

The Hydrides of Aluminium, Gallium, Indium, and Thallium: A Re-evaluation

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1 Introduction

No class of compounds exemplifies better than the hydrides the individualism of the Group 13 elements. In the diversity and profusion of its hydride chemistry,^{1,2} boron gives little hint of the comparative wasteland making up much of the hydride estate of the heavier Group 13 elements.³ At a recent count² about 100 binary boranes are now known, typically as discrete molecules remarkable for their stoichiometries and structures which have done much to challenge and reshape our understanding of chemical bonding at large. By contrast, aluminium forms only one binary hydride stable under normal conditions as a polymeric solid, $[\text{AlH}_3]_n$, the α -form of which is isostructural with AlF_3 , featuring 6-coordinate aluminium atoms.^{3,4} Attempts to prepare the analogous gallium compound have a chequered history,⁵ and it has taken nearly 50 years from the first reported sighting to establish the true credentials of gallane, $[\text{GaH}_3]_n$,⁶ which now emerges as showing obvious affinities to diborane in the vapour state (*i.e.* $n = 2$) while being relatively short-lived under normal conditions. Despite some claims, however, it is unlikely that the hydrides $[\text{InH}_3]_n$ and $[\text{TlH}_3]_n$ have yet materialized.³

In this account we review the current status of the hydrides formed by the Group 13 metals aluminium, gallium, indium, and thallium. Coordinatively saturated derivatives like MH_4^- ($M = \text{Al, Ga, In, or Tl}$) and $\text{Me}_3\text{N} \cdot \text{MH}_3$ ($M = \text{Al or Ga}$) having been known for some years,^{3,4} we are concerned primarily with the parent hydrides, $[\text{MH}_m]_n$ ($m = 1, 2, \text{ or } 3; n = 1, 2, \dots$), and related *unsaturated* derivatives. The last category includes species with more than one Group 13 element, for example tetrahydroborate derivatives like $\text{Al}(\text{BH}_4)_3$ and $\text{H}_m\text{Ga}(\text{BH}_4)_{3-m}$ ($m = 1 \text{ or } 2$) and tetraborane(10) derivatives like $2\text{-R}_2\text{MB}_3\text{H}_8$ ($M = \text{Al, R} = \text{Me}; M = \text{Ga, R} = \text{H or Me}$). It is appropriate first to consider the physical properties of the binary hydrides $[\text{MH}_m]_n$. Hence it is possible to identify not only

feasible methods of synthesizing compounds with $M\text{-H}$ bonds, but also the origins of the thermal lability and reactivity besetting such compounds.

1.1 Theoretical Modelling

Exploration of the Group 13 metal hydrides has been spurred by the greatly enhanced sophistication of modern computational methods which now admit the use of relatively elaborate basis sets, as well as making due allowance for factors like configuration interaction and relativistic corrections.⁷ Where comparisons can be made, such calculations typically yield dimensions and energetics which reproduce closely the experimental findings, and in some cases *improve upon* those findings. Such is the case, for example, with the monohydride molecules MH ($M = \text{B, Al, Ga, In, or Tl}$), which are short-lived under normal conditions.^{8,9} Accordingly we can place some trust in such results to anticipate the *likely* equilibrium molecular structures, vibrational properties, and binding energies of Group 13 hydrides, including numerous species whose existence has yet to be authenticated. Just what inferences are to be drawn will be discussed in Section 2.

1.2 Experimental Methods

In many cases, then, theory appears to lead experiment. In fact, the relation is more nearly a synergistic one, for the recent flurry of theoretical enquiries¹⁰ has been stimulated to a large extent by experiments, and notably by the synthesis and characterization of gallane, $[\text{GaH}_3]_n$.^{5,6} The practical side is apt to be a Sisyphean task. The hydrides of the Group 13 metals are, without exception, unusually susceptible to attack by air or moisture. None is thermally robust and most decompose at ambient temperatures. That the compounds are nearly always handled *in vacuo* is a minimum, not a sufficient requirement. Among the special procedures which it has been necessary to

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reactive-hydrido- and organo-derivatives of typical and transition elements with matrix isolation and various spectroscopic techniques. Following his Ph.D. research at Cambridge on perfluoroorganosulphur compounds, supervised by the late Professor H. J. Emeléus, F.R.S., he held a Salters' Fellowship in 1961–2. Prior to the move to Oxford, he was a Senior Demonstrator (1962–3) then Lecturer (1963–6) at the University of Newcastle upon Tyne.

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Tony Downs. He remained in Oxford for a further two years as a postdoctoral research assistant and as an EPA Cephalosporin Junior Research Fellow at Linacre College. In 1992 he was awarded a Royal Society University Research Fellowship and moved to the University of Edinburgh. His current research interests include structural studies of the Group 13 hydrides in the condensed phases and the development of the hydride chemistry of tin and lead.

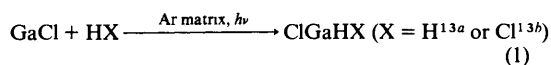
adopt is the use of *all-glass apparatus* individually constructed for each experiment and with provisions (i) for rigorous pre-conditioning (ideally by heating under continuous pumping) and (ii) for close temperature control extending over all the exposed surfaces to which the hydride has access. Manipulation and characterization of the product then depend on keeping the temperature and vapour pressure down to the levels compatible with the experimental needs. As to the detection and specification of a Group 13 metal hydride, there are four aspects which stand out.

1.2.1 Vapour Studies at Low Pressure

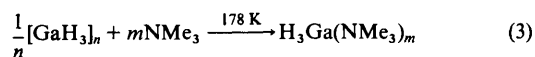
Vapour samples including low partial pressures of the molecules may be generated, usually by high-energy methods involving, for example, the action of an electric discharge on M/H₂ mixtures (as with MH, where M = Al,^{11a} Ga,^{11b} In,^{11c} or Tl,^{11d} and AlH₂^{11e}), but in the case of Ga₂H₆ simply by careful vaporization.^{5,6} The sample can then be interrogated in various ways. For example, the electronic emission spectrum may admit the characterization of various electronic states of MH^{11d} and AlH₂^{11e} molecules. The infrared spectrum measured ideally at high resolution, as in studies using a diode laser, may afford a detailed picture of the dimensions as well as the vibrational and rotational properties of MH molecules in their electronic ground states.^{11b,c} Mass spectroscopy is a third option, which has been exploited to test for the molecules MH₃ (M = Al, Ga, or In) and Al₂H₆ in high-temperature vapours.¹² Yet another method of attack is to appeal to the electron-diffraction pattern of the vapour, as in the case of Ga₂H₆,^{5,6} to determine the vibrationally averaged structure of the molecule.

1.2.2 Trapping Experiments

The tracking and identification of Group 13 metal hydrides have frequently called for trapping. This may be achieved *physically* by quenching the vapour on a cold surface either alone or with an excess of a suitable diluent, or by photolysis of appropriate precursors also trapped in a low-temperature matrix.⁵ For example, the reactions 1 and 2 have been shown to occur on broad-band irradiation of matrix samples.



Alternatively the experimenter may resort to *chemical* trapping of the hydride by treating it with a compound likely to undergo a facile and quantitative reaction yielding a known product. An illustration is provided by the addition reaction 3 which gives rise to the known adducts H₃Ga(NMe₃)_m (m = 1 or 2) and so attests to the identity of the hydride precursor.^{5,6}



1.2.3 Infrared Spectroscopy

Foremost among the properties used to identify and characterize a Group 13 metal hydride is its infrared spectrum. As with the study of metal carbonyls, it is the stretching vibrations which by their energies and intensities are likely to offer the most telling commentary on the molecular identity. Where $\nu(\text{C}-\text{O})$ modes differentiate between terminal and bridging carbonyl functions, so $\nu(\text{M}-\text{H})$ modes differentiate between terminal and bridging M-H functions.⁵ For example, the stretching fundamentals of terminal Ga-H bonds give rise to strong infrared absorptions in the range 1720–2050 cm⁻¹, whereas the corresponding vibrations of bridging Ga-H-Ga units absorb with variable intensity in the range 900–1720 cm⁻¹. In addition, the energies

and intensities of the symmetric and antisymmetric stretching vibrations of an M-H-M bridge give a useful indication of the M-H-M bond angle.^{5,6} Other questions of interpretation affecting, say, the molecular structure can be addressed by examining the response of the spectrum to changes of isotopic composition. Thus, the infrared spectra associated with the different isotopomers MH_xD_{2-x} (M = Al^{14b,15a} or Ga;^{15b} x = 0–2) and AlH_xD_{3-x} (x = 0–3)^{14a} leave little doubt about the equivalence of the hydrogen atoms in each of these molecules.

1.2.4 Structure Determination

Such is the thermal instability of most of the hydrides formed by the Group 13 metals that it would be a brave, and possibly vain venture to attempt to grow single crystals. Preliminary studies of deuteriated gallane do show encouraging signs that crystalline powder samples at low temperatures are amenable to neutron diffraction.¹⁶ However, there is ample circumstantial evidence that aggregation is a primary motif and that the form of such compounds is liable to vary substantially from one phase to another. In practice, definitive measurements of the structures and dimensions of discrete hydride molecules have depended mostly on detailed analyses of the rotational lines associated with specific vibrational transitions. These may appear either in infrared absorption (e.g. for molecules of the type MH^{11b,c}) or in the optical emission spectrum characterizing one or more excited electronic states of the molecule (e.g. MH^{11d} and AlH₂^{11e}). The only other method of structure determination to be enlisted for discrete gaseous molecules is electron diffraction. This has been the principal agent of characterization not only for the binary gallium hydride Ga₂H₆,⁶ but also for mixed hydrides like GaBH₆,¹⁷ HGa(BH₄)₂,¹⁸ and 2-GaB₃H₁₀.¹⁹

2 Physical Properties of the Hydrides

The hydrides of the Group 13 metals carry bonds which are polarized in the sense M^{δ+}-H^{δ-}. The pseudo-anionic hydrogen ligand is thus susceptible to electrophilic attack, and the metal centre to nucleophilic attack, this partly by virtue of the positive charge and partly by virtue of the vacant orbital which it bears. Herein lie the seeds of aggregation and other distinctive properties.

Table 1 lists thermodynamic and vibrational properties, together with dimensions, for Group 13 hydrides of the types MH, MH₂, and [MH₃]_n (n = 1 or 2). The parameters elicited from *ab initio* calculations have been augmented, where possible, by experimental results so that there are some opportunities for testing how well theory imitates nature. All but one of the species are gaseous molecules; the sole exception is the solid polymer [AlH₃]_n which appears to be unique among the binary hydrides of Group 13 in being formed *exothermally* from the constituent elements in their standard states. Analysis of the properties *en bloc* brings out a number of features germane to this class of compounds at large.

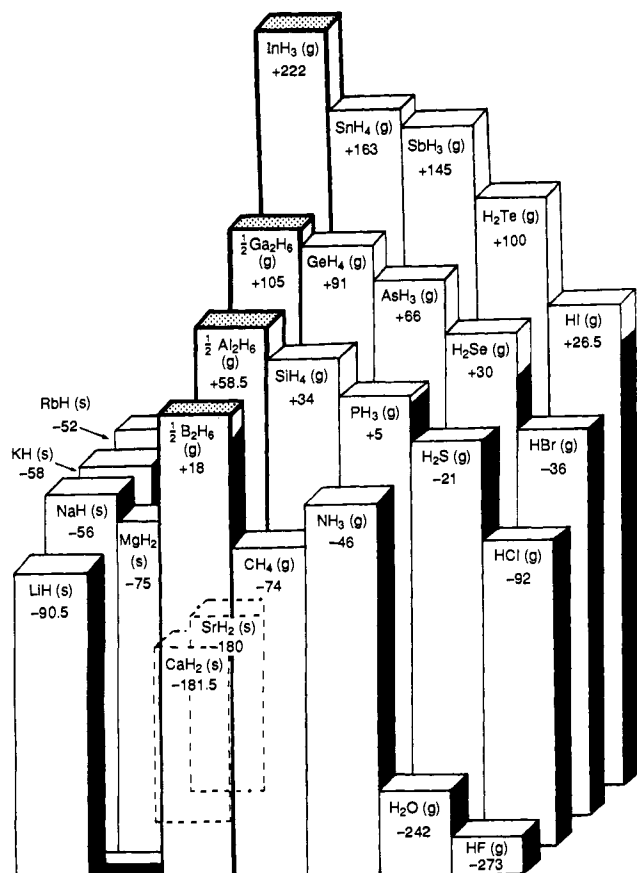
2.1 Heats of Formation

All the gaseous molecules are endothermic with respect to the elements in their standard states; allowance for the effects of entropy indicates that none of them is thermodynamically stable at normal temperatures with respect to the decomposition reaction 4. On the other hand, the unsaturated valence shell of the species MH_n, allied to the relatively electron-rich nature of the hydrogen ligands, means that substantial stabilization is to be found through aggregation with the formation of M-H-M bridges. Thus, the best estimates of the standard enthalpy change associated with reaction 5 are -82, -64.5, and -46 kJ mol⁻¹ for M = B, Al, and Ga, respectively.^{10c} In the case of aluminium such aggregation can continue to give the polymer [AlH₃]_n with each Al atom bound to six bridging H atoms;⁴ that ΔH for reaction 6 is estimated^{8a,20} to be -169 kJ mol⁻¹ must be a major factor governing the stability of the solid hydride.

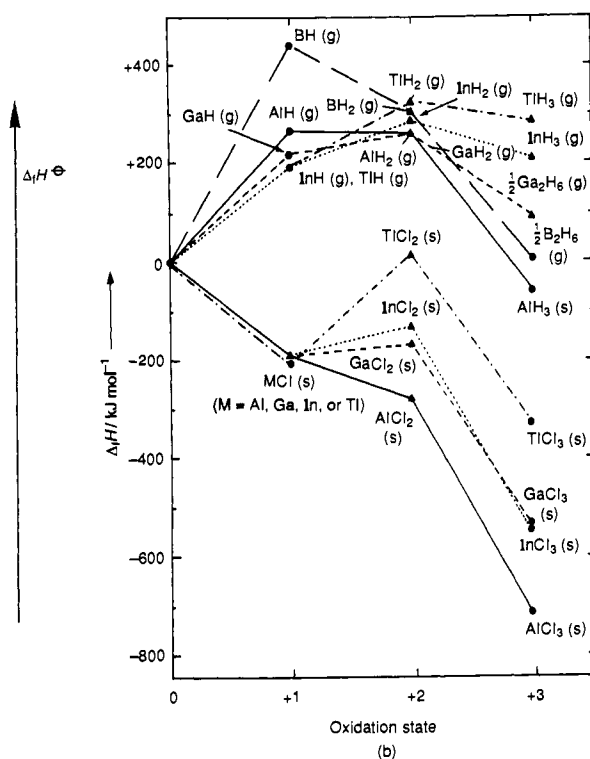
Table 1 Physical properties of the simplest binary hydrides of the Group 13 elements

Molecule	Dimensions ^c			Thermodynamic properties ^b			Vibrational properties, ^c		
	theor		exp	theor		exp	theor		exp
	$r_e(\text{M}-\text{H})/\text{pm}$ (angle/°)	$r_e(\text{M}-\text{H})/\text{pm}$ (angle/°)	$r_e(\text{M}-\text{H})/\text{pm}$ (angle/°)	$B(\text{M}-\text{H})/\text{kJ mol}^{-1}$	$\Delta_f H_{298}^\circ/\text{kJ mol}^{-1}$	$B(\text{M}-\text{H})/\text{kJ mol}^{-1}$	$\Delta_f H_{298}^\circ/\text{kJ mol}^{-1}$	$\nu(\text{M}-\text{H})/\text{cm}^{-1}$	
¹¹ BH ₃ (g)	122.5, ^d 123.0, ^e 124.1, ^f 122.7 ^g	123.24 ^h	123.24 ^h	347.4 ^d	+435.6 ^d	333.9 ⁱ	+449.6 ⁱ	2513, ^{*d} 2532, ^g	2366.90 ^h
¹¹ BH ₂ (g)	118.5 (126.5), ^d 119.4 (127.1) ^g	r_0 118 (131) ^y	—	344 ^d	+313 ^d	ca 400 ^d	+201 ^d	2867, ^{* 2728^{*d}}	—
¹¹ BH ₃ (g)	118.8, ^d 119.3 ^f (120)	—	—	379 ^d	+82.4 ^d	373 ⁱ	+100.0 ⁱ	2813, ^{* 2693^{*d}}	2808, ^{* 2623^{*k}}
$\frac{1}{2}$ ¹¹ B ₂ H ₆ (g)	118.9(t), 132.4(b), ∠B-H _b -B 84.8 ^l	118.4(t), 131.4(b), ∠B-H _b -B 83.1 ^m	—	—	+19.6 ^l	—	+17.8 ^l	2785—1758 ^l	2613—1615 ^{*n}
AlH ₃ (g)	165.2, ^d 166.5, ^e 167.4, ^f 165.1 ^g	164.738 ^o	164.738 ^o	303 ^d	+245 ^d	289 ⁱ	+259.2 ⁱ	1771, ^{*d} 1738 ^g	1682.43 ^o
AlH ₂ (g)	159.5 (118.0), ^d 159.0 (118.7) ^g	r_0 159 (119) ^p	—	249 ^d	+268 ^d	—	—	1976, ^{* 1954^{*d}}	1799, ^{* 1766^{*q}}
AlH ₃ (g)	158.4, ^d 158.6, ^e 159.3, ^f 157.1 ^g (120)	—	—	287 ^d	+123 ^d	—	—	2024, 2021 ^r	1882.7 ^{*r}
$\frac{1}{2}$ Al ₂ H ₆ (g)	156.3(t), 171.9(b), ∠Al-H _b -Al 97.9 ^l	—	—	—	+58.5 ^{d,l}	—	—	2047—1368 ^l	—
$\frac{1}{n}$ [AlH ₃] _n (s)	—	r_0 171.5, ∠Al-H _b -Al 141.2 ^s	—	—	—	—	-46.0 ^r	—	ca 1600 ^{*t}
GaH ₃ (g)	167.5, ^e 169.6, ^f 166.2, ^u 167.2, ^v 167.7 ^g	166.2118 ^w	166.2118 ^w	271 ^u	+224 ^u	270 ⁱ	+225 ^u	1612, ^u 1605 ^e	1603.9566 (6 ^o GaH) ^y
GaH ₂ (g)	158.0 (120.3), ^u 160.0 (119.5), ^v 158.0 (119.7) ^g	r_e — (136) ^z	—	220 ^u	+274 ^u	—	—	—	1799, ^{* 1728^{*x}}
GaH ₃ (g)	157.7, ^e 158.6, ^f 156.5, ^l 155.7, ^u 158.2 ^v (120)	—	—	260 ^u	+151 ^u	—	—	2055, 2028 ^l	—
$\frac{1}{2}$ Ga ₂ H ₆ (g)	155.2(t), 175.3(b), ∠Ga-H _b -Ga 96.1 ^l	r_0 152(t), 171(b), ∠Ga-H _b -Ga 98 ^l	—	—	+105 ^u	—	—	2101—1294 ^l	1993—1202 ^{*y}
InH ₃ (g)	183.8, ^e 185.0, ^f 182.3, ^z 184.9 ^g	183.77630 ^{aa}	183.77630 ^{aa}	250 ^z	+211 ^z	257 ^{bb}	+204 ^{bb}	1469, ^z 1535 ^e	1475.4343 (11 ^o InH) ^{aa}
InH ₂ (g)	178.2 (119.7), ^{bb} 175.5 (119.0) ^g	—	—	191 ^{bb}	+296 ^{bb}	—	—	—	—
InH ₃ (g)	172.5, ^e 173.4, ^f 175.3 ^{bb} (120)	—	—	225 ^{bb}	+222 ^{bb}	—	—	—	—
TlH ₃ (g)	189.9, ^e 191.2, ^f 188.3, ^{cc} 189.9 ^g	187.02 ^h	187.02 ^h	197 ^{bb,cc}	+203 ^{bb,cc}	199 ^{bb}	+201 ^{bb}	1413, ^{cc} 1300, ^{dd} 1383 ^e	1391.2681 (20 ^o TlH) ^{cc}
TlH ₂ (g)	185.4 (121.5), ^{bb} 177.6 (119.9), ^{cc} 176.0 (121.7) ^g	—	—	143 ^{bb}	+332 ^{bb}	—	—	—	—
TlH ₃ (g)	174.5, ^e 175.6, ^f 178.8, ^{bb} 173.9 ^{cc} (120)	—	—	180 ^{bb}	+297 ^{bb}	—	—	—	—

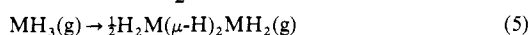
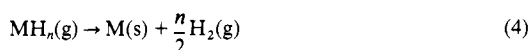
^a b bridging atom, t terminal atom ^b B refers to the actual M-H bond energy for MH, but to the mean M-H bond energy for molecules containing more than one M-H bond ^c Vibrational wavenumbers are for a harmonic oscillator unless labelled with an asterisk which denotes an anharmonic oscillator ^d Ref 8a *ab initio* MO theory, Møller-Plesset theory to full fourth order with a series of extended basis sets ^e Ref 9 *ab initio* relativistic MO theory, Møller-Plesset theory to second order allowing for spin-orbit coupling ^f Ref 9 *ab initio* relativistic MO theory with quadratic configuration interaction and allowing for spin-orbit coupling ^g Ref 8e *ab initio* SCF + CI calculations using effective core potentials and taking account of relativistic effects for the heaviest atoms ^h Ref 11d ⁱ Ref 20 ^j G Herzberg and J W C Johns, *Proc. Roy. Soc.*, 1967, **298A**, 142 ^k A Kaldor and R F Porter, *J. Am. Chem. Soc.*, 1971, **93**, 2140 ^l Ref 10c *ab initio* MO theory, single and double excitation coupled cluster (CCSD) method with DZP basis sets ^m J L Duncan and J Harper, *Mol. Phys.*, 1984, **51**, 371 ⁿ J L Duncan, *J. Mol. Spectrosc.*, 1985, **113**, 63 ^o Ref 11a ^p Ref 11e ^q Ref 15a ^r Ref 14a ^s Ref 4 ^t H Roszinski, R Dautel, and W Zeil, *Z. Phys. Chem. (Frankfurt am Main)*, 1963, **36**, 26 ^u Ref 8b *ab initio* MO theory, complete active space CASCF (CASCF) followed by full second-order configuration interaction (SOC) calculations ^v Ref 8d *ab initio* MO theory, Møller-Plesset correlation corrections to fourth order, MP2 = Full optimization ^w Ref 11b ^x Ref 15b ^y Ref 6 ^z Ref 8c *ab initio* MO theory, complete active space MCSCF (CASCF)/second-order configuration interaction/relativistic CI calculations ^{aa} Ref 11c ^{bb} K Balasubramanian and J X Tao, *J. Chem. Phys.*, 1991, **94**, 3000 *ab initio* MO theory, complete active space multiconfiguration SCF/second-order configuration interaction/relativistic CI calculations ^{cc} P Schwerdtfeger, P D W Boyd, G A Bowmaker, H G Mack, and H Oberhammer, *J. Am. Chem. Soc.*, 1989, **111**, 15 *relativistic pseudopotential MO calculations* ^{dd} P A Christiansen, K Balasubramanian, and K S Pitzer, *J. Chem. Phys.*, 1982, **76**, 5087 *relativistic calculations including spin-orbit coupling and configuration interaction* ^{ee} R-D Urban, A H Bähnmaier, U Magg, and H Jones, *Chem. Phys. Lett.*, 1989, **158**, 443



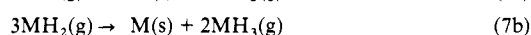
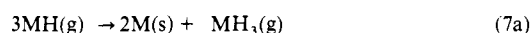
(a)



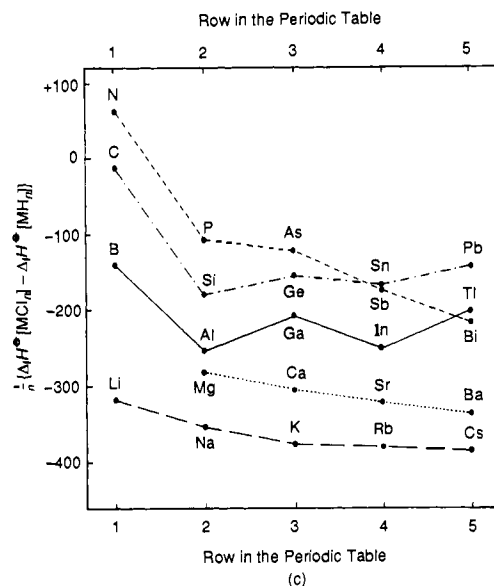
(b)



How the gaseous MH_3 molecules compare in their heats of formation with the hydrides formed by adjacent elements in the Periodic Table is illustrated in Figure 1(a). Hence it is apparent that the Group 13 hydrides are peculiarly high-energy species, the heat of formation of the characteristic hydride formed by each element in a given period rising to a maximum at Group 13. This position is modified somewhat when the hydrides assume their natural forms at room temperature. Thus, the hydrides of the alkali and alkaline-earth metals are typically exothermic compounds by virtue of the large (mainly coulombic) stabilization energies which accrue through hydrogen-bridging on lattice-formation. The corresponding energies, although substantial for AlH_3 (as noted above), are smaller for the other MH_3 species in Group 13, and assume still less importance to the gross stabilities of the hydrides formed by the elements in succeeding Groups.



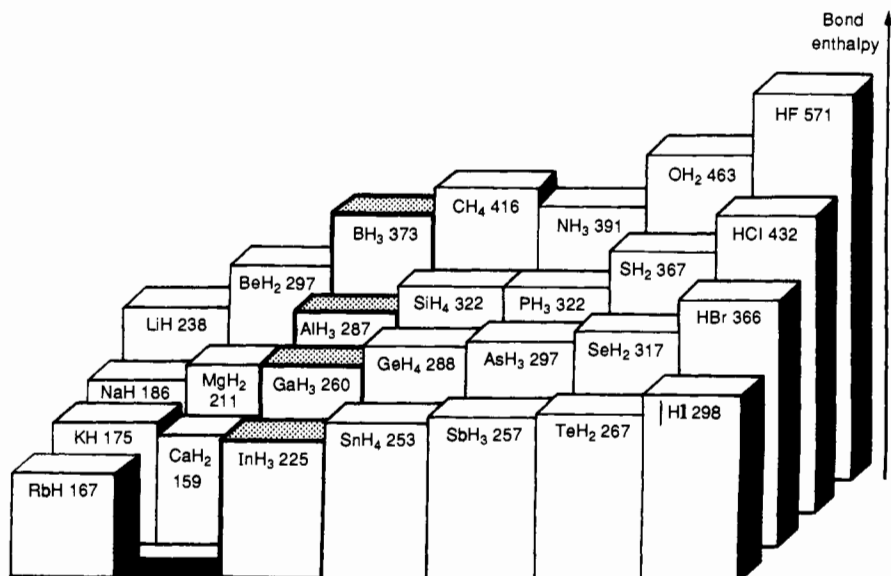
The heats of formation of the different Group 13 hydrides, MH_n , can also be compared, in juxtaposition to those of the solid chlorides, in a thermochemical oxidation state diagram [see Figure 1(b)]. Under normal conditions and for all M, the results show that MH and MH_2 molecules are both highly susceptible to disproportionation in accordance with equations 7a and 7b. By contrast, although solid MCl_2 is invariably unstable with respect to disproportionation, solid MCl is prone to disproportionate when $\text{M} = \text{Al}$ but not when $\text{M} = \text{Tl}$. In this respect,



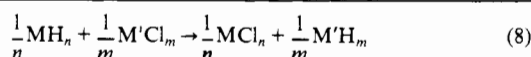
(c)

Figure 1 Thermodynamic properties of Group 13 metal hydrides: (a) standard enthalpies of formation, $\Delta_f H_{298\text{K}}^\circ$ (in kJ mol^{-1}), of *s*- and *p*-block hydrogen compounds; (b) oxidation state diagram giving experimental (●) or estimated (▲) values for the standard enthalpies of formation of compounds of the types MX , MX_2 , and MX_3 ($\text{M} = \text{Group 13 element}$; $\text{X} = \text{H or Cl}$); and (c) standard enthalpy changes for the reaction $\frac{1}{n}\text{MH}_n + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \frac{1}{n}\text{MCl}_n + \frac{1}{2}\text{H}_2(\text{g})$, where M is an *s*- or *p*-block element.

then, hydrogen is akin to CH_3 , being a σ -type ligand with little potential to bring out oxidation states lower than +3, even in an element like thallium. At high temperatures, where entropy changes are likely to have a major voice, however, the thermodynamic balance will inevitably tilt in favour of MH .



(a)



A comparison of the energetics of formation of hydrides and chlorides is revealing too for what it tells us about the feasibility of metathesis reactions of the type shown in equation 8. Figure 1(c) plots periodic variations in the enthalpy change attending

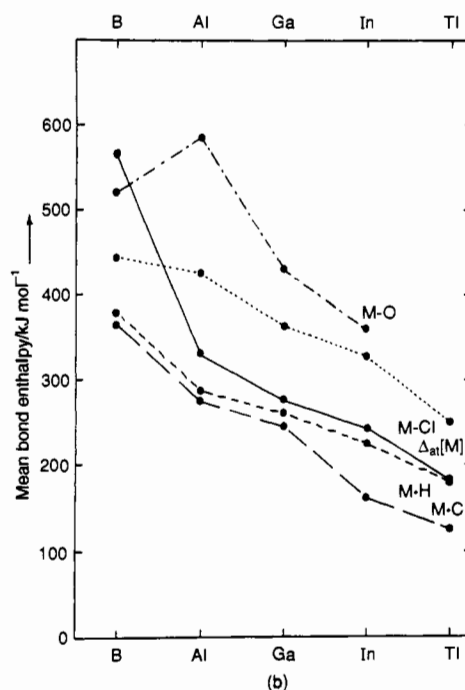
the transformation $\frac{1}{n} \text{MH}_n + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \frac{1}{n} \text{MCl}_n + \frac{1}{2} \text{H}_2(\text{g})$. The

more exothermic the process, the greater is the potential of MH_n —and its derivatives, presumably—as a precursor to the hydrides of other metals. In this respect, as Figure 1(c) demonstrates, the more-or-less ionic hydrides formed by the metals of Groups 1 and 2 are unsurpassed. In practice, for reasons of low solubility, purity, and state of subdivision, they do not always live up to their potential. The Group 13 elements clearly occupy a position intermediate between the *s*-block metals and the less metallic *p*-block elements of Groups 14 and 15. Aluminium stands out in Group 13 as the element which emulates most closely the metals of Groups 1 and 2. This reduces severely the synthetic options for the preparation of aluminium hydrides; for example, reaction 9 which works well as a source of gallium hydrides with $n = 1^{21a}$ or 2^{21b} has no useful counterpart for aluminium, once it is appreciated that the reagent Me_3SiH is itself made by chloride-hydride exchange normally at the expense of the Al-H bonds of LiAlH_4 .



2.2 Bond Enthalpies

The Group 13 metal hydrides, $[\text{MH}_3]_n$, owe their elusiveness, so it is commonly suggested, purely and simply to the weakness of the M-H bonds, as opposed to the strengths of the M-M and H-H bonds in the elements. That 'the truth is rarely pure and never simple' appears to be the principle upheld by the mean bond enthalpies displayed in Figures 2(a) and 2(b). Weak the M-H bonds may be on average, certainly compared with their M-Cl and M-O counterparts (thereby accounting in part for their vulnerability to attack by air and moisture), and also with the bonds to hydrogen formed by adjacent *p*-block elements of Groups 14–17. Yet they are stronger than the metal-hydrogen bonds incorporating neighbouring *s*-block metals (notwithstanding the durability of the solid hydrides formed by these metals); they are also marginally stronger than the analogous M-C bonds²² (notwithstanding the position *vis-à-vis* compounds of the type MMe_3 which, unlike the hydrides, are well authenticated and long-lived at room temperature).



(b)

Figure 2 Mean bond enthalpies (in kJ mol^{-1}) (a) for hydrogen compounds of the *s*- and *p*-block elements, and (b) for the bonds formed by Group 13 elements to H, Cl, O, and C in comparison with $\Delta_f H_{298}^\circ$ for the gaseous metal atoms.

The explanation of these anomalies, which is partly thermodynamic and partly kinetic, hinges on the capacity of the metal M and the ligand X to enter into the formation of M-X-M bridges. Reliable thermodynamic data are sparse but some idea of the strengths of M-X-M bridges for the Group 13 elements B, Al, Ga, and In may be gained from the estimated mean bond enthalpies listed in Table 2. In the case where X = H, the bridges vary in strength in the order $\text{B} > \text{Al} > \text{Ga}$, but for X = Cl or Me the order changes to $\text{B} \ll \text{Al} > \text{Ga}$; with M = Al or Ga the bridges become weaker as X changes in the sequence $\text{Cl} > \text{H} > \text{Me}$. The metals of Groups 1 and 2 are also electronically unsaturated in discrete molecules like MH or MH_2 and they too have the ability to aggregate through M-H-M bridges. The signs are that the individual M-H-M bridges are somewhat weaker than those formed by the Group 13 metals, but the greater degree of unsaturation of the *s*-block elements

Table 2 Strengths of bridging bonds $M-X_b-M$, where $M = B, Al, Ga, \text{ or } In$ and $X = H, Cl, \text{ or } Me$ (mean bond energies, B , in kJ mol^{-1})

Group 13 element, M	$X = H^a$		$X = Cl^a$		$X = Me^a$	
	$B(M-X_b-M)$	$B(M-X_b-M) - B(M-X_t)$	$B(M-X_b-M)$	$B(M-X_b-M) - B(M-X_t)$	$B(M-X_b-M)$	$B(M-X_b-M) - B(M-X_t)$
B	451 ^b	76 ^b	444 ^c	ca. 0	370 ^d	ca. 0
Al	351 ^b	64 ^b	575 ^c	195 ^c	324 ^d	43 ^d
Ga	306 ^b	46 ^b	407 ^c	51 ^e	ca. 259 ^{d,f,g}	ca. 3 ^{f,g}
In	?	?	394 ^b	66 ^b	ca. 233 ^{d,f}	ca. 15 ^f

^a $B(M-X_b-M) = B(M-X_t) + \frac{1}{2}\Delta H[M_2X_6(g) \rightarrow 2MX_3(g)]$. No allowance has been made for the effects of 'reorganization' (see K. Wade, 'Electron Deficient Compounds', Nelson, London, 1971, pp. 128–131). Subscripts: b bridging; t terminal. ^b See Table 1. ^c Ref. 20. ^d Ref. 22. ^e C. Chatillon and C. Bernard, *J. Cryst. Growth*, 1985, 71, 433. ^f Estimate based on the thermodynamics of vaporization. ^g D. S. Matteson, 'Organometallic Reaction Mechanisms', Academic Press, New York, 1974, p. 38. ^h F. Defoort, C. Chatillon, and C. Bernard, *J. Chem. Thermodynamics*, 1988, 20, 1443.

causes this factor to be outweighed by the *number* of such bridges (6 or 8) filling out the coordination shell of the metal in the extended three-dimensional array of the crystalline solid. The same principle is presumably at work with solid $[AlH_3]_n$ which owes its unusual thermodynamic stability ultimately to the propensity of aluminium to rise to six-fold coordination.³ By contrast, gallium tends to follow boron in remaining four-coordinate. Indium and thallium are more prone to assume high coordination numbers but the weakness of In–H and Tl–H interactions then militates against the formation of a solid stable at normal temperatures.

Insofar as decomposition of a discrete molecular hydride MH_n may be initiated by homolytic dissociation of an M–H bond, it is not obvious why a Group 13 hydride like gallane should be so much more labile than, say, stannane [see Figure 2(a)]. Presumably, however, there are circumstances in which an *associative* mechanism, possibly preceding concerted elimination of H_2 , offers a lower barrier to reaction than does a purely dissociative one. In that case the tendency of the hydride to associate or dissociate and the strength of M–H–M bridge bonds are likely to be crucial to the kinetics of decomposition. By contrast, decomposition of the methyl derivatives Me_3M appears typically to be dissociatively activated²² and so to be opposed by a relatively large energy barrier; in this case associative activation is made ineffectual by the weakness of M–Me–M bridges. It would be fascinating to know more about the kinetics of decomposition of a molecule like Ga_2H_6 in the gas phase, particularly in the light of the complex behaviour of B_2H_6 on pyrolysis,^{1,2} but it will be a tall order to prevent heterogeneous surface reactions from playing the dominant rôle.

2.3 Structures

On the accumulated evidence of experimental and theoretical enquiries, the M–H bonds in monomeric Group 13 metal hydrides vary in length in the order $MH > MH_2 \approx MH_3$, the trihydride typically displaying M–H bonds up to 10 pm shorter than that in the monohydride. The MH_2 molecules in their electronic ground states are bent with bond angles close to 120° , as attested experimentally in the case of AlH_2 .^{11e} The MH_3 molecules in their electronic ground states are planar with D_{3h} symmetry, in keeping with the prognosis of VSEPR theory, and that too finds support from the first definite sighting of the AlH_3 molecule,¹⁴ as generated in a low-temperature matrix and identified by its infrared spectrum.

Perhaps the most distinctive property of the hydrides in physical terms is their proclivity for aggregation. With regard to the dimer of MH_3 , a single configuration seems to hold sway, namely the familiar diborane-like one, $H_2M(\mu-H)_2MH_2$, as deduced experimentally for Ga_2H_6 (Figure 3) on the grounds of its infrared spectrum and electron-diffraction pattern.^{5,6}

For the dimers $[MH]_2$ and $[MH_2]_2$, however, the situation is evidently more complicated, although this is an area where hypothesis leads and experiment lags far behind. Diborene, B_2H_2 , the boron analogue of acetylene, has a linear triplet

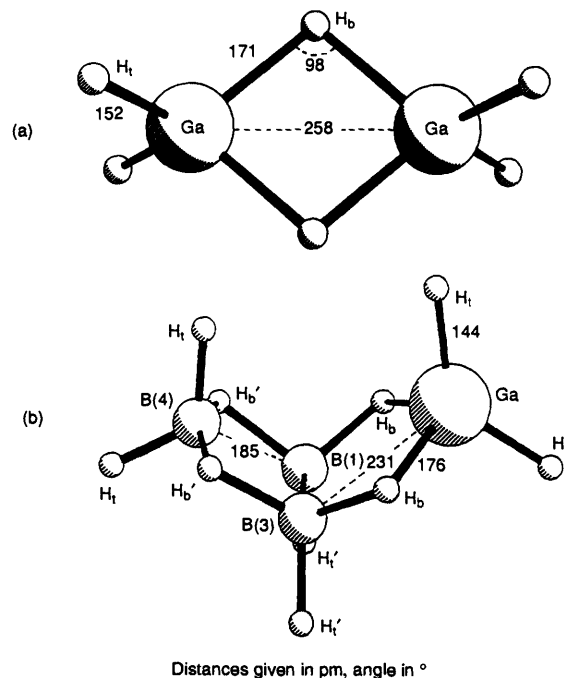
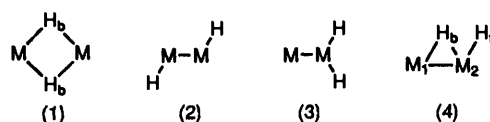
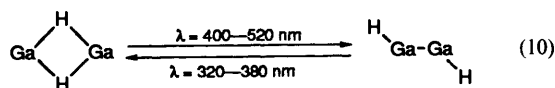


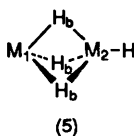
Figure 3 The structures of the gaseous molecules (a) Ga_2H_6 (ref. 6) and (b) $2-GaB_3H_{10}$ (ref. 19) as deduced by electron diffraction.



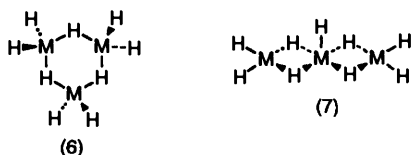
ground-state, with no experimental evidence for significant B–B double-bonding.^{8e} On the other hand, a *bis*(μ -hydrido) structure (1) with D_{2h} symmetry is found to be the most stable form of M_2H_2 for all the other Group 13 elements.^{8e} Instead of the linear form, which is now only a transition state, a *trans*-bent isomer (2) (C_{2h}) appears as a second minimum on the potential energy surface for M_2H_2 where $M = Al, Ga, \text{ or } In$. There are two other possible isomers, namely the asymmetric $M-MH_2$ (3) (C_{2v}) and the mono-H-bridged $HM(\mu-H)M$ (4) (C_s), which typically give minima at energies not far above the global minimum for M_2H_2 . Configuration (3) is relatively accessible to all the Group 13 metals, (4) to all but Tl. Infrared measurements suggest that the dimer of elemental gallium, Ga_2 , reacts spontaneously with H_2 in an argon matrix to form $Ga(\mu-H)_2Ga$ (1) and that this can be converted photoreversibly into a second isomer $HGaGaH$ (2).^{15b} The dimer Tl_2H_2 may be unsubstantiated by experiment, but it has attracted particular attention as a model compound in connection with the vexed question of whether Tl–Tl bonding interactions of significant strength can be established.^{3,8e}



Theoretical calculations^{23a-c} also find quite different properties for molecules of the type M_2H_4 according to whether $M = B$ or $M = Al$ or Ga . Boron favours a classical structure H_2B-BH_2 with D_{2d} symmetry, whereas Al_2H_4 and Ga_2H_4 prefer a tri-H-bridged structure (5) with C_{3v} symmetry, and studies of the mixed hydrides $BGaH_4$ and $AlGaH_4$ lead to analogous global minima.^{23d} Such a structure can be described in terms of more-or-less coulombic interactions between an M^+ cation and a tetrahedral MH_4^- anion, thereby betraying disproportionation of the divalent species.

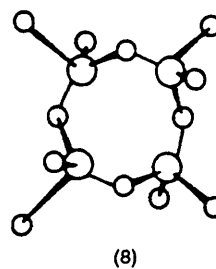


But dimerization need not be the limit to association, whatever the experience of B_2H_6 might suggest. The trimers $[MH_3]_3$ ($M = B, Al, \text{ or } Ga$) are calculated to have substantial binding energies with respect to the monomer MH_3 ,^{10b} the energetically favoured structures of Al_3H_9 and Ga_3H_9 involve planar six-membered $[MH]_3$ rings with D_{3h} symmetry, (6), but these are only slightly more stable than the acyclic structures, (7), conforming to C_2 symmetry and featuring a pentacoordinate central M atom. Whereas the hypothetical reaction 11 is endoergic for $M = B$ (+ 121 kJ), it turns out to be exoergic for $M = Al$ (- 32 kJ) and $M = Ga$ (- 42 kJ).^{10b} No homonuclear molecule of the type M_3H_9 is known, but gallium does form the mixed hydride GaB_2H_9 with the acyclic structure (7) based on a pentacoordinated central Ga atom.¹⁸ Although the compound undergoes some form of weak association in the condensed phases, it maintains a terminal $Ga-H$ unit. By contrast, the corresponding aluminium compound is a strongly associated, involatile liquid in which the unique $Al-H$ bond is involved in bridging, probably to complete six-fold coordination of the metal.²⁴



Regarding the formation of still larger oligomers, there is as yet no guidance to be had from theory. What is known experimentally about aluminium trihydride indicates that polymerization to a three-dimensional network ultimately offers optimum stability. Preliminary studies of the corresponding gallium compound leave little doubt that the Ga_2H_6 molecules present in the vapour also aggregate in the condensed phases.^{5,6} However, the properties of solid gallane (its infrared spectrum, volatility, and solubility in solvents like toluene) point to the formation not of an extended polymer but of a discrete oligomer such as the tetramer $[GaH_3]_4$, (8), which, unlike solid AlH_3 , retains *terminal* $M-H$ bonds.

Direct metal-metal bonding has yet to be established as a significant principle in the hydrides of the Group 13 metals, and there are no known homonuclear analogues of $B-B$ bonded polyborane species like B_4H_{10} , $B_{10}H_{14}$, and $B_{12}H_{12}^{2-}$.¹ Tempting though it may be to invoke $M-M$ bonding in M_2H_6 molecules ($M = Al$ or Ga) in view of the short $M \cdots M$ distance, current theoretical opinion gives little or no weight to such an interaction.¹⁰ The mixed hydride GaB_3H_{10} has been described



recently¹⁹ and its structure is akin to that of B_4H_{10} but with gallium replacing boron at the 2-position so that interaction between the heavy atoms is confined mainly to the $B-B$ hinge of the GaB_3 skeleton (Figure 3). That compounds containing $M-M$ bonds can be made has been demonstrated unequivocally with the isolation and structural characterization of species like $[(Me_3Si)_2CH]_4M_2$ ($M = Al, Ga, \text{ or } In$),^{25a} $[(2,4,6-Pr_3-C_6H_2)_4M_2]^-$ ($M = Al$ or Ga),^{25b} $[(\eta^5-C_5Me_5)Al]_4$,^{25c} and $[Al_{12}Bu_{12}]^{2-}$.^{25d} Evidently, however, large substituents are needed at the metal centres to inhibit more extensive aggregation, usually at the expense of rupturing the metal-ligand bonds. Hence it is far from certain that hypothetical species like $Al_{10}H_{14}$ and $[Ga_{12}H_{12}]^{2-}$, with the potential for kinetic and thermodynamic stabilization of the $M-H$ bonds, will enjoy more than a transient existence under normal conditions, although they may have a part to play in the thermal decomposition of hydrido- and organo-derivatives of the metals. Group 13 metal clusters are already known in intermetallic compounds.³ Typically they are not discrete but interlinked, as with the Ga_{21} and In_{16} units found in the phases $Rb_{0.6}Na_{6.25}Ga_{20.02}$ ^{26a} and $Na_7In_{11.8}$,^{26b} respectively.

3 Chemical Aspects

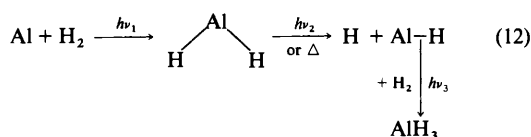
3.1 Synthesis

Most of the routes likely to lead to metal hydrides have been tried at one time or another with the Group 13 metals. Perhaps the most conspicuous exception is the action of a proton source on an electron-rich form of the Group 13 metal (as in an intermetallic compound in combination with a Group 1 or Group 2 metal, *q.v.*), there being no reported parallels to Stock's classical synthesis of the boron hydrides from a metal boride and a protonic acid. On the other hand, compounds containing bonds between hydrogen and a Group 13 metal have been prepared with varying degrees of success by the following methods: (i) addition of H_2 or a hydrogen-containing molecule like HCl to an unsaturated form of the metal; (ii) metathesis involving a hydride source and a halide or other derivative of the metal; (iii) decomposition or elimination reactions; and (iv) acid-base reactions.

3.1.1 Addition of H_2 and Related Reactions

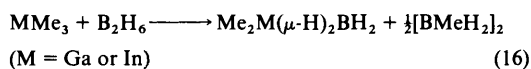
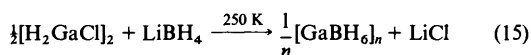
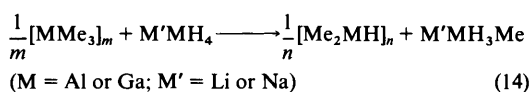
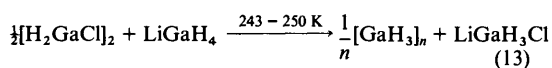
Direct synthesis of a Group 13 metal hydride from the elements is a high-energy process and even the metal atoms seem to require electronic or some other form of excitation before they will add to H_2 . For example, the results of matrix experiments involving photolysis of Al atoms in the presence of H_2 argue for the following mechanism (equation 12).^{14,15a} Similar insertion reactions occur - sometimes spontaneously, more often with photolytic initiation - between a Group 13 metal atom and a hydrogen-containing molecule HX to give the M^{II} hydride HMX (e.g. $X = NH_2$ ²⁷ or Me ^{15b}). Given the appropriate stimulus, molecular derivatives of the univalent metals, such as AlH , $AlCl$, and $GaCl$, will also add to H_2 and HCl to give the corresponding M^{III} hydride, as in equations 1 and 12. So far this strategy has been confined to the small scale of matrix-isolation experiments but it could be viable as a method of synthesis on the larger scale, at least for products with the thermal stability to survive at or near ambient temperatures. An important recent

important recent advance in this direction has been made through the preparation of metastable AlCl_2^{28a} and GaCl_2^{28b} in cooled solutions.



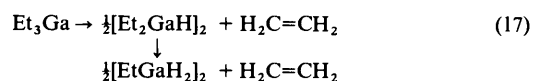
3.1.2 Metathesis

This has been one of the principal agencies of synthesis, with hydride-halide or hydride-methyl exchange being exemplified in reactions 9,²¹ 13,⁶ and 14,^{24b,29} The choice of hydride ion source is dictated by its activity and by the possibility that exchange may also lead to mixed hydride derivatives, as in reactions 15¹⁷ and 16.⁵ The reactions are normally carried out between the neat reagents and in the absence of a solvent, a feature prescribed by the need to avoid contamination of the free hydride, notably by basic impurities.



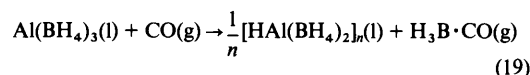
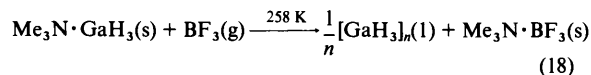
3.1.3 Decomposition/Elimination Reactions

An aluminium hydride is often the first product, accompanying elimination of the appropriate alkene, in the thermal decomposition of a trialkylaluminium compound, although it usually takes a 2-substituted alkene to make this a workable synthetic route.²² Controlled pyrolysis of triethylgallium, brought about by infrared laser radiation, has also been shown to proceed *via* β -elimination (equation 17).³⁰



3.1.4 Acid-Base Reactions

For many years the displacement reaction 18 was believed to afford a route to gallane,⁵ being driven by the preference of Me_3N for coordination to BF_3 rather than GaH_3 . Unfortunately halide-hydride exchange and not displacement turns out to be the dominant pathway. On the other hand, the action of the unusually 'soft' base CO, with its marked affinity for coordination to BH_3 , has been turned to account in reaction 19.^{24b}

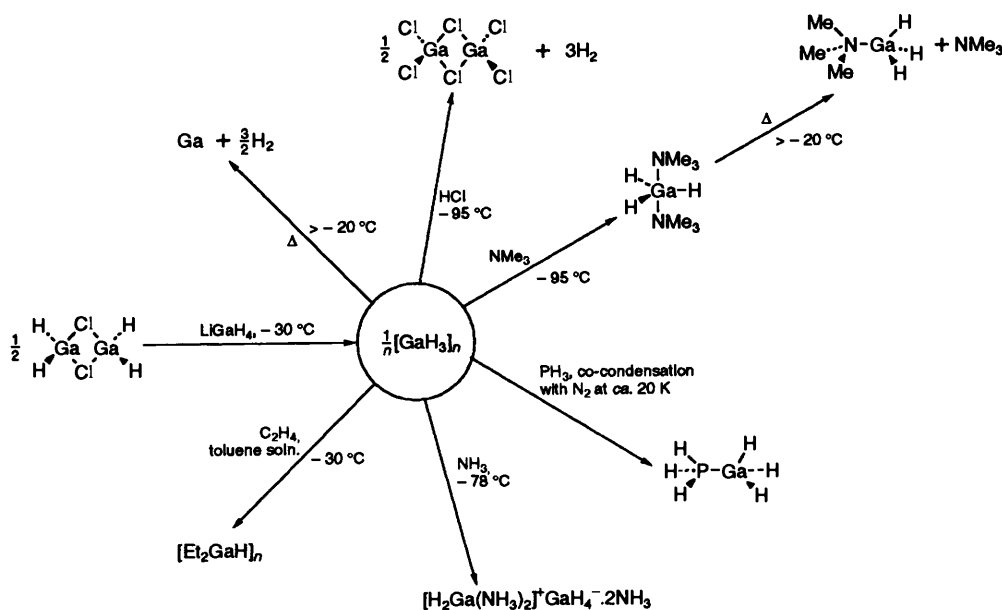


3.2 Reactions

Some of the chemical properties of gallane have now been charted,^{5,6} with the results summarized in Scheme 1. Apart from the obvious parallels with diborane,¹ the reactions seem to typify the behaviour of Group 13 metal hydrides. Reaction pathways of particular note with regard to the wider significance of these compounds are: (i) thermal decomposition to the metal; and (ii) complex-formation with Lewis bases. In addition, the Group 13 metal hydrides are powerful reducing agents, the M-H bonds being highly susceptible to a wide range of oxidation, addition, exchange, or solvolysis reactions. There is the potential appeal of unusual selectivity in the reduction of organic substrates, as shown by AlH_3 and $\text{Bu}'_2\text{AlH}$ for example,³¹ and which may repay the formidable investment which the preparation and handling of such compounds normally demand.

3.2.1 Thermal Decomposition

A recurring theme of this account is the thermal frailty of the known binary hydrides of the Group 13 metals which decompose to the elements at or near ambient temperatures. In fact, it is the ability to deliver the pure metal which confers considerable advantages on the hydrides over more conventional organome-



Scheme 1 Preparation and some reactions of gallane.

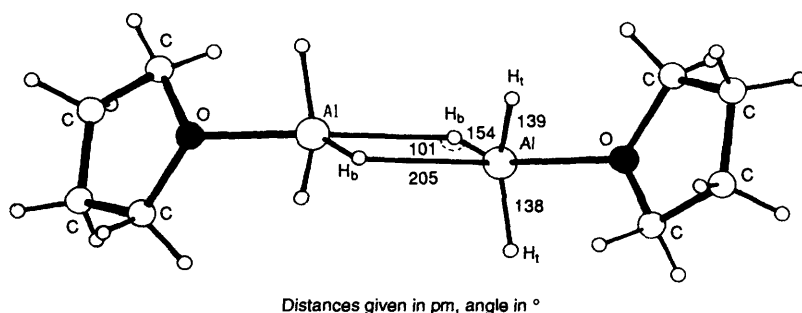
tallic precursors for the creation of thin films of III–V compounds or of the Group 13 metal, as in the growth of GaAlAs and the ‘metallization’ of semiconductor devices.³² In addition, the hydrides may be either active intermediates or parents to such intermediates in the thermolysis reactions associated with useful CVD processes and our current knowledge of which owes more to conjecture than to well substantiated fact. That they may serve as instructive models for surface reactions is borne out by very recent spectroscopic studies of the adsorption of hydrogen atoms on the (1×6) reconstruction of GaAs(100);³³ unmistakable evidence has thus been found for the formation of gallium hydride surface species bearing both terminal and bridging Ga–H functions.

3.2.2 Complex-formation

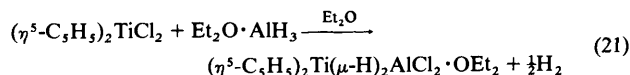
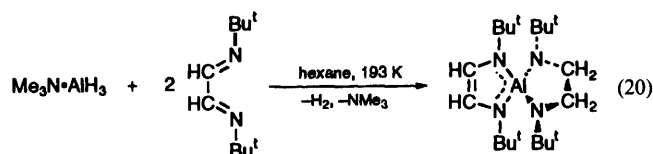
One of the most characteristic reactions of a Group 13 metal hydride is that with a Lewis base. This may proceed with homolytic, symmetrical cleavage of $M(\mu\text{-H})_2M$ bridging units to give the corresponding molecular adduct in which the hydride is coordinated by one or more base molecules, e.g. $(\text{Me}_3\text{N})_n\text{GaH}_3$ ($n = 1$ or 2) and $\text{H}_3\text{P} \cdot \text{GaH}_3$ (see Scheme 1).^{5,6} More or less tetrahedral coordination of the metal centre is the norm in discrete 1:1 complexes like $\text{Me}_3\text{N} \cdot \text{MH}_3$ ($M = \text{Al}$ or Ga) in the gas phase. On the other hand, the greater predisposition of aluminium to rise to coordination numbers greater than 4 is manifested in the dimeric structures assumed by 1:1 complexes like $\text{C}_4\text{H}_8\text{O} \cdot \text{AlH}_3$ ^{34a} in the solid state (see Figure 4). Here we find an Al_2H_6 unit with highly unsymmetrical Al–H...Al bridges, evincing a relationship with the elusive dialane, Al_2H_6 . Complexation can also evolve through an alternative channel, with heterolytic, unsymmetrical cleavage of $M(\mu\text{-H})_2M$ bridging units to give a salt-like product most aptly formulated in terms of cationic and anionic metal hydride moieties, e.g. $[\text{H}_2\text{Ga}(\text{NH}_3)_2]^+[\text{GaH}_4]^-$,^{5,6} and $[\text{H}_2\text{AlL}]^+[\text{AlH}_4]^-$ ($L = N, N, N', N'', N'''$ -pentamethyldiethylenetriamine).^{34b}

Complexes of all kinds are easier of access, more stable and, usually, more tractable than the parent hydrides. Accordingly they are preferred in most of the applications which the Group 13 metal hydrides have found, although they do not necessarily duplicate the behaviour of the parent hydrides. Most familiar is the use of alanes – notably LiAlH_4 and its derivatives – as powerful and selective reducing and hydrogenating agents.^{3,31} Key transformations involve the reduction of organic >C=C< , >C=O , and $\text{-C}\equiv\text{N}$ groups. In inorganic chemistry, too, adducts of alane and gallane have considerable synthetic potential not only as reducing agents, but also as precursors (i) to other compounds of the metals, the generation and survival of which requires that strongly reducing conditions be maintained, as in reaction 20,³⁵ and (ii) to hydride derivatives of other metals, as in reaction 21.³⁶ In addition, compounds like $\text{Me}_3\text{N} \cdot \text{AlH}_3$ are attractive as agents for chemical vapour deposition of the Group 13 metal in thin film technology.³² Here they offer the advantage over more conventional organometallic sources of affording carbon-free deposits.

Figure 4 Molecular structure of the adduct $[\text{C}_4\text{H}_8\text{O} \cdot \text{AlH}_3]_2$ in the crystalline solid.^{34a}



Distances given in pm, angle in °



4 Conclusions

Unlike the boron hydrides, which have waxed more or less strongly since their discovery, the hydrides of the heavier Group 13 elements have suffered fluctuating fortunes. From the first fine careless rapture of the energy-hungry 1950s and 1960s, aluminium hydride has lapsed into semi-obscurity, even while some of its derivatives have gained prominence as commercial and/or laboratory reagents. Gallane, $[\text{GaH}_3]_n$, has had an even more vexed history, with its very existence befogged for nearly 50 years by claims and counter-claims.⁵ However, the recent experimental advances that have led to the synthesis and characterization not only of gallane,^{5,6} but also of various novel adducts of alane and gallane, and to the isolation of discrete molecules like AlH_3 and GaH_2 in solid matrices at low temperatures have breathed new life into an otherwise faltering chemical body. One of the principal consequences has been to stimulate theoretical enquiries at a relatively sophisticated level.^{8–10} From such calculations have come results which have served the dual purpose of testing and supplementing experimental findings on known compounds, and urging the performance of new experiments to seek out other, hitherto undisclosed hydrides whose properties have been foretold. Such is the weakness and reactivity of M–H and M–M bonds that the chemistry of the Group 13 metal hydrides is never going to rival that of the corresponding boranes. On the other hand, this rather thinly populated borderland between the electron-precise regions of conventional ionic and molecular species still raises fundamental issues of structure and bonding, while the very reactivity and thermal instability of the compounds, as exemplified by the adduct $\text{Me}_3\text{N} \cdot \text{AlH}_3$,^{31,32,35} may yet be virtues.

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