

Hydrides of the Main-Group Metals: New Variations on an Old Theme

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I. Introduction

For an atom with such a uniquely simple electronic makeup, hydrogen shows remarkable mutability as a ligand. As a one-electron substituent with no significant potential for π -type interactions, it may function as a medium σ -donor to medium-strong σ -acceptor with respect to one or more metal centers.¹ In that it forms quite strong bonds with many metals, M, comparisons may be made, up to a point, with the methyl group or with fluorine. In their dissociation energies M–H bonds are typically superior to M–CH₃ bonds and invariably inferior to M–F bonds. Fluorine comes closest to matching hydrogen for size, but hydrogen differs from fluorine in at least two important respects. First, a valence orbital energy comparable with that of some metal centers makes hydrogen a much poorer σ -acceptor, resulting in a wide variation in polarity between the extremes represented by Mⁿ⁺...H⁻ and M^{δ-}–H^{δ+}, the precise condition being dependent also on the characters of any other ligands that may be linked to M.^{1–5} This polarizability makes it singularly difficult to ascribe to hydrogen any *general* ligand parameters that reflect meaningfully its size and function. Thus, it is by no means certain that the strong ligand field developed by hydrogen in iron(II) complexes such as [FeH₆]^{4–6} is a common principle of transition-metal hydrides,¹ still less that the strong trans effect which hydrogen exerts^{1–5} has significance extending much beyond the chemistry of platinum(II). There is a second radical difference between hydrogen and fluorine: the thermodynamic stability of M–H bonds is compromised by the strength of the H–H bond (cf. F₂) and of the corresponding M–O bonds. Accordingly, metal hydrides are seldom robust with respect to their response to thermal or oxidative stimuli.

For more than three decades transition-metal hydrides have held the limelight. This is understandable in view of the part played by M–H bonds in the organometallic chemistry of the transition metals, particularly in catalytic processes. Methods of synthesis, structures, spectroscopic and other physical properties, and the chemical reactions of the compounds have been generously detailed in books^{4,5} as

Comment is free but facts are sacred.

C. P. Scott
Manchester Guardian, May 6, 1926

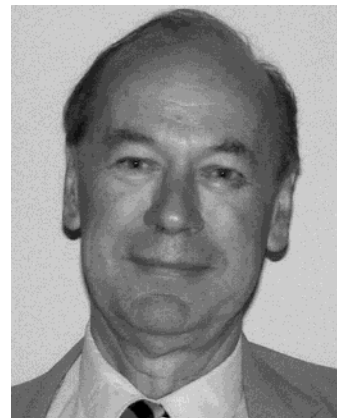
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Simon Aldridge obtained his B.A. and D.Phil. degrees from the University of Oxford, the latter in 1996 for work on group 12 and 13 metal hydrides under the supervision of Professor A. J. (Tony) Downs. He then obtained a Fulbright Scholarship and went to work for Professor T. P. Fehlner at the University of Notre Dame on synthetic and structural aspects of early transition-metal metallaborane clusters. After a short stint working for Professor D. M. P. Mingos at Imperial College London, he took up a lectureship at Cardiff University in September 1998. His current research interests include synthetic, structural, and reactivity studies of transition-metal complexes containing low-coordinate boron ligands and the synthesis of novel Lewis acids of relevance in catalysis and selective anion binding.

well as numerous review articles.^{1–3} Interest in transition-metal hydrides was boosted in 1984 by the discovery of molecular dihydrogen complexes. Numerous reviews^{3,7} attest to the fascination aroused by the subtle balance between the two options ($\eta^2\text{-H}_2\text{M}$ and $(\eta^1\text{-H})_2\text{M}$ (with its implications for catalytic hydrogenation reactions) and by the unusual spectroscopic properties that go with the first option. In addition, significant advances have also been made with the synthesis and characterization of hydride derivatives of the f-block metals which often incorporate hydroborate or -aluminate ligands.⁸

In the same period little has been made of the hydrides formed by the main-group metals, despite their importance in chemical synthesis, notably as precursors to other metal hydrides and as reducing agents for a wide range of inorganic and organic substrates. Ranging from the salt-like hydrides of the s-block metals to the molecular hydrides of the p-block metals, these make up an altogether more diverse body of stoichiometric compounds than do the molecular hydrides of the d- and f-block elements. Where binary derivatives of the latter are known in the condensed phases only as solids of widely varying composition, those of the main-group metals are typically well-defined stoichiometric species. The seeming neglect of the main-group hydrides can be traced to several factors: heterogeneity of compound type and properties; the long established familiarity of many of the compounds, allied to a general lack of synthetic advance since the 1960s and the era of vacuum-line chemists such as Schlesinger, Burg, Wiberg, and Emeléus; the technical problems presented by compounds that are often thermally frail, in addition to being unusually susceptible to attack by air or moisture; the failure of the main-group metals as yet to deliver long-lived dihydrogen complexes analogous to those formed by the transition metals; and the lack of a broader horizon, beyond laboratory synthesis and one or two specialist ap-



Tony Downs gained his first degree and Ph.D. degree from the University of Cambridge, U.K., where his research, concerned with perfluoroorgano-derivatives of sulfur, was supervised by the late Professor H. J. Emeléus and Dr. (now Professor) E. A. V. Ebsworth. Prior to his move to Oxford, he held a Salters' Fellowship (1961–1962) at Cambridge and was appointed a Senior Demonstrator (1962–1963), then Lecturer (1963–1966) in Inorganic Chemistry at the University of Newcastle upon Tyne. At the University of Oxford he was appointed first (1966) a Senior Research Officer, then (in 1971) a Lecturer, and later (1996) a Professor in Inorganic Chemistry; he has been concurrently a Tutorial Fellow of Jesus College. His current research interests focus on reactive intermediates in the shape of hydrido and organo derivatives of both typical and transition elements. Characteristic of this research has been the alliance of synthetic studies (often requiring peculiarly rigorous exclusion of impurities) with a variety of physical techniques, including matrix isolation, vibrational spectroscopy, and electron as well as X-ray diffraction.

plications, to urge more systematic and detailed studies. The picture has changed materially within the past decade or so. Real synthetic progress has been made on several fronts: through a variety of physical methods transient hydride molecules have been tracked, characterized, and, in some cases, preserved; by appropriate molecular design improved stability and/or tractability has been conferred on metal hydride fragments, giving synthetic access to many more compounds that can be isolated and manipulated at ambient temperatures.

The most recent reviews detailing the main-group metal hydrides at large appeared in the early 1970s,⁹ although the situation has been updated for some individual metals, e.g., Al,^{10–12} Ga,^{10–13} In,^{10–12} As,¹⁴ and Sb,¹⁴ and also for compounds containing M–C as well as M–H bonds.¹⁵ In this account we review the current status of the binary and mixed hydrides formed by the metals of groups 1/11, 2/12, 3/13, 14, and 15, as represented in Scheme 1.

Some of the elements thus identified are of rather marginal significance, e.g., Cu, Ag, Au, B, and Ge, but without wishing to pursue their hydride chemistry in any depth (were that even possible), we include them here for the sake of the comparisons they afford with the chief protagonists.

The motivation for the recent research has come not from catalysis-led but from a variety of other sources. Two chief influences have been at work: (i) the need for new precursors in the design and fabrication of a wide range of solid materials or multilayer devices with special electrical, optical, or other; properties and (ii) the investigation of molecules that are transient under normal conditions but potentially important as reaction intermediates in

Scheme 1. Scope of the Present Review: Hydrides of the Following Metals Will Be Discussed

1	11	2	12	3/13	14	15
Li		Be		B		
Na		Mg		Al		
K	Cu ^{a,b}	Ca	Zn	Ga	Ge ^b	As
Rb	Ag ^{a,b}	Sr	Cd	In	Sn	Sb
Cs	Au ^{a,b}	Ba	Hg	Tl	Pb	Bi

^a Only derivatives in which the d¹⁰ shell of the metal stays intact. ^b Included mainly for comparison.

the gas phase (e.g., in plasmas or other energized gas mixtures) or in surface reactions.¹⁶ The search for new, selective agents for reduction and other reactions has also played an important part, and supporting roles have been taken by factors linked variously to the hydrogen economy, new energy sources, astroscience, and the production of pure metals. For example, some of the hydrides hold promise as the means of storing hydrogen, for electrochemical applications, e.g., in fuel cells or for electroplating of metals, and as possible fuels (sometimes in exotic projects such as that involving the powering of a rocket from Mars using CO₂ as the oxidant¹⁷). Above all, it must be said, the chance to explore hitherto uncharted chemical territory has been a vital force. In practice, progress has depended less on intentions and on new ideas than on new or improved techniques. It has commonly demanded the sensitivity and discrimination of modern spectroscopic methods, the ability to operate in a variety of media under extremes of temperature and pressure, recourse to physical or chemical stratagems for preserving MH_{*n*} moieties that are otherwise vulnerable to decomposition, aggregation or other reactions, and the computational armory of contemporary quantum chemical methods. In recognition of the extent to which *technique* has led the way, it is only natural to begin with a brief survey of the methods that have been instrumental in furthering our knowledge of the main-group metal hydrides.

II. Methods of Investigation

A. Gas-Phase Studies

The gas phase at low pressures offers the best opportunity for detailed physical studies of free diatomic MH and other simple hydride molecules, despite what is usually only a fleeting existence even under these conditions. Generated mostly by thermal or discharge reactions between the metal vapor and hydrogen, these may survive at partial pressures high enough and for times long enough to be detected,

identified, and interrogated by an appropriate spectroscopic signature, typically recorded at high resolution. This signature may be the electronic spectrum measured either in absorption, as with BH₂¹⁸ and AlH₂,¹⁹ or in emission, as with BeH.²⁰ Such a spectrum reports on the vibrational and rotational properties of the molecule in its electronic ground and excited states and may provide for an MH molecule good approximations to the dissociation energies in one or more states.^{21–23} The potential of laser-induced fluorescence has also been demonstrated by recent studies of GeH₂²⁴ and GeHX (X = Cl or Br),²⁵ which have thus been probed in both the ground and excited electronic states, having been produced by subjecting the appropriate germane (GeH₄ or GeH₃X) to an electric discharge at the exit of a pulsed nozzle. Another powerful instrument of characterization is the infrared spectrum, again measured either in absorption, for example, with a diode laser spectrometer as in the cases of KH²⁶ and PbH,²⁷ or in emission, as in the cases of BaH²⁸ and AlH.²⁹ Analysis of the resulting rovibrational spectrum affords a detailed picture of the properties, including the dimensions, of an MH molecule in its electronic ground state. Rotational spectroscopy in the submillimeter region offers another important option which has been applied to the characterization of the molecules CuH,³⁰ ZnH,³¹ AsH,³² and AsH₂.³³ Of such studies perhaps the most spectacular has been that involving LiH,³⁴ rotational transitions of which have been fixed with an unprecedented accuracy of a few parts in 10⁸ with the aid of a tunable far-infrared spectrometer, ultimately to yield the Born–Oppenheimer equilibrium bond length of $r_e = 1.594\,908\,11(16)$ Å. Another variation open to paramagnetic species such as GeH³⁵ and SnH³⁶ is laser magnetic resonance in which a CO laser is employed to produce a series of sharp rovibrational lines to one of which a rovibrational line of the radical may be tuned through the application of a magnetic field. A different line of attack exploits mass spectroscopy following ionization by electron impact or photoionization to test for molecules such as AlH, AlH₂, MH₃ (M = Al, Ga, or In), and Al₂H₆.³⁷ Hence, access may also be gained to quantitative estimates of dissociation energies and related thermodynamic parameters, as in the cases of MH (M = Cu, Ag, or Au)³⁸ and AsH_{*n*} (*n* = 1–3).³⁹ To the challenges presented in all these studies by transience, low partial pressure, and the presence of other species, various technical remedies have been found, e.g., (i) continuous generation at elevated temperatures and the use of flow systems; (ii) use of multi-reflection devices to achieve long sample path lengths or, alternatively, formation of the molecule in a noble-gas stream that is then caused to undergo supersonic free jet expansion prior to interception by the analyzing radiation;^{24,25} and (iii) the development of special modulation and phase-sensitive detection techniques to improve both selectivity and sensitivity.^{16,40} Many of these features are well illustrated by the study of MgH,⁴¹ a molecule of some astrophysical importance. Generated by discharging mixtures of H₂ and Ar over magnesium in a heated quartz cell, the molecule has been detected by its infrared spectrum with the aid

of concentration modulation at 3 kHz (f_2) and phase-sensitive detection at $2f_2$.

By contrast, some metal hydrides can be vaporized to give molecules which are more or less long-lived under normal (ambient) conditions and therefore amenable to analysis by a variety of more conventional methods. Such is the case with certain hydrides formed by (a) the group 13 elements B, Al, and Ga {e.g., $(\text{Me}_3\text{N})_n\text{AlH}_3$ ($n = 1$ or 2), $[\text{Me}_2\text{AlH}]_n$ ($n = 2$ or 3), $[\text{GaH}_3]_n$ ($n = 2$ or more), and $\text{HGa}(\text{BH}_4)_2$ }; (b) the group 14 elements Ge and Sn {e.g., $\text{MH}_n\text{X}_{4-n}$ ($\text{M} = \text{Ge}$ or Sn ; $n = 1-4$; $\text{X} = \text{halogen}$ or an organic group)}; and (c) the group 15 elements As and Sb (e.g., AsH_3 and SbH_3). High-resolution studies of rotational and vibrational transitions have yielded much detailed information about the equilibrium structures and dynamic properties but only for a handful of binary hydride molecules, viz. B_2H_6 ,⁴² GeH_4 ,^{43,44} SnH_4 ,⁴³⁻⁴⁵ AsH_3 ,⁴⁶ and SbH_3 .⁴⁷ Rotational spectroscopy has been the mainstay of accurate r_0 structures as determined for AsH_3 ⁴⁶ and SbH_3 ,⁴⁷ despite the nonpolar equilibrium configurations of GeH_4 and SnH_4 , microwave spectra have been measured not only for the partially deuterated isotopomers $\text{MH}_n\text{D}_{4-n}$ ($\text{M} = \text{Ge}$ or Sn ; $n = 1-3$),⁴⁴ but also for the parent molecule SnH_4 through an ingenious infrared-microwave double-resonance experiment depending on the dipole moment developed by the molecule on excitation of a t_2 vibration.⁴⁵ Microwave spectroscopy, often allied to rovibrational studies, has also been a primary agency of structure determination for a number of simple derivatives of GeH_4 and SnH_4 , e.g., GeH_3X ($\text{X} = \text{F}$, Cl , Br , or I),^{43,48} SnH_3X ($\text{X} = \text{Cl}$, Br , or I),⁴³ CH_3MH_3 ($\text{M} = \text{Ge}^{49}$ or Sn^{50}), $\text{C}_2\text{H}_5\text{-SnH}_3$,⁵¹ $(\text{CH}_3)_2\text{GeH}_2$,^{52a} and $\text{H}_3\text{GeC}\equiv\text{CH}$.^{52b} Infrared and microwave measurements yield distinctive signatures by which some of the metal hydrides have been recognized in extraterrestrial sources; these include molecules such as MgH^{53} and AlH^{54} that are quick to decay under normal conditions, as well as more enduring molecules such as AsH_3 and GeH_4 that have been detected in the reducing atmospheres of the larger planets.⁵⁵

The only realistic way of determining the structure of a more elaborate molecule is to appeal to its electron diffraction pattern for a vibrationally averaged picture.⁵⁶ To this method, however, there are distinct limitations: the pattern does not discriminate well between interatomic distances that are comparable in magnitude and the relatively weak scattering of bound or unbound $\text{M}\cdots\text{H}$ atom pairs tends to impair accurate location of the hydrogen atoms. For all but the simplest molecule it is rarely possible to extract good estimates of all the structural and vibrational parameters that determine the molecular scattering. The best response in these circumstances 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, where these are known or can at least be meaningfully approximated. A further improvement has been made recently 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.⁵⁷ Hence, for example, the structures of the gallium hydrides $\text{H}_2\text{GaB}_3\text{H}_8$ ⁵⁸ and $\text{Me}_3\text{N}\cdot\text{GaH}_3$ ⁵⁹ have been determined with some confidence. Other molecules depending wholly or in part on electron diffraction for their structural evaluation include the binary hydrides B_2H_6 ,⁴² Ga_2H_6 ,⁶⁰ and Ge_2H_6 ⁶¹ as well as numerous derivatives, e.g., $[\text{Me}_2\text{AlH}]_n$ ($n = 2$ or 3),⁶² $[\text{Me}_2\text{GaH}]_2$,⁶³ $[\text{Me}_2\text{NGaH}_2]_2$,⁶⁴ $\text{HGa}(\text{BH}_4)_2$,⁶⁵ $(\text{GeH}_3)_2\text{E}$ ($\text{E} = \text{O}$ or S),⁶⁶ $(\text{GeH}_3)_3\text{N}$,⁶⁷ RGeH_3 ($\text{R} = \text{cyclopropyl}$,^{68a} cyclobutyl ,^{68b} or cyclopentadienyl ^{68c}), $\text{Me}_n\text{SnH}_{4-n}$ ($n = 2$ or 3).⁶⁹

Initial identification of a gaseous hydride molecule owes much to its vibrational properties. As with the characterization of metal carbonyls, it is the M-H stretching vibrations that by their energies and intensities offer the most telling commentary on the molecular identity. Just as $\nu(\text{CO})$ modes differentiate terminal from bridging carbonyl functions, so, as indicated in Table 5 (section IV.A), do $\nu(\text{MH})$ modes differentiate terminal from bridging M-H functions.¹³ For example, the first clear sign of the Ga_2H_6 molecule depended on the observation that its infrared spectrum includes not only strong absorptions near 1980 cm^{-1} attributable to the stretching fundamentals of terminal Ga-H bonds, but also two other absorptions no less intense near 1200 cm^{-1} that must arise from the stretching fundamentals of the Ga-H-Ga bridges.^{13,60} The wavenumbers of the M-H stretching fundamentals are also a relatively sensitive function of the dimensions and other properties of MH_n units, although any direct correlation must be of an empirical nature. By partial deuteration to give CHD_{n-1} units, McKean and his colleagues have been able to eliminate the complications of Fermi resonance and determine 'isolated' C-H stretching frequencies, $\nu_{\text{is}}(\text{CH})$, which correlate remarkably well with $r_0(\text{C-H})$, $\angle(\text{H-C-H})$, and $D_0^0(\text{C-H})$, and this provides a relatively precise index to these and other parameters.⁷⁰ The approach has been extended with some success not only to molecules including SiH_n , but also GeH_n ,^{48,71-73} SnH_n ,⁷⁴ and AsH_n ⁷³ fragments. Hence, for example, it has been possible to define more closely the structures of some germanium⁷² and tin⁷⁴ hydrides and to explore the effects of conformational change. In other cases, however, there is a dearth of reliable data on which analogous correlations might be founded.

Elucidation of the electronic structure and bonding has been accomplished by analyzing the valence-shell photoelectron spectra of some molecules, e.g., B_2H_6 ,⁷⁵ Ga_2H_6 ,⁷⁵ MH_4 ($\text{M} = \text{Ge}$ or Sn),⁷⁶ and MH_3 ($\text{M} = \text{As}$ or Sb).⁷⁷ The obvious correlation between the spectra of B_2H_6 , GaBH_6 , and Ga_2H_6 leaves little doubt about the structural kinship of the three molecules.⁷⁵ The spectra of the $(t_2)^{-1}$ ionized states of GeH_4 and SnH_4 , like those of CH_4 and SiH_4 , betray the effect of Jahn-Teller distortion;⁷⁶ Jahn-Teller splitting is also observed for the $(e)^{-1}$ ionized states of AsH_3 and SbH_3 .⁷⁷ Only in a few cases—notably those of GeH_3X ($\text{X} = \text{H}$, CH_3 , Cl , or Br)⁷⁸ and SnH_4 ⁷⁹—has X-ray photoelectron spectroscopy been deployed to examine

Table 1. Main-Group Metal Hydrides Featuring in Matrix-Isolation Studies

species	method of preparation	method of characterization	comments	ref
group 1/11				
H ₂ ···MX (M = Li, Na, K, Rb, or Cs; X = halogen or NO ₃)	codeposition of H ₂ and MX; Ar matrices, ca. 10 K	IR	$\nu(\text{H-H})$ mode IR-active and red-shifted by weak interaction of H ₂ with halide anion of M ⁺ X ⁻ ion pair	83
(η^2 -H ₂)CuCl	codeposition of H ₂ and CuCl; Ar matrices	IR, ^{1,2} H; ab initio calculations	formation of η^2 -H ₂ complex implied	84
CuH	use of hollow-cathode sputtering source to codeposit Cu atoms with H ₂ ; Ar matrices 14 K	IR, ^{1,2} H		85
CuH	photoexcitation of Cu atoms in the presence of H ₂ ; Kr matrices 10–12 K	UV-vis; EPR; IR, ^{1,2} H	CuH reacts thermally with H atoms to regenerate Cu + H ₂	86
CH ₃ CuH	photoexcitation of Cu atoms in the presence of CH ₄ ; CH ₄ matrices, 12 K	UV-vis; EPR; IR, ^{1,2} H, ^{12,13} C	CH ₃ CuH is photolabile	87
group 2/12				
BeH	codeposition of Be and H atoms; Ar matrices, 4 K	EPR, ^{1,2} H; ab initio calculations		88
BeH, BeH ₂ , BeBeH, HBeBeH, HBeHBeH	codeposition of H ₂ with Be atoms formed by pulsed laser ablation; Ar matrices, 10 K	IR, ^{1,2} H; ab initio calculations		89
HBeCN, HBeNC	codeposition of HCN with laser-ablated Be atoms; Ar matrices, 6–7 K	IR, ^{1,2} H, ^{12,13} C; ab initio calculations		90
HBeOH, HBeOBeH	codeposition of H ₂ O with laser-ablated Be atoms; Ar matrices, 10 K	IR, ^{1,2} H, ^{16,18} O; ab initio calculations		91
HBeCCH	codeposition of C ₂ H ₂ with laser-ablated Be atoms; Ar matrices, 10 K	IR, ^{1,2} H, ^{12,13} C; ab initio calculations		92
CH ₃ BeH, H ₂ CBeH, HCB ₂ H, CH ₃ MgH, CH ₃ CaH	codeposition of CH ₄ with laser-ablated Be, Mg, or Ca atoms; Ar matrices, 10 K	IR, ^{1,2} H, ^{12,13} C; ab initio calculations		93
MgH, CaH, SrH, BaH	codeposition of M and H atoms (M = Mg, Ca, Sr, or Ba); Ar matrices, 4 K	EPR, ^{1,2} H, ²⁵ Mg		94
MgH, MgH ₂ , HMgMgH, Mg(μ -H) ₂ Mg, HMg(μ -H) ₂ MgH	codeposition of H ₂ with laser-ablated Mg atoms; Ar matrices, 10 K	IR, ^{1,2} H, ^{24,26} Mg; ab initio calculations		95
MgH ₂ , CH ₃ MgH	photoexcitation of Mg atoms in the presence of H ₂ or CH ₄ ; Ar or CH ₄ matrices	UV-vis; IR, ^{1,2} H, ^{12,13} C		96
CaH ₂ , HC ₂ CaH, HCa(μ -H) ₂ CaH, Ca ₃ H ₂ , ZnH ₂ , HZnZnH	photoexcitation of Ca or Zn atoms in the presence of H ₂ ; Ar, Kr, or Xe matrices, 12 K	IR, ^{1,2} H	some evidence of H ₂ complexes, e.g., Ca ₂ (H ₂) ₂	97
ZnH, CdH, HgH	codeposition of M and H atoms (M = Zn, Cd, or Hg); Ar matrices, 4 K	EPR, ^{1,2} H, ^{111,113} Cd, ^{199,201} Hg		98
ZnH, ZnH ₂ , ZnZnH, HZnZnH, HZnOH, CdH, CdH ₂ , HCdOH	excitation of M atoms (M = Zn or Cd) in the presence of H ₂ ; Ar matrices, 12 K	IR, ^{1,2} H; ab initio calculations	reaction depends on photoexcitation of M atoms; evidence of weak H ₂ complexes	99
HgH, HgH ₂ , HHgCl	photoexcitation of Hg atoms in the presence of H ₂ or HCl; Ar, Kr, H ₂ , or N ₂ matrices, 6 K	IR, ^{1,2} H	insertion into H–H or H–Cl bonds involves ³ P ₁ Hg atoms	100
CH ₃ MH (M = Zn, Cd, or Hg), C ₂ H ₅ HgH	excitation of M atoms in the presence of CH ₄ or C ₂ H ₆ ; Ar matrices, 12 K	IR, ^{1,2} H, ^{12,13} C	³ P ₁ M atoms insert into a C–H bond of CH ₄ or C ₂ H ₆	101
group 3/13				
BH ₂	electron bombardment of B ₂ H ₆ ; Ar matrices, 4 K	EPR, ¹ H, ¹¹ B; ab initio calculations		102
BH, H ₂ ···BH, BH ₃ , H ₂ ···BH ₃ , HBBH, B ₂ H ₆ , BH ₄ ⁻	codeposition of H ₂ with laser-ablated B atoms; Ar matrices, 10 K	IR, ^{1,2} H, ^{10,11} B; ab initio calculations	evidence of H ₂ complexes	103
HBBH	vacuum-UV, X, or laser irradiation or electron bombardment of B ₂ H ₆ ; Ne or Ar matrices, 4 K	EPR, ¹ H, ¹¹ B; ab initio calculations	HBBH has a ³ Σ _g ⁻ electronic ground state	104
BH ₄	codeposition of H ₂ with laser-evaporated B atoms; H ₂ , D ₂ , or HD matrices	EPR, ^{1,2} H, ^{10,11} B	BH ₄ has a C _{2v} structure and, unlike CH ₄ ⁺ , is not fluxional	105
H ₃ B·NH ₃ , H ₂ BNH ₂	pyrolysis of B ₂ H ₆ /NH ₃ mixtures or H ₃ B·NH ₃ ; Ar matrices, 14 K	IR, ^{1,2} H, ^{10,11} B, ^{14,15} N		106
H ₂ BSH, HBS	pyrolysis of B ₂ H ₆ /H ₂ S mixtures; Ar matrices, 14 K	IR, ^{1,2} H, ^{10,11} B		107
AlH ⁺	reactive laser sputtering and photoionization of AlH; Ar matrices, 4 K	EPR, ^{1,2} H, ²⁷ Al; ab initio calculations		108

Table 1 (Continued)

species	method of preparation	method of characterization	comments	ref
HAIOH	codeposition of laser-vaporized Al atoms with H ₂ O; Ar or Ne matrices, 4 K	EPR, ^{1,2} H, ²⁷ Al, ¹⁷ O; ab initio calculations	H–Al–O skeleton is nonlinear	109
AlH	use of hollow-cathode sputtering source to codeposit Al atoms with H ₂ ; Ar matrices, 14 K	IR, ^{1,2} H		85
AlH, AlH ₂ , CH ₃ AlH	photoexcitation of Al atoms in the presence of H ₂ or CH ₄ ; Kr or CH ₄ matrices, 12 K	UV-vis; EPR; IR, ^{1,2} H		110
AlH ₂	photoexcitation of Al atoms in the presence of H ₂ O; Ne matrices, 4 K	EPR, ^{1,2} H, ²⁷ Al; ab initio calculations		111
AlH, AlH ₂ , AlH ₃ , H ₂ ⋯AlH _n	codeposition of laser-ablated Al atoms with H ₂ ; Ar matrices, 10 K	IR, ^{1,2} H; ab initio calculations	evidence of H ₂ complexes of AlH _n species	112
Al ₂ H ₂	codeposition of laser-ablated Al atoms with H ₂ ; Ar matrices, 10 K	IR, ^{1,2} H; ab initio calculations	two different isomers have been identified, viz. Al(μ-H) ₂ Al and Al(μ-H)AlH	112,113
AlH, GaH, InH, AlH ₂ , GaH ₂ , InH ₂	photoexcitation either of M atoms in the presence of H ₂ or of MH ₂ ; Ar matrices, 10 K	IR, ^{1,2} H, ^{69,71} Ga; ab initio calculations		114
AlH ₃ , GaH ₃ , InH ₃	codeposition of M and H atoms or photoexcitation of AlH in the presence of H ₂ ; Ar matrices, 10 K	IR, ^{1,2} H; ab initio calculations	trigonal planar MH ₃ molecules characterized (M = Al, Ga, or In)	115
AlH ₃	photoexcitation of Al atoms in the presence of H ₂ ; Ar and Kr matrices, ca. 16 K	IR, ^{1,2} H; ab initio calculations	trigonal planar AlH ₃ molecules characterized	80
H ₂ ⋯AlH ₂ , AlH ₄ [−]	photoexcitation of H ₂ ⋯AlH ₂ ; Ar matrices, 10 K	IR, ^{1,2} H; ab initio calculations		116
HALX ₂ (X = Cl or Br)	photoexcitation of AlCl in the presence of HCl; ^{117a} thermolysis of Me ₂ N(CH ₂) ₃ AlX ₂ ; ^{117b} Ar matrices	IR, ^{1,2} H, ^{35,37} Cl; ab initio calculations		117
HALCl	codeposition of Al atoms with HCl; Ar matrices, ca. 4 K	EPR, ¹ H, ²⁷ Al, ³⁵ Cl; ab initio calculations		118
HAIOH, HGaOH, HInOH	thermal or photolytic reaction of M atoms (M = Al, Ga, or In) with H ₂ O; Ar or Kr matrices, 15 K	UV-vis; IR, ^{1,2} H, ^{16,18} O	HMOH molecules are photolabile yielding MOH and MO	119
HAlNH ₂ , HAlNH	codeposition of NH ₃ with laser-ablated Al atoms; Ar matrices, 6–7 K	IR, ^{1,2} H, ^{14,15} N; ab initio calculations	bent HAlNH thought to be a minor product	120
Al⋯SiH ₄ , HAlSiH ₃	photoexcitation of Al atoms in the presence of SiH ₄ ; Ar matrices, 12 K	UV-vis; EPR; IR, ^{1,2} H	photoreversible formation of H ₃ SiAlH from Al(² P)⋯SiH ₄	121
GaH, Ga ₂ H ₂ , CH ₃ GaH	photoexcitation of Ga atoms in the presence of H ₂ or CH ₄ ; thermal reactions of Ga ₂ with H ₂ ; Ar or Kr matrices	IR, ^{1,2} H, ^{12,13} C	different forms of Ga ₂ H ₂ are generated on photolysis	122
GaH ₂ , CH ₃ GaH	photoexcitation of Ga atoms in the presence of H ₂ or CH ₄ ; Ne matrices, 4 K	EPR, ^{1,2} H, ^{69,71} Ga; ab initio calculations		123
Ga ₂ H ₆ , H ₃ Ga·PH ₃	deposition of Ga ₂ H ₆ vapor; codeposition of Ga ₂ H ₆ and PH ₃ ; Ar, N ₂ , or CH ₄ matrices, ca. 20 K	IR, Raman, ^{1,2} H; ab initio calculations		60, 124
CH ₃ GaH, CH ₃ InH	photoexcitation of Ga or In atoms in the presence of CH ₄ ; Ar matrices, 12 K	IR, UV-vis, ^{1,2} H; ab initio calculations	CH ₃ GaH and CH ₃ InH are photolabile and yield CH ₃ Ga and CH ₃ In, respectively	125a
HMNH ₂ , H ₂ MNH ₂ (M = Al, Ga, or In)	photoexcitation of M atoms in the presence of NH ₃ ; Ar matrices, 12 K	IR, UV-vis; ^{1,2} H, ^{14,15} N; ab initio calculations	first product is HMNH ₂ which photodissociates to H ⁺ + MNH ₂ giving H ₂ MNH ₂ as a secondary product	125b
HGaX ₂ (X = Cl or Br)	photoexcitation of GaCl in the presence of HCl; ^{126a} thermolysis of Me ₂ N(CH ₂) ₃ GaX ₂ ; ^{126b} Ar matrices	IR, ^{1,2} H, ^{35,37} Cl, ^{69,71} Ga; ab initio calculations		126
H ₂ GaCl	photoexcitation of GaCl in the presence of H ₂ ; Ar matrices	IR, ^{1,2} H, ^{35,37} Cl; ab initio calculations		127
CH ₃ GaH ₂ , (CH ₃) ₂ GaH	thermolysis of [Me ₂ N(CH ₂) ₃]GaMe ₂ ; Ar matrices, 15 K	IR, mass spectrometry; ab initio and DFT calculations	β-hydrogen elimination gives (CH ₃) ₂ GaH and CH ₃ GaH ₂	126c
HInCl ₂ , H ₂ InCl	photoexcitation of InCl in the presence of HCl or H ₂ ; Ar matrices, 12 K	IR, ^{1,2} H, ^{35,37} Cl; ab initio calculations		128
[H ₂ GaCl] ₂	deposition of vapor; Ar, N ₂ , or CH ₄ matrices, 15–20 K	IR, Raman, ^{1,2} H; ab initio calculations		129, 130

Table 1 (Continued)

species	method of preparation	method of characterization	comments	ref
HGa(BH ₄) ₂	deposition of vapor; Ar or N ₂ matrices, ca. 12 K	IR, ^{1,2} H; ab initio calculations		65
group 14				
GeH, GeH ₂ , GeH ₃ , GeH ₄ , Ge ₂ H ₆	vacuum-UV photolysis of GeH ₄ ; Ar matrices, 4–25 K	IR, ^{1,2} H		131a,b
GeH, GeH ₂ , GeH ₃ , GeH ₄ , Ge ₂ H ₆	trapping of neutral species from a GeH ₄ dc discharge	IR		131c
GeH ₃ , SnH ₃	γ-irradiation of MH ₄ (M = Ge or Sn); Kr or Xe matrices, 4.2 K	EPR, ¹ H, ⁷³ Ge, ^{117,119} Sn	MH ₃ radicals are pyramidal	132
GeH ₃ X, GeH ₂ X ₂ , GeH ₂ X, GeHX (X = Cl or Br)	UV photolysis of GeH ₃ X or GeH ₂ X ₂ ; Ar or CO matrices, 4–24 K	IR		131b
GeH ₄ ···HF	codeposition of GeH ₄ and HF; Ne or Ar matrices, 4.5–30 K	IR, ^{1,2} H		133a
group 15				
AsH ₂	γ-irradiation of AsH ₃ ; Kr or Xe matrices, 4.2 K	EPR		132
AsH ₃ , O ₃ ···AsH ₃ , H ₂ AsOH, H ₃ AsO, HAsO(?)	codeposition and photolysis of AsH ₃ and O ₃ ; Ar matrices, 12 K	IR, ^{1,2} H, ^{16,18} O		134
SbH ₂ , SbH ₃ , HSbO ₃ , H ₂ SbOH, H ₃ SbO	codeposition and photolysis of SbH ₃ and O ₃ ; Ar matrices, 12 K	IR, ^{1,2} H, ^{16,18} O	HSbOOO is a major product	135
A···AsH ₃ [A = ClF, Cl ₂ , Me ₂ M (M = Zn or Cd), HCl or TiCl ₄]	codeposition of A and AsH ₃ ; Ar matrices, 14–15 K	IR, ^{1,2} H	weak complexes of AsH ₃ identified	133b
A···MH ₃ [M = As or Sb; A = HF, HCl, or Me ₃ M (M = Ga or In)]	codeposition of A and MH ₃ ; Ar matrices, 12–15 K	IR, ^{1,2} H	weak complexes of AsH ₃ and SbH ₃ identified	133c

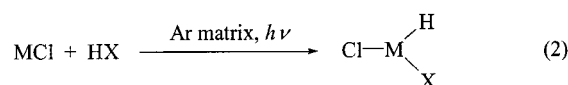
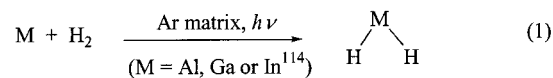
the binding energies of core electrons, e.g., 3d for Ge and 4d for Sn.

B. Trapping

Our heightened acquaintance with molecular hydrides of the main-group metals owes a considerable debt to trapping experiments of one sort or another designed to preserve reactive transients. This may sometimes be compassed by *chemical* means, the transient being intercepted by a reactive substrate to produce a known product that is easily identified by spectroscopic or other means. Some of the first evidence pointing to the formation of the trihydrides of aluminum and gallium came from experiments in which the hydride was trapped with trimethylamine to form the known, relatively stable adducts (Me₃N)_nMH₃ (M = Al^{13,80} or Ga;^{13,60} n = 1 or 2). More often some method of *physical* trapping is sought. One way, already alluded to, involves entrainment in a noble-gas stream and rapid adiabatic cooling in a supersonic jet to produce molecules in an essentially collisionless state and with effective translational, vibrational, and rotational temperatures of a few Kelvin. More exotic are experiments involving *magnetic* trapping of a paramagnetic molecule like CaH which can be sampled by a newly described technique depending on elastic collisions with a cold buffer gas;⁸¹ laser fluorescence and Zeeman spectroscopies have been used to detect the trapped molecule and to establish that temperatures in the milliKelvin range have been achieved.

A more familiar strategy involves matrix isolation,^{16,82} the reactive molecule being entrapped at high dilution in a solid inert host. In principle, a variety of spectroscopic methods can then be used to detect, identify, and characterize the captive molecule: in practice and as indicated in Table 1, infrared and EPR measurements have been the lynchpins of analysis in studies of hydride molecules. These molecules may be quenched from the vapor

phase with an excess of the matrix gas to form a solid condensate at low temperatures; often they are formed within the cold matrix, as exemplified by eqs 1 and 2 involving photoexcitation of M atoms and MCl molecules, respectively. The effects of systematic



(M = Al, X = Cl;^{117a} M = Ga, X = Cl^{126a} or H;¹²⁷ M = In, X = Cl or H¹²⁸)

changes in the conditions may be instructive, but it is the response of the spectrum to the precise isotopic composition of the molecule (whether through isotopic shifts in the IR or through hyperfine splitting in the EPR spectrum) that is likely to be most revealing with regard to the nature of a new molecule. For example, the divalent aluminum radical AlH₂ can be recognized unequivocally by its EPR spectrum;¹¹¹ as illustrated in Figure 1, this consists of a widely spaced sextet [due to the single Al atom (*I* = 5/2)] of 1:2:1 triplets [corresponding to two equivalent H atoms (*I* = 1/2)]. There is a similar ring of confidence about the identification of the trigonal planar GaH₃ molecule as the major product of the co-condensation of gallium and hydrogen atoms with an excess of argon at 10 K.¹¹⁵ As illustrated in Figure 2, experiments with an equimolar mixture of H and D give rise to a total of no less than 8 distinct absorptions in the region associated with ν(GaH_t)/(GaD_t) modes and 10 such absorptions in the region associated with GaH_t/GaD_t bending modes (where t denotes a terminal ligand), findings that can be shown to be wholly in keeping with the postulate that different isotopomers of GaH₃ with *D*_{3h} symmetry are the carriers of these bands. In both cases, characterization is

Table 2. Physical Properties of Gaseous Mononuclear Hydrides of the Main-Group Metals, MH_n

molecule	dimensions ^a		vibrational properties ^b		thermodynamic properties ^c	
	exp	theor	exp	theor	dissociation energy	$\Delta_f H_{298}^\ominus$
	1. MH species					
⁷ LiH	<i>r_e</i> 1.59490811 ³⁴	<i>r_e</i> 1.588–1.63578 ^{253–255}	ω_e 1405.50936 ²²	ω_e 1386–1416 ^{253–255}	234.35 ²² (234–244) ^{253–257}	+139.25 ^{22,258}
²³ NaH	<i>r_e</i> 1.8874 ^{23,259}	<i>r_e</i> 1.864–1.9144 ^{253–255}	ω_e 1171.0946 ^{23,259}	ω_e 1162–1198 ^{253–255}	183.2 ²³ (184–192) ^{253–255}	+138.5 ^{23,258}
³⁹ KH	<i>r_e</i> 2.240164 ^{23,26,260,261}	<i>r_e</i> 2.214–2.313 ^{254,255}	ω_e 986.6484 ^{26,260}	ω_e 954–995 ^{254,255}	170.86 ²³ (162–179) ^{254,255}	+132.4 ^{23,258}
⁸⁵ RbH	<i>r_e</i> 2.366808 ^{23,262}	<i>r_e</i> 2.258–2.467 ^{254,255}	ω_e 937.1046 ^{23,262}	ω_e 894–941 ^{254,255}	169 ²³ (158–182) ^{254,255}	+126 ^{23,258}
¹³³ CsH	<i>r_e</i> 2.4942 ^{23,263}	<i>r_e</i> 2.324–2.624 ^{254,255}	ω_e 891.2511 ^{23,263}	ω_e 834–956 ^{254,255}	171.6 ²³ (161–194) ^{254,255}	+119.1 ^{23,258}
⁹ BeH	<i>r_e</i> 1.345 ²⁰	<i>r_e</i> 1.33–1.34839 ^{253,254,264}	ω_e 2071.87 ²⁰	ω_e 2082–2148 ^{253,254}	196.3 ^{20,258} (199–207) ^{254–257,264}	+342.0 ^{20,258}
²⁴ MgH	<i>r_e</i> 1.729828 ⁴¹	<i>r_e</i> 1.73–1.74859 ^{253,254}	ω_e 1495.2632 ^{41,95}	ω_e 1354–1532 ^{253,254}	129 ²¹ (120–125) ^{253,254}	+232 ^{21,258}
⁴⁰ CaH	<i>r_e</i> 2.00083 ²⁶⁵	<i>r_e</i> 1.99–2.074 ^{254,265–268}	ω_e 1298.3999 ²⁶⁵	ω_e 1253–1284 ^{254,267}	≤ 164 ²¹ (152–164) ^{254,267}	≥ +228 ^{21,258}
⁸⁸ SrH	<i>r_e</i> 2.146097 ²⁶⁹	<i>r_e</i> 2.14–2.228 ^{254,266,270}	ω_e 1206.8912 ²⁶⁹	ω_e 1134–1167 ^{254,270}	≤ 160 ²¹ (142–148) ^{254,270}	≥ +218.5 ^{21,258}
¹³⁸ BaH	<i>r_e</i> 2.231899 ^{28,271}	<i>r_e</i> 2.156–2.376 ^{254,266,272}	ω_e 1168.4245 ^{28,271}	ω_e 1071–1195 ^{254,272}	≤ 188 ²¹ (173) ²⁵⁴	≥ +206 ^{21,258}
⁶³ CuH	<i>r_e</i> 1.462581 ^{30,273}	<i>r_e</i> 1.429–1.568 ^{274–276}	ω_e 1940.7462 ^{30,273}	ω_e 1691–2484 ^{274–276}	251 ²⁷⁴ (135–277) ^{274–276}	+301 ^{258,274}
¹⁰⁷ AgH	<i>r_e</i> 1.617798 ²⁷⁷	<i>r_e</i> 1.584–1.6908 ^{275,278,279}	ω_e 1759.671 ²⁷⁷	ω_e 1779–1882 ^{275,278}	199 ²⁸⁰ (139–230) ^{275,278,279}	+300 ^{258,280}
¹⁹⁷ AuH	<i>r_e</i> 1.52385 ²⁸¹	<i>r_e</i> 1.490–1.56 ^{275,278,281,282}	ω_e 2305.01 ²⁸¹	ω_e 2157–2548 ^{275,278}	288 ²⁸¹ (272–319) ^{275,278}	+292 ^{258,281}
⁶⁴ ZnH	<i>r_e</i> 1.59400 ^{31,283}	<i>r_e</i> 1.607 ²⁸⁴	ω_e 1615.7164 ³⁹	ω_e 1647 ²⁸⁴	82.1 ²¹ (79) ²⁸⁴	+263 ^{21,258}
¹¹⁴ CdH	<i>r_e</i> 1.76107 ²⁸³	<i>r_e</i> 1.778 ²⁸⁵	ω_e 1460.8978 ²⁸³	ω_e 1370 ²⁸⁵	65.4 ²¹ (68) ²⁸⁵	+261 ^{21,258}
²⁰² HgH	[<i>r_e</i> 1.7662 ²¹] ^d	<i>r_e</i> 1.778–1.845 ^{285–287}	ω_e 1203.24 ²⁸⁸	ω_e 1296–1396 ²⁸⁷	36.1 ²¹ (38–46) ²⁸⁵	+239.6 ^{21,258}
¹¹ BH	<i>r_e</i> 1.232179 ²⁸⁹	<i>r_e</i> 1.225–1.241 ^{11,253}	ω_e 2366.7275 ²⁸⁹	ω_e 2513–2532 ¹¹	337.9 ²⁹⁰ (340.8–354.8) ^{253,256,257}	+441.3 ^{258,290}
²⁷ AlH	<i>r_e</i> 1.645362 ²⁹	<i>r_e</i> 1.648–1.674 ^{11,253}	ω_e 1682.3694 ^{291,292}	ω_e 1564–1771 ¹¹	281 ²⁵⁸ (303) ²⁵³	+263 ²⁵⁸
⁶⁹ GaH	<i>r_e</i> 1.662121 ²⁹³	<i>r_e</i> 1.662–1.706 ¹¹	ω_e 1603.9559 ^{292,294}	ω_e 1506–1612 ¹¹	261 ²⁹⁵ (271) ²⁹⁵	+226 ^{258,295}
¹¹⁵ InH	<i>r_e</i> 1.835971 ²⁹⁶	<i>r_e</i> 1.823–1.898 ¹¹	ω_e 1475.4183 ²⁹⁶	ω_e 1405–1535 ¹¹	239 ²¹ (240) ²⁹⁷	+218 ^{21,258}
²⁰⁵ TlH	<i>r_e</i> 1.872651 ²⁹³	<i>r_e</i> 1.883–1.944 ^{11,285}	ω_e 1391.2681 ²⁹⁸	ω_e 1294–1439 ^{11,286}	190 ²¹ (189–202) ^{286,297}	+206 ^{21,258}
⁷⁴ GeH	<i>r_e</i> 1.58724 ³⁵	<i>r_e</i> 1.575–1.628 ²⁹⁹	ω_e 1900.3820 ³⁵	ω_e 1813–1980 ²⁹⁹	≤ 318 ²¹	≥ +268 ^{21,258}
¹²⁰ SnH	<i>r_e</i> 1.76905 ³⁶	<i>r_e</i> 1.766–1.798 ³⁰⁰	ω_e 1718.4231 ³⁶	ω_e 1715–1819 ³⁰⁰	≤ 263 ²¹	≥ +252 ^{21,258}
²⁰⁸ PbH	<i>r_e</i> 1.8393 ²⁷	<i>r_e</i> 1.852–1.880 ²⁸⁶	ω_e 1560.5320 ²⁷	ω_e 1567–1592 ²⁸⁶	≤ 153 ²¹ (147–151) ²⁸⁵	≥ +256 ^{21,258}
⁷⁵ AsH	<i>r_e</i> 1.52237 ³²	<i>r_e</i> 1.511–1.535 ^{39,301,302}	ω_e 2155.503 ³⁰³	ω_e 2130–2163 ^{301,302}	270 ³⁹	+246 ^{39,258}
¹²¹ SbH	<i>r_e</i> 1.71072 ³⁰⁴	<i>r_e</i> 1.702–1.731 ^{301,305}	ω_e 1923.1792 ³⁰⁴	ω_e 1886 ³⁰⁵	(223) ³⁰⁶	(+254) ^{258,306}
²⁰⁹ BiH	<i>r_e</i> 1.8085919 ³⁰⁷	<i>r_e</i> 1.772–1.858 ^{282,286,301}	ω_e 1699.5170 ³⁰⁷	ω_e 1756–1780 ²⁸⁶	≤ 280 ²¹ (183–206) ^{282,286,306}	≥ +238 ^{21,258}

		2. MH₂ species				
⁹ BeH ₂		<i>r</i> _c 1.333–1.344 ^{89,253,264} <i>θ</i> _e 180 ^{89,253,264}	2159.1, 697.9 ⁸⁹	ref 89	(295–302) ^{253,257,264}	(+165) ²⁵³
²⁴ MgH ₂		<i>r</i> _c 1.71768 ^{95,253} <i>θ</i> _e 180 ^{95,253}	1571.9, 439.8 ⁹⁵	ref 95	(206) ²⁵³	(+162) ²⁵³
⁴⁰ CaH ₂		<i>r</i> _c 2.03–2.05 ^{266,268,308} <i>θ</i> _e 157–180 ^{266,269,308}	1267.0, 1192.0 ⁹⁷	ref 266	(ca. 170) ²⁶⁶	
⁸⁸ SrH ₂		<i>r</i> _c 2.174–2.18 ^{266,308} <i>θ</i> _e 137–140 ^{266,308}		ref 266		
¹³⁸ BaH ₂		<i>r</i> _c 2.27–2.278 ^{266,308} <i>θ</i> _e 120 ^{266,308}		ref 266		
⁶⁴ ZnH ₂		<i>r</i> _c 1.505–1.530 ⁹⁹ <i>θ</i> _e 180 ⁹⁹	1870.6, 630.5 ^{97,99}	ref 99	(202) ⁹⁹	(+162) ⁹⁹
¹¹⁴ CdH ₂		<i>r</i> _c 1.668–1.683 ⁹⁹ <i>θ</i> _e 180 ⁹⁹	1753.8, 601.7 ⁹⁹	ref 99	(182) ⁹⁹	(+183) ⁹⁹
²⁰² HgH ₂		<i>r</i> _c 1.629–1.642 ^{99,282} <i>θ</i> _e 180 ^{99,282}	1885–1903, 769–774 ¹⁰⁰	ref 99	(167–169) ^{99,282} ca. 400 ¹¹	(+163–175) ^{99,282}
¹¹ BH ₂	<i>r</i> ₀ 1.181 ¹⁸ <i>θ</i> ₀ 131 ¹⁸	<i>r</i> _c 1.185–1.194 ^{11,102,253} <i>θ</i> _e 126.5–128.6 ^{11,102,253}	954.65 ¹⁸	ref 11	(336.4–344) ^{11,257}	+201 ¹¹
²⁷ AlH ₂	<i>r</i> ₀ 1.591 ¹⁹ <i>θ</i> ₀ 119 ¹⁹	<i>r</i> _c 1.588–1.609 ^{11,111,123,204,253} <i>θ</i> _e 118.0–118.7 ^{11,111,123,204,253}	1806.3, 1769.5, 766.4 ¹¹⁴	ref 114	(236–312) ^{11,204,253}	(+268) ²⁵³
⁶⁹ GaH ₂	<i>θ</i> ca. 120 ¹¹⁴	<i>r</i> _c 1.580–1.616 ^{11,123,253} <i>θ</i> _e 118–120.4 ^{11,123,253}	1799.5, 1727.7, 740.1 ¹¹⁴	ref 114	(220) ¹¹	(+274) ^{11,295}
¹¹⁵ InH ₂		<i>r</i> _c 1.755–1.816 ^{11,114} <i>θ</i> _e 118.9–120.6 ^{11,114}	1615.6, 1548.6, 607.4 ¹¹⁴	ref 114	(191) ¹¹	(+293) ^{11,297}
²⁰⁵ TlH ₂		<i>r</i> _c 1.760–1.869 ¹¹ <i>θ</i> _e 119.9–121.7 ¹¹			(156) ²⁹⁸	(+303) ²⁹⁷
⁷⁴ GeH ₂	<i>r</i> ₀ 1.591 ²⁴ <i>θ</i> ₀ 91.2 ²⁴	<i>r</i> _c 1.553–1.620 ^{24,309–312} <i>θ</i> _e 86.2–93 ^{24,309–312}	1887, 1864, 920 ^{131,313}	ref 312	286–290 ^{314,315}	+229–237 ^{314,315}
¹²⁰ SnH ₂		<i>r</i> _c 1.756–1.801 ^{310–312} <i>θ</i> _e 85.3–93.0 ^{310–312}		ref 312		
²⁰⁸ PbH ₂		<i>r</i> _c 1.866–1.880 ^{282,312} <i>θ</i> _e 90.5–91.5 ^{282,312}		ref 312	(188) ²⁸²	(+265) ²⁸²
⁷⁵ AsH ₂	<i>r</i> ₀ 1.518 ³³ <i>θ</i> ₀ 92.08 ³³	<i>r</i> _c 1.516–1.521 ^{306,316,317} <i>θ</i> _e 90.7–92.7 ^{306,316,317}		ref 317	274 ³⁹ (275) ³¹⁸	+172 ³⁹
¹²¹ SbH ₂		<i>r</i> _c 1.726 ³⁰⁶ <i>θ</i> _e 89.8 ³⁰⁶			(229) ³⁰⁶	(+240) ³⁰⁶
²⁰⁹ BiH ₂		<i>r</i> _c 1.876 ³⁰⁶ <i>θ</i> _e 88.9 ³⁰⁶			(181) ³⁰⁶	(+281) ³⁰⁶
		3. MH₃ species				
¹¹ BH ₃	<i>r</i> ₀ 1.19001 ³¹⁸ <i>θ</i> ₀ 120 ³¹⁸	<i>r</i> _c 1.188–1.198 ^{11,253,319,320} <i>θ</i> _e 120 ^{11,253,319,320}	2601.574, 1196.66, 1147.499 ³¹⁸	refs 11,319,320	371 ²⁵⁸ (369–372) ^{11,257}	+100.0 ²⁵⁸
²⁷ AlH ₃	<i>θ</i> _e 120 ¹¹⁵	<i>r</i> _c 1.571–1.597 ^{11,80,115,253,319,320} <i>θ</i> _e 120 ^{11,80,115,253,319,320}	1882.9, 783.6, 697.7 ^{80,112,115}	refs 80,112,115, 319,320	(282) ¹¹	(+123) ²⁵³
⁶⁹ GaH ₃	<i>θ</i> _e 120 ¹¹⁵	<i>r</i> _c 1.557–1.587 ^{11,115,319,320} <i>θ</i> _e 120 ^{11,115,319,320}	1923.2, 758.7, 717.4 ¹¹⁵	ref 115	(260) ^{282,295}	(+151) ^{282,295}
¹¹⁵ InH ₃	<i>θ</i> _e 120 ¹¹⁵	<i>r</i> _c 1.725–1.753 ^{11,115,321} <i>θ</i> _e 120 ^{11,115,321}	1754.5, 613.2, 607.8 ¹¹⁵	ref 115,321	(225) ¹¹	(+222) ²⁹⁷
²⁰⁵ TlH ₃		<i>r</i> _c 1.739–1.789 ^{11,321} <i>θ</i> _e 120 ^{11,321}		ref 321	(181) ¹¹	(+293) ²⁹⁷
⁷⁴ GeH ₃	<i>θ</i> _e ca. 115 ¹³²	<i>r</i> _c 1.524–1.525 ^{317,322} <i>θ</i> _e 110.5–112.4 ^{317,322}	2049.81 ³²³ 1841, 1814, 663 ^{131,324}	ref 317	(265) ³¹⁷	+229 ³²⁵ (+221) ³¹⁷
¹²¹ SnH ₃	<i>θ</i> _e ca. 117 ¹³²	<i>r</i> _c 1.755 ³²² <i>θ</i> _e 110.6 ³²²				

Table 2 (Continued)

molecule	dimensions ^a		vibrational properties ^b		thermodynamic properties ^c	
	exp	theor	exp	theor	dissociation energy	ΔH_{298}^{\ominus}
⁷⁵ AsH ₃	r_0 1.51106 ⁴⁶	r_e 1.500–1.512 ^{301,317}	3. MH ₃ species ref 301	refs 301, 317	297 ²⁵⁸	+66.4 ²⁵⁸
	θ_0 92.069 ⁴⁶	θ_e 92.4–94.3 ^{301,317}		ref 301	(285) ³¹⁷	+145.1 ²⁵⁸
	r_0 1.7000 ⁴⁷	r_e 1.688–1.719 ^{301,306}		ref 301	257 ²⁵⁸	
	θ_0 91.54 ⁴⁷	θ_e 92.1–93.6 ^{301,306}		ref 301	$\leq 196^{\text{9b}}$ (193–235) ^{282,306}	
²⁰⁹ BiH ₃	r_0 1.760–1.865 ^{282,301,306}	r_e 1.760–1.865 ^{282,301,306}	4. MH ₄ species ref 43	refs 317, 326	288 ²⁵⁸	+90.8 ²⁵⁸
	θ_0 90.3–92.8 ^{282,301,306}	θ_e 90.3–92.8 ^{282,301,306}		ref 43	(288–295) ^{317,328}	+162.8 ²⁵⁸
⁷⁴ GeH ₄	r_0 1.5143 ^{43,44}	r_e 1.525–1.56 ^{317,326–328}	ref 43	ref 326	(256) ³²⁸	$\geq +250^{\text{9b}}$ (+263) ²⁸²
	tetrahedral	tetrahedral		ref 326	$\leq 205^{\text{9b}}$ (206–241) ^{282,328}	
¹²¹ SnH ₄	r_0 1.70285 ^{43–45}	r_e 1.706–1.73 ^{326–328}	ref 43	ref 326		
	tetrahedral	tetrahedral		ref 326		
²⁰⁸ PbH ₄		r_e 1.74–1.78 ^{282,326–328}	ref 326	ref 326		
		tetrahedral				

^a Distances, r , are in Å and interbond angles, θ , in deg. ^b Vibrational wavenumbers are in cm^{-1} . Harmonic wavenumbers, ω_e , are quoted for the diatomic hydrides, but anharmonic (observed) wavenumbers are quoted for the larger molecules. ^c Energies are in kJ mol^{-1} . The dissociation energy quoted is generally D_0^{\ominus} for the diatomic hydrides, but the mean bond energy for the polyatomic hydrides. Values in parentheses are theoretical estimates. ^d Value open to doubt.

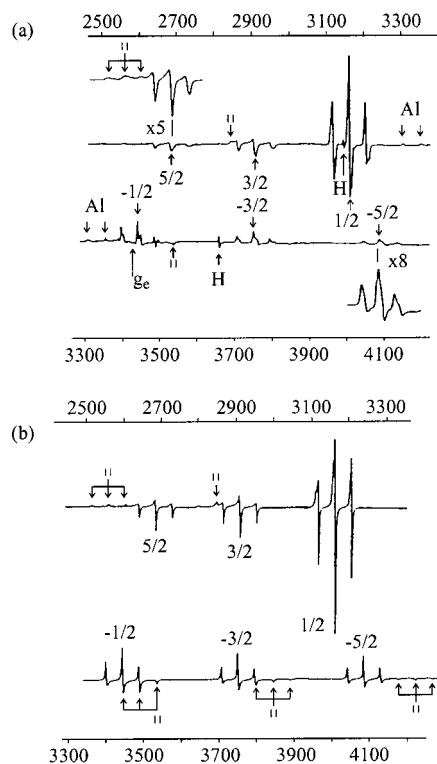


Figure 1. (a) Overall EPR spectrum of AlH_2 trapped in a neon matrix at 4 K; two Al atom lines and the H atom lines are also indicated. The sample was prepared by photolysis ($\lambda = 254 \text{ nm}$) of a neon matrix containing Al atoms and a small amount (ca. 0.1%) of H_2O . (b) Overall computer-simulated EPR spectrum of AlH_2 . Note the relatively large peak height intensity of the Al $M_I = 1/2$ transition and the arrow near 3420 G which indicates the magnetic field position corresponding to g_e . (Adapted from ref 111.)

greatly strengthened by ab initio calculations at a level sufficient to simulate realistically the relevant spectra. Matrix isolation has thus been highly successful as a means of reconnaissance and of providing the first hints of weakly bound complexes. Such complexes include a number in which H_2 appears to be a ligand, e.g., $\text{H}_2 \cdots \text{BH}_3$,¹⁰³ $\text{H}_2 \cdots \text{AlH}_2$,^{112,116} and $\text{H}_2 \cdots \text{ZnH}_n$ ($n = 1$ or 2),⁹⁹ but only in the case of $(\eta^2\text{-H}_2)\text{CuCl}$ is there evidence from a $\nu(\text{HH})$ mode made active in IR absorption that a bond of some substance is established between the metal and H_2 .⁸⁴

Offering an altogether more strongly interactive environment for the trapping of hydride fragments are the surfaces of the metals or of their solid compounds or the interstices of open framework structures, e.g., zeolites. This is not the place to elaborate on adsorption phenomena, but some idea of what is entailed may be gained from recent studies of the adsorption of H atoms on Al (110). Scanning tunneling microscopy (STM) and surface infrared measurements witness the evolution of a variety of surface alanes Al_mH_n with m ranging from 1 to more than 30.¹³⁶ The atomic hydrogen initiates the process by extracting Al atoms from the surface lattice to create mobile monohydride monomers (ad-Al–H) which predominate in the low-coverage regime. At higher hydrogen coverages, multihydride oligomers are produced in company with the ad-Al–H. These alane oligomers are not only relatively immobile, but also more stable than ad-Al–H, remaining at room

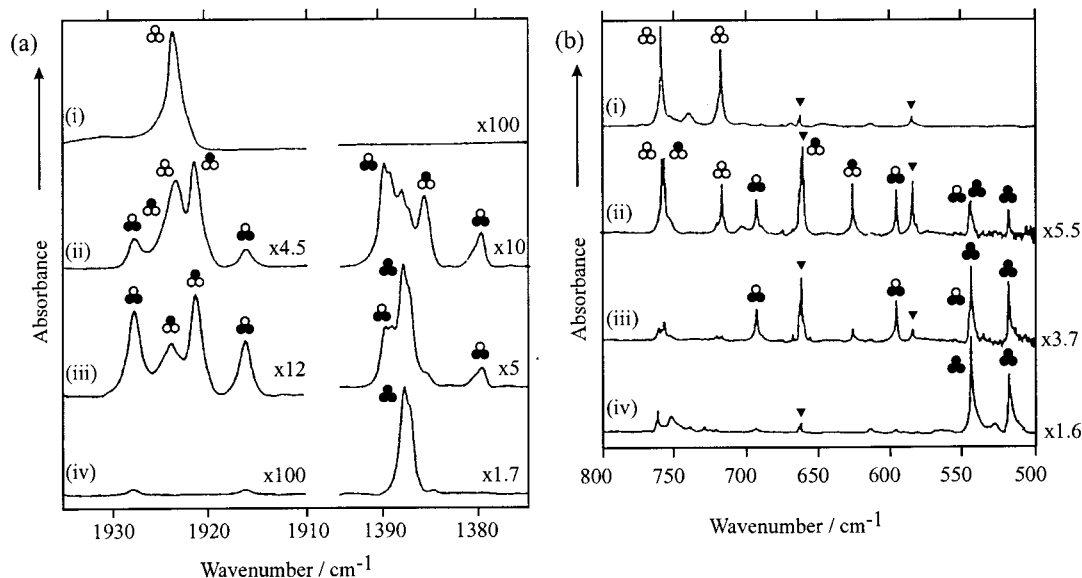


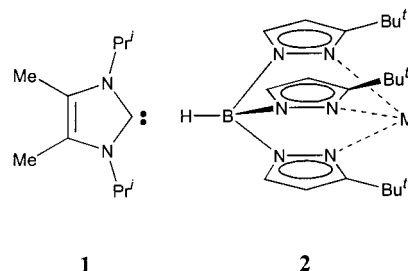
Figure 2. Infrared spectra (i) of the Ga–H and Ga–D stretching modes and (ii) of the deformation modes of the various $\text{GaH}_{3-n}\text{D}_n$ isotopomers as formed after co-deposition of Ga with H and/or D atoms and an excess of argon. The spectra were normalized with respect to the strongest band (see ordinate scale normalization factors). The samples were prepared with argon/hydrogen mixtures which were subjected to the action of a microwave discharge; the mixtures consisted of H_2 , HD, D_2 , Ar in the following proportions: (a) 10:0:0:100, (b) 5:5:0:100, (c) 0:10:0:100, and (d) 0:0:10:100. Bands due to the different isotopomers are identified by $\circ = \text{H}$ and $\bullet = \text{D}$; \blacktriangledown indicates traces of hydroxygallium hydride species. Note that GaHD_2 exhibits two bands in the $\nu(\text{Ga-H})$ region as a result of Fermi resonance. (Adapted from ref 115.)

temperature on the surface where they can be directly imaged. Surface Ga–H but not N–H species have also been identified by high-resolution electron energy loss spectroscopy (HREELS) when H atoms are adsorbed on GaN (0001), a result clearly implying that the surface is Ga-terminated.¹³⁷ Both terminal Ga–H and bridging Ga–H–Ga have been identified, together with As–H units, by the infrared spectra of H atoms adsorbed on the c (2×8) and (2×6) reconstruction of GaAs (100).¹³⁸ Polarized spectra reveal that the Ga–H and As–H bonds orient along the [110] and $[\bar{1}10]$ axes, respectively, a finding that is consistent with a GaAs surface structure composed of Ga and As dimers with the dimer bonds in the [110] and $[\bar{1}10]$ directions. Similar studies give grounds for believing that H atoms also insert into the analogous In_2 dimers present on the metal-rich InP (001) surface, with the assembly of In–H–In bridges.¹³⁹

C. Chemical Control

Stabilization of reactive MH_n fragments, including protection from bimolecular encounters, may be achieved by a variety of chemical means. Reference has already been made to the capacity of complexation to preserve binary molecules such as alane and gallane, and numerous adducts of these electrophilic hydrides with neutral bases or anionic species are lastingly stable at ambient temperatures;^{12,140} in the case of alane, stabilization is perhaps less important than the increased tractability that accompanies the change from the polymeric structure of the parent hydride to the discrete molecular structure of the adduct. For reasons of thermal stability, solubility in common organic solvents, or ease of preparation and manipulation, therefore, species such as $\text{Me}_3\text{N} \cdot \text{MH}_3$ and MH_4^- ($\text{M} = \text{Al}, \text{Ga}, \text{or In}$) make altogether

more convenient synthetic agents than do the base-free hydrides. The binary hydride InH_3 has so far resisted all attempts to prepare it in any but a matrix environment at low temperature,¹¹⁵ but coordination by the highly nucleophilic imidazol-2-ylidene carbene **1** has now led to the isolation of the first example of a structurally authenticated indium trihydride complex, $\text{Pr}^i\text{NC}_2\text{Me}_2\text{N}(\text{Pr}^i)\text{C} \cdot \text{InH}_3$, which survives in the solid state at temperatures up to -5°C .¹⁴¹



Partial replacement of hydride by other ligands tends also 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 mixed hydrides of the types $[\text{RMH}_2]_n$ and $[\text{R}_2\text{MH}]_n$ for $\text{M} = \text{Al}$ or Ga and for a variety of organic substituents R.^{12,142–146} With a sufficiently bulky substituent, e.g., $\text{R} = \text{Mes}^* = 2,4,6\text{-Bu}^i_3\text{C}_6\text{H}_2$, the natural tendency of the MH_n unit to aggregate through the formation of M-H-M bridges may be curbed to furnish monomeric derivatives such as Mes^*GaH_2 and Mes^*_2MH ($\text{M} = \text{Al}$ or Ga).^{143–146} Here steric factors are likely to be the dominant principle of stabilization. Other substituents combine bulk with multidentate coordinating

Table 3. Physical Properties of Gaseous Binuclear Hydrides of the Main-Group Metals, M_2H_n

molecule	geometry and dimensions ^{a,b}		vibrational properties, $\nu(M-H)^{b,c}$		other properties	$\Delta_f H_{298}^{\ominus d}$
	exp	theor	exp	theor		
			1. M_2H_2 species			
HMgMgH		linear ⁹⁵	1491.8 ⁹⁵	1554.7 ⁹⁵		
HZnZnH		linear ⁹⁹	1740.3 ⁹⁹	1884, 1919 ⁹⁹		
HHgHgH		linear ^{100,329} $r_e(\text{Hg}-\text{H})$ 1.74 $r_e(\text{Hg}-\text{Hg})$ 2.73	1792 ¹⁰⁰	ref 329		
HBBH	linear, $^3\Sigma_g^-$ ground state ¹⁰⁴	linear ^{103,104,330} $r_e(\text{B}-\text{H})$ 1.177 $r_e(\text{B}-\text{B})$ 1.516	ref 103	refs 103,330	EPR spectrum ¹⁰⁴	
Al ₂ H ₂		four possible isomers 10–12,14 ^{113,330–332}	ref 113	refs 113, 330–332		
Ga ₂ H ₂		four possible isomers 10–12,14 ^{330,332–334}	ref 122	refs 332,333		
In ₂ H ₂		four possible isomers 10–12,14 ³³⁰	evidence of isomer 10 ^{122c}	ref 122c		
Ge ₂ H ₂		four possible isomers 10–12,14 ^{332,335}		refs 332,335		
HAs=AsH		<i>trans</i> - C_{2h} structure ³³⁶ $r_e(\text{As}=\text{As})$ 2.227 $\angle \text{As}=\text{As}-\text{H}$ 94.4		ref 336		
HSb=SbH		<i>trans</i> - C_{2h} structure ³³⁶ $r_e(\text{Sb}=\text{Sb})$ 2.608 $\angle \text{Sb}=\text{Sb}-\text{H}$ 93.0		ref 336		
HBi=BiH		<i>trans</i> C_{2h} structure ³³⁶ $r_e(\text{Bi}=\text{Bi})$ 2.719 $\angle \text{Bi}=\text{Bi}-\text{H}$ 91.8		ref 336		
			2. M_2H_4 species			
HMg(μ -H) ₂ MgH		D_{2h} structure (15) ³³⁷ $r_e(\text{Mg}-\text{H}_i)$ 1.688 $r_e(\text{Mg}-\text{H}_b)$ 1.870	ref 95	refs 95,337		
HCa(μ -H) ₂ CaH		D_{2h} structure (15) ³³⁷ $r_e(\text{Ca}-\text{H}_i)$ 2.038 $r_e(\text{Ca}-\text{H}_b)$ 2.198	ref 97	ref 337		
HZn(μ -H) ₂ ZnH		D_{2h} structure (15) ⁹⁹ $r_e(\text{Zn}-\text{H}_i)$ 1.498 $r_e(\text{Zn}-\text{H}_b)$ 1.713		ref 99		
H ₂ BBH ₂		lowest energy equilibrium structure has D_{2d} symmetry (16) ³³⁸				
Al ₂ H ₄		lowest energy equilibrium structure is trihydrogen bridged (18) ³³⁹		ref 339		
Ga ₂ H ₄		lowest energy equilibrium structure is trihydrogen bridged (18) ³⁴⁰		ref 340		
Ge ₂ H ₄		lowest energy equilibrium structure is <i>trans</i> - C_{2h} (17) ³⁴¹		ref 341		

Sn ₂ H ₄		lowest energy equilibrium structure is <i>C_{2h}</i> HSn(<i>μ</i> -H) ₂ SnH (15) ³⁴¹		ref 341		
Pb ₂ H ₄		lowest energy equilibrium structure is <i>C_{2h}</i> HPb(<i>μ</i> -H) ₂ PbH (15) ³⁴¹		ref 341		
3. M₂H₆ species						
H ₂ B(<i>μ</i> -H) ₂ BH ₂	<i>r_e</i> (B–H _t) 1.184 ³⁴²	<i>r_e</i> (B–H _t) 1.182–1.194 ^{319,320,343–345}	<i>ν</i> (B–H _t) 2518–2613 ³⁴⁶	refs 319,320, 343–345	dimerization energy for 2BH ₃ : 182 (126–197) ^{319,320,343,345}	+35.6 ²⁵⁸
	<i>r_e</i> (B–H _b) 1.314	<i>r_e</i> (B–H _b) 1.309–1.340	<i>ν</i> (B–H _b) 1615–2096			
H ₂ Al(<i>μ</i> -H) ₂ AlH ₂	∠B–H _b –B 83.1	∠B–H _b –B 84.0–86.1 <i>r_e</i> (Al–H _t) 1.558–1.586 ^{319,320,343,344}		refs 319,320, 343,344	dimerization energy for 2AlH ₃ : (129–157) ^{319,320}	(+92–184)
		<i>r_e</i> (Al–H _b) 1.714–1.750 ∠Al–H _b –Al 96.9–101.2			detected by mass spectrum ³⁷	refs 253,321,343
H ₂ Ga(<i>μ</i> -H) ₂ GaH ₂	<i>r_a</i> (Ga–H _t) 1.52 ⁶⁰	<i>r_e</i> (Ga–H _t) 1.519–1.568 ^{319,320,343,344}	<i>ν</i> (Ga–H _t) 1976–2015 ^{60,124}	refs 319,320, 343,344	dimerization energy for 2GaH ₃ : (88–115) ^{319,320,343}	(+105–118) ^{321,343}
	<i>r_a</i> (Ga–H _b) 1.71	<i>r_e</i> (Ga–H _b) 1.710–1.780	<i>ν</i> (Ga–H _b) 1202–1474		UV-PE spectrum ⁷⁵	
H ₂ In(<i>μ</i> -H) ₂ InH ₂	∠Ga–H _b –Ga 97.9	∠Ga–H _b –Ga 95.4–97.8 <i>r_e</i> (In–H _t) 1.706–1.727 ^{321,345}		refs 321,345	dimerization energy for 2InH ₃ : (62–95) ^{321,345}	(+175) ³²¹
		<i>r_e</i> (In–H _b) 1.940–1.976 ∠In–H _b –In 99.1–99.6				
H ₂ Tl(<i>μ</i> -H) ₂ TlH ₂		<i>r_e</i> (Tl–H _t) 1.701 ³²¹		ref 321	dimerization energy for 2TlH ₃ : (38) ³²¹	(+245) ³²¹
		<i>r_e</i> (Tl–H _b) 2.003 ∠Tl–H _b –Tl 99.8				
H ₃ GeGeH ₃	<i>r_a</i> (Ge–H) 1.541 ⁶¹ <i>r_a</i> (Ge–Ge) 2.403 ∠Ge–Ge–H 112.5	<i>r_e</i> (Ge–H) 1.520–1.546 ^{347–350} <i>r_e</i> (Ge–Ge) 2.419–2.499 ∠Ge–Ge–H 110.2–110.6	ref 351	refs 349, 350	<i>D</i> (Ge–Ge) 276 ³⁵² (256–267) ³⁵³	+162.3 ²⁵⁸
H ₃ SnSnH ₃		<i>r_e</i> (Sn–H) 1.701–1.715 ^{347,348}			detected by mass spectrum ³⁵⁴	+274 ^{9b}
		<i>r_e</i> (Sn–Sn) 2.780–2.850			half-life in vapor 4.7 s at 264–388 K ³⁵⁴	(+160–273) ^{347,348}
H ₃ PbPbH ₃		∠Sn–Sn–H 110.5 <i>r_e</i> (Pb–H) 1.737–1.750 ^{347,348} <i>r_e</i> (Pb–Pb) 2.851–3.012 ∠Pb–Pb–H 110.4–110.6			<i>D</i> (Sn–Sn) (228–234) ³⁵³ <i>D</i> (Pb–Pb) (207–216) ³⁵³	

^a Bond distances, *r*, are in Å and bond angles, ∠, in deg. Bold numbers refer to relevant structural formulae in the text. ^b t = terminal, b = bridging. ^c Vibrational wavenumbers are in cm⁻¹. ^d Energies are in kJ mol⁻¹. *D* = bond dissociation energy.

Table 4. Physical Properties of Binary Hydrides of Main-Group Metals in the Condensed Phases

thermal/thermodynamic properties ^a						
compound	m.p.	b.p.	decomp temp	$\Delta_f H_{298}^\ominus$	crystal structure ^b	other properties
LiH	965 ^{9b}		820 ^c	-90.5 ²⁵⁸	cubic NaCl-type $a = 4.083$ shortest Li \cdots H 2.043 ^{9b}	
NaH			480 ^c	-56.3 ²⁵⁸	cubic NaCl-type $a = 4.879$ shortest Na \cdots H 2.445 ^{9b}	
KH			480 ^c	-57.7 ²⁵⁸	high-pressure phase B2(CsCl) at $p_T \geq 29.3$ GPa ^{188,189} cubic NaCl-type $a = 5.708$ shortest K \cdots H 2.856 ^{9b}	
RbH			440 ^c	-52.3 ²⁵⁸	high-pressure phase B2(CsCl) at $p_T \geq 4.0$ GPa ¹⁸⁹ cubic NaCl-type $a = 6.037$ shortest Rb \cdots H 3.025 ^{9b}	
CsH			440 ^c	-54.2 ²⁵⁸	high-pressure phases: B2(CsCl) at $p_T \geq 2.2-3.1$ GPa ¹⁸⁹ and orthorhombic CrB-structure at $p_T \geq 85$ GPa ³⁵⁵ cubic NaCl-type $a = 6.376$ shortest Cs \cdots H 3.195 ^{9b}	
CuH			<290 ^c		wurtzite structure $a = 2.89$, $c = 4.61$ ³⁵⁶	studied by TEM, powder X-ray diffraction, and DSC ^{d357}
BeH ₂			470 ^{e9b}		body-centered orthorhombic; space group <i>Ibam</i> $a = 9.082$, $b = 4.160$, $c = 7.707$ Be-H 1.38-1.44, \angle Be-H-Be 127, 130 network of corner-sharing BeH ₄ tetrahedra ³⁵⁸ second, low-temperature phase also reported ³⁵⁹	
MgH ₂			360 ^{e9b}	-75.3 ²⁵⁸	rutile structure $a = 4.517$, $c = 3.021$ Mg-H 1.95 ¹⁷⁴	
CaH ₂			1160 ^{e9b}	-181.5 ²⁵⁸	orthorhombic <i>Pnma</i> PbCl ₂ -type $a = 5.925$, $b = 3.581$, $c = 6.776$ Ca \cdots H 2.32, 2.85 ^{175,360}	NMR studies ¹⁷⁵
SrH ₂			860 ^{e9b}	-180.3 ²⁵⁸	high-temperature cubic (β) form ^{9b} orthorhombic <i>Pnma</i> PbCl ₂ -type $a = 6.3706$, $b = 3.8717$, $c = 7.3021$ Sr \cdots H 2.49, 3.06 ^{163,360}	
BaH ₂			500 ^{e9b}	-177.0 ²⁵⁸	high-temperature cubic (β) form ^{9b} orthorhombic <i>Pnma</i> PbCl ₂ -type $a = 6.792$, $b = 4.168$, $c = 7.858$ Ba \cdots H 2.570-2.979 ^{176,361}	
B ₂ H ₆	108.31 ⁴²	180.57 ⁴²	420 ^e	+35.6 ²⁵⁸	high-temperature cubic (β) form ^{9b} β -form, monoclinic $a = 4.40$, $b = 5.72$, $c = 6.50$, $\beta = 105.1$, $Z = 2$ B-H _t 1.06, 1.09; B-H _b 1.24, 1.25; \angle B-H _b -B 90.1 ³⁶²	NMR, vibrational, PE, and other properties ⁴²
AlH ₃			420-470 ^e	-46.0 ²⁵⁸	α -form, trigonal, space group <i>R3c</i> , hexagonal unit cell $a = 4.449$, $c = 11.804$ Al-H 1.715; \angle Al-H _b -Al 141.2 ¹⁷⁷	IR spectrum ³⁶³
GaH ₃	ca. 223 ⁶⁰		240 ^{e60}		structure involves both terminal and bridging Ga-H units ⁶⁰	NMR, vibrational, and PE properties ^{60,75,124}
GeH ₄	107.26 ^{9e}	184.93 ^{9e}	550 ^{e9e}	+90.8 ²⁵⁸	at least three phases reported ^{9e} solid GeD ₄ at 5 K: orthorhombic, space group <i>P2₁2₁2₁</i> (No.19) $a = 7.3549$, $b = 8.1597$, $c = 4.5402$ mean Ge-D 1.522 ³⁶⁵	NMR, vibrational, and other properties ^{9e,43}
Ge ₂ H ₆	164 ^{9e}	304.7 ^{9e}	470 ^{e9e}	+162.3 ²⁵⁸		ref 9e

SnH ₄	123 ³⁶⁴	220.8 ³⁶⁴	300 ^{9e}	+162.8 ²⁵⁸	solid SnD ₄ at 5 K: monoclinic, space group P ₂ ₁ /c (No. 14) a = 8.8737, b = 4.5469, c = 8.7562, β = 119.287; mean Sn–D 1.701 ³⁶⁵	NMR and vibrational properties ^{9e,43}
Sn ₂ H ₆			<273 ^{9b}	+274 ^{9b}		mass spectrum ^{9b,354}
PbH ₄		ca. 260 ^{9b}	<273 ^{9b}	>+250 ^{9b}		mass spectrum ^{9b}
AsH ₃	156.9 ¹⁴	210.8 ¹⁴	523–573 ^{5e}	+66.4 ²⁵⁸		NMR, vibrational, and other properties ¹⁴
As ₂ H ₄		ca. 373 ^{5e}	<273 ^{9b}	+147 ^{9b}		mass spectrum ^{9b}
SbH ₃	185 ¹⁴	254.8 ¹⁴	293 ^{5e}	+145.1 ²⁵⁸		NMR, vibrational, and other properties ¹⁴
Sb ₂ H ₄		(290) ¹⁴	<273 ^{9b}	+239 ^{9b}		mass spectrum ^{9b}
BiH ₃			<238 ^{9b}	>+278 ^{9b}		mass spectrum and tensimetric properties ^{9b}

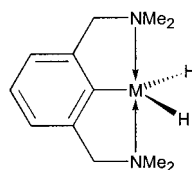
^a Temperatures are in K, enthalpies in kJ mol⁻¹, ^b Distances are in Å, angles in deg, ^c Temperature at which p_{H₂} = 10 mmHg, ^d TEM = transmission electron microscopy; DSC = differential scanning calorimetry, ^e Approximate temperature above which decomposition becomes rapid.

Table 5. Observed (Anharmonic) Wavenumbers and Wavenumber Ranges (in cm⁻¹) of M–H Stretching Fundamentals in Binary Main-Group Metal Hydride Molecules and Their Derivatives

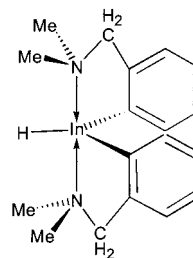
group	M	ν(M–H) ^a	ν(M–H–M)
1	⁷ Li ^I	1359 ²²	
	Na ^I	1133 ²⁵⁹	
	K ^I	955 ^{26,260}	
	Rb ^I	909 ²³	
11	Cs ^I	866 ²³	
	Cu ^I	1866 ²⁷³	
	Ag ^I	1692 ²⁷⁷	
	Au ^I	2219 ²⁸¹	
2	Be ^{II}	1865–2160 ^{89–93,147}	1060–1750 ^{384,385}
	Mg ^{II}	1490–1580 ^{93,95,96}	1250–1300 ¹⁵
	Ca ^{II}	1020–1270 ^{93,97}	590–880 ⁹⁷
	Str ^{II}		
12	Ba ^{II}		
	Zn ^{II}	1690–1960 ^{99,101,148,401}	
	Cd ^{II}	1710–1840 ^{99,101}	
	Hg ^{II}	1885–2092 ^{100,101}	
13	B ^{III}	2200–2650 ^{9e,42,375}	1525–2200 ^{9e,42,375}
	Al ^{III}	1700–1970 ^{9b,9e,10,125b,368d}	930–1790 ^{62b,368d}
	Ga ^{III}	1720–2050 ¹³	900–1720 ¹³
	In ^{III}	1640–1850 ^{125b,141,152,534}	1200–1650 ^{244,245}
14	Tl ^{III}		
	Ge ^{IV}	1950–2180 ^{9e,15,43}	
	Sn ^{IV}	1790–1910 ^{9e,15,43,74,368d}	
	Pb ^{IV}	ca. 1710 ^{9e}	
15	As ^{III}	2040–2350 ^{15,73,160,301,568}	
	Sb ^{III}	1835–2065 ^{15,160,301,569}	
	Bi ^{III}	ca. 1760 ^{301,566}	

^a t = terminal.

ability. Such is the case, for example, with substituted tris(pyrazolyl)borate ligands such as Tp^{Bu^t}, **2**, which chaperones M–H bonds in the monomeric compounds Tp^{Bu^t}BeH,¹⁴⁷ Tp^{Bu^t}ZnH,¹⁴⁸ and Tp^{Bu^t}CdH.¹⁴⁹ The same criteria of space-filling and coordination are met by the substituted aromatic ligands 2-(Me₂NCH₂)C₆H₄ and 2,6-(Me₂NCH₂)₂C₆H₃. Hence, relatively robust monomeric hydrides H₂M[2,6-(Me₂NCH₂)₂C₆H₃], **3**, with pentacoordinated M atoms have been isolated for M = Al¹⁵⁰ or Ga.¹⁵¹ More strikingly still, the first neutral indium hydride, HIn[2-(Me₂NCH₂)C₆H₄]₂, **4**, has been isolated in this way.¹⁵²



3



4

It is a natural extension of the coordination principle that choice of solvent should be important to the preservation and manipulation of some metal hydrides. Just what can be achieved with an appropriate choice of solvent is well illustrated by the synthetic opportunities that have been created by the ability to maintain the univalent group 13 metal halides MX (M = Al, Ga, or In) in solution at

relatively high temperatures.^{10,153} In practice, however, these opportunities have failed as yet to deliver any isolable hydrides of Al, Ga, or In in low formal oxidation states. Nevertheless, basic media—and particularly ethers such as thf and Et₂O—are the rule for synthetic operations with the main-group metal hydrides at ambient temperatures. These are certainly the normal conditions for working with alane, AlH₃,¹⁵⁴ and its derivatives,^{154,155} magnesium hydrides,^{15,156} zinc hydrides,^{15,157} and, most recently, the indium hydride HInCl₂ which is reported to be quite stable in thf solution at ambient temperatures.¹⁵⁸ On the other hand, as the metal becomes increasingly electron-rich, controlled protonation in an acidic medium may be realized. Thus, stannanes with the general formula Me_{4-n}SnH_n (*n* = 1–4) dissolve in fluorosulfonic acid with the release of methane and the formation of the cationic species Me_{3-n}SnH_n⁺, which have been identified by their ¹H, ¹³C, and ¹¹⁹Sn NMR spectra.¹⁵⁹ The altogether more basic hydrides AsH₃ and SbH₃ are protonated in the superacid systems HF/SbF₅ or HF/AsF₅ to give the corresponding MH₄⁺ cations, which have been isolated as MF₆⁻ salts (M = As or Sb) at low temperatures.¹⁶⁰

For some hydrides though there is little life outside the solid state. This is broadly true of the hydrides formed by the metals of groups 1 and 2. The methods of solid-state chemistry¹⁶¹ need, therefore, to be applied to the preparation of some binary and ternary compounds, the latter class including, for example, MH_xX_{2-x} (M = Ca, Sr, or Ba; X = halogen),^{9,162} SrND,¹⁶³ MMgH₄ (M = Sr^{164a} or Ba^{164b}), Ba₂MgH₆,¹⁶⁵ K₂ZnH₄,¹⁶⁶ K₃[ZnH₄]H,¹⁶⁷ and the Zintl phases M₃M'H₂ (M = Ca or Yb; M' = Sn or Pb),¹⁶⁸ Ba₅Ga₆H₂,¹⁶⁹ and M₅M'H (M = Ca, Sr, Ba, Sm, Eu, or Yb; M' = Sb or Bi).¹⁷⁰ The majority of these solids have extended structures, sometimes reflecting the roughly similar sizes of H⁻ and F⁻,^{162,170} but discrete units can occasionally be discerned, as with K₃[ZnH₄]H which adopts the tetragonal Cs₃CoCl₅ structure type and contains tetrahedral [ZnH₄]²⁻ ions.¹⁶⁷ There are also some isolated examples of intercalation of metal hydrides into host lattices. Thus, hydrogen–alkali-metal–graphite intercalation compounds with novel physical properties have been described.¹⁷¹ Introduction of hydrogen to an alkali-metal–graphite host can result in charge transfer from the alkali metal to form M⁺–H⁻–M⁺ triple atomic layer sandwiches which enter between the metallic graphite sheets. Less clear is the nature of the phase with the nominal composition (NaH)₄C₆₀ prepared by direct intercalation of NaH in C₆₀ and which becomes superconducting at temperatures < 15 K.¹⁷²

D. The Condensed Phases: Diffraction of Crystalline Solids and Other Studies

As in so many other areas of chemistry today, X-ray diffraction studies of single crystals have formed the bedrock of characterization of main-group metal hydrides in the condensed phases. Even if a suitable crystal of a given hydride can be grown, however, this technique has its limitations originating mainly in

the low scattering cross-section of hydrogen and the difficulties inherent in locating hydrogen atoms in the vicinity of metal atoms of much higher atomic number. To make matters worse, the vibrational amplitudes associated with the H atoms at room temperature are frequently large with the result that the scattering from these atoms is not only weak but more than usually diffuse. The difficulties are well documented and at worst may mean that the presence of hydrogen atoms has to be inferred, say from the spectroscopic properties of the compound. The indium hydrides testify to the predicament: of the derivatives believed to contain terminal In–H bonds only two—the 2-(dimethylaminomethyl)phenyl derivative HIn[2-(Me₂NCH₂)C₆H₄]₂, **4**,¹⁵² and the phosphine complex (cyclohexyl)₃P·InH₃¹⁷³—have admitted the location of the hydrido ligands on the basis of X-ray diffraction measurements, thereby enabling the In–H bond length to be evaluated. However, even this, in common with similar estimates of other M–H bond lengths, falls short of the values determined by spectroscopic or other means, typically by about 0.1 Å.⁵⁶ The discrepancy arises from the involvement of the single H 1s electron in bonding, so that the electron density departs appreciably from being symmetrical about the nucleus.

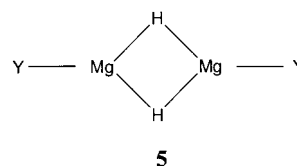
The amplitude problem can often be alleviated by cooling the crystal, but for more accurate location of the hydrogen atoms, neutron diffraction must be the method of choice. Neutron scattering cross-sections for hydrogen and, better still, deuterium offer an altogether superior prospect of locating H atoms precisely; in addition, systematic M–H bond shortening is eliminated. However, the large size of single crystals (0.5–5 mm) normally required, together with the high costs and low intensity of most neutron beams, has restricted the widespread use of the neutron diffraction method in this particular area. By contrast, transition-metal hydrides have attracted numerous neutron-diffraction studies,^{3c} partly because of the particular difficulty of locating H atoms close to metal atoms such as W, partly also because of the intense interest stimulated by dihydrogen complexes such as W(η²-H₂)(CO)₃(PPR₃)₂.⁷ Out of the handful of main-group hydrides that have been the targets of neutron experiments—usually as powders rather than single crystals—the majority feature extended structures, e.g., MgH₂,¹⁷⁴ CaH₂,¹⁷⁵ BaH₂,¹⁷⁶ and AlH₃.¹⁷⁷ The ternary hydrides K₃[ZnH₄]H¹⁶⁷ and [H₂GaNH₂]₃¹⁷⁸ are rare examples of solids containing discrete molecular units that have been interrogated by neutron diffraction. Accordingly, the dimensions of MH_n moieties have seldom been quantified accurately. There is clearly scope for a greater input of neutron-diffraction data; with this, as well as the improved capacity of modern X-ray facilities, it cannot be long before electron densities are being mapped,¹⁷⁹ with an eye to elucidating questions of both primary and secondary bonding. Hence, for example, it may be possible to resolve contentious issues such as the precise roles of direct M···M' versus bridging M–H–M' interactions in units of the type M(μ-H)_nM', and the nature of the unconventional hydrogen bonds Ga–H···H–N that appear to domi-

nate the intermolecular interactions in the solid cyclotrigallazane $[\text{H}_2\text{GaNH}_2]_3$.¹⁷⁸

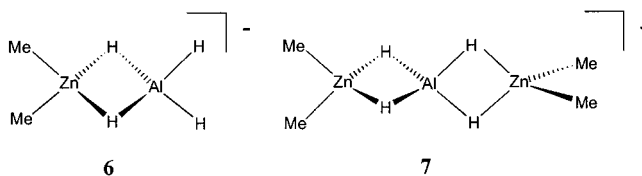
Even where single crystals cannot be grown and structural analysis is not possible, X-ray powder patterns have been extensively used as fingerprints of some of the less well-defined ternary hydrides of copper (e.g., $\text{Li}_m\text{Cu}_n\text{H}_{m+n}$; $m = 1-5$, $n = 1-3$),¹⁸⁰ magnesium [e.g., MMgHR_2 and MMg_2HR_4 ($M =$ alkali metal; $R =$ organic group)],¹⁵ and zinc [e.g., ZnH_2 ,¹⁸¹ NaZnH_3 ,¹⁸² MgZnH_4 ,¹⁸³ $\text{Mg}(\text{ZnH}_3)_2$,¹⁸³ and PhZn_2H_3 ¹⁸⁴]. Thermal methods of analysis, i.e., differential thermal analysis (DTA) and thermogravimetric (TGA) analysis, have frequently supplemented diffraction measurements to gain information about the stability limits of particular phases. Thus, DTA experiments have allowed p , T -state diagrams to be mapped for BeH_2 and AlH_3 , indicating that decomposition of both to the elements is reversible at sufficiently high pressures.¹⁸⁵ The effects of pressure or temperature on the hydrides of the group 1 and group 2 metals and aluminum have also been explored by conventional X-ray^{9,186} or neutron¹⁸⁷ methods and in the cases of NaH ,^{188,189} KH ,¹⁸⁹ RbH ,¹⁸⁹ CsH ,^{189,190} and AlH_3 ¹⁹¹ by energy-dispersive X-ray measurements. In the particular cases of CaH_2 and the biphasic solid electrolyte $\text{CaH}_2\text{-CaCl}_2$, additional information has been sought from the ^1H or ^2H NMR spectrum¹⁷⁵ and electrical conductivity,¹⁹² respectively.

Physical studies of the main-group hydrides in solution have been preoccupied for the most part with the characterization of the solute species with regard to composition and state of aggregation. Infrared, NMR, and colligative properties have been the principal devices of analysis, as exemplified by the notable work of Ashby et al. on the hydrides of magnesium, zinc, and aluminum. Infrared spectra are instructive because of their capacity, already noted, to spot bridging as well as terminal $M\text{-H}$ units. On the other hand, the potential of NMR spectroscopy is somewhat diminished by the susceptibility of hydrogen-bridged frameworks to undergo facile exchange, even at the lowest temperatures accessible to solution measurements. Broadening of the ^1H resonance through coupling to a quadrupolar metal nucleus M may help to identify the presence of an MH_n moiety, as with the complex $\text{Pr}^{\text{III}}\text{NC}_2\text{Me}_2\text{N-}(\text{Pr}^{\text{III}})\text{C-InH}_3$, solutions of which display a ^1H resonance at δ 5.58 with an intensity and breadth implying that it arises from the hydride ligands bound to indium (^{115}In 95%, $I = 9/2$; ^{113}In 5%, $I = 9/2$).¹⁴¹ However, such broadening reduces the sensitivity of the technique as a means of sensing hydride ligands and may ultimately cause the resonance to escape detection. The example of the indium hydride complex illustrates too that hydride ligands bound to main-group metals do not generally share with those bound to transition metals the property of resonating at a distinctively low frequency.² The quadrupolar character of several of the key metal nuclei (e.g., ^{27}Al , ^{69}Ga , and ^{71}Ga) has also impaired the usefulness of these nuclei as NMR probes for hydride derivatives of the relevant metals in any but the most sym-

metrical environments (e.g., AlH_4^- and GaH_4^-).^{153,193,194} Systems which have attracted spectroscopic investigation, frequently together with colligative measurements, include ether solutions of the following species: (i) the magnesium hydrides RMgH , RMg_2H_3 , and HMgX ($R = \text{Me}$, Et , Pr^i , Ph , or Cp ;¹⁹⁵ $X = \text{Cl}$ or Br ¹⁹⁶); (ii) AlH_3 ;¹⁹⁷ and (iii) the bi- and trimetallic species LiMgH_2R ,¹⁵ $\text{LiMg}_2\text{H}_3\text{R}_2$,¹⁵ $\text{Li}_2\text{MgH}_2\text{R}_2$,¹⁵ HMg-MH_4 ($M = \text{B}$ or Al),^{196,198} $\text{Mg}(\text{AlH}_4)(\text{BH}_4)$,^{196,198} $\text{LiZnMe}_2\text{AlH}_4$,¹⁹⁹ and $\text{LiZn}_2\text{Me}_4\text{AlH}_4$.¹⁹⁹ Hence, it ap-



pears, for example, that the species present in thf solutions of HMgY ($Y = \text{Me}$,¹⁹⁵ Cl ,¹⁹⁶ or Br ¹⁹⁶) is the solvated hydride-bridged dimer **5** and that the triple metal hydride complexes $\text{LiZnMe}_2\text{AlH}_4$ and $\text{LiZn}_2\text{Me}_4\text{AlH}_4$ include the anions **6** and **7**, respectively. It



is not uncommon for a given compound to exist in solution in two or more forms that differ in their degree of aggregation and/or composition; such species are often in dynamic equilibrium, the balance of which is critically dependent on the nature of the solvent and the conditions of concentration and temperature. Representative of this behavior are alane, AlH_3 , in ether solutions,¹⁹⁷ and dimethylalane, $[\text{Me}_2\text{AlH}]_n$,^{62b,200} gallane $[\text{GaH}_3]_n$,^{13,60} or the mixed lithium hydride/*tert*-butoxide aggregates, $[(\text{Bu}^o\text{O})_x\text{LiH}_{1-x}]_n$,²⁰¹ in hydrocarbon solutions. Definitive results are still at a premium here, affording ample scope for applying contemporary mass spectrometric techniques, for example, with 'electrospray' ionization,²⁰² to the analysis of some of these systems. Without a detailed knowledge of the solute species there can be no properly informed understanding of the reaction pathways open to a given metal hydride in solution.

E. Theoretical Methods

The simplicity of the hydride ligand facilitates quantum chemical studies, and exploration of the main-group metal hydrides has depended in no small part on the input of modern computational methods. High-level ab initio calculations admitting the use of relatively elaborate basis sets, as well as making due allowance for factors like configuration interaction and relativistic corrections, are now widely accessible, and density functional theory methods have become relatively commonplace. Where comparisons can be made, calculations of this sort typically yield molecular dimensions, energies, vibrational wavenumbers, and intensities in infrared

absorption or Raman scattering and chemical shifts that reproduce closely the experimental findings and sometimes *improve upon* those findings. Such is the case, for example, with the monohydrides and with simple molecules such as GeH_2 , AsH_2 , MH_3 ($M = \text{B}$, As , or Sb), MH_4 ($M = \text{Ge}$ or Sn), B_2H_6 , and Ga_2H_6 , as revealed by the parameters listed in Table 2. Provided that the calculations are carried out at an appropriate level of sophistication—as assessed by largely empirical means—we can now place considerable trust in the results to anticipate the equilibrium structures and spectroscopic properties of main-group metal hydride molecules. For some species—e.g., MH_2 ($M = \text{Sr}$, Ba , Tl , Sn , Pb , Sb , or Bi), MH_3 ($M = \text{Tl}$, Pb , or Bi), PbH_4 , M_2H_2 ($M = \text{Ge}$, As , Sb , or Bi), and M_2H_6 ($M = \text{In}$, Tl , Sn , or Pb)—theoretical predictions are virtually the sole source of information; for others—e.g., MH_2 ($M = \text{Be}$, Mg , Ca , Zn , Cd , Hg , Ga , or In), MH_3 ($M = \text{Al}$, Ga , In , Ge , or Sn), and M_2H_2 ($M = \text{B}$, Al , or Ba)—theory outstrips experiment. The second category is largely made up of molecules that have been characterized with varying degrees of certainty by matrix-isolation experiments. Here it may be possible to draw on isotopic shifts and the relative intensities of IR absorptions or on the hyperfine coupling parameters of EPR signals to estimate the angular dimensions of the trapped molecule. It is unlikely, however, that rough valuations of this sort can now compete in exactitude with the results of appropriate quantum chemical calculations. The recent practice has therefore been to rely on the calculations for the prediction of spectroscopic properties that will provide a benchmark for the identification of a given molecule by experiment. This synergy between experiment and theory has developed still further with methods such as SARACEN⁵⁷ (see section II.A) depending on quantum chemical calculations to guide the analysis of experimental results (provided, for example, by electron-diffraction,^{58,59} rotational, or rovibrational studies of gaseous molecules).²⁰³

III. Formation

A. Dihydrogen Derivatives

Several hundred stable dihydrogen complexes of transition metals have been prepared since the discovery of the first such complex, $\text{W}(\text{H}_2)(\text{CO})_3(\text{PPr}^i)_2$, by Kubas et al. at Los Alamos Laboratory in 1984.⁷ Most have the metal in the d^6 electron configuration, e.g., $\text{Cr}(\text{O})$, $\text{Re}(\text{I})$, $\text{Fe}(\text{II})$, and $\text{Rh}(\text{III})$. Yet there has been no report that any main-group metal forms complexes analogous to these, even when the metal center is strongly acidic. The situation is reminiscent of another celebrated nonevent:

“Is there any other point to which you would wish to draw my attention?”

“To the curious incident of the dog in the night-time.”

“The dog did nothing in the night-time.”

“That was the curious incident,” remarked

Sherlock Holmes

A. Conan Doyle, *The Memoirs of Sherlock Holmes*

Theoretical studies have indeed indicated that a primary interaction in the formation of a dihydrogen complex entails donation of the electron density from the filled σ_g orbital of H_2 to the LUMO of the metal. The failure of main-group Lewis acids such as BH_3 or CH_3^+ to form stable dihydrogen complexes, any more than they form stable dinitrogen or alkene complexes, gives strong circumstantial support to the belief that stability depends crucially on a second bonding component, viz. back-donation of electron density through a π -type interaction between a filled metal orbital of appropriate character and energy and the empty σ_u^* orbital of the H_2 . Main-group metal centers are not equipped for significant back-donation of this sort; the nearest approach is likely to be found in a d^{10} post-transition-metal center like $\text{Cu}(\text{I})$ or $\text{Hg}(\text{II})$, but even here the d-electrons lie too deep in energy to afford significant stabilization of the metal– H_2 interaction. Although it is dangerous to infer too much from the apparent nonexistence of a particular type of compound, such intelligence as we have suggests that dihydrogen binds only weakly to main-group metals, forming complexes that have no more than a transient existence under normal conditions.

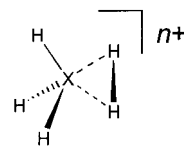
Denied the stimulus of more positive experimental results, the status of dihydrogen complexes of non-transition metals has excited comparatively little theoretical interest. SCF calculations are noteworthy in their finding²⁰⁴ that the neutral Al atom dissociates the H_2 molecule, although the process is far from spontaneous while the metal atom is in its electronic ground state, whereas the Al^+ cation binds the H_2 molecule associatively, albeit with a binding energy of no more than a few kJ.^{204–206} The neutral metal atom can act as a donor, barely at all as an acceptor, of electron density, and transfer of electron density to H_2 can only be to the antibonding σ_u^* orbital. By contrast, charge transfer occurs in the opposite sense for the Al^+ cation, which has negligible donor capacity; in addition, binding is enhanced through polarization of the H–H bond by the electric field created by the cation. As the charge on the cation, Al^{n+} , increases, the $\text{Al}^{n+}\cdots\text{H}-\text{H}$ binding energy increases. Calculations at the SCF and MP2 levels have yielded the following estimates of D_e (in kJ mol^{-1}):²⁰⁶ $\text{Al}^+\cdots\text{H}_2$ 4, $\text{Al}^{2+}\cdots\text{H}_2$ 86, and $\text{Al}^{3+}\cdots\text{H}_2$ 334; simultaneously, the H–H bond is attenuated by 0.003, 0.045, and 0.151 Å and the H–H stretching frequency decreases by 163, 792, and 1906 cm^{-1} , respectively. Side-on interaction of the H_2 molecule to produce an $\text{M}\cdots\text{H}_2$ unit with C_{2v} symmetry seems to be the general rule, and MP4 calculations extending beyond Al and Al^{n+} have yielded the following interaction energies (all in kJ mol^{-1} and allowing for zero-point corrections):²⁰⁴ $\text{Li}^+\cdots\text{H}_2$ 19, $\text{Be}^+\cdots\text{H}_2$ 18, $\text{HBe}^+\cdots\text{H}_2$ 90, $\text{H}_2\text{B}^+\cdots\text{H}_2$ 59, $\text{Na}^+\cdots\text{H}_2$ 10, $\text{Mg}^+\cdots\text{H}_2$ 2.4, $\text{HMg}^+\cdots\text{H}_2$ 26, $\text{H}_2\text{Al}^+\cdots\text{H}_2$ 114. Hence, associative binding of H_2 to any appreciable extent appears to incur the need for a positive charge on the metal atom. Reduction of this charge through ligation of the cation by one or more anionic partners, as in neutral Lewis acids such as BeO and AlF_3 , works strongly to the disadvantage of any $\text{M}\cdots\text{H}_2$ bond. On the evidence of quantum-chemical calculations allowing for single

and double excitation and configuration interaction, BeO stands out for forming a relatively strongly bound complex $\text{H}_2 \cdots \text{BeO}$ but with a binding energy (ca. 100 kJ) only about one-half that of $\text{H}_2 \cdots \text{Be}^{2+}$.²⁰⁷ Altogether more weakly bound are the complexes $\text{H}_2 \cdots \text{MgF}_2$ and $\text{H}_2 \cdots \text{AlF}_3$ with binding energies in the order of only 10 kJ²⁰⁶ (cf. energies of 92 and 334 kJ for $\text{H}_2 \cdots \text{Mg}^{2+}$ ²⁰⁸ and $\text{H}_2 \cdots \text{Al}^{3+}$,²⁰⁶ respectively).

Direct experimental evidence of the coordination of H_2 to a main-group atom comes mostly from the IR and UV-vis spectra of matrixes doped with H_2 and metal atoms or discrete molecules of metal compounds. More often than not, the spectral properties point to very weakly bound complexes—no more than ‘contact pairs’ in some cases—involving minimal perturbation of the H_2 and its partner. Such is the case, for example, with the complexes $\text{M} \cdots \text{H}_2$, $\text{H}_2 \cdots \text{MH}$, and $\text{H}_2 \cdots \text{MH}_2$ ($\text{M} = \text{Ca}$,⁹⁷ Zn ,⁹⁹ or Cd ⁹⁹); $\text{H}_2 \cdots \text{BH}$ and $\text{H}_2 \cdots \text{BH}_3$,¹⁰³ and $\text{H}_2 \cdots \text{AlH}_n$ ($n = 1$ or 2).¹¹² For none of these species is the $\nu(\text{H}-\text{H})$ mode activated in IR absorption, at least to the point where it can be detected. Instead, interaction is inferred from the appearance of more than one set of IR absorptions attributable to the MH_n molecule and which can be differentiated on the basis of their growth and decay properties and particularly on their response to annealing of the H_2 -doped matrix. Thus, broad-band photolysis of Mg atoms in an H_2 -doped argon matrix yields as the primary reaction products MgH and MgH_2 , each of which is trapped either in a matrix cage made up exclusively of argon atoms or in one including an H_2 molecule.⁹⁵ $\text{H}_2 \cdots \text{MgH}$ is characterized by a $\nu(\text{Mg}-\text{H})$ fundamental that is blue-shifted by 33.5 cm^{-1} from its counterpart in MgH , implying a repulsive interaction; conversely, $\text{H}_2 \cdots \text{MgH}_2$ has an antisymmetric $\nu(\text{Mg}-\text{H})$ fundamental that is red-shifted by 15.0 cm^{-1} from the corresponding mode of MgH_2 . By contrast, $\text{H}_2 \cdots \text{AlH}_2$ appears on the evidence of slightly blue-shifted $\nu(\text{Al}-\text{H})$ modes to be no more than a van der Waals aggregate but still with its own distinctive photochemistry, the matrix-trapped species giving rise on irradiation with UV light at wavelengths near 240 nm to AlH_4^- anions.¹¹⁶ The largest red shift for systems of this sort is 112.1 cm^{-1} for ν_3 of BH_3 in the species $\text{H}_2 \cdots \text{BH}_3$ which has legitimate claims to being classed as a dihydrogen complex with a binding energy calculated at high levels of theory to be about 5.9 kJ mol^{-1} .¹⁰³ There are no clear spectroscopic signs of $\text{H}_2 \cdots \text{AlH}_3$,^{80,112,115} which is predicted²⁰⁹ to be marginally more strongly bound ($D_0 = 7.1 \text{ kJ mol}^{-1}$) than $\text{H}_2 \cdots \text{BH}_3$ as a result of an interaction that is largely electrostatic in nature.

BH_5 and AlH_5 are isoelectronic with the CH_5^+ cation, which has become quite a cause célèbre, being formed in the gas phase where it has been characterized by mass²¹⁰ and IR^{210,211} spectroscopic studies and also, according to more circumstantial evidence, in the condensed phase afforded by appropriate superacid media.²¹⁰ Ab initio calculations indicate a common structure **8** with C_s symmetry in which an H_2 molecule is bound to a neutral or cationic XH_3 substrate. Whereas neutral BH_3 and AlH_3 bind H_2 only weakly, the CH_3^+ cation binds it strongly with

an energy of $175\text{--}190 \text{ kJ mol}^{-1}$.²¹⁰ It seems unlikely therefore that the neutral adducts will share the

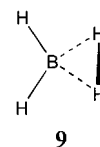


($\text{X} = \text{B}$ or Al , $n = 0$; $\text{X} = \text{C}$, $n = 1$)

8

remarkable fluxionality of the CH_5^+ ion. Quantum chemical studies serve notice that one or more dihydrogen ligands are also present in the equilibrium structures adopted by the following polyhydride cations: XH_4^+ ($\text{X} = \text{B}^{212a}$ or Al^{212b}), XH_5^{2+} ($\text{X} = \text{Al}^{212b}$, P^{212c} or As^{212c}), XH_6^{n+} ($n = 1$ or 3 , $\text{X} = \text{B}^{212a}$ or Al^{212b} , $n = 3$, $\text{X} = \text{P}^{212c}$ or As^{212c}), XH_7^{2+} ($\text{X} = \text{B}^{212a}$ or Al^{212b}), and XH_8^{3+} ($\text{X} = \text{B}^{212a}$ or Al^{212b}). Although such cations are unlikely to be observed as long-lived species even in superacid media, it is possible that some at least feature as, or model, transients formed in superacid-catalyzed processes leading, for example, to hydrogen scrambling.

Just as CH_4^+ has a Jahn-Teller-distorted structure in its electronic ground state, so too it appears does the isoelectronic boron hydride BH_4 which has been trapped in dihydrogen matrixes and there identified by its EPR spectrum.¹⁰⁵ The results are consistent with the C_{2v} structure **9**, implying that the molecule can be regarded as a dihydrogen complex of the BH_2 radical. On the other hand, with an estimated bind-



9

ing energy of about 60 kJ mol^{-1} with respect to BH_2 and H_2 ,²¹³ the resulting complex would appear to have little in common with its aluminum counterpart, $\text{AlH}_2(\text{H}_2)$, wherein, as noted previously, the AlH_2 has but a tenuous hold on its H_2 partner.

In only two cases has it been possible to observe the $\nu(\text{H}-\text{H})$ mode of an H_2 molecule bound to a substrate that does not contain a transition-metal center of the normal kind. One of these involves $(\eta^2\text{-H}_2)\text{CuCl}$ formed by the co-condensation of CuCl and H_2 in a solid argon matrix;⁸⁴ here the $\nu(\text{H}-\text{H})$ mode of the coordinated H_2 molecule is not only activated in IR absorption but also red-shifted by no less than 916 cm^{-1} with respect to the unperturbed molecule. At ca. 90 kJ mol^{-1} the calculated binding energy of the complex bears comparison with that of NiCO . Although it might be thought that π -type interactions play a significant part in this d^{10} metal complex (despite the tight binding of the 3d electrons), ab initio calculations seem to imply that the H_2 is bound to copper by purely σ -type interactions.⁸⁴ The $\nu(\text{H}-\text{H})$ mode is also activated in IR absorption and red-shifted by up to 114 cm^{-1} when H_2 is co-deposited with an alkali halide, also in an argon matrix.⁸³ Analysis of the results suggests that KF binds H_2

most strongly at the fluoride anion, while NaF, KCl, NaCl, and LiCl involve increasing participation of the cation in the binding; except in the case of LiCl though, argon competes successfully with H₂ for binding at the cation site and displaces H₂ from this site.

The conditions favoring the ligation of H₂ to a non-transition-metal center M can thus be seen only as 'through a glass, darkly'. However, the miscellaneous studies reported to date—including a recent experimental and theoretical examination of the binding interactions in Cu⁺(H₂)_n clusters²¹⁴—are beginning to reveal a pattern of sorts manifesting the following features. (a) Binding of H₂ is strengthened by increasing positive charge at M, although these conditions may be difficult in practice to reconcile with the formation of species that are long-lived under normal conditions. (b) The strength of M··H₂ bonding depends on the nature and number of any other ligands coordinated to M (as evidenced by some of the theoretical results already cited). (c) Valence s electrons localized on M develop a repulsive interaction and so disfavor H₂ ligation.^{214,215}

Interaction of H₂ with an appropriately responsive acceptor leads ultimately to cleavage of the H–H bond, with the hydrogen atoms becoming attached to the same or different atoms. This does not rule out the possibility of residual H··H interaction. There is now some weight of evidence to suggest that secondary dihydrogen bonding of this sort can operate between a conventional hydrogen bond donor X–H, such as NH or OH, as the weak acid component and a metal–hydride bond as the weak base component, i.e., X–H^{δ+}···H^{δ-}–M.²¹⁶ H··H distances are typically in the range 1.7–2.2 Å, and the X–H··H unit tends to be linear, while the M–H··H unit is bent. In most of the crystalline solids where bonding of this sort has been identified, M is a transition metal. Several examples make it plain, however, that the phenomenon is not confined to transition-metal hydrides. Thus, boraneamines such as H₃B·NH₃^{217a} tend to be characterized by close N–H··H–B contacts, and crystals of cyclotrigallazane consist of cyclic [H₂GaNH₂]₃ molecules each with a chairlike conformation linked in chains through intermolecular Ga–H··H–N interactions (with H··H distances of 1.97 Å).¹⁷⁸ Calculations on the gallium compound suggest that each H··H bond contributes about 12 kJ mol⁻¹ to the binding energy, implying a strength comparable to that of a conventional hydrogen bond. Accordingly, H··H interactions appear to represent a significant influence not only on the crystal structures assumed by metal hydride derivatives, but also on the reaction pathways open to these derivatives.^{216,217b}

B. Metal Hydrides

There have been changes of the scope and emphasis and important specific developments of chemistry or technique, but the general strategies for forming main-group metal hydrides have not changed in the last three decades. These comprise four routes: (i) addition of H₂ or a hydrogen-containing molecule to the metal in the elemental or a low valent state; (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. Each route will now be considered in turn, with the emphasis on recent developments, even if the boundaries between the different routes are sometimes rather arbitrary.

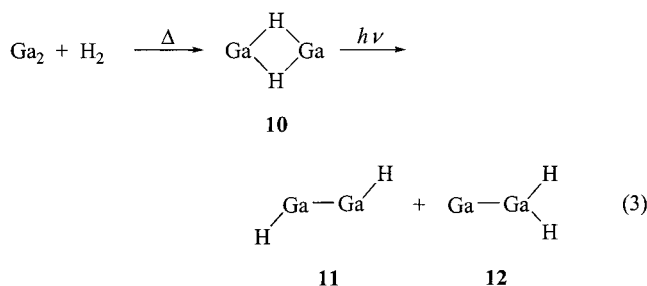
1. Addition of H₂ or an H-Containing Compound

Direct synthesis from the elements is readily achieved for the binary hydrides of the group 1 and heavier group 2 metals; in appropriate (high pressure) circumstances access can also be gained in this way to BeH₂,^{185a} MgH₂,^{156,218,219} and AlH₃,¹⁸⁵ i.e., the only other hydrides which are thermodynamically stable with respect to the elements under anything approaching standard conditions. Elemental hydrogen under pressure is a primary reagent too in the synthesis of certain ternary hydrides, e.g., MMgH₄ (M = Sr^{164a} or Ba^{164b}), Ba₆Mg₇H₂₆,²²⁰ K₂ZnH₄,¹⁶⁶ K₃[ZnH₄]H,¹⁶⁷ and SrND.¹⁶³

Metal atoms offer a considerable thermodynamic advantage over the bulk metal as sources of the relevant hydrides, although reactions with H₂ or H-containing molecules are seldom spontaneous. One exception is provided by Ca atoms which are reported to insert into the C–H bonds of aromatic hydrocarbons, ArH, on co-condensation with the formation of compounds of the type ArCaH.²²¹ More often, however, electronic excitation is needed to promote a reaction of this sort, as demonstrated by matrix-isolation experiments (see Table 1). For example, H₂ evokes no obvious response from Al, Ga, or In atoms in their electronic ground states but is breached by the photoexcited ²S or ²D atoms to form the corresponding metal dihydride (see eq 1).¹¹⁴ Likewise photoexcitation is needed before Zn,⁹⁹ Cd,⁹⁹ or Hg¹⁰⁰ atoms undergo a similar insertion reaction. Metal atoms formed by laser ablation have a wide spread of thermal energies, and some are likely to be electronically excited; these factors probably account for the spontaneous formation of metal hydrides when laser-ablated Be⁸⁹ or Mg⁹⁵ atoms are co-condensed with H₂. Comparable in strength with the H–H bond is the C–H bond of organic compounds such as CH₄, and once again insertion to afford products such as CH₃MH requires excitation of the M atoms; certainly this is the case with M = Be,⁹³ Zn,¹⁰¹ Cd,¹⁰¹ Hg,¹⁰¹ Al,^{110,125a} Ga,^{122,123,125a} or In.^{125a} On the other hand, insertion into the X–H bonds of polar molecules such as H₂O¹¹⁹ or HCl,¹²⁸ which interact more strongly with the ground-state metal atoms and are also potential sources of strong M–X bonds, may proceed spontaneously on co-condensation of the reagents at low temperatures.

Small aggregates or clusters of metal atoms do not necessarily emulate either the bulk metal or the parent atoms in their chemical behavior while perhaps anticipating some of the properties of a metal surface. A remarkable illustration of this point is provided by the Ga₂ dimer. Together with Ga atoms, this is entrained, typically in low but significant concentrations, when gallium vapor is quenched with an excess of an inert matrix gas at low temperatures.

Doping of this gas with H₂ gives a solid deposit which implies by its IR spectrum that Ga₂ has cleaved H₂ spontaneously with the formation of the dihydrido-bridged Ga(*μ*-H)₂Ga, **10**.¹²² Irradiation of the matrix with UV light then brings about photoisomerization, with the formation of the species HGaGaH, **11**, and/or GaGaH₂, **12** (eq 3). Minimal thermal activation

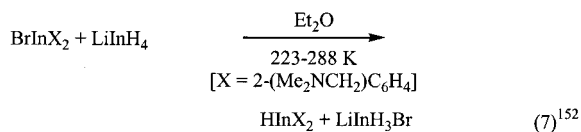
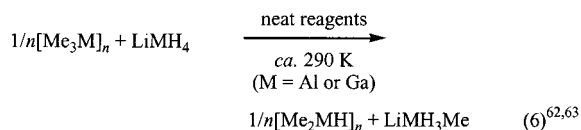
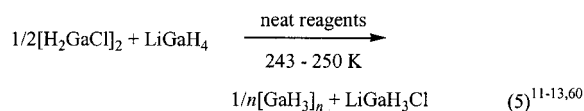
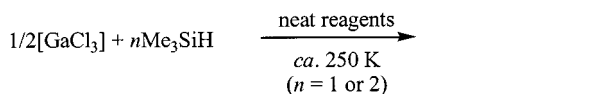


appears likewise to oppose the addition of H₂ to Al₂^{112,113} with similar results.

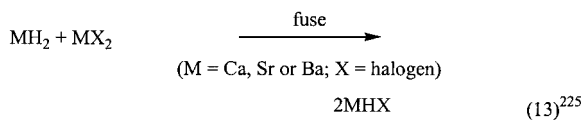
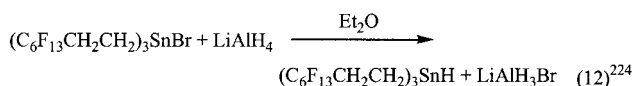
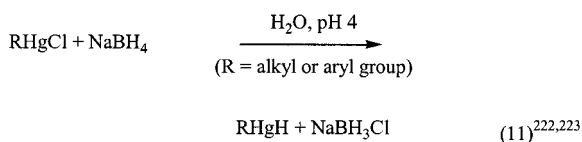
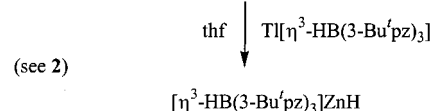
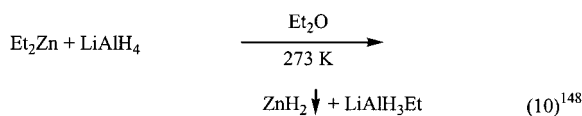
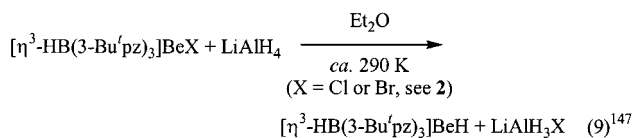
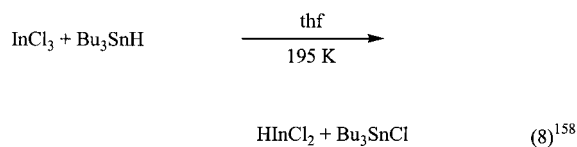
Molecular derivatives of the subvalent metal may also be amenable under photoactivation to the addition of H₂ or HCl, as illustrated, for example, by eq 2 in the cases of AlCl₃,^{117a} GaCl₃,^{126a,127} and InCl₃.¹²⁸ The monohydrides AlH and GaH can similarly be made to deliver AlH₃¹¹⁵ and H₂GaCl,¹²⁸ respectively. So far all such studies have been confined to the small scale of matrix-isolation experiments. Whether the method is viable as a means of synthesis on the large scale is doubtful. Even for substrates such as the monohalides of the group 13 metals which have been successfully handled as synthons for metathesis in cooled, metastable solutions,¹⁵³ the reactivity of the solvent is liable to inhibit the formation of the loosely bound adducts that are the precursors to photoaddition.

2. Metathesis

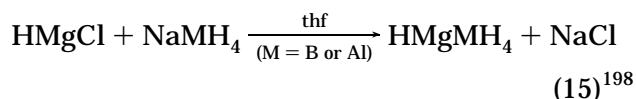
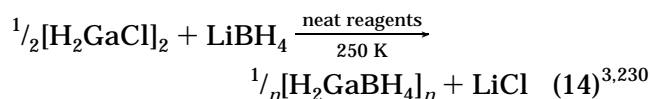
Exchange reactions involving a suitable hydride ion source continue to be the main vehicle of synthesis for hydrides of the s- and p-block metals, with hydride being traded usually for halide or organic ligands. Examples are given in eqs 4–13. LiAlH₄ is



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the most commonly favored hydride ion source, but alkali-metal salts of BH₄⁻, GaH₄⁻, and InH₄⁻ anions have also been used as have silanes such as Me₃SiH and stannanes like Bu₃SnH. Alkali-metal hydrides have found only limited use; despite the development of various stratagems for activating them²²⁶ and/or bringing them into solution,^{157,227–229} they suffer the severe disadvantage of minimal solubility in normal solvents with which they do not react. While the choice of hydride ion source is naturally dictated by its activity, it may be necessary also to guard against the possibility that exchange leads to a mixed-metal hydride, as in eqs 14 and 15.



For this reason there may be distinct merit in restricting the exchange to a common metal center, as in eqs 5–7. The choice of reaction medium is often crucial, not only in supporting the reagents under appropriate conditions but also, as noted earlier, in stabilizing or sometimes precipitating the product, as exemplified by the cases of HInCl₂ (eq 8) and ZnH₂ (eq 10), respectively. To prepare solvent-free samples of some of the more fragile, reactive hydrides, how-

ever, the only realistic option may be to dispense with any solvent and rely on the reaction between the well-mixed neat reagents in rigorously preconditioned all-glass apparatus.^{11–13}

3. Decomposition/Elimination Reactions

An aluminum hydride is often the first product, accompanying β -elimination of the appropriate alkene, in the thermal decomposition of a trialkylaluminum compound, although it usually takes a 2-substituted alkene to make this a workable synthetic route.²³¹ That such a reaction may occur even at low temperatures is shown by the formation of mono-hydridoaluminum derivatives such as $[\text{Bu}^t\text{AlH}]_3$ and $[\text{LiHAlBu}^t]_n$ (when Bu^tLi reacts with AlBr_3)²³² and $[\text{Li}(\text{tmeda})_2]^+ [\text{HAl}\{\text{CH}(\text{SiMe}_3)_2\}_n\text{Bu}^{t_{3-n}}]^-$ [when Bu^tLi reacts with $\text{Al}\{\text{CH}(\text{SiMe}_3)_2\}_n\text{Bu}^{t_{3-n}}$ ($n = 1$ or 2) in the presence of the $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ (tmeda) ligand].^{233,234} The silylaluminum $\text{K}[\text{Me}_3\text{AlSiH}_3]$ also decomposes readily in ether solution with the formation of the corresponding hydroaluminate $\text{K}[\text{Me}_3\text{AlH}]$.²³⁵

Controlled pyrolysis of triethylgallium, brought about by infrared laser radiation, also proceeds with β -elimination and the sequential formation of the hydrides $[\text{Et}_2\text{GaH}]_n$ and $[\text{EtGaH}_2]_n$.^{236–238} Decomposition of a different kind is presumed also to accompany exchange in the reaction between gallium(III) chloride and LiBH_4 under solvent-free conditions, which leads not to $\text{Ga}(\text{BH}_4)_3$ [as might be expected by analogy with the corresponding reaction of aluminum(III) chloride] but to the gallium hydride $\text{HGa}(\text{BH}_4)_2$.^{65,239}

For one other metal only has alkene elimination been exploited to a significant degree, namely, beryllium. Organoberyllium compounds containing branched alkyl chains decompose in this way at moderate temperatures with the formation of the corresponding organoberyllium hydride and, ultimately, the binary hydride BeH_2 .^{9e} For example, decomposition of Bu^t_2Be starts at 40°C , giving first a mixture of $[\text{Bu}^t\text{BeH}]_n$ and $[\text{Bu}^t\text{BeH}]_n$, and proceeds at higher temperatures to BeH_2 , which can thus be prepared in up to 98% mol purity.

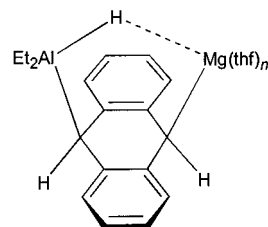
4. Acid–Base Reactions

Representative of this approach are protonation, hydride addition, and displacement reactions.

Where strongly hydridic character is found, as with the derivatives of the more electropositive metals of groups 1, 2, and 13, protonation is likely to result only in attack at the hydride center, with the elimination of dihydrogen. For the more electron-rich metals of groups 14 and 15, however, it remains an option, initial alloying with a more electropositive metal providing the appropriate nucleophilic centers for protonation, and this method has been applied to the synthesis of binary hydrides of Ge,⁹ Sn,⁹ As,^{9,14} and Sb.^{9,14} The same principle has been used to prepare the stibine Mes_2SbH ($\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) by the action of $[\text{Me}_3\text{NH}]\text{Cl}$ on Mes_2SbLi .²⁴⁰ In the highly acidic environment of fluorosulfonic acid or of a superacid like HF/SbF_5 , protonation may even yield

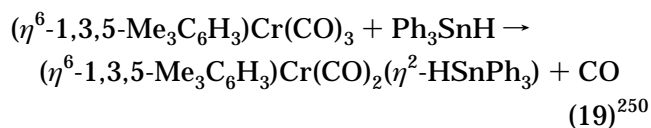
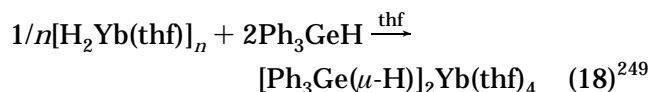
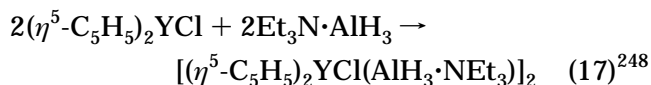
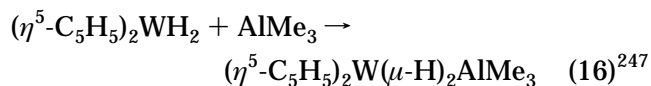
cationic species, e.g., $\text{Me}_{3-n}\text{SnH}_n^+$ ($n = 1–3$)¹⁵⁹ and MH_4^+ ($\text{M} = \text{As}$ or Sb).¹⁶⁰

Hydride addition reactions, frequently to Lewis acidic organometallic substrates, provide a well-beaten path to hydridometalate complexes. For example, LiH or NaH adds to dialkylzinc compounds, R_2Zn , in an appropriate solvent to form complexes of the type $\text{M}[\text{R}_2\text{ZnH}]$, which prove to be unusually powerful and selective as a means of reducing organic carbonyl groups.¹⁵⁷ In the same vein, NaH adds to diethylberyllium in diethyl ether solution to give the structurally authenticated hydridoberyllate complex $[(\text{Et}_2\text{O})\text{Na}]_2 [\text{Et}_2\text{Be}(\mu\text{-H})_2\text{BeEt}_2]$.²⁴¹ Similar treatment of triorgano derivatives of the group 13 metals with an alkali-metal hydride, sometimes in the presence of a crown ether or other complexing ligand designed to sequester the alkali-metal cation, has led to the preparation and characterization of $\text{Na}[\text{Me}_3\text{Al}(\mu\text{-H})\text{-AlMe}_3]$,²⁴¹ $\text{K}[(\text{Me}_3\text{SiCH}_2)_3\text{GaH}]$,²⁴³ $[\text{Li}(\text{tmeda})_2] [\text{Me}_3\text{-In}(\mu\text{-H})\text{InMe}_3]$,²⁴⁴ and $\text{K}[(\text{Me}_3\text{CCH}_2)_3\text{In}(\mu\text{-H})\text{In}(\text{CH}_2\text{-CMe}_3)_3]$.²⁴⁵ When the hydride source is a group 13 metal hydride, in neutral or anionic form, addition is likely to result in a mixed-hydride complex. In tetrahydrofuran solution, for example, AlH_3 adds to the zinc hydrides LiZnMe_2H and $\text{LiZn}_2\text{Me}_4\text{H}$ with the formation of the tetrahydroaluminate complexes $\text{LiZnMe}_2\text{AlH}_4$ (see **6**) and $\text{LiZn}_2\text{Me}_4\text{AlH}_4$ (see **7**), respectively.¹⁹⁹ MgH_2 likewise adds B_2H_6 or AlH_3 in similar circumstances to give products of the type HMgMH_4 ($\text{M} = \text{B}$ or Al),¹⁹⁸ while ‘anthracenemagnesium’ takes up diethylalane to give the unusual 9,10-dihydro-9,10-anthrylene compound **13**, the structure of which implies significant interaction between the magnesium and the hydride of the aluminate anion.²⁴⁶ That hydride addition may sometimes im-



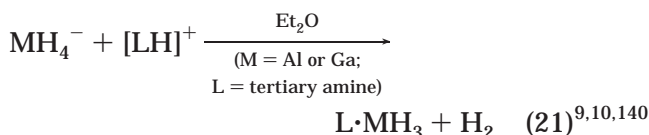
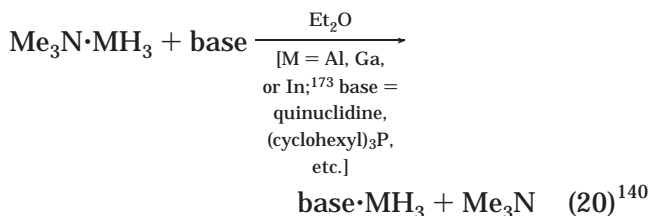
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plicate d- or f-block metal compounds is affirmed by the following examples:



Displacement of one donor ligand by another is a working principle commonly adopted for the synthe-

sis of metal hydride complexes. It is exemplified by eqs 20 and 21, although the second of these strictly entails *double* displacement (and hence exchange) through trading of the bases L and H⁻ between the acids MH₃ and H⁺.



Furthermore, elimination of BH₃ through the formation of either Ph₃P·BH₃ or OC·BH₃ may offer a viable route from a tractable tetrahydroborate to a much less tractable hydride derivative (see eqs 22 and 23, for example).



On the other hand, the history of gallane¹³ testifies that the weakly acidic metal hydride cannot be disengaged satisfactorily from coordination to a donor ligand, e.g., Me₃N, as was once supposed, by the action of a molecular halide which is a strong Lewis acid, e.g., BF₃, since halide–hydride exchange tends to take precedence over displacement.

IV. Physical Properties

A. Binary Compounds

The binary hydrides of the main-group metals incorporate units which are invariably polarized in the sense M^{δ+}–H^{δ-}. The negative charge carried by the hydrogen ligand increases with the reducing power of the metal, i.e., in the order group 15 < group 14 < group 13 < group 2 < group 1 for a given valence shell, and where direct comparisons can be made, the susceptibility to electrophilic (acidic) attack reflects this sequence. The electrophilic character of the metal center depends not only on its positive charge, but also on the availability of one or more vacant orbitals at relatively low energy. Herein lie the seeds of aggregation which characterizes the hydrides of the metals of groups 1, 2, and 13 in their normal valence states.

Table 2 lists the dimensions and vibrational and thermodynamic properties of gaseous mononuclear hydrides of the type MH_{*n*} (*n* = 1–4); Table 3 presents a similar catalog, inevitably less detailed, for gaseous binuclear hydrides M₂H_{*n*} (*n* = 2, 4, or 6). Experimental estimates of the parameters have been augmented by values elicited from quantum chemical calcula-

tions, providing the opportunity for testing how well theory imitates nature. In many cases, however, theory is the chief, sometimes sole, source of information. On the other hand, experiment is the exclusive preserve of Table 4, which details the thermal, thermodynamic, and structural properties of those binary hydrides that have been authenticated more or less well in the condensed phases. Analysis of the properties *en bloc* brings out a number of features characteristic of this class of compounds.

1. Thermodynamic Properties

All the gaseous metal hydride molecules are conspicuously endothermic with respect to the elements in their standard states. On the other hand, the unsaturated valence and coordination shells of the species formed by the metals of groups 1, 2, and 13, allied to the polarity of the M···H unit, means that substantial stabilization is to be gained through aggregation with the formation of M–H–M bridges in oligomeric or, more often, extended arrays. Thus, the best estimates of the standard enthalpy change associated with eq 24 range from ca. –230 kJ mol⁻¹ for M = Li or Mg through –169 kJ mol⁻¹ for M = Al to –82 kJ mol⁻¹ for M = B.



Mainly Coulombic in origin, this stabilization accounts for the exothermicity of the solid hydrides formed by the metals of groups 1 and 2 (with the possible exception of Be) and, uniquely in group 13, by aluminum. By contrast, the gaseous GaH₃ molecule is estimated to be about 30 kJ mol⁻¹ more endothermic than AlH₃ and is likely to benefit less from aggregation; in combination with the unfavorable entropy change attending eq 24, this is evidently sufficient to make gallane unstable with respect to its elements under normal conditions.^{11,13,60,321} For indium and thallium the position is inevitably worse.³²¹ With central atoms having formally saturated valence shells and stronger, less polar M–H bonds, the group 14 and 15 metal hydrides have little to profit from aggregation.

How the compounds compare in their heats of formation and mean bond enthalpies with the hydrides formed by adjacent elements in the Periodic Table are illustrated in Figures 3 and 4, respectively. Hence, it is apparent that the hydrides formed by the metals of groups 13–15 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 or 14. By contrast, the mean M–H bond enthalpies display a more or less steady increase as we progress from left to right across each period, being typically somewhat in excess of the corresponding M–CH₃ bond enthalpies.³⁶⁶ That methyl derivatives are often relatively stable where the corresponding hydrides are unknown cannot therefore be attributed merely to the strengths of the relevant metal–ligand bonds but must depend, at least in part, on differences in mechanism or kinetic barrier to decomposition.¹¹

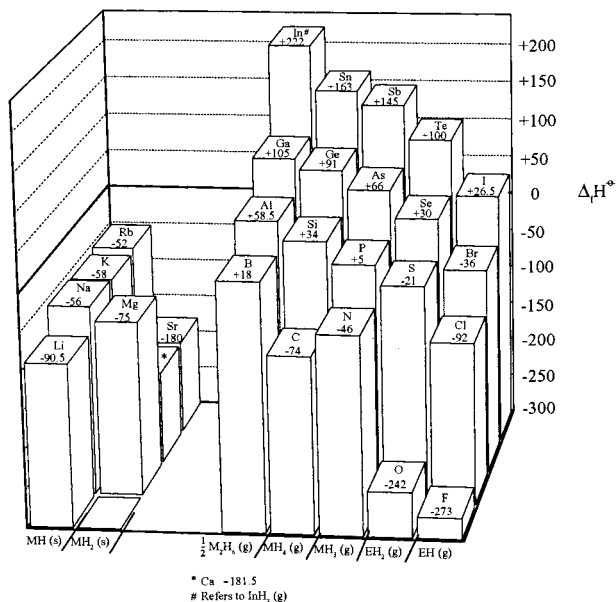


Figure 3. Standard enthalpies of formation, ΔH_{298K}° (in kJ mol^{-1}), of s- and p-block hydrogen compounds.¹¹

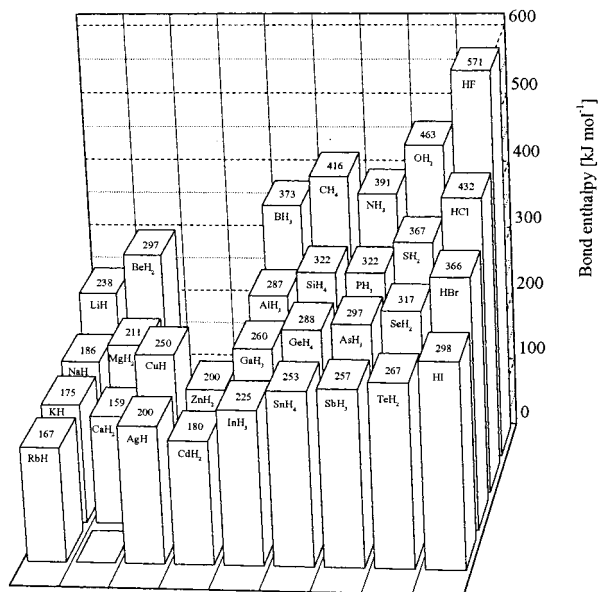
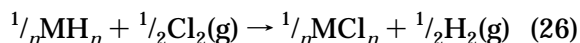
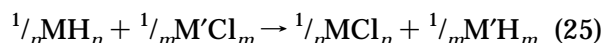


Figure 4. Mean bond enthalpies (in kJ mol^{-1}) for hydrogen compounds of the s- and p-block elements.¹¹

A comparison of the energetics of formation of metal hydrides and chlorides is also revealing for what it implies about the feasibility of metathesis reactions of the type shown in eq 25. Figure 5 plots periodic variations in the enthalpy change attending the reaction represented by eq 26.



The more exothermic this change, the greater is the potential of MH_n —and its derivatives, presumably—as a precursor to the hydrides of other metals. The more-or-less ionic hydrides formed by the metals of groups 1 and 2 are plainly unsurpassed in this respect, whatever limitations their properties may

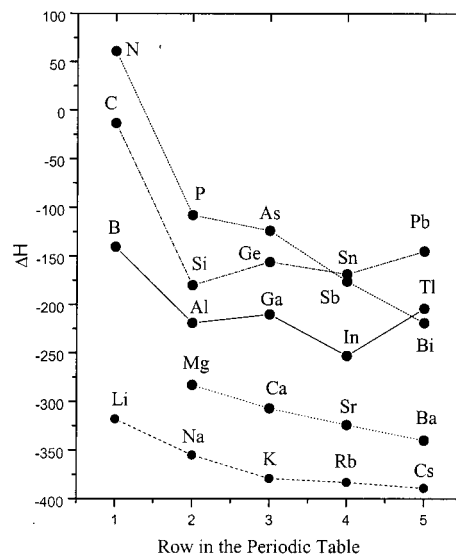


Figure 5. Standard enthalpy changes (ΔH_{298K}° in kJ mol^{-1}) for the reaction $\frac{1}{n}\text{MH}_n(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \frac{1}{n}\text{MCl}_n + \frac{1}{2}\text{H}_2(\text{g})$, where M is an s- or p-block element.¹¹

impose (see section III.B.2). The group 13 elements come next in order of thermodynamic potential, with aluminum standing out as the element that emulates most closely the s-block metals. This, combined with the tractability of alane derivatives such as LiAlH_4 , Bu_2AlH , and $\text{Me}_3\text{N}\cdot\text{AlH}_3$, accounts for the importance of such derivatives as agents for hydride transfer.^{10,154,367} It also reduces the synthetic options for the preparation of aluminum hydrides. For example, whereas Me_3SiH and Bu_3SnH offer through their reactions with the appropriate metal halide a convenient source of gallium^{13,130} and indium¹⁵⁸ hydrides, they are themselves made by halide–hydride exchange, normally at the expense of the Al–H bonds of LiAlH_4 .

2. Vibrational Properties: M–H Stretching Modes

As noted earlier (section II), vibrational spectroscopy, usually in the form of IR absorption, is one of the primary tools of interrogating main-group metal hydrides. The method is crucially important for species that are transient under normal conditions, e.g., BeH_2 ⁸⁹ and AlH_3 ,¹¹⁵ or for long-lived species where the presence of the hydrogen ligand cannot be established by X-ray diffraction, e.g., $\text{H}_3\text{In}\cdot\text{CN}(\text{Pr}^i)\text{-CMe}=\text{CMeN}(\text{Pr}^i)$.¹⁴¹ It is the M–H stretching fundamentals, $\nu(\text{M}-\text{H})$, that offer the most obvious and distinctive signature of the M–H bond. Not only are these modes usually intense in IR absorption, they fall at wavenumbers high enough to enable them to be treated as relatively well-defined localized motions with minimal coupling to other vibrations of the molecule. The wavenumber regime also makes it that much less likely that the $\nu(\text{M}-\text{H})$ modes will be mistaken for any other type of vibration, with the response to deuteration allaying any doubts about the assignment. With regard to the nature of the M–H bond and its surroundings, there are few parameters more sensitive as reporters than the $\nu(\text{M}-\text{H})$ wavenumber. Some idea of its scope and relevance may

be gained from Table 5, which lists wavenumbers or wavenumber ranges for both terminal and, where appropriate, bridging M–H–M units; these data are drawn from binary hydride molecules containing the metals in their normal oxidation states and/or derivatives of these species.

Terminal M–H bonds display $\nu(\text{M–H})$ modes spanning an extraordinarily wide range of wavenumbers—from 866 cm^{-1} for $\text{M} = \text{Cs}^{\text{I}}$ to 2650 cm^{-1} for $\text{M} = \text{B}^{\text{III}}$. The primary influence appears to be the polarity of the bond. The greater the charge separation between M and H and the more Coulombic the resulting interaction, the shallower is the curvature associated with the M–H coordinate at the foot of the relevant potential well. The M–H stretching force constant and wavenumber decrease accordingly. Changes in charge separation, brought about, for example, by partial replacement of hydrogen by another ligand, complexation, or variations in overall charge, then dictate the $\nu(\text{M–H})$ wavenumbers characterizing derivatives of the binary hydrides. Thus, any factor that increases the electron density on the metal may be expected to result in a decrease in the $\nu(\text{M–H})$ wavenumber. Such a trend is exemplified by the following values (in cm^{-1}) for the antisymmetric $\nu(\text{Ga–H})$ mode of gallane and some of its derivatives: H_2GaCl 1978,¹²⁷ GaH_3 1923,¹¹⁵ 2,4,6- $\text{Bu}_3\text{C}_6\text{H}_2\text{-GaH}_2$ 1887,¹⁴⁴ $\text{Me}_3\text{N}\cdot\text{GaH}_3$ ca. 1820,^{368a} $\text{Me}_3\text{P}\cdot\text{GaH}_3$ 1808,^{368b} $(\text{Me}_3\text{N})_2\text{GaH}_3$ 1790,⁶⁰ and LiGaH_4 ca. 1760.^{368c} The same principle holds when the oxidation state of the metal is varied, as attested by the wavenumbers (in cm^{-1}) of the $\nu(\text{Al–H})$ modes of the following molecules each trapped in an argon matrix: AlH_3 1883/1881,¹¹⁵ AlH_2 1806/1770,¹¹⁴ and AlH 1591.¹¹⁴ There are other factors, such as the coordination geometry about the metal and vibrational coupling, that affect the wavenumbers, but these play a secondary role.

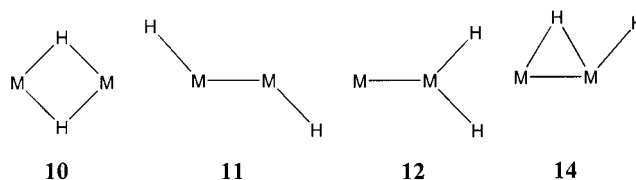
By contrast, bridging M–H–M fragments differ markedly in three respects. First, it is less easy to distinguish stretching from bending motions in what are usually angular M–H–M units. Second, the transitions which correspond most nearly to M–H stretching vibrations occur at wavenumbers significantly lower than those of the corresponding transitions associated with terminal M–H bonds (see Table 5). Third, the wavenumbers and IR intensities of the transitions approximating to the antisymmetric and symmetric stretching fundamentals of the M–H–M unit are highly sensitive functions of the M–H–M bond angle θ .¹³ The wavenumber ratio, $\nu_{\text{as}}/\nu_{\text{s}}$, and intensity ratio, $I_{\text{as}}/I_{\text{s}}$, both tend to unity as θ approaches 90° but increase sharply as θ expands. For example, the dimer $\text{Me}_2(\mu\text{-H})_2\text{AlMe}_2$, in which $\theta = 95.3(6)^\circ$, features IR-active bridge-stretching modes at ca. 1370 (ν_{as}) and 1215 cm^{-1} (ν_{s}), whereas the corresponding modes of the trimer $[\text{Me}_2\text{AlH}]_3$, the skeleton of which is a six-membered $[\text{AlH}]_3$ ring with $\theta = 134(4)^\circ$, occur at 1786 and 939 cm^{-1} .^{62b}

3. Structures

The structures of many of the gaseous hydride molecules are either familiar or unremarkable in their conformity to the expectations of simple bonding

theories. For example, all the dihydrides of the type MH_2 where the valence shell of M includes more than four electrons are known or predicted to be angular molecules. Although the corresponding hydrides of Be, Mg, Zn, Cd, and Hg appear to be linear, those of Ca, Sr, and Ba are expected to flout the conventions of simple VSEPR theory by taking up nonlinear equilibrium structures.^{266,308} Where the metal is capable of forming more than one hydride MH_n , the M–H bonds tend to contract as n increases, e.g., AlH 1.645 Å, AlH_2 1.59 Å, AlH_3 1.57 Å; GeH 1.587 Å, GeH_2 1.591 Å, GeH_3 1.525 Å, GeH_4 1.514 Å; AsH 1.522 Å, AsH_2 1.518 Å, AsH_3 1.511 Å.

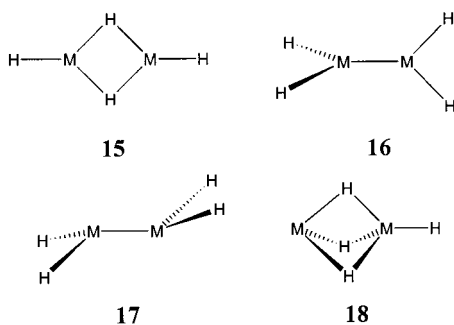
The structures of binuclear hydrides M_2H_n vary according to whether the M atoms are linked by direct metal–metal bonding, as in $\text{H}_3\text{Ge–GeH}_3$,⁶¹ or by hydrogen bridges, as in $\text{H}_2\text{Ga}(\mu\text{-H})_2\text{GaH}_2$.⁶⁰ Variations abound for molecules of the type M_2H_2 . Metal–metal-bonded structures are predicted for some of these species, with linear skeletons in HMg–MgH ,⁹⁵ HZnZnH ,⁹⁹ and HHgHgH ¹⁰⁰ (which have been glimpsed in matrix-isolation studies), and *trans*- C_{2h} structures in HAsAsH , HSbSbH , and HBiBiH ³³⁶ (which have yet to be detected in the laboratory). The elements of groups 13 and 14 offer an intriguing range of structures for molecules of this type. Diborene, B_2H_2 , the boron analogue of acetylene, has a linear triplet ground state with no suggestion of significant B–B double bonding.^{103,104,330} On the other hand, a bis(μ -hydrido) structure (**10**) with D_{2h} symmetry is found to be the most stable form of M_2H_2 for all the heavier group 13 elements;^{330–334} IR bands attributable to this species have been observed in matrix-isolation experiments with $\text{M} = \text{Al}$,¹¹³ Ga ,¹²² or In .^{122c} Instead of the linear form, which is now only a transition state, a *trans*- C_{2h} isomer (**11**) appears as a second minimum on the potential energy surface for M_2H_2 , where $\text{M} = \text{Al}$, Ga , or In . There are two other possible isomers, namely, the mono-H-bridged $\text{M}(\mu\text{-H})\text{MH}$ (**12**) with C_s symmetry and M–MH_2 (**13**) with C_{2v} symmetry, which typically give minima at energies not far above the global minimum. There is



experimental reason, as noted previously, for believing that access to isomer **11** can be gained through photoexcitation of **10** when $\text{M} = \text{Ga}$ or In .¹²² A similar situation exists with the heavier group 14 elements. With Ge_2H_2 , as with Si_2H_2 , there are four possible isomers having structures akin to **10**, **11**, **12**, and **13** but not, remarkably, to that of acetylene.^{332,335} In the case of silicon, isomers $\text{Si}(\mu\text{-H})_2\text{Si}$ (**10** but with a nonplanar butterfly-like framework) and HSiSiH (**14**) have both been characterized by their microwave spectra, being among the products formed in silane plasmas.³⁶⁹

Experimental facts about molecules of the type M_2H_4 are few and far between, although matrix-

isolation experiments have led to the identification of Mg_2H_4 ^{95,337} and Ca_2H_4 ^{97,337} which appear to favor the symmetrical bis(μ -hydrido) structure **15** with D_{2h} symmetry. M_2H_4 molecules featuring a group 13 element remain hypothetical, but theoretical calculations are noteworthy for the different properties they impute according to whether $\text{M} = \text{B}$ or $\text{M} = \text{Al}$ or Ga . Boron favors a classical B–B-bonded structure **16**, whereas Al_2H_4 and Ga_2H_4 prefer a tris(μ -hydrido) structure **18**.^{338–340} This last structure can be de-



scribed in terms of more or less Coulombic interactions between an M^+ cation and a tetrahedral MH_4^- anion, thereby implying disproportionation of the divalent species.

Somewhat surprisingly, structure **18** and not **15** is also predicted *ab initio* for the equilibrium geometries of Sr_2H_4 and Ba_2H_4 ,³³⁷ which must therefore approximate to the ion pairs $\text{M}^{2+}\text{MH}_4^{2-}$. Just as B_2H_4 gives little hint of the geometries preferred by Al_2H_4 and Ga_2H_4 , so the familiar planar structure of ethylene turns out not to be the most stable form for the corresponding hydrides of the heavier members of group 14.³⁴¹ Instead, Si_2H_4 and Ge_2H_4 favor the nonplanar *trans*- C_{2h} structure **17**,³⁴¹ with a relatively short M–M linkage enjoying a degree of multiple bonding; this is in keeping with the known geometries of derivatives M_2R_4 , where R is a bulky organic group, e.g., mesityl or $\text{CH}(\text{SiMe}_3)_2$.³⁷⁰ Despite the fact that $\text{Sn}_2[\text{CH}(\text{SiMe}_3)_2]_4$ follows the precedents set by analogous silicon and germanium compounds, with the $C_2\text{MMC}_2$ skeleton departing increasingly from planarity,³⁷⁰ the hypothetical hydrides Sn_2H_4 and Pb_2H_4 are calculated to be most stable with an HM-(μ -H)₂MH framework akin to **15** but having terminal M–H bonds roughly perpendicular to the plane of the central $\text{M}(\mu\text{-H})_2\text{M}$ ring and *trans* to each other (again in C_{2h} symmetry).³⁴¹ This isomer is computed to lie below the *trans*-bent H_2MMH_2 one by 38 or 100 kJ mol⁻¹ for $\text{M} = \text{Sn}$ or Pb , respectively. Plainly experiment has much ground to make up before it can match hypothesis.

However, dimerization is seldom the limit of association of MH_n molecules formed by the metals of groups 1, 2, and 13. According to *ab initio* calculations, for example, the trimer $[\text{MH}_3]_3$, with a planar six-membered $[\text{MH}]_3$ ring, is formed exoergically from the corresponding dimer when $\text{M} = \text{Al}$ or Ga but not when $\text{M} = \text{B}$.³⁷¹ Even more exoergic is the conversion of the dimer to the tetramer $[\text{MH}_3]_4$ based, it is predicted, on a distinctly nonplanar eight-membered $[\text{MH}]_4$ ring, again when $\text{M} = \text{Al}$ or Ga .³⁷² However, regarding the formation of still larger oligomers and,

ultimately, of extended arrays of these and other MH_n molecules, there is as yet little guidance to be had from theory.

What is well-known experimentally about the alkali-metal hydrides is that they each crystallize under normal conditions in a cubic NaCl-type structure.^{9b} At sufficiently high pressures this typically gives place to a second phase with a B2(CsCl) structure,^{188,189} the threshold decreasing from $p_T = 29.3$ GPa for NaH to 1.2 GPa for CsH. At even higher pressures RbH ³⁵⁵ and CsH ¹⁹⁰ each transform to a third phase with an orthorhombic CrB-type structure featuring zigzag chains of H atoms in a way that suggests significant $\text{H}\cdots\text{H}$ interaction. CuH contrasts with the alkali-metal hydrides in its adoption of a wurtzite-type structure under normal conditions.^{356,357}

The structures of the solid dihydrides of the group 2 metals display a steady increase in the coordination number of the metal from 4 in BeH_2 ,³⁵⁸ through 6 in MgH_2 ,¹⁷⁴ to 7–9 in CaH_2 ,^{175,360} SrH_2 ,^{163,360} and BaH_2 .^{176,361} The beryllium compound has a centered orthorhombic structure comprising a network of corner-sharing BeH_4 tetrahedra with Be–H distances of 1.38–1.44 Å and Be–H–Be angles of 127–130°. ³⁵⁸ There is evidence suggesting the formation of a second phase at low temperatures.³⁵⁹ MgH_2 forms a rutile-type structure with Mg–H distances averaging 1.95 Å.¹⁷⁴ At normal temperatures CaH_2 , SrH_2 , and BaH_2 all have orthorhombic PbCl_2 -type structures with the dimensions indicated in Table 4. This means that the metal has a coordination environment consisting of seven close and two more distant hydride neighbors, though there is in reality an appreciable spread of the interatomic distances. All three of these compounds are reported also to undergo a phase change to a cubic (β) form at high temperatures.^{9b}

Solid aluminum trihydride differs markedly from its boron analogue, a low-melting solid composed of B_2H_6 molecules.³⁶² The α -form of AlH_3 is isostructural with AlF_3 , AlH_6 octahedra having mean Al–H distances of 1.715 Å being linked via hydrogen bridges featuring Al–H–Al angles of 141.2°. ¹⁷⁷ Solid gallane has so far eluded structural characterization, but its properties (and particularly its IR and Raman spectra)^{60,373} imply an oligomeric or, more likely, a polymeric structure different from that of alane in that it features not only Ga–H–Ga bridges but also terminal Ga–H units. A possible model is suggested by the mixed hydride $[\text{GaBH}_6]_n$ the crystal structure of which at 110 K reveals helical chains made up of alternating pseudo-tetrahedral GaH_4 and BH_4 fragments (see Figure 6).³⁷⁴ For few of the other binary hydrides do we have definitive information about the structure of the solid, although the low-melting hydrides formed by the metals of groups 14 and 15 almost certainly follow the example of GeH_4 and SnH_4 ³⁶⁵ in retaining discrete molecules in the solid phase, with only weak dipole–dipole and/or dispersion forces for cohesion.

B. Mixed Hydrides and Complexes

The binary hydrides discussed in the preceding section are parents to many neutral derivatives in

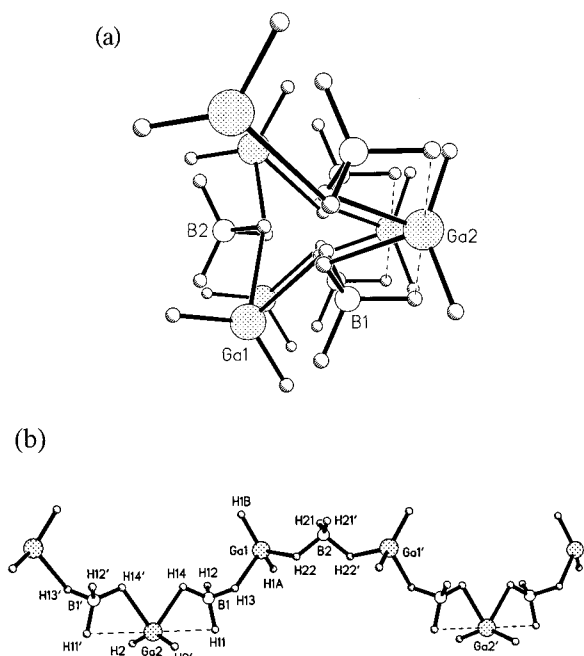


Figure 6. Structure of crystalline gallaborane at 110 K as determined by X-ray diffraction (primed atoms are symmetry-related to nonprimed atoms) showing the helical polymeric arrangement (a) viewed along the axis of the helix and (b) side-on. (Reprinted with permission from ref 374b. Copyright 2001 American Chemical Society.)

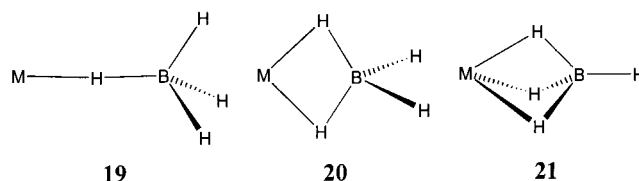
which hydride is partially displaced from the coordination shell of the metal by one or more other ligands, e.g., halide, NR_2 , OR, SR, or R (where R is an organic group). In the event that the binary or mixed hydride carries a metal center with significant acidic character, there is also the possibility of coordination by a neutral or anionic base, with the formation of a complex, e.g., $\text{Me}_3\text{N}\cdot\text{MH}_3$ or MH_4^- ($\text{M} = \text{Al}, \text{Ga}, \text{or In}$). Again, we concentrate mainly on recent developments and on those compounds which have been characterized structurally, usually by X-ray diffraction studies of single crystals. In some cases we draw on the results of spectroscopic studies involving chiefly NMR and IR measurements, but in that these often relate to a phase other than the solid, they cannot be guaranteed to afford structural information outside that phase. Although boron is at the periphery of this review, metal hydroborates³⁷⁵ are often characterized by $\text{M}-\text{H}-\text{B}$ bridges. These too are therefore to be regarded as ‘mixed hydrides’. The different groups of metals will now be treated in turn.

1. The Alkali Metals

The alkali metals offer little scope for the formation of mixed hydrides. The only option open to them involves the formation of mixed *aggregates*, as in the case of the lithium hydride/*tert*-butoxide system, $[(\text{Bu}^t\text{O})_x\text{LiH}_{1-x}]_n$,²⁰¹ on the evidence of the ^6Li and ^1H NMR spectra of cyclopentane solutions, the aggregates contain 10 or 12 Li atoms but with structures yet to be defined.

Alkali-metal hydroborate or hydrometalate derivatives often give the appearance of affording little or no *specific* interaction between the alkali-metal cat-

ion, M^+ , and the hydrogen of the anionic component. That is certainly the impression given by the crystal structures of the tetrahydroborate salts MBH_4 .³⁷⁵ On the other hand, the situation may change if the alkali-metal center is modified through additional coordination by a neutral donor ligand or if the basicity of the complex hydride anion increases. Thus, specific interactions between the metal and the tetrahydroborate anion are typically signaled by the adoption of one of three modes of coordination involving monodentate (**19**), bidentate (**20**), or tridentate (**21**) ligation.³⁷⁵ The smallness of the Li^+ cation may



well be a factor contributing to the $\eta^1\text{-BH}_4^-$ anions found in the binuclear tetrahydroborate (18-crown-6) $\text{Li}_2(\text{BH}_4)_2$.³⁷⁶ On the other hand, η^3 -coordination is found in the complexes $[(\text{tmeda})\text{Li}(\mu\text{-}\eta^3\text{-BH}_4)]_2$,³⁷⁷ $[\text{HC}(3,5\text{-Me}_2\text{pz})_3]\text{Li}(\eta^3\text{-BH}_4)$,³⁷⁸ $\{[\text{H}_2\text{C}(3,5\text{-Me}_2\text{pz})_2]\text{Li}(\mu\text{-}\eta^3\text{-BH}_4)\}_2$,³⁷⁸ and $\{[4,4'\text{-Me}_2\text{bipy}]\text{Li}(\mu\text{-}\eta^3\text{-BH}_4)\}_2$ ³⁷⁸ ($\text{pz} = \text{pyrazolyl}$; $\text{bipy} = \text{bipyridyl}$), all with hexacoordinated lithium atoms. A novel polymeric structure has also been reported for $[(\text{diglyme})\text{NaBH}_4]_n$, the sodium centers being bridged by BH_4^- groups with three types of hydrogen participating in coordination, one of them functioning as a bridge.^{379a} Monomeric, dimeric, and tetrameric assemblies are found among the solvates formed by LiBH_4 and NaBH_4 with various amines (pyridine, *p*-benzylpyridine, 2,4,6-trimethylpyridine, *N,N,N',N'*-pentamethyldiethylenetriamine, trimethylhexahydrotriazine, and trimethyltriazacyclononane).^{379b} Here BH_4^- groups may be bidentate or tridentate and may function in different ways as bridges between the alkali-metal centers according to the number of donor atoms taken up from the amine, as well as the size of the cation.

The hydrogen atoms of hydroaluminate anions are more nucleophilic than those of analogous hydroborate species and are therefore more susceptible to specific interaction with the accompanying cation. This feature is evident in the structure of LiAlH_4 , where the Li^+ cations act as bridges between the AlH_4^- anions, four of the $\text{Li}\cdots\text{H}$ distances (1.88–2.00 Å) being substantially shorter than those in LiH (2.04 Å).³⁸⁰ It is also apparent (i) in the dimeric adduct $\{[\text{HN}(\text{Bu}^t)\text{CH}(\text{Bu}^t)\text{CHNBu}^t]\text{Li}(\mu\text{-H})_2\text{AlH}_2\}_2$ where the $\text{Li}\cdots\text{H}$ distances range from 1.66(9) to 2.04(7) Å³⁸¹ and (ii) in $\{(\text{Me}_2\text{pip})\text{Li}(\mu\text{-H})\text{AlBu}^t[\text{CH}(\text{SiMe}_3)_2]_2\}$ ($\text{Me}_2\text{pip} = \text{N,N}$ -dimethylpiperazine) which has an angled $\text{Li}-\text{H}-\text{Al}$ bridge and an unusually short $\text{Li}\cdots\text{H}$ distance (1.76 Å), as well as an intriguingly short intramolecular contact between Li and the C–H bonds of an Me_3Si group.²³⁴

2. The Group 2 Metals

a. Beryllium. The tendency of beryllium hydrides to form oligomeric or polymeric frameworks in the solid state is amply illustrated not only by the

structure of the binary hydride,³⁵⁸ but also by those of $\text{Be}(\text{BH}_4)_2$,³⁸² M_2BeH_4 ($\text{M} = \text{Li}$ or Na),³⁸³ $[\text{Et}_2\text{BeHN}(\text{OEt}_2)]_n$,²⁴¹ $[\text{PhBe}(\text{NMe}_3)(\mu\text{-H})]_2$,³⁸⁴ and $[\text{MeBe}(\text{OEt}_2)(\mu\text{-H})]_2$.³⁸⁵ Monomeric species are generally found only in conjunction with bridging hydrido linkages to bulky hydroborate cage ligands such as B_3H_8^- ³⁸⁶ and $\text{B}_5\text{H}_{10}^-$.³⁸⁷ Until recently the only example of a crystallographically characterized compound with a terminal Be–H linkage was to be found in the dimeric species $[\text{HBeN}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2]_2$ synthesized by Bell et al. in 1983.³⁸⁸ Measuring 1.39(2) Å, this distance is consistent with the r_0 value of 1.32(1) Å deduced from the microwave spectrum of the gaseous monomer ($\eta^5\text{-C}_5\text{H}_5$)BeH.³⁸⁹

Through the use of sterically bulky substituents at the 3 and 5 positions of the pyrazolyl unit, tris-(pyrazolyl)borate (or scorpionate) ligands have now been developed to the point of offering remarkably close control of the coordination environment of a metal center (see **2**, section II.C).³⁹⁰ The extremely large cone angles of the ligands Tp^{Me} and Tp^{Bu^t} (224 and 244°, respectively)³⁹⁰ restrict severely the opportunity for oligomerization through bridging ligands and so give access to monomeric compounds of the type TpMR , where M is a group 2 or group 12 metal and R a terminal hydride, alkyl, or halide ligand. $\text{Tp}^{\text{Bu}^t}\text{BeH}$, synthesized by eq 9,¹⁴⁷ represents the first example of a monomeric beryllium hydride to be characterized crystallographically. The reported Be–H distance of 1.23(7) Å is not significantly different from those of the other terminal Be–H bonds that have been measured to date; it is close to the sum of the relevant covalent radii (1.26 Å)³⁹¹ and also to the distances calculated for a range of hypothetical beryllium hydrides.³⁹² As expected, appreciably longer distances are found for the bridging Be–H linkages in $\text{B}_5\text{H}_{10}\text{BeBH}_4$ (1.46–1.59 Å),³⁸⁷ $\text{Be}(\text{B}_5\text{H}_{10})_2$ (1.66–1.75 Å),³⁸⁷ $\text{Be}(\text{B}_3\text{H}_8)_2$ (1.47–1.53 Å),³⁸⁶ and $[\text{Et}_2\text{BeHN}(\text{OEt}_2)]_n$ (1.4 Å).²⁴¹ It is worth remarking that $\text{Tp}^{\text{Bu}^t}\text{BeH}$ and $\text{Tp}^{\text{Bu}^t}\text{BeBr}$ do not differ significantly with regard to the dimensions of the $\text{Tp}^{\text{Bu}^t}\text{Be}$ fragment. Hence, the tetrahedral geometry enforced by the Tp^{Bu^t} ligand appears to be able to accommodate substituents as different in size as H and Br, while the tertiary butyl groups provide sufficient steric bulk peripheral to the coordination site to minimize the tendency toward oligomerization.¹⁴⁷

b. Magnesium, Calcium, Strontium, and Barium. For none of the heavier members of group 2 has it been possible to isolate, and authenticate the structure of, any hydride derivative containing a terminal M–H bond. As noted previously, magnesium forms numerous mixed hydrides of the types RMgH ,^{15,195} RMg_2H_3 ,^{15,195} HMgX ,^{196,198} LiMgH_2R ,¹⁵ $\text{LiMg}_2\text{H}_3\text{R}_2$,¹⁵ and $\text{Li}_2\text{MgH}_2\text{R}_2$ ¹⁵ ($\text{R} =$ organic group; $\text{X} =$ halogen, BH_4 , or AlH_4) which appear invariably to be oligomers or polymers containing Mg–H–Mg bridges. Spectroscopic and colligative measurements on solutions have given information about the degree of aggregation and likely composition of the aggregates (which often include solvent molecules), but no definitive structural details are available, with but a single exception. This is the anthrylene complex $[(\text{thf})_n\text{Mg}(\mu\text{-H})(\mu\text{-C}_{14}\text{H}_{10})\text{AlEt}_2]$ already alluded to

(**13**) wherein the unique bridging hydride ligand is more closely associated with the Al than with the Mg center.²⁴⁶ Solid ternary hydrides such as MMgH_4 ($\text{M} = \text{Sr}$,^{164a} Ba ,^{164b} or Eu ^{393a}), Ba_2MgH_6 ,¹⁶⁵ EuMg_2H_6 ,^{393a} $\text{Ba}_2\text{Mg}_3\text{H}_{10}$,^{393b} and $\text{Ba}_6\text{Mg}_7\text{H}_{26}$ ²²⁰ follow the same structural principles as MgH_2 ,¹⁷⁴ being composed of more or less well-defined MgH_6 octahedra with Mg–H distances in the range 1.77–2.28 Å. Calcium, strontium, and barium form mixed hydrides of the type MHX ($\text{M} = \text{Ca}$, Sr , or Ba ; $\text{X} = \text{Cl}$, Br , or I), which are reported typically to adopt the PbClF -type of layer structure, although the hydrogen atoms have not been directly located.^{9b} The similar sizes of hydride and fluoride anions produce a rather different picture when hydride is substituted for fluoride in the cubic fluorite lattices of MF_2 ($\text{M} = \text{Ca}$, Sr , or Ba) to give hydride fluorides $\text{MF}_{2-x}\text{H}_x$ with a statistical distribution of H^- and F^- .¹⁶²

Rather more specific $\text{M}\cdots\text{H}$ interactions are implied by the structures of some of the tetrahydroborate derivatives of these metals, with $\eta^2\text{-BH}_4$ ligands predominating for the smaller magnesium center^{394–396} and $\eta^3\text{-BH}_4$ ligands for the larger strontium and barium ones.³⁹⁷ Calcium takes up an intermediate position, yielding complexes that contain both η^2 - and $\eta^3\text{-BH}_4$ groups.^{398,399} Thus, strontium and barium tetrahydroborates have been reported by Nöth et al.³⁹⁷ to form ether complexes with the stoichiometries $\text{M}(\text{BH}_4)_2(\text{thf})_2$, $\text{M}(\text{BH}_4)_2(\text{diglyme})_2$, and $\text{M}(\text{BH}_4)_2(18\text{-crown-6})$ ($\text{M} = \text{Sr}$ or Ba). Of these $\text{Sr}(\text{BH}_4)_2(\text{thf})_2$ and $\text{Ba}(\text{BH}_4)_2(\text{thf})_2$ are infinite chain coordination polymers in the solid state; successive metal centers are bridged by two BH_4 ligands, each coordinated in η^3 fashion to both metals, and the coordination sphere of the metal is completed by two mutually trans thf ligands to give an overall coordination number of 14 (two thf oxygens and four sets of three bridging hydrides). Recourse to oxygen donor ligands of greater denticity results in the isolation of discrete molecular species in $\text{M}(\text{BH}_4)_2(\text{diglyme})_2$ and $\text{M}(\text{BH}_4)_2(18\text{-crown-6})$. The diglyme solvates feature two tridentate BH_4 ligands and two diglyme molecules each coordinated to the metal center via three oxygen atoms. The coordination number at the metal center is therefore 12. By contrast, the corresponding calcium complex has a decacoordinated metal center.³⁹⁹ The smaller size of the calcium necessitates the adoption by one of the BH_4 units of η^2 -coordination (**20**) and the binding of one of the diglyme ligands through only two oxygen atoms.

3. The Group 12 Metals

Long-lived hydrides of the group 12 metals normally require the stabilizing influence of complexation. Only mercury gives rise to simple monomeric mixed hydrides RHgH containing a variety of organic groups R and which are robust enough to be characterized, usually at low temperatures, by their NMR, vibrational, and mass spectra.^{222,223,400} It is noteworthy that the hydride ligand gives a ^1H NMR signal at uncharacteristically high frequency for a main-group metal hydride. All the signs indicate the linear C–Hg–H skeletons to be expected of molecular mercury(II) compounds, but definitive structural measurements are still awaited.

Complexation may give more durable compounds having terminal M–H linkages. For example, the solid complexes K_2ZnH_4 and K_3ZnH_5 contain more or less discrete tetrahedral $[ZnH_4]^{2-}$ ions with Zn–H distances measuring 1.63–1.67 Å.^{166,167} More often, however, the survival of such units requires the mediation of chelating or bridging ligand frameworks, as in $[(Me_2NCH_2CH_2NMe)ZnH]_2$,^{401a} $[(Me_3PN)ZnH]_4$,^{401b} and $Tp^{Bu}MH$ (where $M = Zn^{148}$ or Cd^{149}). The Zn–H distance in $[(Me_2NCH_2CH_2NMe)ZnH]_2$ is found to be 1.62(6) Å on the basis of neutron-diffraction experiments,⁴⁰¹ but such details about terminal M–H bonds remain generally in short supply.

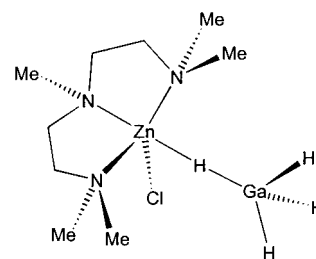
In practice, stable hydrides are more likely to contain hydrido-bridged linkages between the same or different main-group metal atoms or between the group 12 metal and either boron or a transition metal. That is certainly the case with the zinc complex $[\{HC(CMeNAr)_2\}Zn(\mu-H)]_2$, where $Ar = 2,6-Me_2C_6H_3$, with bridging Zn–H bonds measuring 1.766 Å and $\angle Zn-H-Zn = 87.9^\circ$.^{401c} The same structural principle probably applies to many of the zinc hydrides that have been described without structural validation, e.g., $PhZn_2H_3$,¹⁸⁴ $MZnH_3$,^{182,402} Li_2ZnH_4 ,⁴⁰² $Mg(ZnH_3)_2$,¹⁸³ $MgZnH_4$,¹⁸³ $MZnMe_2H$,^{182,402} MZn_2Me_4H ,⁴⁰³ $MZnMe_2AlH_4$ (see **6**),¹⁹⁹ and $MZn_2Me_4AlH_4$ (see **7**),¹⁹⁹ where M is an alkali metal and R is an organic group. Hydroborates often turn out to be more tractable and with appropriate control of coordination at the metal center may be amenable to crystallographic characterization.

A striking example of this is provided by $Tp^{Me}CdBH_4$, the only compound to be prepared to date containing a reasonably well authenticated Cd–H bond.¹⁴⁹ The Tp^{Me} ligand adopts the expected η^3 -coordination mode, but the BH_4 ligand is bidentate, in keeping with the IR spectrum³⁷⁵ and also with the precedents set by earlier studies.⁴⁰⁴ The $Cd\cdots H$ contacts are not reported but must measure about 2.0 Å and are therefore substantially closer than those [2.36(4) Å] within the anion in crystalline $[Bu^t_4N]_2[Cd(\eta^3-B_6H_6)_2]\cdot 2CH_2Cl_2$; the distances in the second case imply no more than a weak $Cd\cdots H-B$ bridging supplement to the primary framework interaction involving two CdB_6H_6 fragments fused about a common Cd vertex.⁴⁰⁵ Use of ‘super hydride’ $LiEt_3BH$ instead of KBH_4 in the reaction with $CdCl_2$ and $Tp^{Me}I$ causes a remarkable change yielding not $Tp^{Me}CdBH_4$ but the dimer $[Tp^{Me}Cd]_2$ for which the measured $^1J(^{113}Cd-^{111}Cd)$ coupling constant of 20 646 Hz points to the existence of a strong Cd–Cd bond.¹⁴⁹ On the other hand, use of the sterically more bulky Tp^{Bu} ligand generates $Tp^{Bu}CdH$ irrespective of whether the hydride source is KBH_4 or $LiEt_3BH$.¹⁴⁹ This compound has been characterized by its NMR and mass spectra; a monomeric structure with a terminal Cd–H bond has been proposed, principally on the evidence of a doublet in the ^{113}Cd NMR spectrum [$^1J(^{113}Cd-H) = 2527$ Hz] which collapses to a singlet on 1H decoupling. Hence, it would appear to be entirely analogous to the corresponding zinc compound described above.¹⁴⁸ That a larger Tp ligand should result in the isolation of the hydride rather than the tetrahydroborate derivative illustrates just

how critical the role of spectator ligand bulk can be in determining the outcome of such a reaction, as well as the structure of the resulting hydride product.

Whereas cadmium and mercury appear to be reluctant partners to hydroborate ligands, zinc is much more cooperative. In the majority of known cases the ligand is BH_4 invariably coordinated to the metal center in an η^2 fashion. The geometry of the $Zn(\mu-H)_2BH_2$ unit varies little among the four crystallographically characterized species containing a terminal BH_4 moiety, viz. $[(MePh_2P)_2VH_2Zn(BH_4)]_2$,⁴⁰⁶ $[Cp_2Nb(CO)(\mu-H)Zn(BH_4)]_2$,⁴⁰⁷ $(tmeda)ZnCl(BH_4)$,⁴⁰⁸ ($tmeda = Me_2NCH_2CH_2NMe_2$), and $[Ph_4P][Zn(BH_4)_3]$.⁴⁰⁹ Averaging 1.85 Å, Zn–(μ -H) distances are ca. 12% longer than the terminal Zn–H one in $[(Me_2NCH_2CH_2NMe)ZnH]_2$ (1.62 Å).⁴⁰¹ A similar increase in Al–H bond length is found for the bridging linkages in solid $Al(BH_4)_3$ [1.73(4)–1.76(4) Å for the α phase⁴¹⁰] compared with terminal Al–H bonds (average length 1.53 Å for the AlH_3 adducts listed in Table 6). The average $Zn\cdots B$ distance (2.25 Å) is somewhat greater than the sum of the covalent radii of zinc and boron (2.15 Å³⁹¹), in support of the view that direct $Zn\cdots B$ interactions play but a minor role in the bonding of the $Zn(\mu-H)_2BH_2$ fragments.

In addition to the tetrahydroborate $(tmeda)ZnCl(BH_4)$, Raston and co-workers also reported the synthesis of the analogous tetrahydrogallate $(tmeda)ZnCl(GaH_4)$, for which bidentate ligation of the GaH_4 moiety was proposed.⁴⁰⁸ Furthermore, use of the tridentate nitrogen donor ligand pentamethyldiethylenetriamine ($pmdeta$, $Me_2NCH_2CH_2N(Me)CH_2-CH_2NMe_2$) leads to the isolation of the tetrahydrogallate $(pmdeta)ZnCl(GaH_4)$, **22**, wherein η^1 -coordination of the GaH_4 unit has been established by X-ray diffraction of a single crystal.⁴⁰⁸



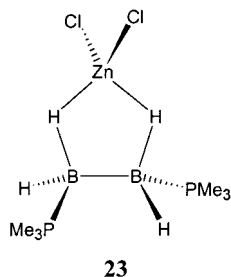
22

In contrast to the terminal $Zn(\mu-H)_2BH_2$ unit found in other zinc tetrahydroborates, bridging BH_4 units are found in crystalline methylzinc tetrahydroborate, presumably as a result of the small steric requirements of the methyl ligand.⁴¹¹ The resulting polymeric chain contains $MeZn$ moieties linked via BH_4 ligands which exhibit bidentate coordination with respect to *both* adjacent metal centers. Similar helical chains are observed in solid $Be(BH_4)_2$ ³⁸² and Me_2AlBH_4 .⁴¹⁰ In each case the $M\cdots B\cdots M$ unit is approximately linear [e.g., $171.9(3)^\circ$ for solid $MeZnBH_4$ ⁴¹¹] with the helical structure resulting from the angle at the metal center [$B\cdots M\cdots B = 98.6(7)^\circ$ for $MeZnBH_4$, $111.7(4)^\circ$ for $Be(BH_4)_2$, and $119.9(2)^\circ$ for Me_2AlBH_4]. The adoption by solid $MeZnBH_4$ ⁴¹¹ and Me_2AlBH_4 ⁴¹⁰ of polymeric structures featuring bis-

(bidentate) BH_4 ligands increases by two the coordination number at the metal center with respect to that found in the monomeric species $\text{MeZn}(\mu\text{-H})_2\text{BH}_2$ ⁴¹² and $\text{Me}_2\text{Al}(\mu\text{-H})_2\text{BH}_2$ ⁴¹³ thought to predominate in the vapor phase at low pressures. This contrasts with the polymeric structure characterizing H_2GaBH_4 in the solid state (Figure 6)³⁷⁴ which retains the approximately tetrahedral four-coordinated geometry of the monomeric molecule $\text{H}_2\text{Ga}(\mu\text{-H})_2\text{BH}_2$ observed in the vapor phase.²³⁰

Finally, we remark upon two unusual zinc hydroborates, namely, $\text{Cl}_2\text{Zn}[\eta^2\text{-B}_2\text{H}_4 \cdot 2(\text{PMe}_3)]$ ⁴¹⁴ and $[(\text{MeZn})_2\text{B}_3\text{H}_7]_2$,⁴¹⁵ each embodying a zinc center linked to a chelating B–B-bonded ligand via two

bridging hydrides to give a five-membered $\text{Zn}(\mu\text{-H})\text{-BB}(\mu\text{-H})$ ring. In the first a chelating *trans*- $\text{B}_2\text{H}_4(\text{PMe}_3)_2$ ligand is bound to a ZnCl_2 unit via two hydride bridges (**23**), the positions of which deviate little from the plane of the ZnB_2 framework.⁴¹⁴ The



$\text{Zn}(\mu\text{-H})$ distances [1.89(5) Å on average] are not significantly different from those found in zinc tetrahydroborate derivatives, although there is a considerable opening up of the H–Zn–H angle {107(2)° for $\text{Cl}_2\text{Zn}[\eta^2\text{-B}_2\text{H}_4(\text{PMe}_3)_2]$; 54–70° for zinc tetrahydroborates^{406–409,411}}, reflecting the very different bite angles of the BH_4 and $\text{B}_2\text{H}_4(\text{PMe}_3)_2$ ligands. $[(\text{MeZn})_2\text{B}_3\text{H}_7]_2$ features discrete centrosymmetric $\text{Me}_4\text{Zn}_4\text{B}_6\text{H}_{14}$ dimers in which two novel $\text{B}_3\text{H}_7\text{ZnMe}$ ligands are linked through hydride bridges about a central $\text{MeZn}\cdots\text{ZnMe}$ vector [3.014(3) Å] in an unusual example of a molecule containing two distinct zinc environments.⁴¹⁵ The pentacoordinated zinc centers are each bound to a single methyl ligand and to four bridging hydrogens, two from each $\text{B}_3\text{H}_7\text{ZnMe}$ ligand. The resulting distorted square pyramidal coordination geometry is similar to that found in solid MeZnBH_4 ,⁴¹¹ although the poorly defined hydrogen atom locations preclude any detailed structural comparison.

4. The Group 13 Metals

The group 13 metals produce a rich tapestry of mixed and complex hydride derivatives. Derivatives of alane are especially numerous, those of gallane less stable and plentiful, and those of indane distinctly scarce. No compounds with significant $\text{Tl}\cdots\text{H}$ interactions have been characterized satisfactorily up to the present time. To produce some kind of framework, the following discussion is presented under five headings: (a) adducts of alane and gallane, (b) alane and gallane derivatives incorporating elements from groups 15–17, (c) organoalanes and -gallanes, (d) hydroborate derivatives, and (e) indium hydrides.

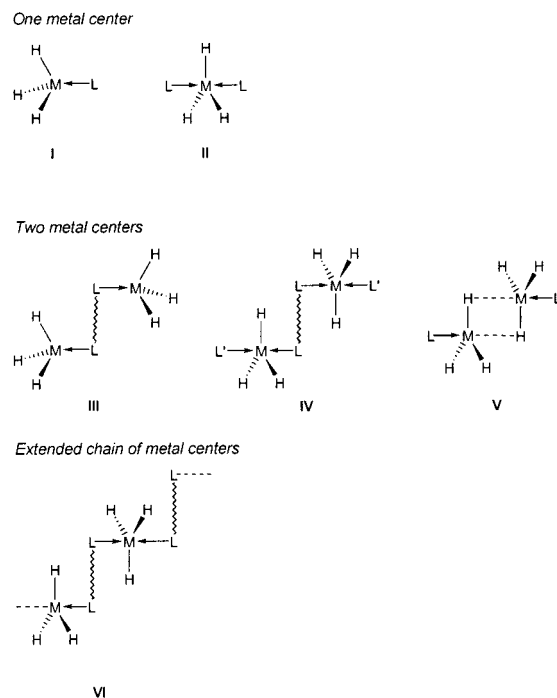


Figure 7. Structural types identified in adducts of AlH_3 and GaH_3 .

a. Adducts of Alane and Gallane. Here we are concerned with the complexes formed by alane, AlH_3 , or gallane, GaH_3 , and a neutral or anionic base partner. Complexation is a key factor in the stabilization of the parent hydride; in the case of aluminum 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, species such as $\text{Me}_3\text{N}\cdot\text{MH}_3$ and LiMH_4 ($\text{M} = \text{Al}, \text{Ga},$ or In) make altogether more convenient synthetic agents than do the base-free hydrides. The neutral complexes of alane and gallane have been reviewed recently by Raston et al.,¹⁴⁰ and no good purpose will be served by going over the same ground. Instead we offer a brief survey of the features that have emerged from structural studies of these compounds.

Structural characterization has been achieved predominantly for the neutral complexes formed with nitrogen, phosphorus, or oxygen donors. In addition, the carbene adducts $\text{H}_3\text{Al}\cdot\text{CN}(\text{Mes})\text{CH}=\text{CHN}(\text{Mes})$ ⁴¹⁶ and $\text{H}_3\text{M}\cdot\text{CN}(\text{Pr}^i)\text{CMe}=\text{CMeN}(\text{Pr}^i)$ (see **1**, $\text{M} = \text{Al}, \text{Ga},$ or In)^{141,417} have recently been reported, the latter including the first adduct of indane, InH_3 , to be characterized crystallographically. In addition to ionic species of the type $[\text{H}_2\text{AlL}]^+[\text{AlH}_4]^-$ [where, for example, $\text{L} = \text{N,N,N,N',N'}$ -pentamethyldiethylenetriamine (pmdeta) or 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4Cyclam)],⁴¹⁸ we find neutral adducts of six structural types on the evidence of the results reported to date. These are represented by the schematic structures **I–VI** in Figure 7. Examples of each type can be found in Table 6, which provides a listing of structurally characterized species.

The balance between 4- and 5-fold coordination at the group 13 metal center and between monomeric

Table 6. Structurally Characterized Adducts of AlH₃ and GaH₃ Containing Group 15 and 16 Donors^a

adduct	mean $r(M-E)/\text{\AA}$	mean $r(M-H)/\text{\AA}$	structural type ^b	ref
AlH₃/nitrogen donors				
H ₃ Al·NMe ₃ (g) ^c	2.063(7)	1.585(2)	I	432
H ₃ Al·quinuclidine	1.991(4)	1.47(5)	I	424
H ₃ Al·NBu ₃	1.979	1.334	I	436
H ₃ Al·NHCMe ₂ CH ₂ CH ₂ CH ₂ CMe ₂	2.04(1)	1.52(9)	I	437
H ₃ Al·2(NMe ₃)	2.18(1)	<i>d</i>	II	420
H ₃ Al·2(tmtz) ^e	2.188(4)	1.67(6)	II	428
[H ₃ Al·NMe ₃] ₂	2.09(2)	<i>d</i>	V	419
[H ₃ Al·NMe ₂ CH ₂ Ph] ₂	2.088(2)	1.56(3) Al-H 1.56(2) Al-μH 2.07(2) Al···μH	V	419
[H ₃ Al·NMe ₂ CH ₂ CH ₂ CH ₂ Cl] ₂	2.068(6)	1.30(7) Al-H 1.84(3) Al-μH 1.99(5) Al···μH	V	438
[H ₃ Al·MeNCH ₂ CHCH ₂ CH ₂] ₂	2.082(4)	1.63(5) Al-H 1.59(4) Al-μH 2.01(4) Al···μH	V	419
[H ₃ Al·Me ₂ NCH ₂ CH ₂ NMe ₂] _∞	2.21	<i>d</i>	VI	439
[H ₃ Al·Me ₂ NCH ₂ CH ₂ CH ₂ NMe ₂] _∞	2.209(4)	1.57(5)	VI	428
[H ₃ Al·tmtz] _∞ ^e	2.215(6)	1.53	VI	428
[H ₃ Al·MeMorph] _∞ ^f	2.15(2) N 2.19(2) O	<i>d</i>	VI	424
[2H ₃ Al·EtMorph] _∞ ^f	2.133(3) N 1.993(3) O	1.52	V ^g	429
[1.5H ₃ Al·EtMorph] _∞ ^f	2.043(3) N 2.103(3) O	1.47	2-D net	429
[H ₃ Al·NMe ₂ H] ₂	2.0281(11)	1.547(11) Al-H 1.543(11) Al-μH 2.075(16) Al···μH	V 2-D net	422
AlH₃/phosphorus donors				
H ₃ Al·PCy ₃	2.467(1)	1.60(4)	I	425
H ₃ Al·PBU ₃	2.471(3)	<i>d</i>	I	427
H ₃ Al·Cy ₂ PCH ₂ CH ₂ PCy ₂ ·AlH ₃	2.406(2)	1.55(2)	III	425
H ₃ Al·Pr ⁱ ₂ PCH ₂ CH ₂ PPR ⁱ ₂ ·AlH ₃	2.451(3)	1.53(10)	III	427
2(Me ₃ N·AlH ₃)·Me ₂ PCH ₂ CH ₂ PMe ₂	2.155(9) N 2.688(5) P	<i>d</i>	IV	424
[H ₃ Al·Pr ⁱ ₂ PCH ₂ CH ₂ PPR ⁱ ₂] _∞	2.732(3)	1.59	VI	425
AlH₃/oxygen donors				
H ₃ Al·2(thf)	2.067(3)	1.51(3)	II	430
[H ₃ Al·thf] ₂	1.967(2)	1.39(4) Al-H 1.54(3) Al-μH 2.05(3) Al···μH	V	430
GaH₃/nitrogen donors				
H ₃ Ga·quinuclidine	2.063(4)	1.62(6)	I	426
H ₃ Ga·NMe ₃ (g) ^h	2.134(4)	1.511(13)	I	59
H ₃ Ga·NMe ₃ (s)	2.081(4)	1.51(6)	I	59
H ₃ Ga·NMe ₂ CH ₂ Ph	2.071(3)	1.52(4)	I	438
H ₃ Ga·Me ₂ NCH ₂ CH ₂ NMe ₂ ·GaH ₃	2.085(3)	1.44(7)	III	426,440
[H ₃ Ga·Me ₂ NCH ₂ CH ₂ CH ₂ NMe ₂] _∞	2.362	1.389	VI	433
[H ₃ Ga·NMe ₂ H] ₂	2.079(3)	1.50(3) Ga-H 1.50(3) Ga-μH 2.87(5) Ga···μH	V	422
GaH₃/phosphorus donors				
H ₃ Ga·PMe ₃	2.403(1)	1.56(2)	I	422
H ₃ Ga·PCy ₃	2.460(2)	1.48	I	441
H ₃ Ga·PBU ₃	2.444(6)	<i>d</i>	I	427
H ₃ Ga·Me ₂ PCH ₂ CH ₂ PMe ₂ ·GaH ₃	2.403(1)	1.45(9)	III	440,441

^a Details relate to crystallographic studies unless stated otherwise. ^b See Figure 7. ^c Microwave study, r_0 distances given. ^d Hydrogen atoms not located. ^e tmtz = 1,3,5-trimethylhexahydro-1,3,5-triazine. ^f MeMorph = *N*-methylmorpholine; EtMorph = *N*-ethylmorpholine. ^g Polymeric version of structure V with coordination of the base via N and O. ^h Determined by a combined analysis of the microwave spectrum and electron diffraction pattern, r_u^0 structure.

and more highly aggregated species is clearly a function of both the electronic and the steric properties of the ligand L and the metal M. Several other points emerge from a survey of the data.

(i) Adducts of alane show a greater propensity toward higher coordination number at the metal than do the analogous gallane adducts. This is clearly

reflected in the structures of the trimethylamine adducts [H₃Al·NMe₃]₂⁴¹⁹ and H₃Ga·NMe₃.⁵⁹ The former molecule adopts the hydrido-bridged dimeric structure V with 5-fold coordination at the aluminum, while the latter retains the tetracoordinated geometry inherent in structure I. Furthermore, whereas alane forms both 1:1 and 1:2 adducts with trimethy-

lamine [the 1:2 adduct $\text{H}_3\text{Al}\cdot 2(\text{NMe}_3)$ adopting structure **II**⁴²⁰], the corresponding 1:2 adduct of GaH_3 decomposes above -23°C to the tetraordinated 1:1 species.⁴²¹ Interestingly, though, a dimeric structure along the lines of **V** has been established very recently for $[\text{H}_3\text{Ga}\cdot\text{NMe}_2\text{H}]_2$,⁴²² while the corresponding alane decomposes rapidly with the elimination of H_2 under comparable conditions. Ab initio studies of the hypothetical complex $\text{H}_3\text{Al}\cdot 2(\text{NH}_3)$ suggest that electronegativity rather than size or access to vacant d-orbitals is the main factor distinguishing aluminum from its neighboring group 13 elements, the Al–NH₃ bonding showing greater Coulombic character.⁴²³

The tendency of aluminum to form pentacoordinated adducts is such that structure type **I** is observed only for strongly σ -donating or sterically bulky ligands. Hence, alane forms a type **I** adduct with the strongly donating quinuclidine ligand [quin, $\text{HC}(\text{CH}_2\text{CH}_2)_3\text{N}$]⁴²⁴ but a hydrido-bridged dimer with trimethylamine⁴¹⁹ and a type **I** adduct with the bulky tricyclohexylphosphine (Cy_3P)⁴²⁵ but a 1:1 pentacoordinated species (type **VI**) with the less sterically demanding $\text{Pr}^i_2\text{PCH}_2\text{CH}_2\text{PPr}^i_2$ ligand.⁴²⁵

(ii) Phosphine ligands tend to bind more strongly to GaH_3 than to AlH_3 , whereas the reverse is found to be the case for nitrogen donor ligands. Hence, the M–N distances for the type **I** adducts $\text{H}_3\text{M}\cdot\text{quinuclidine}$ (M = Al or Ga) are 1.991(4)⁴²⁶ and 2.063(4) Å,⁴²⁶ respectively, whereas the corresponding M–P distances for $\text{H}_3\text{M}\cdot\text{PBu}'_3$ are 2.471(3) and 2.444(6) Å,⁴²⁷ despite the near-identical covalent radii of aluminum and gallium.³⁹¹ Indeed, the coordination of alane by phosphorus donors is sufficiently weak that adducts containing sterically unhindered ligands decompose to polymeric $[\text{AlH}_3]_n$ under relatively mild conditions.⁴²⁴ With this in mind, the loss in vacuo of trimethylamine from the mixed-donor adduct $\text{Me}_3\text{N}\cdot\text{AlH}_3\cdot\text{PBu}'_3$ is highly unusual; the behavior may reflect the exceptionally large steric demand of the phosphine ligand coupled with the volatility of trimethylamine.⁴²⁴

(iii) 1:1 Adducts of alane and gallane with bidentate nitrogen and phosphorus ligands show little or no tendency toward chelation, even in systems such as $[\text{H}_3\text{Al}\cdot\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2]$, where the chelate ring so formed would contain little strain.⁴²⁸ Such systems invariably display polymeric structures of type **VI** in which the sum of the H–Al–H angles approaches 360° . The preference of the AlH_3 moiety for a planar skeleton has been investigated by Atwood et al. using the model system $\text{H}_3\text{Al}\cdot 2(\text{NH}_3)$.⁴²⁸ It was found that a D_{3h} structure featuring a planar AlH_3 unit was most stable, with alternative C_{2v} and C_s arrangements of the ligands being unstable with respect to fragmentation into $\text{H}_3\text{Al}\cdot\text{NH}_3$ and NH_3 (which collectively are 44.9 kJ mol^{-1} less stable than the D_{3h} structure).⁴²⁸ Alane also forms adducts with the mixed-donor ligands *N*-methylmorpholine (MeMorph) and *N*-ethylmorpholine (EtMorph) with the stoichiometries $\text{H}_3\text{Al}\cdot\text{MeMorph}$,⁴²⁴ $2\text{H}_3\text{Al}\cdot\text{EtMorph}$,⁴²⁹ and $1.5\text{H}_3\text{Al}\cdot\text{EtMorph}$.⁴²⁹ All of these self-assemble spontaneously into one- or two-dimensional polymeric structures, the first into a polymeric chain of type **VI**, the second into a polymeric chain formed by the

linking of discrete N- and O-bound AlH_3 units via $\text{Al}\cdots\text{H}-\text{Al}$ bridging, and the third into a two-dimensional net-like array involving three distinct types of AlH_3 unit.

(iv) Adducts of type **V** (which are formed for L = tetrahydrofuran⁴³⁰ or the nitrogen bases NMe_3 ,⁴¹⁹ NMe_2H ,⁴²² $\text{NMe}_2\text{CH}_2\text{Ph}$,⁴¹⁹ or *N*-methyl-2,5,6-tetrahydropyridine⁴¹⁹) can be considered as Lewis base adducts of the elusive dialane, Al_2H_6 . In each case, the sum of the three H–Al–H angles is very close to 360° (e.g., 358° for the $\text{NMe}_2\text{CH}_2\text{Ph}$ adduct), implying trigonal bipyramidal coordination of the aluminum center. The two apical coordination sites are occupied by the donor ligand and by an H atom establishing a weak secondary $\text{Al}\cdots\text{H}$ interaction. The weakness of this mode of coordination is reflected not only by the long $\text{Al}\cdots\text{H}$ distances characterizing the H bridge, but also by the fact that the Al–H bonds forming the bridge are not significantly longer than the terminal Al–H ones. $\text{Al}\cdots\text{Al}$ distances are typically in the order of 2.8 Å, and ab initio calculations on the model compound $[\text{H}_3\text{Al}\cdot\text{NH}_3]_2$ indicate minimal $\text{Al}\cdots\text{Al}$ interaction and a bond order close to zero.⁴¹⁹ The $\text{Ga}\cdots\text{Ga}$ distance in $[\text{H}_3\text{Ga}\cdot\text{NMe}_2\text{H}]_2$ is even longer [3.7519(15) Å] and, with a separation of 2.87(5) Å, the secondary $\text{Ga}\cdots\text{H}$ interaction still more tenuous than the $\text{Al}\cdots\text{H}$ one in the alane complexes.⁴²²

With the exception of the carbene adducts of AlH_3 ,^{416,417} GaH_3 ,⁴¹⁷ and InH_3 ,^{141,417} the tetrahydrofuran complexes $[\text{H}_3\text{Al}\cdot\text{thf}]_2$ ⁴³⁰ and $\text{H}_3\text{Al}\cdot 2(\text{thf})$ ⁴³⁰ represent the only examples of structurally characterized alanes or gallanes not containing a group 15 donor. The weakness of the H_3Al –oxygen donor interaction renders even the 1:1 adduct unstable with respect to polymeric $[\text{AlH}_3]_n$ at temperatures above 60°C , a situation which is presumably responsible for the dearth of well-authenticated species of this type.⁴³⁰

(v) M–E bond lengths for five-coordinated $\text{H}_3\text{M}\cdot 2\text{L}$ complexes (type **II**) are generally longer than those found in $\text{H}_3\text{M}\cdot\text{L}$ complexes of type **I** or in adducts of type **V** which are weakly associated via hydride bridges. Such a trend reflects not only increased steric congestion, but also the reduced acidity of the metal center with the coordination of the first L molecule.⁴³¹ Hence, Al–N distances for the gaseous $\text{H}_3\text{Al}\cdot\text{NMe}_3$ molecule (type **I**) and for $[\text{H}_3\text{Al}\cdot\text{NMe}_2\text{CH}_2\text{Ph}]_2$ (type **V**) and $[\text{H}_3\text{Al}\cdot\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2]_\infty$ (type **VI**) in the solid state are 2.063(8),⁴³² 2.088(2),⁴¹⁹ and 2.209(4) Å,⁴²⁸ respectively. Similarly Ga–N distances for gaseous $\text{H}_3\text{Ga}\cdot\text{NMe}_3$ (type **I**) and solid $[\text{H}_3\text{Ga}\cdot\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2]_\infty$ (type **VI**) are 2.137(4)⁵⁹ and 2.362 Å,⁴³³ respectively.

(vi) Although adducts of AlH_3 with mono- or bidentate nitrogen donor ligands adopt four- or five-coordinated structures incorporating pyramidal or trigonal planar AlH_3 moieties, treatment of $\text{H}_3\text{Al}\cdot\text{NMe}_3$ with tridentate or macrocyclic tetradentate ligands leads to the formation of salts of the type $[\text{H}_2\text{AlL}]^+[\text{AlH}_4]^-$.⁴¹⁸ Two of these derivatives (L = pmdeta or Me_4Cyclam), having the structures reproduced in Figure 8, represent the first authenticated cationic aluminum hydrides.⁴¹⁸ The approximately octahedral coordination adopted by the metal center

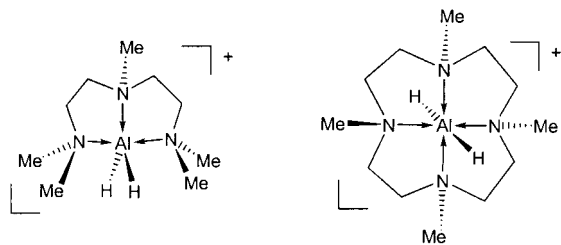


Figure 8. Structures of the cations in $[\text{H}_2\text{Al}(\text{pmdeta})]^+[\text{AlH}_4]^-$ and $[\text{H}_2\text{Al}(\text{Me}_4\text{Cyclam})]^+[\text{AlH}_4]^-$, respectively.⁴¹⁸

in the $[\text{H}_2\text{Al}(\text{Me}_4\text{Cyclam})]^+$ cation contrasts with the tetracoordinated geometry adopted in the 1:4 adduct of the same macrocycle with AlMe_3 .⁴³⁴ That no examples of six-coordinated gallium hydride derivatives have been reported is not altogether surprising.¹⁰

b. Alane and Gallane Derivatives Incorporating Elements from Groups 15–17. Whereas AlH_3 and GaH_3 form a series of tetra- and pentacoordinated adducts with tertiary amine and phosphine ligands, the reactions with primary or secondary amines, $\text{R}_n\text{NH}_{3-n}$ ($n = 1$ or 2), normally give rise to imido or amido derivatives, empirically formulated as $[\text{HMNR}]$ or $[\text{H}_n\text{M}(\text{NR}_2)_{3-n}]$ ($\text{M} = \text{Al}$ or Ga ; $n = 1$ or 2), respectively. Similarly, the reaction with a primary alcohol such as $\text{Bu}'\text{OH}$ leads to the formation of alkoxo species of the types $[\text{H}_2\text{MOR}]$ and $[\text{HM}(\text{OR})_2]$ ($\text{M} = \text{Al}$ or Ga). The reduction in coordination number at the metal center implied by these empirical formulas, and brought about in practice by the loss of dihydrogen across the $\text{M}-\text{E}$ bond, is rectified by the formation of oligomeric units. A survey of structurally characterized aluminum and gallium hydrides featuring monodentate amido, imido, and alkoxo ligands is set out in Table 7. Meriting further comment are four classes of compounds.

(i) *Imidoalanes.* The studies of Cesari and co-workers have provided much insight into the structural chemistry of these aggregates.^{442–450} Three structural motifs (represented as **VII–IX** in Figure 9) are common to many of the species which have been characterized, viz. the cubic tetramer (**VII**),^{442,446} the hexagonal prismatic hexamer (**VIII**),^{443–445,447–449} and the octamer (**IX**).⁴⁴⁴ The last framework can be viewed as being formally derived from the combination of two opened-out cubic tetramers or, conversely, from fusing the square ring of an $[\text{HAlNR}]_2$ dimer onto one of the square faces of the hexamer **VIII**.⁴⁴⁴

Structure **VII** is exemplified by the isopropylimido derivative $[\text{HAlNPr}^i]_4$,⁴⁴² the crystal structure of

which features two conformers (1:1) related by rotation of one of the peripheral Pr^i groups. Each conformer contains strictly planar $(\text{AlN})_2$ faces in which all $\text{Al}-\text{N}$ distances are equivalent within experimental error. The angles $\text{N}-\text{Al}-\text{N}$ [mean $89.9(1)^\circ$] and $\text{Al}-\text{N}-\text{Al}$ [$90.1(2)^\circ$] are also equal. Similar structures are observed for the methyl- and phenylaluminum derivatives $[\text{MeAlNPr}^i]_4$ ⁴⁴² and $[\text{PhAlNPh}]_4$,⁴⁵¹ although steric factors tend to give $\text{Al}-\text{N}$ distances slightly longer than those found in the hydrido analogue [$1.923(5)$ Å on average for the methyl compound vs $1.913(2)$ Å for the hydride⁴⁴²].

Bimetallic cubane species in which one of the four AlH vertexes has formally been substituted by a $(\text{thf})_n\text{M}$ moiety ($\text{M} = \text{Mg}$, $n = 1$; $\text{M} = \text{Ca}$, $n = 3$) have also been characterized.⁴⁴⁶ The resulting clusters $[\text{HAlNBu}^i]_3[(\text{thf})\text{MgNBu}^i]$ and $[\text{HAlNBu}^i]_3[(\text{thf})_3\text{CaNBu}^i]$ are distorted as a result of differing $\text{M}-\text{N}$ distances within the framework. The increased length of the $\text{Mg}-\text{N}$ and $\text{Ca}-\text{N}$ linkages [$2.090(4)$ Å on average for Mg , $2.490(2)$ Å for Ca] compared with the remaining $\text{Al}-\text{N}$ distances [$1.895(2)$ – $1.933(2)$ Å for the magnesium cluster] causes the group 2 metal center to be forced outward and the $\text{N}-\text{M}-\text{N}$ angles to be considerably smaller than those found in the parent $[\text{HAlNPr}^i]_4$ cluster $\{86.3(2)^\circ$ for Mg and $73.2(2)^\circ$ for Ca ⁴⁴⁶ vs $90.1(2)^\circ$ for $[\text{HAlNPr}^i]_4$ ⁴⁴²].

In addition to the cubane-like $[\text{HAlNPr}^i]_4$, the $[\text{AlNPr}^i]$ unit also aggregates into a hexamer of type **VIII**, reflecting the small energy difference between the different oligomers.⁴⁴³ Here too the low potential energy barrier relating to rotation about the $\text{N}-\text{C}$ bond is reflected in the existence of two distinct conformers within the crystal. The structure is based around two $(\text{AlN})_3$ six-membered rings linked by six 'transverse' $\text{Al}-\text{N}$ bonds. The $(\text{AlN})_3$ units are close to planar, although small distortions (ca. 0.04 Å) from this plane are in the direction of a chair-type conformation. $\text{Al}-\text{N}$ bond lengths within the $(\text{AlN})_3$ rings are significantly shorter [$1.898(2)$ Å on average] than those defining the transverse links between the rings [$1.956(2)$ Å]. This disparity in bond lengths has been attributed to the geometry enforced at the nitrogen center by the hexagonal prismatic cluster. Three bond angles at the nitrogen center [those involving the carbon of the isopropyl group and the two aluminum atoms in the $(\text{AlN})_3$ ring] are opened up with respect to the idealized tetrahedral angle. Consequently there is greater s character in these bonds (which are shorter) and greater p character in the remaining transverse $\text{Al}-\text{N}$ linkages (which are therefore longer).⁴⁴³

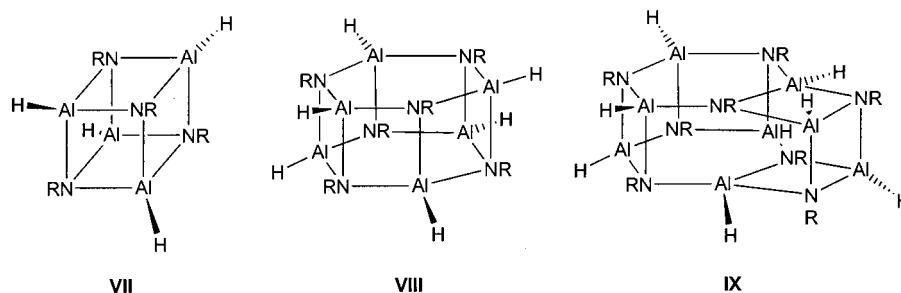


Figure 9. Commonly observed structural motifs for imido derivatives of aluminum hydrides.

Table 7. Structurally Characterized Aluminum and Gallium Hydrides Featuring Monodentate Amido, Imido, Alkoxo, or Halide Ligands

compound	mean $r(\text{M}-\text{E})/\text{\AA}$	mean $r(\text{M}-\text{H})/\text{\AA}$	structural type	ref
amidoalanes and -gallanes				
$[\text{H}_2\text{AlNMe}_2]_3^a$	1.936(3)	1.55	cyclic trimer	452–454
$[\text{HAl}(\text{NMe}_2)_2]_2$	1.966(2) bridge 1.804(2) term.	b	amido-bridged dimer	453
$[\text{H}_2\text{Al}(\text{tmp})_2]^c$	1.835(3)	1.68(2)	hydrido-bridged dimer	455
$[(\text{H}_2\text{Al})_2\{\mu\text{-N}(\text{Bu}^t)\text{CH}_2\}_2]$	1.943(7)	1.40(7)	contains cyclic butterfly Al_2N_2 core	467
$[\text{H}_2\text{Al}\{\mu\text{-N}(\text{CH}_2\text{CH}_2)_2\text{S}\}_2]$	1.962(6) [Al–N] 1.996(6)	1.37(2)	cyclic Al_2N_2 core	486
$[\text{H}_2\text{Al}\{2\text{-}(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_2]$	2.102(4) [Al–N]	1.688 1.928(3)	cyclic Al_2H_2 core, 5-coord. Al	487
$[\text{H}_2\text{Al}\{2,6\text{-}(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}]$	2.277(5) [Al–N] 2.223(5)	1.50(4)	monomeric, 5-coord. Al	488
$[\text{H}_2\text{AlNCMe}_2\text{C}_3\text{H}_6\text{CMe}_2]\cdot\text{NMe}_3$	1.838(2) ^d	1.59(3)	monomeric NMe_3 adduct	437
$[(\text{Me}_3\text{Si})_2\text{NAlH}_3\text{Li}\cdot 2\text{OEt}_2]$	1.858(3)	1.61(5)	cyclic dimer incorporating Li centers	456
$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AlH}_2\text{Li}\cdot 2\text{OEt}_2$	1.862(3)	1.59(2)	monomeric; bridging hydrides to Li center	456
$[\text{Li}\{\text{N}(\text{Bu}^t)\text{CH}(\text{Bu}^t)\text{CH}_2\text{N}(\text{Bu}^t)\}_4\text{AlH}_2]_4$	1.783(6) 1.884(6)	1.58(5)	$\text{Li}_4\text{Al}_2\text{H}_6$ 12-membered heterocycle	457
$[\text{HN}(\text{Bu}^t)\text{CH}(\text{Bu}^t)\text{CH}_2\text{N}(\text{Bu}^t)\text{AlH}_2]$	1.799(9) 2.02(1)	1.60(7)	intramolecularly coordinated secondary amine adduct of an amidoalane	457
$[\text{H}_2\text{GaN}(\text{H})_2]_3$	1.981(7)	1.56(3)	cyclic trimer	178
$[\text{H}_2\text{GaN}(\text{CH}_2\text{CH}_2)_3]_3$	1.97(2)	b	cyclic trimer	458
$[\text{H}_2\text{GaNMe}_2]_2(\text{g})^e$	2.027(4)	1.49(4)	cyclic dimer	64
$[\text{H}_2\text{GaNMe}_2]_3(\text{s})$	1.981(3)	1.51(2)	cyclic trimer	422
$[\text{H}_2\text{GaN}(\text{Et})_2]_2$	2.013	1.72	amido-bridged dimer	459
$[\text{H}_2\text{GaN}(\text{H})\text{NMe}_2]_2$	2.007(5)	1.51(3)	amido-bridged dimer	460
$(\text{HGa})_6(\text{H}_2\text{Ga})_2(\text{NCH}_2\text{CH}_2\text{NMe}_2)_4\text{-}(\text{NHCH}_2\text{CH}_2\text{NMe}_2)_2(\text{O})_2$	1.972	1.46	$\mu_3\text{-O}$, $\mu_3\text{-NR}$ bridged cage	461
$[\text{H}_2\text{Ga}\{2\text{-}(\text{Me}_2\text{N})\text{C}_6\text{H}_4\}]$	2.087(7) [Ga–N]		monomeric, 4-coord. Ga	487
$[\text{H}_2\text{Ga}\{2,6\text{-}(\text{Me}_2\text{N})_2\text{C}_6\text{H}_3\}]$	2.389(6) [Ga–N]		monomeric, 5-coord. Ga	489
$[\text{HGa}(\text{SCH}_2\text{CH}_2\text{NET}_2)_2]$	2.27(1) [Ga–N]	1.33	monomeric, 5-coord. Ga	486
$[(\text{HGa})_2\{(\text{NPr}^i\text{CH}_2)_2\}_2]$	2.005(4) 2.205(4) 1.853(4)	1.62	cyclic Ga_2N_2 core, 5-coord. Ga	490
$[\text{HGa}\{2\text{-}(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4\}_2]$	2.324(7) 2.457(8)	1.150	monomeric, 5-coord. Ga	487
imidoalanes				
$[\text{HAlNPr}^i]_4$	1.913(2)	1.50(5)	cubic tetramer	442
$[\text{HAlNPr}^i]_6$	1.898(2) ^f 1.956(3) ^g	1.49(1)	hexagonal prismatic hexamer	443
$[\text{HAlNPr}^i]_6$	1.850(4) ^f 1.959(8) ^g	1.53(5)	hexagonal prismatic hexamer	444
$[\text{HAlNCH}(\text{Me})\text{Ph}]_6$	1.893(6) ^f 1.981(7) ^g	b	hexagonal prismatic hexamer	445
$[\text{HAlNPr}^i]_8$	1.916(5)	1.50(2)	octamer	444
$[\text{HAlNBu}^i]_3[(\text{thf})_3\text{CaNBu}^i]$	1.901(7)	1.35(2)	pseudo-cubic unit	446
$[\text{HAlNBu}^i]_3[(\text{thf})\text{MgNBu}^i]$	1.906(3)	1.52(1)	pseudo-cubic unit	446
$[\text{HAlNPr}^i]_6\cdot\text{AlH}_3$	1.906(6) ^f 1.950(6) ^g	1.50(1) ^b	AlH_3 bound to square face of hexagonal prismatic hexamer	447
$[\text{H}(\text{HAlNPr}^i)_5\text{AlH}_2]\cdot\text{LiH}\cdot\text{OEt}_2$	1.919(8)	1.54	based on hexagonal prismatic hexamer	448
$[\text{HAlNCH}_2\text{CH}_2\text{CH}_2\text{NMe}_2]_6\cdot 2\text{LiH}$	1.901(13)	1.51(9)	based on hexagonal prismatic hexamer	449
$[\text{HAlNPr}^i]_2[\text{H}_2\text{AlNHP}^i]_3$	1.938(5)	1.48(10)	skew-boat $(\text{AlN})_3$ ring bridged by 2 AlN units	450
$[\text{HAlNPr}^i]_2[\text{H}_2\text{AlNHP}^i]_2\cdot[\text{HAlNCH}(\text{Me})\text{CH}_2\text{NMe}_2]$	1.916(11) ⁱ	1.44	skew-boat $(\text{AlN})_3$ ring bridged by 2 AlN units	449
phosphido- and arsenidoalanes and -gallanes				
$[\text{H}_2\text{AlPMe}_2]_2\cdot\text{NMe}_3$	2.409(3) ^j	1.56(7)	monomeric NMe_3 adduct	484
$[\text{H}_2\text{AlP}(\text{SiMe}_3)_2]_3$	2.398(2)		cyclic trimer	487
$[\text{H}_2\text{AlAs}(\text{SiMe}_3)_2]\cdot\text{NMe}_3$	2.438(2) ^j		monomeric NMe_3 adduct	487
$[\text{H}_2\text{GaPCy}_2]_3$	2.385(2)	1.51(7)	cyclic trimer	485
$[\text{H}_2\text{GaP}(\text{SiMe}_3)_2]_3$	2.392(2)	1.50	cyclic trimer	486
$[\text{H}_2\text{GaAs}(\text{SiMe}_3)_2]_3$	2.474(1)	1.50(3)	cyclic trimer	486
alkoxoalanes and -gallanes				
$[\text{H}_2\text{AlOCH}(\text{Bu}^t)_2]_4$	1.863(2) ^k 1.834(2) ^l		alkoxo-bridged tetramer	495
$[\text{H}_2\text{GaOCH}(\text{Bu}^t)_2]_2$	1.93(1)		alkoxo-bridged dimer	495
$[\text{H}_2\text{AlOBu}^i]_2$	1.813(2)	1.55(5)	alkoxo-bridged dimer	496
$[\text{H}_2\text{GaOBu}^i]_2$	1.905(9)	1.61(12)	alkoxo-bridged dimer	496

Table 7 (Continued)

compound	mean $r(M-E)/\text{\AA}$	mean $r(M-H)/\text{\AA}$	structural type	ref
alkoxoalanes and -gallanes				
[Al(OBu ^o) ₂] ₂	1.817(3) bridge 1.675(3) term.	1.51(5)	alkoxo-bridged dimer	496
[HGa(OBu ^o) ₂] ₂	1.906(4) bridge 1.783(4) term.	1.53(7)	alkoxo-bridged dimer	496
[H ₂ AlOR]·NMe ₃ ^m	1.762(4)	1.81	monomeric NMe ₃ adduct	497
[H ₂ AlOR·NMe ₃] ₂ ^m	1.774(3)	1.52 ⁿ 1.63 ^o 2.01 ^p	hydrido-bridged dimeric NMe ₃ adduct	497
[Al(OR) ₂]·OEt ₂ ^m	1.708(3)	1.47(3)	monomeric NMe ₃ adduct	497
[Al(OR) ₂]·NH ₂ Bu ^t ^m	1.723(5)	1.67(7)	monomeric NH ₂ Bu ^t adduct	497
[(Al) ₅ (Bu ^o O) ₈ O]	1.850(4)	1.44(5)	OBu ^o -bridged, O-centered square pyramid of AlH units	498
chlorogallanes				
[H ₂ GaCl] ₂ ^o	2.350(2) [Ga-Cl]	1.523(20)	Cl-bridged dimer	130
HCl ₂ Ga·quinuclidine	2.017(3) [Ga-N]	1.66(5)	monomeric, 4-coord. Ga	501
HCl ₂ Ga·2quinuclidine	2.254(8) [Ga-N] 2.232(8)		monomeric, 5-coord. Ga	501
H ₂ ClGa·2quinuclidine	2.259(2) [Ga-N]	1.51(2)	monomeric, 5-coord. Ga	501
[HGa(Cl)N ₃] ₄	1.918(17) [Ga-N] 2.063(16)		tetramer with cyclic Ga ₄ N ₄ core	502
<p>^a Values taken from ref 454. ^b Not given. ^c tmp = 2,2,6,6-tetramethylpiperidyl. ^d Amido Al-N linkage only. ^e Electron-diffraction study, r_{α} values. ^f Within (AlN)₃ ring. ^g Between (AlN)₃ rings. ^h Al-H bonds to tetracoordinated aluminum only. ⁱ Al-N bonds to tetracoordinated N only. ^j Al-P or Al-As linkage only. ^k Pentacoordinated aluminum. ^l Tetracoordinated aluminum. ^m R = 2,6-Bu^t-4-MeC₆H₂. ⁿ Terminal Al-H. ^o Al-μH. ^p Al···μH.</p>				

Similar structures are observed for [HAlNPrⁿ]₆⁴⁴⁴ and [HAlNCH(Me)Ph]₆⁴⁴⁵ with slight puckering of the (AlN)₃ rings toward chair conformations being observed in each case. The former molecule shows no significant differences in structural parameters from the Prⁱ derivative,⁴⁴⁴ whereas the latter shows greater variation in the transverse Al-N bond lengths.⁴⁴⁵

Several other imidoalanes feature structures based around a hexagonal prismatic cluster. These include [HAlNPrⁱ]₆·AlH₃,⁴⁴⁷ [H(HAlNPrⁿ)₅AlH₂]·LiH·OEt₂,⁴⁴⁸ and [HAlNCH₂CH₂CH₂NMe₂]₆·2LiH.⁴⁴⁹ The first compound is made up of a type **VIII** hexamer in which one of the six square (AlN)₂ faces is bound to an extra AlH₃ moiety.⁴⁴⁷ The extra Al center is bound to the two nitrogens of this face and thereby increases its coordination number to five (giving an approximately trigonal bipyramidal environment). In addition, two of the AlH₃ hydrides bridge the two facial aluminum centers. There is considerable variation in Al-H distances within the cluster. Terminal Al-H linkages carried by the tetracoordinated aluminum centers of the (AlN)₃ rings [1.50(1) Å, on average] are not significantly shorter than the unique Al-H bond [1.55(5) Å] carried by the pentacoordinated Al center. Bridging Al-H linkages are longer, with distances of 1.92(5) and 1.62(8) Å, indicating closer interaction of the bridging hydrogens with the facial Al centers than with the lone peripheral Al.⁴⁴⁷

The small differences in energy between oligomeric forms is further emphasized by the isolation of the octameric species [HAlNPrⁿ]₈ with the structure **IX**.⁴⁴⁴ The restraint of the extra (AlN)₂ four-membered ring forces the (AlN)₃ six-membered rings to adopt slightly boatlike conformations, in contrast to the slightly chairlike distortions found in the unconstrained [HAlNR]₆ hexamers. The overall octameric structure is also less regular than the hexameric one,

with no clear pattern of inter- and intraring Al-N distances.⁴⁴⁴

There is no discernible trend linking Al-N bond lengths with the nuclearity of the imidoalane cage. Thus, the average Al-N distances for [HAlNPrⁿ]₈ and [HAlNPrⁱ]₄ are equal within the bounds of experimental error [1.913(2)⁴⁴⁴ and 1.916(5) Å,⁴⁴² respectively]. It is also difficult to relate cluster nuclearity to the steric bulk of the imido substituent. With reference to Prⁿ and Prⁱ imidoalanes, it is true that the largest cluster (**IX**) is found only for the less sterically demanding Prⁿ group,⁴⁴⁴ whereas the cubane **VII** is found only in conjunction with the bulkier Prⁱ ligand.⁴⁴² However, the geometries of the hexameric clusters **VIII** found for both alkyl ligands display no significant differences in bond lengths or angles, thereby betraying little influence of substituent bulk on the structural parameters.^{443,444}

Finally, Cesari and co-workers made a general observation regarding imidoalane clusters that Al-N-Al angles tend to be wider than N-Al-N angles for six-membered (AlN)₃ rings, whereas the reverse is true for four-membered (AlN)₂ rings. In many cases, however, the differences between angles at N and those at Al are very small compared with the errors implicit in the crystallographic measurements. For [HAlNPrⁱ]₄, for example, these values are 89.9(1)° and 90.1(2)°, respectively.⁴⁴²

(ii) *Amidoalanes and Amidogallanes.* Numerous amidoalanes and -gallanes have been structurally characterized, and here too there is considerable structural diversity.^{64,178,452-461} In addition to species featuring bidentate amido ligands^{457,462-468} and base-stabilized adducts such as (Me₃Si)₂NAIH₃Li·2OEt₂,⁴⁵⁶ [(Me₃Si)₂N]₂AlH₂Li·2OEt₂,⁴⁵⁶ and [H₂AlNCMe₂CH₂-CH₂CH₂CMe₂]·NMe₃,⁴³⁷ aluminum and gallium hy-

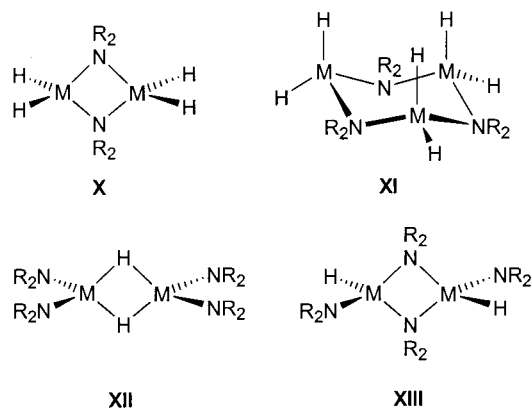


Figure 10. Motifs observed for structurally characterized amido derivatives of group 13 hydrides.

drides including monodentate amido substituents have been detailed, thereby revealing each of the structural motifs **X–XIII** set out in Figure 10.

Simple amidoalanes and -gallanes [H_2MNR_2] and [$HM(NR_2)_2$] have the possibility to augment the coordination of the metal center via either amido- or hydrido-bridged oligomerization; in practice, the former mode of coordination predominates. [H_2GaNEt_2] $_2$,⁴⁵⁹ [$H_2GaN(H)NMe_2$] $_2$,⁴⁶⁰ and [$Al(NMe_2)_2$] $_2$ ⁴⁵³ adopt amido-bridged dimeric structures of type **X** or **XIII**, respectively, whereas [H_2AlNMe_2] $_3$ and [$H_2GaNCH_2CH_2$] $_3$ exist as trimers (**XI**) in the solid state.^{452–454,458} H_2GaNMe_2 is a dimer in the vapor phase at low pressures⁶⁴ but a trimer in the solid state.⁴²² [$Al(tmp)_2$] $_2$ (tmp = 2,2,6,6-tetramethylpiperidyl) is the sole example of this type of compound featuring Al–H–Al bridges and terminal amido ligation (type **XII**).⁴⁵⁵

The trimeric species [H_2AlNMe_2] $_3$,^{452–454} [H_2GaNH_2] $_3$,¹⁷⁸ [H_2GaNMe_2] $_3$,⁴²² and [$H_2GaNCH_2CH_2$] $_3$ ⁴⁵⁸ have as their frameworks six-membered (MN) $_3$ rings with chairlike conformations. The fourth molecule is typical, displaying N–Ga–N–Ga torsion angles (59–61°) in the range characteristic of such a conformation and substantially smaller angles at the larger gallium center [99.9(11)° on average] than at nitrogen [121.5(11)°].⁴⁵⁸ Neutron powder diffraction measurements made on fully deuterated cyclotrigallazane, [D_2GaND_2] $_3$, at 25 °C have been analyzed with Rietveld refinement to give an average bond distance of 1.56(3) Å for Ga–D.¹⁷⁸ Particularly striking, however, are the intermolecular interactions which are dominated by four unconventional Ga–H···H–N hydrogen bonds per molecule which form a chain parallel to the crystallographic *a* axis (see Figure 11 and section III.A). The trimeric structure of [H_2AlNMe_2] $_3$ ^{452–454} and [H_2BNMe_2] $_3$ ⁴⁶⁹ contrasts with the dimeric forms found in crystalline [Me_2AlNMe_2] $_2$,⁴⁷⁰ [$(Me_3Si)_2AlNH_2$] $_2$,⁴⁷¹ [$Al(NMe_2)_2$] $_2$,⁴⁵³ and [$Al(NMe_2)_3$] $_2$.⁴⁵³ The chair conformation finds precedent, however, in the structure favored by *cis*-[$Me_2AlNHMe$] $_3$ ⁴⁷⁰ in the solid state while being at variance with the skew-boat arrangements adopted by *trans*-[$Me_2AlNHMe$] $_3$,⁴⁷⁰ [$H_2AlNCH_2CH_2$] $_3$,⁴⁷² and [Me_2MNH_2] $_3$ (M = Al or Ga)^{473,474} and with the planar ring found in [$Bu^t_2AlNH_2$] $_3$.⁴⁷³ This trend conceivably

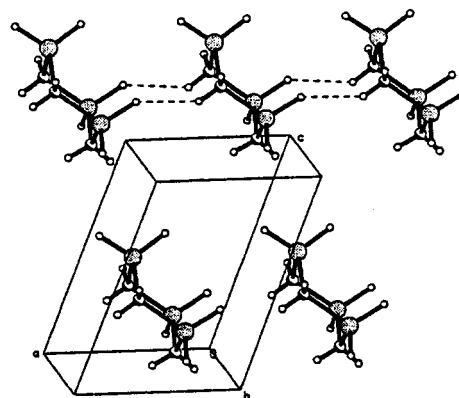


Figure 11. Packing arrangement in one plane of cyclotrigallazane, [H_2GaNH_2] $_3$. (Reprinted with permission from ref 178. Copyright 1998 American Chemical Society.)

reflects the increasing steric demands of the amido substituents. The Al–N distances in [H_2AlNMe_2] $_3$ [1.936(3) Å on average] are similar to those found in other (AlN) $_3$ rings^{470,472,473} and slightly shorter than those found in systems containing cyclic (AlN) $_2$ units {e.g., [$Al(NMe_2)_2$] $_2$, 1.966(2) Å for the bridging Al–N linkages⁴⁵³}.

If one considers a series of amine, amido, and imido derivatives of alane (all containing tetracoordinated aluminum) and even the binary nitride AlN itself, a steady shortening of the Al–N bond length is revealed as the number of substituents attached to the aluminum and nitrogen centers decreases. Thus, the amine adduct H_3Al -quinuclidine has an Al–N distance of 1.991(4) Å,⁴²³ as compared with distances of 1.936(3) and 1.966(2) Å for the amidoalanes [H_2AlNMe_2] $_3$ ^{452–454} and [$Al(NMe_2)_2$] $_2$,⁴⁵³ respectively. The imidoalanes [$AlNR$] $_n$ (R = Prⁱ, *n* = 4 or 6; R = Prⁿ, *n* = 6 or 8) feature average Al–N bond lengths between 1.905(8) and 1.927(3) Å,^{442–444} a figure which falls to 1.893 Å for AlN itself.⁴⁷⁵ Presumably this reflects, at least in part, reduced interligand repulsions as the number of substituent groups decreases, although the bonding of such terminal units cannot be wholly separable from the bonding of the framework, and it has been argued that rehybridization and π -interactions also have a part to play.^{476,477}

[$Al(tmp)_2$] $_2$ represents a rare example of a dimeric alane featuring tetracoordinated aluminum centers bridged by hydrido ligands.⁴⁵⁵ The preference for terminal amido ligation in the solid state almost certainly reflects the high steric demands of the tmp ligand, which also give rise to wide N–Al–N angles [126.9(1)°] and a relatively long Al···Al distance [2.680(2) Å, cf. 2.52 Å for the sum of the covalent radii³⁹¹]. The corresponding parameters determined for the gaseous $Me_2Al(\mu-H)_2AlMe_2$ molecule by electron diffraction are 117.7(4)° (for the C–Al–C angle) and 2.625(6) Å (for the Al···Al distance).⁶² The steric bulk of the tmp ligand is responsible too for Al–N bond lengths [1.835(3) Å on average] which are long compared, for example, with those found in Al–[N(SiMe $_3$) $_2$] $_3$ [1.78(2) Å].⁴⁷⁸ Al–H lengths for the bridging Al($\mu-H$) $_2$ Al unit [1.68(2) Å on average⁴⁵⁵] are similar to those found in the corresponding unit in [Me_2AlH] $_2$ [1.776(7) Å⁶²] and in the cyclic trimer [Bu^t_2AlH] $_3$ [1.726(5) Å²³²]. Indeed, the figure is not sig-

nificantly different from the average Al–H bond length found for the eight other crystallographically characterized species containing an Al(μ -H)₂Al moiety (1.76 Å).^{143,146,429,479–482} As such, the Al–H bonds are patently longer than typical terminal Al–H bonds (1.55 Å)^{380,454} but shorter than the Al $\cdots\mu$ -H contacts found in weakly bound dimers such as [H₃Al·NMe₂-CH₂Ph]₂ [2.07(2) Å⁴¹⁹].

(iii) *Phosphido and Arsenido Derivatives.* Structurally characterized phosphido and arsenido derivatives of aluminum and gallium hydrides number but six.^{484–487} The molecule [H₂GaPCy₂]₃ synthesized by Raston et al. adopts a trimeric structure in the solid phase based around a six-membered (GaP)₃ ring of skew-boat conformation.⁴⁸⁵ The overall molecular geometry and, in particular, the Ga–P distances [2.395(2) and 2.383(2) Å] are similar to those measured for the related compound [Me₂GaPPrⁱ]₃.⁴⁸⁸ Furthermore, the very recently synthesized trimers [H₂GaE(SiMe₃)₂]₃ (E = P or As)⁴⁸⁶ also adopt cyclic (GaE)₃ structures in the solid phase. In the phosphido complex crystallographic constraints impose strict planar symmetry on the six-membered ring, although the thermal parameters of the gallium atoms are unusually large, possibly reflecting a lowering of molecular symmetry due to ring puckering. Similarly, the arsenido derivative is described as having a ‘flattened skew-boat’ geometry, in which the maximum deviation from the best-fit plane is 0.25 Å and the largest Ga–As–Ga–As torsion angle is ca. 17°. In both molecules angles at the gallium centers are significantly smaller than at the group 15 atoms [e.g., average As–Ga–As and Ga–As–Ga angles of 111.0(3)° and 127.1(3)°, respectively, for the arsenido compound], reflecting greater accommodation of ring strain at arsenic or phosphorus.

Increasing substituent bulk in cyclic (AlN)₃ systems results in the adoption of skew-boat^{470,472–474} or even planar ring geometries⁴⁷³ rather than the chair-type conformations found with less sterically demanding ligands.^{452–454,459,470} The skew-boat structures adopted by [H₂GaPCy₂]₃⁴⁸⁵ and [H₂GaAs(SiMe₃)₂]₃⁴⁸⁶ and the near-planar geometry of [H₂GaP(SiMe₃)₂]₃⁴⁸⁶ are consistent with this trend and with the large steric demands imposed by the cyclohexyl or trimethylsilyl substituents.

[H₂GaPCy₂]₃,⁴⁸⁵ [H₂GaP(SiMe₃)₂]₃,⁴⁸⁶ and the monomeric phosphidoalane [H₂AlPMes₂]₃·NMe₃⁴⁸⁴ all display significantly shorter M–P distances than those observed for analogous phosphine complexes {e.g., 2.389(2) Å on average for [H₂GaPCy₂]₃;⁴⁸⁵ 2.460(2) Å for H₃Ga·PCy₃⁴⁴¹}, in line with the trend observed for amine, amido, and imido derivatives of alane.

Very recently Wells and co-workers reported the synthesis of the trimer [H₂AlP(SiMe₃)₂]₃ and the base-stabilized adduct [H₂AlAs(SiMe₃)₂]₃·NMe₃ and investigated their thermal decomposition to nanocrystalline AIP and AlAs, respectively.⁴⁸⁷ The structure of the first molecule is similar in many ways to those reported for the analogous gallium compounds [H₂-GaE(SiMe₃)₂]₃ (E = P or As)⁴⁸⁶ in that each is based around a planar six-membered (ME)₃ ring featuring larger thermal parameters at the group 13 atom than at the group 15 atom. In all three molecules the

E–M–E angle is significantly narrower than the M–E–M angle. [H₂AlAs(SiMe₃)₂]₃·NMe₃, on the other hand, is the first structurally characterized alane arsenide containing the AlH₂ moiety. The extremely short Al–As distance [2.438(2) Å] is attributed, at least in part, to the fact that the molecule contains four-coordinated aluminum bonded to tricoordinated arsenic.

(iv) *Alkoxo Derivatives.* Alkoxoaluminum and -gallium hydrides of the types [H₂MOR] and [HM(OR)₂] have been synthesized by the reaction of alane and gallane adducts such as LiAlH₄ or H₃M·OEt₂ with ROH in the correct stoichiometric ratio.^{489–492} All of the structurally characterized derivatives contain sterically bulky R groups such as Bu^t,⁴⁸⁹ Bu^t,⁴⁹⁰ Bu^tCH₂,⁴⁹¹ and 2,6-Bu^t-4-Me-C₆H₂,⁴⁹² and each fits into one of three distinct structural types.

The base-stabilized adducts [H₂AlOR]·NMe₃, [HAL(OR)₂]₂·OEt₂, and [HAL(OR)₂]₂·NH₂Bu^t (R = 2,6-Bu^t-4-Me-C₆H₂) adopt monomeric structures in the solid state, although the first molecule also exists as a hydrido-bridged dimer, [(H₂AlOR)·NMe₃]₂.⁴⁹² This structure is similar to the one observed for [H₃Al·thf]₂,⁴²⁹ featuring two distinct Al–(μ -H) bond lengths (1.63 and 2.01 Å) reflecting the weakly bound nature of the dimer. As expected, the average Al–N bond lengths are greater for the dimer than for the monomer [2.115(4) vs 2.079(4) Å], in keeping with the increased coordination number at the metal center, although there is little significant change in the Al–O distances [1.774(3) and 1.762(4) Å, respectively].⁴⁹² Finally, the terminal Al–H distances for the monomeric species [H₂AlOR]·NMe₃, [HAL(OR)₂]₂·OEt₂, and [HAL(OR)₂]₂·NH₂Bu^t vary widely (1.47–1.88 Å), reflecting the inherent difficulty in determining hydrogen atom positions by X-ray diffraction methods.⁴⁹²

In the absence of a coordinating amine or ether base, alkoxoalanes and -gallanes adopt alkoxo-bridged oligomeric structures. H₂MOBu^t,⁴⁹⁰ HM(OBu^t)₂ (M = Al or Ga),⁴⁹⁰ and H₂GaOCH₂Bu^t⁴⁹¹ all take up dimeric structures based around a four-membered M₂O₂ ring, whereas H₂AlOCH₂Bu^t has a unique tetrameric structure.⁴⁹¹ That the Bu^tCH₂O–aluminum and –gallium species assume structures of differing nuclearity testifies to the greater tendency of aluminum to increase its coordination number beyond four.¹⁰ Increased coordination at the aluminum centers manifests itself too in the average Al–O distance which is longer for [H₂AlOCH₂Bu^t]₄ than for the dimer [H₂AlOBu^t]₂ [1.849(2)⁴⁹¹ vs 1.813(2) Å⁴⁹⁰] containing only tetracoordinated aluminum.

The gallium complexes H₂GaOBu^t and HGa(OBu^t)₂ display little change in the geometry of the central Ga₂O₂ ring upon substitution of two of the four terminal hydrogens by OBu^t groups.⁴⁹⁰ The terminal alkoxo substituents adopt a trans orientation, with significantly shorter Ga–O distances [by ca. 0.122(4) Å] than those found for the bridging OBu^t groups. The corresponding aluminum complexes [H₂AlOBu^t]₂, [HAL(OBu^t)₂]₂, and [Al(OBu^t)₃]₂ have central Al₂O₂ rings that become progressively more open with increasing alkoxo substitution (average Al–O dis-

tances being 1.812, 1.817, and 1.824 Å, respectively).⁴⁹⁰

The cluster $[(\text{HAl})_5(\text{OBU}^i)_8\text{O}]$ is distinguished by an unusual structure in the solid state, with an oxo-centered square pyramidal arrangement of five AlH moieties being bridged on all eight edges by OBUⁱ ligands.⁴⁸⁹ Each of the basal aluminum centers is pentacoordinated, while the apical aluminum has a coordination number of six and correspondingly longer bonds to bridging alkoxo ligands [1.954(3) vs 1.812(4) Å]. The Al–H distances [1.42(5) Å on average] do not vary significantly between the different aluminum centers.

Finally, a point of further interest concerns the *endo/exo* cavity hydride isomerization observed by Raston et al. for an alane complex of dimetalated 1,3-dimethyl ether *p-tert*-butylcalix[4]arene.⁴¹² An Al–H moiety is complexed to the calixarene unit via two alkoxo linkages and two ether donor/acceptor bonds. The thermodynamically more stable *endo* form (Al–H bond located within the calixarene cavity) is formed from the *exo* isomer on treatment with $\text{H}_3\text{Al}\cdot\text{NMe}_3$.

(v) *Chlorogallanes*. Halide derivatives of alane and gallane are not generally well characterized mainly because of their tendency to take on intractable polymeric forms in the condensed phase. The compounds H_2GaCl ,^{13,130} HGaCl_2 ,¹³ and HGaBr_2 ¹³ have been described, and their vibrational spectra suggest the existence of more or less well-defined dimeric units linked together by halide bridges. Certainly the dimeric molecule $\text{H}_2\text{Ga}(\mu\text{-Cl})_2\text{GaH}_2$ has been shown to be the predominant component in the vapor of monochlorogallane at low pressures with bridging Ga–Cl bonds measuring 2.350(2) Å.¹³⁰ This compound has played a central role as a precursor to other compounds containing the GaH_2 unit, including the binary hydride,⁶⁰ $[\text{H}_2\text{GaBH}_4]_n$,³⁷⁴ and $[\text{H}_2\text{GaN}_3]_n$.⁴⁹³ Coordination by a suitable donor results not only in stabilization of the $\text{GaH}_n\text{Cl}_{3-n}$ moiety ($n = 1$ or 2), but also in the formation of more tractable products, typically with discrete mononuclear structures. Thus, quinuclidine forms the monomeric complexes $\text{HCl}_2\text{-Ga}\cdot\text{quinuclidine}$, $\text{HCl}_2\text{Ga}\cdot 2\text{quinuclidine}$, and $\text{H}_2\text{ClGa}\cdot 2\text{quinuclidine}$;⁴⁹⁴ the last two, with pentacoordinated gallium centers, testify to the enhanced acidity of GaHCl_2 and GaH_2Cl over GaH_3 . The mixed chloride azide $\text{HGa}(\text{Cl})\text{N}_3$, prepared by the metathesis of dichlorogallane and LiN_3 , is noteworthy for being a tetramer with azide rather than chloride bridges and a cyclooctane-like Ga_4N_4 skeleton.⁴⁹³

c. Organoalanes and -gallanes. Organoaluminum and -gallium hydrides can be divided into three broad types reflecting not only the structural entities present but also the sorts of synthetic method employed. These encompass species featuring (i) hydride bridges to the same or another metal or to boron, (ii) extremely bulky alkyl or aryl substituents designed to reduce the extent of molecular aggregation, and (iii) intramolecular coordination of a nitrogen base as a means of stabilization. In addition, several organoindium hydrides have been characterized; these are dealt with in section e.

(i) *Species with Hydride Bridges.* Organoaluminum and -gallium hydrides are compounds which become

increasingly labile in the order $\text{R}_2\text{MH} < \text{RMH}_2 < \text{MH}_3$ and which normally exist as hydride-bridged oligomers on the evidence of their physical and spectroscopic properties.¹⁵ For example, the compounds Me_2AlH and Me_2GaH exist as the diborane-like molecules $\text{Me}_2\text{M}(\mu\text{-H})_2\text{MMe}_2$ ($\text{M} = \text{Al}^{62}$ or Ga^{63}) in the vapor phase at low pressures. As the molecular concentration increases, further aggregation is likely to occur. In the case of dimethylalane, the trimer $[\text{Me}_2\text{AlH}]_3$ has been detected in the vapor and partially characterized by its electron-diffraction pattern; it appears to have a planar, cyclic Al_3H_3 core with Al–H and $\text{Al}\cdots\text{Al}$ distances of 1.71(2) and 3.153(8) Å, respectively (cf. 1.776(7) and 2.625(6) Å for the corresponding dimensions in the dimer).⁶² Solution studies suggest, however, that the trimer is not the limit of aggregation.^{62,200} The compounds are found usually to form viscous liquids, and their reluctance to crystallize has thwarted attempts to investigate the structures they assume in the solid state. However, the propensity for aggregation can be restricted by varying the bulk of the organic substituent, a theme to be developed in section ii. Hydride bridges are also met in complexes such as $\text{Na}[\text{Me}_3\text{Al}(\mu\text{-H})\text{-AlMe}_3]$.²⁴²

Some compounds containing organoaluminum fragments linked by one or more hydride bridges to another main-group element have proved more amenable to crystallographic analysis. Thus, several examples of such linkages to boron are known; these will be reviewed in section d. The sole representative featuring a bridging hydride linkage to magnesium, viz. the complex $(\text{thf})_n\text{Mg}(\mu\text{-H})(\mu\text{-C}_{14}\text{H}_{10})\text{AlEt}_2$ (**13**),²⁴⁶ has been mentioned already. In addition, there are now known numerous compounds in which an organoaluminum fragment is bound through one or more hydride bridges to a transition-metal center.^{495,496} These involve most commonly the group 4 metals $\text{Ti}^{497-501}$ and $\text{Zr}^{502-504}$ with particularly significant research contributions having come from the groups of Erker^{502,503} and Bulychev.^{496,499-501} The titanium compounds are typically oligomeric with metallocene fragments linked by $\text{Ti}(\mu\text{-H})\text{Al}(\mu\text{-H})\text{Ti}$ bridges. Among later transition metals similar structural motifs have been demonstrated crystallographically for W^{247} , Re^{505} and Ni^{506} .

(ii) *Species with Bulky Organic Substituents.* Hydride bridges tend to be a recurring motif with organoaluminum and -gallium hydrides, and it has been partly with the aim of restricting aggregation through these bridges that extremely bulky substituents such as Mes^* ($2,4,6\text{-Bu}'_3\text{C}_6\text{H}_2$) have been employed chiefly by the groups of Power and Cowley.^{142-146,479,507} With the dialkylalanes, R_2AlH , for example, increasing steric bulk of the R group from methyl⁶² to *tert*-butyl²³² is not sufficient to prevent oligomerization, and $[\text{Bu}'_2\text{AlH}]_3$ is a cyclic trimer featuring a planar six-membered $(\text{AlH})_3$ heterocycle. Perversely, for the anionic species $[\text{R}_3\text{AlH}]^-$, the methyl derivative $\text{K}[\text{Me}_3\text{AlH}]$ is monomeric in the solid state²³⁵ whereas the *tert*-butyl analogue $\text{Li}[\text{Bu}'_3\text{-AlH}]$ is a dimer centered around a cyclic $(\text{LiH})_2$ bridging unit.²³² The nature of the cation presumably plays a significant role in such aggregation processes.

Accordingly, complexation of the lithium center by a bidentate nitrogen base such as tetramethylethylenediamine (tmeda) and/or use of the sterically more demanding (trimethylsilyl)methyl ligands $(\text{Me}_3\text{Si})_2\text{CH}$ or Me_3SiCH_2 yields monomeric species such as $\text{Li}(\text{tmeda})\{[(\text{Me}_3\text{Si})_2\text{CH}]_2\text{Bu}^t\text{AlH}\}^{233,234}$ and $\text{K}[(\text{Me}_3\text{SiCH}_2)_3\text{GaH}]$.²⁴³ Worthy of note also is the complex $\text{Li}(\text{tmeda})[\text{R}_2\text{AlAlR}_2\text{H}]$ [$\text{R} = (\text{Me}_3\text{Si})_2\text{CH}$], the anion of which features two distinct aluminum centers (one tricoordinated, the other tetracoordinated) linked by an unbridged Al–Al bond.⁵⁰⁸

As the number of alkyl substituents attached to the metal center decreases, so the chances of isolating monomeric complexes are reduced. Hence, even with the extremely bulky tris(phenyldimethylsilyl)methyl $[(\text{Me}_2\text{PhSi})_3\text{C}]$ or tris(trimethylsilyl)methyl $[(\text{Me}_3\text{Si})_3\text{C}]$ ligands (R), the complexes $\text{Li}(\text{thf})_2[\text{RAlH}_3]$ are dimeric featuring four bridging Al–H–Li linkages.⁵⁰⁹ Interestingly, though, reaction of $\text{Li}(\text{thf})_2[(\text{Me}_3\text{Si})_3\text{CAlH}_3]$ with tmeda gives the compound $\text{Li}(\text{tmeda})\text{-}[\text{RAlH}_3]$ composed of solvent-separated $[\text{Li}(\text{tmeda})]^+[\text{H}_3\text{AlR}]^-$ ion pairs.⁵¹⁰

Attempts made over the last five years to synthesize monomeric organoaluminum and -gallium hydrides of the types R_2MH and RMH_2 have focused upon the use of phenyl substituents, R, in which significant steric shielding of the metal center is effected by the introduction of bulky groups at the 2,6 and sometimes 4 positions of the phenyl ring.^{142–146,479,507} Use of the supermesityl (Mes^*) ligand, for example, has enabled Cowley and co-workers to isolate the base-free organogallium hydride Mes^*GaH_2 by reaction of the corresponding dichloride with LiGaH_4 .¹⁴⁴ The monomeric nature of the compound in the solid state was confirmed by X-ray diffraction, although location of the hydrogen atoms proved impossible. The analogous reaction with $\text{Mes}^*_2\text{GaCl}$ yielded not the expected product Mes^*_2GaH but its isomer $\text{Mes}^*(3,5\text{-Bu}^t\text{C}_6\text{H}_3\text{CMe}_2\text{CH}_2)\text{GaH}$.¹⁴⁴ The trigonal planar coordination of the gallium center is reported to be augmented by two agostic interactions involving C–H bonds of the *ortho* Bu^t groups of the Mes^* ligand. Location of the hydrogen atom enabled a Ga–H bond length of 1.43(10) Å to be established. Power and co-workers managed to synthesize Mes^*_2GaH by an alternative route, namely, the reaction of $\text{Mes}^*_2\text{GaCl}$ with Bu^tLi in hexane at 0 °C.¹⁴⁶ The crystal structure of this compound shows it to consist of discrete molecules featuring trigonal planar gallium and a Ga–H bond length of 1.572(48) Å.

The corresponding aluminum compounds $\text{Mes}^*_2\text{-AlH}$ and Mes^*AlH_2 have also been synthesized.^{143,145} The former compound, which is formed by the transmetalation reaction of either $\text{Mes}^*_2\text{GaCl}$ or $\text{Mes}^*_2\text{-InCl}$ with LiAlH_4 , is monomeric and, in common with the gallium analogue, incorporates a trigonal planar metal center.¹⁴⁵ This compound represents the only example of a structurally authenticated base-free aluminum hydride monomer, a feature the authors ascribe to partial shielding of the terminal Al–H bond by the *ortho* Bu^t groups of the Mes^* ligand. On the other hand, the dihydride Mes^*AlH_2 is dimeric in both the solid and solution phases.¹⁴³ This con-

trasts with the monomeric structure found for Mes^*GaH_2 and is in line with the greater tendency toward aggregation distinguishing aluminum compounds at large.¹⁰ The structure of the $\text{Mes}^*\text{Al}(\text{H})(\mu\text{-H})_2\text{Al}(\text{H})\text{Mes}^*$ molecule in the solid state includes trans Mes^* ligands and symmetric $\text{Al}(\mu\text{-H})\text{Al}$ bridges; Al–H_b distances are equivalent within experimental error averaging 1.695(36) Å. The terminal Al–H linkages [1.498(37) Å] are not significantly different in length from those found in Mes^*_2AlH [1.53(4) Å], despite the differing coordination numbers of the aluminum centers. The geometry of the $\text{Al}(\mu\text{-H})_2\text{Al}$ bridging unit is similar to that found in $[(\text{tmp})_2\text{AlH}]_2$ ($\text{tmp} = 2,2,6,6\text{-tetramethylpiperidyl}$; a type **XII** dimer, see Figure 10) in which the high steric demands of the piperidyl substituents force the amide to adopt a terminal rather than the more common bridging mode of coordination.⁴⁵⁵ The Al–H_b {1.695(36) Å for $[\text{Mes}^*\text{AlH}_2]_2$; 1.68(2) Å for $[(\text{tmp})_2\text{AlH}]_2$ } and Al···Al distances {2.652(2) Å for $[\text{Mes}^*\text{AlH}_2]_2$; 2.680(2) Å for $[(\text{tmp})_2\text{AlH}]_2$ } for the two compounds are in close agreement. Formal replacement of one of the hydride ligands in Mes^*AlH_2 by chloride reduces the tendency of the molecule to oligomerize.⁵⁰⁷ Hence, $\text{Mes}^*\text{Al}(\text{Cl})\text{H}$ and $\text{Mes}^*\text{Al}(\text{Cl})\text{H}(\text{thf})$ are monomeric in the solid state, although interpretation of the crystal structure of the former compound is complicated by its contamination with $\text{Mes}^*\text{AlCl}_2$.⁵⁰⁷ Of note too is the aluminate complex $\text{Li}(\text{thf})_2[\text{H}_3\text{AlMes}^*]$,¹⁴⁶ which has a dimeric structure involving two terminal and four Al–H–Li bridging hydrides analogous to that found for the corresponding complex with $\text{R} = (\text{Me}_2\text{-PhSi})_3\text{C}$.⁵⁰⁹

Power et al. also investigated the use of the slightly less sterically crowded Trip ligand ($\text{Trip} = 2,4,6\text{-Pr}^i\text{C}_6\text{H}_2$) in organoaluminum and -gallium hydride chemistry.¹⁴⁶ The reduction in steric bulk compared to the supermesityl ligand is sufficient to induce dimerization for R_2MH ($\text{R} = \text{Trip}$; $\text{M} = \text{Al}$ or Ga), in contrast to the monomeric structures found for the analogous compounds with $\text{R} = \text{Mes}^*$. The $[\text{Trip}_2\text{-MH}]_2$ dimers ($\text{M} = \text{Al}$ or Ga) are made up of similar $\text{M}(\mu\text{-H})_2\text{M}$ bridging units with $\text{M}\cdots\text{M}$ contacts of 2.698(2) and 2.638(2) Å, respectively; Ga–H_b bond lengths range from 1.650(70) to 1.792(70) Å, although crystallographic disorder renders analogous parameters for the aluminum compound of little significance.⁵⁰⁷

A further development in the design of sterically encumbered ligands has seen the use of so-called terphenyl ligands in the synthesis of aluminum hydrides.^{146,479} Power and co-workers synthesized the alanes $\text{RH}_2\text{Al}\cdot\text{L}$ [$\text{R} = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$, $\text{L} = \text{Et}_2\text{O}$; $\text{R} = 2,6\text{-Trip}_2\text{C}_6\text{H}_3$, $\text{L} = \text{Et}_2\text{O}$; $\text{R} = 2,6\text{-(4-Bu}^t\text{C}_6\text{H}_4)_2\text{C}_6\text{H}_3$, $\text{L} = \text{Me}_3\text{N}$] and $[\text{RAlH}_2]_2$ ($\text{R} = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$ or $2,6\text{-Trip}_2\text{C}_6\text{H}_3$), as well as the aluminate $\text{Li}_2(\text{Et}_2\text{O})_3\{2,4,6\text{-Ph}_3\text{C}_6\text{H}_2\}\text{AlH}_3\}_2$, each of which features a phenyl ligand bearing two further aryl substituents at the *ortho* positions. Significantly, monomeric species are observed only in the solid state for the base-stabilized adducts $\text{RH}_2\text{Al}\cdot\text{L}$, with dimeric structures analogous to that of Mes^*AlH_2 being adopted by the base-free alanes. In fact, the authors conclude that a single terphenyl ligand is not as effective as Mes^* in

preventing further coordination at aluminum. This reflects not only the lack of significant interaction between *ortho* aryl groups and the metal center, but also the ability of these inherently planar groups to rotate into an orientation which provides minimal steric and electronic masking of the metal center.⁴⁷⁹

(iii) *Species with Intramolecular Base Stabilization.* Several mononuclear alane and gallane complexes have been isolated by making use of the steric and electronic saturation brought about by coordination of an external base to the metal center. An extension of this approach has seen the synthesis of organoaluminum and -gallium hydrides in which the stabilizing base is tethered to the organic ligand.^{150,151,481,511–514}

Cowley and co-workers made use of the 'pincer' ligand 2,6-(Me₂NCH₂)₂C₆H₃ in order to fortify monomeric dihydrides of the type 2,6-(Me₂NCH₂)₂C₆H₃-MH₂ (M = Al or Ga).^{150,151} In each case the crystal structure reveals a distorted trigonal bipyramidal geometry at the metal center in which the two axial sites are occupied by the nitrogen atoms and the three equatorial sites by the two hydrides and the aryl carbon. The thermal stability of the gallium compound (surviving at 350 °C in the vapor phase) is in marked contrast to that of H₃Ga·2NMe₃ which decomposes to the more stable four-coordinated adduct H₃Ga·NMe₃ at temperatures in excess of -23 °C.⁴²¹ As might be expected, the Ga-N distances found for 2,6-(Me₂NCH₂)₂C₆H₃GaH₂ [2.380(6) and 2.398(6) Å] are significantly longer than those found in four-coordinated nitrogen donor adducts of GaH₃ [which fall within the range 2.063(4)–2.085(3) Å^{59,422,426,433,438,440}] but are very similar to those found in the sole five-coordinated adduct to be structurally authenticated, viz. [H₃Ga·Me₂NCH₂CH₂CH₂NMe₂]_∞ (2.362 Å).⁴³³ The propensity of gallium hydrides to adopt four-coordinated geometries is reflected in the reaction of 2,6-(Me₂NCH₂)₂C₆H₃GaH₂ with three equivalents of triflic acid, CF₃SO₃H (TfOH). This yields the salt [2,6-(HMe₂NCH₂)₂C₆H₃GaH(OTf)₂]⁺OTf⁻ in which the nitrogen centers are protonated and the gallium atom is linked to the aryl carbon, a single hydride, and the oxygens of two triflate ligands.¹⁵¹

Use of aryl ligands bearing only a single 'pincer' arm results in a diminished ability to satisfy the steric and electronic requirements of the metal center.^{481,512–514} Consequently, whereas the gallanes 2-(Me₂NCH₂)C₆H₄GaH₂ and [2-(Me₂NCH₂)C₆H₄]₂GaH are monomeric in the solid phase incorporating four- and five-coordinated gallium centers, respectively,⁴⁸¹ the alanes 2-(Me₂NCH₂)C₆H₄AlH₂, Me₂N(CH₂)₃AlH₂ and [8-(dimethylamino)-1-naphthyl]AlH₂ are dimeric.^{481,512,513} Each of the alanes features two bridging and two terminal hydrides and has a structure reminiscent of the dimeric type V AlH₃ adducts [H₃-Al-L]₂ (L = NMe₃,⁴¹⁹ NMe₂CH₂Ph,⁴¹⁹ MeNCH₂CHCH-CH₂CH₂,⁴¹⁹ or NMe₂CH₂CH₂CH₂Cl,⁴³⁸ see Figure 7). As such, the bridging hydrides are asymmetrically linked to the two adjacent aluminum centers, giving Al-H_b distances of 1.688 and 1.928(3) Å for [2-(Me₂NCH₂)C₆H₄AlH₂]₂, 1.60(1) and 1.95(2) Å for [Me₂N(CH₂)₃AlH₂]₂, and 1.61(2) and 1.91(2) Å for [8-

(dimethylamino)-1-naphthyl]AlH₂]₂. The coordination spheres of the aluminum centers can be described in terms of a distorted trigonal bipyramid with the carbon of the organo ligand, the terminal hydride, and the more closely bound bridging hydride occupying the three equatorial sites and the nitrogen atom of the pincer arm and the more distant bridging hydrogen occupying the axial vertexes. The sum of the angles between the ligands occupying the equatorial sites is in each case equal to 360° within the bounds of experimental error.^{481,512,513} By contrast, the (*N,N*-dialkylaminoethyl)cyclopentadienyl group sustains monomeric alane and gallane derivatives of the type [(R₂NCH₂CH₂)C₅H₄]MH₂ (R = Me, M = Al or Ga; R = Prⁱ, M = Al).⁵¹⁴ The coordinative and electronic saturation of the metal center in these compounds leads to a drastic reduction in the susceptibility to attack by air and moisture as compared with analogous cyclopentadienyl derivatives that lack base stabilization. The compounds are also volatile enough to suggest that they may be useful precursors for the deposition of metal films by MOCVD methods.

Within this category one further compound deserving of note is the intramolecularly base-stabilized diorganogallane HGa(CH₂CH₂CH₂)₂NMe in which the coordination sphere of the gallium center is made up of a single hydride ligand, the carbon atoms of two organo 'arms', and the nitrogen atom tethered in position by the two 'arms'. The N→Ga donor/acceptor interaction distorts the eight-membered GaC₃NC₃ heterocycle into a pseudo-boat-shaped geometry.⁵¹¹

Finally, another complex of some consequence is the hydride-bridged anion [Me₃Al(μ-H)AlMe₃]⁻ synthesized as the sodium salt by Atwood and co-workers in 1981.²⁴² Unlike the vast majority of species containing an M-H-M linkage (M = group 13 element),⁵¹⁶ this is characterized by a linear Al-H-Al skeleton. The B-H-B angle found, for example, in the anion of [PPN]⁺[B₂H₇]⁻ is in the order of 130° (136.6° by X-ray diffraction, 127.2° by neutron diffraction).⁵²⁷ The Al-H distances (1.65 Å) in [Me₃-Al(μ-H)AlMe₃]⁻ are not significantly different from those found in bent Al-H-Al bridges {e.g., 1.695(36) Å for the Al-H_b bonds in the [Mes*AlH₂]₂ dimer, for which the Al-H-Al angles average 103(2)°¹⁴³}, and the authors argue that the long Al...Al distance (3.30 Å), taken together with the relative invariance of Al-H bond length to changes in Al-H-Al angle, tends to discount a significant bonding contribution from direct Al-Al interactions.²⁴²

d. Hydroborate Derivatives of Aluminum and Gallium. Despite their thermal frailty, the volatility of many aluminum and gallium hydrides at low-to-moderate temperatures, coupled with the comparatively high symmetries of the gaseous molecules, has made them amenable to investigation by gas-phase electron diffraction (GED).^{11,13} Hence, it has been possible to determine the structures of gaseous hydrides such as Ga₂H₆,⁶⁰ [Me₂GaH]₂,⁶³ and [Me₂-AlH]_n,⁶² of tetrahydroborates such as H₂GaBH₄,^{230,374} HGa(BH₄)₂,⁶⁵ Me₂GaBH₄,⁴¹³ Me₂AlBH₄,⁴¹³ MeAl(BH₄)₂,⁵¹⁷ and Al(BH₄)₃,⁵¹⁸ and of tetraborane(10)-like

species such as $\text{H}_2\text{GaB}_3\text{H}_8$,⁵⁸ $\text{Me}_2\text{GaB}_3\text{H}_8$,⁵¹⁹ and $\text{Me}_2\text{-AlB}_3\text{H}_8$.⁵¹⁹ Properties of some of these compounds have been reviewed in detail elsewhere^{11,13} and will not be discussed here at length. The possibility of investigating such compounds in the solid phase has been hampered by their thermal lability and, in some cases, by the amorphous nature of the solid phases formed at low temperature. Only in a few cases has structural characterization been achieved for both solid and vapor phases, thereby shedding some light on the roles of crystal packing and molecular aggregation processes in the assembly of the solid state.^{374,410} The compounds Me_2AlBH_4 ,^{410,413} $\text{Al}(\text{BH}_4)_3$,^{410,518} and H_2GaBH_4 ^{230,374} represent rare examples of mixed group 13 hydrides for which diffraction studies have elucidated structures in both the solid and vapor phases. In the case of $\text{Al}(\text{BH}_4)_3$, the monomeric hexacoordinated structure incorporating three bidentate BH_4 ligands determined for the molecule in the vapor phase persists more or less unchanged with the transition into the condensed phase; the principal differences between the α and β phases of the solid relate more to the *packing* of the molecular units. Interestingly, although there are no $\text{Al}\cdots\text{H}$ intermolecular contacts shorter than 3.6 Å, the packing of molecular units in the α phase about a 2_1 crystallographic screw axis is reminiscent of the behavior of polymeric species such as $\text{Be}(\text{BH}_4)_2$,³⁸² MeZnBH_4 ,⁴¹¹ and Me_2AlBH_4 .⁴¹⁰ The GED study carried out on the gaseous $\text{Al}(\text{BH}_4)_3$ molecule by Haaland et al. could not differentiate conclusively between D_{3h} and D_3 models for the molecule; an angle θ of 72.8–(24)° between AlB_2 and $\text{Al}(\mu\text{-H})\text{B}$ planes was found to give the best account of the experimental scattering.⁵¹⁸ Subsequent *ab initio* calculations have suggested that the D_{3h} structure is a transition state between two minima of D_3 symmetry with an energy minimum occurring for $\theta = 66.8^\circ$.⁵²⁰ The corresponding angles in the α and β phases of the solid (90.3° and 89.5°) conform within the limits of experimental error to 90°,⁴¹⁰ although the relevance of this figure to the gaseous molecule is clearly dependent on crystal packing forces, particularly as the barrier to synchronous rotation of the three BH_4 groups is calculated to be very low (0.3–3.7 kJ mol⁻¹ 520).

The dimethyl derivative Me_2AlBH_4 exists as discrete $\text{Me}_2\text{Al}(\mu\text{-H})_2\text{BH}_2$ molecules in the vapor but as a helical polymer in the solid state. The structure of the solid resembles closely those of $\text{Be}(\text{BH}_4)_2$ ³⁸² and MeZnBH_4 ⁴¹¹ and features Me_2Al units linked by BH_4 groups exhibiting bidentate ligation with respect to each of the adjacent metal centers. Comparison of the two structures reveals several differences consistent with the change from discrete molecular entities to a polymer incorporating alternate Me_2Al^+ and BH_4^- ions. Thus, the $\text{Al}\cdots\text{B}$ and $\text{Al}\text{-H}$ distances are appreciably longer in the solid phase [2.392(6), 2.419(6), and 1.82(4)–2.22(5) Å⁴¹⁰] than in the vapor [2.128(8) and 1.77(3) Å⁴¹³].

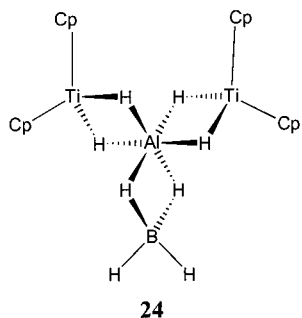
Like Me_2AlBH_4 , gallaborane, H_2GaBH_4 , also exists as discrete molecular entities, $\text{H}_2\text{Ga}(\mu\text{-H})_2\text{BH}_2$, in the vapor but as a BH_4 -bridged polymer in the solid phase (see Figure 6).^{230,374} In addition, NMR measurements in solution imply an equilibrium between

species of different nuclearity.²³⁰ Unlike Me_2AlBH_4 , however, solid H_2GaBH_4 features two distinct types of bridging BH_4 group: one linkage involves a $\text{Ga}(\mu\text{-H})_2\text{B}$ unit with dimensions very similar to those of the $\text{Al}(\mu\text{-H})_2\text{B}$ unit in solid Me_2AlBH_4 , while the other consists of GaH_2 units bridged by bis(monodentate) $(\mu\text{-H})\text{BH}_2(\mu\text{-H})$ groups.³⁷⁴ Although the former (bidentate) mode of coordination of the BH_4 group is common and finds precedent in gallium chemistry in $\text{CpFe}(\text{CO})_2\text{Ga}(\text{BH}_4)(\text{C}_3\text{H}_6\text{NMe}_2)$,⁵²¹ the latter is highly unusual while finding precedent in the structure of the dimeric iridium complex $(\text{Cp}^*\text{Ir})_2\text{-H}_3(\text{BH}_4)$.⁵²² It is interesting to note that whereas the aluminum center in solid Me_2AlBH_4 exploits all four hydrogens to increase its coordination number to six, one of the gallium centers in solid H_2GaBH_4 retains the tetracoordinated geometry seen in the vapor phase (albeit with considerable distortion from idealized tetrahedral geometry), with the consequence that each BH_4 ligand bears two terminal hydrogen atoms. This difference in coordination geometry is consistent with the structural properties of many other aluminum and gallium compounds, for example, solid AlCl_3 and GaCl_3 .¹⁰

Among the mixed hydrides of the group 13 elements, aluminum tetrahydroborate derivatives have attracted the most crystallographic studies. These have included not only $\text{Al}(\text{BH}_4)_3$ itself,⁴¹⁰ but also $\text{Al}(\text{BH}_4)_3\cdot\text{L}$ ($\text{L} = \text{NMe}_3$ ⁵²³ or NH_2Me ⁵²⁴), $[\text{Al}(\text{BH}_4)_4]^-$,⁵²⁵ $[\text{Al}(\text{BH}_4)_2\text{X}]_2$ ($\text{X} = \text{OSiMe}_3$,⁵²⁶ NCH_2CH_2 ⁵²⁷), and $[\text{Al}(\text{BH}_4)(\text{H}_2\text{TiCp}_2)_2]$.⁵²⁸ $\text{Al}(\text{BH}_4)_3\cdot\text{NMe}_3$ ⁵²³ and $\text{Al}(\text{BH}_4)_3\cdot\text{NH}_2\text{Me}$ ⁵²⁴ contain rare examples of heptacoordinated aluminum centers, being linked to the six bridging hydrides of three bidentate BH_4 ligands and to the nitrogen atom of the donor molecule. In the case of $\text{Al}(\text{BH}_4)_3\cdot\text{NMe}_3$, an X-ray structure determination at 113 K revealed an approximately pentagonal bipyramidal arrangement of ligands at aluminum with the NMe_3 group and one of the bridging hydrides occupying the axial coordination sites.⁵²³ The $\text{Al}\cdots\text{B}$ and $\text{Al}\text{-N}$ distances [2.23(1)/2.26(1) and 1.989(8) Å] are similar to those found for solid $\text{Al}(\text{BH}_4)_3$ ⁴¹⁰ and AlH_3 adducts [e.g., $\text{H}_3\text{Al}\cdot\text{quinuclidine}$, 1.991(4) Å⁴²⁴], respectively. An even more crowded aluminum coordination sphere is found in the anionic species $\text{L}^+[\text{Al}(\text{BH}_4)_4]^-$ ($\text{L}^+ = [\text{Ph}_3\text{MeP}]^+$ or $[\text{PPN}]^+$) synthesized by Shore et al.⁵²⁵ Here four bidentate BH_4 ligands are arranged such that the eight bridging hydrides define a distorted dodecahedral coordination geometry. $\text{B}\text{-H}_t$ and $\text{B}\text{-H}_b$ distances [0.95(5)–1.22(5) and 0.80(5)–1.07(5) Å] are very similar to those found in solid $\text{Al}(\text{BH}_4)_3$,⁴¹⁰ differences in the $\text{Al}\text{-H}$ and $\text{Al}\cdots\text{B}$ distances for the two compounds and the existence of less symmetrical $\text{Al}(\mu\text{-H})_2\text{B}$ bridges in $[\text{Al}(\text{BH}_4)_4]^-$ are almost certainly manifestations of the greater steric congestion and distorted dodecahedral geometry peculiar to the anion.

The dimeric species $[\text{Al}(\text{BH}_4)_2\text{OSiMe}_3]_2$ ⁵²⁶ and $[\text{Al}(\text{BH}_4)_2\text{NCH}_2\text{CH}_2]_2$ ⁵²⁷ feature approximately planar Al_2E_2 rings ($\text{E} = \text{O}$ or N) with the distorted octahedral coordination sphere of each aluminum center being completed by four hydrides from two bidentate BH_4 ligands. In the case of $[\text{Al}(\text{BH}_4)_2\text{OSiMe}_3]_2$,⁵²⁶ the

resulting centrosymmetric dimer has an Al...Al distance of 2.720(2) Å, which is somewhat greater than the sum of the covalent radii for the two aluminum centers (2.52 Å³⁹¹) and similar to that found in other dimeric species for which no direct Al...Al interaction is postulated. The geometry of the aluminum center in [Al(BH₄)(H₂TiCp₂)₂] (**24**) is reminiscent of that found in Al(BH₄)₃ itself, with two Cp₂Ti units having formally replaced two BH₂ fragments.⁵²⁸ In contrast



to solid Al(BH₄)₃, however, the angle between the Al-(μ-H)B and AlTi₂ planes is ca. 59.3°, a figure remarkably close to that calculated for the gaseous Al(BH₄)₃ molecule by Demachy and Volatron (66.8°).⁵²⁰

Finally, we note that relatively long M...H-B contacts have also been observed not only in the carborane complex [Al(C₂B₉H₁₁)₂AlEt₂],⁵²⁹ but also in the indium species [1-PrⁱIn-2,3-(Me₃Si)₂-2,3-C₂B₄H₄]⁵³⁰ and Me₂InB₃H₈⁵³¹ to be described in the next section.

e. Indium Hydrides. Despite the comparative weakness of the In-H bond,^{10–12,321} several structurally characterized indium hydrides have been reported over the last 10 years (see refs 12, 141, 152, 244, 245, 417, and 530–535). Of these six feature terminal In-H linkages, viz. K₃[K(Me₂SiO)₇][HInPp₃]₄ (Np = neopentyl, Me₃CCH₂),⁵³³ HIn(2-Me₂NCH₂-C₆H₄)₂,¹⁵² [Li(thf)₂][Tsi₂In₂H₅] (Tsi = tris(trimethylsilyl)methyl, (Me₃Si)₃C),⁵³² [Cy₂PInH₂]₃,⁵³⁴ and the carbene and tricyclohexylphosphine adducts H₃In·CNPrⁱC₂Me₂NPrⁱ¹⁴¹ and H₃In·PCy₃,⁵³⁵ respectively. Only in the cases of HIn(2-Me₂NCH₂-C₆H₄)₂, [Cy₂-PInH₂]₃, and the phosphine adduct has the location of the hydrido ligand been established on the basis of the diffraction data, yielding In-H bond lengths close to 1.70 Å. This figure can be compared with average Al-H and Ga-H bond lengths of 1.53 and 1.48 Å, respectively, as determined for MH₃ adducts (see Table 6); the trend in M-H bond lengths is thus consistent with the increase in the tetrahedral covalent radius of indium compared with aluminum and gallium.³⁹¹ The structure of HIn(2-Me₂NCH₂-C₆H₄)₂ is unusual in embodying a trigonal bipyramidal indium center (**4**) with an N-In-N angle of 177.3° and equatorial angles summing to 360°, within experimental error.¹⁵²

Although it proved impossible to locate the hydrogen atoms in the carbene complex H₃In·CNPrⁱC₂-Me₂NPrⁱ by crystallographic methods, the presence of these atoms could be inferred from the spectroscopic properties of the compound.¹⁴¹ In addition to the ¹H NMR signal (see section II.D), there is a strong

absorption at 1640 cm⁻¹ in the IR spectrum which can be assigned to the antisymmetric In-H stretching mode of the InH₃ moiety, being at somewhat lower frequency than the corresponding mode in matrix-isolated InH₃ (1754.5 cm⁻¹ for ν₃¹¹⁵). A similar reduction in M-H stretching frequency is observed for the AlH₃ moiety on coordination of a carbene ligand.⁴¹⁶ Jones and co-workers recently extended this synthetic approach to the analogous alane and

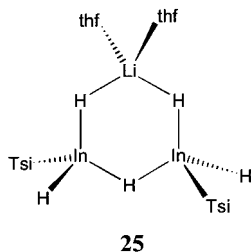
gallane adducts, H₃M·CNPrⁱC₂Me₂NPrⁱ (M = Al or Ga).⁴¹⁷

By contrast, location of the hydrogen atoms in the crystal structure of the carbene-alane H₃Al·CN-(Mes)₂C₂H₂N(Mes) has revealed a distorted tetrahedral geometry at the group 13 metal center.⁴¹⁶ In both the carbene-alane and -indane adducts, the M-C distance [2.034(3)⁴¹⁶ or 2.260(6) Å¹⁴¹ for M = Al or In, respectively] is longer than expected for typical M-C bonds {e.g., 1.958 Å on average for the terminal Al-C distances in [AlPh₃]₂⁵³⁶ and 2.174 Å in Me₃In·quinuclidine⁵³⁷}, a trend consistent with the bond lengths found in other group 13 carbene complexes.⁵³⁸ In both complexes, too, the NMR and crystallographic properties of the carbene moiety indicate a degree of delocalization within the imidazole ring (**1**).

The carbene complex of InH₃ is thermally frail; the solid decomposes at temperatures above -5 °C, and solutions are unstable above -20 °C. Given the comparative 'hardness' of indium as an acid center, it is surprising that the solid tricyclohexylphosphine adduct H₃In·PCy₃, which also contains a four-coordinated metal core,^{534,535} should be relatively long-lived at temperatures up to 50 °C. The properties of this and other phosphine complexes of InH₃ imply that the stabilization is a feature of the solid state and of a comparatively low solubility in the normal solvents, depending partly on the bulk and partly on the nucleophilicity of the phosphine. The first examples of phosphine complexes of the type H₃-In(PR₃)₂ have also been prepared, and H₃In(PCy₃)₂ has been characterized by its crystal structure which comprises discrete molecules with trigonal bipyramidal InH₃P₂ skeletons, the phosphine ligands occupying the apical sites (structure type **II**, Figure 7); strikingly the In-P distances are almost 0.34 Å longer than those in H₃In·PCy₃.^{534,535} Comparable in thermal stability with H₃In·PCy₃ is the phosphido derivative [Cy₂PInH₂]₃ which can be prepared by treating Me₃N·InH₃ with LiPCy₂; here the X-ray crystal structure reveals a cyclic trimer akin to its gallium analogue, the In₃P₃ core adopting a flattened or twisted boat conformation with In-P distances [2.596(1) Å on average] in the normal range for an indium phosphido compound.⁵³⁴ There are good grounds therefore for believing that indium hydrides do indeed have a future.

Other structurally characterized compounds have been shown to feature hydrido ligands bridging between indium and lithium {[Li(thf)₂][Tsi₂In₂H₅]}, Tsi = (Me₃Si)₃C⁵³²}, indium and boron {[1-PrⁱIn-2,3-(Me₃Si)₂-2,3-C₂B₄H₄]⁵³⁰ and Me₂InB₃H₈⁵³¹}, and two indium atoms {[Li(thf)₂][Tsi₂In₂H₅],⁵³² K[H(InPp₃)₂]

(Np = Me₃CCH₂),²⁴⁵ and [Li(tmeda)₂][H(InMe₃)₂].²⁴⁴ In the case of [Li(thf)₂][Tsi₂In₂H₅] (**25**), the first



structurally characterized complex containing an In–H linkage, a six-membered $\text{In}(\mu\text{-H})\text{In}(\mu\text{-H})\text{Li}(\mu\text{-H})$ ring is proposed, although the locations of the hydrido ligands could not be established from the crystallographic data.⁵³² Instead, the suggested H atom positions were based on the evidence of IR and $^7\text{Li}\{\text{H}\}$ NMR spectra for solutions of the compound in toluene or thf. The proposed bent $\text{In}(\mu\text{-H})\text{In}$ unit finds analogies in the crystal structures of $\text{K}[\text{H}(\text{In-Np}_3)_2]$ ²⁴⁵ and $[\text{Li}(\text{tmeda})_2][\text{H}(\text{InMe}_3)_2]$,²⁴⁴ the anions of which consist of somewhat flattened InR_3 fragments linked via a hydrido ligand. The average In–H–In angle is $156(5)^\circ$ for $\text{R} = \text{Np}$ or ca. 149° for $\text{R} = \text{Me}$, and the mean $\text{In}\cdots\text{In}$ distance at 3.796 \AA ($\text{R} = \text{Np}$) or 3.591 \AA ($\text{R} = \text{Me}$) is slightly longer than that found in $[\text{Li}(\text{thf})_2][\text{Tsi}_2\text{In}_2\text{H}_5]$ [$3.482(3) \text{ \AA}$]⁵³². As expected, In–($\mu\text{-H}$) distances [$1.94(2) \text{ \AA}$ on average] are appreciably longer than the terminal In–H ones found in $\text{HIn}(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2$ ¹⁵² and $\text{H}_3\text{In-PCy}_3$ ⁵³⁵ ($1.68\text{--}1.69 \text{ \AA}$).

Significantly longer $\text{In}\cdots\text{H}$ distances are found for the $\text{In}\cdots\text{H-B}$ moieties in $[1\text{-Pr}^i\text{In-2,3-(Me}_3\text{Si)}_2\text{-2,3-C}_2\text{B}_4\text{H}_4]_2$ ⁵³⁰ and $\text{Me}_2\text{InB}_3\text{H}_8$.⁵³¹ The $\text{In}\cdots\text{H}$ contacts in the former compound [shortest distance 2.48 \AA , mean 2.79 \AA] imply a very weak bridging interaction holding together the dimeric assembly. The structure of $\text{Me}_2\text{InB}_3\text{H}_8$, on the other hand, formally resembles that of the *arachno* tetraborane, B_4H_{10} , in which a wingtip BH_2 moiety has been replaced by a dimethylindium unit. In the solid state the indium coordination sphere is augmented by secondary $\text{In}\cdots\text{H}$ intermolecular contacts (ca. 2.53 \AA), the *intramolecular* In–($\mu\text{-H}$) distances at $2.18(4) \text{ \AA}$ are long, and the C–In–C angle at $158.6(2)^\circ$ is unusually wide (cf. angles of 132.0° and 132.3° determined for the analogous aluminum and gallium compounds in the gas phase⁵¹⁹).

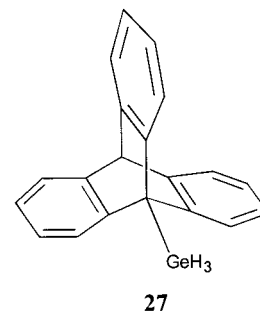
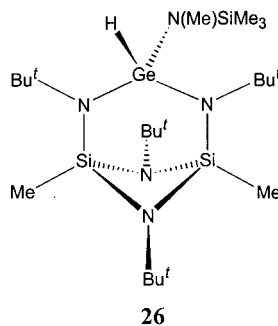
5. The Group 14 Metals

a. Germanium. At the edge of our field of survey, germanium forms numerous mixed hydrides in which up to three hydrogen atoms of GeH_4 are replaced by other substituents, e.g., halogen or, more commonly, organic groups. These are nearly always molecular compounds with Ge–H bonds of low polarity showing minimal acid/base character and therefore offering little potential for aggregation. The Ge–H bond is not only less polar but also more robust than the Ga–H one (estimated mean bond enthalpies 288 and ca. 260 kJ mol^{-1}),¹¹ and although weaker than the Si–H bond (322 kJ mol^{-1}),¹¹ it tends to be more

sluggish in its reactions. Organogermanium hydrides are of some note mainly through their capacity to undergo hydrogermylation reactions with unsaturated organic compounds.⁵³⁹

No long-lived germanium(II) hydride has been characterized to date. The facility with which GeH_2 inserts into $\text{Ge}^{\text{IV}}\text{-H}$ bonds³¹⁵ testifies to the unusual reactivity of such compounds. The transients HGeX and DGeX ($\text{X} = \text{Cl}$ or Br) are formed by the action of an electric discharge on the appropriate monohalogenogermane,²⁵ and analysis of the laser-induced fluorescence spectra of the jet-cooled molecules gives the following dimensions: HGeCl , $r_0(\text{Ge-H}) = 1.592(1) \text{ \AA}$ and $\angle\text{H-Ge-Cl} = 94.3^\circ$; HGeBr , $r_0(\text{Ge-H}) = 1.598(6) \text{ \AA}$ and $\angle\text{H-Ge-Br} = 93.9^\circ$. The Ge–H bonds do not differ significantly in length from those in GeH_2 ,²⁴ and the H–Ge–X angles are only about 3° larger than the H–Ge–H one (91.2°).

By contrast, Ge–H bonds in germanium(IV) compounds measure 1.52 \AA on average with a deviation not exceeding 0.04 \AA . This is the consensus of microwave, infrared, and electron-diffraction studies carried out on a number of gaseous molecules [$\text{H}_3\text{-GeX}$ ($\text{X} = \text{halogen}$,^{43,48,72} Me ,^{49,72} cyclopropyl,^{68a} cyclobutyl,^{68b} cyclopentadienyl,^{68c} or $\text{C}\equiv\text{CH}$ ^{52b}), $(\text{GeH}_3)_2\text{E}$ ($\text{E} = \text{O}$ or S),⁶⁶ $(\text{GeH}_3)_3\text{N}$,⁶⁷ $\text{H}_2\text{Ge-}(\text{CH}_2)_4\text{CH}_2$,⁵⁴⁰ MeGeH_2Cl ,⁷² and Me_3GeH ⁷²]. Among the better defined values in the range $r_0(\text{Ge-H}) = 1.518\text{--}1.538 \text{ \AA}$, it appears that halogen substitution brings about a modest strengthening of the Ge–H bond.⁷² Accurate values of $r_0(\text{Ge-H})$ are at a premium, however, and unfortunately ‘isolated’ Ge–H stretching frequencies $\nu_{\text{is}}(\text{GeH})$, unlike their C–H counterparts,⁷⁰ do not appear generally to be a reliable quantitative guide to Ge–H distances. There have been few crystallographic studies of germanium hydrides giving estimated Ge–H distances [e.g., for $(\text{C}_5\text{H}_5)\text{GeH}_3$,^{68c} $\text{HGe}\{\text{CH}(\text{SiMe}_3)_2\}_2(\text{OEt})$,⁵⁴¹ $(2\text{-Me}_2\text{-NCH}_2\text{C}_6\text{H}_4)_3\text{GeH}$,⁵⁴² and the compound **26**⁵⁴³] that are typically subject to substantial uncertainties. With due allowance for this and for the systematic deviations between distances determined by different methods, the average distance of 1.50 \AA derived from the crystallographic studies tends to argue that Ge–H bonds are not greatly affected either by the other substituents or by change of phase. On the other hand, the ability of very bulky organic substituents to screen the GeH_n moiety is plainly in evidence in tribenzobarellenegermane, **27**, which forms air-stable crystals, mp 232°C , whose structure has also been reported.⁵⁴⁴



Acid–base reactions and complexation do not come naturally to germanes. GeH_4 is a very weak acid which can be metalated nevertheless by an alkali metal in liquid ammonia or 1,2-dimethoxyethane; thermally frail germyl derivatives MGeH_3 can be isolated as crystalline solids which have been characterized by X-ray powder diffraction and ^1H NMR studies.⁵⁴⁵ KGeH_3 and RbGeH_3 form cubic crystals isostructural with the corresponding silyl derivatives, but CsGeH_3 is reported to form orthorhombic crystals with the TII-type structure. That GeH_4 should also form only loosely bound adducts with HF (identified in matrix-isolation experiments, see Table 1)^{133a} bears witness to the slight basicity of the hydrogen atoms. d-Block and f-block metals may be better able to exploit this basicity, however, and the structure of the triphenylgermane complex $(\text{Ph}_3\text{GeH})_2\text{Yb}(\text{thf})_4$ reveals unsymmetrical μ_2 -H bridges between the Yb and Ge centers, even if the Ge–H distances, at 1.48 and 1.56 Å, are not out of line with those in uncomplexed germanes.²⁴⁹ There is circumstantial evidence too that interaction, possibly with η^2 -coordination of a Ge–H bond, occurs in $(\eta^2\text{-MeC}_5\text{H}_4)\text{Mn}(\text{CO})_2\cdot\text{HGePh}_3$,⁵⁴⁶ with behavior reminiscent of so-called ‘agostic’ C–H bonds.⁵⁴⁷ This phenomenon, which may well be a general feature of group 14 hydrides, will be elaborated more fully in the next section, studies with organotin hydrides affording more compelling signs of η^2 -coordination of the Sn–H fragment.

b. Tin. Despite the weakness of the Sn–H bond, with a mean bond energy of only 253 kJ mol⁻¹,¹¹ and the lability of the binary hydride SnH_4 , tin is one of the more prolific main-group metals in the range of mixed hydrides that it forms. Simple inorganic derivatives such as H_3SnX , where X = Cl, Br, or I, tend to be no more robust than SnH_4 itself, but some organostannanes—and particularly those carrying just a single Sn–H bond—are not only more stalwart but also of much consequence in their role as strong reducing agents.⁵⁴⁸ According to the conditions, the Sn–H bond of organotin hydrides may react heterolytically or, more often, homolytically to provide either nucleophilic or electrophilic hydrogen. Recent studies have focused heavily on the use of tributyltin hydride in organic synthesis as an initiator of chain reactions involving the tributyltin radical which may undergo homolytic addition to a multiple bond or substitution at a functional group. The use of tributyltin hydride in this way is not without problems, mainly associated with the difficulties of separating the organotin byproducts from the organic material. No little effort has been invested in modifying the tin hydride reagents in an attempt to facilitate separation and/or minimize toxicity hazards. One recent result²²⁴ has been the advocacy of highly fluorinated organotin hydrides of the types $[\text{R}_f(\text{CH}_2)_n]_3\text{SnH}$ and $[\text{R}_f(\text{CH}_2)_n]\text{Me}_2\text{SnH}$ ($\text{R}_f = \text{C}_4\text{F}_9$, C_6F_{13} , C_8F_{17} , or $\text{C}_{10}\text{F}_{21}$; $n = 2$ or 3) for the performance of reductive radical and hydrostannation reactions.

Of tin(II) hydrides there has been little sign, even as fleeting intermediates, and the susceptibility of tin(IV) hydrides to decomposition has hampered studies of the gaseous molecules. The apparent instability of tin(II) hydrides might seem to confirm

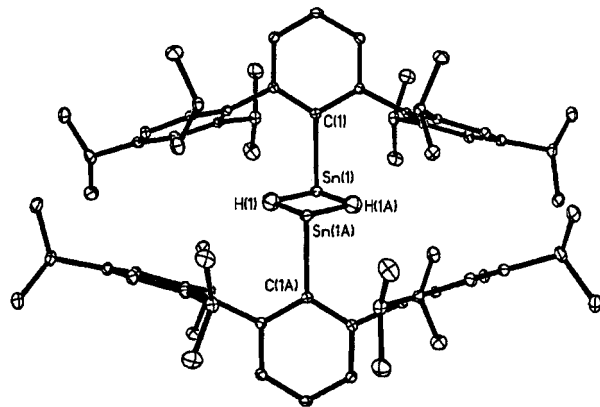


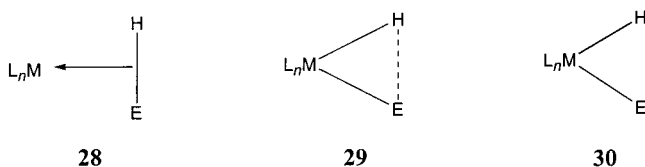
Figure 12. Structure of the tin(II) hydride molecule $[(2,6\text{-Trip}_2\text{C}_6\text{H}_3)\text{Sn}(\mu\text{-H})_2]$ as deduced by X-ray diffraction of a single crystal. (Reprinted with permission from ref 550. Copyright 2000 American Chemical Society.)

the expectation that Sn(II)–H bonds are weaker than Sn(IV)–H ones. This view is certainly supported by the bonds to many other ligands which are slightly longer for tin(II) than for tin(IV), although thermochemical studies of amido derivatives imply stronger bonding not for the higher but for the lower valent species.⁵⁴⁹ In a very recent study involving the mediation of the sterically highly encumbering ligand 2,6-Trip₂C₆H₃– (where Trip = 2,4,6-Prⁱ₃C₆H₂–), Power and his group reported⁵⁵⁰ the preparation of the tin(II) hydride $[(2,6\text{-Trip}_2\text{C}_6\text{H}_3)\text{Sn}(\mu\text{-H})_2]$ by hydride transfer to the corresponding chloride. This, the first subvalent hydride of a heavier group 14 element to be isolated, is an orange, crystalline solid which melts at 174–177 °C and is thermally quite robust. In the crystal it exists as a di- μ -hydrogen-bridged dimer with the aryl groups in the trans positions, as illustrated in Figure 12; the Sn–H distances are 1.89(3) and 1.95(3) Å. Such a structure is consistent with the *trans*-dihydrogen bridged geometry calculated to be the most stable for $[\text{SnH}_2]_2$ (see section IV.A.2).³⁴¹ However, dissolution in a hydrocarbon solvent yields a blue solution in which the predominant species is the monomer.

On the evidence of microwave and IR spectroscopic or electron-diffraction measurements on the molecules $\text{Me}_n\text{SnH}_{4-n}$ ($n = 1$ –3),^{50,69} EtSnH_3 ,⁵¹ and $\text{H}_3\text{-SnX}$ (X = Cl, Br, or I),^{43,551} the Sn–H bond distances all approximate to 1.70 Å, corresponding closely with the r_0 value of 1.702 85 Å^{43–45} in SnH_4 and with the sum of the relevant covalent radii.³⁹¹ There are insufficient accurate data to establish whether a useful linear relationship exists between $\nu_{\text{is}}(\text{SnH})$ and $r_0(\text{Sn–H})$, but measurements of $\nu_{\text{is}}(\text{SnH})$ have been used to investigate the conformational properties of specific stannane derivatives.⁷⁴ Few crystal structures have been described for organotin hydrides,⁵⁵² and still fewer offer a means of locating the hydrogen atoms; a rare example is afforded by *tert*-butyl-8-dimethylaminonaphthyl(–)-menthyltin hydride, the unit cell of which includes two distinct molecules each featuring a pentacoordinated metal atom with an Sn–H bond length of 1.52(5) or 1.63(5) Å.^{552a}

The reducing power of tin hydrides hints at hydrogen ligands which are more nucleophilic than those in the corresponding germanes. In terms of identifi-

able complexes, however, the basic properties of Sn–H bonds are far from obvious. The possibility of coordination to appropriately receptive transition-metal centers has been revealed in recent studies, though with some weight of evidence that it may proceed through η^2 -coordination of the Sn–H bond. Again this brings to mind ‘agostic’ C–H bonds which have been the subject of intense interest in the past 15 years, partly because of the influence they appear to exert on the structures of numerous organometallic complexes, and partly because of their potential mediation in some important chemical changes.⁵⁴⁷ As originally formulated, the interaction involves three-center, two-electron bonding between C–H and L_nM fragments, where M is an electron-deficient transition-metal center. This has been represented by either **28** or **29** (where E = C), the former emphasizing the chemical origin of the fragments and the latter the delocalized nature of the interaction,⁵⁵³ although the most recent results imply that there is little direct $M\cdots H$ interaction, in some systems at least.⁵⁵⁴ Agostic C–H bonds can also be viewed as “chemical snapshots” on the reaction coordinate linking discrete L_nM and C–H entities and the oxidative addition product **30**.⁵⁵³ It has also become



apparent that this form of coordination is not unique to carbon, with examples of analogous behavior being found for E = Si,⁵⁵⁵ E = Ge,⁵⁴⁶ and E = Sn.^{250,553,556–558} Thus, complexes with η^2 -coordination of Sn–H bonds have been structurally characterized in a number of cases, with results that have enabled Schubert et al. to ascertain the extent to which the E–H bond has travelled along the pathway of oxidative addition and how this varies with the identity of the group 14 element E.⁵⁵³

Single-crystal X-ray diffraction studies have been carried out for the triply bridged species $(EtPh_2P)_3Fe(\mu-H)_3SnPh_3$ ⁵⁵⁶ and for the complexes $(\eta^5-MeC_5H_4)Mn(CO)_2(HSnPh_3)$,⁵⁵³ $(\eta^6-1,3,5-Me_3C_6H_3)Cr(CO)_2(HSnPh_3)$,²⁵⁰ $Os_3SnH_2(CO)_{10}[CH(SiMe_3)_2]_2$,⁵⁵⁷ and $CpCr(PPh_3)(NO)(HSnPh_3)$.⁵⁵⁸ In each case the nature of the interaction between the transition metal and Sn–H moieties has been probed not only by analysis of the metrical data, but also by examination of the NMR spectra of the molecules in solution. η^2 -Coordination of an Sn–H bond has been unambiguously established for $(\eta^5-MeC_5H_4)Mn(CO)_2(HSnPh_3)$ ⁵⁵³ and $(\eta^6-1,3,5-Me_3C_6H_3)Cr(CO)_2(HSnPh_3)$,²⁵⁰ both prepared by photolysis of the corresponding tricarbonyl derivative in the presence of $HSnPh_3$ in a nonpolar solvent. $^{119}Sn-^1H$ and $^{117}Sn-^1H$ coupling constants have proved particularly instructive in determining the mode of coordination of the stannane;^{250,553} in each case the magnitudes are consistent with η^2 -coordination, being intermediate in value between $^1J(Sn-H)$ expected for the free stannane⁵⁵⁹ and $^2J(Sn-M-H)$ expected for a stannyl hydride, (R_3Sn)–

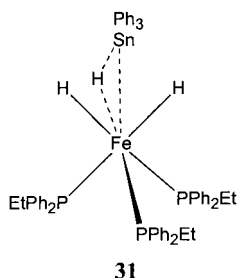
$ML_n(H)$.⁵⁶⁰ Hence, it is found that $J(^{119}Sn-^1H) = 270$ and 327.6 Hz for $(\eta^5-MeC_5H_4)Mn(CO)_2(HSnPh_3)$ ⁵⁵³ and $(\eta^6-1,3,5-Me_3C_6H_3)Cr(CO)_2(HSnPh_3)$,²⁵⁰ respectively, whereas $^1J(Sn-H) = 1500-1800$ Hz for alkyltin hydrides⁵⁵⁹ and $^2J(^{119}Sn-Os-^1H) = 136$ Hz for the stannyl hydride $(OC)_4Os(H)SnCl_3$, which has no direct Sn–H interaction.⁵⁶⁰ The structural inferences drawn on the basis of the NMR spectra of solutions are corroborated for the solid phase by crystallographic studies. Thus, in $(\eta^5-MeC_5H_4)Mn(CO)_2(HSnPh_3)$ for which hydrogen atoms could be located and refined, the Sn–H distance [2.16(4) Å,⁵⁵¹ ca. 0.45 Å (21%) longer than in methylstannanes^{50,69}] is indicative of a bonding interaction between the Sn and H centers, displaying as it does an increase in E–H bond length on complexation similar to that of η^2 -Si–H-bound moieties.^{555,561} The Mn–Sn distance is also longer than expected for a two-center, two-electron linkage.⁵⁵³ Structural parameters for $(\eta^6-1,3,5-Me_3C_6H_3)Cr(CO)_2(HSnPh_3)$ [$r(Sn-H) = 2.02(4)$ Å, $r(Cr-Sn) = 2.702(1)$ Å²⁵⁰] are similarly suggestive of η^2 -coordination. Furthermore, the geometry of the (ring)M(CO)₂ unit in each case is characteristic of a three- rather than a four-legged piano-stool structure^{250,553} and hence supports a description of $HSnPh_3$ as a single η^2 -bound ligand rather than as distinct hydrido and stannyl entities.

Comparison of the structural parameters of $(\eta^5-MeC_5H_4)Mn(CO)_2(HSnPh_3)$ with the very similar silyl complex $CpMn(CO)_2(HSiPh_3)$ ⁵⁶² reveals an Mn–Sn distance which is shorter than might be expected on the basis of the Mn–Si bond length and the differences in covalent radii between Si and Sn.^{391,553} Closer approach of the Mn and Sn centers is consistent with the η^2 -Sn–H moiety being further along the reaction coordinate to oxidative addition than is the corresponding silyl species. Interestingly, NMR studies carried out by Schubert and co-workers with the compounds $(OC)_3(dppe)M(HSnPh_3)$ (M = Cr, Mo, or W) reveal that, whereas the chromium and molybdenum species are best viewed as η^2 -Sn–H complexes, the tungsten compound displays much smaller Sn–H coupling constants (ca. 70 Hz) and is better viewed as a stannyl hydride.²⁵⁰ That the extent of oxidative addition is much greater for the tungsten compound is consistent with the relative magnitudes of the M–H bond strengths.

In the compounds $CpCr(PPh_3)(NO)(HSnPh_3)$,⁵⁵⁸ $FeH_3(PPh_2Et)_3(SnPh_3)$,⁵⁵⁶ and $Os_3SnH_2(CO)_{10}[CH(SiMe_3)_2]_2$,⁵⁵⁷ the mode of coordination of the Sn–H bond is less clear. The measured Sn–H coupling constant for $CpCr(PPh_3)(NO)(HSnPh_3)$ (23.7 Hz) argues for a stannyl hydride, although the structural parameters relating to the (poorly defined) hydrogen atom location lead Legzdins et al. to suggest a structure “approaching an η^2 -stannane complex” in the solid state.⁵⁵⁸ Conversely, for the cluster $Os_3SnH_2(CO)_{10}[CH(SiMe_3)_2]_2$, Sn–H coupling constants of 258.7 (^{117}Sn) and 298.0 Hz (^{119}Sn) point to an η^2 -Sn–H unit, although the crystallographic data are such that no metal-bound hydrogens could be located in the final difference map.⁵⁵⁷

Finally, the Sn–H coupling constant measured for the iron complex $(EtPh_2P)_3Fe(\mu-H)_3SnPh_3$ at room

temperature is consistent with a structure, **31**, in which two terminal Fe–H linkages and a single three-center, two-electron Sn–H–Fe moiety are rapidly interchanging among the three hydrogens.⁵⁵⁶ The



measured value of 175 Hz for $J(\text{Sn}-\text{H})$ is appropriate for the average of two stannyl hydride linkages (ca. 100 Hz⁵⁶⁰) and a single η^2 -bound Sn–H moiety (ca. 325 Hz²⁵⁰). Intriguingly, though, the crystal structure of $\text{FeH}_3(\text{PPh}_2\text{Et})_3(\text{SnPh}_3)$ reveals a skeleton approximating to C_3 symmetry with symmetric bridging of the Fe–Sn vector by all three hydrogen atoms.⁵⁵⁶

c. Lead. Inorganic derivatives of plumbane retaining Pb–H bonds are no more durable than the parent compound. Organic derivatives of the types R_2PbH_2 and R_3PbH , where R is an alkyl group, are somewhat more manageable,⁵⁶³ they can be prepared by the reduction of the corresponding chloride or bromide using LiAlH_4 in an ether solvent at low temperatures ($\leq -60^\circ\text{C}$). Me_3PbH and Et_3PbH are also formed in the decomposition of the ammoniate of the corresponding tetrahydroborate.⁵⁶³ All such compounds exhibit very low thermal stability, methyl- and ethyllead hydrides decomposing at temperatures between -20 and -50°C . Trialkyllead hydrides readily undergo hydroplumbylation reactions with unsaturated substrates at low temperatures and without catalytic assistance. As yet, however, no lead(IV) hydride has yielded to structural authentication and experiment gives no guide to the dimensions of PbH_n units, with the single exception of the gaseous PbH radical.²⁷

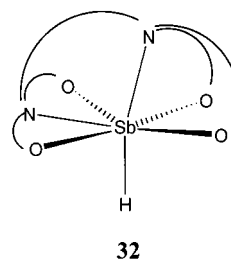
6. The Group 15 Metals

Mixed hydrides of the group 15 metals are neither numerous nor generally well characterized. Organometal(III) hydrides, $\text{R}_n\text{MH}_{3-n}$, are better known than any other class,⁵⁶⁴ but pentavalent metal hydrides in any form remain obdurately unknown. Hydrides of As, Sb, and Bi have been prepared from a variety of oxide and halide sources, with reduction being effected by zinc and acid (for As), by hydrides such as LiAlH_4 and NaBH_4 , and sometimes also by electrolysis.⁵⁶⁴ Organoarsenic hydrides resist attack by water and dilute acid, whereas organoantimony and -bismuth hydrides react with Brønsted acids. The thermal stabilities of compounds of the type $\text{R}_n\text{MH}_{3-n}$ vary in the orders $\text{As} > \text{Sb} > \text{Bi}$ and $n = 2 > 1 > 0$. Thus, very low temperatures are necessary for the preparation of bismuth hydrides by halide–hydride exchange using LiAlH_4 ,⁵⁶⁵ the methylbismuthanes MeBiH_2 and Me_2BiH made in this way decompose rapidly at temperatures above ca. -20°C . By contrast, Me_2SbH decomposes only slowly at room temperature. Although As–H and Sb–H bonds add to

alkenes and alkynes, little or no practical use has been made of the reaction.

Apart from the gaseous diatomic molecules MH ($\text{M} = \text{As},^{32} \text{Sb},^{304} \text{or Bi}^{307}$) and the trihydrides AsH_3^{46} and SbH_3 ,⁴⁷ structurally characterized derivatives featuring an M–H bond are few and far between and were confined until very recently to cases where $\text{M} = \text{As}$ or Sb . With the isolation of the bismuthane $(2,6\text{-Mes}_2\text{C}_6\text{H}_3)_2\text{BiH}$,⁵⁶⁶ however, a stable bismuth hydride has at last found a place on the chemical map, and been authenticated by crystallographic analysis. The strategies used in synthesizing hydrides of the heavier group 15 elements can be divided into two broad approaches.

(i) Comparatively stable monomeric species of the types RMH_2 ($\text{M} = \text{As}$ or Sb) and R_2MH ($\text{M} = \text{As}, \text{Sb}$, or Bi) have been formed by the device of using substituents R which may be either an alkyl group containing no β -hydrogen atoms, e.g., Me_3CCH_2- or $\text{Me}_3\text{SiCH}_2-$, or a bulky group like mesityl or $(\text{Me}_3\text{Si})_2\text{N}-$. This approach has been adopted by Hendershot et al. to make $\text{Me}_3\text{CCH}_2\text{SbH}_2$ and $\text{Me}_3\text{SiCH}_2\text{SbH}_2$,⁵⁶⁷ by Cowley et al. in the synthesis of $\text{Mes}_2\text{-SbH}$,²⁴⁰ by Power et al. to make $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AsH}$,⁵⁶⁸ $(2,6\text{-Trip}_2\text{C}_6\text{H}_3)\text{SbH}_2$,⁵⁶⁹ and $(2,6\text{-Mes}_2\text{C}_6\text{H}_3)_2\text{BiH}$,⁵⁶⁶ and by Hu and Lin who employed the hexadentate polylenediaminetetraacetate ligand in the synthesis of $[(\text{O}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}(\text{Me})(\text{CH}_2\text{CO}_2)_2]\text{SbH}$ (**32**).⁵⁷⁰



$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{AsH}$ adopts a monomeric pyramidal structure in the solid state, in contrast to the analogous phosphine complex which is a dimer, $\{[(\text{Me}_3\text{Si})_2\text{N}]_2\text{PH}\}_2$, featuring bridging hydrogen atoms and a unique planar P_2H_2 core.⁵⁶⁸ The arsenic compound displays no close intermolecular contacts, a feature the authors ascribe to poorer overlap between arsenic and hydrogen orbitals, and hence to weaker M–H–M bridging interactions. The As–H bond length is 1.5(1) Å, and the mean As–N bond length [1.877(3) Å] is shorter than would be expected on the basis of the covalent radii of arsenic and nitrogen, possibly as a result of N–As $p\pi$ – $d\pi$ bonding.⁵⁶⁸

The crystal structure of Mes_2SbH features discrete molecular units.²⁴⁰ The planes of the mesityl ligands are rotated by ca. 68° with respect to the plane of the C–Sb–C unit, presumably to minimize intramolecular steric repulsions. The molecule possesses a C_2 axis bisecting the C–Sb–C angle, although the hydrogen atom could not be located from the crystallographic analysis and its presence had to be inferred from the IR and NMR spectra. Use of the terphenyl ligand 2,6-Trip₂C₆H₃⁵⁷¹ enables the isolation of the primary stibane 2,6-Trip₂C₆H₃SbH₂, a white crystalline solid which does not decompose in the absence

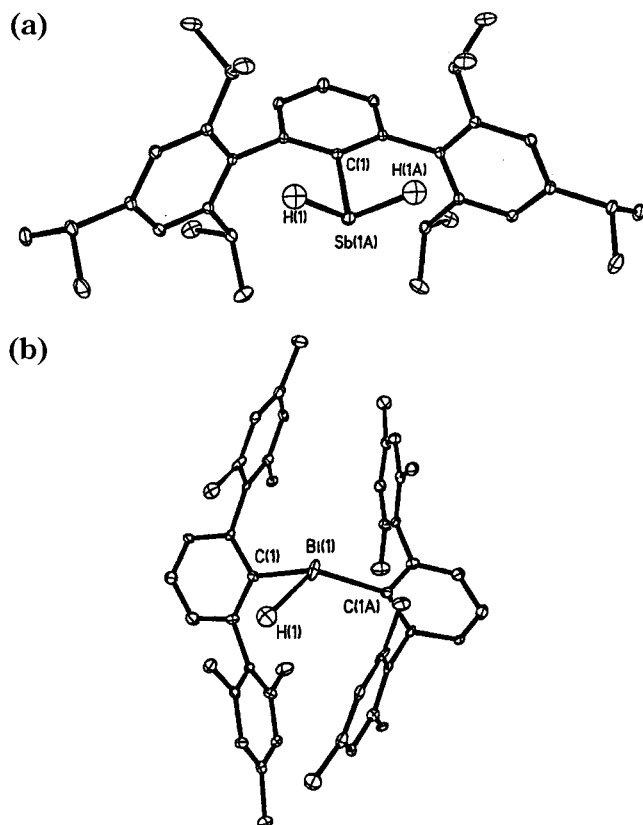


Figure 13. Structures of (a) the primary stibane 2,6-Trip₂C₆H₃SbH₂ and (b) the secondary bismuthane (2,6-Mes₂C₆H₃)₂BiH as deduced by X-ray diffraction of single crystals. (Reprinted with permission from refs 569 and 566, respectively. Copyright 2000 Elsevier Science and Wiley-VCH.)

of light at temperatures up to 195 °C.⁵⁶⁹ The X-ray crystal structure has identified the monomeric structure of the molecule (see Figure 13a) in which the hydrogen atoms have been located, giving an Sb–H distance of 1.67(4) Å (*cf.* $r_e = 1.7000$ Å in SbH₃⁴⁷).

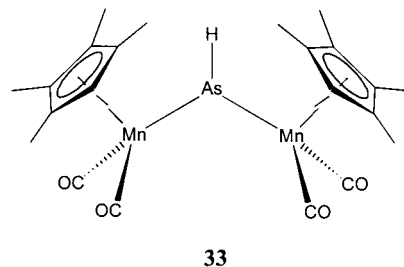
Through the stabilizing influence of a different terphenyl ligand, the first long-lived bismuthane, (2,6-Mes₂C₆H₃)₂BiH, has been synthesized by the reaction of LiAlH₄ with the corresponding chloride.⁵⁶⁶ It is a colorless, crystalline solid that reveals the presence of the Bi–H bond not only through its IR spectrum [which features a strong absorption at 1759 cm⁻¹ attributable to the $\nu(\text{Bi-H})$ mode], but also through its X-ray crystal structure. The latter identifies the monomeric molecule illustrated in Figure 13b and gives the first experimental measure of a Bi(III)–H distance, viz. 1.79(8) Å. In that no hydride derivative of the elements Hg, Tl, Pb, or Bi has been isolated previously at ambient temperatures, it is a remarkable testimony to the stabilizing effect of a sterically crowding terphenyl substituent⁵⁷¹ that this compound should decompose only as it melts at 135–136 °C.

(ii) Complexes have been synthesized in which MH_{*n*} moieties are linked to one or more centers, which are usually, but not invariably, transition metals. Structurally authenticated molecules in this class include (a) straightforward donor/acceptor complexes featuring AsH₂R, AsHR₂, and As₂H₂R₂ ligands, exemplified by (OC)₅Cr(AsH₂Ph),⁵⁷² (OC)₅Cr[AsH(Ph)CH₂CMe=

CMe₂],⁵⁷³ and the bridged system [(C₅H₅)Mn(CO)₂]₂-(μ -As₂H₂Ph₂),⁵⁷⁴ (b) compounds incorporating a terminal arsenido (AsH₂) unit and a direct M–As bond, as exemplified by the sterically bolstered silane derivative (Trip)(Bu^{*t*})Si(AsH₂)₂⁵⁷⁵ and the iridium(III) species *trans*-(Et₃P)₂IrCl(CO)H(AsH₂) formed by oxidative addition of AsH₃ to the Ir(I) precursor,⁵⁷⁶ and (c) species in which an MH moiety bridges two or more centers, as exemplified by the μ_2 -AsH units found in (Trip)(Bu^{*t*})Si(μ -AsH)₂Ge(Mes)(Bu^{*t*})⁵⁷⁵ and [Cp^{***}Mn(CO)₂]₂AsH (Cp^{***} = C₅Me₅ or C₅H₄Me)^{577,578} and the μ_3 -MH unit found in the dianion [(OC)₄Fe]₃MH²⁻ (M = As or Sb).^{579–581}

Complexes containing arsines with terminal As–H bonds are rare, and no examples of structurally characterized species containing the AsH₃ ligand have yet been reported. This has been attributed to the lability of the As–H bond, with spontaneous elimination of H₂ to give As–As-bonded species being a likely route of decomposition.⁵⁷⁷ The only examples of terminal arsenido ligands to be structurally characterized are those found in (Trip)(Bu^{*t*})Si(AsH₂)₂⁵⁷⁵ and the octahedral complex *trans*-(Et₃P)₂IrCl(CO)H(AsH₂),⁵⁷⁶ although in neither case have the positions of the hydrogen atoms been located with any certainty. Reaction of the iridium complex with the ruthenium dimer [(η^6 -Me-4-Pr^{*i*}C₆H₄)RuCl₂]₂ gives rise to the arsenido-bridged bimetallic species *trans*-(Et₃P)₂IrCl(CO)H(μ -AsH₂)RuCl₂(η^6 -Me-4-Pr^{*i*}C₆H₄) for which As–H distances of 1.48(8) and 1.37(8) Å are reported.⁵⁷⁶ These compare with an r_e distance of 1.511 Å in the gaseous AsH₃ molecule (see Table 2).⁴⁶

Transition-metal complexes containing the bridging arsenediyl ligand (μ -AsH) have been reported by the groups of both Herrmann⁵⁷⁷ and Huttner.⁵⁷⁸ The very air-sensitive, deep blue complex [Cp^{***}Mn(CO)₂]₂-(μ -AsH), **33**, is formed by the reaction of Cp^{***}Mn(CO)₂(thf) with AsH₃. Dihydrogen is evolved during the course of the reaction, and the lability of the As–H bond is further emphasized by the decomposition of **33** with further loss of H₂ to give the butterfly cluster [Cp^{***}Mn(CO)₂]₂(μ_2 , η^2 -As₂). The molecular structure of **33** includes short Mn–As distances of 2.247(1) Å and an Mn–As–Mn angle of 139.3(1)°, while the bonding of the arsenediyl ligand to the two manganese centers has been described in terms of a three-center, four-electron model. In the case of the analogous cyclo-



33

pentadienyl compound [CpMn(CO)₂]₂(μ -AsH) formed by the reaction of arsine with CpMn(CO)₂(thf), an intermediate thought to involve coordination of the AsH₃ ligand to the metal center has been identified but not fully characterized.⁵⁷⁷

The bridging M–H unit has also been found in a class of complexes (L⁺)₂{[(OC)₄Fe]₃MH}²⁻ (L⁺ =

PPh_4^+ or $[\text{Ph}_3\text{P}=\text{N}=\text{PPh}_3]^+$, PPN^+ ; $\text{M} = \text{As}$ or Sb) synthesized by the groups of both Burns⁵⁷⁹ and Whitmire.^{580,581} In each case the ligand bridges three iron centers and the coordination geometry at the group 15 atom approximates to C_3 symmetry, with $\text{Fe}-\text{M}-\text{Fe}$ angles in the region of 115° . The arsenic or antimony ligand occupies one of the axial sites of the trigonal bipyramid enclosing the iron center, which thereby attains an 18e configuration. In no examples were hydrogen atoms located crystallographically, their existence being inferred from spectroscopic data. These mixed-metal species can be viewed as being formally derived from the corresponding base $\{[(\text{OC})_4\text{Fe}]_3\text{M}\}^{3-}$, and in the case of $[\text{PPN}^+]_2\{[(\text{OC})_4\text{Fe}]_3\text{AsH}\}^{2-}$ Whitmire et al. proposed that the reaction does in fact proceed via protonation of the corresponding trianion.⁵⁸¹

V. Chemical Aspects

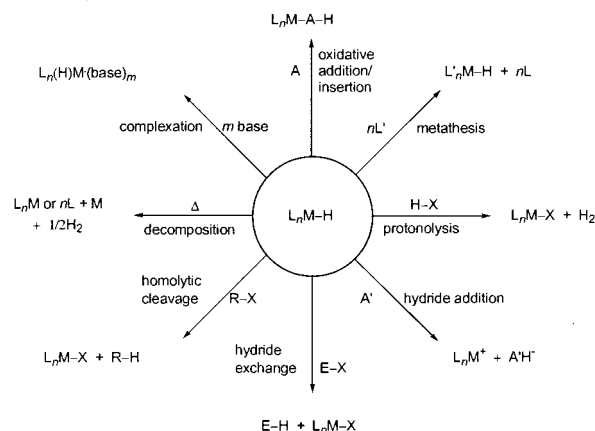
"Simplicity, simplicity, simplicity! I say, let your affairs be as two or three, not a hundred or a thousand; instead of a million count half a dozen, and keep your accounts on your thumb nail."

H. D. Thoreau, *Walden*

Legion are the reactions of main-group metal hydrides,^{9b,e} with their reducing action as the dominant principle and finding widespread application in chemical synthesis. Numerous books and reviews^{154,367,548,582} testify to the importance of hydrides such as LiAlH_4 , 'Red-Al' $\{\text{Na}[(\text{CH}_3\text{OC}_2\text{H}_4\text{O})_2\text{AlH}_2]\}$, 'DIBAL-H' ($\text{Bu}'_2\text{AlH}$), AlH_3 , and Bu_3SnH as agents for the reduction of organic compounds. Reduction at centers other than carbon, nitrogen, or oxygen may have been less systematically developed but is applicable none-the-less to a wide range of inorganic and organometallic substrates. To catalog all the different reactions in which main-group metal hydrides have been reported to engage lies beyond the scope of the present review. Instead, we present no more than an *overview* of the essential chemistry, the main features of which are illustrated by representative examples. Applications of certain reactions will be signaled, but we do not pretend to record more than a fraction of the exploitable features, either established or attributed.

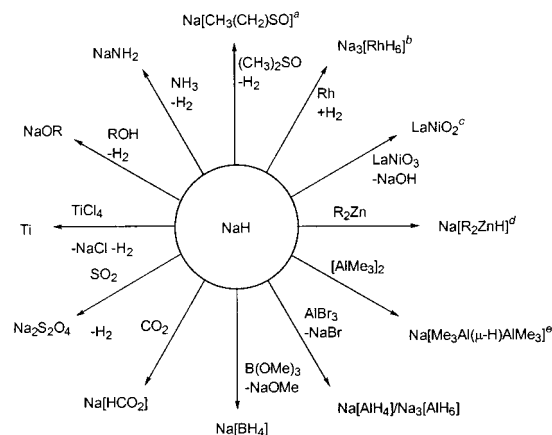
Scheme 2 takes as an example a mixed hydride in which hydrogen and a second ligand L compete for the coordination of a main-group metal M, and indicates the characteristic reaction pathways open in varying degrees to such a compound. Some of these reactions are then exemplified in Schemes 3–7, which depict representative chemical properties reported for the binary hydrides NaH ^{9b,e} and $[\text{GaH}_3]_n$ ^{13,60} and for the mixed hydrides $\text{Me}_3\text{N}\cdot\text{AlH}_3$,^{12,140} $[\eta^3\text{-HB}(3\text{-Bu}'\text{pz})_3]\text{BeH}$,¹⁴⁷ and $[\eta^3\text{-HB}(3\text{-Bu}'\text{pz})_3]\text{ZnH}$.¹⁴⁸ The chemistry of a mixed hydride with the general formula L_nMH is distinguished by reactivity of four main types, namely, (a) homolytic cleavage of the M–H bond, (b) heterolytic cleavage of the M–H bond, usually in the sense M^+H^- , (c) metathesis reactions of the ML_n fragment preserving intact the M–H bond, and (d) coordinative saturation of the metal center through aggregation or complexation.

Scheme 2. Typical Reactions of a Main-Group Metal Hydride $\text{L}_n\text{M}-\text{H}^a$



^a A, A' = acid/unsaturated substrate; E = metal or nonmetal; L, L' = ligand; R = organic group.

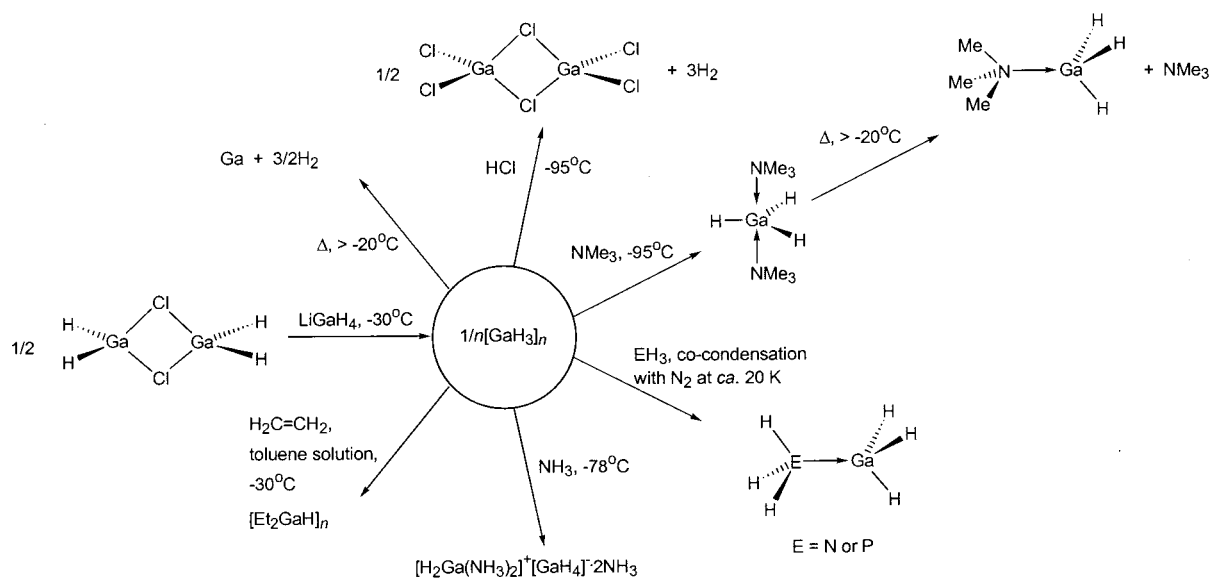
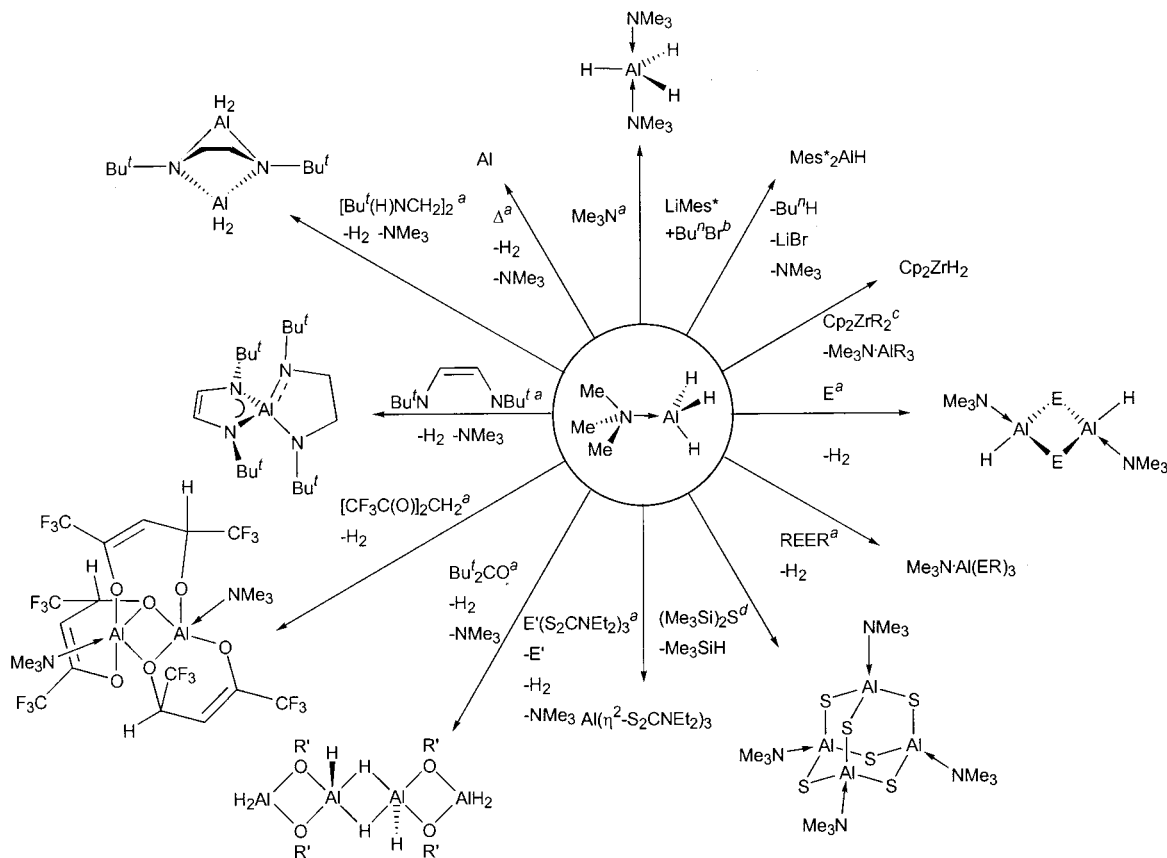
Scheme 3. Some Typical Reactions of NaH



^a Reference 582. ^b Reference 602. ^c Reference 593. ^d Reference 157. ^e Reference 242.

A. Homolytic Cleavage of the M–H Bond and Decomposition

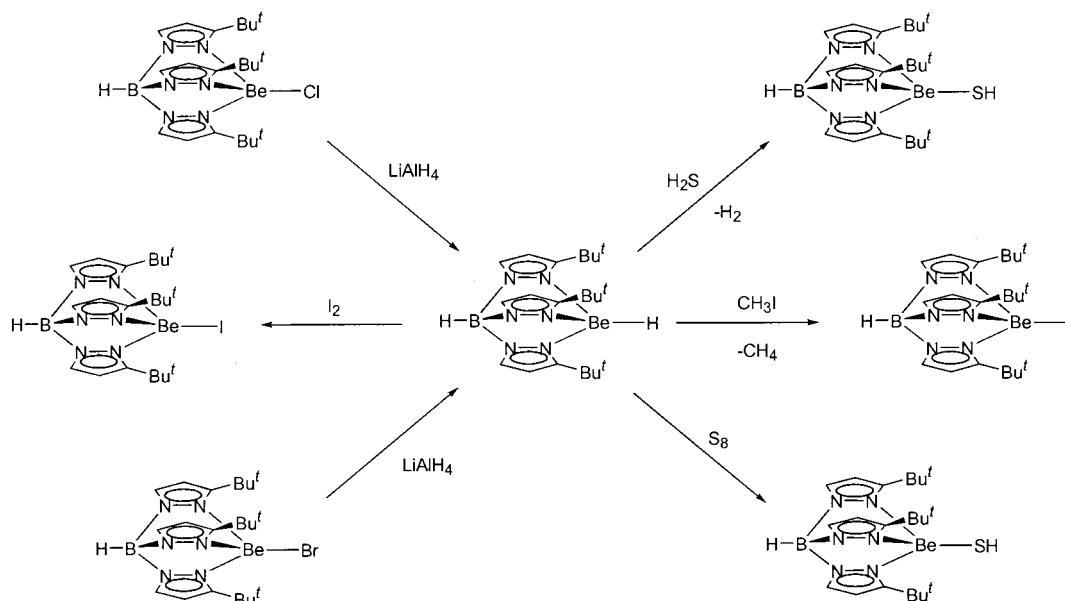
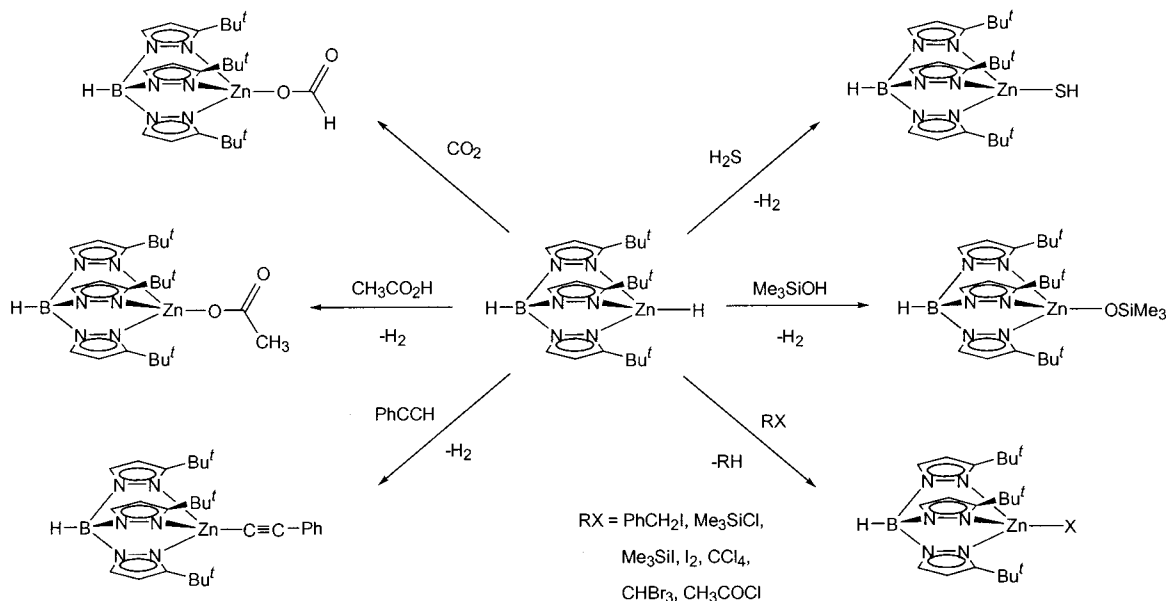
As noted in section IV.A, M–H bonds are not particularly weak and homolytic cleavage is normally opposed by a substantial energy barrier. Indeed, M–H bonds are marginally stronger than M–C bonds. Yet rupture of the M–H bond with the formation of the metal or a lower valent derivative of the metal, e.g., ML_n , is a reaction path more or less readily taken than the corresponding path, say, for a compound of the type L_nMCH_3 . In that the H–H bond energy is about 88 kJ mol^{-1} greater than the mean C–C bond energy, thermodynamics obviously play a part in dictating the relative thermal stabilities of compounds such as GaMe_3 and $[\text{GaH}_3]_n$,^{11,13} but major kinetic differences are also apparent. Firm mechanistic information is scarce, but there is reason to believe that decomposition of $\text{L}_n\text{M}-\text{H}$, unlike that of $\text{L}_n\text{M}-\text{CH}_3$, is likely to be *associatively* activated and dependent therefore on the ability of hydrogen to form at least a transient bridge between two M atoms. Accordingly, the thermal stability of L_nMH can be controlled to some extent by varying the electronic and spatial design of L so as to limit or enhance the acceptor action of M.

Scheme 4. Preparation and Reactions of Gallane⁶⁰Scheme 5. Some Reactions of the Alane Complex $\text{Me}_3\text{N} \cdot \text{AlH}_3$ ($\text{Mes}^* = 2,4,6\text{-Bu}^t\text{C}_6\text{H}_2$; $\text{R} = \text{Organic Group}$; $\text{R}' = \text{CHBu}^t_2$; $\text{E} = \text{Se or Te}$; $\text{E}' = \text{As or Sb}$)

^a References 12 and 140. ^b Reference 598a. ^c Reference 598b. ^d Reference 598c.

Only with a heavy metal atom which forms weak bonds to hydrogen, while achieving an 8-electron valence shell, does homolytic fission compete effectively with other modes of reaction. Such is the case, for example, with tin hydrides, the reactions of which commonly carry the hallmarks of radical intermediates. The net effect may be oxidative addition to an unsaturated substrate A, with insertion of A into the M–H bond, as in ‘hydrostannylation’

reactions.⁵⁴⁸ In practice, however, this type of reaction is more likely to proceed initially by *concerted* addition of the M–H moiety to A in a way that reflects its polarity. A very recent development challenges the supremacy of organotin hydrides as radical reagents in this area of synthetic organic chemistry. Oshima et al. report that dichlorogallane, HGaCl_2 , also acts as an efficient radical mediator which has been successfully exploited, for example, (i) for the radical

Scheme 6. Formation and Some Reactions of the Beryllium Hydride $\text{Tp}^{\text{Bu}^t}\text{BeH}^{147}$ **Scheme 7. Some Reactions of the Zinc Hydride $\text{Tp}^{\text{Bu}^t}\text{ZnH}^{148}$** 

reduction of haloalkanes to alkanes and (ii) for the radical cyclization of haloacetals to substituted furans.⁵⁸³

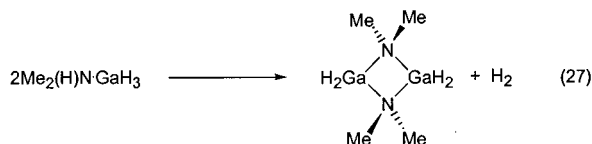
Thermal decomposition is of practical importance on two counts, namely, (a) as a source of H_2 and (b) as a source of the metal or one of its binary compounds.

(a) The release of elemental dihydrogen suggests the use of the hydride as a compact and relatively safe means of storing, transporting, and delivering hydrogen as a fuel. Thus, the use of a metal hydride for hydrogen generation in man-portable fuel cells has been identified as having significant promise to replace batteries in specific applications.^{378,584} One test assembly has involved the hydrolysis of solid LiH^{585a} and another the hydrolysis of CaH_2 in a hydrogen-fueled air-breathing PEM fuel cell.^{585b}

(b) Decomposition may be of strategic value too for the solid product it delivers, often the metal itself or

a binary compound of the metal in a pure state. In this context, hydrides have attracted considerable attention as source materials for the metals or for semiconductors such as the III–V compounds, typically required at a high level of purity and in the form of thin films to be formed epitaxially on a suitable substrate.⁵⁸⁶ As a prospective leaving group, particularly in chemical vapor deposition (CVD) processes, the hydride ligand has much to commend it:¹² it engages normally in only weak intermolecular interactions (thereby favoring volatility); it forms thermally labile bonds with the metals; decomposition of the metal derivatives yields in H_2 a highly volatile coproduct unlikely to enter into further reactions with the solid product; and there is little opportunity for the formation of intermediate decomposition products likely to impair the purity of the solid product (cf. the behavior of some organometallic precursors). Neutral complexes of alane and gallane

have been investigated in some detail for their performance as CVD precursors.^{12,140,587} The weakest bond in such a complex is almost certain to be the coordinate link between the metal and the donor atom of the Lewis base, so that 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 such as GaN—a promised land of much recent research—unless there is a mechanism for elimination of H_2 or some other simple molecule to take place, as in eq 27, thus permitting a normal covalent linkage to be established between the metal and the donor atom.

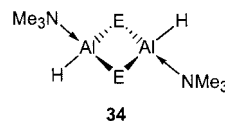


Nevertheless, several tertiary amine complexes of alane—most notably $\text{Me}_3\text{N}\cdot\text{AlH}_3$ and $\text{Me}_2\text{EtN}\cdot\text{AlH}_3$ —have been successfully used to deposit aluminum from the gas phase for the growth of GaAlAs, AlGaN, and Al-containing heterostructures, or for the metalization of semiconductor devices.^{587,588} Thermal decomposition of such complexes in solution also offers a means of producing nanometer-sized aluminum powders.⁵⁸⁹ By contrast, the inferior thermal stabilities of the corresponding gallane complexes make them less viable as sources of gallium, while the properties reported to date offer little promise that indane complexes can be exploited in this way.⁵³⁴ The complex quinuclidine $\cdot\text{GaH}_3$ appears to be the best prospect for deposition of gallium: it is long-lived at normal temperatures and does not decompose at temperatures below 100 °C.¹⁴⁰ Exploratory studies suggest that it may indeed be used with advantage as the gallium source for the growth of thin films of GaAs and GaSb.⁵⁹⁰

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 focusing on the interaction of $\text{Me}_3\text{N}\cdot\text{AlH}_3$ with hydroxyl-free oxidized silicon surfaces under UHV conditions indicate that the metal center expands its coordination shell by binding as a pentacoordinated species $\text{Me}_3\text{N}\cdot\text{AlH}_3(\text{O}=\text{})$, where $\text{O}=\text{}$ denotes a surface oxygen center, with a higher partial pressure of the alane resulting in the formation of a hydride-bridged species $\text{H}_2\text{Al}(\text{NMe}_3)-(\mu\text{-H})_2\text{AlH}_2(\text{O}=\text{})$.^{140c} On the other hand, dissociative adsorption occurs with $\text{Me}_3\text{N}\cdot\text{GaH}_3$ under similar conditions yielding the four-coordinated species $\text{H}_3\text{-Ga}(\text{O}=\text{})$.

A single-source precursor to a III–V or other binary compound ME needs then to have a strong bond between M and E atoms or at least facile access to an intermediate of this sort. In this respect, the neutral gallane derivatives $[\text{H}_2\text{GaNH}_2]_3$,^{178,591} $[\text{HGa}(\text{Cl})\text{N}_3]_4$,⁴⁹³ and $[\text{H}_2\text{GaN}_3]_n$ ⁴⁹³ show distinct promise as precursors to gallium nitride. Thus, pyrolysis of powdered samples of $[\text{H}_2\text{GaNH}_2]_3$ under a variety of conditions leads to nanocrystalline gallium nitride

with neither the pure wurtzite nor 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 structure of the precursor (*q.v.*).¹⁷⁸ The polymeric imido derivative $[\text{HGaNH}]_n$, formed as an intermediate in the decomposition of $[\text{H}_2\text{GaNH}_2]_3$ under rather different conditions, namely, in supercritical ammonia,⁵⁹² can also be converted to nanocrystalline GaN. Similar control may well determine the unusual morphology and microstructure reported for the crystalline samples of GaN delivered by the decomposition of $[\text{H}_2\text{GaN}_3]_n$.⁴⁹³ Other newly reported compounds include $[\text{H}_2\text{ME}(\text{SiMe}_3)_2]_3$ ($\text{M} = \text{Al}$, $\text{E} = \text{P}$,⁴⁸⁷ $\text{M} = \text{Ga}$, $\text{E} = \text{P}$ or As ⁴⁸⁶) and $\text{H}_2\text{AlAs}(\text{SiMe}_3)_2\cdot\text{NMe}_3$,⁴⁸⁷ which also undergo decomposition; in this case the reaction proceeds with the elimination not of H_2 or N_2 but of Me_3SiH and formation of nanocrystalline samples of the relevant III–V compound ME, albeit at widely different temperatures according to whether $\text{M} = \text{Al}$ or Ga and at the cost of some contamination associated with competing decomposition pathways. Compounds such as $[\text{Me}_3\text{N}\cdot\text{Al}(\text{H})\text{E}]_2$, prepared by the reaction of the elemental chalcogen $\text{E} = \text{Se}$ or Te with $\text{Me}_3\text{N}\cdot\text{AlH}_3$ (see Scheme 5) and having the structure **34**, may well function as a source of the binary metal chalcogenide, a possibility that is still under investigation.^{140c}



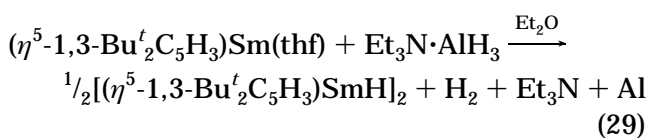
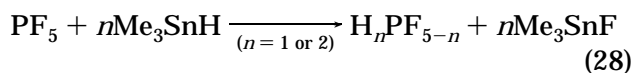
B. Heterolytic Cleavage of the M–H Bond

Polarization in the sense $\text{M}^{\delta+}-\text{H}^{\delta-}$ means that most main-group metal hydrides are typically real or latent sources of the hydride anion, at once one of the most powerful bases and reducing agents known. According to the degree of polarization, heterolytic cleavage of the M–H bond may then be brought about in one of three ways: (a) through nucleophilic substitution, (b) through oxidative addition to an unsaturated substrate (*q.v.*), and (c) through protonolysis, sometimes by Brønsted acids as weak as $(\text{CH}_3)_2\text{SO}$.⁵⁸² Herein lie the principal seeds of the reducing, metalating, activating, or drying action for which the main-group metal hydrides are best known (see Schemes 3 and 5, in particular). While this action has usually been confined to solution chemistry, the reducing power of an alkali-metal hydride can also be harnessed in solid-state reactions, as exemplified by the use of NaH in the topotactic reduction of the nickel(III) perovskite LaNiO_3 to the highly metastable nickel(I) phase LaNiO_2 .⁵⁹³

Many and well-known are the uses of alanes, often in the form of adducts with ethers or amines or as hydrido complexes (particularly LiAlH_4 and $\text{Na}[(\text{CH}_3\text{OC}_2\text{H}_4\text{O})_2\text{AlH}_2]$) as powerful and more or less selective reducing agents for both organic and inorganic

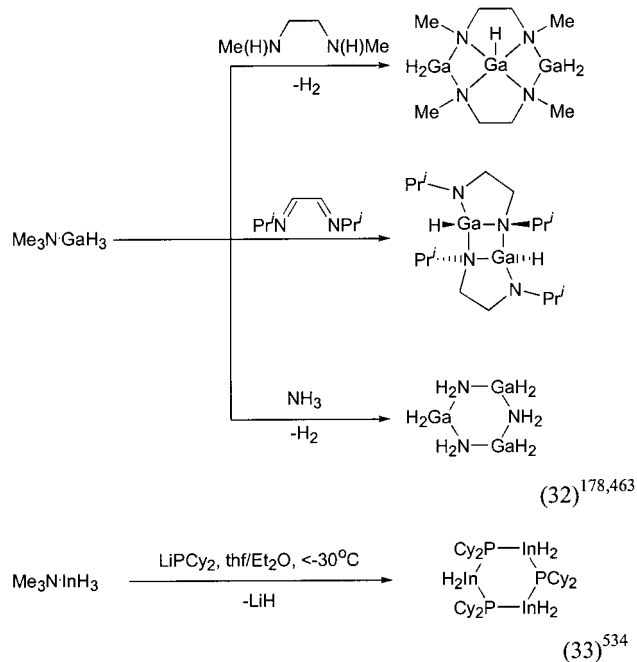
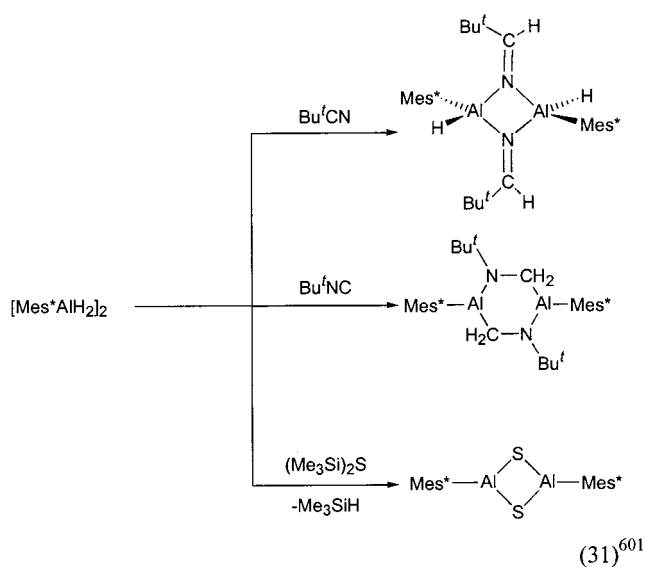
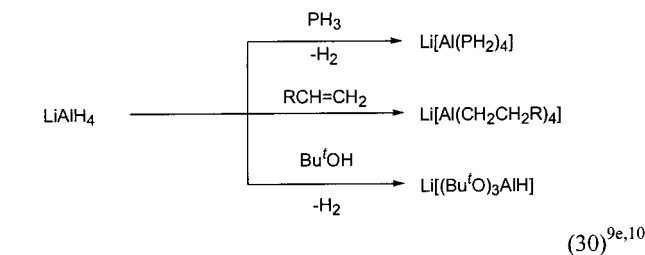
compounds (see Scheme 5, for example).^{10,154,155,367,582} Of the various groups open to reduction in organic compounds, carbonyl groups have been the principal targets, but other potential reaction centers include carbon-halogen, C=C, epoxide, -CN, -NO₂, and sulfur functionalities. By contrast, rather little attention has so far been paid to the reducing properties of gallium and indium hydrides. It is noteworthy therefore that preliminary studies should find gallane complexes to be milder, more selective reducing agents than similar alane complexes.^{140c,594} For example, Me₃N·GaH₃ selectively reduces the carbonyl group in 4-BrC₆H₄COBr, whereas quinuclidine·AlH₃ reduces not only this group but also the adjacent C-Br bond. Whether indium hydrides such as HInCl₂(thf)_n¹⁵⁸ or LiInH₄⁵⁹⁵ offer any major advantages over their aluminum and gallium counterparts has yet to be demonstrated. More convenient in many ways are the zinc hydride complexes of the type M[R₂ZnH], where M is an alkali metal and R an organic group.¹⁵⁷ as noted earlier, these are powerful yet selective agents for the reduction of the carbonyl group in esters and amides, as well as aldehydes and ketones. Just how selective they may be is attested by the 1,2-reduction of α,β-unsaturated carbonyl compounds, the regioselective ring-opening reduction of epoxides, and the chemoselective reduction of aldehydes in the presence of ketones. By contrast, tin hydrides are more prone to react homolytically, although there are circumstances in which they function as 'hydride' sources (*q. v.*)^{9e,224,548}

From the inorganic or organometallic standpoint, the hydrides are exploited primarily as hydride sources, as in the formation of nonmetal and d- or f-block metal hydrides (see, for example, eqs 28⁵⁹⁶ and 29⁵⁹⁷).



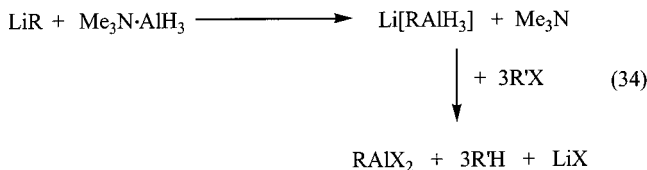
The lability of the M-H bond can also be turned to advantage to bring about metalation and hydro-metalation reactions, typically by protonolysis or oxidative addition.⁵⁹⁸ Representative examples are included in Schemes 5-7 and also in eqs 30-33. A characteristic feature is the addition of the M-H fragment across CC, CN, and CO multiple bonds in what will often be the first stage of reduction of these units (see eqs 30-32, for example). The reaction is seldom fast but highly susceptible to the precise natures of the reagents.^{9e} Mechanistic details are generally sparse, but addition is most likely to proceed through a four-center transition state similar to that invoked for hydroboration, so that the identity of the product reflects the polarization of both the M-H and multiple bonds (witness, for example, the addition of Tp^{Bu}ZnH to CO₂ in Scheme 7).

Access to a metal hydride being gained more often than not from the corresponding halide, metathesis in the reverse sense might seem to be of little profit.



Yet where the particular target is an aluminum halide, hydride-to-halide conversion may offer distinct advantages. A case in point is provided by the organoaluminum halides R_nAlX_{3-n} (X = halogen, n = 1 or 2) and particularly where the organic group is a sterically encumbered one in what are key precursors to a variety of compounds with unusual bonding and/or structures.⁵⁹⁹ Such compounds are often difficult to make and purify following the direct reaction of an organolithium or Grignard reagent with the parent aluminum halide, mainly as a result of the formation of anionic complexes of the type

$[R_nAlX_{4-n}]^-$ in these circumstances. The problem is much less likely to arise if an organoaluminum hydride is first formed and then made to exchange hydrogen for halogen with an organic or organosilicon halide, as in eq 34, for example.



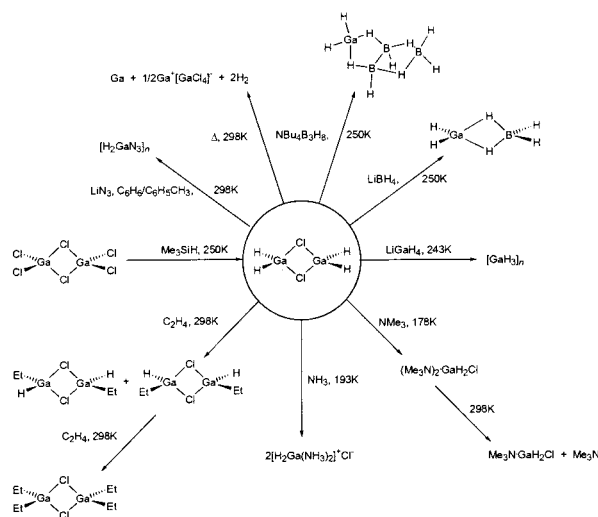
e.g. $R = 2,4,6\text{-Bu}^t_3\text{C}_6\text{H}_2^{507}$ or a terphenyl ligand such as $2,6\text{-Mes}_2\text{C}_6\text{H}_3$, $2,6\text{-Trip}_2\text{C}_6\text{H}_3$, or $2,4,6\text{-Ph}_3\text{C}_6\text{H}_2$; 479,600 $R'X = Me_3SiCl$

Reactions of $LiAlH_4$ or alane adducts with transition-metal and actinide compounds are prone to yield mixed-metal derivatives in which aluminum is linked to the d- or f-block metal through one or more hydrogen bridges.^{8,248,495,496} Analogous gallane and indane derivatives have yet to make an appearance, although the zinc tetrahydrogallate complex ($pmdeta$) $Zn(\eta^1\text{-GaH}_4)Cl$ ($pmdeta = Me_2NC_2H_4N(Me)C_2H_4NMe_2$) has been described.⁴⁰⁸

C. Metathesis Reactions Preserving the M–H Bond

In principle, mixed-metal hydrides of the type $L_n\text{-MH}$ may undergo a variety of reactions in which the supporting ligands L are replaced while the $M\text{-H}$ bond remains a spectator. That this can in fact be achieved in practice is demonstrated by some of the reactions of monochlorogallane, $[H_2GaCl]_n$,^{12,13} as set out in Scheme 8. On the other hand, the reactivity of the $M\text{-H}$ bond is apt to intrude by offering alternative reaction channels, and the reactions tend to be restricted to those involving metathesis at the hands of reagents of minimal acidic or oxidizing character, e.g., BH_4^- or N_3^- . Even then, it is noteworthy that although azidogallane, $[H_2GaN_3]_n$, can be prepared by metathesis between $[H_2GaCl]_n$ and LiN_3 , it is formed more easily and more efficiently

Scheme 8. Preparation and Some Reactions of Monochlorogallane^{13,493}



via $[Cl_2GaN_3]_n$ with hydride replacing chloride ligands only in the final stage.⁴⁹³ Where mixed hydrides are required, this is likely to be the preferred strategy.

D. Coordination Chemistry: Aggregation and Complexation

The characteristic polarization $M^{\delta+}\text{-H}^{\delta-}$ of $M\text{-H}$ bonds carries the implication that the metal is open to coordination by suitable neutral or anionic bases; in the absence of such a reaction partner, the molecule L_nMH is liable to aggregate in order to achieve a closer approach to electroneutrality. This has been a recurring theme in preceding sections treating the preparation, physical properties, and chemistry of the hydrides formed by the metals of groups 1, 2, 12, and 13 (see sections III.B, IV.A, and IV.B). Particular emphasis has been given to the role of complexation in modifying the properties of metal hydrides of this sort, e.g., with regard to thermal stability, nuclearity, solubility, and reactivity. As noted and illustrated previously, the character of the product is strongly influenced by such factors as the strength, denticity, detailed architecture, and spatial requirements of the base (see, for example, sections II.C, IV.B, and V.B). On the other hand, the modest electron-withdrawing properties of hydrogen as a ligand combine with an 8-electron valence shell to deny the group 14 or group 15 metal atom significant acceptor character in hydrides such as Bu_3SnH or Mes_2SbH .²⁴⁰

As sources of hydride anions, the hydrides of the more electropositive metals of groups 1 and 2 may also act as bases toward appropriate acidic substrates to form hydride complexes, e.g., $Na[Me_3Al(\mu\text{-H})\text{-AlMe}_3]$,²⁴² $[(Et_2O)Na]_2[Et_2Be(\mu\text{-H})_2BeEt_2]$,²⁴¹ and $M[R_2\text{-ZnH}]$ ($M = Li$ or Na ; $R =$ alkyl group).¹⁵⁷ Similar principles apply to the formation of anionic transition-metal hydride derivatives, e.g., $M[(\eta^5\text{-C}_5\text{Me}_5)_2\text{-ZrH}_3]$ ($M = Li$ or K),⁶⁰² although solution methods of synthesis are more likely to employ a hydride source like $NaBH_4$ or $LiAlH_4$ rather than the binary hydride.^{1,2} The acidic substrate may be no more than a formalism or at best an intermediate, but solid-state methods, typically involving the sintering of a powdered mixture of a group 1 or 2 metal hydride with a transition metal under a high pressure of hydrogen (up to 160 bar), have also given access to a wide range of ternary or quaternary transition-metal hydrides.⁶⁰³ With the general formula $M'_xM''_yH_z$ ($M' =$ group 1 or group 2 metal; $M'' =$ transition metal), these vary from insulators containing more or less discrete $[M''H_z]^{n-}$ anions, e.g., $[FeH_6]^{4-}$,^{6,603} $[MH_6]^{3-}$ ($M = Rh$ or Ir),⁶⁰³ and $[MH_4]^{2-}$ ($M = Pd$ or Pt),⁶⁰³ to metals, e.g., Ba_2PdH_4 .^{603,604} The puzzling variety of compositions, coordination geometries, and electron counts taxes our understanding of the electronic structures,^{604,605} but the highly polarizable character of the H^- anion appears to be a key factor. Under appropriate conditions, even the group 13 metal hydrides can be made to trade hydride anions, as revealed, for example, by the complexes $[H_2AlL]^+[AlH_4]^-$ ($L = pmdeta$ or $Me_4Cyclam$)⁴¹⁸ and $[H_2Ga(NH_3)_n]^-$ $[GaH_4]^-$.^{13,60} However, the reduced basicity of the hydride ligand in these and other, more overtly

molecular metal hydrides will often favor hydrogen bridging {found, for example, in $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Y}(\text{Cl})(\mu\text{-H})\text{AlH}_2\text{-NEt}_3]_2$ ⁸ and $(\eta^6\text{-1,3,5-Me}_3\text{C}_6\text{H}_3)\text{Cr}(\text{CO})_2(\eta^2\text{-HSnPh}_3)$ ²⁵⁰} more than outright hydride transfer.

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