}$$

1.2.3.4. Metathesis and displacement. Nucleophilic substitution remains one of the principal agencies of synthesis, being exemplified in reactions (11)–(14).

$$1/m[H_2GaCl]_m + MX \rightarrow 1/n[H_2GaX]_n + MCl \tag{11}$$

($X = GaH_4$, BH_4, B_3H_8 [10–12], or N_3 [33]; $M = Li$ or NR_4)

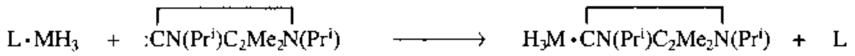
$$4Me_3N{\cdot}AlH_3 + 6(Me_3Si)_2S \rightarrow Al_4S_6(NMe_3)_4 + 12Me_3SiH \text{ [35]} \tag{12}$$

$$GaBr + LiC_5Me_5 \rightarrow Ga(C_5Me_5) + LiBr \text{ [20]} \tag{13}$$

$$\text{'GaI'} + Na(Tp^{Bu^t}2) \rightarrow Ga(Tp^{Bu^t}2) + NaI \text{ [36]} \tag{14}$$

Displacement of one base by another which is stronger or in large excess has also been a regular working principle in the synthesis of new adducts of the binary or substituted metal hydrides, as in Eq. (15).

(15)



$$L{\cdot}MH_3 + :CN(Pr^i)C_2Me_2N(Pr^i) \longrightarrow H_3M{\cdot}CN(Pr^i)C_2Me_2N(Pr^i) + L$$

($M = Al$, Ga or In; $L = H^-$ or NMe_3 [23])

1.2.3.5. Aggregation. Aggregation is a distinctive feature in the chemistry of the Group 13 metals, reflecting the electrophilicity of the metal centre in relation to its ligands. It can be curbed by the coordinating action of suitable donor species or by the steric bulk of appropriate ligands. Thus, the hydrides typically take up hydrogen-bridged oligomeric or polymeric structures under normal conditions, e.g. AlH_3 [1], GaH_3 [10–12] and $GaBH_6$ [10,37], but form discrete mononuclear complexes in association with suitable donors, e.g. $Me_3N{\cdot}GaH_3$ [38]. That the degree of aggregation can also be controlled by the size of spectator ligands is well illustrated by the monomeric characters of the hydrides Mes^*_2MH and Mes^*GaH_2, where $M = Al$ or Ga [25–27]. Aggregation is also the norm in compounds where the Group 13 metal is bound to an element from Group 15 or Group 16 and where a degree of π-interaction may be anticipated. Here, too, the natural order of things can be varied by complexation or by the judicious introduction of bulky ligands. Thus, when synthesised in the presence of trimethylamine, aluminium(III) sulphide forms not its usual three-dimensional structure but a discrete cluster $[Al_4S_6(NMe_3)_4]$

based on an adamantane-like Al_4S_6 core [35]. How the specific spatial demands of the tris(pyrazolyl)borate ligand **2** result in mononuclear species bearing terminal metal–chalcogen bonds has already been noted (reaction (5) [28]). Moreover, the attachment of sufficiently bulky substituents to the Group 15 or Group 16 atom opens the way to monomeric tri-coordinated derivatives of the Group 13 metals, e.g. $M(EMes^*)_3$, where $M = Al$, Ga or In and $E = S$ or Se [39].

2. Hydride derivatives

2.1. Binary hydrides

There are but two hydrides of the Group 13 metals that can be isolated in the normal way at or near ambient temperatures [1,10,12]. One of them, alane $[AlH_3]_n$, is quite robust in thermal terms but, being a polymeric solid, it is relatively intractable in the absence of a suitable base. The other, gallane $[GaH_3]_n$, is much more tractable but thermally frail, decomposing at temperatures above ca. 240 K [1,10,11]. That gallane vaporises at low pressures as the diborane-like molecule $H_2Ga(\mu\text{-}H)_2GaH_2$ with more or less well defined dimensions cannot be doubted, and the Raman [61] and UV photoelectron [62] spectra of the molecule have now been measured. Less clear is the form of the compound in the condensed phase, although IR spectra indicate that the solid differs from alane in retaining *terminal* M–H bonds. The crystal structure of the related compound gallaborane, $[GaBH_6]_n$, at 110 K consists of helical chains made up of alternating pseudotetrahedral GaH_4 and BH_4 units (Fig. 1) [37], and this may well foreshadow the structure of solid gallane. Exploration of the chemistry of gallane is hampered by its thermal lability, but most of the features established to date find obvious parallels in the chemistry of diborane. On the evidence of recent ab initio MP2 studies [57], though, the prospects of isolating the corresponding indium and thallium hydrides seem bleak. In thermodynamic terms, In_2H_6 and Tl_2H_6 appear to be highly unstable in both the gas and solid states, although modest kinetic stability in the gas phase may give a glimmer of hope.

Thermodynamic stability does not improve for any of the mononuclear hydrides MH, MH_2 or MH_3. Nevertheless, each of the monohydride molecules may be generated by high-energy methods (involving, for example, the action of an electric discharge on M/H_2 mixtures) in the gas phase at low pressures, and here it may be interrogated by a variety of high-resolution spectroscopic techniques (see Table 1). As a result, the physical properties of these molecules have been determined with an accuracy unmatched by any other studies of the Group 13 metal hydrides [12,13]. Nor has thermodynamic stability prevented the molecules from being generated in solid noble gas matrices, for example *via* a series of photochemical reactions set in train by excitation of M atoms ($M = Al$, Ga or In) to the ^2S and ^2D states in the presence of H_2 molecules (Eq. (4)). The molecules have all been identified unambiguously and characterised by the IR spectra of their normal and deuterated forms, the conclusions being strongly endorsed by the results of quantum chemical calculations [17,18]. EPR measurements testify to the paramagnetism and genuinely divalent character of AlH_2 [42] and GaH_2 [43].

The molecules MH and MH_2 are susceptible to aggregation and the dimers $[MH]_2$ and $[MH_2]_2$ have attracted considerable theoretical attention, despite a dearth of hard experimental fact. Diborene, B_2H_2, the boron analogue of acetylene,

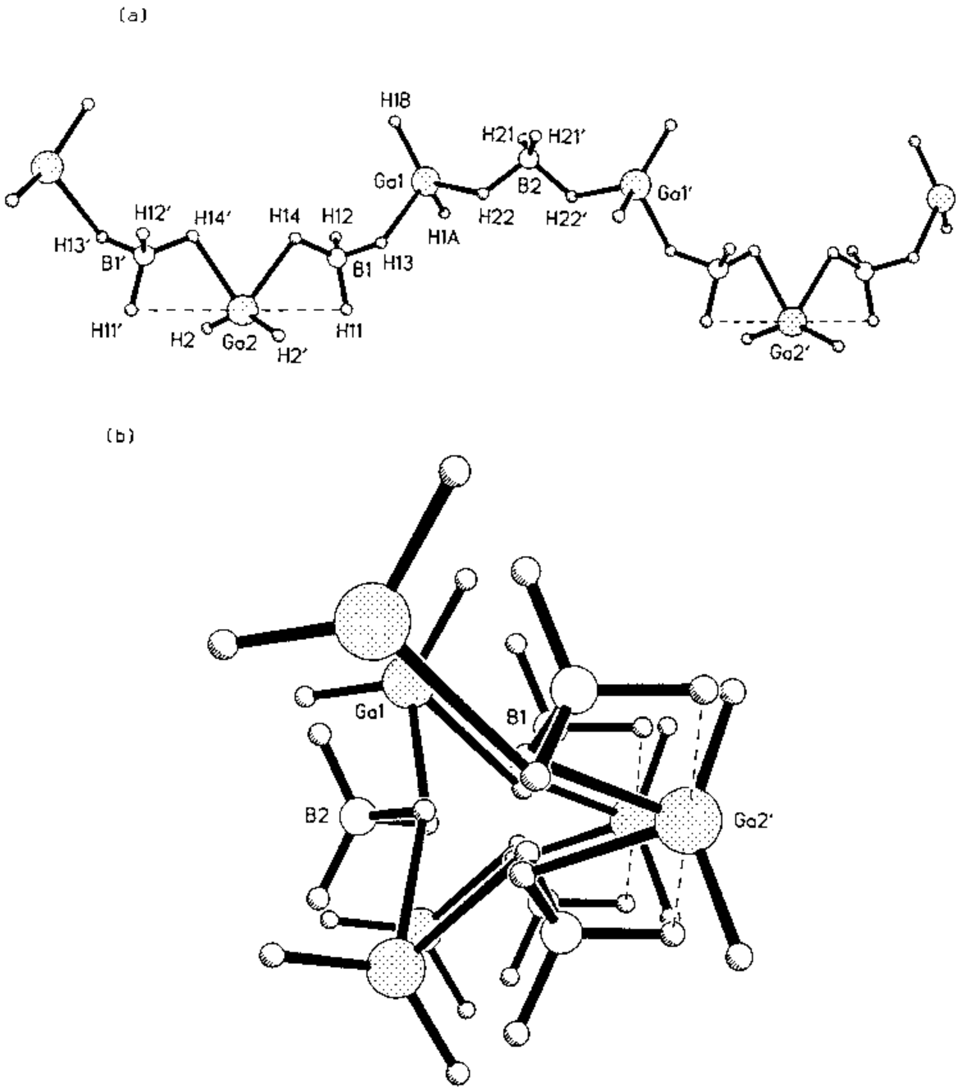
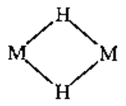


Fig. 1. Structure of crystalline gallaborane at 110 K as determined by X-ray diffraction (primed atoms are symmetry-related to non-primed atoms) showing the helical polymeric arrangement (a) side-on; and (b) viewed along the axis of the helix. Reproduced with permission from Ref. [37].

has a linear triplet ground state involving little or no B–B double-bonding [63]. By contrast, a bis(μ-hydrido) structure (**4a**) with D_{2h} symmetry is calculated to be the most stable form of M_2H_2 for all the other Group 13 elements [12,64]. Instead of the linear form, which is now only a transition state, a *trans*-bent isomer (**4b**) (C_{2h}) appears as a second minimum on the potential energy surface for M_2H_2 where M = Al, Ga or In. There are two other possible isomers, namely the asymmetric $M-MH_2$ (**4c**, C_{2v}) and the mono-H-bridged HM(μ-H)M (**4d**, C_s) which typically give minima at energies not far above the global minimum for M_2H_2. IR studies of the matrices formed by condensing laser-ablated Al atoms with H_2 and an excess of argon may well have revealed absorptions due to the isomers **4a** and **4d** for M = Al [65]. Similar experiments with thermally evaporated gallium suggest that the dimer Ga_2 reacts *spontaneously* with H_2 to form the isomer **4a** and that this can be converted photoreversibly into a second isomer **4b** for M = Ga [66].



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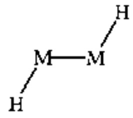

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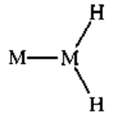

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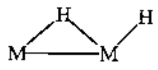


4d

2.2. Mixed hydrides $[MH_2X]_n$ and $[MHX_2]_n$

Replacement of hydrogen in the parent trihydride by other ligands tends to improve the thermal stability of the system, whether thermodynamically or kinetically, and whether from electronic or from steric causes. The past decade has brought a flurry of activity resulting in the isolation of numerous hydrides of the types $[MH_2X]_n$ and $[MHX_2]_n$ for M = Al or Ga and for a variety of organic and inorganic substituents X. Table 2 lists a selection of these compounds, drawn mainly from the results of recent studies. The research groups of Power (at Davis, California), Cowley (at Austin, Texas) and Raston (now at Monash University, Melbourne) have been major players, and some of the work on organo-aluminium and -gallium hydrides carried out by the Austin group was reviewed in 1995 [67].

The routes to mixed hydrides most commonly followed involve either metathesis, usually starting from an appropriate halide [e.g. reaction (11) or the reaction of an organometal halide with a hydride source like $LiAlH_4$ or $LiGaH_4$], or displacement by a base carrying an acidic hydrogen atom followed by elimination of H_2, as, for example, in Eq. (16) [49]. Addition reactions represented by

$$Me_3N{\cdot}GaH_3 + NH_3 \xrightarrow{\text{liquid } NH_3} 1/3[H_2GaNH_2]_3 + NMe_3 + H_2 \qquad (16)$$

Eq. (1) give access to the molecules H_2GaCl and $HGaCl_2$ which can be preserved as monomers by isolation in solid noble gas matrices [22]. However, unless the substituent X is sufficiently bulky (e.g. Mes* [24–27]) or tailored to function as a multidentate ligand (e.g. 2-$(Me_2NCH_2)C_6H_4$ or 2,6-$(Me_2NCH_2)_2C_6H_3$ [67–71]), the base-free hydrides exist as oligomers under normal conditions, with N, P, As, O, Cl

Table 2
Structures of selected base-free compounds of the types $[H_2MX]_n$ or $[HMX_2]_n$ (M = Al, Ga or In; X = an organic or inorganic substituent)

Compound[a]	Method[b]	Structure	Mean distance (Å)		Reference
			r(M–E)	r(M–H)	
$[H_2AlNMe_2]_3$	X	Cyclic Al_3N_3 core	1.936(3) (E=N)	1.55	[75]
$[H_2Al(tmp)]_2$	X	Cyclic Al_2H_2 core	1.836(3) (E=N)	1.68(2)[c]	[72]
$[(H_2Al)_2\{\mu\text{-}N(Bu^t)CH_2\}_2]$	X	Contains cyclic butterfly Al_2N_2 core	1.943(7) (E=N)	1.40(7)	[76]
$[H_2Al\{\mu\text{-}N(CH_2CH_2)_2S\}]_2$	X	Cyclic Al_2N_2 core	1.962(6), 1.996(6) (E=N)	1.37(2)	[77]
$[H_2Al\{2\text{-}(Me_2NCH_2)C_6H_4\}]_2$	X	Cyclic Al_2H_2 core, 5-coordinated Al	1.974(5) (E=C)	1.688[c], 1.928(3)[c]	[68]
			2.102(4) (E=N)		
$[H_2Al\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}]$	X	Monomeric, 5-coordinated Al	1.949(5) (E=C)	1.50(4)	[69]
			2.277(5), 2.233(5) (E=N)		
$H_2AlP(SiMe_3)_2]_3$	X	Cyclic, planar Al_3P_3 core	2.398(2) (E=P)		[51]
$[H_2AlOBu^t]_2$	X	Cyclic Al_2O_2 core	1.813(3) (E=O)	1.55(5)	[78]
$H_2AlOCHBu^t_2]_4$	X	Cyclic Al_2O_2 cores with symmetrical $Al(\mu\text{-}H)_2Al$ bridges	1.863(2)[d] (E=O)		[79]
			1.834(2)[e] (E=O)		
$[2,6\text{-}Mes_2C_6H_3AlH_2]_2$	X	Cyclic Al_2H_2 core	1.956(3) (E=C)	1.44(4), 1.65(5)[c]	[80]
$[2,6\text{-}Trip_2C_6H_3AlH_2]_2$	X	Cyclic Al_2H_2 core	1.963(4) (E=C)	1.46(4), 1.74(5)[c]	[80]
			1.966(2) (E=C)	1.36(4), 1.62(8)[c]	
$[Mes^*AlH_2]_2$	X	Cyclic Al_2H_2 core	1.966(3) (E=C)	1.50(4), 1.69(4)[c]	[24]
$[H_2GaNH_2]_3$	X, N	Cyclic Ga_3N_3 core	1.981(7) (E=N)	1.56(3) (Ga–D)	[49]
$[H_2GaNMe_2]_2$	ED	Cyclic Ga_2N_2 core	2.027(4)[f] (E=N)	1.49(4)[f]	[81]
$[H_2GaNEt_2]_2$	X	Cyclic Ga_2N_2 core	2.017(5) (E=N)	1.72	[82]
$[H_2Ga\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}]$	X	Monomeric, 5-coordinated Ga	1.968(7) (E=C)		[70]
			2.389(6) (E=N)		
$[H_2Ga\{2\text{-}(Me_2NCH_2)C_6H_4\}]$	X	Monomeric, 4-coordinated Ga	1.92(1) (E=C)		[68]
			2.087(7) (E=N)		
$[H_2GaPCy_2]_3$	X	Cyclic Ga_3P_3 core	2.385(2) (E=P)	1.51(7)	[83]
$[H_2GaP(SiMe_3)_2]_3$	X	Cyclic Ga_3P_3 core	2.392(2) (E=P)	1.50[g]	[52]

Table 2 (Continued)

Compound[a]	Method[b]	Structure	Mean distance (Å)		Reference
			r(M–E)	r(M–H)	
[$H_2GaAs(SiMe_3)_2]_3$	X	Cyclic Ga_3As_3 core	2.474(1) (E=As)	1.50(3)	[52]
[$H_2GaOBu^t]_2$	X	Cyclic Ga_2O_2 core	1.905(9) (E=O)	1.61(12)	[78]
[$H_2GaOCHBu^t_2]_2$	X	Cyclic Ga_2O_2 core	1.93(1) (E=O)		[79]
[Mes*GaH_2]	X	Monomeric, 3-coordinated Ga	1.942(7) (E=C)		[25]
[$H_2GaCl]_2$	ED	Cyclic Ga_2Cl_2 core	2.353(3)^{c,h} (E=Cl)	1.514(33)^{h}	[73]
[H_2GaBH_4]	ED	Cyclic Ga(μ-H)$_2$B core	2.179(2)^{f} (E=B)	1.586(8)^{f} 1.826(8)^{c,f}	[37]
[$H_2GaBH_4]_\infty$	X	Helical polymeric chains made up of alternating GaH_4 and BH_4 units	2.473(7) (E=B)	1.41(5), 1.93(7)^{c}	[37]
[$H_2GaB_3H_8$]	ED	2-Ga-substituted B_4H_{10} structure	2.310(2)^{i} (E=B)	1.493(14)^{i}, 1.81(4)^{c,i}	[54]
[$Hal(SCH_2CH_2NEt_2)_2$]	X	Monomeric, 5-coordinated Al	2.179(2) (E=N) 2.275(1) (E=S)	1.62(2)	[77]
[$Hal\{PhC(NSiMe_3)_2\}_2$]	X	Monomeric, 5-coordinated Al	1.932(2), 2.032(2) (E=N)	1.55(2)	[84]
[Mes*Al(H)N(SiMe$_3$)$_2$]	X	Monomeric, 3-coordinated Al	1.819(2) (E=N) 1.974(2) (E=C)	1.51(3)	[85]
[$Hal(Obu^t)_2]_2$	X	Cyclic Al_2O_2 core	1.675(3), 1.817(3)^{c} (E=O)	1.51(5)	[78]
[$Trip_2AlH]_2\cdot PhMe$	X	Cyclic Al_2H_2 core	1.980(3) (E=C)		[27]
[Mes$_2^*$AlH]	X	Monomeric, 3-coordinated Al	1.992(6) (E=C)	1.53(4)	[26]
[Mes*Al(H)Cl]^{j}	X	Monomeric, 3-coordinated Al	1.946(4) (E=C) 2.14(1) (E=Cl)	1.53(12)	[86]
[Me_2AlH]	ED	Cyclic Al_2H_2 core	1.953(1)^{f} (E=C)	1.779(8)^{c,f}	[87]
[$Bu^t_2AlH]_3$	X	Cyclic, planar Al_3H_3 core	2.001(2) (E=C)	1.726(5)^{c}	[88]
[$HGa(SCH_2CH_2NEt_2)_2$]	X	Monomeric, 5-coordinated Ga	2.27(1) (E=N) 2.289(3) (E=S)	1.33	[77]
[$(HGa)_2\{(NPr^iCH_2)_2\}_2$]	X	Cyclic Ga_2N_2 core, 5-coordinated Ga	2.005(4)^{c}, 2.205(4)^{c} 1.853(4) (E=N)	1.62	[89]
[$HGa(Cl)N_3]_4$	X	Cyclic Ga_4N_4 core	1.918(17)–2.063(16) (E=N) 2.134(11)–2.184(5) (E=Cl)		[33]
[$HGa\{2\text{-}(Me_2NCH_2)C_6H_4\}_2$]	X	Monomeric, 5-coordinated Ga	2.324(7), 2.457(8) (E=N) 1.966(9), 1.993(9) (E=C)	1.150	[68]

Table 2 (Continued)

Compound[a]	Method[b]	Structure	Mean distance (Å)		Reference
			r(M–E)	r(M–H)	
$[\mathrm{HGa(Obu^t)_2}]_2$	X	Cyclic Ga_2O_2 core	1.783(4), 1.906(4)^c (E=O)	1.53(7)	[78]
$[\mathrm{Trip_2GaH}]_2$	X	Cyclic Ga_2H_2 core	1.977(7) (E=C)	1.72(7)^c	[27]
$[\mathrm{Mes^*_2GaH}]$	X	Monomeric, 3-coordinated Ga	2.002(3) (E=C)	1.57(5)	[27]
$[\mathrm{Mes^*(3,5\text{-}Bu^t_2C_6H_3CMe_2CH_2)GaH}]$	X	Monomeric, 3-coordinated Ga but with short Ga···H contracts	1.978(17) (E=C)	1.43(10)	[25]
$[\mathrm{Me_2GaH_2}]$	ED	Cyclic Ga_2H_2 core	1.954(4)^f (E=C)	1.708(14)^{c,f}	[90]
$[\mathrm{HGa(BH_4)_2}]$	ED	Monomeric, 5-coordinated Ga with bidentate BH_4 groups	2.185(2)^f (E=B)	1.50(4)^f, 1.788(7)^{c,f}	[55]
$[\mathrm{HIn\{2\text{-}(Me_2NCH_2)C_6H_4\}_2}]$	X	Monomeric, 5-coordinated In	2.487(3), 2.560(3) (E=N) 2.185(4) (E=C)	1.69(3)	[71]

[a] tmp, 2,2,6,6-tetramethylpiperidinyl; Mes, 2,4,6-$Me_3C_6H_2$; Trip, 2,4,6-$Pr^i_3C_6H_2$; Mes*, 2,4,6-$Bu^t_3C_6H_2$; Cy, cyclohexyl.

[b] X, X-ray diffraction; N, neutron diffraction; ED, electron diffraction (of vapour).

[c] Bridging M–H or other distance.

[d] 5-coordinated Al.

[e] 4-coordinated Al.

[f] r_a distance.

[g] Assumed value.

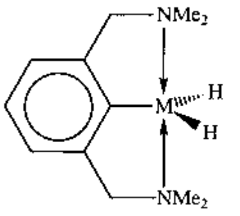
[h] $r_g$distance.

[i] r_α distance.

[j] Contaminated with some [Mes*$AlCl_2$].

or H atoms bridging the metal atoms usually, as indicated in Table 2, in four- or six-membered cyclic arrays. Hydrogen is superior only to organic groups as a bridging agent, so that hydrogen bridges tend to be formed in the absence of any other realistic option. Nevertheless, the inherent attractions of an amido bridge may be diminished by steric congestion at the nitrogen atom to the point where hydrogen bridging is preferred; such is the case, for example, with $[H_2Al(tmp)]$ where tmp = $2,2,6,6\text{-}Me_4C_5H_6N-$ [72]. Hence the structural picture is one of considerable diversity, with additional variety coming from the conformations of the cyclic structures, and particularly the six-membered ones which may adopt chair, skew-boat or planar conformations according to the dictates of the atoms in the heterocycle and the substituents they bear.

Outside a matrix environment, monomeric base-free derivatives can be prepared only with the assistance of very bulky aryl groups like Mes* or Trip = $2,4,6\text{-}Pr^i_3C_6H_2$. It is of interest that whereas Mes^*_2MH molecules are monomeric with tri-coordinated metal atoms for both M = Al and Ga [26,27], Mes^*MH_2 is monomeric only when M = Ga [25], succumbing to dimerisation when M = Al to give four-coordinated metal atoms and both terminal and bridging hydrido ligands [24]. This finding illustrates well the propensity of aluminium more than gallium to enter into oligomeric or polymeric arrays and so seek out environments with relatively high coordination numbers (≥ 4). The steric bulk of the organic group serves to increase the thermal stability of the intrinsically fragile metal hydride fragment. Another way of inhibiting thermal decomposition involves coordination of the metal centre by a suitable Lewis base, and by the judicious introduction of basic substituents into the aromatic ligand the roles of space-filling and coordination can be combined. Hence relatively robust monomeric hydrides $H_2M[2,6\text{-}(Me_2NCH_2)_2C_6H_3]$, **5**, with penta-coordinated M atoms have been isolated for M = Al [69] or Ga [70]. More strikingly still, the first neutral indium hydride, $HIn[2\text{-}(Me_2NCH_2)\text{-}C_6H_4]_2$, **6**, has been brought to book in this way [71].



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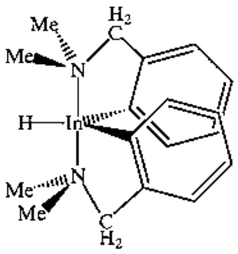
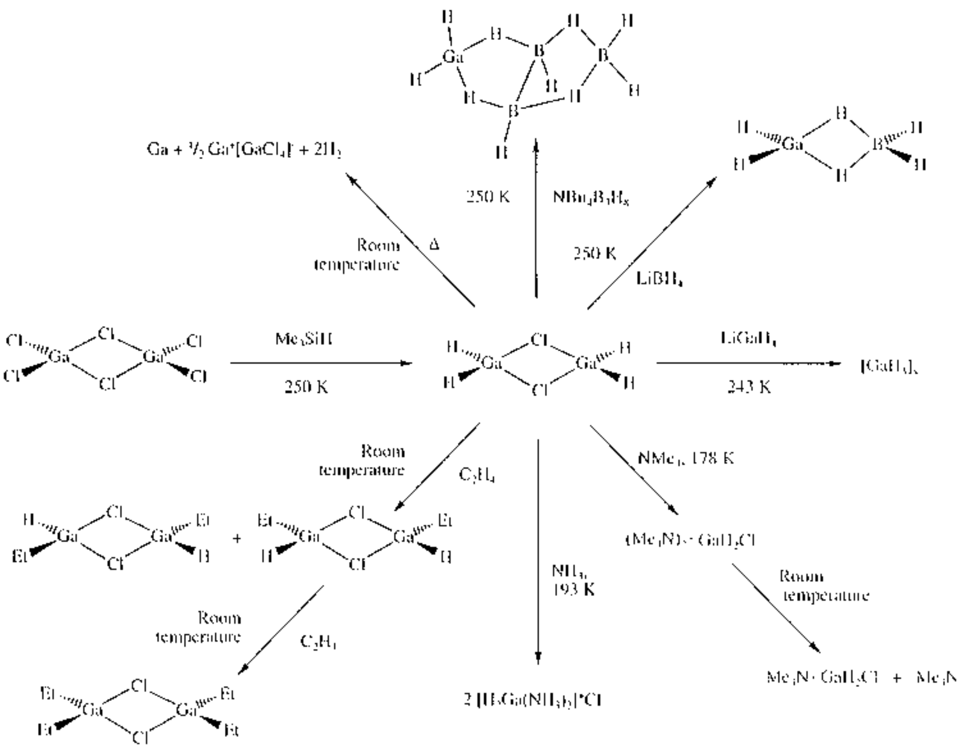


6

The chemical properties of mixed hydrides attracting most attention are thermal decomposition and complexation. Some, like monochlorogallane, $[H_2GaCl]_n$, are potentially useful as synthetic precursors to other compounds containing the MH or MH_2 unit, as illustrated in Scheme 1 [10,73]. Alkenes insert into the M–H bonds to give the corresponding metal alkyl derivative, but relatively little has so far been



Scheme 1. The preparation and some reactions of monochlorogallane.

made of this or of the reducing power of the mixed hydrides. A possible exception is the indium hydride $[HInCl_2]_n$, prepared by transmetallation between indium(III) chloride and Bu^n_3SnH at $-78°C$ [74]. Tetrahydrofuran solutions of the compound, which are relatively stable at ambient temperatures, have been investigated as a means of reducing organic carbonyl and halide derivatives.

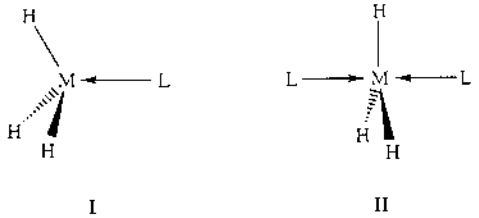
2.3. Complexes

Hydrides of the Group 13 metals act as Lewis acids and numerous adducts with neutral bases or anionic species have been characterised to date. Complexation is a key factor in the stabilisation of the parent hydride; in the case of aluminium this is perhaps less important than the increased tractability of the adducts. For reasons of thermal stability, solubility in common organic solvents, or ease of preparation and manipulation, therefore, species like $Me_3N{\cdot}MH_3$ and MH_4^- ($M = Al$, Ga or In) make altogether more convenient synthetic agents than base-free hydrides do. The neutral complexes of alane and gallane have been the subject of more than one recent review by Raston et al. [48,91], and no good purpose will be served by going over the same ground. Instead, it will be sufficient to survey briefly the principal features that have emerged from structural studies of these compounds, and to outline the progress that has been made with complexes of indium hydrides.

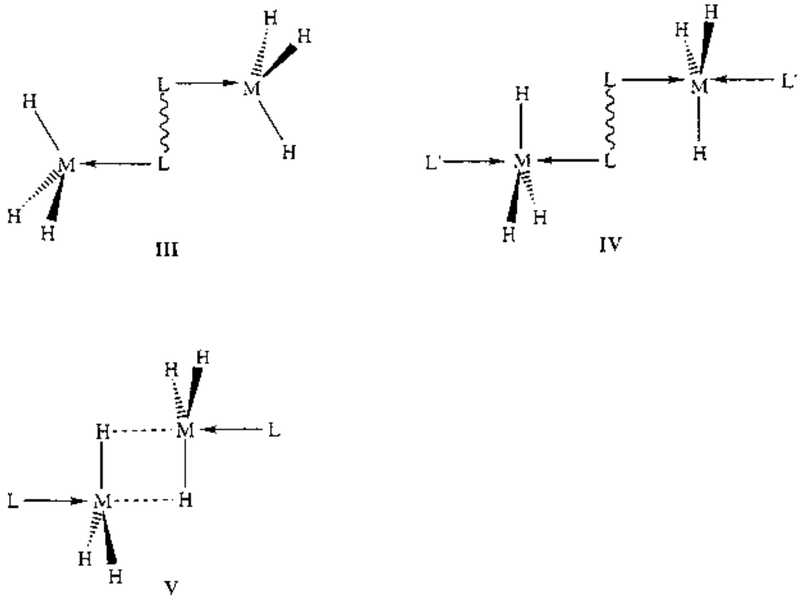
Six structural types are revealed by crystallographic studies of alane and gallane complexes, as represented by the schematic structures **I**–**VI** in Fig. 2. The balance between four- and five-fold coordination of the metal centre and between monomeric and dimeric or more aggregated species is clearly a function of the electronic and steric properties of both the donor ligand and the metal host. Adducts of alane show a greater disposition towards structures in which the coordination number of the metal exceeds four than do the analogous adducts of gallane. This is reflected in the crystal structures of $[Me_3N\cdot AlH_3]_2$ [92] and $Me_3N\cdot GaH_3$ [38]. The former adopts the hydrido-bridged dimeric structure **V** while the latter is composed of essentially the same discrete monomeric molecules that enter the vapour with the tetra-coordinated structure **I**. $[Me_3N\cdot AlH_3]_2$, in common with other complexes of the type $[L\cdot AlH_3]_2$ ($L = Me_2(PhCH_2)$*N*,*N*-methyl-2,4,6-tetrahydropyridine, or tetrahydrofuran), can be considered to be a Lewis base adduct of the elusive dialane, Al_2H_6; the structure is characterised by trigonal bipyramidal coordination at the metal centre, with the equatorial sites accommodating the hydrogen atoms, one apical site the donor ligand, and the other apical site a weak secondary Al···H interaction. Here and elsewhere the AlH_3 molecule shows a distinct preference for retaining its planarity in the face of complexation. Furthermore, whereas alane forms both 1:1 and 1:2 adducts with trimethylamine, with the 1:2 adduct adopting structure **II**, the corresponding 1:2 adduct of gallane decomposes at temperatures above − 23°C to $Me_3N\cdot GaH_3$ and free Me_3N. Indeed, the tendency of aluminium to form penta-coordinated adducts is such that structure **I** is observed only for strongly σ-donating bases like quinuclidine or sterically bulky ones like tricyclohexylphosphine [48,91].

Phosphine ligands tend to bind more strongly to GaH_3 than to AlH_3, whereas the reverse holds for nitrogen donor ligands. Hence the M–N distances for the type **I** adducts quinuclidine·MH_3 are 1.991(4) and 2.063(4) Å for M = Al and Ga, respectively [93]: the corresponding M–P distances for $Bu^t_3P\cdot MH_3$ are 2.471(3) and 2.444(6) Å [94], despite the near-identical covalent radii of aluminium and gallium in tetra-coordinated environments. However, the MH_3 molecules are not particularly strong Lewis acids and the coordinate links they form are seldom strong, as demonstrated by the comparative ease of dissociation to release the free base. The same point is made by the structure of $Me_3N\cdot GaH_3$, a representative type **I** complex, where the GaH_3 fragment is a relatively flat pyramid with N–Ga–H bond angles of 99.3(8)° [38]. In general, though, the dimensions of the MH_3 moiety are insufficiently well defined to offer a wider view of just how the metal hydride molecule responds to complexation.

Adducts of alane and gallane with bidentate nitrogen and phosphorus ligands show little taste for chelation, even in systems like $[H_3Al\cdot tmen]$ ($tmen = Me_2NCH_2CH_2NMe_2$) where the chelate ring so formed would entail little strain [95]. Such systems are more likely to display polymeric structures of type **VI**, but bulky substituents at the donor atom may oblige the metal to adopt the tetra-coordinated structure **III** (as in $[H_3Al\cdot PCy_2C_2H_4PCy_2\cdot AlH_3]$ (Cy = cyclohexyl) [96], and a combi-



Two metal centres



Extended Chain of Metal Centres

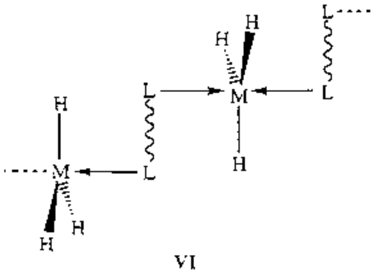


Fig. 2. Structural types identified in crystallographically characterised adducts of AlH_3 and GaH_3. Reproduced with permission from S. Aldridge, A.J. Downs, Chem. Rev. (in preparation).

nation of bidentate and monodentate ligands may lead to the structure **IV** {as in $[Me_3N{\cdot}AlH_3{\cdot}PMe_2C_2H_4PMe_2{\cdot}AlH_3{\cdot}NMe_3]$ [93]}.

Despite the weakness of the In–H bond and the unpropitious properties forecast for the base-free hydride InH_3 in one form or another, several structurally characterised indium hydrides have now come to light, all but one of these benefiting from the stabilising influences of *inter*molecular complexation. The compounds are listed in Table 3. Four of them feature terminal In–H linkages, viz. $K_3[K(Me_2SiO)_7]$ $[HIn(CH_2CMe_3)_3]_4$ [97], $[HIn\{2\text{-}(Me_2NCH_2)C_6H_4\}_2]$ (**5**, see Section 2.2) [71], $[Li(THF)_2][\{(Me_3Si)_3C\}_2In_2H_5]$ [98], and the carbene adduct $[Pr^iNC_2Me_2(Pr^i)NC{\cdot}InH_3]$ [23]. Unfortunately only in the case of $[HIn\{2\text{-}(Me_2NCH_2)C_6H_4\}_2]$ has the hydrido ligand been located, yielding an In–H bond length of 1.69(3) Å; this figure contrasts with average Al–H and Ga–H bond lengths of 1.53 and 1.48 Å, respectively, determined by X-ray diffraction measurements spanning a range of alane and gallane complexes [48]. The carbene complex $[Pr^iNC_2Me_2(Pr^i)NC{\cdot}InH_3]$ represents the sole adduct of InH_3 to be isolated so far and although the hydrogen atoms could not be positioned by crystallographic methods, their presence was clearly implied by the ^1H-NMR and IR spectra of the compound [23]. The NMR and structural properties of the carbene moiety indicate a degree of delocalisation within the ring and a structure intermediate between those of the free imidazolylidene **1** and the imidazolium cation $[Pr^iNC_2Me_2(Pr^i)NCH]^+$.

Among the indium hydrides to be isolated several have hydrido ligands bridging indium and another atom. That atom is lithium in $[Li(THF)_2][\{(Me_3Si)_3C\}_2In_2H_5]$ which is believed to have the structure **7**, although the positions of the hydrido ligands could not be fixed by the crystallographicdata [98]. It is boron in $[Me_2InB_3H_8]$ [99] and $[1\text{-}Pr^iIn\text{-}2,3\text{-}(Me_3Si)_2\text{–}2,3\text{-}C_2B_4H_4]_2$ [100]. The first of these has a structure akin to that of the *arachno* tetraborane B_4H_{10} in which a wingtip BH_2 has been replaced by an Me_2In moiety [99]; here the intramolecular In-μH distances measure 2.18(4) Å but the coordination sphere of the indium is augmented by secondary In···H intermolecular contacts measuring ca. 2.53 Å. Long-range indium–hydrogen contacts, no shorter than 2.48 Å, are also found in the solid indacarborane, where they provide a very weak bridging interaction holding together the dimeric structure, as illustrated in Fig. 3 [100]. In three cases the hydrido bridge spans two indium atoms. One is the lithium complex **7** already alluded to. The bent In(μ-H)In unit proposed here anticipates the crystal structures of $[Li(tmen)_2][Me_3InHInMe_3]$ [101] and $K[(Me_3CCH_2)_3$

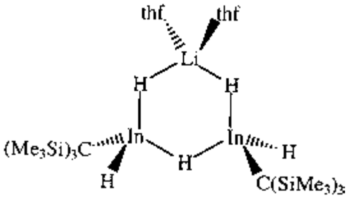


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Table 3
Structures of some indium hydrides determined by X-ray crystallography

Compound[a]	Structure	Salient distances (Å) and angles (°)	Reference
$[Li(thf)_2]\ [\{(Me_3Si)_3C\}_2In_2H_5]$	As in **6** with both bridging and terminal H atoms; H atoms not located	r(In–C) 2.20(3), r(In···In) 3.482(3), r(In···Li) 3.38(9)	[98]
$K_3[K(Me_2SiO)_7][HIn(CH_2CMe_3)_3]_4$	Contains $[HIn(CH_2CMe_3)_3]^-$ ions; H atoms not located	No details about the anions given	[97]
$HIn[2\text{-}(Me_2NCH_2)C_6H_4]_2$	As in **5** with 5-coordinated In and terminal In–H bonds.	r(IN–H) 1.69(3), r(In–C) 2.185(4), r(In–N) 2.487(3), 2.560(3)	[71]
$Pr^i\overline{NC_2Me_2(Pr^i)NC}\cdot InH_3$	Monomeric species of structure type **I** (Fig. 2); H atoms not located	r(In–C) 2.260(6)	[23]
$Me_2InB_3H_8$	B_4H_{10}-like structure with Me_2In unit in the 2-position; bridging In–H–B units and weak intermolecular In···H–B bridges	r(In–H) 2.18(4), r(In···H) 2.53, 2.61, r(In–C) 2.105(5), r(In···B) 2.745(6), ∠C–In–C 158.6(2)	
$[1\text{-}Pr^iIn\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4]_2$	Dimeric cluster composed of *closo* InC_2B_4 units linked through weak In···H–B bridges	2.668(5), r(In–B) 2.428(6), 2.297(5)	
$[Li(tmen)_2]\ [Me_3InHIMe_3]$	Two Me_3In units linked by a non-linear In–H–In bridge	r(In–H) 1.87(4), r(In–C) 2.172(7), r(In···In) 3.591(4), ∠In–H–In 148.6(10)	[101]
$K[(CMe_3CH_2)_3InHIn(CH_2CMe_3)_3]$	Two $(Me_3CCH_2)_3In$ units linked by a non-linear In–H–In bridge	R(In–H) 1.94(2), r(In–C) 2.213(6), ∠In–H–In 156(5)	[102]

[a] tmen, $Me_2NCH_2CH_2NMe_2$.

contrasting with the analogous aluminium compound $Na[Me_3AlHAlMe_3]$ [103] which displays a linear Al–H–Al bridge in the solid state.

2.4. Applications

Recent developments in the chemistry of Group 13 metal hydrides have been stimulated mainly by their possible applications in synthesis and as volatile precursors in chemical vapour deposition and other areas of current materials science.

2.4.1. Synthesis

Well known and legion are the uses of alanes, usually in the form of adducts with ethers or amines or as hydrido complexes (particularly $LiAlH_4$), as powerful and more or less selective reducing agents for both organic and inorganic compounds [1,104,105]. Of the various groups open to reduction in organic compounds, carbonyl groups have been the main reaction centres, but other potential targets include carbon–halogen, C=C, epoxide, –CN, $-NO_2$, and sulphur functionalities. By contrast, rather little attention has so far been paid to the reducing properties of gallium and indium hydrides. It is interesting therefore that preliminary studies should find gallane complexes to be milder, more selective reducing agents than alane complexes [48,106]. For example, $Me_3N{\cdot}GaH_3$ selectively reduces the carbonyl group in $4\text{-}BrC_6H_4COBr$, whereas quinuclidine·AlH_3 reduces not only this group but also the adjacent C–Br bond. Whether indium hydrides like $HInCl_2(THF)_n$ [74] or $LiInH_4$ [107] offer any advantages over their aluminium and gallium counterparts has yet to be demonstrated.

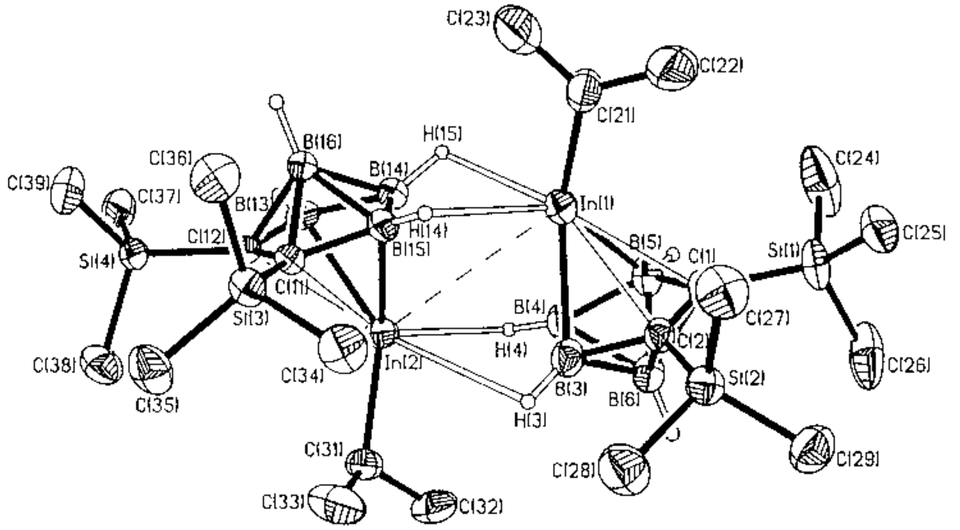
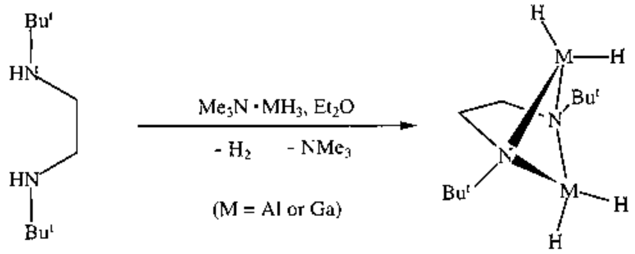


Fig. 3. Perspective view of *closo*-$[1\text{-}Pr^i\text{-}1\text{-}In\text{-}2,3\text{-}(Me_3Si)_2\text{-}2,3\text{-}C_2B_4H_4]$ showing the In···H–B bridges holding the dimeric unit together. Reproduced with permission from Ref. [100].

From the inorganic standpoint, the hydrides are noteworthy primarily as hydride sources and in metallation and hydrometallation reactions. Representative examples are provided by Eqs. (17)–(20). A significant development in alane chemistry has come through the reactions of $LiAlH_4$ and alane [76,108]



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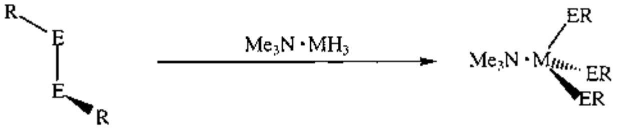
(17)



[108]

(18)

(M = Al or Ga; E = Se or Te; R = alkyl or aryl group)

$$E(SiMe_3)_3 \xrightarrow[-\,Me_3SiH\,-\,NMe_3]{Me_3N{\cdot}MH_3,\ Et_2O} 1/3[H_2ME(SiMe_3)_2]_3 \ [51,52]$$

$$(M = Al\ or\ Ga;\ E = P\ or\ As) \qquad (19)$$

$$(\eta^5 - 1{,}3 - Bu^t_s - C_5H_3)_2Sm(thf) \xrightarrow[-\,Al\,-\,NEt_3\,-\,H_2]{Et_3N{\cdot}AlH_3,\ Et_2O} [(\eta^5 - 1{,}3 - Bu^t_2 - C_5H_3)_2SmH]_2$$

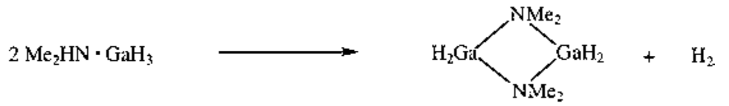
[109] (20)

adducts with transition-metal, lanthanide and actinide compounds to yield not only hydride but also a variety of aluminohydride derivatives in which aluminium is linked to the d- or f-block metal through one or more hydrogen bridges [109,110]. Although the zinc gallohydride complex $[Zn(\eta^1\text{-}GaH_4)Cl\text{–}(pmdeta)]$ (pmdeta = $Me_2NCH_2CH_2N(Me)CH_2CH_2NMe_2$) has been prepared [111], gallane and indane chemistry has yet to follow suit.

2.4.2. Chemical vapour deposition and other applications in materials science

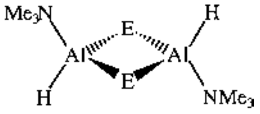
The Group 13 metals are of strategic importance as the parents of the **III–V** compounds, ranging in properties from refractory, wide-bandgap (> 3 eV) semiconductors like GaN, through narrow-bandgap (1–2 eV) semiconductors like the ubiquitous GaAs and InP (with all their applications in circuitry, optoelectronic devices and communications), to intermetallic species like TlBi [1]. Some of the binary chalcogenides, e.g. GaS [46], also possess useful electronic and optoelectronic properties. Much effort has been invested in seeking out optimum methods of preparing these compounds in a pure state and often in the form of thin films to be formed epitaxially on a suitable substrate. One of the most generally effective procedures involves chemical vapour deposition (CVD), and the search for suitable precursors has therefore focused on volatile compounds which decompose cleanly to the parent metal or directly to the desired binary compound. In this context, the hydride ligand has much to commend it: it engages normally in only weak intermolecular interactions (to favour volatility); it forms comparatively weak bonds to the Group 13 metals (to give thermal lability); its derivatives yield a highly volatile product, H_2, on decomposition; and there is little opportunity for the formation of intermediate decomposition products (cf. the decomposition of organometallic compounds like trimethylaluminium).

Seemingly well set to meet these desiderata are some of the neutral complexes of alane and gallane, whose performance as CVD precursors has been explored in some detail [48,112]. The weakest bond in such a complex is likely to be the coordinate link between the metal and the donor atom of the Lewis base, and thermal decomposition usually proceeds to give the metal, dihydrogen, and the free base at temperatures in the range −10 to 200°C. Hence the complexes do not function as single source precursors to binary compounds of the metals—a prized aim of much current research—unless there is a mechanism for elimination of H_2 or some other simple molecule to take place and so permit the establishment of a normal covalent bond between the metal and donor atom, as in Eq. (21) [81]. Nevertheless, several tertiary amine complexes of alane—most notably $Me_3N{\cdot}AlH_3$ and $Me_2EtN{\cdot}AlH_3$—have been successfully used to deposit aluminium from the gas phase for the growth of GaAlAs, AlGaN and Al-containing heterostructures or for the metallisation of semiconductor devices [112,113]. Thermal decomposition of such complexes in solution also offers a means of producing nanometre-sized aluminium powders [114]. By contrast, the inferior thermal stability of the corresponding gallane complexes makes them less manageable as a source of gallium. The complex quinuclidine·GaH_3 appears to be the best prospect; it is long-lived at normal temperatures and does not decompose at temperatures below 100°C. Exploratory studies suggest that this may indeed be used with advantage as the gallium source for the growth of thin films of GaAs and GaSb [115]. In processes involving the deposition of thin films, the hydrides may have a further important part to play in *modifying* the surface of the substrate. Indeed, adsorption studies on the interaction of $Me_3N{\cdot}AlH_3$ with hydroxyl-free oxidised silicon surfaces under UHV conditions indicate that the metal centre expands its coordination shell by binding as a penta-coordinated species $Me_3N{\cdot}AlH_3(O{=})$, where O= denotes a surface O-centre, with a higher partial pressure of the alane resulting in the formation of a hydride bridge species $H_2Al(NMe_3)(\mu\text{-}H)_2AlH_2(O{=})$ [48]. On the other hand, dissociative adsorption occurs with $Me_3N{\cdot}GaH_3$ under similar conditions yielding the four-coordinated species $H_3Ga(O{=})$.



(21)

A single-source precursor to a **III**–**V** or other binary compound ME needs, then, to have a strong bond already in place between the M and E atoms, or at least to have facile access to an intermediate of this sort. The neutral gallane derivatives $[H_2GaNH_2]_3$ [32,49], $[HGa(Cl)N_3]_4$ [33], and $[H_2GaN_3]_n$ [33] show distinct promise as precursors to gallium nitride. Of particular note is the ability of the precursor to dictate the morphology of the solid product. Thus pyrolysis of powdered samples of $[H_2GaNH_2]_3$ under a variety of conditions leads to nanocrystalline gallium nitride with neither the pure wurtzite nor the pure zinc blend structure, but probably with a random arrangement of stacking planes and equal proportions of cubic and hexagonal phases. This synthesis of metastable samples of the nitride is probably the result of topochemical reaction in which the hydrogen elimination (with concomitant Ga–N bond formation) occurs along a reaction coordinate established by the crystal and molecular structure of the precursor [49]. Similar control certainly appears to operate at a molecular level in the formation of cubic GaS from $[Bu^tGa(\mu_3\text{-}S)]_4$ [46], and may well determine the unusual morphology and microstructure reported for the crystalline samples of gallium nitride delivered by the decomposition of azidogallane, $[H_2GaN_3]_n$ [33]. The newly reported compounds $[H_2ME(SiMe_3)_2]_3$ (M = Al, E = P [51]; M = Ga, E = P or As [52]) and $[H_2AlAs(SiMe_3)_2]\cdot NMe_3$ [51] also undergo decomposition, in this case with the elimination of Me_3SiH and formation of nanocrystalline samples of the relevant **III**–**V** compound ME, albeit at widely different temperatures according to whether M = Al or Ga and at the cost of some contamination associated with competing decomposition pathways. Compounds such as $[Me_3N\cdot Al(H)E]_2$, prepared by the reaction of the elemental chalcogen E = Se or Te with $Me_3N\cdot AlH_3$ and having the structure **8**, may well function as sources of the binary metal chalcogenides, a possibility that is still under investigation [48].



8

3. Multiple bonding involving the Group 13 metals

3.1. Introduction

The engagement of the heavier p-block elements in multiple bonding has been a theme underlying much research in the past two decades. At the centre of the action have been the elements of Groups 14–16 [116]; the chemical map now carries a host of well-defined compounds incorporating what are generally acknowledged to be valence multiple bonds [117] to many of these elements. The Group 13 metals M have been relatively late to enter the fray, but their status as regards multiple bonding has lately come under close scrutiny with the discovery that they can be made to spawn numerous compounds with the *potential* for multiple bonding to M.

What the issue may lack in hard facts and unambiguous evidence, however, is amply compensated by the controversy it has created, rising at times to fever pitch [118]. The subject has been authoritatively reviewed by Brothers and Power on the basis of literature published up to mid-1995 [41]. The purpose of this brief survey is not to go over the same ground, but to sketch in the latest developments.

Quite aside from the teasing question of what exactly is meant by multiple or π bonds in a polynuclear assembly, the Group 13 metals pose several problems when we come to weigh their chances of supplementing the σ-bonds they form by a π-type component.

1. The electrophilicity usually characterising the Group 13 metal centre in its compounds means that any *heteronuclear* multiple bonding in which M may engage is likely to have significant *dative* character [117].
2. In addition, M–E bonds are often highly polar and coulombic contributions result in shorter bonds, as well as other structural and energetic features that may be indistinguishable from the effects of π-bonding.
3. The size and natural electrophilicity of M atoms in combination make them prey to complexation or aggregation (q.v.). To produce compounds in which M has a coordination number of three or less, and thereby create the conditions optimising π-type interactions, it is necessary therefore not only to avoid donor solvents but also to seek the steric protection of very bulky organic or other substitutents (see Section 1.2). The very size and shape of these substituents may well result in steric crowding, at the cost of lengthening adjacent putative multiple bonds.
4. Since bond distances are a function of coordination number, the assumption by the metal of a two- or three-coordinated environment must of itself be expected to lead to shorter bonds, irrespective of any other factors determining the bond length.
5. Covalent bonding is favoured (a) by minimising the difference in electronegativity between M and its substituent E, and best of all when $M = E$; and (b) by increasing the electron density on M, e.g. through partial reduction to produce species that may be regarded formally as M^{I} or M^{II} derivatives. Heteronuclear systems involving M in a partially reduced state are liable to give rise to further ambiguities of interpretation, particularly regarding the exact function of the M-centred fragment in relation to the groups it partners.

In the circumstances, it is not surprising that few clear-cut inferences can be drawn as regards the role of multiple bonding in the chemistry of the Group 13 metals. Bond lengths, the usual yardstick, offer little help because they are subject to other influences, although the detailed configuration of the molecule may give some clues to the π-type interactions (through the geometries about the atoms forming the bond and the mutual orientations of the substituents carried by those atoms). Variable temperature NMR studies designed to determine the barrier to rotation about a supposed multiple bond are not always straightforward since there may be other conformational changes open to the molecule. On the evidence from this source as recorded up to mid-1995, no barrier to rotation in excess of 50 kJ mol^{-1} has been found for heteronuclear bonds between tri-coordinated aluminium

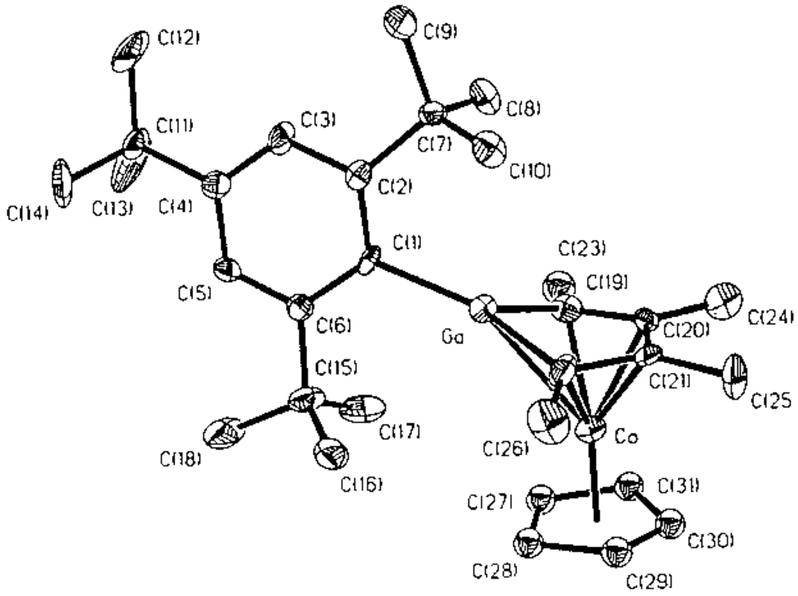
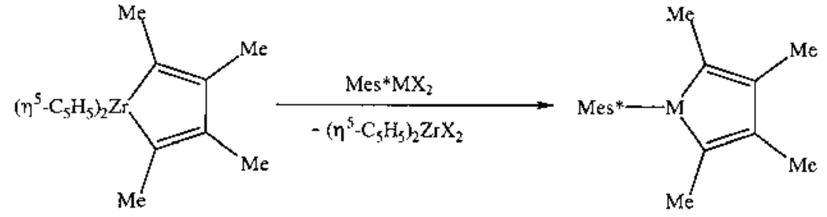


Fig. 4. Skeleton of the complex $[(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-Mes*GaC}_4\text{Me}_4)\text{Co}]$ (Mes* = 2,4,6-$\text{Bu}^t_3\text{C}_6\text{H}_2$) showing the envelope conformation of the previously planar gallacyclopentadiene ring (angle between the C(19)–Ga–C(22) and C(19)–C(20)–C(21)–C(22) planes 21.8°). Reproduced with permission from Ref. [119].

or gallium and an N, P or S atom, e.g. in molecules like $[\text{Bu}^t_2\text{AlN(Dipp)(SiPh}_3)]$ (Dipp = 2,6-$\text{Pr}^i_2\text{C}_6\text{H}_3$–) and $[\text{Mes}^*_2\text{GaSMe}]$ [41].

3.2. Heteronuclear bonds to other main Group elements

The possibility of incorporating a Group 13 metal into a delocalised cyclic array has been explored by the research groups of both Cowley and Power. With the aid of bulky aromatic substituents for protection and the transmetallation Eq. (22), galla- and inda-cyclopentadiene derivatives, **9**, have been prepared [119]. Despite the tri-coordinated geometry at the metal and the planarity of the GaC_4 ring in the gallium compound, the Ga–C distances fall in the normal range for single bonds. Neither by this nor by the mixed sandwich complex $[(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-Mes*GaC}_4\text{Me}_4)$ Co], the structure of which is illustrated in Fig. 4, do we detect any suggestion that delocalisation within the metallacycle extends to the metal atom, although the cobalt complex *can* be viewed as a *nido* cluster provided



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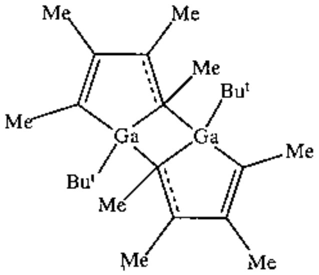
(M = Ga, X = Cl; M = In, X = Br) (22)

the Mes*Ga moiety is included in the framework. If Mes* is replaced by the less bulky Bu^t group, the resulting gallacyclopentadiene forms a rather weakly bound dimer with the structure **10**, quite different from that of the analogous boron compound $[\mathrm{PhBC_4Me_4}]_2$ [120].



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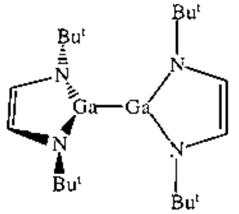
However, attempts to prepare the dianions of these metallacyclopentadienes, which would be isoelectronic with the cyclopentadienide anion, have been unsuccessful. Instead attention has switched to diazabutadiene derivatives of gallium which are also isoelectronic with the cyclopentadienide anion and therefore potentially aromatic. Both monomeric and gallium–gallium bonded diazabutadiene derivatives, exemplified by **11**, have indeed been made [121], but all the structural signs point to the conclusion that delocalisation is confined to the N–C–C–N fragment. Another formal analogue of the cyclopentadienide anion is the aluminium complex **12** which has been prepared by the reaction of azobenzene with $[\mathrm{Mes^*AlH_2}]_2$ in accordance with Eq. (23) [122]. However, the bond lengths, the envelope structure about the non-planar $\mathrm{Al_2N_3}$ ring and the slightly pyramidal geometries at the two adjacent N atoms give little grounds for invoking significant delocalisation in the $\mathrm{Al_2N_3}$ ring.



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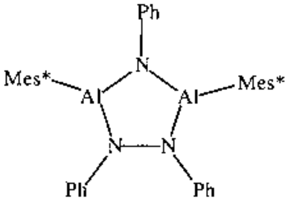


12

$$3/2[\mathrm{Mes^*AlH_2}]_2 + 2\mathrm{PhNNPh} \rightarrow \mathrm{Mes^*}\overline{\mathrm{AlN(Ph)Al(Mes^*)N(ph)N}}\mathrm{Ph} + 1/2[\mathrm{Mes^*AlNPh}]_2 + 3\mathrm{H_2} \qquad (23)$$

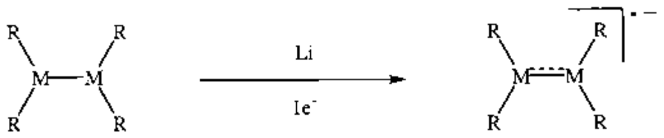
Other heterocycles containing tri-coordinated aluminium bound to a Group 15 or Group 16 atom have been described. These involve four-membered rings for $[\mathrm{Mes^*AlX}]_2$ (X = NPh [123] or S [124]), non-planar six-membered rings for $[\mathrm{Mes^*AlEPh}]_3$ (E = P or As [123]), and an almost planar eight-membered ring for $[\mathrm{Mes^*AlO}]_4$ [125]. However, there is nothing about the geometries or dimensions of these molecules to suggest that π-bonding is at work. Quantum chemical calculations impute only a weak π-interaction to the model monomeric compounds HAlNH and H_2AlNH_2 while denying the existence of a second π-bond in the former [126]. Elaboration of these calculations to take in $[HAlNH]_n$ ($n = 2$ or 4) finds, moreover, that π-interactions play at best a minor role in the oligomerisation of HAlNH [127]. For molecules of the type $R_2MER'_n$ [R, R′ = H, Me; M = Al or Ga; E = N ($n = 2$), O or S ($n = 1$)] ab initio methods have also been exploited to estimate barriers to rotation about the M–E bond as a measure of the π-interactions in these compounds [128]. The barriers being consistently one to two orders of magnitude smaller than that for ethene, it would appear that the π-interactions are indeed weak, with little influence beyond the contribution they make to the conformational equilibrium geometries in the final analysis.

Parkin and his group at Columbia University have followed quite a different path to prepare complexes of gallium and indium in which terminal bonds to selenium or tellurium are supported by the ligating action of the spatially demanding tris(3,5-di-*tert*-butylpyrazolyl)hydroborate ligand $Tp_2^{Bu^t}$, **2** [28]. The method of preparation involves oxidation of the relevant gallium(I) or indium(I) complex by the elemental chalcogen [as in reaction (5), Section 1.2]. Each of the metal–chalcogen bonds is certainly shorter than any other previously reported for that combination of elements. Once again, the effects of the coordination environment and bond polarity must cloud the picture, but it seems reasonable to view the terminal metal–chalcogen bonds as semipolar double bonds [28].

3.3. Homonuclear bonds and bonds to other metal atoms

The best prospects for establishing true valence multiple bonds free from polar effects must be in homonuclear interactions involving two or more Group 13 metal atoms. Such bonds, whether single or multiple, are invariably weak, and their survival hinges typically on the choice of appropriate supporting ligands and anaerobic, base-free conditions. To achieve two- or three-fold coordination of the metal in the face of the natural tendency otherwise to aggregate calls for very bulky substituents.

The best evidence for multiple bonding predating Brothers and Power's review [41] comes from the one-electron reduction (Eq. (24)) of a tetraorganodimetal compound R_2MMR_2, where M = Al or Ga



and R = $CH(SiMe_3)_2$ or 2,4,6-$Pr^i_3C_6H_2$. The paramagnetic anionic product has been isolated, e.g. as $[Li(12\text{-crown-}4)_2]^+[M_2(2,4,6\text{-}Pr^i_3C_6H_2)_4]^-$, and structural studies revealed that reduction causes the M_2C_4 skeleton to become more or less planar and the M–M bond distance to contract by 0.13–0.18 Å to an unprecedentedly short value. The formation of a one-electron π-bond thus implied is also warranted by the EPR properties of the compounds. However, all attempts to bring about a two-electron reduction of the parent compound and so generate an alkene-like dianion have as yet been to no avail.

Of recent advances, none has been more dramatic than the growth of our knowledge of the Group 13 metals Al, Ga and In in the univalent state [1,20,129]. The combination of an appropriately chosen ligand R [e.g. R = C_5Me_5, $C(SiMe_3)_3$, 2,6-(2,4,6-$Pr^i_3C_6H_2)_2C_6H_3$ (**3**), or $Tp_2^{Bu^t}$ (**2**)] and a synthetic strategy depending either on metathesis [starting from a monohalide dissolved in a stabilising solvent, cf. Eqs. (13) and (14)] or on reduction of a trivalent halide (e.g. RMX_2 or R_2MX) has unearthed a rich seam of new compounds of the type RM [20]. Unless R is unusually demanding of space, the RM molecules are associated in the form of oligomeric or polymeric arrays. However, the M···M interactions are only weak, as testified by the volatility of compounds like $[(\eta^5\text{-}C_5Me_5)M]_n$ and $[Ga\{C(SiMe_3)_3\}]_4$ which vaporise as the monomers, and by the dimensions of the monomers which are not perceptibly affected by aggregation. Strikingly, too, the Ga···Ga distances in the octahedral cluster $[(\eta^5\text{-}C_5Me_5)Ga]_6$ are not shorter but slightly *longer* than those in the analogous indium species [47], presumably because the packing requirements of the six C_5Me_5 ligands take precedence over metal–metal interactions in determining the dimensions of the clusters. The compounds are highly reactive, being particularly susceptible to a wide range of addition reactions, frequently to form novel cluster compounds, such as $[\{(\eta^5\text{-}C_5Me_5)Al\}_6P_4]$ [20] and $[RME]_4$ (M = Al, R = C_5Me_5, E = Se or Te [20]; M = In, R = $C(SiMe_3)_3$, E = O [130]), or unwonted compounds founded on homonuclear metal–metal bonds which play havoc with conventional notions of oxidation or valence states, e.g. $[Et_3P{\cdot}GaI_2{\cdot}GaI(PEt_3){\cdot}GaI_2{\cdot}PEt_3]$ [131] and $[(\eta^5\text{-}C_5Me_5)Al{\cdot}AlI_2{\cdot}Al(\eta^5\text{-}C_5Me_5)]^+[(\eta^5\text{-}C_5Me_5)AlI{\cdot}AlI_3]^-$ [132]. Largely through the highly original and technically accomplished research of the groups led by Schnöckel, Uhl and others in Germany, a new chemical landscape is only now starting to materialise.

However, that is another story. What concerns us most in the present context is the possibility of reducing RM aggregates to form species $[RM]_n^{m-}$ having the opportunity for M–M multiple bonding, bearing in mind that $[RMMR]^{2-}$ and cyclic $[R_6M_6]^{6-}$ are formally isoelectronic with ethyne and benzene, respectively. Robinson and his group, now at the University of Georgia, have sprung some truly astounding surprises in this area through the discovery of reduced di- and trigallium complexes in which each gallium atom is deliberately encumbered by the ultrabulky ligand Ar* = 2,6-(2,4,6-$Pr^i_3C_6H_2)_2C_6H_3$ (**3**).

First on the scene came compounds of the type $M_2[Ar^*Ga]_3$ (M = Na or K) prepared by alkali metal reduction, as represented by the transformations (Eq. (25a)) and also (Eq. (25b)) (where metathesis and disproport-

$$3Ar^*GaCl_2 \xrightarrow[-6\ McL]{8M} M_2[Ar^*Ga_3] \quad M = Na\ \text{or}\ K \tag{25a}$$

$$Ga_2Cl_4 \xrightarrow[-LiCl]{Ar^*Li} \xrightarrow[KCl]{K} K_2[Ar^*Ga]_3 \tag{25b}$$

ionation are also implicated) [133]. The dark red crystals are the first examples of a cyclogallane, being composed of regular planar Ga_3 rings with alkali metal atoms sited above and below each ring to complete a trigonal bipyramid (see Fig. 5). The mean Ga–Ga distances [2.441(1) and 2.4255(5) Å in the sodium and potassium compounds, respectively] are unquestionably on the short side compared with the corresponding distances in other compounds known to incorporate Ga–Ga bonds, as listed in Table 4. The structure of what is presumed to be the $[Ar^*Ga]_3^{2-}$ anion has been seized upon as a rare example of a metallic ring system possessing aromatic character, a view supported by calculations at the SCF and DFT levels of theory [134]. Still one cannot help remarking that the Ga–Ga bonds are not as short as those in radical anions of the type $[R_2MMR_2]^-$ [2.343(2) Å, q.v.] or in the neutral compound **11** [2.333(1) Å] where π-bonding is actually *precluded* by the mutual orthogonality of the two GaN_2C_2 planes. That the compounds $M_2[Ar^*Ga]_3$ should be more or less discrete clusters also gives grounds for wondering whether the role of the alkali metal atoms has been accurately assessed.

Whether metallaromatics or not, cyclogallanes were but the preludes to greater surprises, and more heated debate. For the sodium reduction of Ar^*GaCl_2 has been found under appropriate conditions [see reaction (7), Section 1.2] to deliver the compound $Na_2[Ar^*GaGaAr^*]$, hailed at the time as the first Group 13 metal analogue of ethyne [31]. The structure of the deeply coloured crystals, as illustrated in Fig. 6, consists of two Ar* ligands bridged by a pair of gallium atoms separated

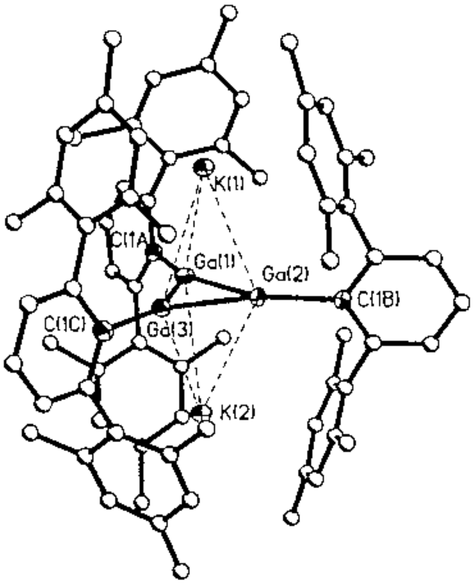


Fig. 5. Molecular structure of $K_2[Ar^*Ga]_3$ in the compound $K_2[Ar^*Ga]_3{\cdot}2Et_2O$ [$Ar^* = 2{,}6\text{-}(Pr^i_3C_6H_2)_2C_6H_3$] showing the trigonal bipyramid formed by the five metal atoms. Reproduced with permission from Ref. [133].

Table 4
Structures and dimensions of selected compounds containing gallium–gallium bonds

Compound[a]	Geometry at gallium	Overall geometry—conformation	Average r(Ga–Ga) (Å)	Reference
$[(\eta^5\text{-}C_5Me_5)Ga]_6$	6-coordinated, pentagonal-based pyramid	Roughly octahedral Ga_6 core; Ga-centroid vectors do *not* point towards the centre of the Ga_6 cluster	4.073(3) –4.173(3)	[47]
$[\{(Me_3Si)_3C\}Ga]_4$	4-coordinated, pseudo-tetrahedral	Tetrahedral Ga_4 core	2.688(4)	[20]
$[(Me_3Si)_2CH]_2GaGa[CH(SiMe_3)_2]_2$	3-coordinated planar	Ga_2C_4 skeleton roughly planar	2.541(1)	[41]
$TMP_2GaGaTMP_2$	3-coordinated planar	Dihedral angle between GaN_2 planes 31°	2.525(1)	[41]
$Trip_2GaGaTrip_2$	3-coordinated planar	Dihedral angle between GaC_2 planes 43.8°	2.515(3)	[41]
$\{(Et_3P)I_2Ga\}_2GaI\cdot PEt_3$	All Ga atoms 4-coordinated, pseudo-tetrahedral	Ga–Ga–Ga skeleton	2.456(1)	[131]
$\{(Et_2O)_2ClGa\}Ga\{GaCl_2(OEt_2)\}_3$	All Ga atoms 4-coordinated, pseudo-tetrahedral	Central G atoms bound to four Ga-centred ligands	2.417(2) –2.450(2)	[20]
$(Et_3P)I_2GaGaI_2(PEt_3)$	4-coordinated, pseudo-tetrahedral	*Trans* staggered geometry overall	2.436(2)	[131]
$K_2[Ar^*Ga]_3$	3-coordinated planar but ∠Ga–Ga–C = 143–147° giving approximately c_{3h} symmetry for the Ga_3C_3 unit	Metal atoms form K_2Ga_3 trigonal bipyramidal cluster (Fig. 5)	2.4255(5)	[133]
$(Pyridine)Br_2GaGaBr_2(pyridine)$	4-coordinated, pseudo-tetrahedral	*Trans* staggered geometry overall	2.421(3)	[1]
$[Pr_4N]_2[Ga_2Br_6]$	4-coordinated, pseudo-tetrahedral	Staggered geometry overall	2.419(5)	[1]
$(Dioxane)Cl_2GaGaCl_2(dioxane)$	4-coordinated, pseudo-tetrahedral	Eclipsed geometry overall with dioxane ligands *gauche*	2.406(1)	[1]
$[Me_4N]_2[Ga_2Cl_6]$	4-coordinated, pseudo-tetrahedral	Staggered geometry overall	2.390(2)	[1]
$Ga_2[Ga_2I_6]$	4-coordinated, pseudo-tetrahedral	Staggered geometry overall	2.387(5)	[1]
$[Li(12\text{-}crown\text{-}4)_2]^+\ [Trip_2GaGaTrip_2]^-$	3-coordinated planar	Dihedral angle between GaC_2 planes 15.5°	2.343(2)	[41]
$(Me_3SiC)_2B_4H_8GaGaB_4H_8(CSiMe_3)_2$	6-coordinated, pentagonal-based pyramid	Two *closo* GaB_4C_2 cages linked via a Ga–Ga bond	2.340(2)	[41]
$Bu^t\overline{NCHCH(Bu^t)NG}a\overline{GaN(Bu^t)CHCHN}Bu^t$	3-coordinated planar	Dihedral angle between GaN_2 planes 90°	2.333(1)	[121]
$Na_2[Ar^*GaGaAr^*]$	2-coordinated, non-linear; ∠Ga–Ga–C = 133.5°	Na_2Ga_2 4-membered ring (Fig. 6)	2.319(3)	[31]

[a] Trip, 2,4,6-$Pr^i_3C_6H_2$; TMP, 2,2,6,6-tetramethylpiperidinyl; Ar*, 2,6-(2,4,6-$Pr^i_3C_6H_2)C_6H_3$ (**3**).

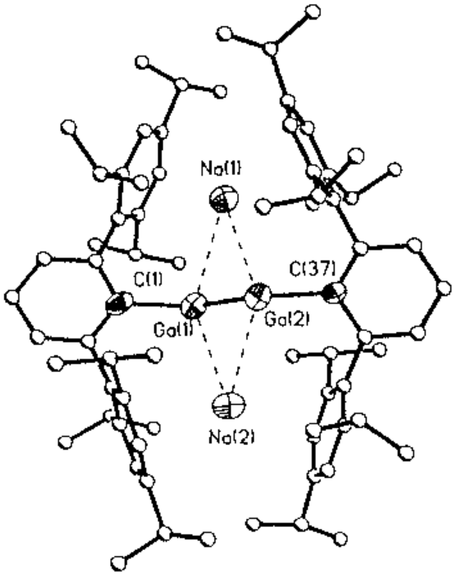
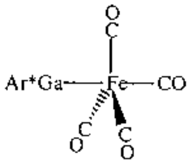


Fig. 6. Molecular structure of $Na_2[Ar^*GaGaAr^*]$ [$Ar^* = 2,6\text{-}(Pr^i_3C_6H_2)_2C_6H_3$] showing the non-linear C–Ga–Ga–C skeleton and the arrangement of the four metal atoms. Reproduced with permission from Ref. [31].

by 2.319(3) Å, with the core being completed by a pair of sodium atoms residing on either side of the Ga–Ga bond and together constituting a nearly planar Ga_2Na_2 four-membered ring. To a first approximation, each gallium atom is indeed two-coordinated, but the case for the so-called gallyne formulation with its implied triple bond, is necessarily marred by a non-linear C–Ga–Ga–C skeleton [with $\angle$Ga–Ga–C = 133.5(4)°]. It has been argued that a triple bond can survive this geometry [31,58,59], with a similar *trans*-bent configuration being predicted for the model compound HGeGeH. The findings that the Ga–Ga distance is not as short as might be expected and that the C–Ga–Ga–C skeleton conforms not to D_h but to C_{2h} symmetry have given rise to doubts in some quarters [80] that two hydrogen atoms have been overlooked, and that the compound is in reality $Na_2[Ar^*(H)GaGa(H)Ar^*]$, i.e. an analogue of ethene rather than ethyne. In any event, the consensus of theoretical wisdom appears to be moving towards a double-bond description of the Ga–Ga linkage in $Na_2[Ar^*GaGaAr^*]$, with a significant part being played in all probability by non-covalent interactions [59,60,118]. Neither experiment nor theory is able to deduce much from the Ga–Ga bond length which shows no obvious correlation with conventional notions of bond order. Without this yardstick, there is perhaps more to be gained from the analogies presented by the characterisation of the radical anion $[Ar^*SnSnAr^*]^-$, i.e. a singly reduced distannyne to all appearances [135]. This, too, is found in the salts that have been isolated to have a *trans*-bent structure similar to the one established for the gallium compound, but all the signs point to weak π-interactions and to the presence of lone pairs on the metal atoms as the principal authors of the angular geometry.

But the Pandora's box opened by Robinson's group is by no means empty. For Ar*$GaCl_2$ is observed also to react with $Na_2[Fe(CO)_4]$ in ether solution with the precipitation of NaCl, leading to the isolation of yellow crystals of the neutral iron–gallium compound [Ar*$GaFe(CO)_4$] [136]. Quite robust under anaerobic conditions, this has the structure **13** with a linear C–Ga–Fe unit and an Fe–Ga bond length of 2.2248(7) Å so short as to encourage the belief in some quarters that a triple bond exists between the metal atoms. There is no denying the intrinsic interest of this compound with its two-coordinated gallium atom. Furthermore, the apparent stabilisation of the Fe–Ga bond may enable the compound to function as a single source precursor, say to FeGa, and so find applications in the fabrication of advanced electronic devices [136]. What is certain is that the notion of an Fe–Ga triple bond has created another furore [118]. In truth, it is difficult to sustain this view. Were there to be such highly developed multiple bonding, one would expect the Ar*Ga substituent to take up an equatorial and not an apical site in the trigonal bipyramidal framework, and the stretching frequencies of the CO groups to be unusually high. Neither of these conditions being met, and for other reasons too [137], it seems more realistic to view the Ar*Ga unit as a two-electron *donor* with minimal π-bonding potential. Such a description assuredly receives support from DFT calculations [137], and the Ga–Fe bonding appears on this evidence to parallel closely the Al–Fe bonding in the analogous compound $[(\eta^5\text{-}C_5H_5)AlFe(CO)_4]$ described by nothing more ambitious than a single Al → Fe bond [138].



13

But experiment shall have the last word in this matter. In the case of indium, the organoindium(I) compound [Ar*In] has been prepared via the metathesis reaction (26) and isolated as

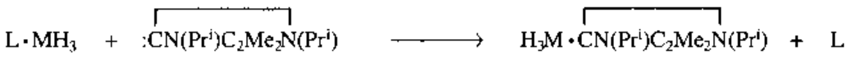
$$InCl + (Et_2O)LiAr^* \xrightarrow{\text{thf, ca. } -78^\circ C} Ar^*In + LiCl + Et_2O \qquad (26)$$

bright orange crystals which are very air-sensitive but thermally stable at temperatures up to 216°C [139]. The crystal structure reveals well separated monomeric Ar*In molecules despite the presence of uni-coordinated indium atoms. The compound acts, moreover, as a Lewis base, displacing THF from $[(\eta^2\text{-}C_5H_5)Mn(CO)_2(THF)]$ to give orange crystals of the manganese–indium complex $[(\eta^5\text{-}C_5H_5)Mn(CO)_2(InAr^*)]$. All the essential features of the gallium complex [Ar*$GaFe(CO)_4$] are reproduced, with a near-linear C–In–Mn linkage and a short In–Mn bond. However, the isolation and characterisation of the parent indium(I) compound puts a different complexion on the findings, clearly endorsing the view that MAr* simply acts as a two-electron σ-donor, while the Ga–Fe and In–Mn bonds owe their deceptive shortness to nothing more extraordinary than the low coordination number of the environment in which the Group 13 metal atom finds itself.

3.4. Epilogue

When the dust of argument has settled, the weight of experimental and theoretical evidence is hard to deny: the Group 13 metals are no match for boron in forming homonuclear or heteronuclear multiple bonds that are appreciably stronger than the corresponding single bonds. In the comparatively rare event that the skeletal symmetry of the molecule admits the drawing of a clear distinction between σ- and π-type interactions, the contribution of the π-component is comparatively slight, being at best comparable with the effects of coulombic or non-bonded interactions. Any such multiple bonding is almost impossible to assess therefore on conclusive experimental grounds; it affects the equilibrium geometry and dimensions of the molecule, but so do the other, non-covalent forces that may be no less decisive in the final analysis. To that extent, there can be little prospect of gauging multiple bonding by the measured interatomic distances.

Where the overall interaction is weak, as in compounds containing homonuclear bonds involving the Group 13 metals, the energy separation between the occupied and unoccupied frontier orbitals is small; as a result, the idealised molecular framework is, at best, highly susceptible to conformational change, and may well give way as a global minimum to a less symmetrical configuration. For example, the model system $[HMMH]^{2-}$ (M = Group 13 metal), which may be presumed at the outset to adopt an ethyne-like structure with D_h symmetry, would have access to a low-lying Π_g excited state (through the promotion of a σ_g electron to a vacant π_g orbital, see Fig. 7). The second-order Jahn–Teller model [1,140] then implies that the π_g bending mode of the H–M–M–H skeleton (**14**) will have an unusually low, possibly negative, force constant. The action of this normal mode mixes together the previously orthogonal σ_g and π_g orbitals with a resultant stabilisation of the occupied orbital. If the promotion energy is sufficiently small, therefore, the preferred equilibrium structure will cease to be linear D_h, transforming instead under the action prescribed by the π_g normal coordinate to *trans*-bent C_{2h}, as found in $Na_2[Ar^*GaGaAr^*]$ [31]. However, once the idealised geometry has been lost, the distinction between σ- and π-type interactions largely disappears, and with it the issue of multiple bonding becomes something of a dead-letter.



$$L\cdot MH_3 + :\overline{CN(Pr^i)C_2Me_2N(Pr^i)} \longrightarrow H_3M\cdot\overline{CN(Pr^i)C_2Me_2N(Pr^i)} + L$$

(M = Al, Ga or In; L = H^- or NMe_3 [23])

Charge-density studies [14] may yet shed light on the true nature of any multiple bonding in which the Group 13 metal atoms are supposed to engage. Otherwise, there is a distinct feeling that the issue is due to join electron deficiency and vacant d-orbital participation (involving main Group elements) as a matter of exegetic more than practical importance. This is not to devalue the intrinsic attraction of compounds like $Na_2[Ar^*GaGaAr^*]$, $K_2[Ar^*Ga]_3$, $[Li(12\text{-crown-}4)_2]^+[M_2(2,4,6\text{-}Pr^i_3C_6H_2)_4]^-$, and $(Tp_2^{Bu^t})GaSe$. Much more is to be gained, however, from explor-

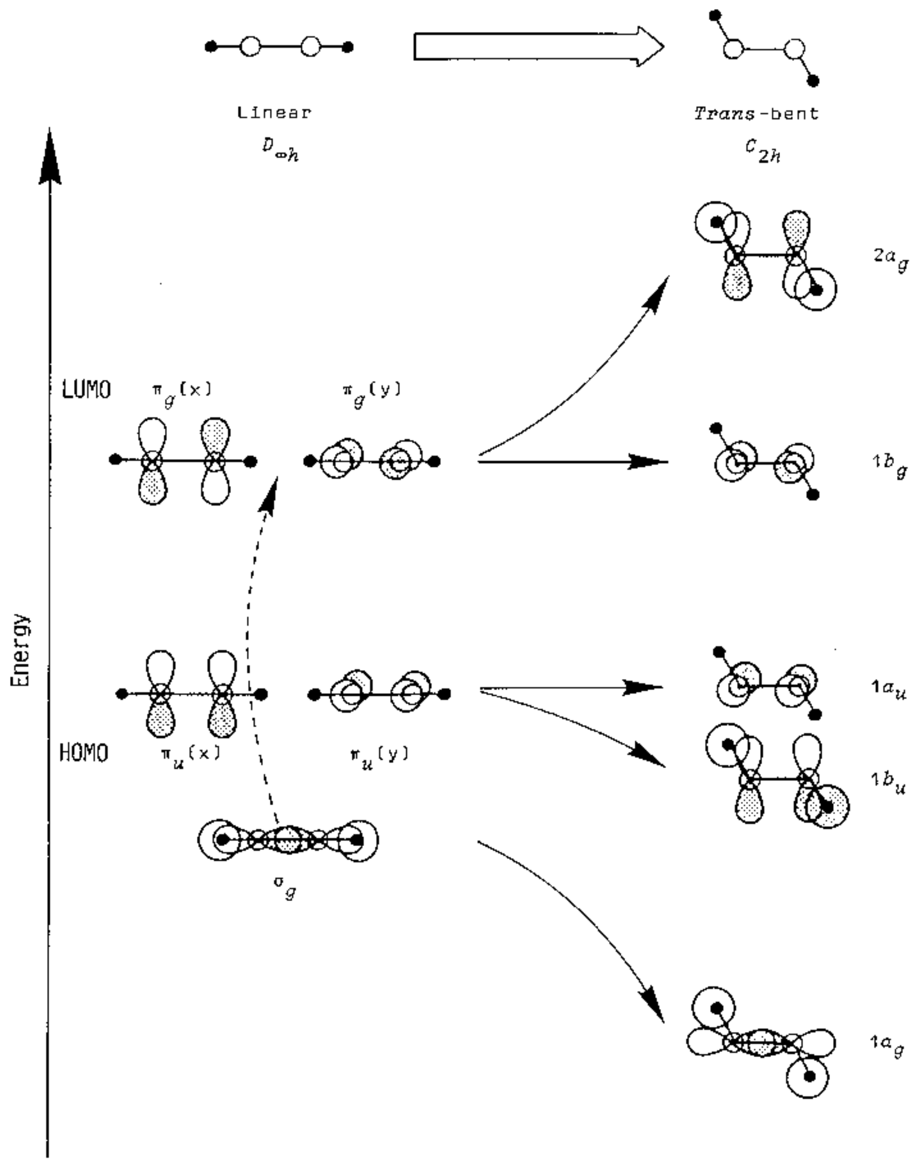


Fig. 7. Qualitative energy diagram for the frontier molecular orbitals of $[HMMH]^{2-}$ (M = Group 13 metal atom) showing the correlation between the linear (D_{h}) and *trans*-bent (C_{2h}) forms.

ing, and elaborating on, not the bonding but the *chemistry* of these highly reactive species which often contain the Group 13 metal in an unusually nucleophilic form. Analysis and models are no substitute for discovery and invention.

4. Conclusions

This review has taken as its text the latest advances in just two areas of Group 13 metal chemistry, namely hydride derivatives and compounds that may engage the metal atoms in multiple bonds. Accordingly, the emphasis has been on discrete molecular, more than macromolecular, compounds, although aggregation and elimination may well give rise to extended solid structures, thereby providing one of the recurring themes of current research. In other respects, hydrides might be thought to have little in common with multiply bound species: the hydride ligand has no propensity itself to enter into significant multiple bonding and is ill adapted to support multiple bonding of the Group 13 metal to which it is bound. There are, however, several features linking the two types of compound. Both typically contain reactive functional groups that are highly susceptible to oxidation, hydrolysis or aggregation. As a result, developments in both areas have depended on similar experimental strategies and on a similar blend of theoretical and practical measures (as indicated by Table 1). Protection of the characteristic functional group has been a central principle with M–H and multiply bonded M atoms alike, experimental progress relying critically on an appropriate choice of reaction medium and/or supporting ligands. In the chemical reactions leading to, or disposing of, the compounds, too, similar patterns of behaviour are found, with addition, aggregation, metathesis and elimination as prevalent reaction pathways.

The present survey has focused on how the different types of compounds are formed, how they have been characterised, with particular reference to the structures they assume, and how they respond to thermal, photolytic and chemical stimuli. Some of the hydrides have potential as synthetic reagents, notably for the reduction of organic and inorganic substrates and in metallation and hydrometallation reactions. Some hold promise as sources of the metal or metal compounds in CVD and other processes giving access to solid materials or assemblies with specific physical properties; here and elsewhere, we find a growing awareness of how the morphology of the solid product can be made to vary with the precursor from which it is derived. By contrast, interest in systems where the Group 13 metal has the opportunity to form multiple bonds has been directed mainly to synthesis and physical characterisation and to analysis of what the bonding actually entails. On the evidence accumulated to date, π-type interactions play only a minor role in the chemistry of the Group 13 metals, their contribution being obscured, at least in part, by the effects of non-covalent interactions. Altogether more promising, though, are the chemical options now created, most notably by the isolation of numerous compounds of the Group 13 metals in low formal oxidation states [20], and including highly reduced species like $Na_2[Ar^*GaGaAr^*]$.

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