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Lewis Base Adducts of Heavier Group 13 Halohydrides – *Not Just Aspiring Trihydrides!*

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The chemistries of the heavier group 13 halohydrides have been scarcely studied relative to those of their trihydride and trihalide counterparts. This short review summarises the literature concerning these compounds and seeks to highlight their distinct reactivities such that they may find increasing application in other fields of science.

Introduction

The binary hydrides of the metallic group 13 elements have been a source of fundamental interest to main group chemists for over 80 years.[1] Despite the early studies of uncoordinated alane (AlH_3)[2] and gallane (GaH_3),[3] in 1947 and 1963 respectively, and the plentiful studies of the Lewis base adduct chemistries of both,[4] relatively little attention has been given to partially halogenated variants, e.g. the mono- and dihalogenometallanes; MXH_2 and MX_2H, where M = metallic group 13 metal and X = halogen. Likewise, while the related chemistry of indane (InH_3) is still in its infancy,[5] very little attention has been paid to the chemistries of haloindanes.[6]

It may be argued that the relative ease of preparation of metallic group 13 metal trihydrides and trihalides[1b,2,3] vs. the difficulties involved in isolating mixed species has contributed largely to the imbalance in study; however, a second factor has been the perception that such species possess little synthetic use beyond those already satisfied by the aforementioned MH_3 or MX_3 complexes. As detailed herein, we strongly believe this is not the case and that halohydrides are valid targets in their own right with properties that differ from and, for some applications, are superior to metallic group 13 trihydrides. We hope this short review will encourage researchers to apply them in their field of science and/or materials.

Aspects of Note

Stability

It is well known that the stability of group 13 metal hydrides diminishes rapidly as the group is descended[7] such

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that there are a few contentious[3,8] reports of thallium hydrides.[9] Although this decrease in stability is commonly attributed to a decline in metal–hydride bond enthalpies,[7] this cannot be the sole causative factor as the metal–carbon bond enthalpies of the respective trimethyl species;[1b] $AlMe_3$, $GaMe_3$, $InMe_3$ and $TlMe_3$ are without exception lower than their metal–hydride counterparts and yet all four compounds are known (Table 1). Rather, aggregation of the metal trihydrides by hydride-bridging is thought to provide a low energy pathway to reductive dehydrogenation with the deposition of group 13 metal.[7] By contrast, methyl bridging and aggregation with the elimination of ethane is not favoured for the trimethyl species. Furthermore, hydride bridging is promoted by declining M–H bond enthalpies and increased metallic radii, as per the heavier group 13 elements. Consistent with this notion is the effectiveness of strategies to isolate heavy group 13 hydrides by sterically enshrouding terminal hydrides using spatially bulky ligands.[10] This has been particularly successful for the isolation of rare indium trihydride complexes.[11]

Table 1. Comparative thermodynamic data for the M–H and M–C bond enthalpies of Lewis base free MH_3 and MMe_3. The M–H bond enthalpies of InH_3 and TlH_3 are based on theoretical calculations.[14]

	Al	Ga	In	Tl
Mean M–C bond enthalpy of MMe_3 [kJ mol^{-1}]	281	256	162	151
Mean M–H bond enthalpy of MH_3 (g) [kJ mol^{-1}]	287[12]	260[13]	225[14]	180[14]

Further to steric shielding of metal hydrides, two less established means of increasing metal–hydride bond stability are:

(i) the use of inductive effects, whereby hydrides are partially substituted by donors of greater electronegativity.[15] The success of this strategy is evidenced by the superior air and thermal stability of mono- and dichlorogallane species ($[GaClH_2(L)]$ and $[GaCl_2H(L)]$, L = Lewis base) relative to their gallane ($[GaH_3(L)]$) counterparts (Figure 1).[15b,16]

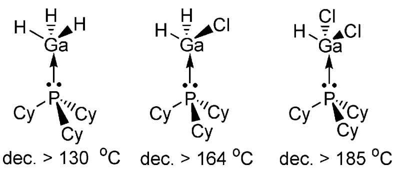


Figure 1. The decomposition temperatures of a series of gallium chlorohydrides.[15b,16]

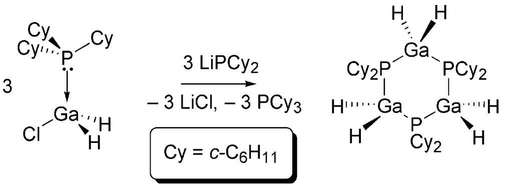
(ii) the coordination of more Lewis base donors. The thermal decomposition of Lewis base group 13 trihydride adducts is generally thought to proceed by dissociation of the Lewis base. Thus, bis adducts are more stable than their respective mono adducts.

The substitution of hydrides by halide ligands, as per halohydrides, accomplishes stabilisation type (i) and further enables type (ii) stabilisation. Thus, the outcome of the partial hydride substitution by halides is a hydride species of superior thermal and air stability, with increased Lewis acidity and a greater M–H bond enthalpy.

Reactivity in Brief

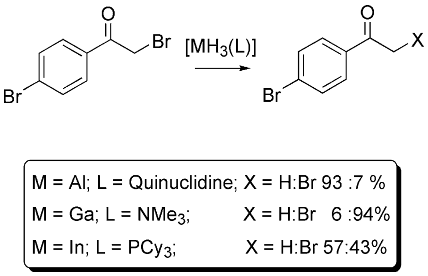
A separate, more comprehensive section on reactivity is included as Section 3.

(i) It is widely accepted that *p*-, *d*- and *f*-block metal halides can be functionalised by salt-elimination using *s*-block alkyls, aryls, organoamides and organooxides, as-well-as a multitude of anionic group 14–16 ligands. Although the respective metal hydride complexes may undergo similar reactions, the elimination of *s*-block hydrides is less favourable, thereby reducing the synthetic utility of group 13 hydrides. Several group 13 hydride derivatives have been accessed using group 13 halohydrides. One example can be seen in Scheme 1 where a phosphide functionalised trimeric gallium dihydride is synthesised from the reaction of a monochlorogallane and a lithium phosphide.[15b] It is noteworthy that protolytic derivatisation is not considered a useful route to mono- and disubstituted group 13 hydrides using trihydride starting materials due to poor selectivity and the isolation of trisubstituted species.[17]



Scheme 1. The synthesis of a phosphide functionalised trimeric gallium dihydride using a monochlorogallane precursor.[15b]

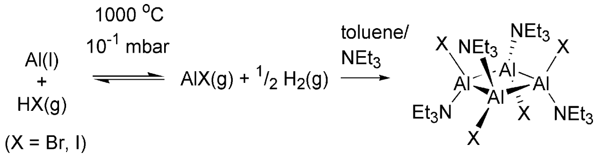
(ii) Halide ligands alter the polarity and nature of the metal–hydride bond by the aforementioned inductive effects. This is amply demonstrated by the variation in metal–hydride IR stretching absorptions, which indicate strengthening of the bonding interaction with increased halide substitution of hydrides (see Section 2).[15b] Accordingly, one might reasonably expect the hydrometallation character of halohydrides to be distinct to that of trihydrides. This is



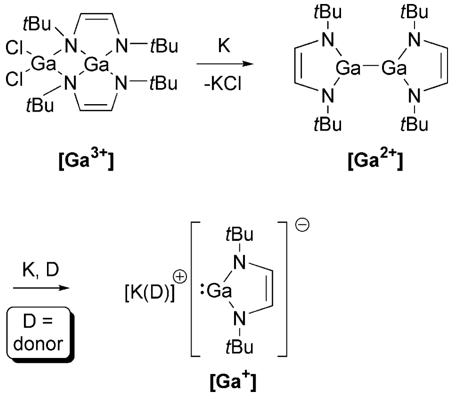
Scheme 2. A representative reaction of an α-bromomethyl ketone with Lewis base adducts of alane, gallane and indane. The disparate hydrometallation outcomes (see X in legend) are invoked by changes in M–H bond enthalpy and metal electronegativity.[18]

true of Lewis base adducted alanes, gallanes and indanes which differ in terms of hydrometallation character based on the Lewis acidity of the MH_3 unit. This acidity in turn results from differences in metal electronegativity and M–H bond enthalpy (Scheme 2).[18] To the best of our knowledge, there are no reported studies of the hydrometallating character of halogenated group 13 hydrides with which to contrast the reactivities of trihydrides.

(iii) The chemistry of low-valent group 13 metal complexes has received considerable attention over the past decade. Early methods for the preparation of such species involved the pioneering low temperature handling of metastable monovalent halides, such as $Al^{I}Br$ and $Ga^{I}Cl$, by Schnöckel and co-workers (Scheme 3).[19] Despite the bountiful success of this route, today the most widely used method for the preparation of low-valent complexes is the reduction of trivalent halide coordinated precursors with alkali metals or magnesium (Scheme 4).[20] An alternative to these approaches is the reductive dehydrogenation of substituted hydride complexes.[6b,21] This method has been successful for the formation of both low-valent gallium (Scheme 5) and indium complexes, providing an access route to low-valent species that has not, as yet, been successful for trihydride congeners. This access route to subvalent group 13 halide chemistry complements the Schnöckel methods, particularly for the heavier group 13 elements where lower oxidation states become more favourable.[1b]

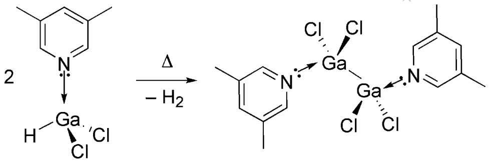


Scheme 3. An example Schnöckel preparation of a low-valent aluminium(I) complex.[22]



Scheme 4. An example preparation of Ga^{I} and Ga^{II} complexes by reductive dehalogenation of a Ga^{III} complex.[23]

Section 3 provides a more in-depth discussion of the reactivities of metallic group 13 halohydrides and their Lewis base adducts.



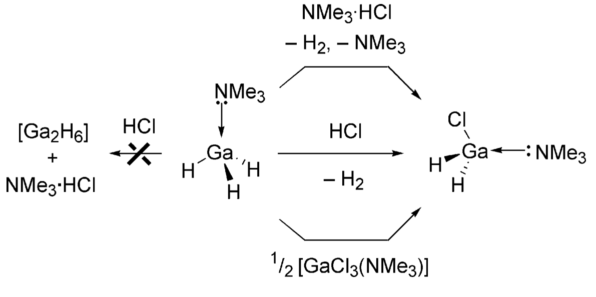
Scheme 5. An example preparation of a Ga^{II} complex by reductive dehydrogenation of a dichlorogallane.[21]

1. Known Complexes and Syntheses of Heavier Group 13 Halohydrides

There are relatively few preparations of metallic group 13 halohydrides in stark contrast to the numerous syntheses of aluminium and gallium trihydride species. The following overview concerns the reported preparative methods and is ordered in terms of the "relative" development of halohydrides. For this reason the discussion of gallium compounds precedes that of aluminium complexes.

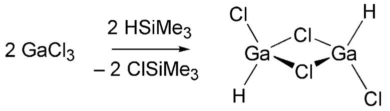
Gallium Halohydrides

Although it took until 1989 to confirm the structure of gallane as a dimer,[24] two distinct methods for the preparation of halogallanes were reported as early as 1965 by the groups of Greenwood[25] and Schmidbaur.[26] The former of these resulted from an attempt to isolate uncoordinated gallane ($\{GaH_3\}_n$) by the treatment of solid $[GaH_3(NMe_3)]$ with anhydrous hydrogen chloride gas. Instead of the anticipated ammonium salt ($NMe_3{\cdot}HCl$) and gallane this reaction afforded the monochlorogallane $[GaClH_2(NMe_3)]$ (Scheme 6). The dichloro- and bromogallane analogues were also prepared by the same method using 2 equiv. of hydrogen chloride and hydrogen bromide respectively.[25] The authors reported two further means of accessing halogenated gallanes; (i) the treatment of a tertiary amine adduct of gallane with a sparingly soluble trialkylammonium halide salt as a source of HX (Scheme 6), and (ii) hydride-halide ligand redistribution of Lewis base adducted gallane with a trihalide congener (Scheme 6). For the latter, it was observed that, whilst a half equivalent of the trihalide (to gallane) was sufficient to access monohalogenogallanes, greater than two equivalents of trihalide (to gallane) were required to produce the dihalogenated species.



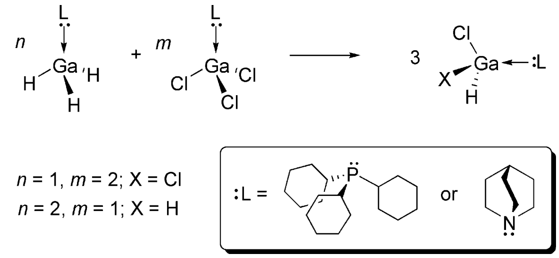
Scheme 6. The Greenwood preparations of chlorogallane.[25]

In the same year as the Greenwood report, Schmidbaur and co-workers reported the preparation of the uncoordinated dichlorogallane dimer ([{$GaCl_2H$}$_2$]) from the reaction of gallium trichloride with trimethylsilane (Scheme 7). The same group structurally characterised this compound along with its triethylphosphane adduct in 2002.[27] The preparation of the uncoordinated monochlorogallane dimer ({$GaClH_2$}$_2$) was achieved in 1988 by Downs and co-workers using the same preparative route with two stoichiometric equivalents of silane.[28]



Scheme 7. The Schmidbaur preparation of dichlorogallane.[26]

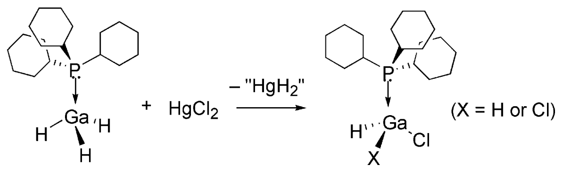
Since 1965, Schmidbaur in particular has published extensively on the chemistry of [{$GaCl_2H$}$_2$] and its use as a precursor to molecular halides,[27] chalcogenides[29] and pnictides.[21,27,30] By contrast, the synthetic routes disclosed by Greenwood have been employed limitedly, perhaps due to their requirement for thermally unstable gallane precursors. None the less, Raston[15b] and Gladfelter[15a] have independently reported on the application of Greenwood's redistribution pathway (Scheme 6) to access N- and P-donor adducts of mono- and dichlorogallane (Scheme 8). In contrast to Greenwood's original report,[25] which highlighted a requirement for excess gallium trihalide to access dichlorogallane complexes, both groups reported the formation of dichlorogallanes using a 1:2 stoichiometry of gallane to gallium trichloride.



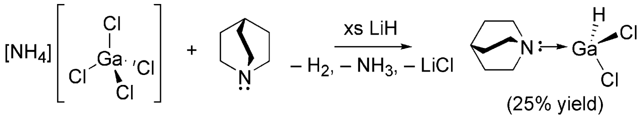
Scheme 8. The chlorogallane complexes of Raston (L = tricyclohexylphosphane)[15b] and Gladfelter (L = quinuclidine).[15a]

Further to this preparation, Raston utilised the direct treatment of phosphane stabilised gallane complexes with ethereal hydrogen chloride to access [$GaClH_2(PR_3)$] and [$GaCl_2H(PR_3)$].[15b] The same group added to the portfolio of halogallane syntheses with the use of mercuric chloride as a chlorinating agent (Scheme 9). Unfortunately this reaction demonstrates low selectivity, affording mixtures of products.

Gladfelter and co-workers have also added to the number of paths available to halogallanes with the successful preparation of quinuclidine complexed monochlorogallane using ammonium tetrachlorogallate, lithium hydride and free quinuclidine (Scheme 10).[15a] Despite the success of this method, it was subsequently shown to be lower yielding than the reaction of Lewis base adducts of gallane with Lewis base "free" gallium trichloride (Scheme 8; $GaCl_3$ replaces [$GaCl_3(L)$]), with **:**L added post redistribution. This "modification" of Greenwood's redistribution path[25] was both higher yielding and more rapid than the original redistribution synthesis (Scheme 6). The authors rationalised the increased rate of formation on the basis of coordination number at gallium, whereby chloride-hydride exchange is achieved more rapidly and cleanly at a three coordinate gallium centre.

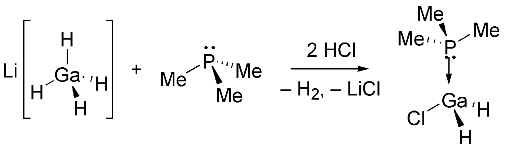


Scheme 9. A mercurial preparation of chlorogallane complexes from a gallane precursor.[15b]



Scheme 10. The low yielding preparation of [$GaCl_2H$(quinuclidine)] from ammonium tetrachlorogallate.[15b]

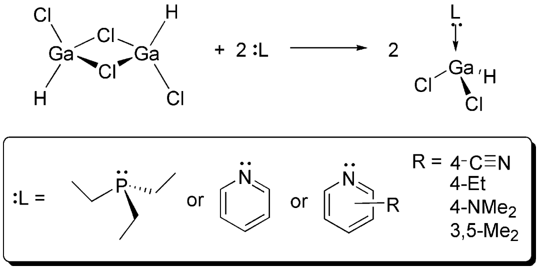
More recently Downs and co-workers have published the synthesis of a trimethylphosphane adduct of monochlorogallane accessed by reaction of $LiGaH_4$ with PMe_3 followed by two equivalents of hydrogen chloride (Scheme 11).[31] Attempts to prepare similar complexes using bulky primary amines under the same reaction conditions afforded the ionic gallane species [$GaH_2(NH_2R)_2$][Cl] (R = *t*Bu or *s*Bu), which were both characterised by single-crystal X-ray structure determination.[31] These complexes represent the first examples of structurally authenticated GaH_2^+ cations.



Scheme 11. The preparation of a trimethylphosphane adduct of monochlorogallane.[31]

Since their landmark synthesis of dichlorogallane,[26] Schmidbaur and co-workers have prepared several dichlorogallanes supported by pyridine[21,30a] or phosphane ligands[27] (Scheme 12) by addition of the free ligands to the dichlorogallane dimer. Many of these products have been the subject of reactivity studies (see Section 3).

During the pyridine studies it was noted that the Ga–N bonding contacts of 1:1 dichlorogallane adducts were between those of the respective gallane and gallium trichloride adducts of the same ligands.[30a] This is indicative of the stronger acceptor character of dichlorogallane relative to its



Scheme 12. The pyridyl and phosphanyl dichlorogallanes prepared by Schmidbaur and co-workers.[27,30a]

chlorine free relative. It is noteworthy that regardless of steric and electronic modulation of the pyridines by modification of 4-substituents (R = H, Et, C≡N or NMe_2) and steric imposition of *meta*-methyl substituents (R = 3,5-Me_2), the reaction outcomes were not altered and the Ga–H IR stretching frequencies were remarkably consistent (see Table 2, Section 2). However, the respective Ga–N contacts did indicate increased donor character in the sequence (R =) 4-NMe_2 > 3,5-Me_2 > 4-H > 4-C≡N.[30a]

Bis(phosphane) adducts of dichlorogallane were not reported during Schmidbaur's investigations, however corresponding to the successful quinuclidine studies of Gladfelter and co-workers,[15a] an uncommon five-coordinate bis(3,5-dimethylpyridine) adduct of dichlorogallane; $[GaCl_2H(3,5\text{-}Me_2Py)_2]$ was prepared and structurally characterised.[21,30a] Attempts to prepare a related gallane complex resulted in hydrometallation of the pyridine (see Section 3), again demonstrating the lower coordination preference of gallane.[21] Furthermore, although the related gallium trichloride species $GaCl_3Py_2$ (Py = pyridine) is ionic in composition; $[GaCl_2Py_4][GaCl_4]$,[32] the authors noted that there was no evidence for equilibration of $[GaCl_2H(3,5\text{-}Me_2Py)_2]$ with an ionic counterpart; $[GaH_2(3,5\text{-}Me_2Py)_4][GaCl_4]$. It could be reasoned that such a composition is sterically prohibited.

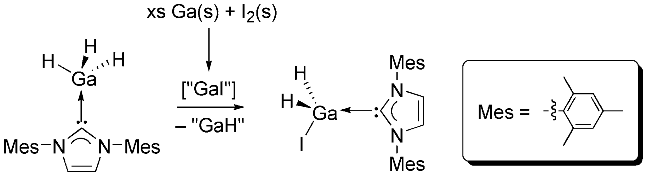
In 2003, an *N*-heterocyclic carbene (NHC) coordinated monoiodogallane was reported by Jones and Baker.[33] The reaction of $[GaH_3(IMes)]$ [IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] with a source of monovalent "$Ga^{I}I$", generated by the reaction of excess gallium with

Table 2. The reported IR M–H stretching absorbance(s) for Lewis base adducts of metallic group 13 halohydrides and analogous absorbances for related MH_3 species.

Compound	[a]IR ν M–H [cm^{-1}]	Reference	Related MH_3 IR ν M–H [cm^{-1}]	Reference
$[AlCl_2H(OEt_2)]$	1920	[40a,51a]	1801[h]	[64]
$[AlCl_2H(OMe_2)]$	1923[c]	[51a]	–	–
$[AlBr_2H(OEt_2)$	1912[c]	[40a]	1801[h]	[64]
$[AlH_2I(OEt_2)]$	1901[d]	[40a]	1801[h]	[64]
$[AlClH_2(thf)_2]$	1836 m, 1755 s[e]	[46]	1802[d] (one thf)	[65]
$[AlCl_2H(thf)_2]$	1838 vs, 1753 vs[e]	[46]	1802[d] (one thf)	[65]
$[AlBrH_2(thf)_2]$	1842 w, 1772 s[e]	[46]	1802[d] (one thf)	[65]
$[AlBr_2H(thf)_2]$	1848 vs, 1753 vs[e]	[46]	1802[d] (one thf)	[65]
$[AlH_2I(thf)_2]$	1782 m[e]	[46]	1802[d] (one thf)	[65]
$[AlHI_2(thf)_2]$	1796 sh, 1746 s[e]	[46]	1802[d] (one thf)	[65]
$[AlCl_2H\{O(CH_2)_5\}]$	1908[c]	[51a]	–	–
$[AlCl_2H\{O(CH_2CH_2)O\}]$	1785[d]	[51a]	1748[d]	[65]
$[AlCl_2H\{(CH_3OCH_2)_2\}]$	1835, 1770[d]	[51a]	–	–
$[AlClH_2(NEt_3)]$	1835, 1773[e]	[46]	1778[c]	[66]
$[AlCl_2H(NEt_3)]$	1866, 1812[e]	[46]	1778[c]	[66]
$[AlClH_2(quin)_2]$	1745 s[d]	[50]	1685 s[d]	[67]
$[AlClH_2(tmpH)]$[b]	1891 vs, 1831 vs[d]	[47]	1773 s[d]	[68]
$[GaCl_2H(py)]$	1970 s[d]	[30a]	–	–
$[GaCl_2H(3,5\text{-}Me_2Py)]$	1978 s[d]	[30a]	1822 s[d]	[30a]
$[GaCl_2H(3,5\text{-}Me_2Py)_2]$	1873 s[d]	[30a]	–	–
$[GaCl_2H(4\text{-}C{\equiv}NPy)]$	1977 m[d]	[30a]	–	–
$[GaCl_2H(4\text{-}NMe_2Py)]$	1979 m[d]	[30a]	–	–
$[GaClH_2(quin)]$	1882 s[f]	[15a]	1810	[69]
$[GaCl_2H(quin)]$	1946 s[f]	[15a]	1810	[69]
$[GaClH_2(quin)_2]$	1892 s[f]	[15a]	–	–
$[GaCl_2H(quin)_2]$	1852 m, 1817 w[f]	[15a]	–	–
$[GaClH_2(PCy_3)]$	1880 s[d]	[15(b]	1800 s	[16]
$[GaCl_2H(PMe_3)]$	1890 s[g]	[31]	1837 s, 1801 s[i]	[70]
$[GaCl_2H(PEt_3)]$	1930 s[c]	[27]	–	–
$[GaCl_2H(PPh_3)]$	1940 s[f]	[29b]	1880 s	[70]
$[GaCl_2H(PCy_3)]$	1920 s nm/1925 s[d]	[15b, 29b]	1800 s	
$[\{GaCl_2H\}_2\{PPh_2CH_2\}_2]$	1951 s[f]	[29b]	1800 s	[71]
$[GaH_2I(IMes)]$[b]	1863 s[d]	[33]	1780 s[d]	[6a]
$[InClH_2(IMes)]$[b]	1737 s	[6a]	1650 s	[6a]
$[InBrH_2(quin)_2]$	1707 s	[6a]	1640 s	[61]

[a] Relative intensity information and medium used provided where available. [b] tmpH = 2,2,6,6-tetramethylpiperidine, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene. [c] Liquid film. [d] Nujol mull. [e] Fluorolube. [f] KBr disk. [g] Raman spectrum. [h] Et_2O solution. [i] Benzene solution.

iodine, afforded [$GaIH_2$(IMes)] (Scheme 13).[33] This reaction was accompanied by the deposition of gallium metal and the evolution of a gas, presumably H_2 generated by the decomposition of a "Ga^IH" co-product. The direct reaction of [GaH_3(IMes)] with elemental iodine has not been reported to date (see aluminium studies below).

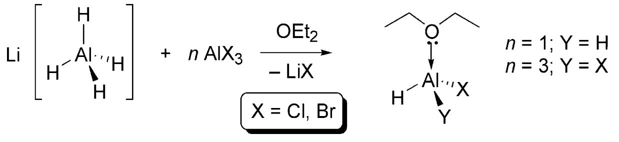


Scheme 13. The preparation of an NHC complex of iodogallane.[33]

Recently, Himmel and co-workers[34] have prepared the complex [$GaClH_2(NMe_3)$], previously reported by Greenwood and co-workers,[25] from the reaction of trimethylamine hydrochloride with [$LiGaH_nCl_{4-n}$], the latter prepared in situ from the incomplete reaction of gallium chloride with lithium hydride.

Aluminium Halohydrides

Despite the considerable interest in the coordination chemistry of alane of Wiberg,[35] Greenwood,[36] Brown[37] and Ruff,[38] amongst others, in the mid 1900s, it was not until 1973 that Lewis base adducts of haloalanes were structurally authenticated by Semenenko and co-workers (Scheme 14).[39]



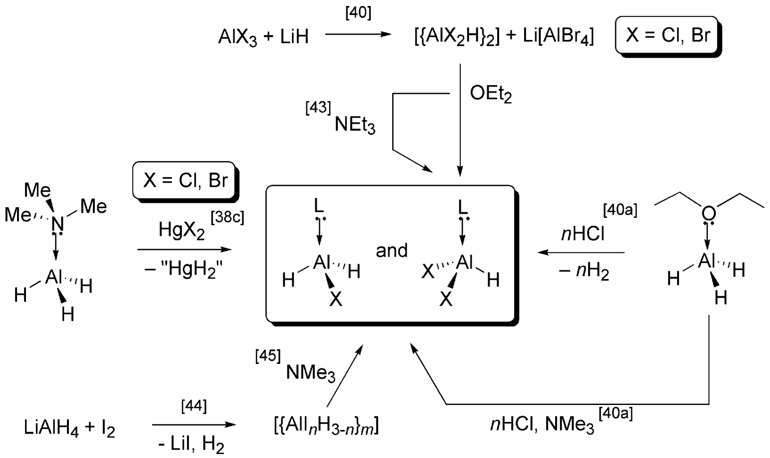
Scheme 14. The preparation of the first structurally characterised haloalanes.[38]

Prior to 1973 the groups of Wiberg[40] (1950s) and Ruff[38c,41] (1960s) had published reports of mono- and dichloroalanes, and Marconi and co-workers had reported extensively on the application of chloroalanes as olefin polymerisation co-catalysts during the mid to late 1960s.[42] The preparative routes used by these groups and others in the field are summarised in Scheme 15. Aside from the success of employing anhydrous hydrogen halides to halogenate alane, it is clear that the paths used to access haloalanes are distinct from those of halogallanes (see above). For instance, the reaction of silanes with aluminium trihalides does not feature while the selective preparation of haloalanes using mercurial halides[38] contrasts with the poor specificity reported by Raston and co-workers for the gallane counterparts.[15b]

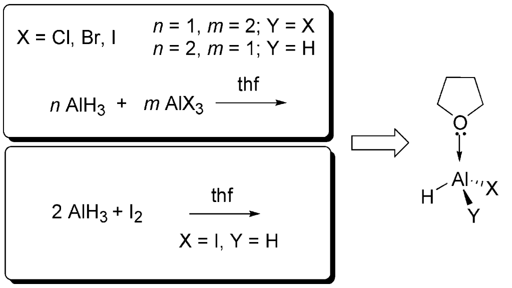
Schmidt and Flagg[46] reported the preparation of tetrahydrofuran (thf) supported chloroalane using the same synthetic route as Semenenko with thf as solvent (Scheme 14).[39] Interestingly, during this work, the authors also noted that halide-hydride redistribution could be accomplished using neutral aluminium trihalides in tetrahydrofuran (Scheme 16) [cf. Greenwood's redistribution preparation of halogallanes (Scheme 6)],[25] although no yields were reported. They also reported the direct treatment of alane with elemental iodine as a means of accessing thf coordinated iodoalanes (Scheme 16).[46] Despite the apparent success of Schmidt and Flagg's "redistribution" using neutral precursors, we know of only one report in which a thf adduct of a haloalane has been used as a synthetic reagent (see Section 3).[47]

The ring opening of cyclic ethers such as thf[48] to afford *n*-alkoxide complexes has long been a suspected decomposition path for metallic group 13 hydrides, albeit with limited precedent.[49] As such, there are very few group 13 metal hydride syntheses that use thf as a solvent. Attempts to repeat the thf studies of Schmidt and Flagg using acyclic ethers have been unsuccessful to date.[50]

The coordination number preference of aluminium (five- or six-coordinate), which is greater than that of gallium



Scheme 15. The haloalane syntheses reported by Wiberg, Ruff and Marconi during the 1950s and 1960s, and related preparations. References listed in square parentheses.[43–45]

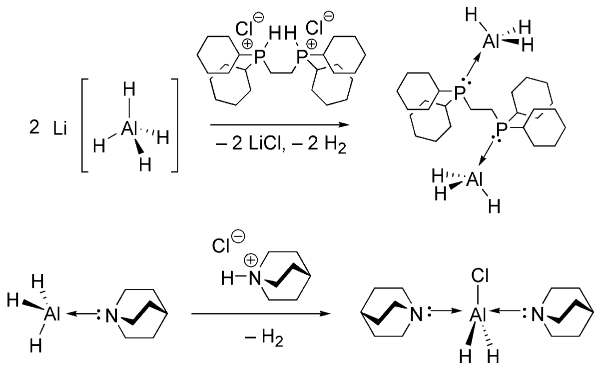


Scheme 16. The synthetic routes to haloalanes reported by Schmidt and Flagg.[46]

(four-coordinate) due to its lower electronegativity, complicates the equilibria established during aluminium halide-hydride redistribution. Furthermore, these equilibria are greatly perturbed by the partial introduction of other Lewis bases, such as tertiary amines or bidentate ethers,[51] which compete with the solvent for coordination of the metal centre. By contrast, it is likely that the successful stoichiometrically controlled ethereal preparation of haloalanes using coordinatively saturated tetrahydridoaluminate complexes, as reported by Wiberg,[40] Semenenko[39,52] and Schmidt and Flagg,[46] results from the superior capacity of the [AlH_4] anion to act as a source of hydride for halide-hydride exchange vs. neutral alane (AlH_3). Ruff has eported that tetrahydridoaluminate (AlH_4^-) reacts with mercurial compounds more rapidly than trimethylaminealane ([$AlH_3(NMe_3)$]) (Scheme 15),[38c] and that rates of reaction were slower still for *N*,*N*′-dimethylamidoalane ([$AlH_2(NMe_2)$]). This suggests a definite trend in reactivity with the number of associated hydrides.

In 1997 Raston reported the mixed alane-monochloroalane adduct of *N*-ethylmorpholine depicted in Scheme 17.[53] This unusual polymeric complex was prepared by the reduction of 4-(2-chloroethyl)morpholine hydrochloride with two equivalents of lithium tetrahydridoaluminate. The ensuing reaction results in chloride-hydride transfer at the chloroethyl functionality, a cleavage pathway previously described by Marconi and co-workers using chloromethylmethylether.[51] The one-dimensionality of this hydride-bridged polymer contrasts with the two-dimensional supramolecular structure of the alane (AlH_3) adduct of the same ligand (Scheme 17).[53] This latter polymer was prepared using a non-chlorinated 4-ethylmorpholine ammonium salt reacted with two equivalents of alane that was prepared in situ from the reaction of lithium tetrahydridoaluminate with sulfuric acid.[54]

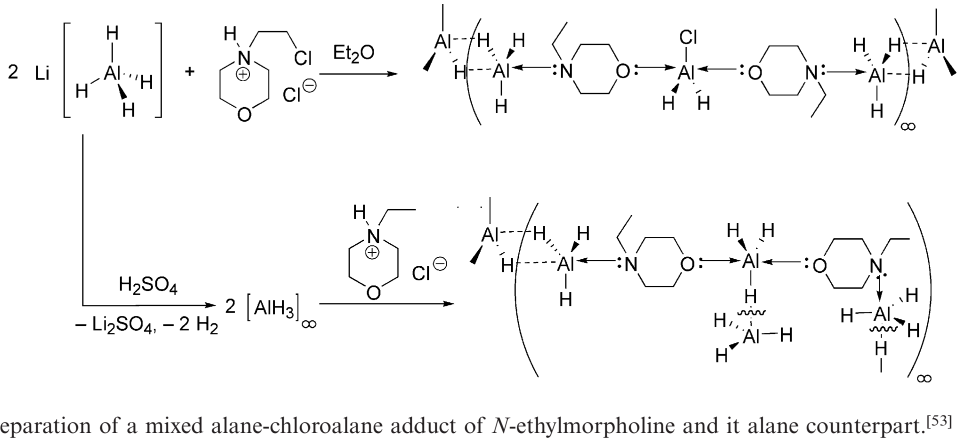
As outlined above, ammonium halides have been used prodigiously as a source of hydrogen halide in gallane chemistry and, combined with phosphonium salts, are used extensively to prepare nitrogen and phosphorus donor adducts of alane and gallane (see Scheme 18 and Scheme 11 respectively). It is therefore surprising that the first use of an ammonium halide as a source of sparingly soluble HX in alane chemistry was reported by Jones in 2001 (Scheme 18).[55] As per the gallane pyridine studies of Schmidbaur (see above),[30a] the shortened Al–N bonding parameters of this species correspond with an increase in acceptor character of the chloroalane relative to that of the alane complex [$AlH_3(quin)_2$].[56]



Scheme 18. The preparation of an alane[57] and chloroalane[55] complex using ammonium/phosphonium chloride salts.

Indium Halohydrides

Indane, InH_3, and tetrahydridoindanate were first reported by Wiberg in 1951[58] in tandem with thallane, TlH_3, and tetrahydridothallate, [TlH_4]⁻.[9] The chemistry of indane has been studied in depth by Jones and co-workers



Scheme 17. The preparation of a mixed alane-chloroalane adduct of *N*-ethylmorpholine and it alane counterpart.[53]

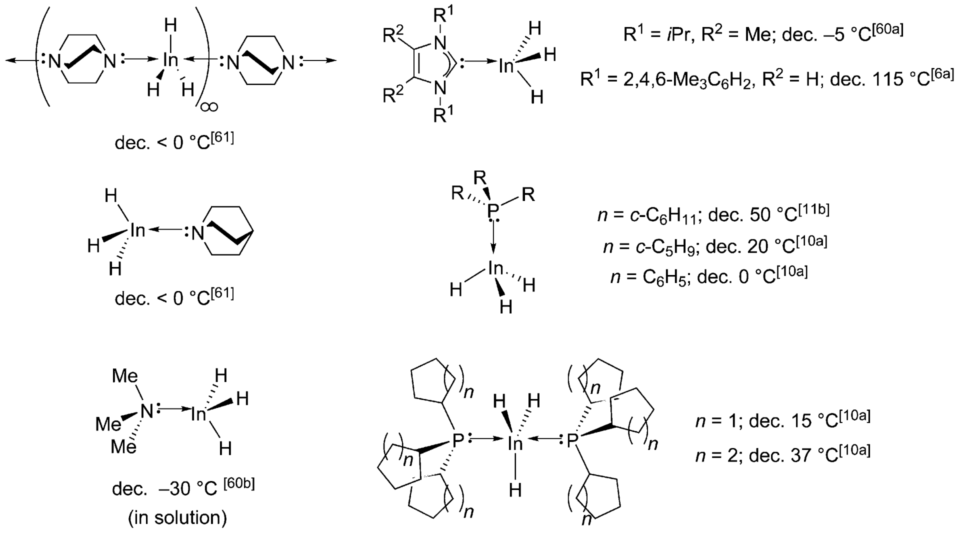
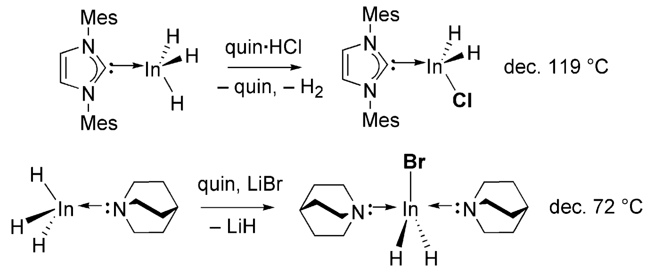


Figure 2. The known Lewis base adducts of indane (InH_3) and their respective decomposition temperatures.[6a,11b,60,61] References provided in square parentheses.

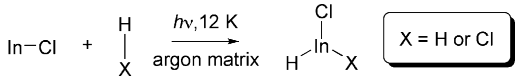
over the past decade.[5,6b,59] From these studies, it is well known that the decomposition of tertiary amine adducts of indane, e.g. [$InH_3(NMe_3)$],[60] occurs at temperatures below 0 °C. Figure 2 displays the known indane Lewis base adducts and their decomposition temperatures. A prominent feature of these stabilities is their correlation with donor strength and the capacity of the donor to sterically shield the indane moiety.

In view of the enhanced thermal stabilities of chlorogallanes relative to gallane counterparts (Figure 1), as reported by Raston,[15b] Gladfelter[15a] and Schmidbaur,[30a] Lewis base coordinated haloindanes represent attractive targets for room temperature stable indium hydrides. To date, two such Lewis base coordinated monohaloindanes have been prepared as outlined in Scheme 19. These compounds exhibit higher decomposition temperatures than their respective trihydrides, in particular that of five-coordinate [$InBrH_2(quin)_2$] (quin = quinuclidine), which is some 75 °C greater than that of four-coordinate [$InH_3(quin)$] (< 0 °C). Note, the five-coordinate bis(quinuclidine) adduct of indane cannot be prepared due to the insufficient Lewis acidity of [$InH_3(quin)$].[61]



Scheme 19. The known Lewis base adducts of haloindanes and their respective solid-state decomposition temperatures.[6]

Concurrent to these studies, Himmel and Downs have reported the successful preparation and argon matrix isolation of both mono- and dichloroindane by the photolytic reaction of indium(I) chloride with dihydrogen and hydrogen chloride respectively at low temperature (Scheme 20). Both species were studied using vibrational spectrocopies and DFT methods, as were their deuteride analogues.[62]



Scheme 20. Photolytic preparation of monochloro- and dichloroindane in an argon matrix.[62]

2. Infrared Spectroscopy and Heavier Group 13 Halohydrides

Molecular structure determination of group 13 hydrides provides an opportunity to assess the impact of halogenation on the parent metal trihydrides. As mentioned in Section 1, the metal to donor bonding contacts of group 13 halohydrides relative to those of trihydrides provided by single-crystal X-ray structure determination have been used to great effect to evidence the increased acceptor capacity of the former. However, X-ray techniques are not ideal for the study of metal hydride interactions due to the disparity in electron density between hydrogen and the group 13 metal, and the low electron density of the hydride ligand. Thus, in the absence of suitable neutron diffraction facilities, most research groups have turned to infrared spectroscopy as a readily available means of probing group 13 metal to hydride interactions.

Like the carbonyl functionality, group 13 metal–hydride bonds absorb strongly in the 2000–1600 cm^{-1} region of the infrared spectrum. IR spectroscopy is therefore an extremely useful technique for probing the strength and nature, e.g. terminal or bridging hydride, of the M–H interaction without the need for single crystal samples. In addition, the number and intensity of such absorptions are highly diagnostic of the coordination environment and symmetry at the metal centre.

Table 2 collates the reported stretching absorbances for the known Lewis base stabilised group 13 halometallanes and, where possible, the analogous absorptions of the alane, gallane or indane congeners. As one can see where comparative data are available, there is an increase in stretching frequency upon sequential substitution of hydrogen by a halogen. Although it may be argued on the basis of classical mechanics that this increase results from "weighting" down the non-hydridic function of the MX_n-H_{3-n} moiety, it is generally accepted that the increasing force constant of a M–H stretching absorption reflects increasing metal–hydride bond strength. This is borne out by the absence of any correlation between the mass of the Lewis base in $[MH_3(L)]$ (M = B, Al, Ga or In) and the energy of absorption. There is also a noticeable correlation between coordination number and absorbance, wherein lower coordinate species absorb at higher wavenumber.

Although the ramifications of bond stretching frequency to metal hydride reactivity are yet to be studied, recent results from our lab suggest that modification of the strength and polarity of the M–H bond results in distinct reactivity for the halometallanes and a reductive character that contrasts that of related trihydrides.[71]

3. The Reactivity of Heavier Group 13 Halohydrides

While it is true that many reactions undertaken by group 13 halometallanes are similar to those of trihydride counterparts, their modified M–H bond strength (Table 2) and increased capacity to accept Lewis base donors[15b,30] leads to a number of reactivities that are distinct to that of the trihydrides.[21,63] Furthermore, in principle the presence of one or more halogen ligands provides an "arrester" point for thermal decomposition by hydrogen elimination,[6b,21] thereby permitting access to low-valent compounds. The following section compiles the known reactivities of group 13 halometallanes and, where relevant, the contrasting chemistry of the corresponding Lewis base adducted metal trihydride.

(i) Lewis Base Adducts of Halometallanes

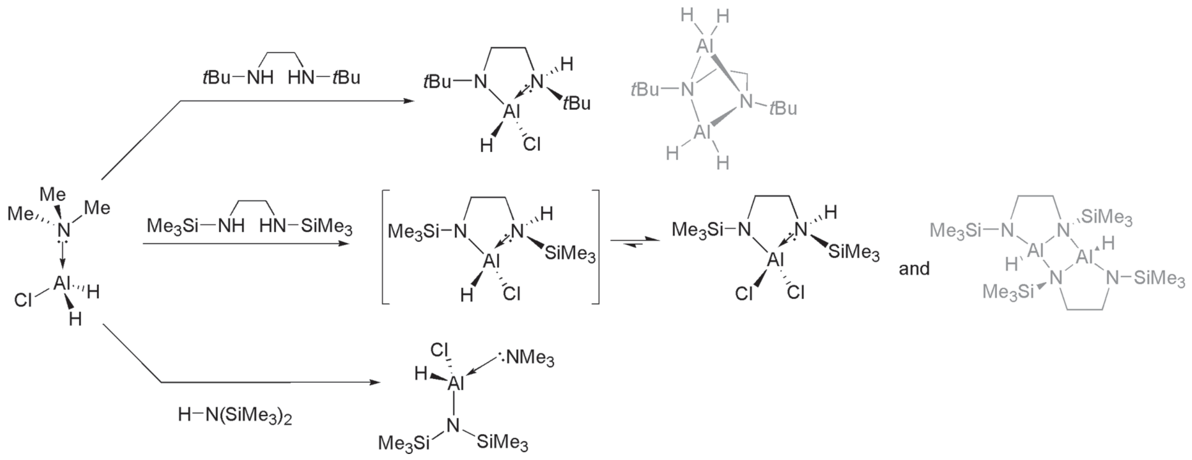
During the 1990s, Raston and co-workers published prodigiously on the reactions of Lewis base supported alanes.[4] The trimethylamine adduct of chloroalane, $[AlClH_2(NMe_3)]$, generated by the mercurial chloride path of Ruff,[38c] featured in several of these studies.[72] The compounds prepared using this starting material are summarised in Scheme 21, with alane ($[AlH_3(L)]$, L = Lewis base) derived products depicted in grey where the reaction outcome contrasts that of $[AlClH_2(NMe_3)]$.[72bc] Differences in reaction outcome can be attributed to the superior Lewis acidity of chloroalane relative to alane, which reduces the availability of the pendant amine functionality by more robust coordination to aluminium.

H. Roesky and co-workers have used $[AlClH_2(NMe_3)]$, prepared by the reaction of trimethylsilylchloride with trimethylaminealane, as a precursor to several carbaalanate complexes (vide infra).[73] This chlorination method mirrors the Schmidbaur preparation of dichlorogallane using a metal trichloride and trimethylsilane.[26] The chlorination of an aluminium hydride using silylchlorides was first reported by Power and co-workers.[74]

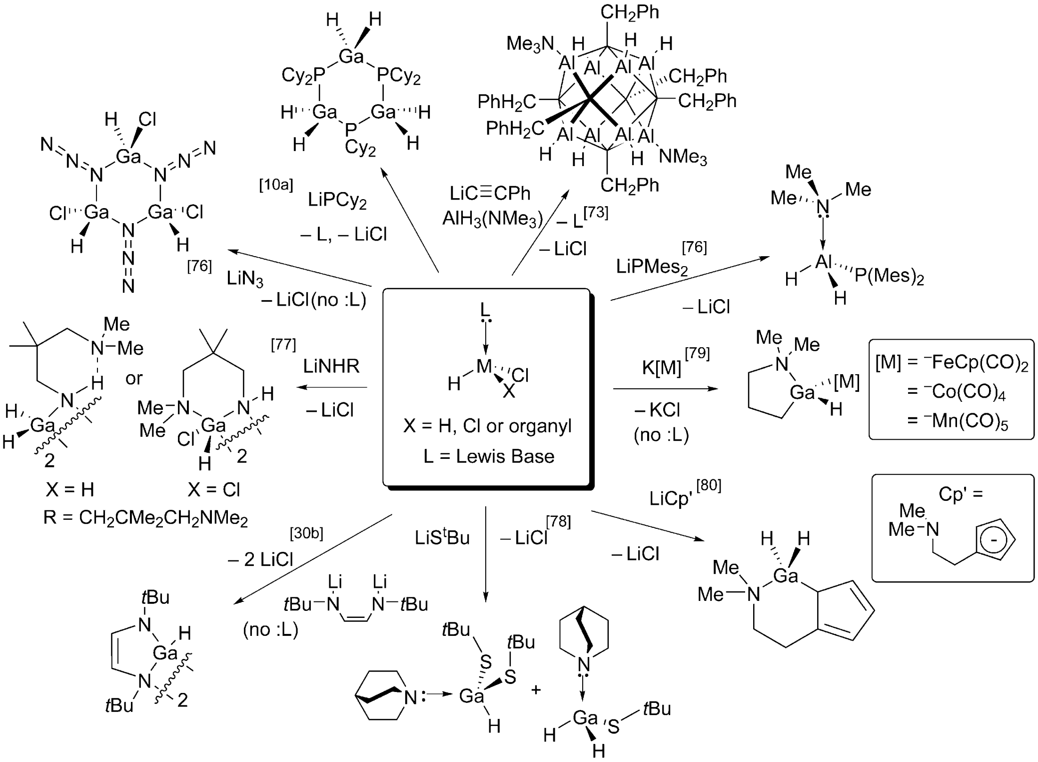
Lastly, tetrahydrofuran coordinated monochloroalane, $[AlClH_2(thf)_2]$,[46] has been used by Nöth and co-workers to prepare an adduct of 2,2,6,6-tetramethylpiperdine.[47]

(ii) Functionalisation by Salt Elimination/Metathesis

The presence of a M–X bond in halometallanes provides an immediate entry point for derivatisation by salt elimination/metathesis methods. While similar reactions can be accomplished at trihydrides by elimination of an *s*-block hydride(s),[10a,75] the method is not broadly applicable and is typically low yielding.



Scheme 21. Example preparations from the group of Raston using $[AlClH_2(NMe_3)]$. $[AlH_3(NMe_3)]$ counterpart illustrated in grey if the reaction outcome differs to that of the chloroalane.[72]



Scheme 22. The known functionalised heavier group 13 hydrides accessed by salt elimination methods.[10a,73,76–80] References provided in square parentheses.

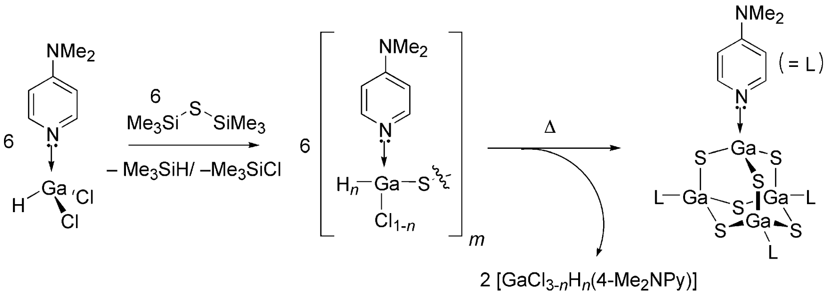
Scheme 22 outlines the known functionalised heavier group 13 hydrides accessed by salt elimination methods. This list of species is dominated by gallium complexes, in part because of the ease and speed of access provided by the Schmidbaur preparation of chlorogallanes (Scheme 7).[26]

The genesis of the trimeric species $[\{GaH_2(PCy_2)\}_3]$ (Cy = c-C_6H_{11})[15b] and $[\{GaHCl(N_3)\}_3]$[81] (top left of Scheme 22) is noteworthy. These compounds were prepared as potential single source precursors to gallium phosphide (GaP) and nitride (GaN) respectively, whereby controlled elimination of cyclohexane or nitrogen was to be induced thermally. In the case of the former, attempts to eliminate the alkane led to formation of dicyclohexylphosphane, gallium metal and hydrogen gas. Meanwhile, the azidogallane afforded nanocrystalline GaN upon thermolysis.

In 2004, Schmidbaur and Nogai reported the reaction of bis(trimethylsilyl) sulfide with a 4-(dimethylamino)pyridine adduct of dichlorogallane.[29b] This gave access to aggregated gallium sulfides with elimination of chlorotrimethylsilane and trimethylsilane in a mixed ratio (Scheme 23). Well defined heavy group 13 sulfides are a rare class of compounds[82] that are of interest for the construction of clusters, nanoparticles and frameworks[83] suitable for III/VI semiconductor, optoelectronic or materials applications (e.g. GaS and Ga_2S_3).[84] In principle, these species are accessible using gallium trihalides, however, the increased solubility of chlorogallanes, which contrasts that of gallium trichloride, is likely to encourage the future application of halogallanes as an access point to this chemistry.

(iii) Reductive Dehydrogenation and Low-valent Group 13 Chemistry

There has been a recent surge in articles concerning low-valent group 13 compounds.[85] The metal–metal bonding and reactivity exhibited by these species remains at the fron-



Scheme 23. The preparation of an aggregated gallium sulfide using a dichlorogallane precursor.[29b]

tier of contemporary bonding theories, and the preparative challenge they pose continues to fascinate, enthral and challenge main group chemists.

The development of low-valent group 13 chemistry has been seeded by two factors; the groundbreaking studies of metastable monovalent aluminium and gallium halides by Schnöckel and co-workers,[19,86] and the search for improved precursors to group 13 metal films and functional materials containing group 13 elements.[81,87] The former of these has been reviewed extensively,[19,85d,86] while the latter has experienced significant interest as an access path to high purity 1D and zero-D[88] nanoscale materials with optoelectronic applications.[89]

Presently, the most common route to thin films or functional materials containing group 13 metals is the chemical vapour deposition (CVD) of metal trialkyls at high temperature (> 700 °C) in the presence of a carrier gas, such as argon, and additional components specific to the material, e.g. phosphane for GaP preparations.[87] For example, deposition of the wide bandgap (3.39 eV, 365 nm) optoelectronic material gallium nitride (GaN) using trimethylgallium takes place at temperatures greater than 1000 °C in combination with a vast excess of ammonia vapour.[90] Aside from the inconvenience, associated hazards and cost of specialist equipment, this method is atom inefficient and generates materials rich in carbonaceous contaminant with high nitrogen vacancies.[91] In the context of applications, these defects hinder particle/film growth, doping capability and narrow the operation characteristics of the material. The drive to further shrink microelectronic technologies and increase computational power and energy efficiency has led to single source “organic free” precursor materials being prized targets in this field. Several research groups have focused their attention on the preparation of gallane and indane complexes coordinated by group 15 or 16 ligands as single source precursors to GaN,[91] Ga_2S_3,[29b] GaP,[15b,90] GaAs,[91,93,94] InN,[5] InP[10a] and other hybrid III/V[95] or III/VI materials.[96] This approach, which invariably utilises a halohydride precursor that is functionalised by salt-elimination, capitalises on the lower temperature stability of hydride bonding contacts to the group 13 metal vis-à-vis alkyl donors, and the incorporation of both elements. Furthermore, use of an anionic group 15 or 16 ligand reduces co-ligand lability and, potentially, organic content relative to simple Lewis base adducts. Figure 3 contains some the group 13 metal complexes that have been generated as single source precursors for this purpose in addition to those previously mentioned in the preceding subsection.

Among these substrates, $[\{GaH_2(N_3)\}_3]$,[98] $[\{GaH_2(P(SiMe_3)_2)\}_3]$ and $[\{GaH_2(As(SiMe_3)_2)\}_3]$[93] have been used to prepare GaN (H_2 and N_2 loss), GaP ($HSiMe_3$ loss) and GaAs ($HSiMe_3$ loss), respectively, by thermally induced reductive dehydrogenation/nitrogenation or dehydrosilylation. Attempts to induce alkane elimination, as per $[\{MH_2ER_2\}_3]$, where M = In; $ER_2 = PCy_2$,[10a] M = Ga; $ER_2 = NMe_2$[99] or NHMe,[100] M = Al; ER_2 = 2-$PH_2C(SiMe_2)_2Py$,[97] have thus far failed.

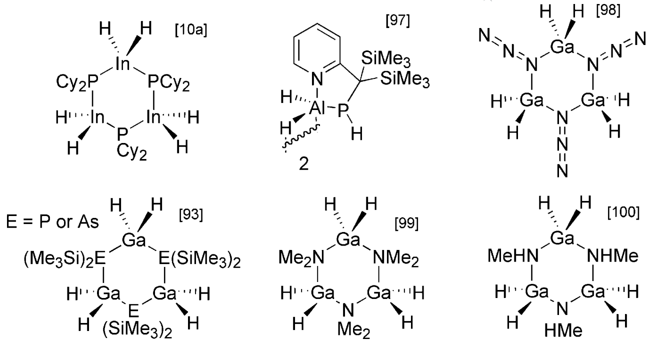
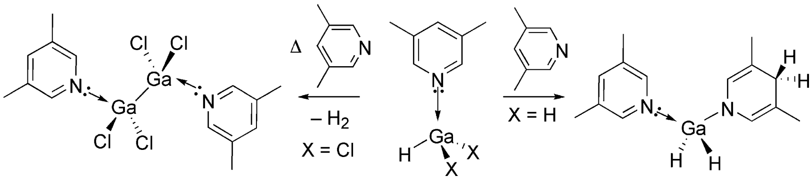


Figure 3. Potential single source heavier group 13 hydride precursors to III/V semiconductor materials.[97]

Further to microelectronics applications, there have been several fundamental studies of reductive dehydrogenation of group 13 halometallanes. Following on from his pioneering studies of $Ga^{II}Br_2$,[101] in 2002 Schmidbaur reported the reductive dehydrogenation of dichlorogallane at 150 °C to give the known crystalline compound “$GaCl_2$”.[29b] This compound exists as ionic mixed oxidation state $Ga^I[Ga^{III}Cl_4]$ in the solid-state[102] and in aromatic hydrocarbon solution[103] without Ga–Ga bonding interactions. In the latter, the Ga^I exists as an arene coordinated cation. This readily accessible source of “$GaCl_2$” generates symmetrical gallium–gallium bonded $LGaCl_2$ dimers upon addition of suitable Lewis bases.[21,27]

Recently Nogai and Schmidbaur have succeeded in applying this dehydrogenative approach to Lewis base adducted dichlorogallane, wherein the heating of toluene solutions of $[GaCl_2H(3,5\text{-}Me_2C_5H_3)]$[30a] and 3,5-dimethylpyridine to reflux affords the dimer $[\{GaCl_2(3,5\text{-}Me_2C_5H_3)\}_2]$ with the concomitant evolution of dihydrogen and release of excess ligand (Scheme 24).[21] Interestingly, the four-coordinate mono pyridine adduct, $[GaCl_2H(3,5\text{-}Me_2C_5H_3N)]$, is thermally stable under the same conditions suggesting a five coordinate species is responsible for activation of the Ga–H bond to reductive dehydrogenation. By contrast, the addition of a second equivalent of the same pyridine to $[GaH_3(3,5\text{-}Me_2C_5H_3N)]$ at ambient temperature results in hydrogallation of one coordinated pyridine to yield $[GaH_2\{N(CH{=}CMe)_2CH_2\}(3,5\text{-}Me_2C_5H_3N)]$ (Scheme 24). This further emphasises the distinct reactivity of halogenated gallanes relative to trihydride counterparts.[21]

Schnöckel’s landmark studies of metastable aluminium and gallium monohalides have, to date, provided the most successful means of accessing subvalent aluminium and gallium halide clusters, some of which incorporating 50+ group 13 metal centres.[104] Using this technique, wherein elemental group 13 metal is heated to ca. 1000 °C and treated with gaseous hydrogen halide under reduced pressure ($\approx 10^{-2}$ mbar),[19,86] Schnöckel and co-workers have isolated many group 13 metal halide clusters for which the bonding cannot be satisfactorily explained using simple bonding theories. Examples include $[Al_{22}X_{20}(thf)_{12}]$ (X = Cl or Br),[105] $[Al_5Br_6(thf)_6][Al_5Br_8(thf)_4]$[106] and $[Ga_{24}Br_{22}(thf)_{10}]$ (Figure 4),[107] all of which isolated by gradual



Scheme 24. The reductive dehydrogenation of a dichlorogallane pyridyl complex and the hydrogallation product of its gallane counterpart.[21]

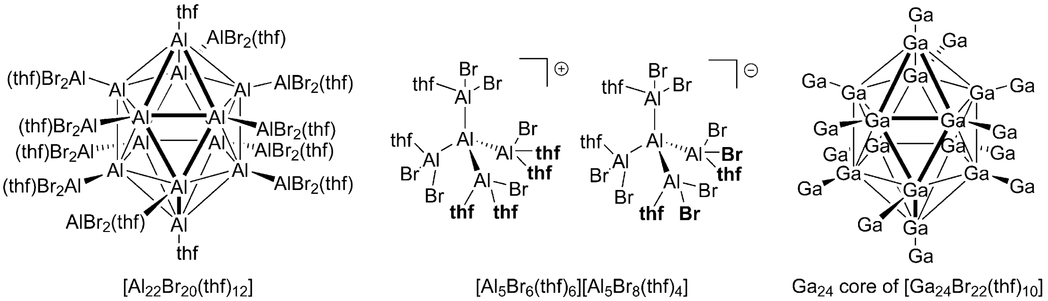
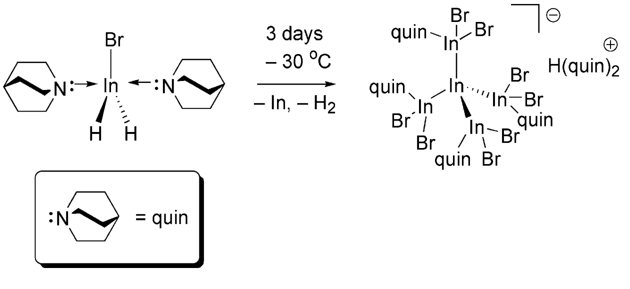


Figure 4. Example subvalent group 13 clusters accessed by Schnöckel and co-workers.[105–107]

warming of condensed M^IX (–196 °C) in the presence of thf. Despite the success of this method, the specialist equipment employed precludes general usage.

In 2005 Jones reported the first example of an indium subhalide anion; [(quin)$_2$H][In$_5$Br$_8$(quin)$_4$] (Scheme 25).[6b] This complex, which structurally resembles the anion of [Al$_5$Br$_6$(thf)$_6$][Al$_5$Br$_8$(thf)$_4$],[106] was accessed by the reductive dehydrogenation of a rare bromoindane-(bis)quinuclidine adduct (see Scheme 19).



Scheme 25. Reductive dehydrogenation of [InH$_2$Br(quin)] to afford the subvalent anion [In$_5$Br$_8$(quin)$_4$]$^-$.[6b]

Pure samples of the indane [InH$_3$(quin)] are unstable above –5 °C in either solution phase or the solid-state.[61] Addition of anhydrous lithium bromide to [InH$_3$(quin)] in the presence of excess quinuclidine affords five-coordinate [InBrH$_2$(quin)$_2$], which decomposes in the solid state at 72 °C.[6b] This haloindane preparation is reminiscent of Ruff's early alane studies using organolithiums to prepare organoaluminium complexes,[38c] and is most likely driven by the insolubility of the lithium hydride by-product in diethyl ether. Despite its significant solid-state stability, solutions of [InBrH$_2$(quin)$_2$] stored at low temperature (–30 °C) evolve hydrogen and deposit indium metal to yield exclusively [(quin)$_2$H][In$_5$Br$_8$(quin)$_4$], which itself disproportionates to [InBr$_3$(quin)$_2$],[108] indium metal and dihydrogen above –15 °C.[6b] In combination with Schmidbaur's dichlorogallane studies, this outcome suggests that dehydrogenation of group 13 halometallanes may be a "general" pathway to low-valent heavy group 13 halides.

Conclusion and Closing Remarks

There is a growing catalogue of Lewis base coordinated group 13 halometallanes, with new species coming forward regularly. One-pot syntheses of these species, particularly those of gallium, are available and positioned for application in other fields of synthetic endeavour. To date, there has been limited use of heavier group 13 halohydrides in this regard. It is likely this will be addressed in the near future, particularly as the unique physical character of these compounds ideally places them for organic hydrometallation studies, as precursors to group 13 materials, and starting materials for low-valent group-13 metal species. Accordingly, it would appear Lewis base adducts of heavier group 13 halohydrides have a bright future and we very much hope other researchers will attempt to apply them in their sphere of synthesis and materials science.

Acknowledgments

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