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NHC-supported mixed halohydrides of aluminium and related studies

A thesis submitted towards the degree of Doctor of Philosophy

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Table of Contents

Abstract

Chapter 1. General introduction

This chapter comprises a comprehensive overview of group 13 chemistry, including the elements of group 13, the trihydrides of aluminium and gallium and their Lewis base adducts, and a brief overview of aluminium and gallium trihalides and their respective Lewis base adducts.

Chapter 2. Lewis base adducts of group 13 mixed halide-hydrides

This chapter consists of an overview of the existing mixed halohydrides of aluminium and gallium, and an introduction to carbenes, including NHCs. The synthesis and discussion of numerous new mixed halohydrides of aluminium and gallium is presented.

Chapter 3. Selected reductions with mixed halohydride reagents

This chapter discusses the application of compounds from Chapter 2 as organic reducing agents and comparison with literature concerning hydrometallation with trihydride congeners.

Chapter 4. Triazenide complexes of alane and gallane

This chapter includes the synthesis of several new triazene species and their precursors, and their application as support ligands for aluminium and gallium mono- and dihydrides.

Chapter 5.

This chapter includes the synthesis of several “super-bulky” NHCs, their precursor diazabutadienes and terphenyls, and preliminary use in coordination chemistry.

Declaration

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Acknowledgements

Like many things in my life, these acknowledgements probably don’t follow any established trend. I figured I’d run through a few relevant times in my life and point out the people that have been influential. Basically, if you’re mentioned below, you have my thanks.

Probably my earliest major influence was Robert Peck, my grade 6/7 primary school teacher. He taught me something about being a man, even as a kid. He taught me about courage, integrity and taking your medicine sometimes. After I left school I ended up working on a farm for year or so, where the farmer’s wife Dianne Freebairn sent me to a career psychologist and encouraged me to go to uni. Due to financial difficulty I only spent one year there but this laid the path for my eventual return. In the 12 years between first and second year uni I was privileged to have Hayley and Annie Davis along with Stan and Vicki Manners as major influences in my life. Also during that period Mark Tilbrook put me on the path to getting my mechanic’s trade, and taught me much about having pride in one’s work. He taught me what tradesmanship is.

My return to uni was prompted by Stephen and Janine Campbell, two amazing people that have taught me more than they realise over the years. I suddenly found myself having to catch up a whole lot of learning, and the transition back into uni was made much easier by Sarah Farrelly. Sarah pushed me in the right directions and gave me the faith to keep going. My idea of quickly finishing an undergrad degree and the Dip Ed to be a high school teacher gradually dissolved, and I was lucky enough to do my Honours degree under Simon Pyke, one of the most inspirational lecturers I know. And then of course the prospect of Ye Olde PhD came along, and here I am. My initial reasons to study under Marcus Cole were mostly because he was young, and a bit of a gun. My rationale was that he would be motivated and helpful, and he has proven to be this and much more. He’s even a good bloke. Along with this, Jonathan Morris has been a most helpful co-supervisor and his enthusiasm for chemistry is inspiring. Now somewhere along the line Kristina Konstas joined our group. “Dr KK” and her amazing energy and enthusiasm made our lab a fun place to be indeed. On top of this her help with the triazenide research made Chapter 4 possible- it wouldn’t have happened without her.

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It’s been fun ☺

Chapter 1: General Introduction

1.1 Group 13 chemistry

The elements of group 13, namely boron, aluminium, gallium, indium and thallium, are a collection of elements with a diverse range of properties; so much so that the group has been described as the worst for easily read trends.[1] Although the elements all possess the ground state valence electron configuration of ns^2np^1, their properties deviate considerably from expected trends as the group is descended.

Boron, the lightest element of group 13, is the only non-metal in the group. It is classed as a metalloid since it possesses properties intermediate to metals and non-metals. Crystalline elemental boron has a high melting point and exists in a variety of allotropic forms, all of which containing B_{12} units that exhibit multicentre B-B bonding.[2] This bonding, a feature of lighter group 13 chemistry, is a result of the inherent electron deficiency of boron; it has four valence orbitals yet only three valence electrons.

The remaining group 13 elements are all soft, low melting point metals. A summary of the physical and chemical properties of the group 13 elements is included in Table 1. This table highlights some of the anomalies in typical main group trends. A striking aberration is the low melting points of both gallium and indium. By looking at group 1, it can be seen that melting points decrease incrementally down a group from 181 °C for lithium to 28 °C for caesium.[3] In group 13 this is clearly not the case, as gallium and indium possess melting points of 30° C and 156 °C respectively. It is necessary to examine the metallic structures of the group 13 elements in order to explain this deviation. Although all four of the metallic group 13 elements exhibit close-packed structures, where each metal atom has 12 neighbours, indium has a slightly distorted close-packed structure with four atoms slightly closer than the remaining eight. Gallium has an unusual structure in that each atom has one near neighbour (2.44 Å) with the other atoms occurring in pairs at distances of 2.70, 2.73 and 2.79 Å respectively.[2] The structure of solid gallium has been compared to that of solid iodine, with its discrete I_2 units,[2] and there is evidence to suggest that weakly bonded Ga_2 molecules persist in gallium melts.[4] Metalloids typically have this incipient bond localisation, and this partly explains the low melting points of both gallium and indium, i.e. the small radii of gallium and indium impart some metalloid character to both elements.

Table 1. Physical and chemical properties of the group 13 elements

	B	**Al**	**Ga**	**In**	**Tl**
Atomic Number	5	13	31	49	81
Covalent Radius (Å)[5]	0.81	1.25	1.25	1.50	1.55
Ionisation Energy (kJmol^{-1}) (1st 3 electrons)	6887	5044	5521	5084	5439
Electronegativity (Allred and Rochow)	2.01	1.47	1.82	1.49	1.44
Melting Point (ºC)[5]	2300	660.1	29.8	156.2	302.4

The ionisation energies (3+) of the group 13 metals (Table 1) are another area of interest. The variation in these can be explained on the basis of the electronic configurations of the respective elements, in particular the “core” electrons present. Ordinarily, one would expect that ionisation energies decrease as a group is descended, based on the premise that the increasing distance of the valence electrons from the nucleus overshadows the increased effective nuclear charge. This trend is observed between boron and aluminium, where a considerable reduction in ionisation energy occurs. The corresponding move from aluminium to gallium, however, fails to follow this trend. This is rationalised by the ‘*d*-block contraction’, or ‘scandide contraction’, where the atomic radius of a period 4 element is smaller than expected due to the poorer shielding properties of *d*-electrons when compared to those of *s*- and *p*-electrons. Essentially, highly directional *d*-orbitals, once filled, fail to compensate for the increased effective nuclear charge. This manifests as a more compact atom due to the drawing of the valence electrons closer to the nucleus, and can be seen in the identical atomic radii of aluminium and gallium. In turn, the increased effective nuclear charge experienced by the valence electrons results in an increased ionisation energy.[3]

A similar phenomenon exists upon descending from indium to thallium as a result of the ‘*f*-block contraction’, or ‘lanthanide contraction’. The filling of the *f*-block orbitals results in a minimal increase in atomic radii between indium and thallium, the end result being a more compact atom and higher ionisation energies for the elements thallium to radon.[3]

The oxidation states of the heavier group 13 elements highlight a trend known as the ‘inert pair effect’. This term refers to the situation where innermost valence electrons, in particular those of the *ns* orbitals, display a reluctance to be involved in covalent bonding, leaving only the outermost valence electrons to participate in bonding. Accordingly, the +3 oxidation state (ns^0 np^0) conventionally assigned to group 13 is increasingly outweighed by a preference for the +1 oxidation state (ns^2np^0) as the group is descended. A partial explanation for this is the large effective nuclear charge of thallium due to filled 4*d* and 5*f* orbitals, and its reduced ionic radius; this coupled with relativistic effects lead to a substantially stabilised 6*s* orbital relative to the 6*p* orbital. This cannot be the sole reason behind the phenomenon, as the 6*s* orbital could not be regarded as too low in energy to participate in bonding. The other contributing factor behind this effect is the low strength of bonds formed by an element of relatively large size. For an element such as boron, the extra energy required to involve the 2*s* electrons is easily offset by the formation of three (rather than one) strong covalent bonds, whereas in the case of thallium, the formation of two additional relatively weak bonds does not offset the promotion energy: in other words, *s*- and *p*-orbital hybridisation is less energetically beneficial for heavy elements. This leads to weaker covalent bonding, and the “inert pair” effect.[2]

1.2 Trihydrides of aluminium and gallium

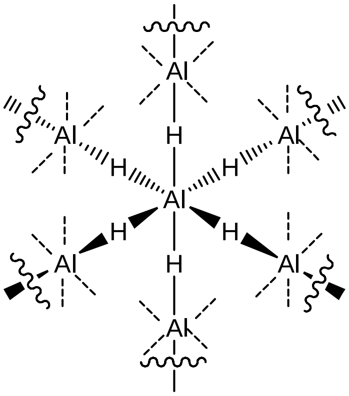
1.2.1 Background

After several reports around 1940 on the existence of Al-H species,[6] polymeric alane of the form $[AlH_3]_\infty$ was first reported in 1942,[7] followed by reports of the trimethylamine and diethyl ether adducts of alane, $[AlH_3(NMe_3)]$[8] and $[AlH_3(Et_2O)]$ respectively.[7] Prior to 1966 alane was difficult to synthesise, however in this year a new process was reported involving the reaction of $Li[AlH_4]$ and H_2SO_4 in THF (Scheme 1).[9] Interest in this area waned during the early 1970s but increased in the 1980s due to newfound applications of this type of compound. The majority of these have been in the semiconductor industry[10-13] and organic synthesis.[14] The latter will be discussed in a later chapter.

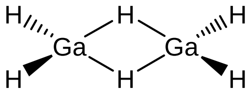
Scheme 1

$$LiAlH_4 + H_2SO_4 \xrightarrow{THF} Li_2SO_{4(s)} + \{AlH_3\}_n$$

Gallium trihydride species have enjoyed some popularity in recent years. A transient gas-phase gallane (GaH_3) species was reported as early as 1965,[15] however it was only in 1989 that digallane [Ga_2H_6] (**1**), the native form of gallane, was characterised,[16] followed by a $(GaH_3)_4$ tetramer in 1994 (**2**).[17] Since then gallium hydride chemistry has been extensively explored in the interests of developing precursor materials for gallium film deposition and semiconductor materials such as gallium nitride, phosphide, and arsenide.



(**1**)



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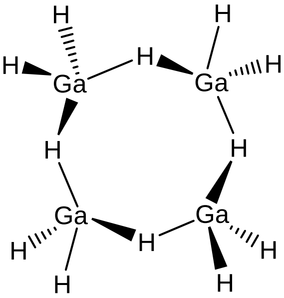


(**3**)

1.2.2 The thermodynamics of alane and gallane

The formation of alane and gallane from the respective metal and hydrogen is an endothermic process and, given allowances for entropy, should not occur at room temperature.[17] The fact that alane and gallane exist under these conditions infers that there is a further stabilising factor. It is believed that the formation of M-H-M bridges, enabled by the empty valence orbital of the metal and the electron rich hydride ligands, provide this stabilisation.[17] This is particularly true in the case of alane, which in at least one of its solid-state forms has all aluminium atoms coordinated by six hydride bridges (**3**).[17]

It is commonly suggested that the instability of alane and gallane is due to the inherent frailty of the M-H bond. However, although these bonds are weaker when compared to their M-Cl or M-O counterparts, this cannot completely explain their instability as M-H bonds are in fact stronger than analogous M-C bonds and the respective M-H bonds of *s*-block hydrides in their period (Table 2).

Compounds containing these bonds are well known, hence there must be another reason for the instability of group 13 metal hydrides. The presently favoured explanation is based on both thermodynamic and kinetic rationales and involves the aforementioned M-H-M bridges. Whilst these bridges play an essential part in the formation of donor-free alane and gallane, they are also believed to be a key factor in decomposition processes. Although decomposition may be initiated by cleavage of a single M-H bond, it has been suggested that decomposition primarily proceeds by an associative mechanism that precedes the loss of hydrogen.[17] Calculations suggest this to be a lower energy pathway than M-H cleavage.[17] Conversely, this is not seen in the alkyl derivatives, where M-C-M bridging is less common, and thus decomposition appears to be initiated by M-C bond dissociation. This means a correspondingly higher energy barrier results and the associative activation is rendered ineffective by weak M-C-M bridges.[17] It has been shown that the coordination of bulky non-hydride ligands about the metal centre frustrates the formation of M-H-M bridges and renders this decomposition process unfavourable.[18, 19]

Table 2. Mean enthalpies of selected bonds

Mean bond enthalpies in kJmol^{-1}	**Al**	**Ga**	**Na/K**	**Mg/Ca**
M – H[17]	287	260	186/175	126/168
M – C[20]	274	245	—	—
M – Cl[21]	511	481	—	—
M – O[21]	511	353	—	—

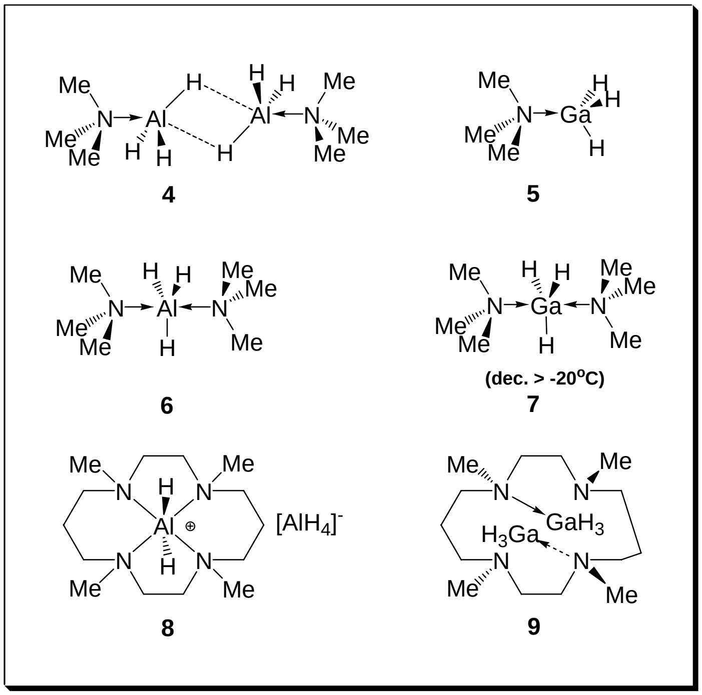
1.2.3 Structural trends in aluminium and gallium hydride complexes

The hydrides of aluminium and gallium display bonding and structures indicative of their respective electronegativities. In their monomeric non-condensed forms, both alane and gallane are sp^2 hybridised and have an unoccupied *p*-orbital. This orbital provides for their Lewis acidity. In the solid state, however, these compounds take on very different structures.

Alane, due to the lower electronegativity of aluminium, forms multiple intermolecular M-H-M bridges to satisfy aluminium electronically. The commonly accepted form is a three dimensional polymeric framework containing six bridges to six adjacent aluminium atoms (**3**).[17] Gallane, due to gallium's higher electronegativity, has less need for intermolecular M-H-M bridging and hence does not readily form large aggregates. In the gas and liquid phase gallane exists as a dimer (**1**) and in the solid state, a tetramer (**2**), both containing four-coordinate, *sp*^{3}, gallium centres.[16, 17]

1.3 Lewis base adducts of alane and gallane

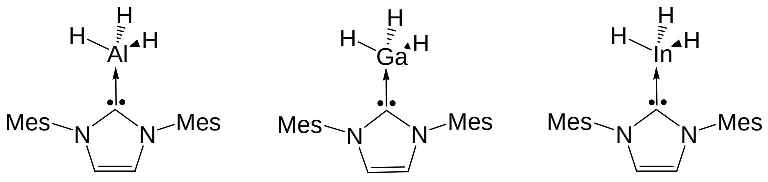
A similar pattern of structure to that in **1.2.3** exists with adduct species of alane and gallane. The aluminium of alane, due to aluminium's lower electronegativity, is more Lewis acidic than the gallium of gallane, and is hence likely to accept more than one Lewis base. Although numerous five-coordinate adducts of alane have been reported,[22] four-coordinate adducts can be prepared, some exhibiting a "tetrahedral" geometry stabilised by intermolecular hydride bridges in the solid state (**4**).[23] Gallane prefers four coordination,[22] although a five-coordinate adduct of NMe_3 has been prepared at low temperature (**7**).[24] A summary of some adducts of both alane and gallane is shown below.



Structure **4**[25] demonstrates the reluctance of aluminium to form four-coordinate adducts; the higher electronegativity of aluminium encourages the formation of the aforementioned intermolecular hydride bridges. Structures **5-9**[22, 23, 26-28] highlight the change in coordination preference of aluminium and gallium, in line with their differing electronegativities.

By far the most thermally stable of the group 13 trihydrides are those coordinated to N-heterocyclic carbenes (NHCs). Of these, those coordinated to 1,3-dimesitylimidazol-2-ylidene display remarkable thermal stability (Figure 1). A detailed discussion of carbenes, including NHCs and their involvement in group 13 chemistry, is included in Chapter 2.

Figure 1

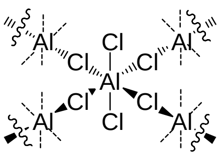


m.p. 246 °C **dec. 214 °C** **dec. 115 °C**

1.4 Aluminium and gallium trihalides

As per their respective trihydrides, both aluminium and gallium trihalides display differing structural preferences as a function of their electronegativity. In the solid state, both the trichloride (**10**) and trifluoride of aluminium adopt a distorted six-coordinate layer framework.[5] Under conditions of higher temperature and pressure, aluminium trichloride has been observed to form a four-coordinate dimer on melting, which can persist into the gas phase. At higher temperatures, gaseous aluminium chloride becomes monomeric, adopting a trigonal planar conformation. Aluminium trifluoride sublimes at 1270 °C and is also trigonal planar in the gas phase. In contrast, aluminium tribromide and triiodide both exist as dimers in all three phases, and become monomeric only at higher temperatures.[29]

Gallium trifluoride, like its aluminium congener, is a high melting point solid (sublimes at 950 °C, m.p. > 1000°C) that displays a distorted six-coordinate geometry.[29] Conversely, gallium trichloride (**11**) exists as a stable (m.p. 78 °C) four-coordinate dimer in the solid and liquid state, and as a monomer in the gas phase; the aforementioned higher electronegativity of gallium leads to the lower coordination numbers.[29] Gallium tribromide and triiodide also exist as stable four coordinate dimers (m.p. 122°C and 212 °C respectively).[30]



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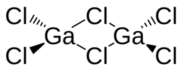
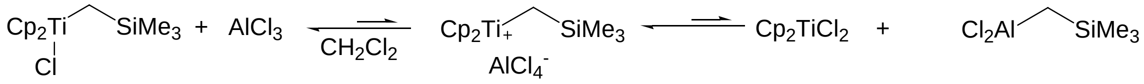


11

Group 13 trihalides, in particular those of aluminium, are utilised for their Lewis acid properties. These properties are successfully exploited in the chemical synthesis industry, as a catalyst for acylation and alkylation reactions, and for hydrocarbon polymerisation and isomerisation.[31, 32] Ligand abstraction is another important use of these species, as in the example below (Scheme 2), wherein the generation of the equilibrating solvent-separated and contact ion pairs results in a catalyst that facilitates the polymerisation of ethylene and poorly-favoured ligand exchange of trimethylsilyl and chloride.[33]

Scheme 2

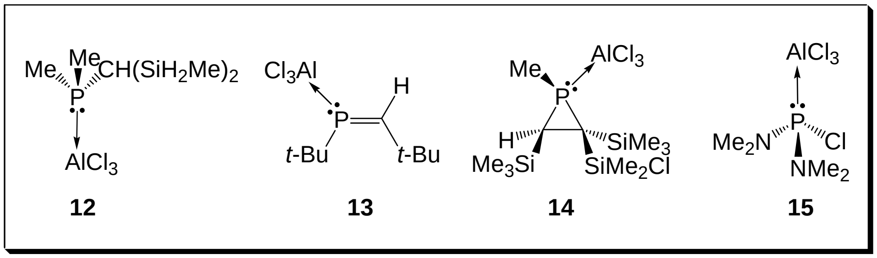


1.4.1 Selected Lewis base adducts of aluminium and gallium trihalides

A rich array of Lewis base adducts of aluminium and gallium trihalides have been reported in the literature, although only those involving group 15 donors will be discussed here. In contrast to their trihydrides, Lewis base adducts of gallium trihalides are more numerous than those of aluminium.

Several N-donor aluminium trichlorides have been prepared, many to demonstrate another compound's reactivity toward Lewis acids. This Lewis acidity is demonstrated by the series of known aluminium trichloride-pyridine adducts, wherein up to three pyridine ligands can be attached to the metal centre when stirred in benzene.[34] Both the mono- and bis-trimethylamine adducts of aluminium trichloride have also been reported, the former's m.p. of 157 °C demonstrating the thermal stability of this type of adduct.[29] In contrast, the trimethylamine adduct of alane, [$AlH_3(NMe_3)$], melts at 76 °C.[35]

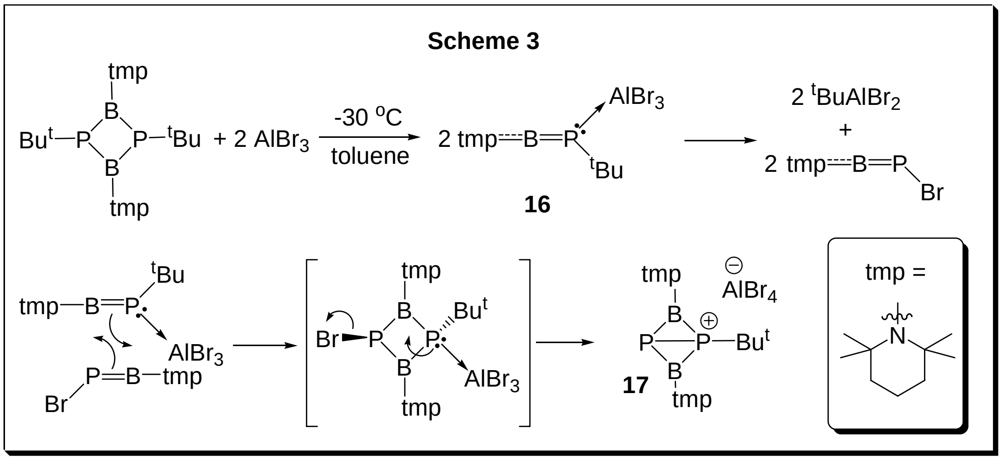
Several phosphine-based complexes have also been reported, usually as intermediates or side-products of other reactions (**12-15**). [36-39]



12 **13** **14** **15**

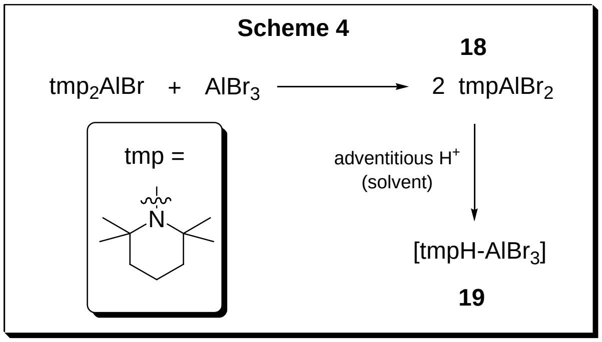
Phosphorus donor tribromides and triiodides of aluminium are relatively scarce. One of the few aluminium tribromide adducts reported is the unstable 2,2,6,6-tetramethylpiperidino-tert-butylphosphinideneborane (tmpB=P^{t}Bu) adduct (**16**) prepared by the reaction of the phosphinideneborane dimer, {tmpBP^{t}Bu}$_2$, with aluminium tribromide (Scheme 3). Compound **16** subsequently decomposes via bromide-alkane exchange to give *tert*-butyl aluminium dibromide and 2,2,6,6-tetramethylpiperidinobromophosphidene borane, which forms an adduct with **16** releasing tetrabromoaluminate and a diphosphadiboratane counterion (**17**).[40]

Scheme 3



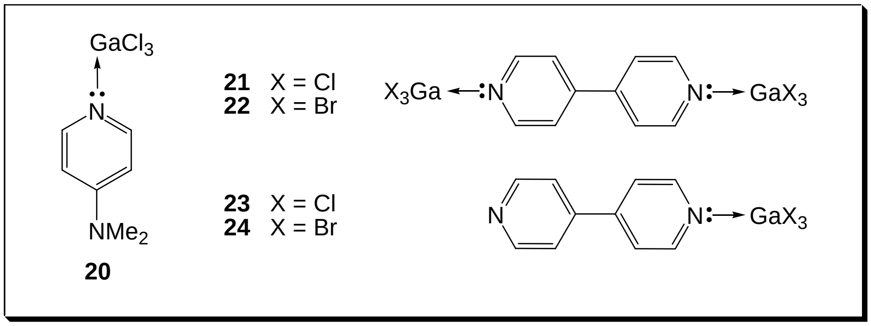
16 **17**

Few nitrogen donor compounds of aluminium triiodide and tribromide have been reported. The 2,2,6,6-tetramethylpiperidine (tmpH) adduct of aluminium tribromide was recently reported by Knabel *et al.* as a serendipitous outcome of the dibrominated species [tmpAlBr$_2$] (**18**) (Scheme 4).[41] According to the authors, whilst **18** could be prepared from [tmp$_2$AlBr] and AlBr$_3$ at 90 °C in the absence of solvent, stirring in either hexane or benzene resulted in a side-reaction with the solvent, producing the protonated species **19**. To date, there are no reported phosphorus or nitrogen adducts of aluminium triiodide.

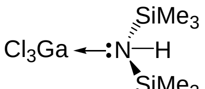

Scheme 4

Nitrogen and phosphorus adducts of gallium trihalides also exist; a search of the literature shows that nitrogen-donor compounds predominate. The dimethyl-4-aminopyridine (DMAP) adduct of gallium trichloride [$GaCl_3$(DMAP)] (**20**) was synthesised by Nogai *et al.* purely as a reference compound in the preparation of the dimeric [$GaCl_2(PEt_3)]_2$, as was the triethylphosphine adduct [$GaCl_3(PEt_3)$].[42, 43]

Of particular interest is the 1:2 and 1:1 4,4′-bipyridine adducts of gallium tribromide and trichloride (**21-24**), synthesised as potential precursors to the semiconductor material GaN. It was proposed that compounds such as these could be used to create materials with specific properties via MOCVD (metal organic chemical vapour deposition), where gas-phase precursors are passed over a substrate wafer, depositing a high-purity metal film.[44, 45]



Recently, Carmalt *et al.* reported a range of gallium tribromide and trichloride amine adducts, also as potential CVD precursors to GaN (**25-28**).[46] The 1:2 and 1:1 pyrazine adducts of gallium trichloride (**29-30**) have also been prepared for the same reason.[47]



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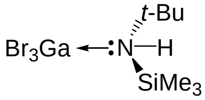

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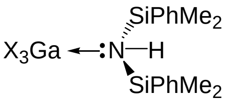
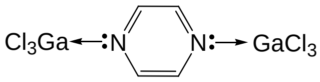


27 X = Cl
28 X = Br



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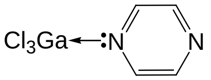

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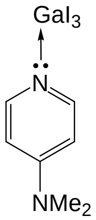
As with aluminium triiodide, Lewis base adducts of gallium triiodide are rare; only two nitrogen donor complexes are known, including the recently-reported[48] DMAP species (**31**)[49] (c.f. **20**). Similarly, only two phosphine adducts have been reported; a triphosphabenzene species (**32**) and a 2:1 adduct of an isomerised 1,2-diphosphino-Z-alkene (**33**). As yet, no nitrogen or phosphorus adducts of gallium trifluoride have been reported.



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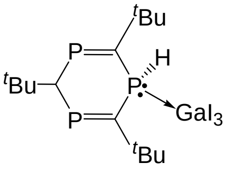

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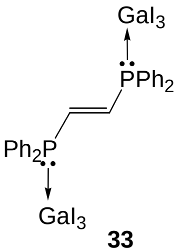


33

Chapter 2: Lewis base adducts of group 13 mixed halohydrides

2.1 Introduction

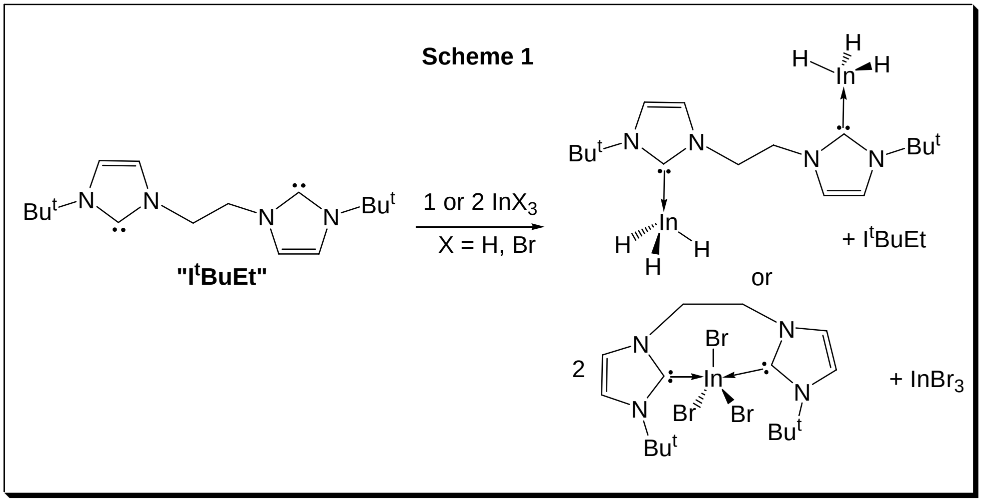
This chapter comprises a comprehensive study of mixed halohydride Lewis base complexes of aluminium and gallium. A key component of this research is the utilisation of *N*-heterocyclic carbenes (NHCs) as stabilising ligands. As mentioned in Chapter 1, the thermal stability of NHC complexes of group 13 trihydrides is without match; this class of Lewis base donors is thermally stable, highly nucleophilic and to date have enabled the preparation of the most thermally stable MH_3 species reported. This chapter's introductory sections consist of two main areas; an overview of existing mixed halohydrides and synthetic methods, and an introduction to carbenes with particular emphasis on *N*-heterocyclic carbenes (NHCs).

2.2 Significance of research

It is anticipated that the chemistry of Group 13 mixed halohydrides will be significantly different to that of their trihydride counterparts for the following reasons.

(i) Group 13 mixed halohydrides should display an increased thermal stability. This has been previously demonstrated with phosphine adducts of gallane $[GaHX_2(PCy_3)]$, where X_2 = H_2, HCl, Cl_2, Cy = c-C_6H_{11}. Replacement of one and two hydrides with chloride ligands results in a significant increase in the thermal stability; decomposition points 130 °C ($X_2 = H_2$), 164 °C (X_2 = HCl) and 185 °C ($X_2 = Cl_2$) respectively.[50]

(ii) It is expected that mixed halohydrides of aluminium and gallium will display greater Lewis acidity than their trihydride counterparts, as this is true of the trihalides.[51] An example of this can be seen in Scheme 1, wherein a bidentate Lewis base preferentially coordinates two trihydrides (InH_3) but chelates the related tribromide ($InBr_3$) due to its greater Lewis acidity, irrespective of the reaction stoichiometry.[51]



Scheme 1

Given the higher electronegativity of halides than hydrides, it follows that this greater electron-withdrawing potential should increase the effective positive charge on the metal centre. Greater Lewis acidity of a metal centre encourages higher coordination numbers (as per the example above), potentially leading to greater control of the metal coordination sphere, providing scope for increased thermal stability. For instance, the quinuclidine adduct of gallane [GaH_3(quin)] is known (dec. 100 °C),[23] however a bis-quinuclidine adduct [GaH_3(quin)$_2$] has not been reported. Bis-quinuclidine adducts of both chloro- and dichlorogallane, [$GaClH_2$(quin)$_2$] and [$GaCl_2H$(quin)$_2$], have been reported, with the latter having a decomposition point of 174 °C.[52]

(iii) Mixed halohydrides of aluminium and gallium have greater potential for derivatisation by salt elimination reactions than analogous trihydrides (Equation 1). The functionalisation of metal halides may be facilitated by addition of an alkali metal reagent, as the loss of an alkali metal halide is typically favoured by precipitation from solution. This is not typical for metal hydrides, thus, salt-elimination syntheses cannot generally be achieved with Group 13 trihydrides. Protolysis is also not considered a useful option for derivatisation of trihydrides, as it has been shown to lack selectivity.[53]

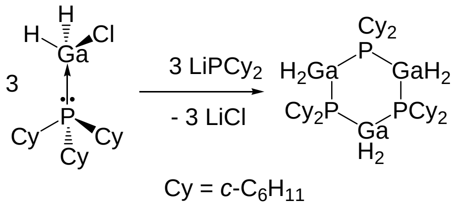
Equation 1

$$\mathrm{M'R + ML_nX \longrightarrow M'X + ML_nR}\ (\mathrm{M'} = \mathrm{Li, Na, K};\ \mathrm{X} = \text{Halide})$$

M = p-block metal

This process has been used previously to generate a trimeric dihydridogalliumphosphide (Scheme 2), where the loss of LiCl facilitates phosphide functionalisation at gallium.[50]

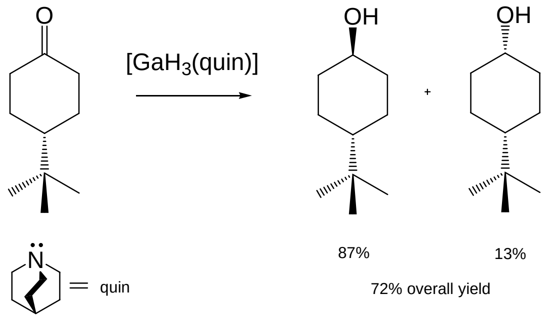
Scheme 2



(iv) By replacing hydrides with halides, it is expected that the remaining metal-hydride bonds will possess properties different to those of the "parent" trihydride. The electronegative halide ligand(s) should, through inductive effects, strengthen the metal-hydride bond. This change in bond character has potential to affect the nature of hydride delivery in the hydrometallation of organic substrates, opening up the potential for distinct chemo- and regioselectivities relative to trihydride species. The quinuclidine adducts of gallane, chlorogallane and dichlorogallane show an increasing wavenumber for the metal-hydride stretching frequency ($\upsilon_{Ga\text{-}H}$ (cm^{-1}): [GaH_3(quin)] 1810; [$GaClH_2$(quin)] 1852; [$GaCl_2H$(quin)] 1891). Although on the basis of classical mechanics this can be attributed to 'weighing' down the ML_2-H moiety, it is generally accepted that in this instance increasing wavenumber reflects increasing metal-hydride bond strength as more halides are introduced.[23, 52] It is anticipated that this will significantly impact on the reactivity of such compounds.

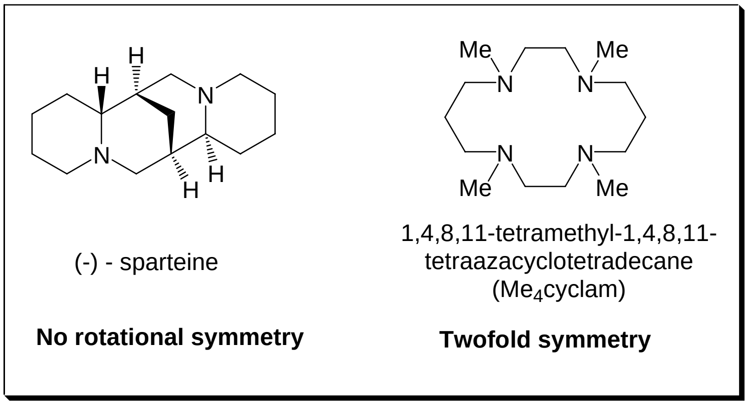
(v) Mixed halohydrides of aluminium and gallium also have greater potential as precursors to stereoselective organic reducing agents than their trihydride analogues. Trihydride adducts of aluminium and gallium are known to demonstrate diastereoselective hydrometallation (see Scheme 3).[54] This selectivity is either brought about by a stabilised transition state, as per the example in Scheme 3,[55] or coordination of the substrate prior to hydrometallation.[54]

Scheme 3



An alternative way to achieve stereoselectivity is by the introduction of chiral ligands to the metal centre. Most importantly, this functionalisation is the most likely means of introducing enantioselectivity to such reagents for the reasons outlined as follows.

Due to the threefold symmetry of a generic Lewis base adducted Group 13 trihydride [$MH_3(L)$], a threefold symmetric Lewis base, a rare class of ligand, is required to maintain a "single" hydride environment. Departing from this symmetry results in up to three hydride environments, reducing the stereoselectivity and control of hydride delivery to an organic substrate. If one or two of the hydrides is replaced by a halide, the requirement for a threefold symmetric ligand is removed. Under these circumstances, ligands with twofold and no rotational symmetry can, in principle, generate single hydride environments for MH_2X and MHX_2 species respectively. Some examples of ligands with these symmetries are shown below.



(-) - sparteine

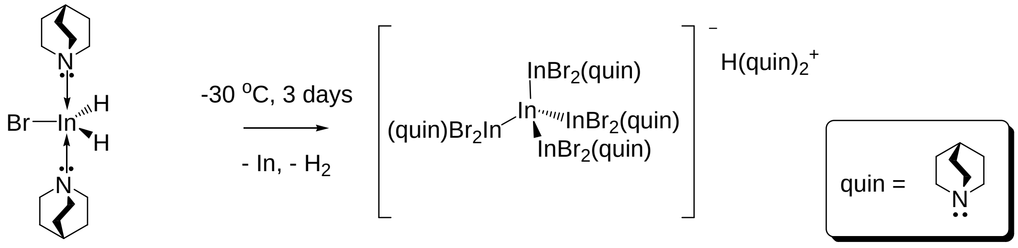
No rotational symmetry

1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4cyclam)

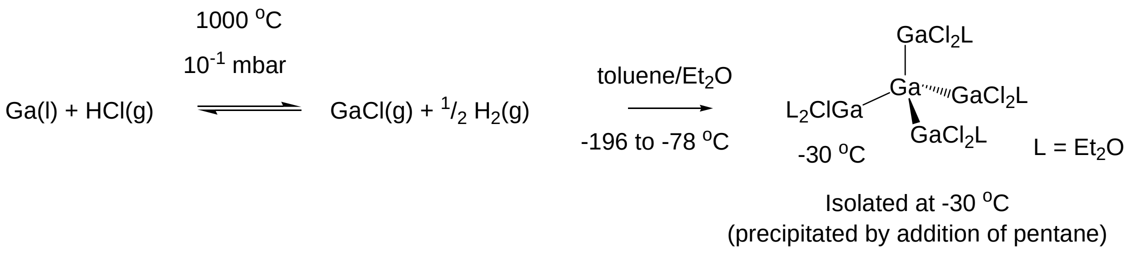
Twofold symmetry

(vi) Mixed halohydrides of aluminium and gallium also have applications in the preparation of complexes of low-valent Group 13 elements. Recently a mixed oxidation state indium complex, $[In_5Br_8(quin)_4]^-$ has been reported, which contains a tetrahedral In_5 unit (Scheme 4).[56] The preparation of this species is noteworthy in that the method of preparation used a stable In(III) precursor, rather than an unstable low-valent species. Previously, aluminium and gallium analogues have been difficult to access due to a requirement for extremely low temperature preparations when handling monovalent precursors, such as that in Scheme 5.[57] This species was prepared from a monovalent precursor at -196 °C and slowly warmed to produce a species of a higher oxidation state. In contrast, the indium species was prepared from [$InH_2Br(quin)_2$] and warmed to produce a species with a lower oxidation state via hydrogen loss. The trivalent precursor for this latter reaction was prepared via addition of one equivalent each of lithium bromide and quinuclidine to [$InH_3(quin)$].[58]

Scheme 4

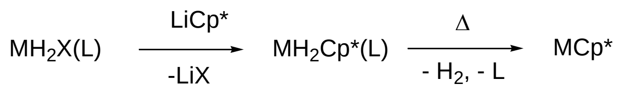


Scheme 5



These preparations rely on the controlled thermal dehydrogenation of “parent” hydride complexes using a non-hydride ligand to arrest the decomposition to M(0). It is therefore plausible that low valent Group 13 species can be accessed using the method outlined in Scheme 6.

Scheme 6



Cp* = *c*-$C_5Me_5^-$
M = Al, Ga. X = Cl, Br.

In this scenario, the halide ligand can be substituted by a Cp* anion, which is known to stabilise low-valent Group 13 complexes,[59] followed by controlled thermally induced hydrogen loss to afford a monovalent species.

2.3 Mixed halohydrides of aluminium and gallium

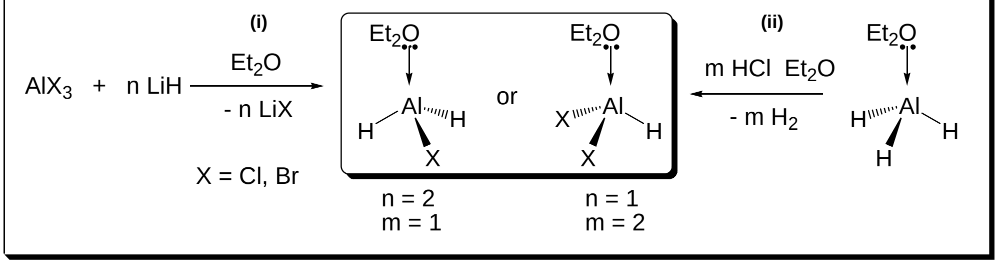
2.3.1 Known compounds and synthetic methods

Whilst numerous trihydride adducts of aluminium and gallium have been reported, relatively few mixed halohydrides are known. The following overview concerns the reported preparative methods and is listed by metal in chronological order, except where discussion of salient compounds is of benefit.

2.3.1.1 Aluminium

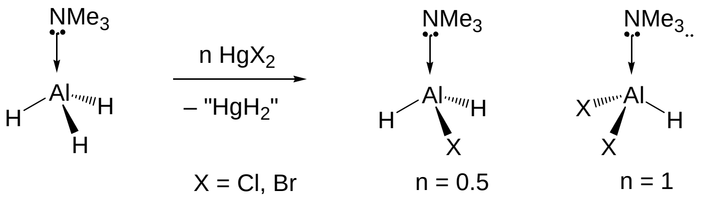
Mixed halohydrides of aluminium were first reported in 1954 by Wiberg *et al.*, who prepared diethyl ether adducts of mixed chloro- and bromoalanes from the relevant aluminium trihalide and lithium hydride ((i) in Scheme 7). An alternate method used anhydrous HCl to produce the same species via loss of hydrogen (ii).[60, 61]

Scheme 7

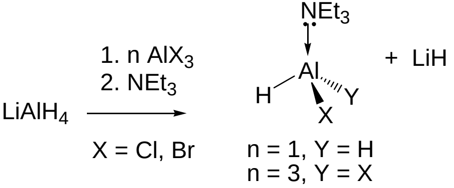


The trimethylamine adducts of these species were subsequently prepared in 1961 by the group of Ruff[62] using mercuric halides (Scheme 8), and the triethylamine analogues in 1966 (Scheme 9).[63] The latter preparation employed the reaction of Li[AlH_4] and one or three equivalents of the respective trihalide in diethyl ether, utilising the Lewis-basic aluminate anion's capacity as a more readily available source of hydride for halohydride exchange. This represents the first reported example of an aluminium halide-hydride redistribution reaction.

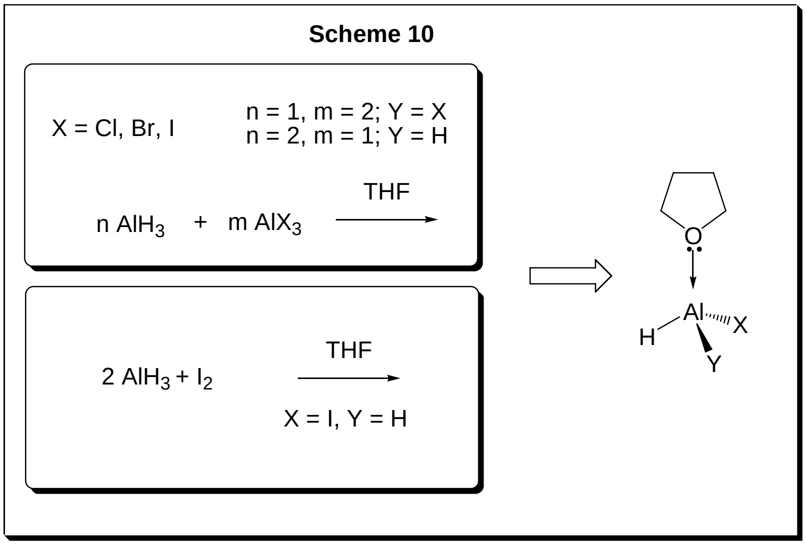
Scheme 8



Scheme 9



In the following year the THF-adducted analogues were prepared via addition of THF to the respective diethyl ether adduct. Interestingly, during this work the authors also noted that halide-hydride redistribution could be accomplished using neutral aluminium trihalides in THF, 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 10).[64]

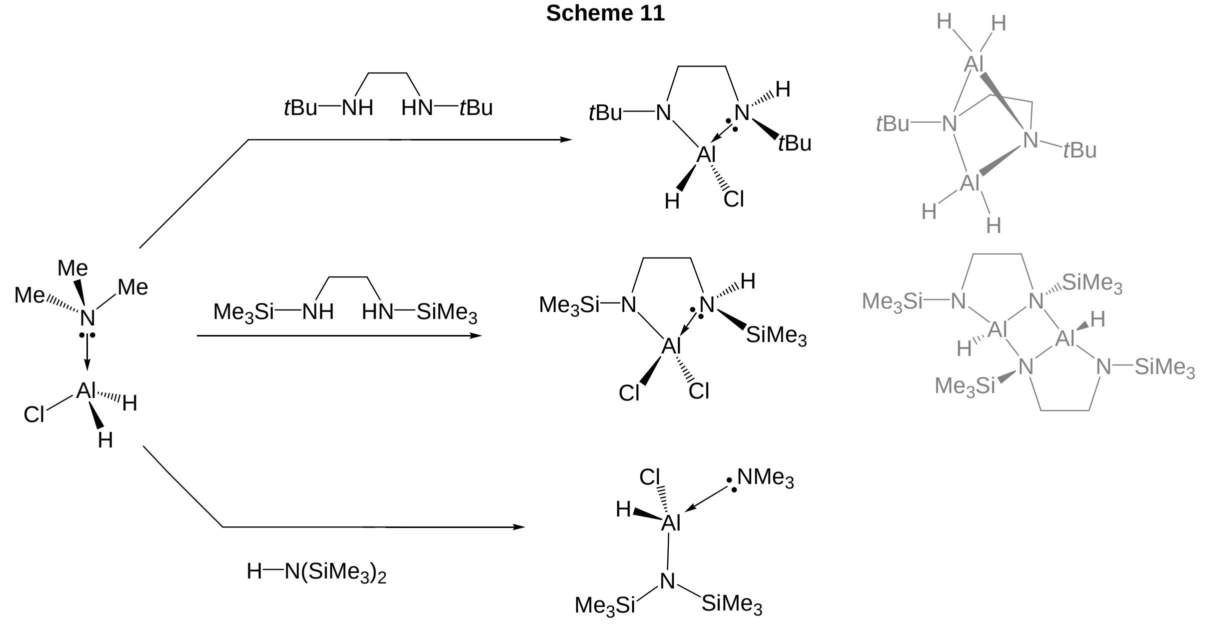


Despite this work, it was not until 1973 that mixed halohydrides were first structurally characterised. Semenenko *et al.*[65] published the single crystal X-ray diffraction structures of both [$AlCl_2H(Et_2O)$] and [$AlBr_2H(Et_2O)$], prepared using the same synthetic route as that used by Ashby (Scheme 10).

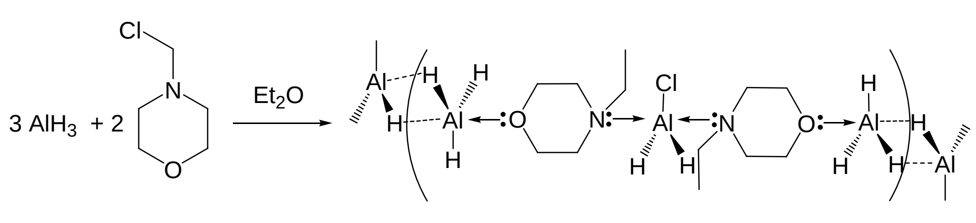
The trimethylamine adduct of chloroalane, [$AlClH_2(NMe_3)$], featured in several studies by the group of Raston.[66-69] The compounds prepared using this starting material are summarised in Scheme 11, with alane ([$AlH_3(L)$], L = Lewis base) derived products depicted in grey if the outcome observed contrasts that of [$AlClH_2(NMe_3)$]. H. Roesky and co-workers have also used [$AlClH_2(NMe_3)$] as a precursor to several carbaalanate complexes.[70]

In 1997 Raston *et al.* synthesised an unusual polymeric *N*-ethylmorpholine adduct containing both alane and monochloroalane. Reaction of alane and 4-(2-chloroethyl)morpholine hydrochloride by two equivalents of Li[AlH_4] resulted in a chloride-hydride transfer at the chloroethyl functionality to form the product (Scheme 12).[71] This cleavage pathway was previously reported by Marconi *et al.*, in that instance using chloromethylmethylether.[6]

Scheme 11

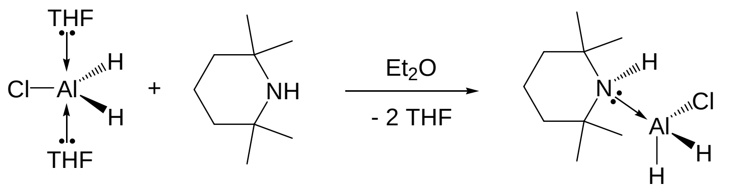


Scheme 12



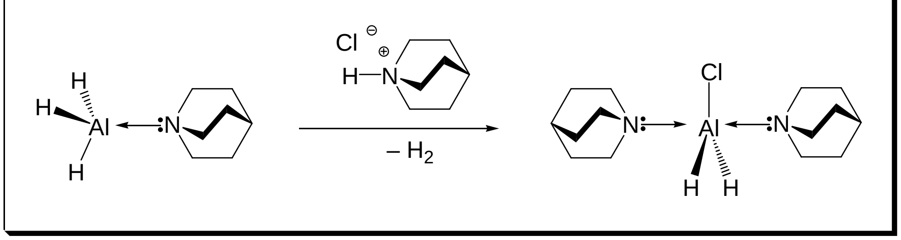
As part of a study of 2,2,6,6-tetramethylpiperidine (TMP) adducts of Group 13 trihalides, Krossing *et al*. reported a mixed halohydride of aluminium, (2,2,6,6-tetramethylpiperidine)-chloro-dihydrido-aluminium. The reaction proceeded via addition of TMP to [$AlClH_2(THF)_2$] however the authors did not elaborate on the preparation of the aluminium starting material (Scheme 13).[72]

Scheme 13



As will be outlined in Section 2.3.1.2, 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. It is therefore surprising that the first use of an ammonium halide as a source of sparingly soluble HX in alane chemistry was reported as recently as 2001 by Jones *et al.* (Scheme 14).[73] The shortened Al-N bonding parameters of [$AlClH_2(quin)_2$] (2.1354(17) Å) correspond with an increase in acceptor character of the chloroalane relative to that of the known alane complex [$AlH_3(quin)_2$] (2.155(3) Å).[74]

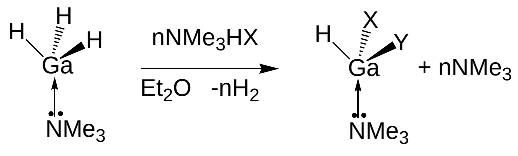
Scheme 14



2.3.1.2 Gallium

As early as 1965, mixed halohydrides of gallium were reported by Greenwood *et al.*[75] in a study initiated by the product of a failed attempt to prepare uncoordinated gallane (GaH_3), wherein the authors attempted the addition of anhydrous HCl gas to solid [$GaH_3(NMe_3)$]. Instead of the HCl displacing the ligand (as $NMe_3.HCl$), the reaction led to the monochloro species [$GaClH_2(NMe_3)$] and the evolution of dihydrogen. The dichloro species and bromo analogues were subsequently prepared by the same method.[75] The authors also reported two other methods for halogenating gallane, the first of which involved the use of a trialkylammonium salt as a source of HX (Scheme 15). This process utilised the lower solubility of the ammonium species to slow the rate of reaction and enhance selectivity.

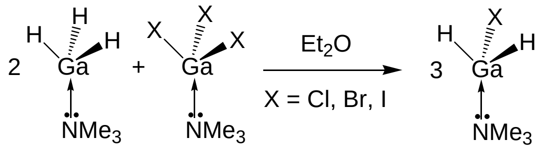
Scheme 15



X = Cl, Br
n = 1, Y = H
n = 2, Y = X

The second alternative method entailed the halohydride ligand redistribution (*cf.* Prather's redistribution preparation of chloroalanes in Scheme 10) of trialkylamine-adducted gallane and an appropriate ratio of either the trichloride, tribromide and triiodide congener (Scheme 16). The authors observed that whilst a 0.5 equivalent of the trihalide was sufficient to successfully synthesise the monohalogenated compounds, an excess was required to produce the dihalogenated species.[75]

Scheme 16



Recently, Himmel and co-workers have also prepared the complex [GaClH$_2$(NMe$_3$)], from the reaction of trimethylamine hydrochloride with [LiGaH$_n$Cl$_{4-n}$], the latter prepared *in situ* from the incomplete reaction of gallium chloride with excess lithium hydride.[76]

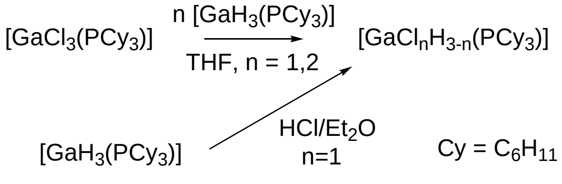
In the same year as the Greenwood report, the group of Schmidbaur reported the synthesis of uncoordinated dichlorogallane via chloride abstraction from gallium trichloride with trimethylsilane (Scheme 17).[77] In 2002 the same group structurally characterised this species along with its triethylphosphine adduct.[43] The synthesis of uncoordinated monochlorogallane was achieved in 1988 via a similar method using silane.[78]

Scheme 17

$$GaCl_3 + SiMe_3H \xrightarrow[-\ 20\ ^{o}C]{} (GaCl_2H)_2 + SiMe_3Cl$$

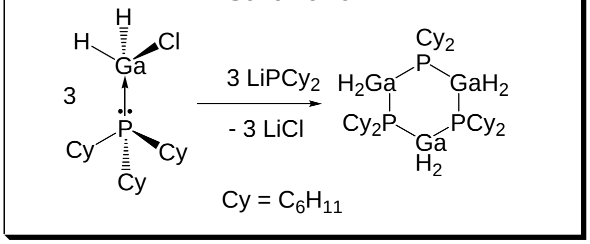
In 1995 Raston *et al.* used a redistribution process to synthesise the tricyclohexylphosphine adducts of both mono- and dichlorogallane as part of their research into potential semiconductor precursors (Scheme 18).[50]

Scheme 18

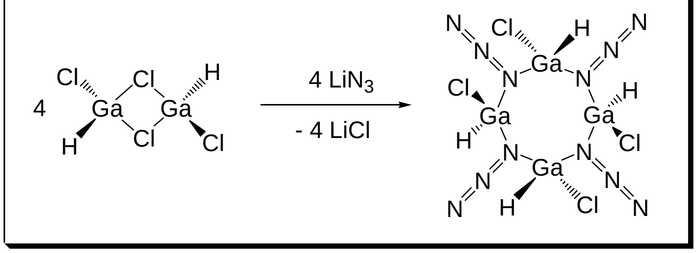


Contrary to the excess gallium trichloride used by Greenwood and co-workers,[75] these preparations were achieved using stoichiometric amounts of trichloride and trihydride species. The same species were also prepared using ethereal HCl as the source of chloride. In contrast, the reaction of mercuric chloride with [$GaH_3(PCy)_3$] yielded a mixture of products, indicating that the process was poorly selective; this contrasts the analogous aluminium reaction of Ruff (Scheme 8).[62] It was noted at the time that phosphine ligand exchange would occur in benzene solvents, but not in THF. However, chloride-hydride exchange would occur in THF, but not in benzene solvents. The species generated using these halohydride precursors, [{$GaH_2(PCy_2)_3$]}[50] (Cy = c-C_6H_{11}) and [{$GaHCl(N_3)$}$_4$][79] (Schemes 19 and 20), were prepared as precursors to gallium phosphide and gallium nitride respectively. Although the latter product yielded nanocrystalline GaN upon thermolysis, the former led to formation of dicyclohexylphosphane, gallium metal and hydrogen gas upon heating.

Scheme 19



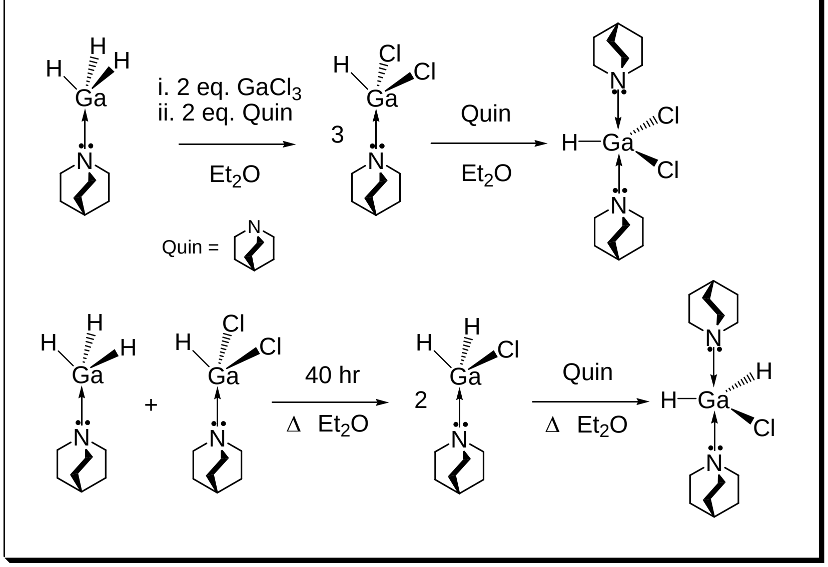
Scheme 20



In 1999 Gladfelter *et al.* reported the mono- and bis-quinuclidine adducts of monochlorogallane and dichlorogallane (Scheme 21)[52] using the established redistribution path of Raston[50] and Greenwood.[75] During the synthesis of [$GaCl_2H$(quin)], reaction of [GaH_3(quin)] with two equivalents of uncoordinated $GaCl_3$ followed by quinuclidine addition was found to achieve improved yields relative to addition of [$GaCl_3$(quin)]. The authors rationalised this by suggesting that due to the preference of gallium for four- and not five-coordination,[22] chloride-hydride exchange is less likely at a four coordinate gallium such as [$GaCl_3$(quin)].

An alternative but lower yielding method for the preparation of [$GaCl_2H$(quin)] was reported concurrently. This comprised the addition of four equivalents of LiH to the salt [NH_4][$GaCl_4$]. The synthesis of the monochlorogallane-monoquinuclidine species was accomplished by the redistribution reaction of [$GaCl_2H$(quin)] and [GaH_3(quin)] in diethyl ether.[52]

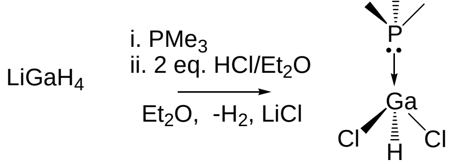
Scheme 21



It is interesting to note that despite the efforts of the authors, $[GaCl_3(quin)_2]$ could not be prepared; reactions resulted in near quantitative isolation of the four coordinate $[GaCl_3(quin)]$. The authors rationalised this outcome by proposing that although the increasing Lewis acidity encouraged higher coordination numbers, it was in this case outweighed by the steric influence of the larger chloride ligands.[52]

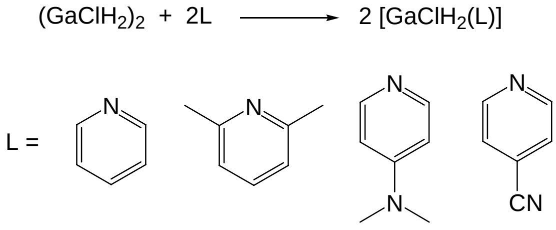
In a 2005 study of monochlorogallane, Downs *et al.* reported the synthesis of its trimethylphosphine adduct, accessed via reaction of $Li[GaH_4]$ with the phosphine base followed by two equivalents of ethereal HCl (Scheme 22). Although this species was prepared in a straightforward manner, attempts to prepare bis-complexes with bulky amines resulted in cationic gallane derivatives $[GaH_2(NH_2R)_2]Cl$, where R = ^{t}Bu or ^{s}Bu. The former of these was characterised by X-ray structure determination to give the first structurally authenticated Lewis base coordinated GaH_2^+ cation.[80]

Scheme 22

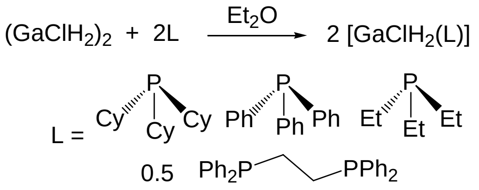


The group of Schmidbaur has prepared numerous mixed halohydrides of gallium utilising various nitrogen and phosphorus-based ligands (Schemes 23 and 24).[42, 81] The former complexes were prepared in order to investigate the donor and acceptor properties of main group metals towards ligands that are weak bases, but strong nucleophiles. Various pyridine analogues were prepared, and despite the changes in the basic/nucleophilic character of the pyridines, induced by either different para-substituents or steric effects of ortho-substituents, the course of the reaction was not altered (Scheme 23). In a similar vein, the phosphine analogues were also prepared (Scheme 24).

Scheme 23

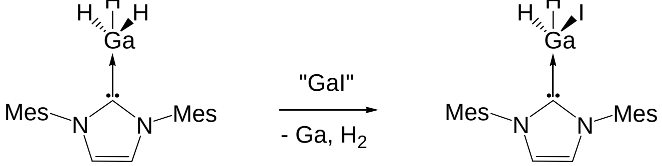


Scheme 24



A single example of an *N*-heterocyclic carbene (NHC) supported mixed halohydride of gallium was reported recently by Jones and Baker. The reaction of [GaH$_3$(IMes)] with a toluene solution of “GaI” resulted in the formation of [GaH$_2$I(IMes)], accompanied by the deposition of gallium metal and, presumably, the evolution of hydrogen gas (Scheme 24).[82] Despite the formation of an iodohydride via direct reaction of elemental iodine with alane,[64] an analogous reaction with gallium has not been reported. A detailed account of NHCs as ligands follows in Section 2.6.2.

Scheme 25



2.3.2 Uncoordinated halohydrides of aluminium and gallium

As aforementioned, dichlorogallane was first reported in 1965 as a result of a reaction between gallium trichloride and trimethylsilane at low temperature,[77] and structurally characterised in 2002.[43] Monochlorogallane was prepared analogously and structurally characterised as a dimer by Goode *et al*. in 1988.[78] As yet, uncoordinated mono- and dichloroalane have not been reported.

2.3.3 General comments

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[62] contrasts with the poor specificity reported by Raston and co-workers for the gallane counterparts.[50]

2.4 Infrared spectroscopy of halohydrides of aluminium and gallium

The molecular structure determination of group 13 trihydrides and halohydrides provides an opportunity to assess the impact of halogenation on the parent trihydride. 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.[52, 73, 81] 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 at the hydride ligand. Thus, in the absence of suitable neutron diffraction facilities, most research groups have turned to infrared spectroscopy as a routine and 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 1 collates the reported stretching absorbances for the known Lewis base stabilised group 13 halometallanes and, where possible, the analogous absorptions of the alane or gallane 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 'weighing' 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.[17]

Table 1. 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	**IR *v* M-H (cm^{-1})[a]**	**Related MH_3 IR *v* M-H (cm^{-1})**
$[AlCl_2H(OEt_2)]$	1920[60, 83]	1801[84][b]
$[AlCl_2H(OMe_2)]$	1923[83][c]	-
$[AlBr_2H(OEt_2)$	1912[60][c]	1801[84][b]
$[AlH_2I(OEt_2)]$	1901[60][d]	1801[84][b]
$[AlClH_2(THF)_2]$	1836m, 1755s[64][e]	1802 (one THF)[85][d]
$[AlCl_2H(THF)_2]$	1838vs, 1753vs[64][e]	1802 (one THF)[85][d]
$[AlBrH_2(THF)_2]$	1842w, 1772s[64][e]	1802 (one THF)[85][d]
$[AlBr_2H(THF)_2]$	1848vs, 1753vs[64][e]	1802 (one THF)[85][d]
$[AlH_2I(THF)_2]$	1782m[64][e]	1802 (one THF)[85][d]
$[AlHI_2(THF)_2]$	1796sh, 1746s[64][e]	1802 (one THF)[85][d]
$[AlCl_2H(OEt)_2]$	1908[83][c]	-
$[AlCl_2H\{O(CH_2CH_2)O\}]$	1785[83][d]	1748[85][d]
$[AlCl_2H\{(CH_3OCH_2)_2\}]$	1835, 1770[83][d]	-
$[AlClH_2(NEt_3)]$	1835, 1773[64][e]	1778[86][c]
$[AlCl_2H(NEt_3)]$	1866, 1812[64][e]	1778[86][c]
$[AlClH_2(quin)_2]$	1745s[d]	1685s[87][d]
$[AlClH_2(TMPH)$[f]	1891vs, 1831vs[72][d]	1773s[23][d]
$[GaCl_2H(py)]$	1970s[81][d]	-
$[GaCl_2H(3,5\text{-}Me_2Py)]$	1978s[81][d]	1822s[81][d]
$[GaCl_2H(3,5\text{-}Me_2Py)_2]$	1873s[81][d]	-
$[GaCl_2H(4\text{-}C{\equiv}NPy)]$	1977m[81][d]	-
$[GaCl_2H(4\text{-}NMe_2Py)]$	1979m[81][d]	-
$[GaClH_2(quin)]$	1882s[52][g]	1810[88]
$[GaCl_2H(quin)]$	1946s[52][g]	1810[88]
$[GaClH_2(quin)_2]$	1892s[52][g]	-
$[GaCl_2H(quin)_2]$	1852m, 1817w[52][f]	-
$[GaClH_2(PCy_3)]$	1880s[50][d]	1800s[89]
$[GaCl_2H(PMe_3)]$	1890s[80][h]	1837s, 1801s[90][j]
$[GaCl_2H(PEt_3)]$	1930s[43][c]	-
$[GaCl_2H(PPh_3)]$	1940s[42][g]	1880s[90]
$[GaCl_2H(PCy_3)]$	1920s [42, 50][d]	1800s[89]
$[\{GaCl_2H\}_2\{PPh_2CH_2\}_2]$	1951s[42][g]	1800s[66-69]
$[GaH_2I(IMes)]$[b]	1863s[82][d]	1780s[91][d]

a) Relative intensity information and medium used provided where available.

b) Et_2O solution.

c) Liquid film.

d) Nujol mull.

e) Fluorolube.

f) TMPH = 2,2,6,6-tetramethylpiperidine, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene.

g) KBr disc.

h) Raman spectrum.

j) Benzene solution.

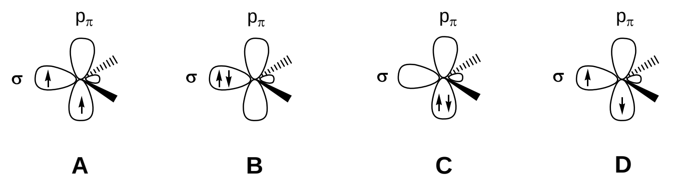
2.5 Stable carbenes

Over the past five decades carbenes have moved from being little-understood chemical curiosities to important compounds of high synthetic interest. Originally introduced into organic chemistry by Doering in the 1950s, and then discovered during the early stages of organometallic chemistry by Fischer in 1964,[92] the last 20 years has seen major advances in our understanding of these highly reactive divalent carbon species.[93] The isolation of a stable *N*-heterocyclic carbene (NHC) by Arduengo in 1991[93] paved the way for a wave of organometallic syntheses utilising ‘free’ carbene ligands. Since this time, NHCs have found broad utility in homogenous catalysis and coordination chemistry.[94]

2.4.1 Ground-state carbene spin multiplicity

Carbenes are, by definition, neutral compounds containing a divalent carbon with six electrons in its valence shell.[92] This simple arrangement permits compounds with markedly different chemical and physical properties. These properties depend on the placement of the six electrons in the four valence orbitals, which relies on the substituents about the carbenic carbon. For instance a carbene can be linear or bent depending on the hybridisation of the carbon. A linear geometry necessitates an *sp*-hybridised centre with two non-bonding degenerate orbitals (formally p_x and p_y), whilst a bent molecule breaks the degeneracy and forces the molecule to adopt an sp^2-type hybridisation. In this case the original p_y orbital remains virtually unchanged, and is commonly referred to as the p_π orbital due to its symmetry relative to the X-C-X plane. The original p_x orbital, which acquires *s* character by bending, is stabilised and commonly referred to as the σ-orbital (see Figure 1).[92]

Figure 1



This generates four possibilities for the arrangement of the two electrons in a bent molecule (see Figure 1). A triplet state is possible, where the two non-bonding electrons are in two different orbitals and have parallel spins (**A**), as are two singlet states; the σ^2 (**B**) is generally considered lower in energy than the π^2 (**C**), due to the lower energy of the σ-orbital. An excited singlet state is also possible but extremely rare. In this instance, the electrons reside in different orbitals with opposite spins (**D**). The reactivity of a carbene is dictated by its ground-state spin multiplicity;[95] singlet carbenes, by virtue of having an unfilled and filled orbital, can be regarded as ambiphilic, whereas triplet carbenes are di-radicals.

The ground-state multiplicity of a carbene is controlled by the relative energy of the σ and p_π orbitals. It is believed that a large gap in energy ($\geq$ 2 eV) leads to a singlet ground state, whereas a value below 1.5 eV results in a triplet state as electron-electron repulsion becomes greater than the σ- p_π gap.[96]

2.4.2 Electronic effects of carbene substituents

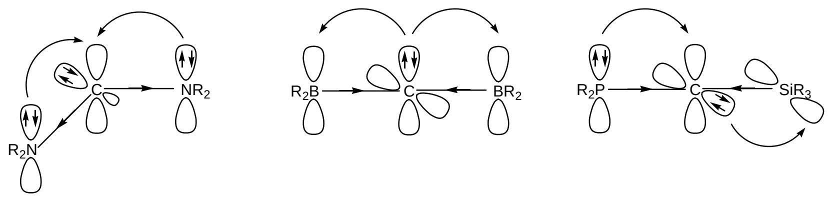
The electronic effects on carbenes can be divided into two categories: inductive effects and mesomeric effects.

It is well established that σ-electron-withdrawing substituents favour a singlet state by inductively stabilising the σ-orbital (increased *s* character). Conversely, electron-donating substituents decrease the energy gap between the *s* and p_π orbitals, favouring the triplet state.[92]

Mesomeric effects are thought to play a more significant role in dictating the ground-state multiplicity of carbenes than inductive effects. Substituents can be divided into two types: p_π-donating, such as -NR$_2$, -Cl, -OR, -PR$_2$, or p_π- withdrawing, such as -COR, -CN, -BR$_2$. Carbenic carbons flanked with either of these types of groups (or one of each) favour a singlet carbene. This is achieved through interactions between the carbenic carbon orbitals (*s*, p_π or p_x, p_y) and the relevant *p* or π orbitals of the substituents (Figure 2). A diaminocarbene, for example, having two π-donating substituents, will have the energy of the "p_π-orbital" raised, due to the π-overlap with the nitrogen lone pair orbitals. This increases the σ-p_π gap and thereby stabilises the singlet state.[92] By contrast, a diborylcarbene, with two π-withdrawing substituents, is predicted to be linear to enable optimal π-orbital overlap of the non-bonding carbon lone pair orbital with the vacant boron *p*-orbitals. As shown in Figure 2, overlap with the vacant substituent *p*-orbitals breaks the (p_x, p_y) degeneracy by lowering the energy of the p_x orbital and favours a singlet state.[92] A combination of these two types of interactions is seen in the case of a phosphinosilylcarbene, i.e., a π-acceptor and donor substituent. In this instance, the vacant p_y

orbital is raised in energy by its interaction with the phosphine lone pair, and the p_x orbital energy is lowered by interaction with the vacant p_π-orbital of the silicon. This again favours a linear singlet state.[92]

Figure 2



Diaminocarbenes Diborylcarbenes Phosphinosilylcarbenes

2.4.3 Steric effects of carbene substituents

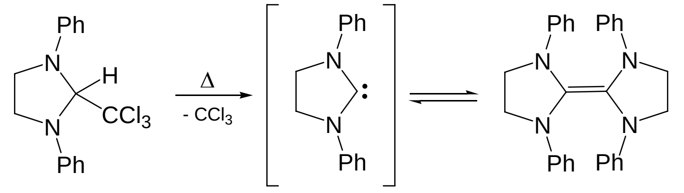
Bulky substituents kinetically stabilise a carbene by shielding the reactive carbon. If electronic influences are negligible, the steric effects of substituents can determine the ground-state multiplicity of the carbene.[92] Suitably bulky substituents favour a linear arrangement, and hence the triplet state. For instance, while dimethylcarbene (CH_3-C-CH_3) has a singlet ground state with a C-C-C angle of 111°,[97] both di(*tert*-butyl)-[98] and diadamantylcarbenes[99] (R-C-R, R = ^{t}Bu and 1-adamantyl respectively) have triplet ground states with C-C-C angles of 143° and 152° respectively. Cyclised carbenes such as cyclopentylidene[100] have singlet ground states due to their angular constraints.

2.6 N-heterocyclic carbenes

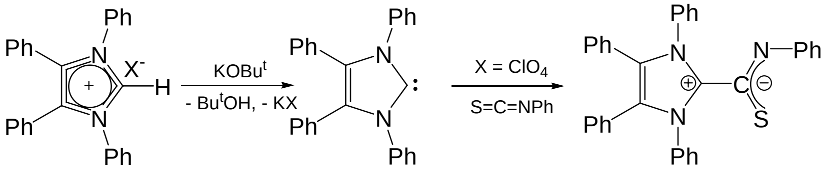
As early as 1960 Wanzlick and co-workers proposed that the stability of carbenes would be enhanced by the presence of π-donating amino substituents. Attempts to prepare 1,3-diphenylimidazolidin-2-ylidene by thermal elimination of chloroform (Scheme 26) were frustrated by the equilibrium of the putative NHC to an electron-rich olefin. Furthermore, cross-coupling experiments undertaken to support formation of the "free" NHC prior to dimerisation did not support the existence of the target carbene.[101] Subsequently, Denk *et al.* have demonstrated the existence of a monomeric carbene-dimer equilibrium using imidazolidin-2-ylidenes with smaller substituents such as methyl, ethyl and isopropyl groups.[102]

In 1970 Wanzlick and co-workers developed on the seminal imidazolin-2-ylidene studies above with the deprotonation of an imidazolium salt using potassium *tert*-butoxide to form the "free" imidazol-2-ylidene. Attempts to isolate the carbene were not made in this instance; instead it was trapped using phenylthioisocyanide as proof of initial NHC formation (Scheme 27).[103]

Scheme 26

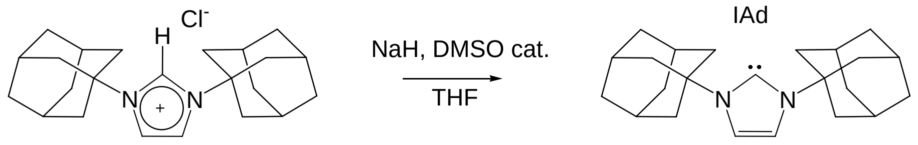


Scheme 27

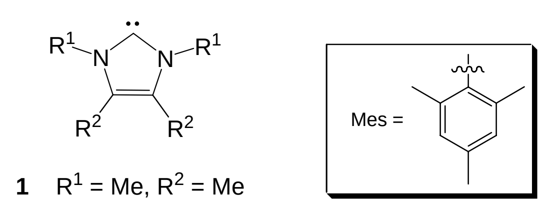


Almost 20 years later, Arduengo isolated a related stable crystalline carbene; 1,3-bis-(1-adamantyl)imidazol-2-ylidene, IAd.[93] The preparation of IAd was similar to that of Wanzlick's method, instead using the dimsyl anion ($^{-}CH_2S(O)CH_3$) as a base in the presence of sodium hydride (Scheme 28). The thermal stability of IAd is considerable, melting at 240 – 241 °C without decomposition.

Scheme 28



Arduengo rationalised the unusual stability of IAd on steric and electronic grounds. At the time it was suggested that these aided isolation. However, he later reported the thermally stable 1,3,4,5-tetramethylimidazol-2-ylidene (IMeMe, **1**) and 1,3-dimethylimidazol-2-ylidene (IMe, **2**), both lacking large N-substituents (m.p. 109-110 °C and dec. < 0 °C respectively).[104] At this time the remarkable stability of imidazol-2-ylidene carbenes was thought to be predominantly electronic with steric bulk at nitrogen augmenting thermal stability. One noteworthy NHC, 1,3-dimesitylimidazol-2-ylidene (IMes, **3**), reported by Arduengo at the same time as IMeMe and IMe, features heavily in this thesis, and is also thermally stable (dec. 150 °C).[104]



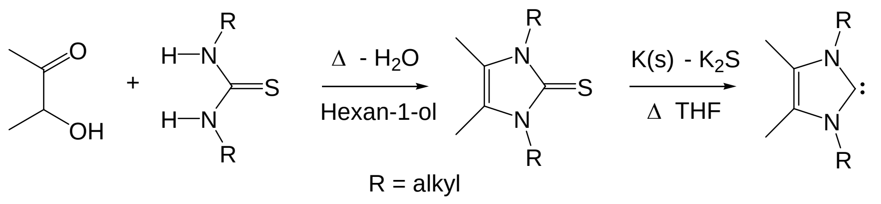
1 R^1 = Me, R^2 = Me
2 R^1 = Me, R^2 = H
3 R^1 = Mes, R^2 = H

2.6.1 Other synthetic routes to free NHCs

Although deprotonation of the corresponding imidazolium salt remains the major method of NHC preparation, several other methods have been reported.

A completely new synthesis of NHCs was reported by Kuhn and Kratz in 1993.[105] This method entailed the reduction of imidazol-2-thiones with potassium. The thione precursors were synthesised by the condensation of an appropriate thiourea with 3-hydroxy-2-butanone in hexan-1-ol at reflux, and potassium reduction was achieved in THF at reflux (Scheme 29).

Scheme 29

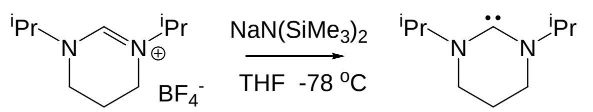


In 1997, this dechalcogenation path was used by Denk *et al*. to prepare imidazolin-2-ylidenes[106] (*cf*. early work of Wanzlick).[103]

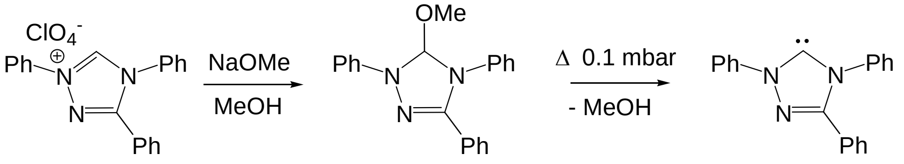
In 1999 Alders *et al.* published the synthesis of an NHC using hexamethyldisilazide as a base to deprotonate a cationic 6-membered NHC precursor (Scheme 30). Azeotropic removal of the by-product $HN(SiMe_3)_2$ with toluene, and purification by distillation afforded the NHC in 40% yield. The resulting six-membered saturated NHC is resistant to dimerisation, unlike saturated 5-membered congeners with nitrogen substituents of similar bulk.[107]

Relating to the aforementioned Wanzlick synthesis of an NHC by reductive elimination of chloroform, Enders *et al*. have used vacuum thermolysis to isolate a 1,2,4-triazol-5-ylidene after treatment of a triazolium perchlorate with sodium methoxide in methanol. This facilitated NHC formation via reductive elimination of methanol (Scheme 31).[108]

Scheme 30



Scheme 31



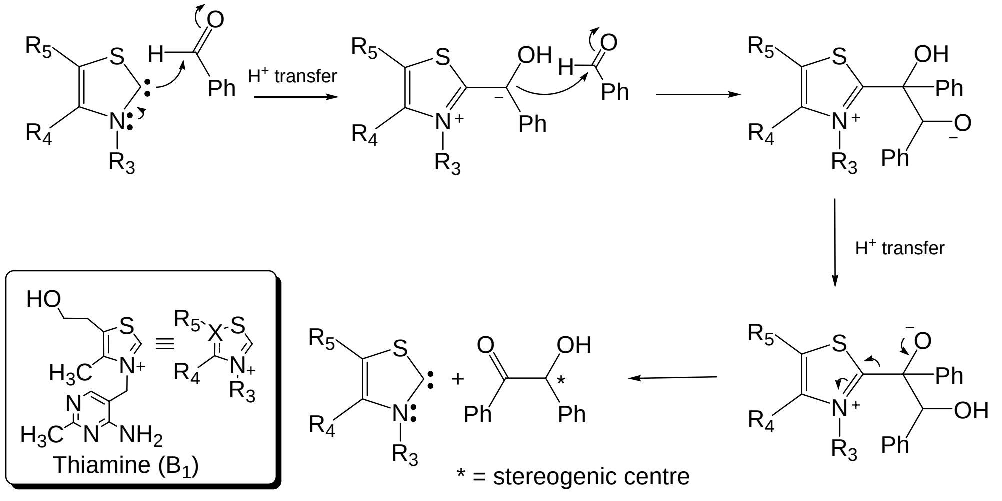
2.6.2 Uses of NHCs up to 2010

2.6.2.1 Organocatalysts

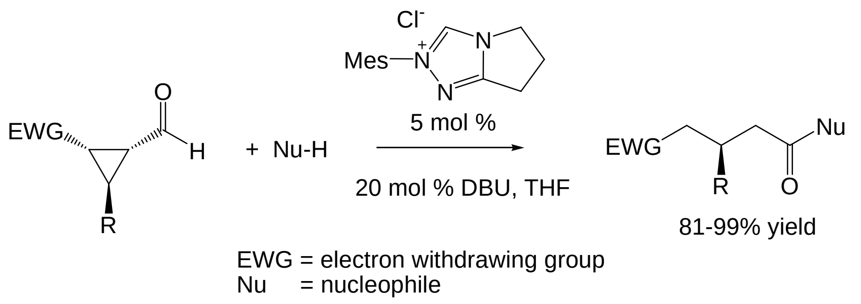
As early as 1958, compounds capable of generating “NHCs” as reactive intermediates have been identified as important catalysts in their own right. For instance, Breslow demonstrated that the vitamin A cofactor thiamine diphosphate catalyses the self-addition of benzaldehyde to form benzoin (Scheme 32).[109] This reaction proceeds by intramolecular removal of the labile 1,3-thiazolium 5-proton of thiamine, to generate a thiazol-2-ylidene NHC. This adds to the carbonyl carbon of benzaldehyde, in turn generating an *umpolung* synthon.[109] Similar reactions have also been studied by Stetter, Rovis, Nolan and others in the synthesis of 1,4-dicarbonyls, [110, 111] including asymmetric variants.[112]

This work has been extended to include conjugate addition reactions of functionalised aldehydes,[113] including α-haloaldehydes,[114] α,β-unsaturated aldehydes,[115] and α,β-epoxaldehydes,[116] conjugate addition to cyclopropane carboxaldehydes,[117] as well as a chiral variation of Breslow’s benzoin condensation.[118] The latter process (Scheme 33) provides a high-yielding, stereoselective pathway to ring-opened small strained molecules under mild conditions without the need for potentially expensive stoichiometric reagents.[116]

Scheme 32



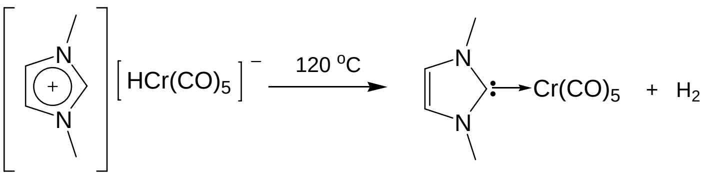
Scheme 33



2.6.2.2 Support ligands in homogeneous organometallic catalysis

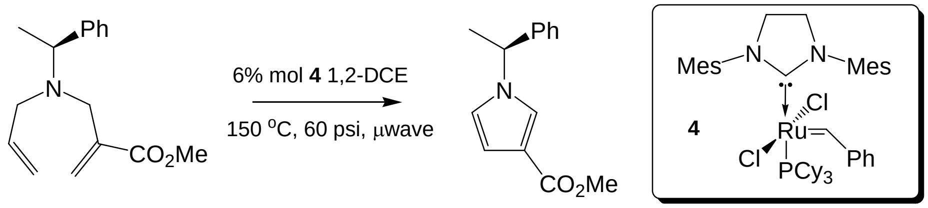
Since the first reported isolation of an NHC-metal complex (Scheme 34),[119] NHC-containing species have been studied extensively and are now regarded as excellent co-ligands in homogenous molecular catalysis.[112, 120] They coordinate transition metals in low or high oxidation states, p-block elements (including beryllium, sulfur and cationic iodine species, see below) and f-block metals.[92, 121] A consequence of their poor π-acceptor nature but superior nucleophilicity is that NHCs can stabilise and activate metal centres in multiple oxidation states in a variety of catalytic steps.[122]

Scheme 34

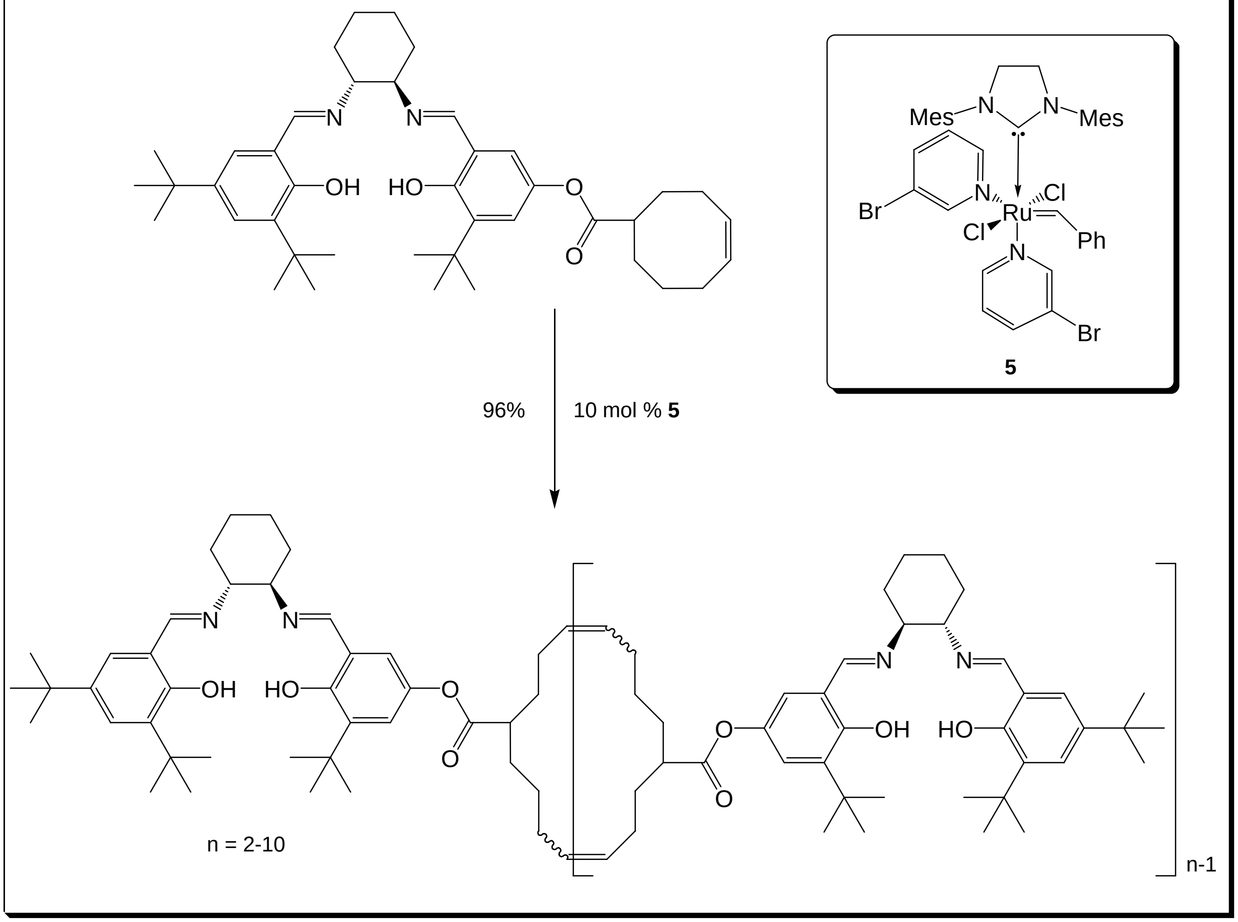


Significant examples of catalysts containing NHC ligands include Grubbs' 2nd and 3rd generation catalysts (Schemes 35[123] and 36[124] respectively). Similarly, NHC-supported palladium complexes are known to catalyse Heck couplings in 99% yield with catalyst concentrations as low as 10^{-4} % (Scheme 37).[122, 125] NHC-palladium complexes have also been utilised in Suzuki coupling reactions to afford high yields at room temperature (Scheme 38).[126, 127]

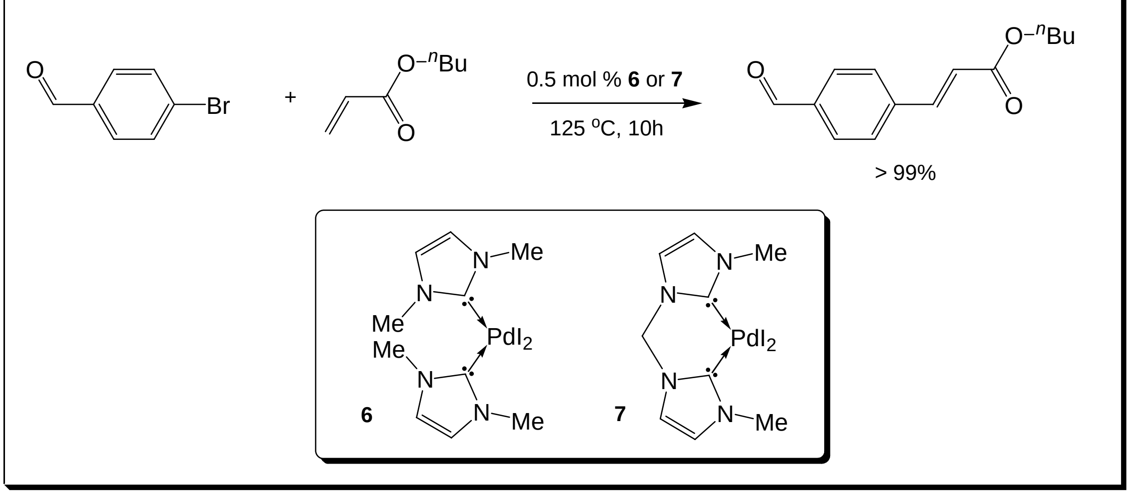
Scheme 35



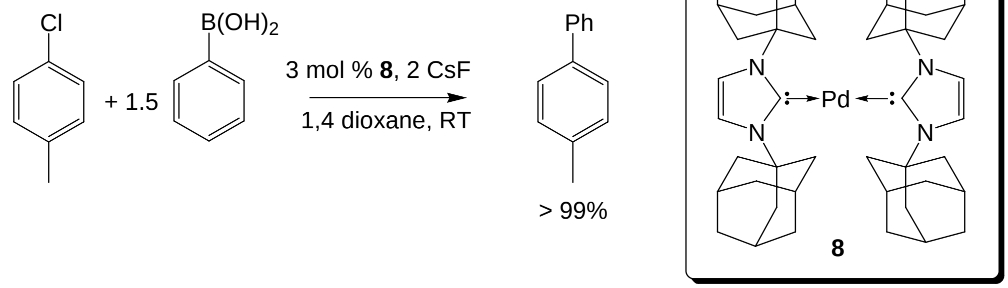
Scheme 36



Scheme 37



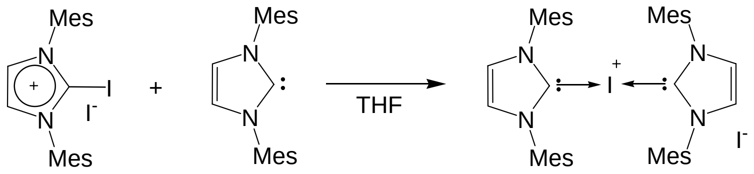
Scheme 38



2.6.2.3 NHCs as stabilising ligands for unusual p-block species

NHCs have been used extensively as stabilising ligands in several unusual p-block species. Arduengo *et al*. reported a bis-NHC adduct of the iodine cation, using the NHC IMes (Scheme 39), whereby reaction of a 2-iodoimidazolium salt of IMes with IMes itself afforded the complex $[(IMes)_2I][I]$.[128]

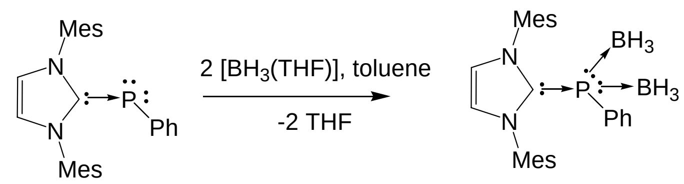
Scheme 39



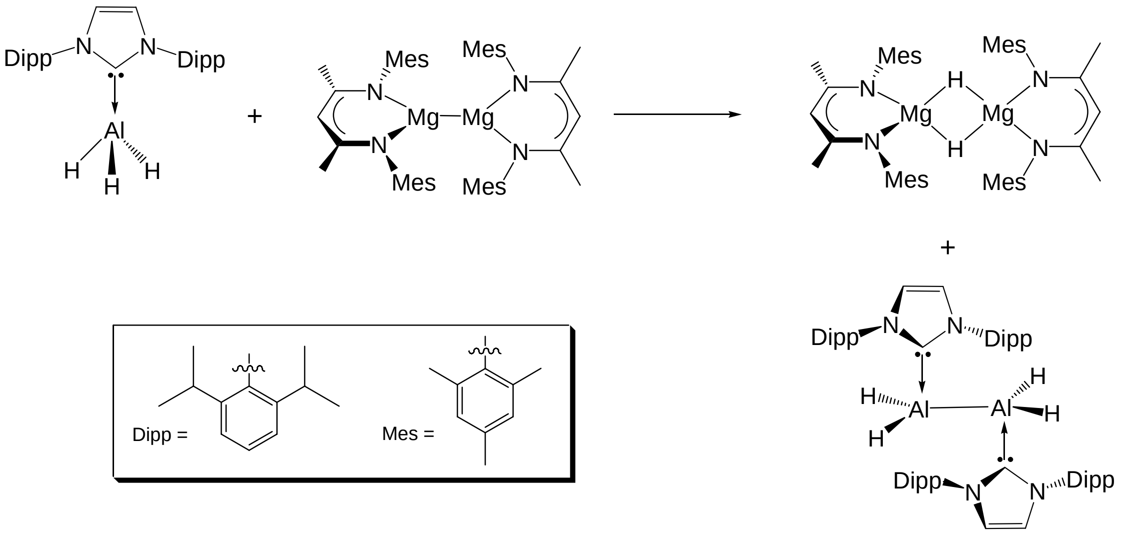
Arduengo, Cowley and co-workers also demonstrated the nucleophilicity of IMes by deoligomerising the cyclopolyphosphines $(PPh)_5$ and $(P(CF_3))_4$ to form carbene-phosphorus adducts of the form “carbene-PR”. The carbenic C-P bond lengths were only marginally longer (*ca*. 4%) than that of a normal C-P single bond, indicating minimal *pπ-pπ* double bond character. This bond length and the slightly twisted conformation of the molecule suggests two lone pairs at phosphorus. This was confirmed by addition of $[BH_3(THF)]$ in toluene to give the bis-borane adduct (Scheme 40).[129]

A recent report from Jones *et al*. details the preparation of an NHC-supported aluminium(II) complex during a study of potential hydrogen-storage materials.[130] A reaction involving hydride transfer to a *β*-diketiminate-supported magnesium dimer resulted in a thermally stable (dec. 190-192 ºC) species with a dimeric Al_2H_4 subunit (Scheme 41).

Scheme 40



Scheme 41



2.6.3 NHC adducts of group 13 metals

In addition to the group 15 donor complexes of aluminium and gallium covered in Chapter 1, NHC complexes of group 13 metals have been the subject of several reports in the literature. The following overview covers the known NHC complexes of group 13 metals organised by anionic ligand, with exceptions where particular compounds are discussed at a relevant stage.

2.6.3.1 Group 13 trihydrides

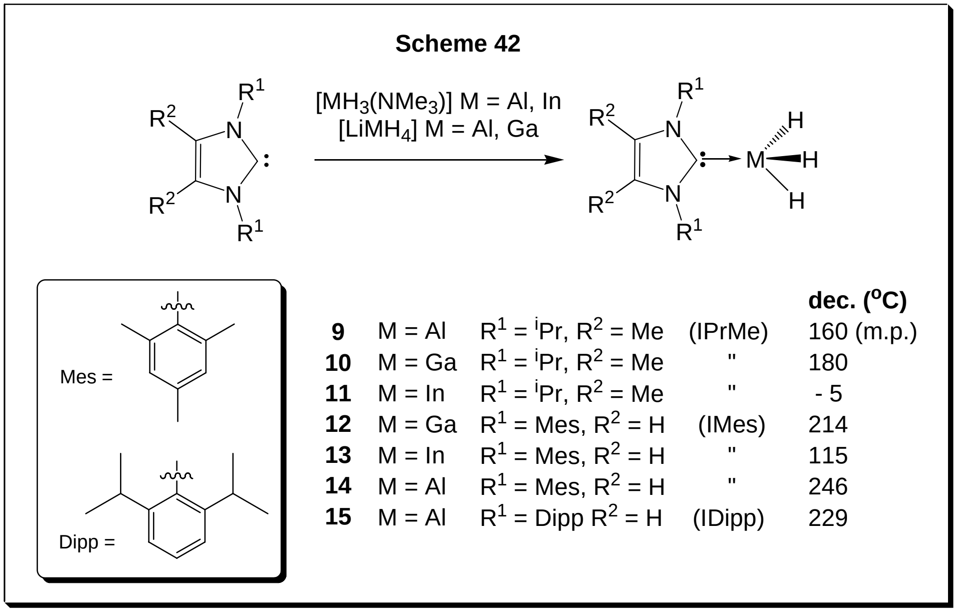
The landmark carbene complex [AlH_3(IMes)] was the first main group complex of an imidazol-2-ylidene.[131] To date, this is the most thermally stable aluminium trihydride complex known (m.p. 246 ºC, dec. not reported). At the time of publication, this stability was attributed to the high nucleophilicity of IMes. Based on spectroscopic and structural data (Table 2), Arduengo *et al.* proposed that the bonding exhibited by the carbene ligand was intermediate between the free carbene and its imidazolium salt, IMes·HCl.

Table 2. Structural and spectroscopic data of IMes and related species.

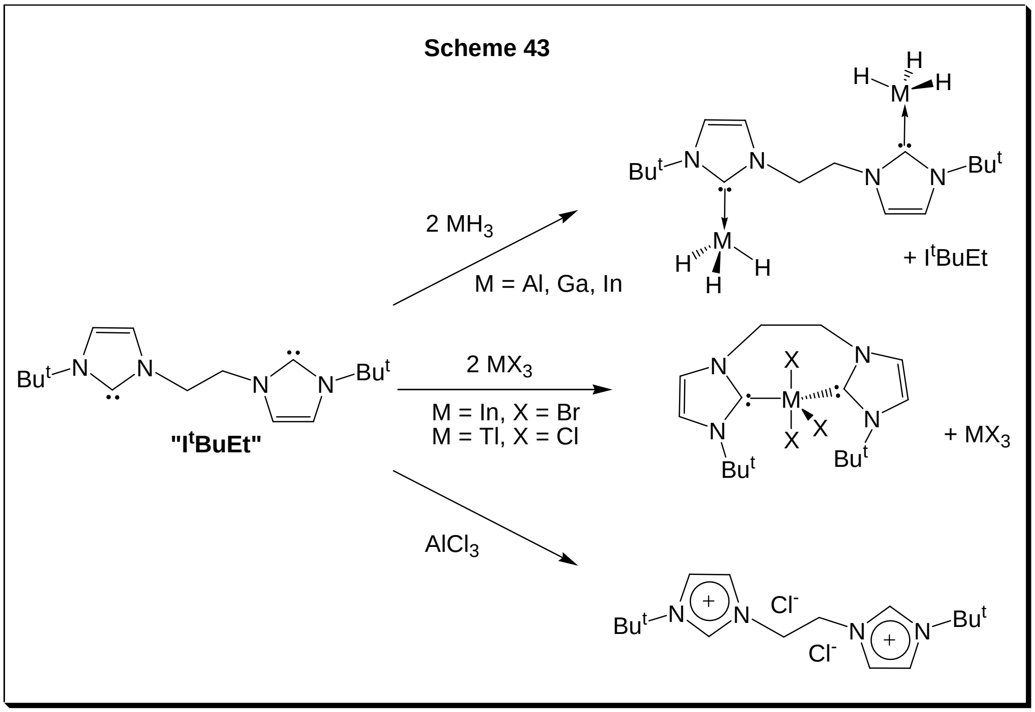
	IMes[104]	**[AlH$_3$(IMes)][131]**	**IMes·HCl[104]**
Carbenic carbon ^{13}C NMR signal (ppm, d^8 THF)	220	175	150
N-C-N angle (degrees)	101.4(2)	104.2(2)	109.2 (phenyl)

In 1998, this work was extended by the group of Jones *et al.* with the preparation of [AlH$_3$(I^{i}PrMe))] (**9**), [GaH$_3$(I^{i}PrMe)][132] (**10**) and [InH$_3$(I^{i}PrMe)] (**11**) (I^{i}PrMe = 1,3-bis(2,6-diisopropyl)-4,5-dimethylimidazol-2-ylidene, Scheme 42).[133] This was followed by a report from the same group on the IMes analogues [GaH$_3$(IMes)] (**12**) and [InH$_3$(IMes)] (**13**)[91] that, like [AlH$_3$(IMes)] (**14**), are considerably more thermally stable than their smaller congeners. In 2002 the bulky complex [AlH$_3$(IDipp)] (Dipp = 2,6-diisopropylphenyl) (**15**) was reported, which also shows considerable thermal stability.[134] Scheme 42 describes the preparation of these species and their respective decomposition points.

In 2002 the Jones group reported a series of complexes utilising the bis-carbene 1,2-ethylene-3,3′-di-*tert*-butyl-diimidazol-2,2′-diylidene (I^{t}BuEt).[51] Addition of the bis-carbene to [MH$_3$(NMe$_3$)] (M = Al, Ga, In) led to the formation of the metal-rich 2:1 adducts (Scheme 43). Addition of a further equivalent of ligand could not encourage formation of their respective 5-coordinate species. In contrast, the 1:1 or 1:2 reactions of I^{t}BuEt with MX$_3$ (M = In or Tl, X = Br or Cl) yielded only the 5-coordinate 1:1 adducts [MX$_3$(I^{t}BuEt)]. In the case of the indium species, this provided direct evidence of the higher Lewis acidity of the trihalide over the trihydride. The analogous aluminium and gallium reactions led to decomposition of the products. In the case of aluminium, a bis-imidazolium salt resulted (Scheme 43). The authors proposed that the imidazolium protons had come from the solvent (THF), but no further data was provided to support the formation of this species other than its significant insolubility.[51]


Scheme 42

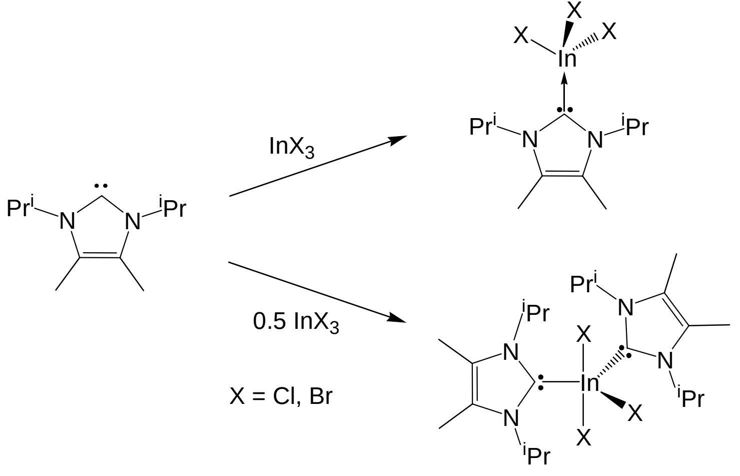
				dec. (^oC)
9	M = Al	R^1 = ^{i}Pr, R^2 = Me	(IPrMe)	160 (m.p.)
10	M = Ga	R^1 = ^{i}Pr, R^2 = Me	"	180
11	M = In	R^1 = ^{i}Pr, R^2 = Me	"	- 5
12	M = Ga	R^1 = Mes, R^2 = H	(IMes)	214
13	M = In	R^1 = Mes, R^2 = H	"	115
14	M = Al	R^1 = Mes, R^2 = H	"	246
15	M = Al	R^1 = Dipp R^2 = H	(IDipp)	229


Scheme 43

2.6.3.2 NHC adducts of group 13 trihalides

Prior to the aforementioned trihalide species, Jones *et al*. reported a series of NHC complexes of indium trihalides in 1997.[135] Treatment of InX_3 (X = Cl, Br) with one equivalent of the bulky NHC 1,3-bis(2,6-diisopropyl)-4,5-dimethylimidazol-2-ylidene (I^iPrMe) yielded 1:1 complexes (Scheme 44).

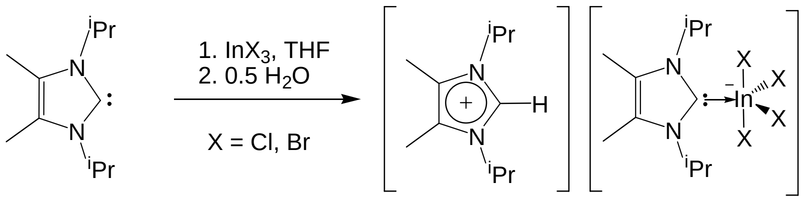
Scheme 44



Addition of two equivalents of carbene to the same trihalides brought about the formation of the relevant 5-coordinate bis-adducts, but with an unusual structural feature. Instead of the bulky ligands adopting the expected apical positions, a distorted trigonal bipyramidal geometry resulted with the carbenes and one halide occupying the equatorial positions.[135]

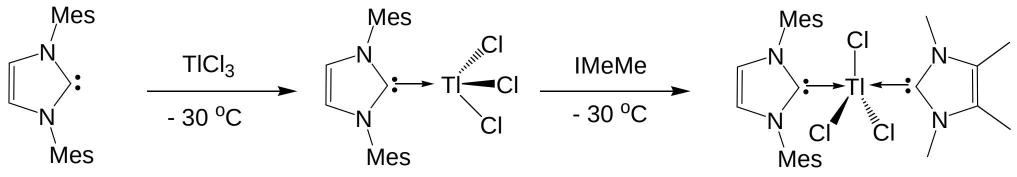
The high nucleophilicity of imidazol-2-ylidenes was demonstrated by reaction of the 1:1 adducts with 0.5 equivalent water, which resulted in imidazolium salts of the respective tetrahaloindanate ions, i.e., adducts of InX_4^- (Scheme 45).[135]

Scheme 45

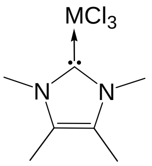


As part of several studies, including some previously mentioned, Jones *et al.* have reported several NHC adducts of group 13 trihalides. These include the IMes adducts of $InCl_3$,[91] $InBr_3$[134] and $TlCl_3$,[136] and also [$InBr_3$(IDipp)] (IDipp = 1,3-bis(2,6-diisopropyl-phenyl)imidazol-2-ylidene).[134] [$InCl_3$(IMes)] was prepared via chloride abstraction by simply stirring the trihydride precursor [InH_3(IMes)] in dichloromethane. The related halohydride [$InClH_2$(IMes)] was accessed by addition of quinuclidine hydrochloride to the same trihydride,[91] and both [$InBr_3$(IMes)][134] and [$TlCl_3$(IMes)][136] were accessed via simple addition of IMes to the trihalide. A bis-adduct of $TlCl_3$[136] was also prepared; an initial attempt was made to include two IMes ligands, which was unsuccessful presumably due to steric limitations. Use of the smaller carbene IMeMe (IMeMe = 1,3,4,5-tetramethylimidazol-2-ylidene) successfully yielded [$TlCl_3$(IMes)(IMeMe)] (Scheme 46).[136]

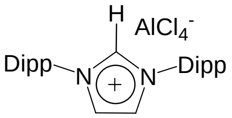
Scheme 46



In 2004 Roesky *et al.* published the synthesis of the IMeMe adducts of gallium and aluminium trichloride (**16**-**17**).[137] As part of their findings the authors revealed that although the aluminium adducts containing a smaller carbene such as IMeMe could be easily synthesised, attempts to use bulkier NHCs for aluminium resulted in the formation of an imidazolium salt and a tetrachloroaluminate counterion (**18**). No report was made of the analogous gallium reactions.



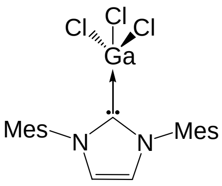
16 M = Al
17 M = Ga



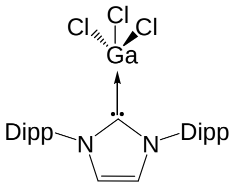
18

Dipp = 2,6-^{i}PrC_6H_3

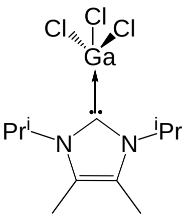
Recently Nolan *et al.* published a series of NHC adducts of gallium trichloride (**18**-**20**) whilst investigating their catalytic potential. One aim of the research was to investigate the air stability of these compounds; the rationale being that sterically encumbered four-coordinate complexes would be more stable. All three of these species demonstrated indefinite air and moisture stability and did not decompose upon dissolution in polychlorinated solvents.[138]



19



20



21

2.6.3.3 NHC-supported group 13 trialkyl species

In contrast to the recent reports of NHC- supported group 13 metal trihydrides and trihalides (see above), very few trialkyls have been reported. In 1996 the group of Robinson prepared NHC complexes of both trimethyl aluminium and gallium via addition of the trialkyl reagents directly to a solution of the carbene I^{i}PrMe.[139] The resultant 1:1 NHC-metal complexes once again demonstrated the high nucleophilicity of NHCs. The IMeMe adduct of trimethylaluminium, also monomeric, has recently been prepared via transmetallation using [TiF_4(IMeMe)].[140]

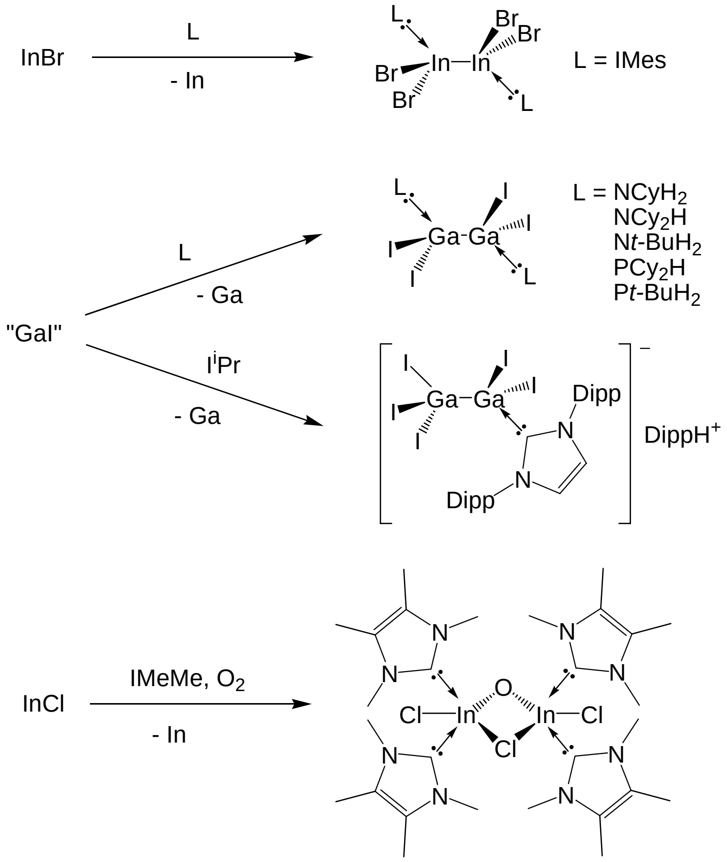
2.6.3.4 Reactions of NHCs with subvalent group 13 halides

As previously mentioned in Section 2.3.1.2, Jones *et al.* have reported the preparation of the NHC-supported gallium halohydride [GaH_2I(IMes)] using a gallium(I) precursor.[82] Further work by the same group has yielded some interesting outcomes. For instance, in a 2002 study of the reactions of amines, phosphines and NHCs with low-valent gallium(I) iodide, “GaI”,[141] the amines and phosphines all afforded gallium(II) products with the general form [$Ga_2I_4(L)_2$]. By contrast, addition of IDipp yielded a novel salt of the form [Ga_2I_5(L)][LH]. At the time of publication, it was assumed that the imidazolium proton was abstracted from the solvent (toluene); this was subsequently confirmed by the reproducibility of the reaction under strict anhydrous conditions. It is noteworthy that this result contrasts the reaction of indium(I) bromide with IMes, which affords the indium(II) complex [$InBr_4IMes_2$] (Scheme 47).[142]

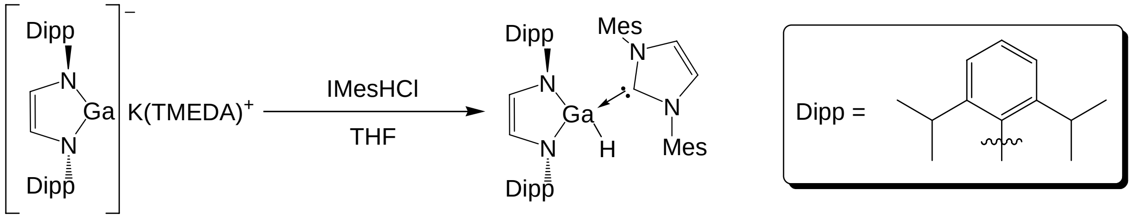
This difference in reactivity was rationalised on the basis of gallium’s smaller atomic radius, and the extra bulk of the carbene used. The 2002 study also detailed the reaction of IMeMe with indium(I) chloride, which resulted in an oxo-bridged dimer via adventitious inclusion of oxygen. Neither this nor the intended product could be isolated when performed under more stringent air-sensitive conditions.[141]

A subsequent report by Jones detailed the preparation of an unusual NHC adduct of a gallium hydride. Whilst the NHC IMes fails to react with an anionic gallium NHC analogue, reaction occurs with its imidazolium salt precursor, IMesHCl, where gallium oxidatively inserts into the imidazolium C-H bond (Scheme 48).[143]

Scheme 47

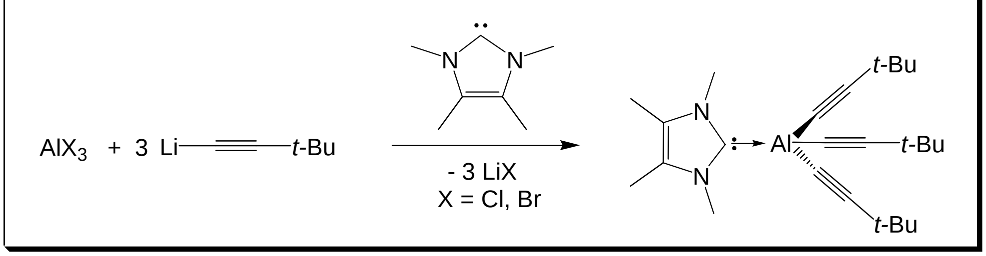


Scheme 48

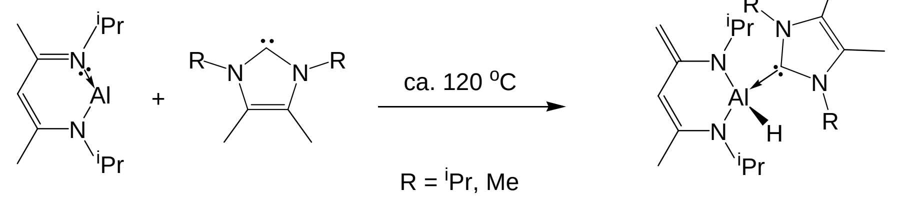


Recent studies by Roesky *et al.* using alane reagents, as part of a study of aluminium hydride cluster precursors (Scheme 49), afforded a unique trialkynylaluminium-NHC complex by a salt-elimination reaction.[144] This compound displays excellent thermal stability (m.p. 162 °C). The same group has also reported two NHC-supported aluminium species as part of a reactivity study of a low valent aluminium(I) precursor.[145] Solid-state mixing of either I^{i}PrMe or IMeMe and LAl (L = HC{(CMe)(NAr)}$_2$, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) at elevated temperature results in hydrogen abstraction from the ketamine methyl and coordination of the NHC to the oxidised aluminium(III) centre (Scheme 50).

Scheme 49

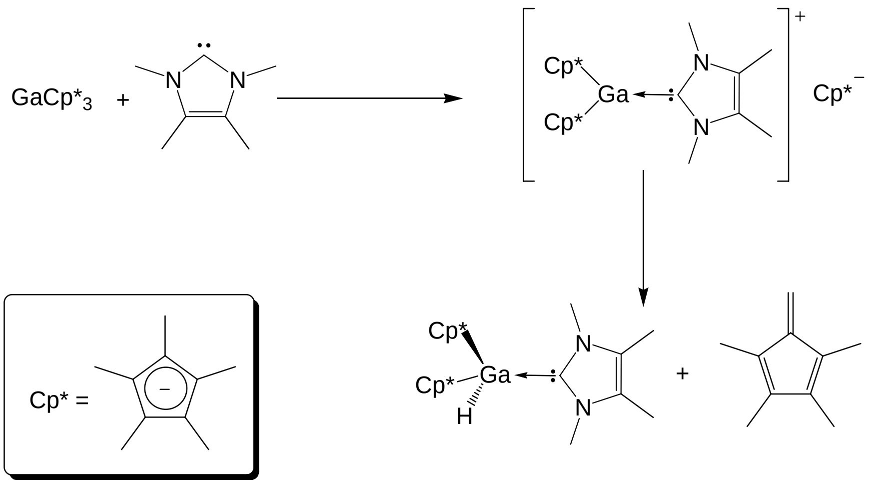


Scheme 50



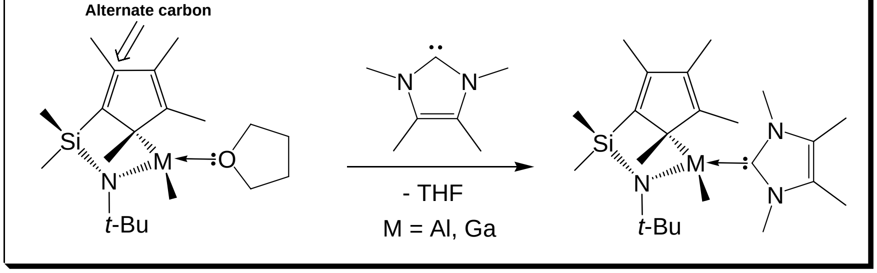
Hydrogen abstraction by a group 13 centre has also been observed by the group of Cowley. Reaction between $Ga(C_5Me_5)_3$ and IMeMe results in displacement of a $(C_5Me_5)^-$ anion by the carbene to form an unstable decamethylgallocenium cation intermediate, followed by hydride transfer to yield a neutral adduct by elimination of tetramethylfulvalene (Scheme 51).[146]

Scheme 51



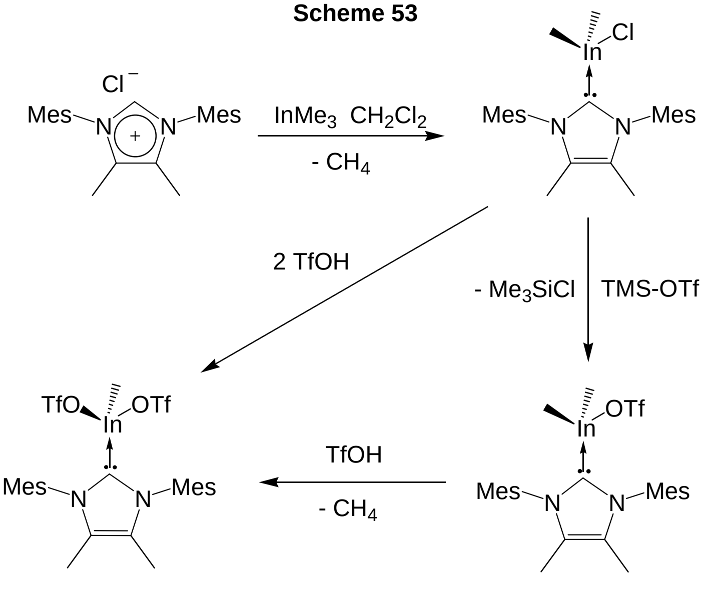
The same group has also reported NHC complexes of group 13 metals with a bridged amidocyclopentadienide ligand, $[Me_2Si(\eta\text{-}C_5Me_4)\text{-}(N\text{-}^tBu)]^{2-}$ (Scheme 52).[147] These species resulted from a simple substitution reaction to displace THF, which was weakly coordinated to the parent complex. NMR spectroscopy of the THF-coordinated species revealed only two methyl signals for the cyclopentadienyl ligand, rather than the expected four. The researchers proposed a fluxional process involving rapid dissociation/re-association of the THF molecule, and a reversible migration of the metal centre to a second carbon (labelled in Scheme 52) By contrast, NMR analysis of the carbene-coordinated species evidenced four distinct cyclopentadiene methyl signals, indicative of the superior donor strength of the carbene over THF providing sufficient impediment to the aforementioned Cp-migration fluxional process.

Scheme 52



As part of an investigation into alternative indium triflate Lewis acid catalysts, several new NHC-indium complexes were prepared.[148] The first of these, a precursor, was prepared via reaction of trimethyl indium with IMesHCl, yielding [InClMe$_2$(IMes)], an air-stable but moisture-sensitive monomer (Scheme 53).[148]

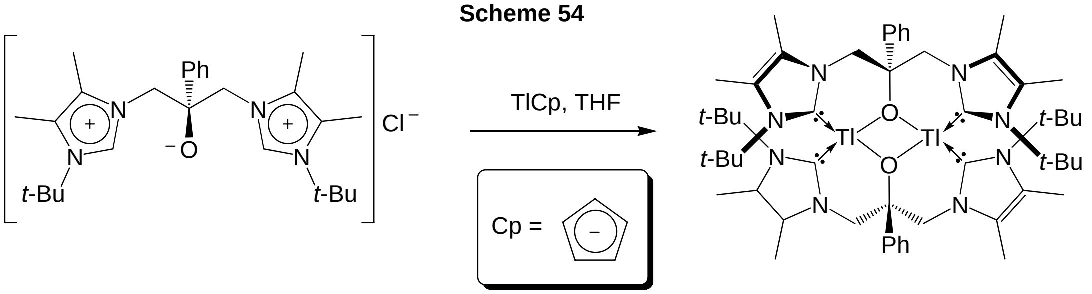
Scheme 53



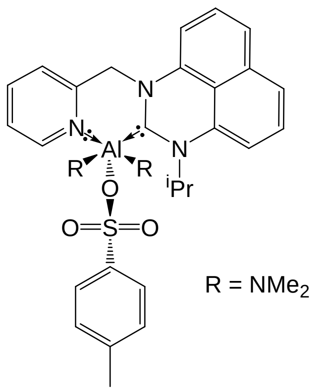
Addition of trimethylsilyltriflate (TMS-OTf) to this product resulted in the NHC-indium triflate complex (InMe$_2$OTf(IMes)] via loss of TMS chloride. Solid-state analysis of this species revealed it to be polymeric, but it was anticipated that this was unlikely to be the case in solution due its high solubility in dichloromethane. Addition of another equivalent of TMS-OTf failed to further substitute the complex; this was achieved via addition of triflic acid (TfOH) with loss of methane. This latter species could also be accessed by addition of two equivalents of TfOH to [InClMe$_{2(}$IMes)]. The use of these species as Lewis acid catalysts was not discussed.[148]

In 2004 Arnold *et al*. reported an unusual tetra-NHC dithallium complex, which was prepared as a transfer reagent. Addition of TlCp to the chloride salt of a bis-imidazolium alkoxide yielded an NHC-supported thallium dimer (Scheme 54).[149] Of note in this report was the combination of an alkoxide functionality with the strongly ligating NHC.

Scheme 54



A tricyclic pyrimidine-based NHC adduct of aluminium with a pendant pyridine donor, anionic sulfonate and amide ligands was reported in a patent application from Richeson *et al.* filed in 2004 (below).[150] No synthetic or spectroscopic details were provided, however it should be noted that the same authors recently described the preparation and reactivity of this ligand type in more detail, including its application as a co-ligand in rhodium catalysed syntheses.[151]



2.7 Research proposal

The aims of this chapter are as follows:

(i) To expand and optimise existing paths to Lewis base adducts of group 13 mixed halohydrides.

(ii) To assess the increased thermal stability and Lewis acidity of group 13 mixed halohydrides.

(iii) To generate a library of compounds for subsequent study as reagents in organic synthesis (see Chapter 3).

2.8 Results and discussion

2.8.1 The preparation of tertiary amine adducts of chloroalanes

The lability and volatility of the amine donor in [$AlH_3(NMe_3)$][62, 86] suggest complexes of the form [$AlCl_nH_{3-n}(NMe_3)_m$] (n = 1 or 2, m = 1 or 2) will be useful precursors to Lewis base adducts of mono- and dichloroalane. Furthermore, the low molecular weight of these species may permit sublimation as a means of purification. It is noteworthy that Wiberg and co-workers reported the putative syntheses of mono(trimethylamine) mono- and dichloroalane by reaction of diethyl ether alane with hydrogen chloride followed by treatment with trimethylamine.[60] Unfortunately, aside from 'active' hydrogen data, this report did not disclose any spectroscopic structural or physical data.

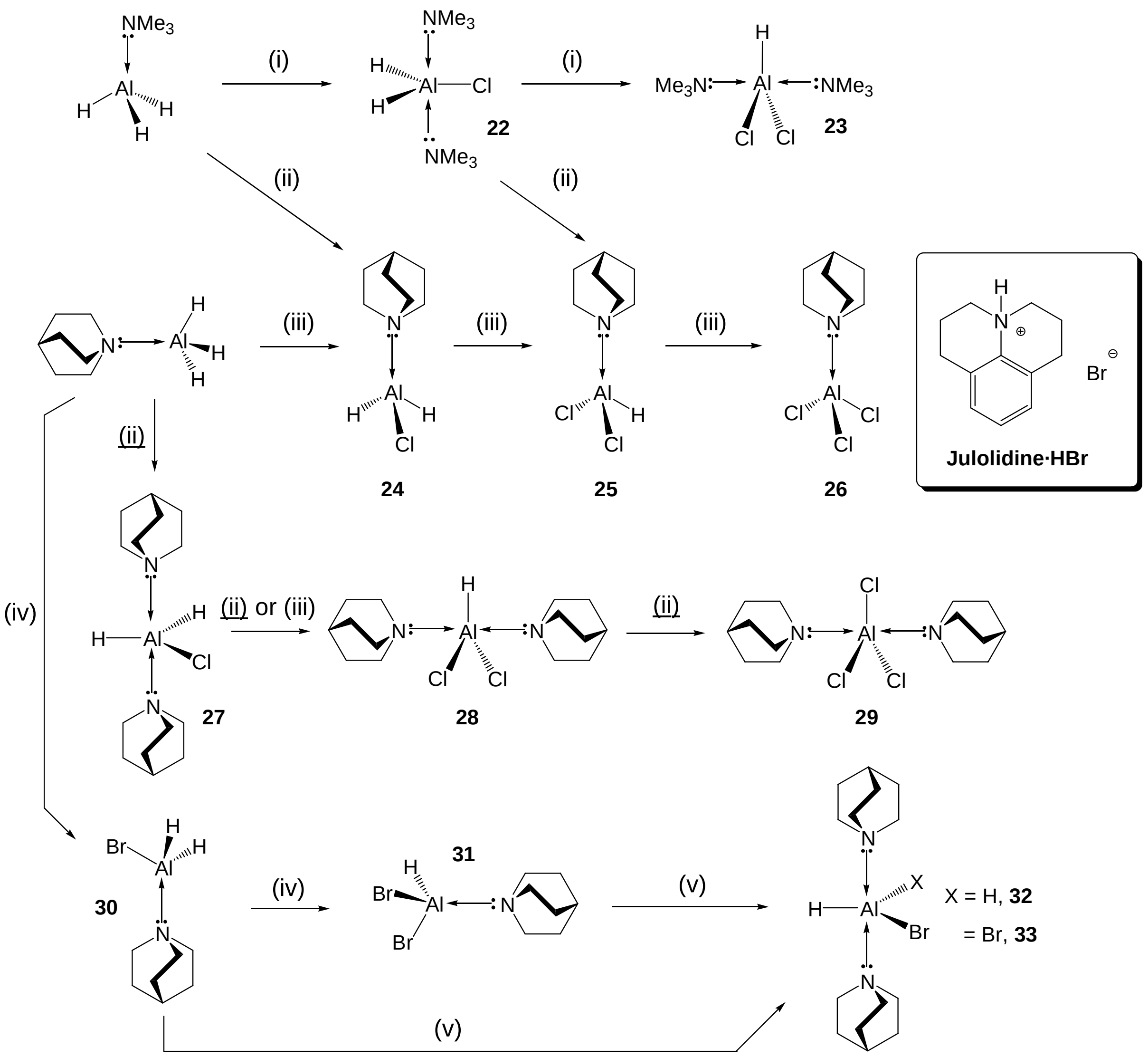
Diethyl ether solutions of freshly sublimed [$AlH_3(NMe_3)$][62, 86] were treated with one or two equivalents of trimethylamine hydrochloride (Scheme 54) at low temperature (-78 ºC) to afford the air and moisture sensitive chloroalanes [$AlClH_2(NMe_3)_2$] (**22**) and [$AlCl_2H(NMe_3)_2$] (**23**). These were purified by sublimation (**22**; 30 ºC, 1.0×10^{-4} bar, **23**; 40 ºC, 1.0×10^{-4} bar) in high yield (86 and 90% respectively). Both preparations can be undertaken in gram scale quantities without diminishment of yield. Sublimation proved to be the superior method of purification of these species; attempts to purify them by fractional crystallisation consistently led to a mixture of products.

The isolation of **22** and **23** as bis(trimethylamine) adducts despite purification by sublimation is noteworthy, and is presumably enabled by the low sublimation temperatures used at the pressure employed, which permits retention of both donors. The melting and decomposition points of **22** and **23** (101-3, 140 ºC, and 105-7, 154 ºC respectively) are above that of [$AlH_3(NMe_3)_2$] (m.p. 76 ºC,[62] dec. 94 ºC) and therefore consistent with 5-coordination (Table 3).

Despite the easy isolation of compounds **22** and **23**, difficulties were experienced with the corrosive vapours of both compounds during sublimation. For instance, neither compound can be sublimed with concurrent use of a Pirani pressure gauge due to reaction with the nickel, platinum or tungsten filament. This necessitates the use of ceramic capacitance diaphragm sensors with an associated increase in cost and decreased universal availability to the synthetic community.

Accordingly, an alternative access route to mono- and dihaloalanes was developed as described in Scheme 55.

Scheme 55



The preparations of tertiary amine coordinated haloalanes. Reagents and conditions: (i) 1.0 eq. $NMe_3{\cdot}HCl$, Et_2O, -78 °C to rt, - H_2; (ii) 1.0 eq. quin·HCl, Et_2O or toluene, -78 °C to rt, - H_2; (iii) 1.0 eq. HCl, toluene, -78 °C to rt, - H_2; (iv) 1.0 eq. julolidine·HBr, toluene, -78 °C to rt, - H_2; and (v) 1.0 eq. quinuclidine, toluene, rt.

Jones and co-workers successfully prepared bis(quinuclidine) monochloroalane using a preparative route akin to that used for **22**.[152, 153] Combining these approaches; one equivalent of quinuclidine hydrochloride was reacted with trimethylamine alane at low temperature (-78 ºC) (Scheme 55) to yield a new hydride in high yield (85%) that analyses as [$AlClH_2$(quin)] (**24**) by

C, H, N elemental analysis and possesses a thermal stability (m.p. 120-2 ºC, dec. 190 ºC) in excess of **22**, **23** and quinuclidine alane (dec. 140, 154 and 160 ºC[154] respectively) (Table 3).

Table 3. Selected solid-state physical and spectroscopic data for complexes and relevant literature compounds.[a]

Compound	m.p. (°C)[b]	IR *v* M-H (cm^{-1})[c]	^{1}H NMR (ppm)[d]
$[AlH_3(NMe_3)]$	76[73] (dec. 94)	1792[86]	1.83
$[AlH_3(NMe_3)_2]$	94-6 (dec. 100)	1709[86]	-
$[AlClH_2(NMe_3)_2]$ (**22**)	101-3 (dec. 140)	1745	2.13
$[AlCl_2H(NMe_3)_2]$ (**23**)	105-7 (dec. 154)	1802	2.11
$[AlH_3(quin)]$	110-2[154] (dec. 160)	1760[60]	0.99, 1.25, 2.78
$[AlClH_2(quin)]$ (**24**)	120-2 (dec. 190)	1822	0.80, 1.05, 2.59
$[AlCl_2H(quin)]$ (**25**)	174-6 (dec. 197)	1861	0.79, 1.05, 2.69
$[AlCl_3(quin)]$ (**26**)	203-5 (dec. 223)	-	0.84, 1.06, 2.85
$[AlH_3(quin)_2]$	175[86](dec. 190)	1685[86]	1.14, 1.33, 2.96
$[AlClH_2(quin)_2]$[73] (**27**)	194-5 (dec. 211)	1741	1.16, 1.35, 3.01
$[AlCl_2H(quin)_2]$ (**28**)	205-7 (dec. 223)	1789	1.15, 1.30, 3.09
$[AlCl_3(quin)_2]$ (**29**)	336 (dec.)	-	1.13, 1.28, 3.20
$[AlBrH_2(quin)]$ (**30**)	122-4 (dec. 175)	1827	0.81, 1.06, 2.60
$[AlBr_2H(quin)]$ (**31**)	164-6 (dec. 189)	1865	0.83, 1.07, 2.72
$[AlBrH_2(quin)_2]$ (**32**)	185-7 (dec. 221)	1745	1.18, 1.33, 3.04
$[AlBr_2H(quin)_2]$ (**33**)	199-201 (dec. 260)	1789	1.09, 1.28, 3.08
$[AlH_3(IMes)]$	246-7[131] (dec. 256)	1743[131]	6.01
$[AlClH_2(IMes)]$ (**34**)	268 (dec.)	1798	5.93
$[AlCl_2H(IMes)]$ (**35**)	320 (dec.)	1865	5.86
$[AlCl_3(IMes)]$ (**37**)	192 (dec.)[58]	-	5.78
$[AlBr_2H(IMes)]$ (**36**)	272 (dec.)	1888	5.86

a) All literature data listed with reference citation.

b) Melting points and decomposition temperatures conducted using capillary sealed samples under UHP argon.

c) All IR spectroscopy conducted as a Nujol mull with sodium chloride plates.

d) Resonance(s) listed are that/those of NMe_3, quin or IMes 4,5-C_2H_2 hydrogens.

For the purposes of method comparison, quinuclidine alane was also reacted dropwise with a highly dilute diethyl ether solution of hydrogen chloride (~ 0.05 M) at low temperature (-78 ºC) (Scheme 55), *cf.* Wiberg preparation of $[AlCl_nH_{3-n}(NMe_3)]$ (n = 1 or 2),[61, 62] to afford crude reaction media that repeatedly characterised as mixtures of **24** (Scheme 55), quinuclidine dichloroalane, quinuclidine aluminium trichloride and starting material. The highest isolated yield of **24** from this route, achieved by repeated fractional crystallisation, was 49%. The reduced selectivity of ‘free’ hydrogen chloride was further evidenced by the reactions of **24** with ethereal hydrogen chloride, and **22** with quinuclidine hydrochloride, to afford $[AlCl_2H(quin)]$

(**25**) (Scheme 55) in 53 and 86% yield respectively, the former after fractional crystallisation from a mixture of products and the latter directly from the filtered, vacuum dried reaction mixture.

Compound **25** is exceptionally stable in the solid-state, decomposing at 197 ºC and melting at 174-6 ºC, *cf.* **24**; m.p. 120-2 ºC, dec. 190 ºC (Table 3). Indeed, the stabilities of **24** and **25** exceed that of the reported decomposition temperature for [$AlClH_2(quin)_2$] (**27**) (182 ºC).[73] Compound **27** and its dichloroalane cousin [$AlCl_2H(quin)_2$] (**28**) were prepared by a stepwise modified version of Jones' synthesis of **27**,[152, 153] whereby quinuclidine alane was reacted with quinuclidine hydrochloride (**27**), and then further reacted with dilute (< 0.07 M) hydrogen chloride (**28**) in diethyl ether at low temperature (-78 ºC) (Scheme 55). This afforded isolated yields of 76 and 77% respectively after recrystallisation from toluene, although the latter was subsequently improved by replacement of 'free' hydrogen chloride with quinuclidine hydrochloride (88%). Both **27** and **28** were heated under UHP argon in sealed glass capillaries to give melting point and decomposition temperatures of **27**; 194-5 ºC, 211 ºC (lit. dec. 182 ºC),[73] **28**; 205-7 ºC, 223 ºC (Table 3). These data are consistent with those expected relative to compounds **24** and **25** *viz* **22** and **23** relative to Wiberg's mono(trimethylamine) chloroalanes (Table 3),[61, 62] and correspond well to the decomposition temperature of bis(quinuclidine) alane (190 ºC) as reported by Raston and co-workers.[155]

2.8.2 The preparation of tertiary amine adducts of bromoalanes

To increase the overall scope of haloalanes, bromo analogues of compounds **24**, **25**, **27** and **28** were prepared by the reaction of quinuclidine alane with one and two stoichiometric equivalents of julolidine hydrobromide in toluene at -78 ºC, to afford the bromoalanes [$AlBrH_2(quin)$] (**30**) and [$AlBr_2H(quin)$] (**31**) in good yield (84 and 82% respectively). This was followed by reaction with one equivalent of quinuclidine to give [$AlBrH_2(quin)_2$] (**32**) and [$AlBr_2H(quin)_2$] (**33**) in reasonable yield (71 and 78% respectively) after recrystallisation from toluene (Scheme 55). The coordination of the tertiary amine julolidine (Scheme 55) was not observed, most likely due to the inferior donor characteristics of this base relative to quinuclidine, and/or steric impediment.

Related tertiary amine adducts of bromoalanes were reported by Ashby (NEt_3)[63] and Ruff (NMe_3)[62] but, as per the aforementioned Wiberg studies,[61] no spectroscopic characterisation was provided at publication.

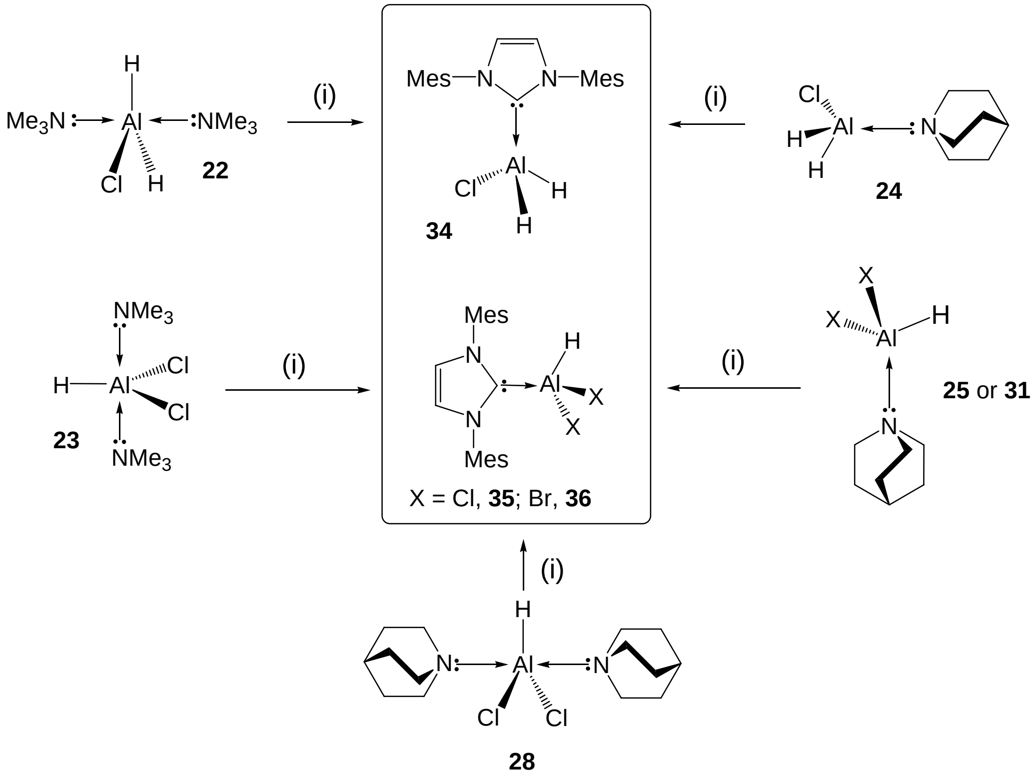
The melting point and solid-state decomposition temperature data collected for **30-33** (Table 3) are comparable to those of their chloro counterparts with the possible exception of **33** (dec. 260 °C), which decomposes some 40 ºC above the decomposition temperature of **28** (dec. 223 °C). This exceeds the solid-state decomposition temperature of the most thermally stable AlH_3 adduct known [AlH_3(IMes)][104] (256 °C) (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), making **33** one of the most thermally stable molecular aluminium hydrides reported (Table 3).

2.8.3 The preparation of NHC adducts of haloalanes

The *N*-heterocyclic carbene complex [AlH_3(IMes)][104] possesses a thermal stability above that of tertiary group 15 ligated alane compounds (Table 3) and, although not air stable, may be handled in air for brief periods without appreciable decomposition. Thus, IMes coordinated mono- and dihaloalanes were targeted as potential air stable aluminium hydrides in order to combine the thermal stabilities of the haloalanes above with that engendered by IMes coordination.

Diethyl ether solutions of **22** and **23** were treated with a single equivalent of IMes resulting in precipitation of the chloroalane complexes [$AlClH_2$(IMes)] (**34**) and [$AlCl_2H$(IMes)] (**35**) respectively from solution, as evidenced by spectroscopic analysis of the solids isolated by filtration. (Table 3, Scheme 56). Analytically pure **34** and **35** were isolated in high yield (84 and 91% respectively) after recrystallisation from toluene or vacuum drying respectively. Both compounds were also accessed by the reaction of IMes with **24** and **25** respectively, or the reaction of IMes with **28** (to give **35**) (Scheme 55), in yields comparable to the aforementioned bis(trimethylamine) route after recrystallisation from toluene (89, 87 and 74% respectively). The bromo analogue of **35**, [$AlBr_2H$(IMes)] (**36**) was also prepared in reasonable yield by the reaction of **31** with IMes as per the preparation of **35** using **25**. No five-coordinate complexes of composition [AlX_nH_{3-n}(IMes)(NR_3)] (n = 1 or 2, NR_3 = quinuclidine or NMe_3) were isolated, indicating the donation and spatial characteristics of IMes thwart retention of tertiary amine in the aluminium coordination sphere. While this is consistent with the preparation of [AlH_3(IMes)] from a trimethylamine alane precursor,[131] the presumed increase in Lewis acidity of the metal centres concerned here may have enabled further coordination. It should be noted that attempts to generate bis(IMes) adducts of $AlCl_nH_{3-n}$, by addition of two equivalents of IMes to tertiary amine precursors, universally met with failure, again presumably due to the bulk of IMes. Furthermore, unlike related gallium species,[156] equimolar solutions of $[AlH_3(IMes)]$ and **35** do not equilibrate to **34**, even when heated to reflux in toluene, eliminating solution phase redistribution as a route to specific chloroalane complexes.

Scheme 56



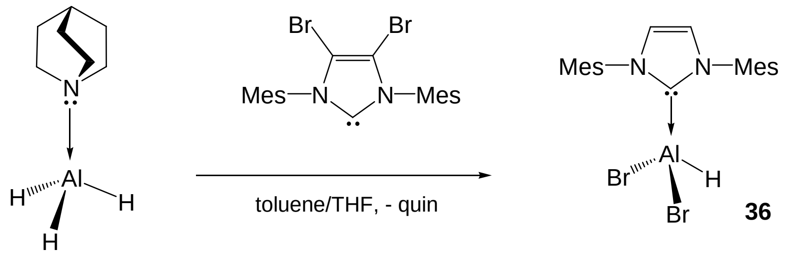
The preparations of NHC-coordinated haloalanes discussed in this section. Reagents and conditions: (i) 1.0 eq. IMes, Et_2O or toluene, rt, - labile amine donor.

Compound **35** expectedly exhibits superior thermal stability over its monochloro and dibromo relatives, **34** and **36**, with a decomposition temperature of 320 °C (**34** 265 °C, **36** 272 °C). This is exceptionally high; indeed **35** is the most thermally stable molecular aluminium hydride known (Table 3).

To assess the solution phase thermal stabilities of **34** and **35**, both compounds were heated to reflux in toluene for periods in excess of two hours without decomposition. Both compounds may also be handled under moisture free conditions, e.g. in a desiccator, without observable decomposition. However, exposure of toluene solutions of **34** or **35** to water in trace amounts (<1 equivalent) results in the deposition of an as-yet unidentified aluminium rich precipitate and the formation of the known 2-dihydroimidazole 1,3-bis(trimethylphenyl)-2-dihydroimidazole (IMesH$_2$),[155] which remains in solution. Thus, while both **34** and **35** are aerobically stable, neither compound tolerates water.

Compound **36** was also prepared via an alternative route using the 4,5-dibrominated derivative of IMes, IMesBr[157] (Scheme 57). The treatment of [AlH$_3$(quin)] with an equimolar quantity of IMesBr in toluene-THF respectively affords **36** via a process involving both NHC coordination and hydride-bromide exchange. This latter process is most likely to occur after NHC coordination, as the corresponding gallium reaction yields the 4,5-bromoimidazol-2-ylidene adduct [GaH$_3$(IMesBr)], which undergoes hydride-bromide exchange upon heating to afford the dibromogallane species [GaBr$_2$H(IMes)].[158] Subsequent deutero-labelling experiments using [MD$_3$(quin)] (M = Al, Ga) confirmed the metal centre as the source of the hydrogens in both reactions.[158] The mechanism of this reaction was not explored, but it is proposed that it involves a binuclear species as a result of coordination of an MH$_3$ species to one of the electron lone pairs on a bromine ligand.

Scheme 57



2.8.4 Spectroscopic data

Despite concerted effort, the ^{1}H NMR hydride resonances for compounds **22**, **23**, **25**, **27**, **28**, **30**, **31**, **34**, and **36** could not be located in the ^{1}H NMR spectra (C_6D_6) of these compounds. This is not unusual for alane Lewis base complexes and understandable due to the reduced symmetries of the complexes relative to their trihydride counterparts, and may also be attributed to the quadrupolar aluminium centre, which broadens any Al-*H* resonance considerably. The hydride resonances of alane complexes are often observed with such broadening.[74, 154] The broad hydride resonances of compounds **24**, **32** and **33** were observed at δ = 4.20, 3.30 and 3.60 ppm respectively. The downfield shift of these resonances (relative to those of mono- and bis(quinuclidine) alane) is consistent with the shift observed upon dibromination of the gallium of [GaH_3(IMes)] to afford [$GaBr_2H$(IMes)] (^{1}H NMR Ga-*H*: δ = 3.96[91] to 4.50 ppm),[158] and is most likely induced by the greater electronegativity halide ligands at the metal *viz* the aforementioned trihydrides. The presence of halide ligands also serves to strengthen the aluminium-hydride bonds by negative inductive effects in all of the hydride compounds disclosed. This is clearly evidenced in the IR spectra of these compounds (Table 3), where the Al-H stretching modes are seen to (i) increase in frequency with the number of halide ligands, (ii) increase in frequency for tertiary amine donors relative to the stronger donor NHC IMes, and (iii) dramatically decrease on addition of a second amine donor (Table 3). Comparison between the impact of chloride and bromide ligands reveals little difference, e.g. IR (Nujol), *v* Al-H stretch: **24** 1822 cm^{-1}, **30** 1827 cm^{-1}, despite the increased electronegativity of chlorine. Thus, in consolidating the data in Table 3, the substitution of a hydride with either chloride or bromide about a tertiary amine adduct of alane results in a *ca*. +55 cm^{-1} shift in Al-H stretching absorption frequency, and addition of a second halide induces a lesser shift of *ca*. +45 cm^{-1}. The associated shifts for the related NHC adducts **34** and **35** relative to [AlH_3(IMes)] are +55 and +67 cm^{-1} (+122 cm^{-1} combined) respectively, while the Al-H stretching absorption of **36** indicates that dibromination invokes a shift of +145 cm^{-1}. There is also a decrease in the frequency of the metal-hydride stretching absorption on the addition of a second tertiary amine donor that can be approximated as -80 cm^{-1}. This is consistent with reduced electron deficiency at the Lewis acidic aluminium and weakening of the Al-H bond(s). Similar decreases are observed for mono- and bis(amine) adducts of alane (Table 3). There is no evidence of hydride bridged Al-H-Al stretching bands in the IR spectra of the complexes described,[61] consistent with mononuclearity. In several instances this has been confirmed by the X-ray diffraction structure determination (see below).

Further to the focus on the spectroscopy of the aluminium-hydride bond above, the resonances attributable to the ligands of the same compounds exhibit chemical shift trends that are also noteworthy (Table 3). For instance, there is distinct downfield shift for the methyl hydrogen resonances of **22** and **23** relative to trimethylamine alane (Table 3). This is consistent with increased electron density at the methyl groups, which corresponds to the five- *versus* four-coordination of the metal centre concerned and, hence, a lesser lone pair donation. Analogous shifts are also observed for the mono- and bis(quinuclidine) adducts **24-33**, where the three ^{1}H NMR resonances of quinuclidine may be used as a guide to the coordination number of the metal (Table 3).

To provide a complete series for [$AlCl_nH_{3-n}$(quin)] and [$AlCl_nH_{3-n}$(quin)$_2$] (n = 0-3) for spectroscopic comparison, the aluminium trichloride complexes [$AlCl_3$(quin)] (**27**) and [$AlCl_3$(quin)$_2$] (**29**) were prepared by addition of ethereal HCl to **25** and quinuclidine hydrochloride to **28** respectively. As described by the ^{1}H NMR data of Table 3, it is clear that there is a marked increase in Lewis acidity upon substitution of the final hydride ligand of **25** and **28** by chloride. This manifests as a downfield shift of the methylene resonance attributable to the NCH_2 of quinuclidine, and an upfield shift of the remaining methylene and methine resonances for bis(quinuclidine) adducts **27**, **28**, **32** and **33**, and downfield shift of the same resonances for the related mono(quinuclidine) adducts **24-26**, **30** and **31**.

Perhaps the most useful ^{1}H NMR data provided in Table 3 is that of the 4,5-C_2H_2 singlet resonance of compounds **34**, **35** and **36**. This resonance, which is intimately associated with the degree of NHC donation to the metal via the delocalised heterocycle of IMes,[92, 121] can be used to determine the number of halide ligands at the coordinated aluminium centre. As per compounds **27** and **29** above, the aluminium trichloride complex [$AlCl_3$(IMes)][58] (**37**) was prepared to complete the hydride-chloride series [$AlCl_nH_{3-n}$(IMes)] (n = 0-3) such that a full series of 4,5-C_2H_2 singlet resonances could be catalogued. Thus, the complete 4,5-C_2H_2 singlet resonance series is ^{1}H NMR (C_6D_6) 4,5-C_2H_2 = δ singlet resonance 6.01 (n = 0), 5.93 (n = 1), 5.86 (n = 2) and 5.78 ppm (n = 3). For comparison, the corresponding resonances for **35** and **36** are identical. The upfield shift on increasing chloride content can be attributed to the increased Lewis acidity of the metal centre induced by increased halide substitution. Moreover, the simple addition of IMes to ethereal chloroalane reaction mixtures (see Scheme 55), which results in immediate precipitation of all [$AlCl_nH_{3-n}$(IMes)] adducts irrespective of 'n', allows the ^{1}H NMR 4,5-C_2H_2 resonances above to be used to assess the "specificity" of routes to chloroalanes (as IMes adducts of alane and chloroalanes do not redistribute in solution, see above). For instance, during the preparation of **24** by reaction of quinuclidine alane with ethereal hydrogen chloride (see above), the addition of IMes to the reaction mixture, removal of volatiles and acquisition of a ^{1}H NMR spectrum (C_6D_6) highlights the low specificity of this route by the observation of 4,5-$C_2\mathit{H}_2$ resonances for all four statistically possible compounds [$AlCl_nH_{3-n}$(IMes)], n = 0-3.

2.8.5 Crystallographic studies

With the exception of **22**, **23** and **28**, all of the aluminium hydride complexes reported herein have been characterised by single crystal X-ray diffraction and their molecular structures are depicted in Figures 3, 4 and 6-12. In all cases, excepting **33,** the hydride ligands were located from difference maps and refined isotropically. Selected bond lengths (Å) and angles (º) are provided in Table 4 along with relevant bond distances and angles for literature compounds such as **27**[73] and [AlH_3(quin)].[74] Further specific bonding parameters, such as aluminium-hydride bond lengths, are provided in figure captions. Due to disorder of the hydride and halide ligands of dichloroalane complex **25**, aluminium trichloride complex **26** was also characterised by single crystal X-ray structure determination (Figure 5). Table 4 contains a summary of crystal measurement and refinement data for the molecular structures in this chapter.

Table 4.[a] Selected bond lengths (Å) and angles (º) for prepared complexes and relevant literature compounds.

Compound	Al-N/C (Å)	Al-Cl/Br (Å)	N/C-Al-Cl/Br (°)	Cl/Br-Al-Cl/Br (°)
$[AlH_3(quin)]$[154]	1.991(4)	-	-	-
$[AlClH_2(quin)]$ (**24**)	1.9782(16)	2.1517(8)	105.13(5)	-
$[AlCl_2H(quin)]$ (**25**)[b]	1.958(4)	2.124(2) [c]	105.64(13) [d]	111.50(12) [e]
$[AlCl_3(quin)]$ (**26**)	1.9436(11)	2.1160(3), 2.1133(5)	106.79(2), 106.22(4)	112.26(2), 112.143(14)
$[AlH_3(quin)_2]$[74]	2.155(3)	-	-	-
$[AlClH_2(quin)_2]$[73](**27**)	2.1354(17)	2.2145(13)	92.05(5)	-
$[AlBrH_2(quin)]$ (**30**)	1.9739(17)	2.3070(7)	106.01(6)	-
$[AlBr_2H(quin)]$ (**31**)	1.959(5)	2.2880(14)	105.82(11)	109.81(10)
$[AlBrH_2(quin)_2]$ (**32**)	2.1238(13)	2.3956(7)	92.00(4)	-
$[AlBr_2H(quin)_2]$ (**33**)	2.145(6), 2.152(6)	2.4148(16)	91.03(10), 91.04(11)	115.48(12)
$[AlH_3(IMes)]$[131]	2.034(3)	-	-	-
$[AlClH_2(IMes)]$ (**34**)	2.039(2)	2.1635(10)	105.19(8)	-
$[AlCl_2H(IMes)]$[f] (**35**)	2.020(7)	2.147(3), 2.136(3)	109.15(19), 107.4(2)	110.21(13)
$[AlBr_2H(IMes)]$ (**36**)	2.028(4)	2.3164(13), 2.2973(13)	107.93(12), 107.15(12)	110.01(5)

a) All bonding parameters listed in numerical order relative to numbering of relevant figure. All data complete, thus, unique bonds are listed without symmetry related bonding parameters. In instances where there is more than one unique molecule in the asymmetric unit, only the bonding parameters for the lowest numbered unit have been included. For bonding data not listed, consult relevant figure caption.

b) One hydride and one chloride disordered; only bonding parameters for the highest atom occupancy are listed here.

c) One Al-Cl bond length, that of disordered chloride ligand (disordered with hydride), not listed.

d) One N-Al-Cl angle, that of disordered chloride ligand (disordered with hydride), not listed.

e) Note: angle calculated using disordered chloride Cl(2).

f) Due to the hydride-chloride disorder of **35**, only bonding parameters for the highest atom occupancy are listed here.

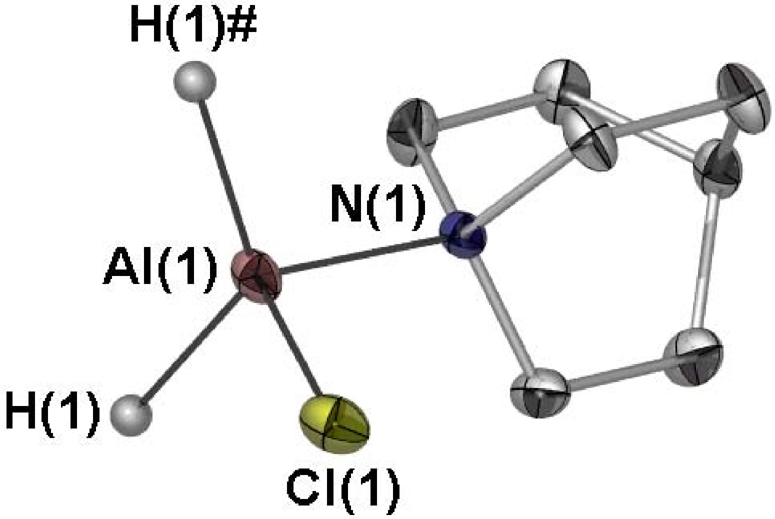


Figure 3. Molecular structure of [$AlClH_2$(quin)] (**24**) (50% thermal ellipsoids POV-RAY illustration). All hydrogen atoms excepting H(1) and H(1)# omitted for clarity. Symmetry transformation used to generate '#' atoms: *x*, ½ - *y*, *z*. Selected bond lengths (Å) and angles (º): Al(1)-H(1) 1.780(13), H(1)-Al(1)-N(1) 107.2(4), H(1)-Al(1)-Cl(1) 104.0(4) (see Table 4 for further bonding parameters).

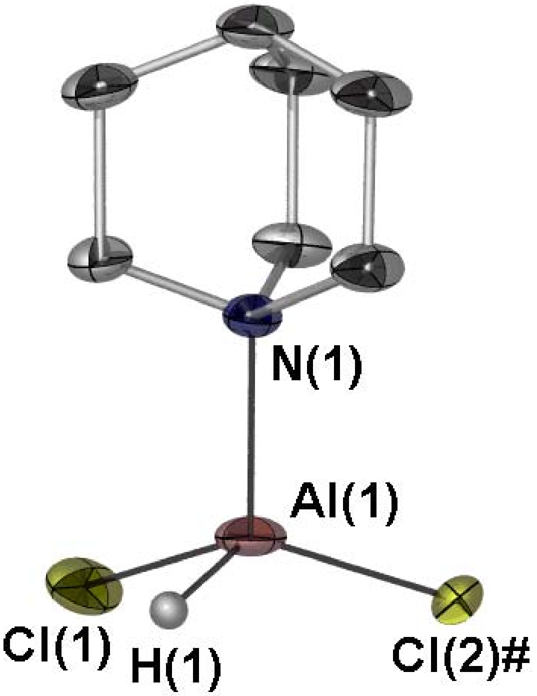


Figure 4. Molecular structure of [$AlCl_2H$(quin)] (**25**) (50% thermal ellipsoids POV-RAY illustration). All hydrogen atoms excepting H(1) omitted for clarity. One of two H(1)/Cl(2) occupancies shown. Symmetry transformation used to generate '#' atoms: *x*, ½ - *y*, *z*. Selected bond lengths (Å) and angles (º): Al(1)-H(1) 1.93(11), H(1)-Al(1)-N(1) 106(3), H(1)-Al(1)-Cl(1) 105(3), H(1)-Al(1)-Cl(2)# 121(3) (see Table 4 for further bonding parameters).

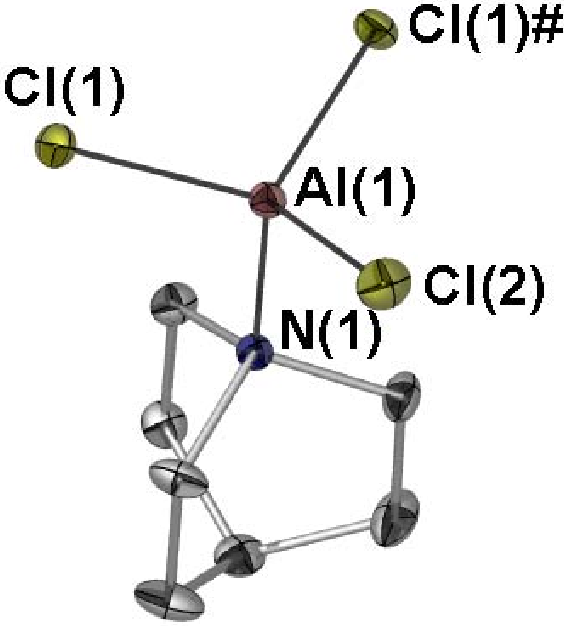


Figure 5. Molecular structure of [$AlCl_3$(quin)] (**26**) (50% thermal ellipsoids POV-RAY illustration). All hydrogen atoms omitted for clarity. Symmetry transformation used to generate '#' atoms: x, ½ - y, z**.** See Table 4 for selected bond lengths (Å) and angles (º).

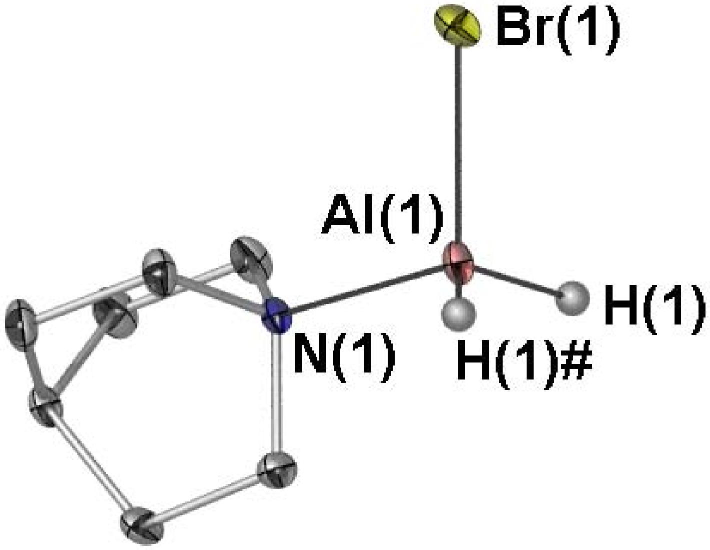


Figure 6. Molecular structure of [$AlBrH_2$(quin)] (**30**) (50% thermal ellipsoids POV-RAY illustration). All hydrogen atoms excepting H(1) and H(1)# omitted for clarity. Symmetry transformation used to generate '#' atoms: *x, ½ - y, z.* Selected bond lengths (Å) and angles (º): Al(1)-H(1) 1.69(2), H(1)-Al(1)-N(1) 105.9(7), H(1)-Al(1)-Br(1) 106.01(6) (see Table 4 for further bonding parameters).

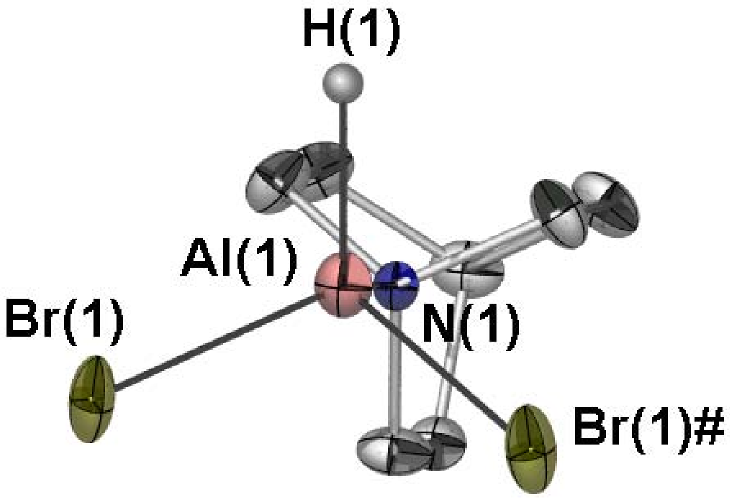


Figure 7. Molecular structure of [$AlBr_2H$(quin)] (**31**) (50% thermal ellipsoids POV-RAY illustration). All hydrogen atoms excepting H(1) omitted for clarity. Symmetry transformation used to generate '#' atoms: *x*, *y*, ½ - *z*. Selected bond lengths (Å) and angles (º): Al(1)-H(1) 1.85(6), H(1)-Al(1)-N(1) 116(2), H(1)-Al(1)-Br(1) 109.7(10) (see Table 4 for further bonding parameters).

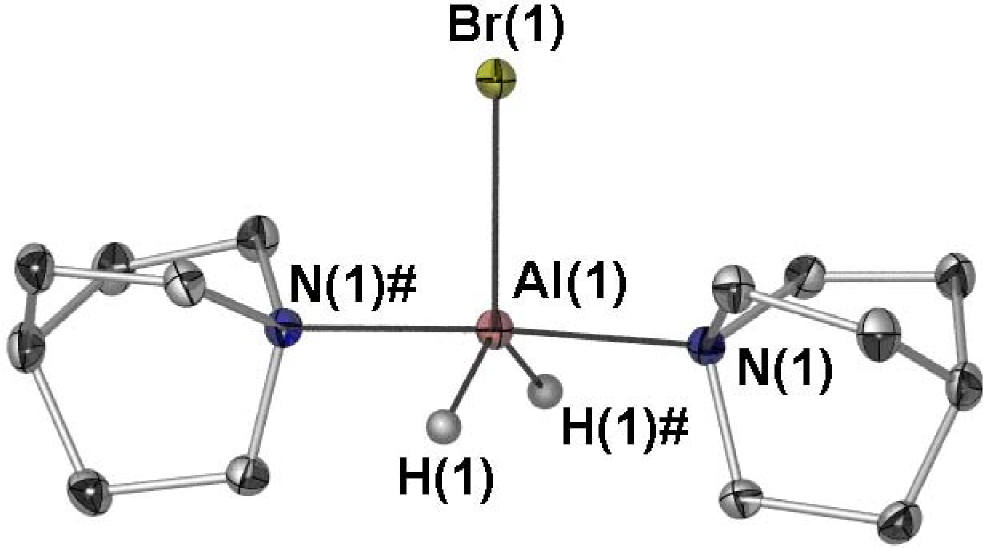


Figure 8. Molecular structure of [$AlBrH_2$(quin)$_2$] (**32**) (50% thermal ellipsoids POV-RAY illustration). All hydrogen atoms excepting H(1) and H(1)# omitted for clarity. Symmetry transformation used to generate '#' atoms: -*x*, *y*, $^1/_2$ - *z*. Selected bond lengths (Å) and angles (º): Al(1)-H(1) 1.695(18), H(1)-Al(1)-H(1)# 126.2(1), H(1)-Al(1)-N(1) 89.7(6), H(1)-Al(1)-N(1)# 88.5(6), H(1)-Al(1)-Br(1) 116.9(6), N(1)-Al(1)-N(1)# 176.01(7) (see Table 4 for further bonding parameters).

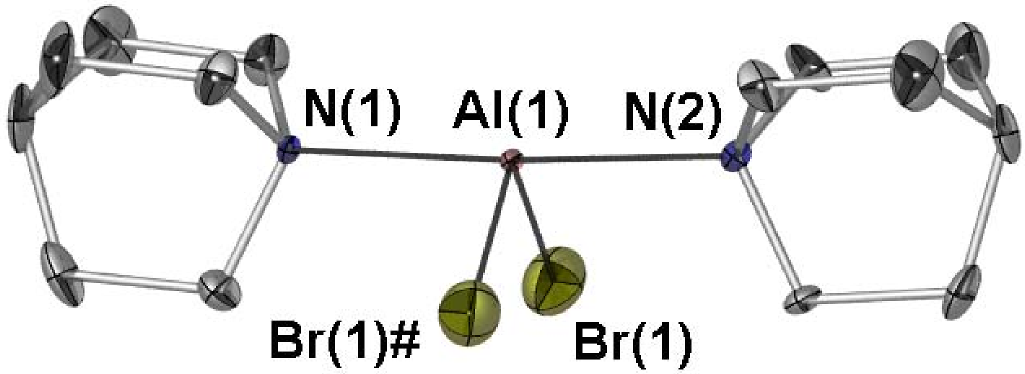


Figure 9. Molecular structure of [$AlBr_2H(quin)_2$] (**33**) (70% thermal ellipsoids POV-RAY illustration). All hydrogen atoms omitted for clarity. Symmetry transformation used to generate '#' atoms: *2 - x, y, z.* See Table 4 for selected bonding parameters. Bond angle N(1)-Al(1)-N(1)# 176.1(2)°.

2.8.5.1 Tertiary amine adducts of chloro- and bromoalanes

Without exception, the mono- and bis(quinuclidine) complexes **24-26** and **30-33** crystallise with half a molecule in the asymmetric unit. For five-coordinate **32**, the crystallographically unique unit includes one complete quinuclidine ligand, while for **33** the related unit includes two halves of the quinuclidine donors. Both **32** and **33** exhibit apical quinuclidine donors with the bromide and hydride ligands situated in the trigonal plane of the trigonal bipyramidal metal coordination geometry. The mono(quinuclidine) mono- and dihaloalane complexes **24**, **25**, **30** and **31** exhibit quinuclidine bonding parameters that are unremarkable with the exception of the metal to nitrogen donor bond and the distorted tetrahedral geometries about their aluminium centres (Table 4). For instance, the Al-N bonds of **24** and **25**, and **30** and **31** respectively denote a 15-20 pm decrease for the dihaloalane adduct. This contraction is comparable to that which occurs on hydride substitution of [AlH_3(quin)][154] with chloride or bromide, and is similar to the shortening of the Al-N contact observed for **35**, which is some 15 pm shorter than that of **25**. Analogous shortening of the aluminium to nitrogen contacts of **32** and **33** is also observed relative to the parent trihydride [$AlH_3(quin)_2$] reported by Barron (**32**; 2.1238(13), **33**; 2.145(6), 2.152(6), [$AlH_3(quin)_2$] 2.155(3) Å).[74] Comparison of **32** with the reported structure of **27** from Jones and co-workers,[19] indicates that the larger halogen of **32** does not extend the Al-N contact of this compound relative to **27** (2.1354(17) Å).[73] Instead, the Al-N bond of **32** is somewhat shorter. The impact of coordination number is seen in the trends observed for the aluminium-halide contacts of **24-26** and **30-33**. For instance, there is a reduction in aluminium to chloride bonds from monochloroalane **24** to aluminium trichloride **35** (Table 4), and similarly from mono(quinuclidine) bromoalane to dibromoalane, but for five-coordinate complexes **32** and **33** the reverse trend is observed. In terms of aluminium to hydride bonding contacts, despite their questionable accuracy as determined by X-ray methods, monochloroalane **24** has a shorter bonding contact than that determined for dichloroalane **25** (1.780(13) vs. 1.93(11) Å, [AlH_3(quin)]; 1.38(5) and 1.56(3) Å) likewise, on going from bromoalane to dibromoalane, the Al-H contacts of **30** and **31** suggest lengthening with increased halogen content (**30**; 1.69(2), **31** 1.85(6) Å). If one considers extension of this contact as indicative of the lessening of bond strength, these data are contrary to those obtained by IR methods (Table 3). The Al-H bonding contact of **32** is surprisingly similar to that of **30** (**32**; 1.695(18), **30**; 1.69(2) Å).

With regard to the regularity of the coordination geometries adopted by **24-26** and **30-33**, it is clear from the N-Al-X (X = Cl or Br) angle that all seven complexes tend toward angles that are consistent with regular sp^3 or sp^3d hybridisation (four- and five-coordinate complexes respectively). To this end, the N-Al-X/H bonds of tetrahedral species **24-26** gradually open from 105.13(5) (**24**) to 106.79(2) and 106.22(4)° (**35**), although there is very little statistical difference between the related bonding parameters of **30** and **31**. It is also clear that the angles about the polyhedra exhibit patterns consistent with Bent's rule,[159] wherein the X-Al-X bonds of **25**, **35**, **30** and **33** are above those expected for tetrahedral (**25**, **35**, **30**) and equatorial trigonal bipyramid (**33**) ligand-metal-ligand angles (Table 4). For **32** and **33**, the axial quinuclidine donors generate a close to linear angle across aluminium (N-Al-N **32**; 176.01(7), **33**; 176.1(2)°), while the equatorial plane H-Al-H and H-Al-Br angles of **32** also follow Bent's rule: **32**; H-Al-H 126.2(1), H-Al-Br 116.9(6)°.

2.8.5.2 NHC adducts of mono- and dihaloalanes

The four-coordinate IMes complexes **34** and **35** crystallise with one and two molecular units in the asymmetric unit respectively. The two distinct units of **35** exhibit comparable bonding parameters. Accordingly, only one molecule is discussed here.

The "Al(IMes)" subunits of **34, 35,** and **36** are similar to those of their trihydride congener [AlH_3(IMes)].[131] For instance, the Al-C bonding contact and endocyclic NCN angles of **34** (2.039(4) Å and 104.2(3)°), **35** (mean 2.01 Å, 105.1(6)°) and **36** (2.028(4) Å and 104.2(3)°) compare well with those of [AlH_3(IMes)] (2.034(3) Å and 104.23(18)°).[131] It could be argued that the bonding of **35** is consistent with greater NHC donation, *cf.* N-C-N angle of IMes imidazolium cation ([IMesH][Cl]·H_2O N-C-N 108.3(1)°, IMes N-C-N 101.4(2)°).[160] It is probable that the increased Lewis acidity of the dibromoalane unit of **36**, which one would expect to shorten the Al–C contact relative to that of [AlH_3(IMes)] (*cf.* **35**; mean Al–C 2.01 A˚), is counterbalanced by the spatial bulk of the bromide ligands over that of the hydrides.

The hydride ligands of **34** **35** and **36** were located and refined isotropically. However, the hydride-chloride disorder of compound **35** necessitated the refinement of the hydride ligands at coincident positions to the disordered chloride. As such, the unreliable Al-H contact of **35** is not discussed here. The Al-H contacts of **34** are of length 1.59(3) and 1.86(2) Å, in which the longer contact lies coplanar with "Al(IMes)" subunit. As per the quinuclidine complexes discussed earlier, the Al-Cl contacts of IMes-dichloroalane are short relative to those of IMes-coordinated chloroalane (**35**; 2.147(3) and 2.136(3), **34**; 2.1635(10) Å) despite the increased size of the ligands about aluminium. In turn, these bonds are extended relative to those of the four-coordinate chloroalanes **24** and **25** (Table 4). The Al-H contact distance for **36** (2.07(3) Å), although unreliably determined by XRD methods, is within the range of Al–H bonding contacts established by X-ray methods.[161] The aluminium of **35** exhibits increased pyramidalisation relative that to that of **34** (Table 4), which supports greater donation by the NHC of **35** relative to **34**, *cf.* shorter Al-C bond and greater N-C-N_{NHC} angle of the former. Unlike quinuclidine complexes **24-26** and **30-33**, the relative bond angles of the two chlorides of **35** or hydrides of **34**, cannot be compared as in both instances one such bond lies coplanar or near coplanar with the "Al(IMes)" unit, with the other bond projecting out of the plane. This leads to an inherent disparity in their respective solid-state environments. The Al-Br distances of **36** (2.3164(13) Å Br(1) and 2.2973(13) Å Br(2)) are similar to those of four-coordinate dibromoaluminiumaryls such as [$AlBr_2(2,4,6\text{-}^iPr_3C_6H_2)(OEt_2)$] (2.311(6) Å),[162] reported by Power and co-workers.

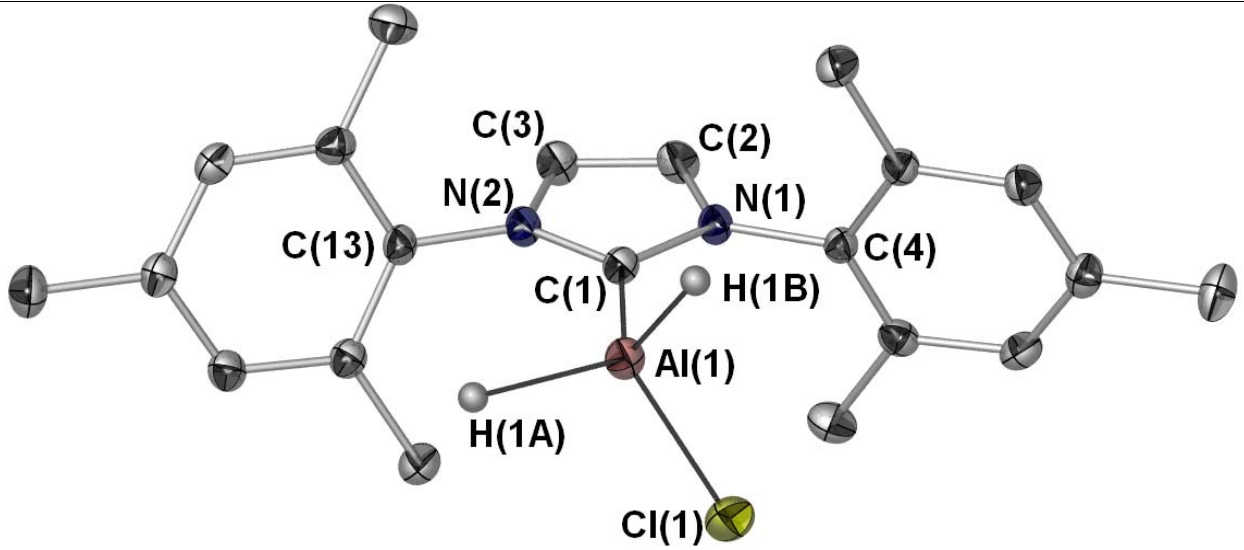


Figure 10. Molecular structure of [$AlClH_2$(IMes)] (**34**) (50% thermal ellipsoids POV-RAY illustration). All hydrogen atoms excepting H(1A) and H(1B) omitted for clarity. Selected bond lengths (Å) and angles (º): Al(1)-H(1A) 1.86(2), Al(1)-H(1B) 1.59(3), H(1A)-Al(1)-C(1) 113.5(6), H(1B)-Al(1)-C(1) 109.0(10), H(1A)-Al(1)-Cl(1) 105.19(8), H(1B)-Al(1)-Cl(1) 107.8(10), H(1A)-Al(1)-H(1B) 109.7(12) , N(1)-C(1)-N(2) 104.23(18) (see Table 4 for further bonding parameters).

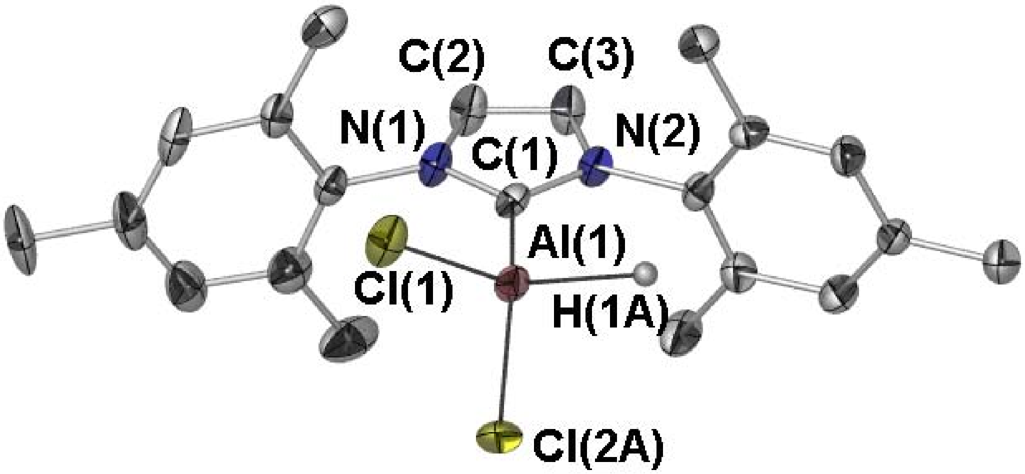


Figure 11. Molecular structure of [$AlCl_2H$(IMes)] (**35**) (40% thermal ellipsoids POV-RAY illustration). All hydrogen atoms excepting H(1A) omitted for clarity. Lowest numbered molecule of two in asymmetric unit shown, highest occupancy disordered atoms displayed. See Table 4 for selected bond lengths (Å) and angles (º). Bond angle N(1)-C(1)-N(2) 105.1(6)°. (Bonding parameters for H(1A) not listed due to coincident refinement with lesser occupancy disordered chloride).

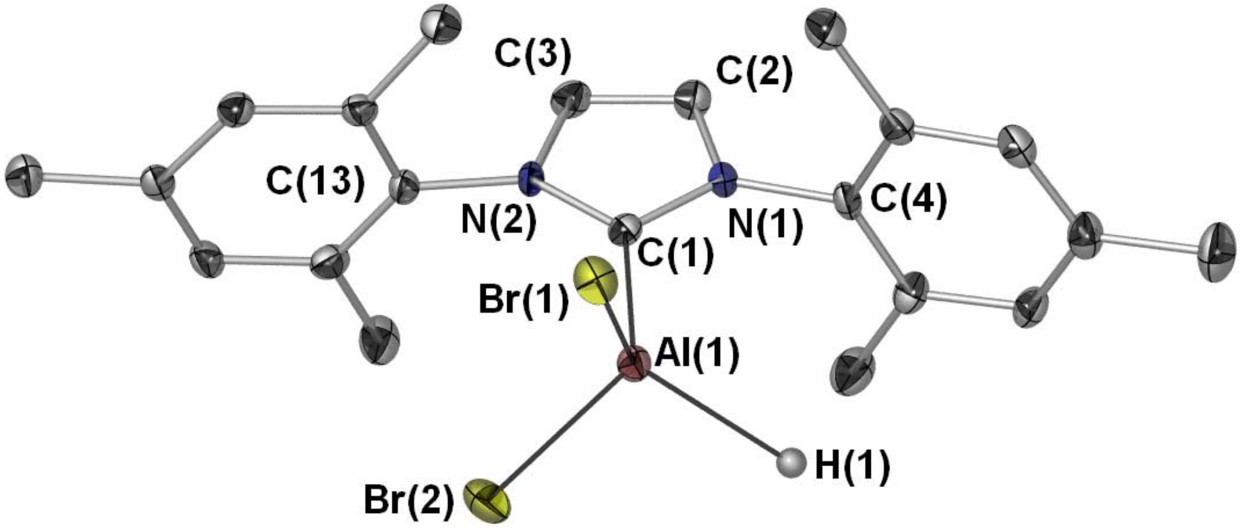


Figure 12. Molecular structure of [$AlBr_2H(IMes)$] (**36**) (40% thermal ellipsoids POV-RAY illustration). All hydrogen atoms excepting H(1A) omitted for clarity. See Table 4 for selected bond lengths (Å) and angles (º). Bond angle N(1)-C(1)-N(2) 104.2(3)°.

2.9 Conclusion

The preparation of chloro- and bromoalanes has been studied and optimised and a catalogue of synthetically useful compounds that can be accessed in gram quantities has been generated. The spectroscopic and structural properties of these compounds clearly demonstrate that the substitution of one or two hydride ligands for halides about a Lewis base adduct of alane results in a marked increase in Lewis acidity and aluminohydride stability. The structures of the compounds studied by X-ray methods exhibit trends consistent with Bent's rule and distorted tetrahedral or trigonal bipyramidal geometries are adopted for four- and five-coordinate complexes respectively. The NHC compounds **34**, **35** and **36** display the greatest thermal and aerobic stabilities reported for molecular aluminium hydrides. All may be handled in dry air and show no sign of decomposition after heating to reflux in toluene for 12 hours. Chapter 3 details the use of these compounds in hydrometallation studies.

2.10 Experimental

General

Diethyl ether, THF and hexane were dried over sodium and freshly distilled from sodium benzophenone ketyl before freeze-thaw degassing prior to use. Toluene was dried over sodium and freshly distilled from potassium before freeze-thaw degassing prior to use. Trimethylamine alane,[86, 163] quinuclidine alane,[86, 154, 163] IMes alane,[131] and IMes[104] were prepared by literature procedures. Trimethylamine hydrochloride, quinuclidine hydrochloride and julolidine hydrobromide were purchased from Sigma-Aldrich and heated at 200 °C under vacuum for 12 hours prior to use. All other materials were acquired from Sigma-Aldrich and used as received. All manipulations were performed using conventional Schlenk or glovebox techniques under an atmosphere of ultra high purity argon in flame-dried glassware. Infrared spectra were recorded as Nujol mulls using sodium chloride plates on a Nicolet Nexus FTIR spectrophotometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 300.13 MHz and 75.46 MHz respectively using a Varian 2000 spectrometer with chemical shifts referenced to the residual ^{1}H resonances of the *deutero*-benzene solvent (δ 7.16 and 128.39 ppm respectively). Melting points were determined in sealed glass capillaries under argon and are uncorrected. Microanalyses were attempted for all compounds and are reported below when the complex in question proved sufficiently stable from transportation in a sealed glass ampoule under UHP argon. All microanalyses were conducted by the Campbell Microanalytical Laboratory, Chemistry Department, University of Otago, P.O. Box 56, Dunedin, New Zealand. Single crystal X-ray data collections were undertaken at Monash University and refined at the University of New South Wales and the University of Adelaide, for which further details are listed in a separate section below.

X-ray structure determination

All single crystal X-ray structure determinations were undertaken using samples mounted on glass fibres in silicone oil by Dr Craig Forsyth at Monash University. Data were collected using graphite monochromated Mo$_{K\alpha}$ X-ray radiation (λ = 0.71073 Å) at 123(2)K on a Bruker X8 Apex diffractometer. Structural solution and refinement was carried out using the SHELX suite of programs.[164]

$[AlClH_2(NMe_3)_2]$ (22)

A slurry of trimethylamine hydrochloride (0.73 g, 7.64 mmol) in diethyl ether (100 cm^3) was added to a solution of $[AlH_3(NMe_3)]$ (0.68 g, 7.63 mmol), also in diethyl ether (100 cm^3), at -78 °C. The stirred slurry was gradually warmed to room temperature over a period of 3 hours, whereupon hydrogen evolution had ceased and the solvent was removed *in vacuo* to yield a colourless solid. The title compound was purified by sublimation (30 °C, 1.0 x 10^{-4} bar) to afford a crystalline solid (1.12 g, 86%), m.p. 101-103 °C (dec. 140 °C). ^1H NMR (C_6D_6): δ 2.13 (s, NCH_3, 18H); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 46.7 (NCH_3); IR (Nujol, cm^{-1}), ν Al-H stretch: 1745 br s.

$[AlCl_2H(NMe_3)_2]$ (23)

A slurry of trimethylamine hydrochloride (0.18 g, 1.88 mmol) in diethyl ether (50 cm^3) was added to a solution of $[AlH_3(NMe_3)]$ (0.17 g, 1.91 mmol), also in diethyl ether (50 cm^3), at -78 °C. The effervescing solution was warmed to room temperature over a period of 3 hours during which hydrogen evolution ceased. A further equivalent of trimethylamine hydrochloride was added in the same manner and, once effervescence had stopped, volatiles were removed *in vacuo* to give crude colourless **23**. Compound **23** was purified by sublimation of $[AlClH_2(NMe_3)_2]$ and residual starting material at 30 °C, 1.0 x 10^{-4} bar, followed by sublimation of pure **23** at 40 °C, 1.0 x 10^{-4} bar, as a white solid (0.37 g, 90%), m.p. 105-107 °C (dec. 154 °C). ^1H NMR (C_6D_6): δ 2.11 (s, NCH_3, 18H); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 46.1 (NCH_3); IR (Nujol, cm^{-1}), ν Al-H stretch: 1802 br s.

$[AlClH_2(quin)]$ (24)

Method (i): A slurry of quinuclidine hydrochloride (0.99 g, 6.71 mmol) in diethyl ether (50 cm^3) was added to a solution of $[AlH_3(NMe_3)]$ (0.60 g, 6.73 mmol) in diethyl ether (50 cm^3) at -78 °C. The effervescing slurry was warmed to room temperature with stirring over 4 hours and dried *in vacuo* to afford a white solid. **24** was recrystallised from toluene to afford small colourless plates (0.95 g, 81%) spectroscopically equivalent to that from method (ii) below.

Method (ii): A cooled (-78 °C) diethyl ether (50 cm^3) solution of 2 M HCl in diethyl ether (1.35 cm^3, 2.70 mmol) was added drop wise by canula to a cooled solution of $[AlH_3(quin)]$ (0.383 g, 2.71 mmol) in toluene (50 cm^3) at -78 °C. The effervescing solution was warmed to room temperature over a period of 2 hours and the volatiles removed *in vacuo* once hydrogen evolution had ceased. The product was recrystallised from toluene to afford small colourless plates (0.23 g, 49%), m.p. 120-122 °C (dec. 190 °C). Elemental analysis calculated (%) for $C_7H_{15}AlClN$: C 47.87; H 8.61; N 7.97. Found: C 48.09; H 8.38; N 8.03; ^1H NMR (C_6D_6): δ 0.80 (m, C*H*$_2$, 6H), 1.05 (m, C*H*, 1H), 2.59 (m, NC*H*$_2$, 6H), 4.20 (br s, Al-*H*, 2H); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 20.2 (*C*H), 24.2 (*C*H$_2$), 46.6 (N*C*H$_2$); IR (Nujol, cm^{-1}), ν Al-H stretch: 1822 br s.

[AlCl$_2$H(quin)] (25)

Method (i): A cooled (-78 °C) diethyl ether (25 cm^3) solution of 2 M HCl in diethyl ether (1.38 cm^3, 2.76 mmol) was added drop wise to a solution of [AlClH$_2$(quin)] (0.485 g, 2.76 mmol) in toluene (25 cm^3), also at -78 °C. The solution was warmed to room temperature over 2 hours, whereupon hydrogen evolution subsided, and then re-cooled to -78 °C followed by addition of a further equivalent of HCl in the same manner as the above. Removal of volatiles *in vacuo* yielded crude **25** as a colourless solid. Crystallisation from toluene afforded **25** as large square colourless plates (0.31 g, 53%) spectroscopically equivalent to that from method (ii) below.

Method (ii): A slurry of quinuclidine hydrochloride (0.45 g, 3.05 mmol) in diethyl ether (25 cm^3) was added to a solution of [AlClH$_2$(NMe$_3$)$_2$] (0.56 g, 3.07 mmol) in diethyl ether (50 cm^3) at -78 °C. The effervescing slurry was warmed to room temperature with stirring over 4 hours and dried *in vacuo* to afford a white solid. **25** was recrystallised from toluene to afford small colourless plates (0.55 g, 86%) m.p. 174-176 °C (dec. 197 °C). Elemental analysis calculated (%) for $C_7H_{14}AlCl_2N$: C 40.02; H 6.72; N 6.67. Found: C 40.50; H 6.74; N 6.64; ^1H NMR (C_6D_6): δ 0.79 (m, C*H*$_2$, 6H), 1.05 (m, C*H*, 1H), 2.69 (m, NC*H*$_2$, 6H); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 20.3 (*C*H), 24.0 (*C*H$_2$), 46.2 (N*C*H$_2$); IR (Nujol, cm^{-1}), ν Al-H stretch: 1861 s. Repeated attempts to obtain a satisfactory microanalysis were unsuccessful.

[AlCl$_3$(quin)] (26)

A cooled (-78 °C) diethyl ether solution (50 cm^3) of 2 M HCl in diethyl ether (1.60 cm^3, 3.20 mmol) was added to a toluene solution (40 cm^3) of [AlCl$_2$H(quin)] (0.68 g, 3.24 mmol), also at -78 °C. The effervescing solution was warmed to room temperature over 2h, filtered and solvent removed *in vacuo* to afford **26** as a white powdery solid. **26** was recrystallised from toluene to afford colourless needles (0.61 g, 78%) m.p. 203-205 °C (dec. 223 °C). ^1H NMR (C_6D_6): δ 0.84 (m, C*H*$_2$, 6H), 1.06 (m, C*H*, 1H), 2.85 (m, NC*H*$_2$, 6H); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 19.8 (*C*H), 23.9 (*C*H$_2$), 46.7 (N*C*H$_2$); IR (Nujol, cm^{-1}), ν 1342 s, 1318 s, 1283 s, 1262 m, 1204 s, 1170 w, 1119 w, 1067 s, 1040 s, 1012 s, 966 s, 900 w, 826 s, 802 s, 652 m, 627 m.

$[AlClH_2(quin)_2]$[73] (27)

A cooled (-78 °C), stirred diethyl ether (50 cm^3) slurry of quinuclidine hydrochloride (1.37 g, 9.28 mmol) was added to a toluene solution (100 cm^3) of $[AlH_3(quin)]$ (1.31 g, 9.28 mmol) at low temperature (-78 °C). The resulting effervescent solution, which gradually became cloudy with precipitated product, was warmed to room temperature over a period of 1 hour and dried *in vacuo* to give impure **27**. Recrystallisation from the minimum volume of toluene afforded the title compound as colourless prisms (2.01 g, 76%), m.p. 194-195 °C (dec. 211 °C, lit. 182 °C).[73] Elemental analysis calculated (%) for $C_{14}H_{28}AlClN_2$: C 58.63; H 9.84; N 9.77. Found: C 57.69; H 9.72; N 9.71; ^1H NMR (C_6D_6): δ 1.16 (m, CH_2, 12H), 1.35 (m, C*H*, 2H), 3.01 (m, NCH_2, 12H); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 22.2 (*C*H), 25.8 (CH_2), 46.2 (NCH_2); IR (Nujol, cm^{-1}), *ν* Al-H stretch: 1741 s.

$[AlCl_2H(quin)_2]$ (28)

Method (i): A cooled (-78 °C) diethyl ether (50 cm^3) solution of 2 M HCl in diethyl ether (1.59 cm^3, 3.18 mmol) was added drop wise to stirred, cooled (-78 °C) toluene (50 cm^3) solution of $[AlClH_2(quin)_2]$ (0.91 g, 3.17 mmol) by canula. The resulting effervescent solution was warmed to room temperature over a period of 2 hours, followed by drying *in vacuo* to afford analytically pure **28** (0.78 g, 77%) spectroscopically equivalent to that from method (ii) below.

Method (ii): As per method (i) using quinuclidine hydrochloride (0.47 g, 3.18 mmol) in place of ethereal hydrogen chloride. Added as a cooled (-78 °C) slurry in diethyl ether (50 cm^3). **28** isolated as colourless prisms after recrystallisation of the vacuum dried reaction medium from toluene (0.90 g, 88%), m.p. 205-207 °C (dec. 223 °C). Elemental analysis calculated (%) for $C_{14}H_{27}AlCl_2N_2$: C 52.34; H 8.47; N 8.72. Found: C 52.58; H 8.50; N 8.69; ^1H NMR (C_6D_6): δ 1.15 (m, CH_2, 12H), 1.30 (m, C*H*, 2H), 3.09 (m, NCH_2, 12H); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 21.6 (*C*H), 25.5 (CH_2), 46.4 (NCH_2); IR (Nujol, cm^{-1}), *ν* Al-H stretch: 1789 s.

$[AlCl_3(quin)_2]$ (29)

A slurry of quinuclidine hydrochloride (0.46 g, 3.12 mmol) in toluene (20 cm^3), at -78 °C, was added to a solution of $[AlCl_2H(quin)_2]$ (1.00 g, 3.11 mmol) in toluene (100 cm^3) cooled to -30 °C, and stirred overnight. Removal of volatiles *in vacuo*, washing with hexane (20 cm^3), and recrystallisation from toluene afforded **29** as rectangular plates (0.61 g, 55%), dec. 336 °C. Elemental analysis calculated (%) for $C_{14}H_{26}AlCl_3N_2$: C 47.27; H 7.37; N 7.88. Found: C 47.27;

H 7.57; N 7.86; ^{1}H NMR (C_6D_6): δ 1.13 (m, CH_2, 12H), 1.28 (m, CH, 2H), 3.20 (m, NCH_2, 12H); ^{13}C{^{1}H} NMR (C_6D_6): δ 21.1 (CH), 25.3 (CH$_2$), 46.9 (NCH$_2$); IR (Nujol, cm^{-1}), v 1352 m, 1336 s, 1317 s, 1279 s, 1197 s, 1166 m, 1112 w, 1043 m, 1021 m, 1003 s, 973 s, 901 w, 832 m, 816 s, 767 s, 626 s.

[AlBrH$_2$(quin)] (30)

A cooled (-78 °C) slurry of julolidine hydrobromide (2.18 g, 8.58 mmol) in toluene (50 cm^3) was added to a stirred solution of [AlH$_3$(quin)] (1.21 g, 8.57 mmol) in toluene (150 cm^3) at -78 °C. The solution was warmed to room temperature with stirring for 12 hours. After removal of volatiles *in vacuo*, the colourless solid was washed with hexane (4 × 5 cm^3), and recrystallised from the minimum volume of toluene as colourless blocks (1.58 g, 84%), m.p. 122-124 °C (dec. 175 °C). Elemental analysis calculated (%) for $C_7H_{15}AlBrN$: C 38.20; H 6.87; N 6.36. Found: C 38.79; H 6.99; N 6.48; ^{1}H NMR (C_6D_6): δ 0.81 (m, CH_2, 6H), 1.06 (m, CH, 1H), 2.60 (m, NCH_2, 6H); ^{13}C{^{1}H} NMR (C_6D_6): δ 20.2 (CH), 24.2 (CH$_2$), 46.8 (NCH$_2$); IR (Nujol, cm^{-1}), v Al-H stretch: 1827 br s.

[AlBr$_2$H(quin)] (31)

A cooled (-78 °C) slurry of julolidine hydrobromide (1.89 g, 7.44 mmol) in toluene (50 cm^3) was added to a stirred solution of [AlBrH$_2$(quin)] (1.64 g, 7.45 mmol) in toluene (150 cm^3) at -78 °C. After stirring and warming to room temperature over a period of 4 hours, all volatiles were removed *in vacuo* and the white solid was washed with hexane (4 × 5 cm^3). The title compound was recrystallised from the minimum volume of toluene as large colourless prisms (1.83 g, 82%), m.p. 164-166 °C (dec. 189 °C). Elemental analysis calculated (%) for $C_7H_{14}AlBr_2N$: C 28.12; H 4.72; N 4.68. Found: C 27.87; H 4.78; N 4.66; ^{1}H NMR (C_6D_6): δ 0.83 (m, CH_2, 6H), 1.07 (m, CH, 1H), 2.72 (m, NCH_2, 6H). ^{13}C{^{1}H} NMR (C_6D_6): δ 20.2 (CH), 23.9 (CH$_2$), 46.5 (NCH$_2$); IR (Nujol, cm^{-1}), v Al-H stretch: 1865 br s.

[AlBrH$_2$(quin)$_2$] (32)

A toluene (20 cm^3) solution of quinuclidine (0.20 g, 1.80 mmol) was added to a stirred solution of [AlBrH$_2$(quin)] (0.39 g, 1.77 mmol), also in toluene (50 cm^3), at ambient temperature. After stirring for 3 hours, volatiles were removed *in vacuo* and the resulting colourless solid was recrystallised from toluene as colourless blocks (0.42 g, 71%), m.p. 185-187 °C (dec. 221 °C).

Elemental analysis calculated (%) for $C_{14}H_{28}AlBrN_2$: C 50.76; H 8.52; N 8.46. Found: C 50.82; H 8.45; N 8.40; ^{1}H NMR (C_6D_6): δ 1.18 (m, C*H*$_2$, 12H), 1.33 (m, C*H*, 2H), 3.04 (m, NC*H*$_2$, 12H), 3.30 (bs, Al-*H*, 2H); ^{13}C{^{1}H} NMR (C_6D_6): δ 22.2 (*C*H), 25.7 (*C*H$_2$), 46.1 (N*C*H$_2$); IR (Nujol, cm^{-1}), *v* Al-H stretch: 1745 br s.

[AlBr$_2$H(quin)$_2$] (33)

A toluene (20 cm^3) solution of quinuclidine (0.30 g, 2.70 mmol) was added to a stirred solution of [AlBr$_2$H(quin)] (0.81 g, 2.71 mmol), also in toluene (20 cm^3), at ambient temperature. The mixture was stirred for 3 hours, stripped of volatiles *in vacuo*, and recrystallised from toluene to yield **33** as small colourless tabular crystals (0.87 g, 78%), m.p. 199-201 °C (dec. 260 °C). Elemental analysis calculated (%) for $C_{14}H_{27}AlBr_2N_2$: C 41.00; H 6.63; N 6.83. Found: C 41.19; H 6.57; N 6.73; ^{1}H NMR (C_6D_6): δ 1.09 (m, C*H*$_2$, 12H), 1.28 (m, C*H*, 2H), 3.08 (m, NC*H*$_2$, 12H), 3.60 (bs, Al-*H*, 1H); ^{13}C{^{1}H} NMR (C_6D_6): δ 21.7 (*C*H), 25.3 (*C*H$_2$), 46.2 (N*C*H$_2$); IR (Nujol, cm^{-1}), *v* Al-H stretch: 1789 br s.

[AlClH$_2$(IMes)] (34)

Method (i): A solution of IMes (1.53 g, 5.03 mmol) in toluene (100 cm^3) was added dropwise to a solution of [AlClH$_2$(quin)] (1.05 g, 5.00 mmol), also in toluene (50 cm^3). The solution was stirred for 1.5 h at room temperature, filtered and the solvent removed *in vacuo.* The resultant pale brown solid was washed with hexane (30cm^3) and recrystallised from toluene to afford **34** as colourless prisms (1.64 g, 89%) spectroscopically equivalent to that from method (ii) below.

Method (ii): A solution of IMes (2.00 g, 6.57 mmol) in diethyl ether (50 cm^3) was added to a solution of [AlClH$_2$(NMe$_3$)$_2$] (1.21 g, 6.62 mmol) in diethyl ether (50 cm^3) with immediate formation of a white precipitate. Further stirring for 1 h, followed by filtration afforded **34** as an off-white powder (2.05 g, 84%), dec. 268 °C. Elemental analysis calculated (%) for $C_{21}H_{26}AlClN_2$: C 68.38; H 7.10; N 7.59. Found: C 68.59; H 7.11; N 7.74; ^{1}H NMR (C_6D_6): δ 2.03 (s, *o*-C*H*$_3$, 12H), 2.05 (s, *p*-C*H*$_3$, 6H), 5.93 (s, 4,5-C$_2$*H*$_2$, 2H), 6.71 (s, *m*-ArC*H*, 4H); ^{13}C{^{1}H} NMR (C_6D_6): δ 17.0 (*o*-*C*H$_3$), 20.5 (*p*-*C*H$_3$), 122.3 (4,5-*C*$_2$H$_2$), 128.9 (Ar*C*), 129.41, 134.5, 139.3 (Ar*C*H); IR (Nujol, cm^{-1}), *v* Al-H stretch: 1798 s.

[$AlCl_2H$(IMes)] (35)

Method (i): A solution of IMes (2.00 g, 6.57 mmol) in diethyl ether (50 cm^3) was added to a solution of [$AlCl_2H(NMe_3)_2$] (1.43 g, 6.59 mmol) in diethyl ether (50 cm^3) with immediate formation of a white precipitate. Further stirring for 1 h, followed by filtration afforded **35** as an off-white solid (2.42 g, 91%) spectroscopically equivalent to that from method (iii) below.

Method (ii): A solution of IMes (1.47 g, 4.83 mmol) in toluene (100 cm^3) was added to a solution of [$AlCl_2H$(quin)] (1.01 g, 4.81 mmol), also in toluene (100 cm^3), and stirred for 1.5 h at ambient temperature. Removal of volatiles *in vacuo* afforded a pale brown solid that was washed with hexane (2 x 20 cm^3) and recrystallised from toluene to yield **35** as colourless needles (1.68 g, 87%) spectroscopically equivalent to that from method (iii) below.

Method (iii): A solution of IMes (2.10 g, 6.90 mmol) in THF (50 cm^3) was added to a solution of [$AlCl_2H(quin)_2$] (2.23 g, 6.94 mmol) in toluene (150 cm^3). The solution was stirred for 12 hours at room temperature, dried *in vacuo,* and the resultant pale yellow solid washed with hexane (2 x 10 cm^3) and extracted into fresh toluene (150 cm^3). Concentration to the point of crystallisation and placement at -20 ºC yielded **35** as fine colourless needles (2.06 g, 74%), dec 320 °C. Elemental analysis calculated (%) for $C_{21}H_{25}AlCl_2N_2$: C 62.54; H 6.25; N 6.95. Found: C 61.66; H 5.65; N 6.45; ^{1}H NMR (C_6D_6): δ 2.03 (s, *o*-CH_3, 12H), 2.06 (s, *p*-CH_3, 6H), 5.86 (s, 4,5-C_2H_2, 2H), 6.71 (s, *m*-ArC*H,* 4H); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 18.0 (*o*-*C*H_3), 21.4 (*p*-*C*H_3), 123.7 (4,5-C_2H_2), 129.9 (Ar*C*), 130.0, 135.5, 140.6 (Ar*C*H); IR (Nujol, cm^{-1}), *ν* Al-H stretch: 1851 s.

[$AlBr_2H$(IMes)] (36)

Method (i): A solution of IMes (0.83 g, 2.73 mmol) in THF (20 cm^3) was added drop wise to a stirred solution of [$AlBr_2H$(quin)] (0.82 g, 2.74 mmol), in toluene (100 cm^3), at room temperature. The pale orange reaction mixture was stirred for 12 hours, stripped *in vacuo*, washed with hexane (2 x 5 cm^3) and extracted into toluene (50 cm^3). Concentration *in vacuo* (*ca.* 20 cm^3) and placement at -20 ºC overnight afforded **36** as colourless prisms (0.89 g, 66 %) spectroscopically equivalent to that from method (ii) below.

Method (ii): A THF solution (20 mL) of IMesBr (1.25 g, 2.7 mmol) was added dropwise to a stirred solution of [AlH_3(quin)] (0.38 g, 2.7 mmol) in toluene (100 mL) at room temperature. The pale orange reaction mixture was stirred for 12 h and volatiles were removed *in vacuo.* Washing with hexane (10 mL) and extraction into toluene (50 mL) afforded **36** as colourless prisms after placement at -30 ◦C for several days (0.89 g, 67%), m.p. 272 ◦C (dec.). Elemental analysis calculated (%) for $C_{21}H_{25}AlBr_2N_2$: C 51.24, H 5.12, N 5.69; Found: C 51.92, H 5.09, N 5.67; ^{1}H NMR (C_6D_6): δ 2.03 (s, 12H, *o*-CH_3), 2.05 (s, 6H, *p*-CH_3), 5.86 (s, 2H, 4,5-C_2H_2), 6.71 (s, 4H, *m*-ArC*H*); IR (Nujol, cm^{-1}), *v* Al-H stretch 1888.

[AlCl$_3$(IMes)] (37)

A solution of IMes (1.77 g, 5.81 mmol) in diethyl ether (50 cm^3) was added to a solution of $AlCl_3$ (0.78 g, 5.85 mmol) in diethyl ether (20 cm^3) resulting in immediate precipitation of colourless **37**. Stirring overnight, followed by filtration and washing with diethyl ether (2 x 10 cm^3) gave **37** as a white solid (2.14 g, 84%), dec. 192 °C. ^{1}H NMR (C_6D_6): δ 2.00 (s, 12H, *o*-CH_3), 2.06 (s, 6H, *p*-CH_3), 5.78 (s, 2H, C=C*H*) 6.71 (s, 4H, *m*-ArC*H*,). ^{13}C{^{1}H} NMR (C_6D_6): δ 18.0 (*o*-CH_3), 21.4 (*p*-CH_3), 126.3 (4,5-C_2H_2), 130.0 (Ar*C*), 130.3, 135.7, 140.5 (Ar*C*H). Repeated attempts to obtain a satisfactory microanalysis were unsuccessful.

Chapter 3: Selected reductions using aluminohalohydrides

3.1 Introduction

This chapter describes the use of mixed halohydrides of aluminium as reducing agents for organic synthesis. The extensive application of boro- and aluminohydrides to this process has generated a library of available reagents that are described in the following sections. Much of this work was conducted by H.C. Brown from about 1940 into the 1960s and few reports followed this. In recent years, this has been supplemented by a wide range of Lewis base adducts of group 13 halohydrides due to a growth in this area (see earlier chapters).[22, 54, 165, 166] Despite the intrinsic instability of the heavier group 13 hydrides, hydrides of gallium and indium have also been applied to this task.[54, 167] A literature search reveals that there are very few reports of related applications of halohydrides, principally due to an absence of paths to such materials in high purity. This dearth was addressed in Chapter 2.

3.2 Significance of research

It is anticipated that the hydrometallation chemistry of aluminohalohydrides will be different to that of alane, due to the expected difference in electronic saturation and subsequent increase in Lewis acidity and hydride bond strength. The effect of such parameters on the outcomes of organic reductions has been observed previously by Jones *et al*., [167] wherein the IMes adduct of indane, [InH_3(IMes)], was shown to behave in an intermediate fashion to IMes adducts of gallane and alane due to an intermediate electronegativity at the metal and size differences. The diastereoselectivity of the reactions also suggested the strong chelation of certain substrates to the metal centre prior to hydride delivery.

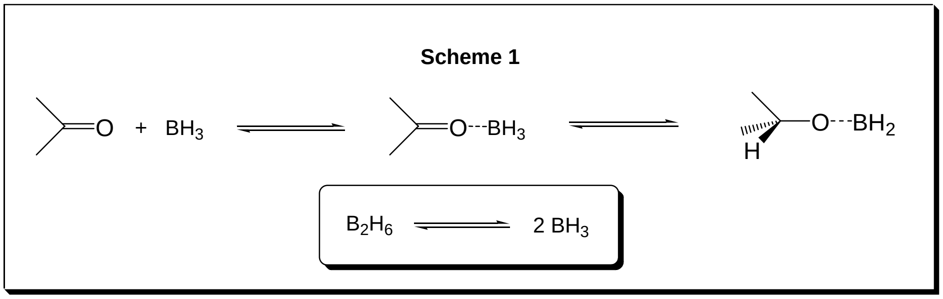
It may be reasonably assumed that the greater Lewis acidity of aluminohalohydrides will lead to new and perhaps distinct reactivities.

3.3 Reductions using borohydrides

3.3.1 Diborane

As early as 1939 H.C. Brown investigated the reducing nature of diborane, $(BH_3)_2$.[168] Brown classified substrates into three broad groups based on their reactivity with diborane; fast-reacting (reaction complete within 15 minutes), slow-reacting (reaction requiring several hours), and non reactive. Amongst the results was a puzzling anomaly; whilst the reaction of acetaldehyde with diborane was very fast, chloral (Cl_3CCHO) failed to react. An initial supposition that this was a steric phenomenon was quickly dismissed, as borane was known to rapidly reduce 2,2-dimethylpropanal, and the steric requirements of chloro and methyl substituents are very similar. This fast reaction ruled out the steric hypothesis and led Brown to propose a mechanism involving coordination of borane to the carbonyl oxygen followed by hydride delivery (Scheme 1). The lack of reactivity of diborane towards chloral was rationalised on the grounds of the reduced donor properties of the carbonyl oxygen due to the electron-withdrawing chloro-substituents.[169]

Scheme 1



3.3.2 Sodium borohydride

Brown reported the synthesis of sodium borohydride in 1953 during efforts to prepare uranium borohydride.[169, 170] Unlike the extremely potent and often non-selective lithium aluminium hydride,[8] this new species was found to be a mild reducing agent that readily reacts with aldehydes, ketones and acid chlorides.[171, 172] Indeed, sodium borohydride can be used in aqueous conditions, where it reacts slowly with the bulk solvent, especially under basic conditions.[170] This feature has proven very useful in the exploration of carbonium ion chemistry.[173]

At the time of its discovery, the large disparity between the reactivities of tetrahydroaluminate and tetrahydroborate posed a problem in terms of selectively reducing functions of intermediate reactivity. To address this, Brown commenced a comprehensive program aimed at exploring variables such as the solvent, the accompanying cation and the addition of substituent groups to the reducing agent. Over a period of approximately 10 years Brown and co-workers reported numerous new hydride reagents and reduction protocols that significantly expanded the synthetic organic chemistry of boro- and aluminohydrides.

Some salient features of this research are as follows:

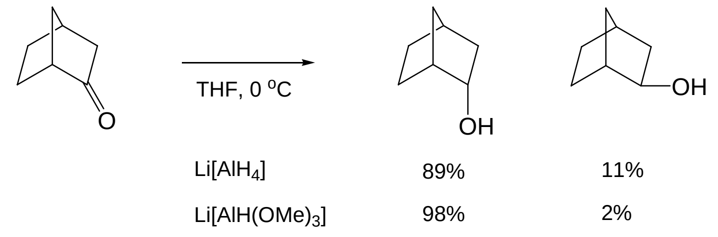
Solvent effects: Sodium borohydride is highly soluble in methanol and ethanol,[170] however it reacts with the former.[174] It is moderately soluble in isopropyl alcohol but stable toward it, allowing reductions on a preparative scale. Diglyme solutions diminish the reducing power of sodium borohydride to the point where aldehydes could be selectively reduced in the presence of ketones.[169]

Cation effects: Early observations of lithium and sodium borohydride highlighted the differences in their reactivity. Whilst the former reduces esters such as ethyl acetate rapidly, the latter reduces esters slowly.[175] This difference is also highlighted by the reduction of acetone.[176] Work by Kollonitsch *et al.* had previously demonstrated that the presence of lithium and magnesium iodides enables sodium borohydride to reduce simple esters more rapidly. Later, the same group reported increased rates of reaction for calcium, strontium and barium borohydrides.[177]

Substituent effects: Brown demonstrated the effect of substituents on sodium borohydride by preparing sodium triisopropoxyborohydride, $Na[AlH(O^iPr)_3]$, and studying its reaction with acetone in diglyme. Whilst the corresponding reduction with sodium borohydride at room temperature gives no reaction, the new species reacts rapidly at 0 °C. Unfortunately, sodium triisopropoxyborohydride readily disproportionates in certain solvents to form the tetrahydride and tetraalkylborate. This diminishes the utility of $Na[AlH(O^iPr)_3]$.[178] By contrast, the trialkyl-substituted species lithium trimethylborohydride and sodium triethylborohydride are much more stable in solution and do not redistribute.[169] These reagents were described by Brown as "interesting possibilities" for selective reducing agents, especially for achieving steric control in the reduction of ketones.[169]

Substituents effects on the reducing nature of lithium aluminium hydride were also examined by Brown. Lithium tri-*t*-butoxyaluminohydride was found to have remarkably diminished reducing power reminiscent of sodium borohydride. For instance, while aldehydes and ketones are reduced to alcohols at 0 °C, lactones and epoxides react slowly.[179] No reduction was observed for carboxylic acids, nitriles, nitro and olefin functions.[179] This reagent is also capable of reducing acid chlorides to their corresponding aldehyde.[180]

Trimethoxy substitution of Li[AlH_4] affords a reagent with similar reductive qualities to the parent tetrahydride with added stereoselective control. For instance, aldehydes, ketones and acid chlorides are reduced to the corresponding alcohols in comparable yields,[181] and bicyclic ketones such as norborane are reduced with greater stereodiscrimination relative to lithium aluminium hydride (Scheme 2).[182]



Scheme 2

3.3 Reductions using Lewis base adducts of alane and gallane

3.3.3 THF adduct of alane

The powerful reducing nature of lithium aluminium hydride was well established by the 1940s and 50s,[171, 172] and quantitatively assessed by H.C. Brown in the 1960s.[9, 169, 183, 184] Greater control and selectivity was achieved by the introduction of alkoxy groups to the metal centre.[180, 185, 186] As with the differing reactivities of diborane and sodium tetrahydroborate highlighted in Section 3.2, the reactivity of alane was expected to be different to that of Li[AlH_4]; alane, being a Lewis acid, would not act in the nucleophilic fashion of the tetrahydride anion.

Prior to the mid-1960s, the standard method of producing alane was the reaction of Li[AlH_4] with aluminium chloride in diethyl ether, yielding alane and lithium chloride (Scheme 3).[8] Unfortunately this species, which is most likely an etherate, precipitates from solution on standing. This uncertainty as to composition discouraged earlier research of its reducing capabilities.

Scheme 3

$$3\ Li[AlH_4]\ +\ AlCl_3 \xrightarrow{Et_2O} 4\ AlH_3\ +\ 3\ LiCl$$

A method previously used to stabilise solutions of alane was the addition of excess aluminium chloride,[187] however this risked generation of such species as [$AlClH_2$] and [$AlCl_2H$].[188-191] H.C. Brown proposed that the presence of these species would surely have diminished the credibility of any reports quantifying the reducing capability of alane.[9] Previously it had been reported that precipitated alane would dissolve in THF to yield [AlH_3(THF)] (**1**);[192] despite this Brown devised a new method of generating this species that was free of any possible halide contamination. This was by the addition of sulfuric acid to Li[AlH_4] in THF, a method that although low yielding, ensured a clean product (Scheme 4). Due to the propensity of alane to ring-open THF (forming *n*-butyl alcohol) on standing or under reflux,[193] Brown used only fresh samples of alane prepared by this method.[9]

Scheme 4

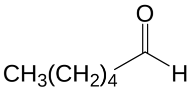
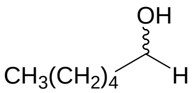
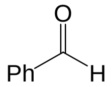
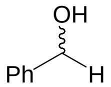
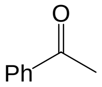
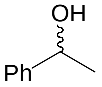
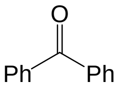
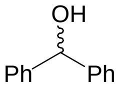
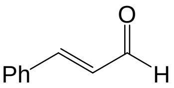
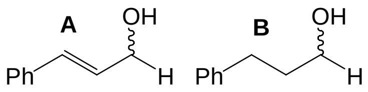
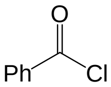
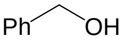
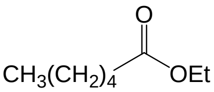
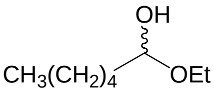
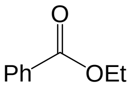
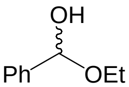
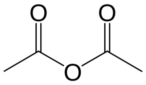
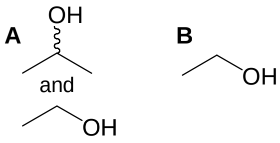
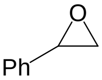
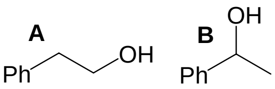
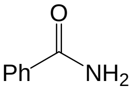
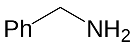
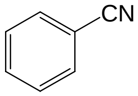
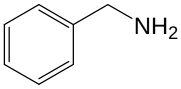
$$2\ Li[AlH_4]\ +\ H_2SO_4 \xrightarrow{THF} 2\ AlH_3\ +\ 3\ Li_2SO_4\ +\ H_2$$

The results of a subsequent reduction study demonstrated an expected difference in reactivity. The reduction character of alane (**1**) was compared with that of Li[AlH_4], (**2**),[183] Li[AlH(OMe)$_3$] (**3**)[194] and Li[AlH(O^{t}Bu)$_3$] (**4**)[186] against a standard list of compounds with functional groups including epoxide, nitrile and a range of carbonyl derivatives. The salient outcomes with respect to **1** of this assay are discussed as follows and summarised in Table 1.

Aldehydes and ketones

As expected, aldehydes and ketones of diverse structure, such as benzaldehyde, norcamphor, *n*-hexanal, benzophenone and acetophenone, were reduced quantitatively in under an hour at 0° C by all reagents. Although **2** and **3** reduced the double bond in cinnamaldehyde, **1** and **4** did not, and hence were classed as suitable for selective reduction of *α,β*-unsaturated carbonyl compounds. Brown reported that **1** was more stereoselective than **2** in the reduction of norcamphor (7:93 *exo-endo*, vs. 10:90), but was less selective than **3** (1:99).[182]

Table 1. Organic reductions using aluminium hydride species.

Substrate	**Product(s)**	**Reductant/% yield**			
		$[AlH_3(THF)]$[9]	$Li[AlH_4]$[184]	$Li[AlH(OMe)_3]$[195]	$Li[AlH(O^tBu)_3)]$[187]
		>99	>99	>99	98
		96	96	>99	86
		98	>99	>99	96
		98	>99	93	89
		>99 (A)	>99 (B)	>99 (B)	>99 (A)
		99	98	>99	>99
		>99	>99	>99	45
		>99	98	>99	0
		99 (B)	99 (A)	94 (A)	58(B)
		>99 (24% A)	>99 (4% A)	86 (1% A)	>99 (0% A)
		98	>99	90	0
		>99	97	92	0

Carboxylic acids and derivatives

1, **3** and **2** and quickly reduced carboxylic acids to their corresponding alcohols, although no such reduction occurred using **4**, and as such the latter was shown to be suitable for reduction of other functional groups in the presence of a carboxylic acid. Little difference was observed between the three active reagents, and **2** was the preferred option when selectivity was not important. If, however, selectivity was desirable, the use of **1** was preferred due to its faster rate of reaction, analogous to the use of diborane on carboxylic acids in the presence of other carbonyl moieties.[195] This trend was also borne out in the reduction of acid chlorides; **2** was the preferred option for non-selective reduction, and **1** for selective reduction.

Esters and lactones

1, 2, and **3** rapidly reduced esters and lactones. By contrast, **4** was either sluggish or gave no reaction.[179] When using **2** and **3**, reduction of isopropenyl acetate utilised three equivalents of hydride. In contrast, only two hydrides were used from **1**, suggesting that the use of **1** retained the enolate fragment. Measurement of evolved hydrogen demonstrated that transfer of the first hydride to some reagents was rapid, whilst the second was quite slow; this had previously been highlighted[196] during the conversion of carboxylic acids to their corresponding aldehydes.

Epoxides

All four reagents reduced epoxides to alcohols; **2** and **1** rapidly, whilst **4** and **3** less so. The reduced activity of the latter two manifested as greater selectivity, for example in the reduction of styrene oxide. Whilst **2** and **1** resulted in 4% and 24% secondary alcohol respectively, use of **3** and **4** yielded 1% and 0% respectively, highlighting their use as suitable reagents for selective reduction of epoxides to primary alcohols. The use of **1** on a hindered epoxide proceeded rapidly despite the steric concerns; 1-methyl-1,2-cyclohexene oxide was reduced to 1-methylcyclohexanol in quantitative yield and free of its other isomer, 2-methylcyclohexanol.

Amides and nitriles

A range of primary amides were reduced to amines by **1**, **2** and **3**, as were tertiary amides, the latter with considerably faster reaction times. Nitriles were quickly reduced to amines by **1**, but **2** and **3** had slower reaction times, whilst **4** did not react with either amides or nitriles. In general, **2** was the preferred reagent except in those situations where nitrile substrates contained acidic α-hydrogens, where simple deprotonation occurred.

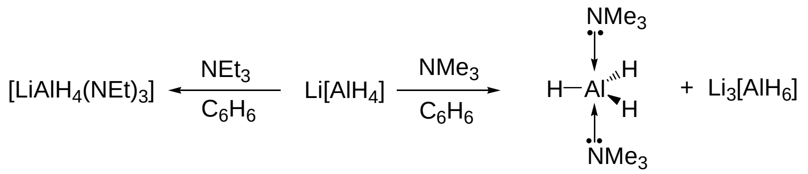
Summary

Overall, **2** is a highly useful reagent, in most part due to its ease of availability and use. Reagents such as **1** have particular application in situations where its increased activity reduces the likelihood of the reduction of secondary functional groups. From the research that Brown and others conducted,[9, 14, 179, 183, 186, 194] generalisations about the behaviour of aluminohydride reagents and the conditions under which they can be used has presented, and continues to present, a wide range of options for the reduction of functional groups.

3.3.4 Tertiary amine adducts of alane and gallane

In 1990, using the synthesis of Dilts and Ashby,[197] the group of Park prepared several tertiary amine adducts of alane (Scheme 5).[198] The method used has the advantages of not requiring exact control over the addition of sulfuric acid *cf*. Scheme 4, and avoids the use of THF with its inherent risk of ring-opening. Addition of trimethylamine to $Li[AlH_4]$ in benzene yields $[AlH_3(NMe_3)_2]$ and trilithium aluminium hexahydride. In contrast, addition of triethylamine to $Li[AlH_4]$ in benzene yields a triethylamine- $Li[AlH_4]$ adduct (Scheme 5).[197, 199]

Scheme 5



To explore the extraction of alane from $Li[AlH_4]$, Park and Marlett reacted a range of tertiary amines with $Li[AlH_4]$. The authors reported that the yield of the extraction reaction, carried out for 16 hours at 25° C in toluene, was dependent on the tertiary amine used (Scheme 6). Of the tertiary amines, dimethylethylamine and N-methylpyrrolidine were the most efficient, and the dimethylethylamine adduct of alane, $[AlH_3(NMe_2Et)]$ was chosen for an organic reduction study. The results of this study are represented in Table 2, and demonstrate a remarkable similarity to the reducing ability of **1**. Thus, it was demonstrated that a tertiary amine adduct of alane could replace **1** as a reducing agent without significant impact on organic reduction outcomes.[198]

Scheme 6

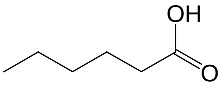
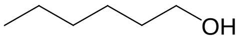
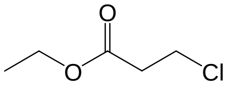
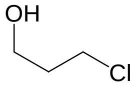
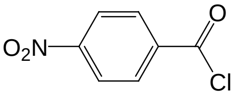
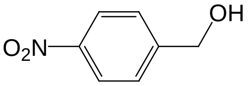
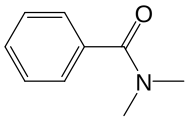
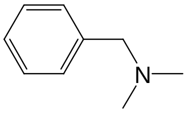
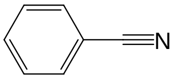
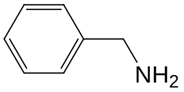
$$Li[AlH_4] \xrightarrow[\text{toluene}]{NR_3} [AlH_3(NR_3)_n] + Li_3[AlH_6]$$

n = 2 for NMe_3, n = 1 for all others

NMe_2Et > $NMe(CH_2)_4$ > NMe_3 > $NMeEt_2$ > NEt_3

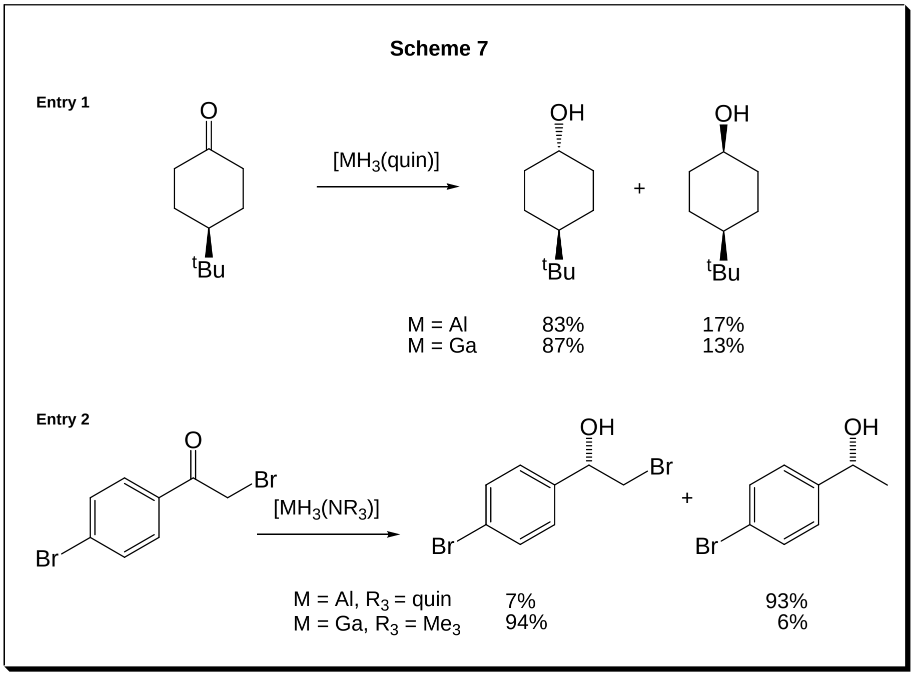
90% 83% 48% 12% 1%

Table 2: Organic reductions using $[AlH_3(NMe_2Et)]$

Substrate	Product	yield (%)	comparison yield using $[AlH_3(THF)]$ (%)
		99	98.5[9]
		99	100[14]
		90	92[14]
		98	98[14]
		98	96.8[14]

The group of Raston subsequently reported a series of reductions using the trimethylamine, tricyclohexylphosphine and quinuclidine adducts of alane and gallane.[54] Reduction of *tert*-butylcyclohexanone by $[AlH_3(quin)]$ (**5**) afforded an 83:17 ratio of the trans and cis alcohol products, whilst use of $[GaH_3(quin)]$ (**6**) afforded an 87:13 ratio (Scheme 7, Entry 1). The former reagent quantitatively reduced 2-cyclohexenone to the allylic alcohol without any reduction of the alkene functionality. The authors commented that the lack of any observable conjugate addition indicates that **5** is a relatively "hard" reagent on the HSAB scale.[200]

No reduction of an ester functionality was observed in the reaction of **6** with ethyl 4-oxocyclohexanecarboxylate, and also between that of [$GaH_3(NMe_3)$] (**7**) and ethyl benzoate. However, the reaction of [$AlH_3(NMe_3)$] and ethyl benzoate afforded benzyl alcohol in 80% yield.



[$GaH_3(NMe_3)$] reduced 1,4′-dibromoacetophenone to the corresponding alcohol without significant debromination (6%), however use of **5** resulted in significant (93%) cleavage of the α-carbon-bromine bond (Scheme 7 Entry 2).[54] These differences in reactivity were rationalised on the grounds of gallium's higher electronegativity and the decreased reactivity of the M-H bond.

Reduction of styrene oxide also highlighted this difference in electronegativities. Whilst the gallane species [$GaH_3(PCy_3)$] resulted in almost exclusively 1-phenylethanol, reduction using **5** resulted in a significant proportion of 2-phenylethanol (37%).[54] The authors commented that this suggested oxygen-aluminium coordination as the initial process in the mechanism, accompanied by the development of positive charge at the benzylic carbon prior to hydride addition. This trend is also demonstrated with the corresponding reaction with [$AlH_3(NEt_3)$],[201] and also the work of Eliel and Delmonte;[187] reduction via Li[AlH_4] yields predominantly the secondary alcohol, whereas more electropositive reagents such as Li[AlH_4]/$AlCl_3$[187] and

BH_3/BF_3[202] produce the opposite stereochemistry. These latter hydride/halide reagent combinations will be discussed in Section 3.44.

3.3.5 Lewis base adducts of indane

Due to the increasing inherent frailty of the M-H bond as group 13 is descended, very few hydride complexes of the heavier group 13 metals have been used in organic synthesis. A report by Jones is the only study of NHC-supported group indane species as reducing agents.[167] The air and room-temperature stability of $[InH_3(IMes)]$ prompted a reduction survey of simple and bifunctional substrates; previous reports[203-205] of supposed In-H reactions utilised reagents that were poorly characterised and difficult to handle due to air-sensitivity and low thermal stability. It was proposed that the In-H bond would have a polarity intermediate to that of the analogous Ga-H and Al-H bonds, due to indium's electronegativity lying between that of gallium and aluminium (In = 1.49, Ga = 1.82, Al = 1.47).[5] The larger covalent radius of indium (In 1.5 Å, Ga, Al 1.25 Å)[5] also encourages a greater participation in higher-coordinate bonding, and hence opens up the possibility of higher diastereoselectivity during the reduction of bifunctional substrates.[167]

Reduction of activated ketones such as benzil, benzoin and benzoin methyl ether proceeded with excellent diastereoselectivity (all > 99%) and in substantially better yields than with the unstable complex $Li[InH_4]$ (dec. 0° C).[203, 204] This diastereoselectivity indicated a strong chelation of the substrate to the metal centre, allowing a directed hydride delivery. In addition, attempted reduction of ethyl benzoate gave no reaction. This contrasts the reaction with $[AlH_3(NMe_3)]$, which yields 80% benzyl alcohol.[54]

Reactions with styrene oxide and 2,4′-dibromoacetophenone demonstrated the intermediate reducing nature of $[InH_3(IMes)]$. In the case of 2,4′-dibromoacetophenone, 57% α-C-Br cleavage occurred; by contrast, the alane congener effects quantitative cleavage whereas the gallane species effects minimal cleavage (see above).[167] In the case of styrene oxide, the reaction yielded roughly equal proportions of the primary and secondary alcohol (44% 2-phenylethanol, 56% 1-phenylethanol). The analogous with quinuclidinealane yields the products in a 37/63 ratio, whilst tricyclohexylphosphinegallane effects the secondary alcohol with >99% selectivity.[54]

3.3.6 Reductions using group 13 mixed halohydrides

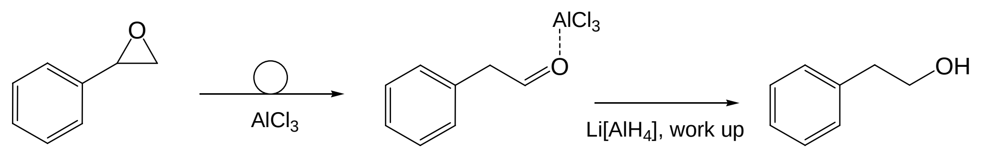
There have been few reports of reductions using group 13 mixed halohydrides, which are all "*in situ*" prepared species. The details of these are discussed as follows.

3.3.6.1 "Mixed" systems

As noted in previous sections, combinations of Li[AlH_4] and a halide source such as aluminium chloride or allyl bromide have been used to perform organic reductions, and numerous reports of this system indicate its usefulness.[189, 206, 207] Both Wiberg[207, 208] and Eliel[187] have indicated that aluminium halohydrides are formed during the use of a mixed system, however the proportions formed were not discussed. In the 1958 report by Eliel and Delmonte[187] on the use of this system, it became apparent that the formation of halohydrides would have had little effect on the outcome of the reactions (see later). The authors used a combination of Li[AlH_4] and either aluminium chloride or allyl bromide to perform reductions of halohydrins and epoxides. Reduction of several epoxides produced alcohol products with the opposite regiochemistry to that of when only Li[AlH_4] was used (Table 3).

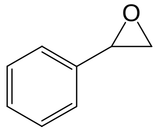
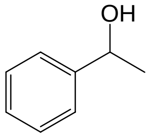
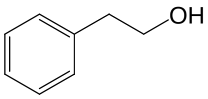
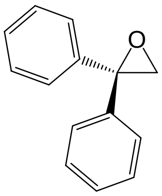
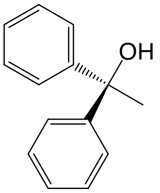
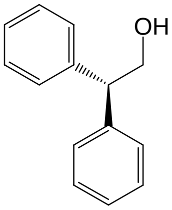
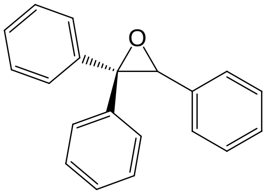
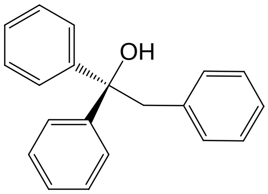
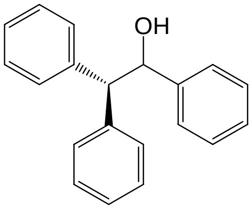
During the course of the study, the mechanism of the reaction was deduced via a deuterium labelling experiment; rapid formation of an activated carbonyl intermediate by the Lewis acid was followed by hydride reduction (Scheme 8). This rearrangement was likened to that of the reactions of epoxides with Grignard reagents, previously reported by Kharasch and Clapp in 1938.[209] The authors commented that although aluminium halohydrides may have been present in the reaction mixture, their "sluggish" nature, borne out of electronic unsaturation, would have ensured very little reduction relative to nucleophilic Li[AlH_4].

Scheme 8



In 1956 H.C. Brown observed that 1:3 solutions of aluminium chloride and sodium borohydride, intended to produce Al[BH_4]$_3$, exhibited increased reducing power over that of the borohydride alone.[210] Solutions of this new reagent rapidly reduced a variety of functional groups, including ketones, aldehydes, lactones, oxides, acid chlorides, acid anhydrides, primary amides and disulfides. The lack of precipitated sodium chloride in these solutions argued against the complete formation of aluminium borohydride, but Brown intimated that small amounts of the latter would be formed and assist in the reduction process.[210] Ultimately, the exact nature of this reductant was not confirmed or studied in detail, but it is likely that an aluminohydride was formed during preparation of the 'mixed' system.

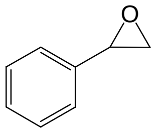
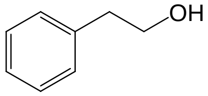
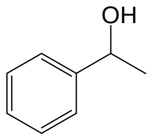
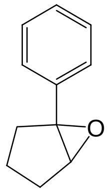
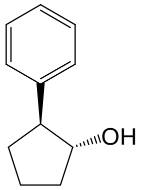
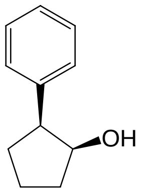
Table 3: Organic reductions using aluminium hydrides and halide sources

Substrate	**Reductant**	**Products and ratio (%)***	
			
	Li[AlH_4]	90-95	5-10
	Li[AlH_4], 4 $AlCl_3$	2-5	95-98
			
	Li[AlH_4]	100	0
	Li[AlH_4], 4 $AlCl_3$	0	100
			
	Li[AlH_4]	100	0
	2.64 Li[AlH_4], CH_2CHCH_2Br	0	100

* some unexplained uncertainty due to method used

In 1968 Brown also investigated the effect of boron trifluoride on the reducing nature of diborane.[202] Diborane alone reduced styrene oxide to afford a mixture of products, including the expected 2-phenylethanol and compounds with partial hydrogenation of the aromatic ring. Reaction with 1-phenylcyclopentene oxide produced none of the expected products; NMR analysis of the reaction mixture revealed a marked decrease in aromatic proton resonances, suggesting involvement of the aromatic ring in the reaction. However, inclusion of boron trifluoride in the same reactions gave remarkably different results (Table 4). In the case of styrene oxide, almost quantitative conversion to the primary alcohol was achieved with only traces of the secondary alcohol observed. Reaction with 1-phenylcyclopentene oxide led to a quantitative ring opening with an anti-Markovnikov product ratio (82:18 trans:cis).[202] The authors commented on the milder conditions of this system; the analogous reaction of styrene oxide with $Li[AlH_4]/AlCl_3$ requires heating to reflux and gives a lower yield and selectivity.[187]

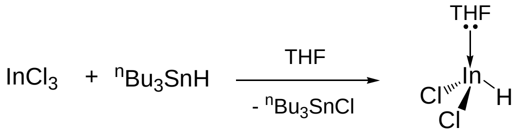
Table 4: Organic reductions using B_2H_6/BF_3

Substrate	**Reductant**	**Products and yield (%)**	
			
	B_2H_6	28	0
	B_2H_6/BF_3	99	trace amount
			
	B_2H_6	0	0
	B_2H_6/BF_3	82	18

3.3.6.2 "True" mixed halohydride reductions

Baba and co-workers have reported the *in situ* preparation of an indium halohydride and its application to organic synthesis.[205] $[InCl_2H(THF)]$ was prepared by a transmetallation between indium trichloride and tributylstannane in THF (Scheme 9).

Scheme 9



Although the hydride was not isolated *in situ*, NMR and IR measurements supported its preparation.[205] This hydride was applied to a range of organic substrates and the results of these experiments are summarised in Table 5.

Aldehydes were reduced to alcohols in high yield without reduction of alkene, ester, nitrile or aromatic nitro functionalities. Reduction of chalcone proceeded in a 1,4 fashion, as opposed to the 1,2-reduction afforded from hydroalumination.[211] Benzoin methyl ether was also reduced in good yield (82%), and the high diastereoselectivity (99% *d.e.*) of this reduction indicated a chelation of the metal centre to the methoxy oxygen. Reduction of alkyl bromides was effected in high yields, and this along with the reduction of chalcone indicated a possible radical nature of the indium-hydride bond. This postulate was tested with the radical inhibitor galvinoxyl; inclusion of this compound suppressed the reduction of both chalcone and aryl bromides, and the authors concluded that [$InCl_2H(THF)$] possessed radical properties. A later study by the same group demonstrated similar results with organic halides with only catalytic amounts of indium chloride.[212]

The same group extended this work in 2002, when they investigated the role of indium chloride in these reactions.[213] The authors proposed that an *in situ* generated [$InCl_2H$] species was responsible for the reduction, however needed to exclude the possibility that the indium chloride was simply assisting tributylstannane in a radical reduction process. The authors used hydride sources that were known not to perform the reduction unassisted (Scheme 10). Of the various hydride reagents trialled, sodium borohydride in acetonitrile proved to be superior, and the yield (81%) could be increased to 90% using 1.5 equivalents (Table 6). This process could also be stopped with 0.1 equivalents of *p*-dinitrobenzene (PNB), a radical scavenger, demonstrating the radical nature of the reduction.[213]

Scheme 10

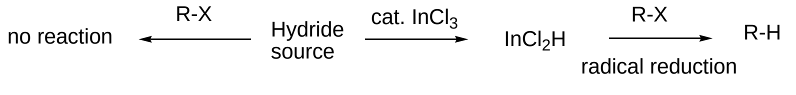


Table 5: Organic reductions using [$InCl_2H(THF)$].

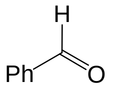
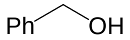
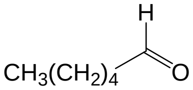
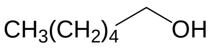
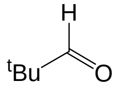
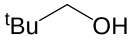
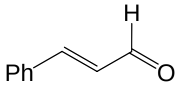
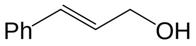
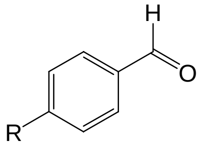
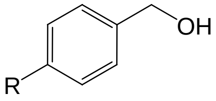
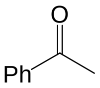
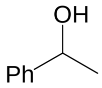
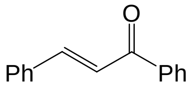
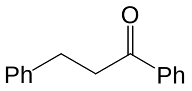
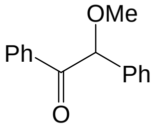
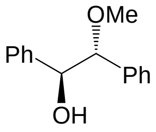
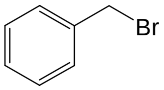
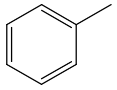
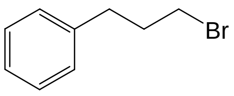
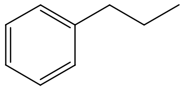
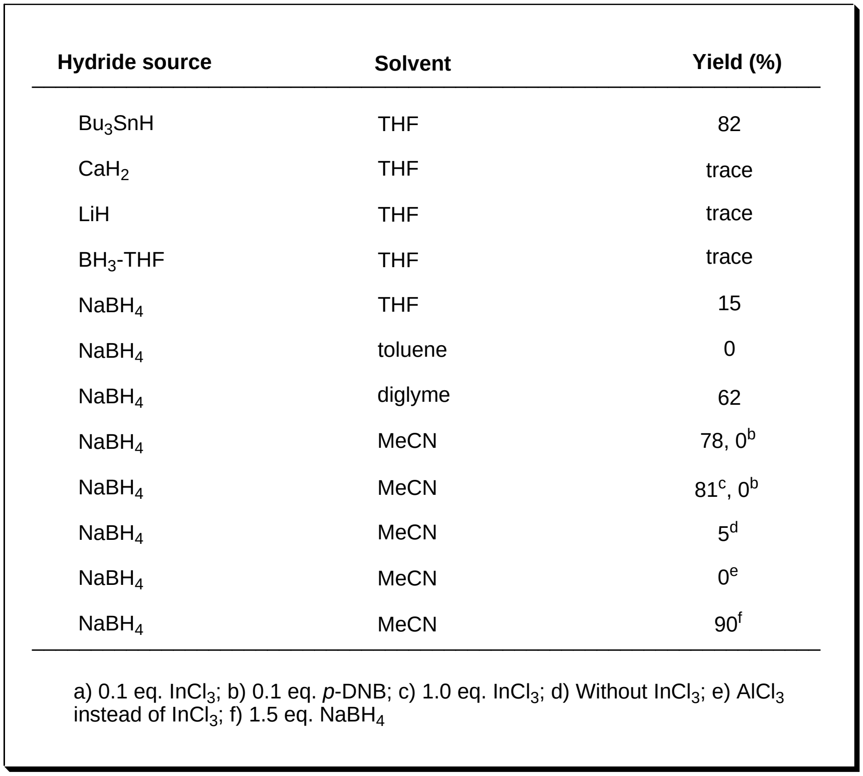
Substrate	Product	Yield (%)
		93
		78
		84
		99
		R = NO$_2$ 75 CN 76 CO$_2$Me 96 Cl 93
		23
		93
		82 (>99% *d.e.*)
		99
		77

Table 6: Indium-catalysed reductions of 2-bromopropylbenzene[a]



Hydride source	**Solvent**	**Yield (%)**
Bu_3SnH	THF	82
CaH_2	THF	trace
LiH	THF	trace
BH_3-THF	THF	trace
$NaBH_4$	THF	15
$NaBH_4$	toluene	0
$NaBH_4$	diglyme	62
$NaBH_4$	MeCN	78, 0[b]
$NaBH_4$	MeCN	81[c], 0[b]
$NaBH_4$	MeCN	5[d]
$NaBH_4$	MeCN	0[e]
$NaBH_4$	MeCN	90[f]

a) 0.1 eq. $InCl_3$; b) 0.1 eq. *p*-DNB; c) 1.0 eq. $InCl_3$; d) Without $InCl_3$; e) $AlCl_3$ instead of $InCl_3$; f) 1.5 eq. $NaBH_4$

3.4 Research proposal

Equipped with the series of aluminohalohydrides outlined in Chapter 2, it is proposed that these species be applied to a comprehensive organic reduction survey. Particular emphasis will be placed on selective transformations using substrates referred to in earlier sections to elucidate chemo-, regio-, and diastereoselective hydrometallation, and evaluate reducing character. The success of these reductions will be compared to those of the related trihydride, tetrahydride and, where possible, alumino- and metallohydrides substituted at the metal by alkoxy and halide functions.

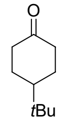
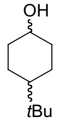
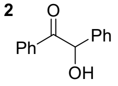
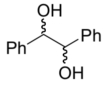
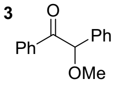
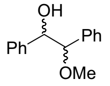
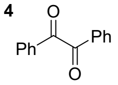
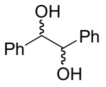
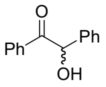
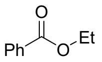
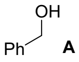
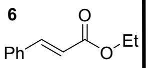
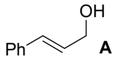
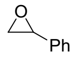
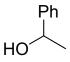
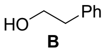
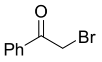
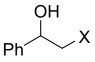
3.5 Results and discussion

3.5.1 Reaction with carbonyls and epoxides

The chloroalane compounds [$AlClH_2$(quin)] (**8**), [$AlClH_2$(quin)$_2$] (**9**),[73] [$AlCl_2H$(Quin)$_2$] (**10**), [$AlClH_2$(IMes)] (**11**) and [$AlCl_2H$(IMes)] (**12**) were chosen for hydroalumination study in order to provide reactivity comparisons between mono- and dichloroalane reagents **9**[73] and **10**, and **11** and **12**), four- and five-coordinate reagents (**8** and **9**)[73] and the influence of the bulky NHC IMes on hydroalumination reactivity (**11**/**12** and **8**, **9**,[73] **10**). These species also provide a broad range of Al-H bond strengths (see IR data in Table 3 of Chapter 2) and, in **11** and **12**, represent two of the most stable molecular aluminium hydrides known. Organic substrates for reduction (see Table 7) were chosen on the basis of (i) the carbonyl or epoxide functionality contained, (ii) the existence of literature outcomes for related trihydride compounds of boron, aluminium, gallium or indium,[54, 167, 169, 201, 203] and (iii) to highlight the selectivities of the chloroalanes at hand. All hydrometallation experiments were performed under an atmosphere of ultra high purity argon with a 2:1 stoichiometric ratio of chloroalane reagent to substrate, except where indicated (Table 7). All reactions were undertaken in dried, degassed THF at room temp over a period of 15-18 hours with stirring. Reactions were worked up by quenching with dilute aqueous acid and extraction into diethyl ether. The outcomes of similar hydrometallations or –borations using Lewis base adducts of group 13 trihydrides are also provided in Table 7 for ready comparison with the data disclosed here.

The reduction of simple ketones, such as aceto- and benzophenone, with compounds **8**, **9**,[73] **10**, **11** and **12** (not listed in Table 7) goes to completion without such complications as halogenation at the carbonyl. The reduction of 4-*tert*-butylcyclohexanone (substrate 1) with the same reagents leads to near quantitative hydrometallation in all cases with appreciable diastereoselectivity for the *trans*-product. This *trans*-selectivity is consistent with those observed for Lewis base adducts of alane, gallane[54, 169, 201] and indane[167] with noticeably decreased selectivity for adducts **9**[73] and **12** and reduced yields for five-coordinate **9**,[73] **10** and bulky dichloroalane **12**. Furthermore, a decrease in hydride reagent:substrate ratio to 1:1 using dichloroalane **10** results in a 20% decrease in yield and a dramatic decline in stereoselectivity (*trans*:*cis ca.* 8:1 to 2:1) under the same reaction conditions. The selectivity of these hydrometallations arises from stabilisation by a heteroallylic transition state.[55]

Table 7. Outcomes for the hydroalumination of substrates 1-8 by the chloroalane reagents **8**, **9**,[73] **10**, **11** and **12**, and relevant examples of hydrometallations undertaken using boron, aluminium, gallium or indium hydride reagents.

Substrate	**Products**	**Hydride Reagent**								
		8	**9**	**10**	**11**	**12**	**L·BH$_3$**	**L·AlH$_3$**	**L·GaH$_3$**	**PCy$_3$·InH$_3$**
		Isolated Yields →								
1 	 *cis* **A** *trans* **B**	17:83	31:52	11:76 (22:46)[#]	18:78	27:57	-	17:83[a]	13:87[a]	19:81
2 	 *meso* **A** *R,R/S,S* **B**	56:36	-	7:2	89:10	72:7	5:1[e]	91:9[e]	-	>99:1
3 	 *R,S/S,R* **A** *R,R/S,S* **B**	93:7	94:6	88:2	78:7	20:64	-	-	-	65:0
4 	 *meso* **A** *R,R/S,S* **B**  **C**	36:30:6	22:8:4	5:1:66	70:6:10	31:7:6	96:2:0[e]	93:2:0[e]	-	69:0
5 	 **A**	100	-	-	-	4	-	80[b]	0[b]	0
6 	 **A**	90	58	49	43	16	-	-	-	0
7 	 **A**  **B**	12:88	8:92	19:81	29:71	17:75	A>>B[b]	63:37[ac]	>99:1[d]	45:35
8 	 X= Br **A** X = H **B**	4:95	20:76	21:78	21:54	13:72	0[b]	7:93[a]	94:6[b]	43:57

a) L = quinuclidine; b) L = trimethylamine; c) L = triethylamine; d) L = tricyclohexylphosphine; e) L = H-; references in text

1:1 ratio reagent:substrate

The diastereoselective reactivities of compounds **8**, **9**,[73] **10**, **11** and **12** are also apparent in their reaction with the α-dicarbonyl or α–hydroxyl/methoxylcarbonyl substrates benzil, benzoin and benzoin methyl ether (substrates 4, 2 and 3 respectively) (Table 7).[54, 167, 169, 201, 203] The reduction of benzoin (substrate 2) and benzil (substrate 4) with Lewis basic group 13 tetrahydride reagents and Lewis base adducts of indane[54, 167, 169, 201, 203] results in *meso*-diols due to spatially directed hydride delivery. It has been proposed that this results from the formation of a cyclic alkoxymetal substrate chelate intermediate, resulting in *meso*:(*R*,*R*/*S*,*S*) ratios for the products of >80% *d.e.*, and frequently > 95% *d.e.*[54, 167, 169, 201, 203] In the present cases, the reduction of substrate 2 by IMes compounds **11** and **12** affords similar selectivities to literature reagents,[54, 167, 169, 201, 203] but reduction by five coordinate **9**[73] and **10** is low yielding. This is consistent with the higher coordination numbers of the latter complexes, which presumably do not freely permit reduction of the C=O bond and prohibit the coordination of the substrate that is required for diastereoselective reduction. It is also likely that the Al-H bonds of **9**[73] and **10** react with the hydroxyl group of this substrate inhibiting hydrometallation by the 2nd equivalent of hydride reagent, *cf.* 2:1 stoichiometry. This is borne out by the successful hydrometallation of methylated substrate 2 by both reagents (**9**; >99 %, **10**; 90 % yield), which occurs in decreasing yield across compounds **8**, **9**,[73] **10**, **11** to **12**. The relative ratio of *R*,*S*/*S*,*R*:*R*,*R*/*S*,*S* products for monochloroalane **11** relative to **8** also indicates that the significant bulk of IMes enhances selectivity during reaction with substrate 2 but not with 3. Interestingly, the selectivity of hydrometallation is reversed for **12** with substrate 3 relative to the selectivity observed with substrate 2. Studies of benzil (substrate 4) hydrometallation provide the most unusual outcome, this being the significant quantity of benzoin (substrate 2) formed upon reaction with bis(quinuclidine) dichloroalane **10**. This reaction outcome, i.e. half reduction, is unprecedented among hydrides of the main group elements.[5, 18, 19, 22, 152, 153, 165, 214]

The ester functionality provides a useful test bed to assess the limitations of hydrometallation by group 13 reagents. Unsubstituted Lewis base adducts of boranes, gallane[54, 169, 201] and indane[167] are unreactive toward esters. By contrast, the reduction of esters to alcohols can be achieved in reasonable yield by reagents such as trimethylamine alane (Table 7).[152, 153] To this end, the four coordinate chloroalanes **8** and **12**, representing the least hindered, least chlorinated and most hindered, most chlorinated four-coordinate hydrides studied respectively, were reacted with ethyl benzoate (substrate 5). The outcome of this was the full reduction of the substrate by **8** and minimal reduction by **12**, suggesting that increased steric bulk and chlorination at aluminium drastically decrease the hydrometallation of esters. To elaborate on this finding, the *E*-cinnamate ester 6 was treated with compounds **8**, **9**,[73] **10**, **11** and **12** resulting in sequentially decreasing yields of the 1,2-hydroalumination product without 1,4-reduction. This is consistent with the outcomes for substrate 5 and indicates that as chloride content and Lewis base donor strength increase, the hydroalumination of esters becomes less favourable.

Corresponding to the aforementioned chemoselectivity studies, the reduction of 1-bromoacetophenone (substrate 7) with compounds **8**, **9**,[73] **10**, **11** and **12** was attempted (Table 7). Lewis base adducts of alane, gallane[54, 169, 201] and indane[167] are known to reduce the related substrate 1,4'-dibromoacetophenone to afford mixtures of the methyl or α-bromomethyl alcohol (α-CH_3:α-CH_2Br; [AlH_3(quin)] 93:7, [$GaH_3(NMe_3)$] 6:94,[54, 169, 201] [$InH_3(PCy_3)$] 57:43 (Cy = *c*-C_6H_{11})).[167] The outcome of reactions with compounds **8**, **9**,[73] **10**, **11** and **12** indicates that the reagents used here are generally less selective than their alane counterparts, and that **9**[73] **10**, **11** and **12** afford appreciable amounts of the α-bromoalcohol unlike quinuclidine alane.

In order to qualitatively establish the Lewis acidities of hydrides **8**, **9**,[73] **10**, **11** and **12**, the regiochemistry of the hydromalumination of styrene oxide (substrate 8, Table 7) was assessed by monitoring the proportion of primary and secondary alcohols generated. The relative ratio of these products results from the degree of metal coordination that occurs prior to hydride delivery.[54, 167, 169, 187, 201, 202] Prior coordination of styrene oxide to the metal results in positive charge build-up leading to preferential hydride delivery at the benzylic carbon and primary alcohol formation (**B** Table 7). By contrast, non-coordination of the epoxide manifests in formation of the secondary alcohol (**A** Table 7), whereby the hydride attacks the least hindered carbon. Lewis base adducts of borane, alane, gallane and indane afford differing ratios of the primary and secondary alcohols, as described in Table 7, with a preference for the secondary 'non-coordinating' product. Gallane, the least Lewis acidic of the trihydrides, yields almost entirely secondary alcohol (A); alane yields roughly a 2:1 ratio of secondary alcohol to primary (A:B). Chloroalanes **8**, **9**,[73] **10**, **11** and **12** afford between 8-29% primary alcohol (B). This is consistent with the outcomes for poorly characterised *in situ* generated systems like

Li[AlH$_4$]/AlCl$_3$ and BH$_3$/BF$_3$. As aforementioned, these systems are thought to react with the substrate independently rather than as discrete mixed halohydride compounds.[187, 202]

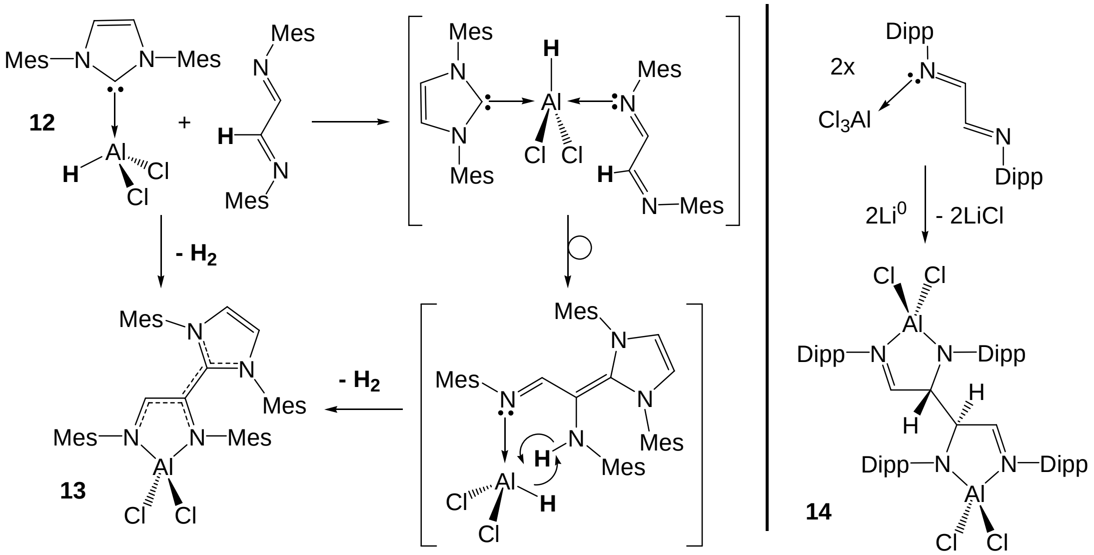
In summary, this investigation of hydroalumination by coordinated mono- and dichloroalanes indicates that the non-pyrophoric reagents prepared in Chapter 2 may be used to selectively reduce several cyclic or carbonyl containing organic substrates. Overall, it is clear that reagent **8** is typically more selective than the related bis(quinuclidine) species **9**[73] and **10**, and that monochloroalanes **9**[73] and **11** are typically more selective and higher yielding than their dichloro-counterparts **10** and **12**. There is a noticeable decrease in reactivity upon moving across the series **8**, **9**,[73] **10**, **11** and **12**. This most likely results from a combination of strengthening of the hydride-metal bond and increased steric buttressing for the latter. The decrease in reactivity also manifests in terms of ester reduction, in which reagent **8** is markedly more active than **9**,[73] **10**, **11** and **12**, with **12** barely active toward ethyl benzoate (substrate 5) and ethyl cinnamate (substrate 6). The hydrometallation of activated difunctionalised substrates such as 2-4 (Table 7) affords some selectivity for the *meso*:*R,S*/*S,R* products, but significantly lower selectivity than that reported for indium hydride[167] or the tetrahydride anions of boron and aluminium.[54, 167, 169, 201] A clear rationale for the haphazard selectivities observed cannot be made based on the data presented herein, as it would appear that both Lewis base size, Al-H bond strength and aluminium Lewis acidity play a contributing role. It is noteworthy that reagent **10** reacts with benzil (substrate 4) to give benzoin (substrate 2) in good yield. Based on reaction outcomes using styrene oxide, compounds **8**, **9**,[73] **10**, **11** and **12** possess Lewis acidities comparable to less well characterised group 13 hydride systems like BH$_3$/BF$_3$ and Li[AlH$_4$]/AlCl$_3$.[187, 202]

3.5.2 Reaction with an α-diimine

As observed by Brown and co-workers, amides and nitriles can be reduced to amines by [AlH$_3$(THF)] and a range of alkoxysubstituted tetrahydroaluminates along with Li[AlH$_4$] (Chapter 2). To expand the survey of hydroalumination using chloroalanes, **12** was reacted with the α-diimine {MesN=CH}$_2$ (Mes = 2,4,6-Me$_3$C$_6$H$_2$), MesDAB (Scheme 11) in a 1:1 reaction. Raston and co-workers have investigated the hydrometallation of several α-diimines using aluminium and gallium trihydrides.[215, 216] From these studies it was anticipated that the mono- or dihydroaluminated complexes [AlCl$_2${(Mes)NCH$_2$C(H)=N(Mes)}] or [{AlCl$_2$N(Mes)CH$_2$}$_2$] would result. The reaction was completed without acidic work-up due to a significant colour change from yellow to deep orange. This was unexpected, as reduction of the C=N should have eliminated the yellow chromophore. Work-up of the reaction mixture afforded the NHC transfer product [AlCl$_2${MesNC(=IMes)C(H)NMes}] (**13**) (Scheme 11), as evidenced by a single crystal X-ray structure determination (Figure 1). The analogous 1:1 reaction of MesDAB with [AlH$_3$(IMes)] affords a symmetrical non-IMes containing complex based on preliminary NMR and IR data. The outcome of this reaction was not pursued further.

Compound **13** contains a two-carbon bridged dinitrogen chelate ligand functionalised at carbon by an NHC-imidazole. The formation of **13** may be rationalised by the mechanism illustrated in Scheme 11 (left side), which has precedent in the organocatalytic applications of NHCs in *umpolung* (polarity inversion) reactions.[217]

Scheme 11



Left: Preparation of **13** and proposed mechanism for its formation.
Right: Preparation of related ligand system to that of **13**.

The distorted tetrahedral metal coordination environment of **13** (Figure 1) may be compared to that of [(AlCl$_2$)$_2${DippN=C(H)-C(=NDipp)}$_2$] (**14**) (Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$) recently reported by Mair *et al.* (Scheme 11, right side).[218] Compound **14** was obtained during attempts to access monovalent light group 13 species by alkali metal reduction of trivalent metal halides.[219-222] The bond lengths of **13** and **14** indicate anionic charge delocalisation and localisation across the dinitrogen ligands respectively. Consistent with this notion are the nitrogen to aluminium bonding contacts of **13** (1.856(3) and 1.846(3) Å), which vary less than the contacts of **14**

(1.824(4) and 1.953(4) Å), the latter two being representative of localised Al-N_{amido} and Al-N_{imino} bonds. Delocalisation is similarly evidenced by the contracted N(1)-C(1) and C(1)-C(2), and elongated N(2)-C(2) bond lengths of **13** (1.365(4), 1.364(5) and 1.424(5) Å) relative to the analogous contacts of **14** (1.286(6), 1.498(7) and 1.462(6) Å).

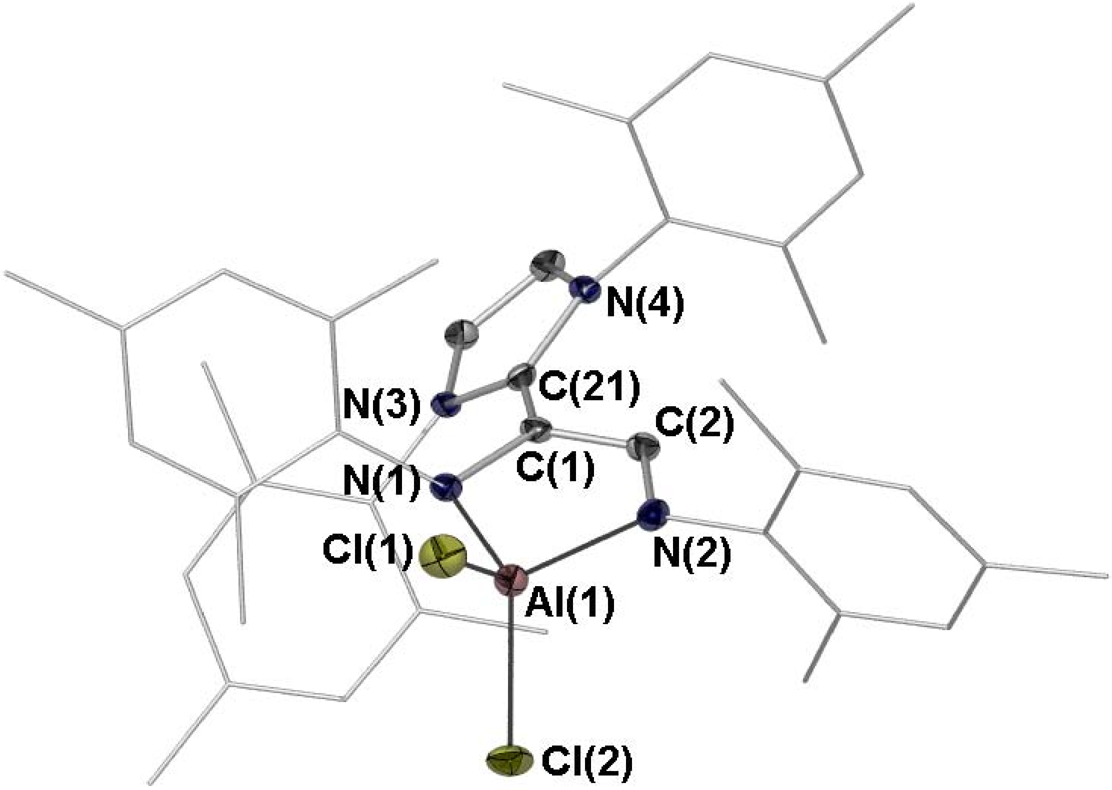


Figure 1. Molecular structure of **13** (POV-RAY illustration 40% thermal ellipsoids). Mesityl groups represented as wire frames and all hydrogen atoms omitted for clarity. Selected bond lengths (Å) for compound **13**: Al(1)-Cl(1) 2.1346(15), Al(1)-Cl(2) 2.1524(15), Al(1)-N(1) 1.846(3), Al(1)-N(2) 1.856(3), C(1)-N(1) 1.424(5), C(2)-N(2) 1.365(4), C(1)-C(2) 1.364(5), C(1)-C(21) 1.454(5).

The hybridisation of **13** at C(1), which is bonded to the 'transferred' NHC moiety, is best described as sp^2 based on the planarity and bonding of C(1) (sum of angles about C(1) 358.6(9)°, C(1) 0.226(6) Å out of the N(2),C(2),C(21) plane). Charge delocalisation most likely includes the imidazole moiety (C(1)-C(21) 1.454(5) Å) although, as denoted by the substantial pyramidalisation of N(1) (sits 0.287(3) Å out of the Al(1),C(3),C(1) plane), the buttressing of aryl substituents at N(1) and N(3) extend the C(1)-C(21) bonding interaction (1.454(5) Å). It is noteworthy that the IR spectrum of **13** contains a strong C=N stretching absorption at 1713 cm^{-1} and does not display an absorbance in the N-H stretching region (**13**; 3394 cm^{-1} *vide supra*) as is consistent with the formulation proposed.

The non-hydroalumination of MesDAB by **12** indicates chloroalanes possess contrasting chemistry to trihydride counterparts. In relation to the NHC transfer that results in **13**, which necessitates IMes dissociation from **12** as illustrated in Scheme 11, it is useful to note that NHC 'lability' has been observed previously during the hydroalumination of β-diketones using NHC-stabilised alanes.[223]

3.6 Conclusion

Outcomes from the application of five chloroalane compounds to hydroalumination indicate that, while the selectivities observed may be duplicated in part by reported group 13 hydride systems, it is clear that complexes such as **8**, **9**,[73] **10**, **11** and **12** exhibit distinct reactivities relative to trihydride counterparts. It is therefore contended that hydrometallation using chloroalanes, and indeed the other halometallanes of group 13, warrants more thorough investigation in the quest for new, selective synthetic reagents.

3.7 Experimental

General

Diethyl ether, THF and hexane were dried over sodium and freshly distilled from sodium diphenylketyl before freeze-thaw degassing prior to use. Toluene was dried over sodium and freshly distilled from potassium before freeze-thaw degassing prior to use. All other materials, including the substrates for the hydroalumination studies, were acquired from Sigma-Aldrich and used as received. All manipulations, excepting the work-up procedures for the hydroalumination studies, were performed using conventional Schlenk or glovebox techniques under an atmosphere of ultra high purity argon in flame-dried glassware. The infrared spectrum of **13** was recorded as a Nujol mull using sodium chloride plates on a Nicolet Nexus FTIR spectrophotometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 300.13 MHz and 75.46 MHz respectively using a Varian 2000 spectrometer with chemical shifts referenced to the residual ^{1}H resonances of the *deutero*-benzene solvent (δ 7.16 and 128.39 ppm respectively). The melting point of **13** was determined in a sealed glass capillary under argon and is uncorrected. The microanalysis of **13** was conducted by the Campbell Microanalytical Laboratory, Chemistry Department, University of Otago, P.O. Box 56, Dunedin, New Zealand. The single crystal X-ray data collection of **13** was undertaken at Monash University. Further details are listed below.

X-ray structure determination

The single crystal X-ray structure determination of **13** was undertaken using a sample mounted on a glass fibre in silicone oil. Data were collected using graphite monochromated $Mo_{K\alpha}$ X-ray radiation (λ = 0.71073 Å) at 123(2)K on a Bruker X8 Apex diffractometer. Structural solution and refinement was carried out using the SHELX suite of programs.[164]

General hydroalumination procedure

A THF solution of chloroalane reagent (2.0 eq.) in THF was added to a substrate (*ca.*1.40 mmol, total volume 30 mL). The resulting solution was stirred for 15-18 hours before quenching with dilute acid and removal of volatiles by fractional distillation (substrates 5-8) or rotary evaporation. Products were isolated by diethyl ether/aqueous or brine work-up, followed by drying over anhydrous magnesium sulfate. All product analyses were initially carried out by ^{1}H NMR in $CDCl_3$, with signals referenced to the residual protic solvent reference. Indicative ^{1}H NMR signals were identified using the Sigma-Aldrich reference library except where unavailable. In such cases, the necessary reagent(s) was purchased from distributors and its ^{1}H NMR spectrum recorded for comparison. Where necessary, volatile hydroalumination products were analysed by GCMS using a Hewlett-Packard 5890A instrument.

Compound 13

A bright yellow solution of MesDAB (0.17 g, 0.58 mmol) in toluene (15 mL) was added drop wise to a stirred colourless solution of **2** (0.24 g, 0.60 mmol), also in toluene (25 mL). The resulting solution darkened over a period of two hours to dark brown. Filtration followed by removal of volatiles *in vacuo* gave a deep orange solid that was washed with diethyl ether (2 x 3 mL) and recrystallised from THF-hexane to afford **13** as dark yellow-orange prismatic crystals (0.16 g, 40%), m.p. 330 °C. Elemental analysis calculated (%) for $C_{31}H_{47}N_4AlCl_2$: C 70.98, H 6.83, N 8.08; Found: C 70.62, H 6.74, N 7.67; ^{1}H NMR (300.14 MHz, C_6D_6, 300 K): δ 1.83 (br s, 12H; IMes *o*-C*H*$_3$), 1.91 (s, 6H; 2 x *p*-C*H*$_3$/1 x *o*-C*H*$_3$), 2.01 (s, 6H; 2 x *p*-C*H*$_3$/1 x *o*-C*H*$_3$), 2.06 (s, 6H; 2 x *p*-C*H*$_3$/1 x *o*-C*H*$_3$), 2.18 (s, 3H; *p*-C*H*$_3$), 2.21 (s, 3H; *p*-C*H*$_3$), 5.72 (s, 1H; 4/5-IMes C*H*), 5.80 (s, 1H; 4/5-IMes C*H*), 6.66 (s, 2H; *m*-Ar*H*), 6.74 (s, 4H; 2 x *m*-Ar*H*), 6.83 (s, 2H; *m*-Ar*H*), 6.87 (s, 1H; C(*H*)=N); IR IR (Nujol, cm^{-1}), v 1713 (s), 1608 (w), 1530 (w), 1306 (m), 1261 (m), 1230 (m), 1155 (m), 1084 (w), 1015 (m), 963 (w), 932 (m), 852 (w), 800 (w), 762 (w). ^{13}C NMR data was not obtainable due to insufficient product material.

Crystal data for **13**: $C_{41}H_{47}AlCl_2N_4$, M = 693.71, monoclinic, $P2_1/n$ (No. 14), a = 10.0810(2), b = 18.3266(4), c = 21.1938(4) Å, β = 91.942(1)°, V = 3913.32(14) Å^3, Z = 4, D_c = 1.177 g cm^{-3}, F_{000} = 1472, μ = 0.221 mm^{-1}, $2\theta_{\max}$ = 56.70°, 47016 reflections collected, 9591 unique (R_{int} = 0.1163). Final $GooF$ = 1.001, R_1 = 0.0961, wR_2 = 0.2571, R indices based on 5219 reflections with $I > 2\sigma(I)$ (refinement on F^2), 445 parameters, 0 restraints.

Chapter 4: *N*-terphenyl-substituted triazenide adducts of aluminium and gallium

4.1 Introduction

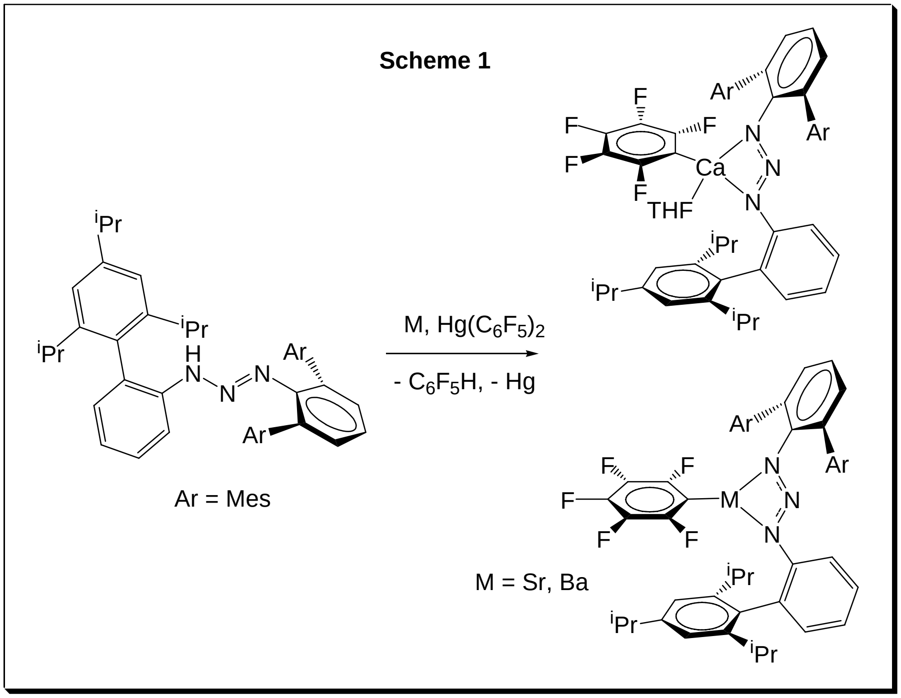
This chapter includes the preparation of several *N*-terphenyl substituted triazenes and their reactions with lithium tetrahydridoaluminate and tetrahydridogallate. The resulting alumino- and gallohydride complexes have been characterised by infrared and NMR spectroscopies (^{1}H and {^{1}H}^{13}C) and, where possible, X-ray structure determination. The structures and thermal stabilities of these complexes are rationalised in terms of triazenide size, metal and metal-hydride coordination environment.

4.2 Significance of research

It is anticipated that the increased steric bulk of *N*-2,6-terphenyl-substituted triazenes will enable greater kinetic stabilisation of group 13 species. Despite concerted attempts internationally to introduce 2,6-terphenyl groups to amidinates at nitrogen to exploit their inherent kinetic stabilisation ability, *N*-2,6-terphenyl substituted amidinates have so far not been reported.[224] The group of Niemeyer have prepared several *N*-terphenyl-substituted triazenes, discussed in Section 4.4. In 2005 Niemeyer also reported several *N*-2,6-terphenyl triazene complexes of alkaline earth metals (Scheme 1).[225] During this study, it was observed that pentafluorophenyl substituents could not be replaced by a second triazenide ligand; the authors proposed that the steric bulk of these species prevented formation of bis(triazenides) by both further substitution and ligand redistribution.

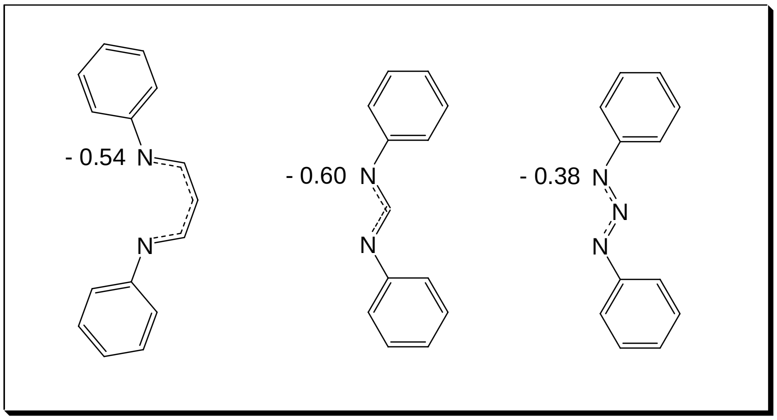
According to Gantzel and Walsh, triazenides are weaker donors and should induce greater electrophilicity at a bonded metal atom when compared to the isoelectronic amidinates and the related β-diketiminates.[226] Niemeyer *et al.* conducted a natural bond orbitals analysis of the energy optimised structures of the model anions 1,3-diphenyl-1,3-diketiminate, 1,3- diphenyl-1,3-diazaallyl, and 1,3-diphenyltriazenide (Figure 1). The results of this showed a natural population analysis charge on the chelating nitrogen of -0.54, -0.60, and -0.38 respectively.[225]

Scheme 1



It has been proposed that the reduced negative charge of triazenides at nitrogen is suited to the stabilisation of low valent metal complexes.[5] This feature stabilises low valent metals due to the increased margin between valence *s* and *p* orbitals, brought about by low charge.[5]

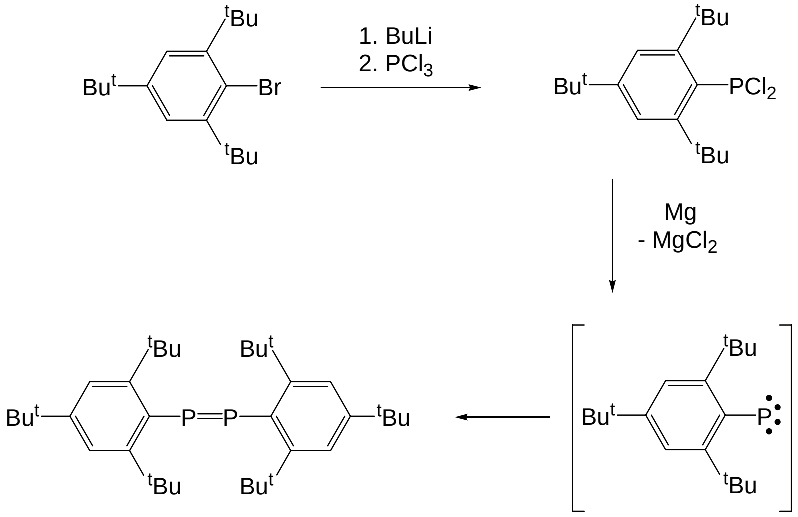
Figure 1: Natural population analysis of the chelating nitrogen atoms of ligands that may be used to stabilise group 13 compounds.



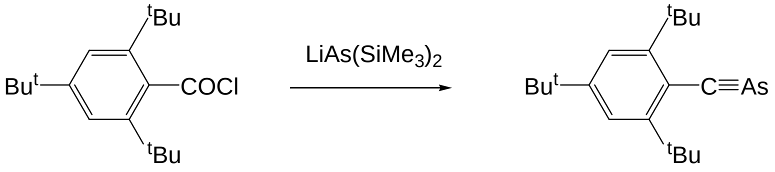
4.3 Sterically hindered ligands

The use of sterically bulky substituents to assist in the stabilisation of low-coordinate main group elements has proven very successful.[227-231] In a famous early example, the first phosphorus-phosphorus double bond, reported in 1981, was stabilised using 2,4,6-tri-*tert*-butylphenyl groups to protect the central phosphorus atoms (Scheme 2).[227] Despite the steric congestion within this molecule, the P-P bond distance (2.034(2) Å) is considerably shorter than those in $(PR)_n$ species such as $(C_6H_5P)_5$ (2.217(6) Å) and $(C_6H_5P)_6$ (2.237(3) Å), inferring an increased P-P bond order relative to these species. The same ligand was also used in 1986 to support the first arsenic-carbon triple bond (Scheme 3).[228]

Scheme 2



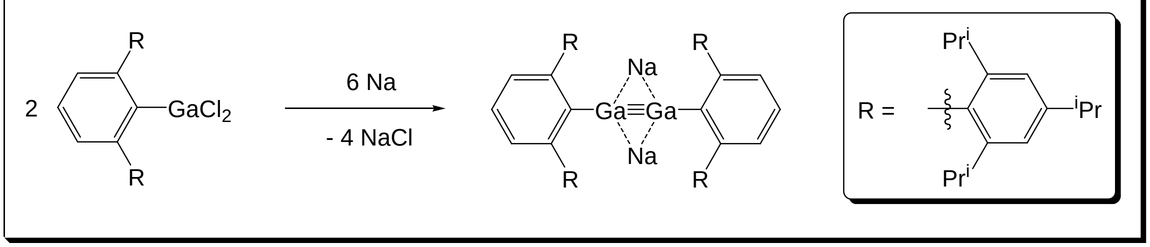
Scheme 3



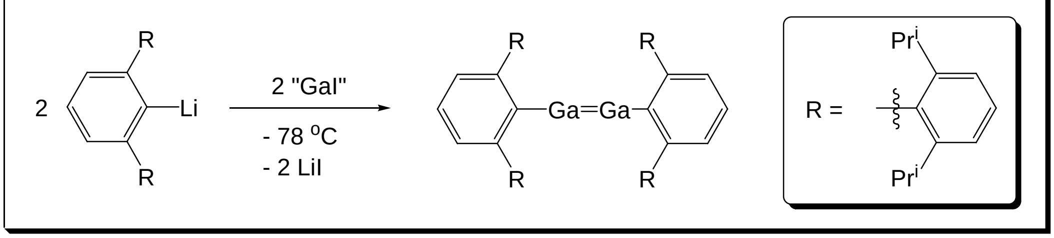
In 1997 Robinson *et al.* reported a species containing a putative gallium-gallium triple bond, which sparked a spirited debate (Scheme 4).[229] This species was stabilised using the "super-bulky" ligand 2,6-(2,4,6-$^iPr_3C_6H_2)_2C_6H_3$. In 2002 Power *et al.* reported the use of a similarly bulky ligand to stabilise the first neutral "digallene", R-Ga=Ga-R (R = 2,6-(2,6-$^iPr_2C_6H_3)_2C_6H_3$) prepared by direct reaction of an aryllithium with gallium(I) iodide (Scheme 5).[230]

As well as providing stability to inherently unstable species, "super-bulky" ligands have also been applied to chemical functionalities that do not need them for stabilisation in order to observe structural modifications. In 1998 Boere *et al.* proposed that direct comparison between crowded and non-crowded molecules could be used to demonstrate the knock-on influence of steric bulk on reactivity and compound structure, thereby enabling the impact of “super-bulky” systems to be quantified.[231]

Scheme 4



Scheme 5



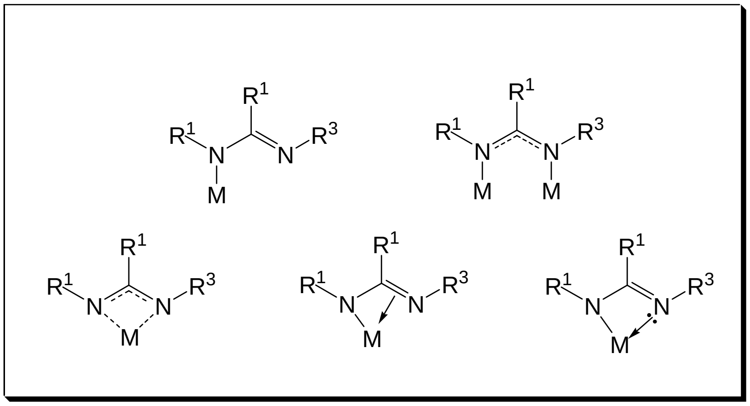
4.3.1 Amidinate chemistry

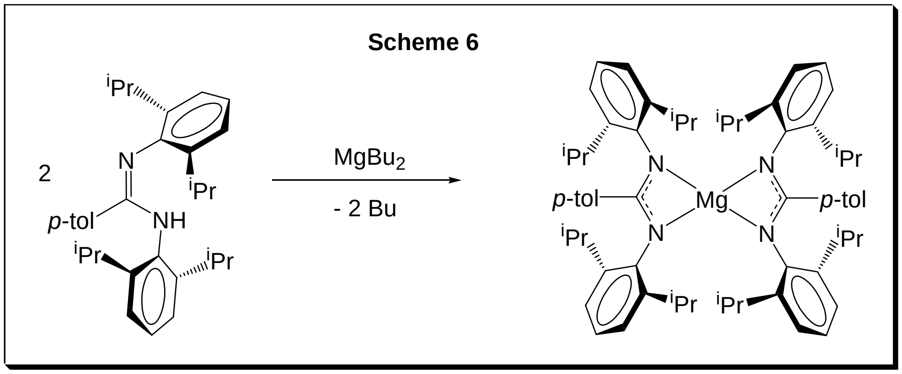
The amidinate ($[R^1NC(R^2)NR^3]^-$) class of ligand (including the formamidinates, where R^2 = H) has been used to good effect to stabilise a wide range of transition metal species.[224, 232, 233] Stabilising structural features include an ability to chelate the metal centre, and an ability to modify sterics by tuning of substituents at the nitrogen and carbon.

1,3-Disubstituted amidines (AmH), the parent compounds of amidinates, can act as simple two-electron donors via the more sterically hindered and less basic imine lone pair, thereby generating simple adducts such as $[CoCl_2(AmH)_2]$.[232] However, when the amine substituent is deprotonated to yield an amidinate of the form $[R^1NC(R^2)NR^3]^-$, multiple metal-bonding modes are enabled (Figure 2).[224]

Bis(aryl)formamidinate ligands, which enable further metal-ligand interactions via π-interactions from the aryl substituents, have also been used to good effect in this regard.[224, 234] Junk *et al.* have prepared numerous alkali metal complexes that demonstrate the coordinative potential of these ligands and their ability to effect a range of synthetic applications.[224] In one case, reaction of the bulky amidinate ligand DippAm with dibutylmagnesium in a 2:1 ratio resulted in a rare "square-planar" magnesium species, in which the considerable steric influences of the ligand dictated the unusual geometry of the complex (Scheme 6).[234]

Figure 2. Possible binding modes of mono- and dinuclear metal amidinate complexes




Scheme 6

4.3.2 Stabilisation of group 13 species using bulky dinitrogen ligands

4.3.2.1 Amidinates

In recent years, extensive research into the amidinate chemistries of the group 13 metal alkyls and halides [234-243] has led to application as olefin polymerisation catalysts[236-239, 243] and chemical vapour deposition (CVD) precursors.[235] Surprisingly, the first structurally authenticated group 13 amidinate complex was reported in 1996 (Scheme 7).[244]

As detailed in earlier chapters, heavy group 13 hydrides may be stabilised by sterically enshrouding the metal hydride bond and thereby frustrating possible metal to hydride bridging interactions that may aid dihydrogen elimination.[17, 245] Employing this rationale, Jones and co-workers have prepared several *N,N'*-bis(aryl)formamidinate complexes of group 13 hydrides that possess some of the highest thermal stabilities recorded (Figure 3).[246, 247]

Scheme 7

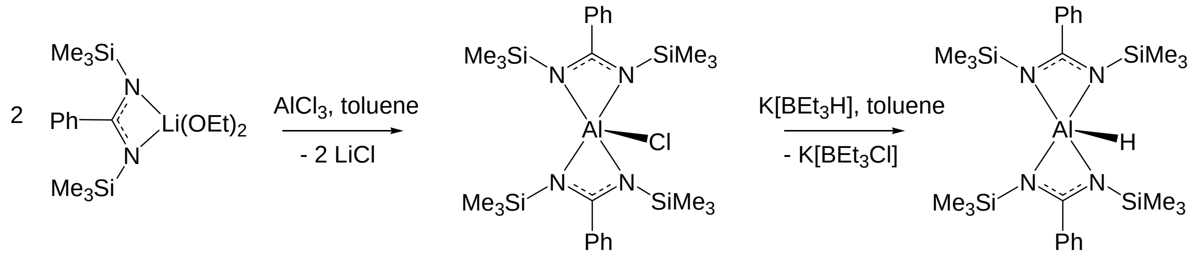
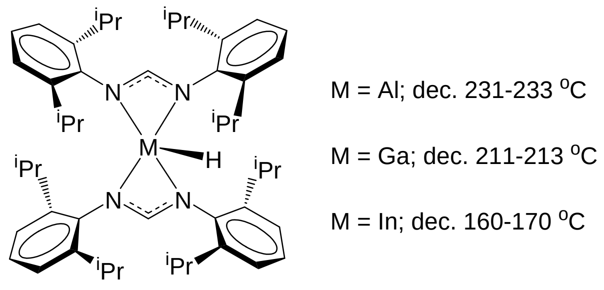
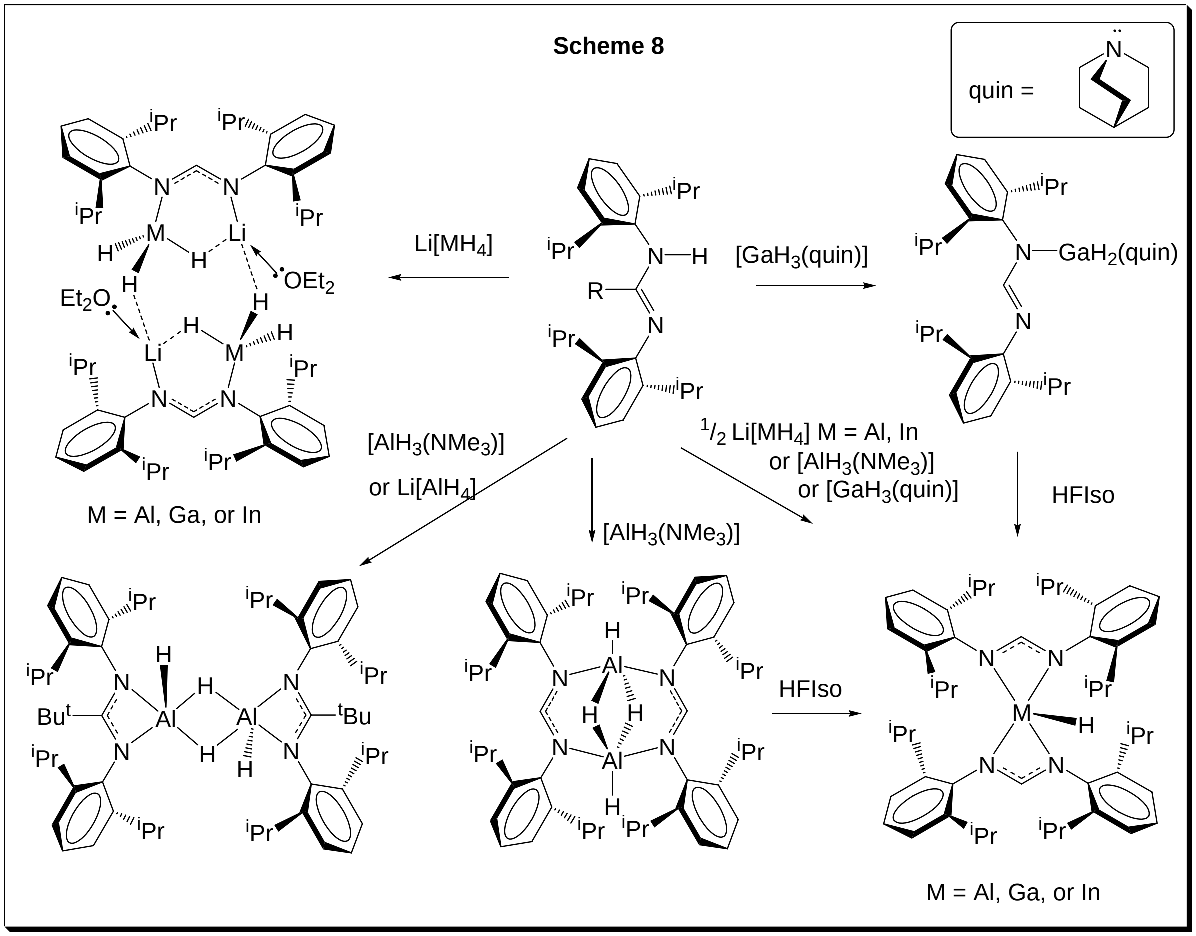


Figure 3. Thermally stable *N,N'*-bis(aryl)formamidinate complexes of group 13 hydrides

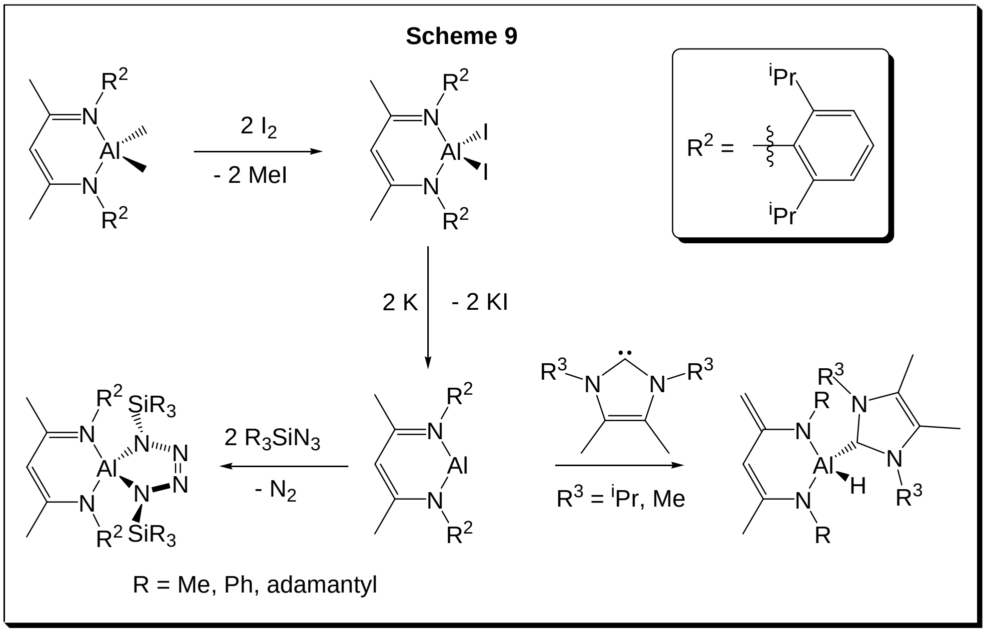


In a 2004 study, Jones *et al.* utilised the bulky formamidinate $[ArNC(H)NAr]^-$ (FIso, Ar = 2,6-$^iPr_2C_6H_3$) to prepare the thermally stable indium hydride species $[InH(FIso)_2]$ from $Li[InH_4]$.[246] The preparation of this species was broken down stepwise with the addition of one equivalent of HFIso to form an initial amidotrihydroindate complex, which further reacts with another equivalent of HFIso to form $[InH(FIso)_2]$ (Scheme 8). The analogous gallium reaction does not proceed in the same manner. Thus, while $Li[GaH_4]$ reacts with one equivalent of HFIso to form an amidogallate, no reaction occurs with a second equivalent, presumably due to gallium's preference for 4-coordination (see Chapter 1) and the reluctance of the complex to eliminate LiH (Scheme 8).[246] In a later study by the same group,[247] the corresponding $Li[AlH_4]$ reaction afforded the analogous 1:1 and 2:1 products to those of indium. Reaction of the alane adduct $[AlH_3(NMe_3)]$ with one equivalent of HFIso yielded a dimer, while the 2:1 reaction of HFIso with $[GaH_3(quin)]$ afforded the previously unobtainable 5-coordinate $[GaH(FIso)_2]$ (Scheme 8). Use of an even bulkier amidinate, the pivamidinate $DippN(C^tBu)NDipp$, with either $[AlH_3(NMe_3)]$ or $Li[AlH_4]$ yielded a related but distinct dimer, which exhibits metal-amidinate chelation rather than bridging due to the increased steric bulk of the central NCN carbon substituent (Scheme 8).[247] At the time of the 2004 report the authors rationalised that the unprecedented thermal stability of the bis(amidinate) hydride species arose from the steric buttressing afforded by the ligands; this not only shielded the M-H fragment from chemical attack, but also negated the formation of M-H-M bridges as a prelude to dihydrogen loss.[17]

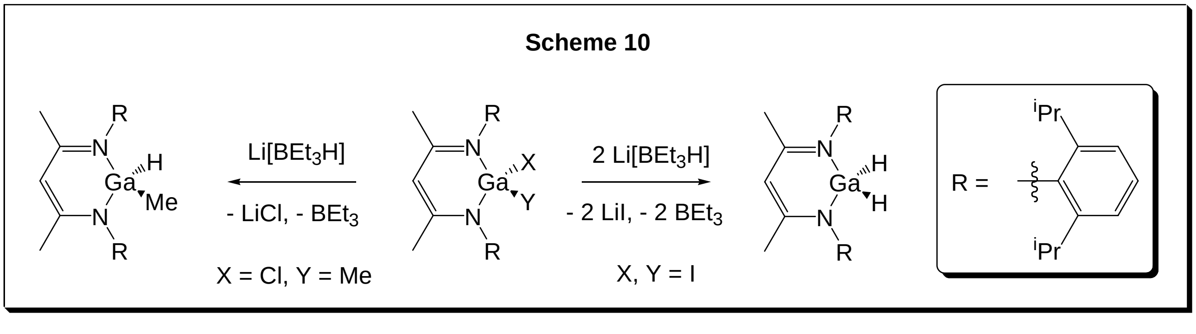


4.3.2.2 *β*-Diketiminates in group 13 chemistry

Since the first example of a group 13 *β*-diketiminate complex,[248] the utilisation of these anionic ligands for the stabilisation of tri- and monovalent group 13 compounds has been studied extensively.[249] The group of Roesky has reported numerous low valent group 13 complexes in recent times. In 2000, when only a handful of Al(I) complexes had been structurally characterised at the time, Roesky *et al.* reported the preparation of a thermally stable (dec 150 °C) *β*-diketiminate supported aluminium(I) NHC analogue via potassium reduction of the corresponding dihalide species (Scheme 9).[250] A subsequent report on the reactivity of this species detailed the preparation of the first AlN_4 ring system via its reaction with two equivalents of Me_3SiN_3 (Scheme 9).[251] In a later study this result was generalised to the bulkier reagents Ad_3SiN_3 (Ad = adamantyl) and Ph_3SiN_3.[252] The authors proposed that the mechanism of this reaction was the addition of one equivalent of R_3SiN_3 accompanied by loss of dinitrogen to form an intermediate, which underwent a second addition. Another report described the reaction of the Al(I) species with two NHC species to yield aluminium hydrides (Scheme 9). In these NHC reactions, addition of the carbene to the metal centre led to hydride abstraction from a methyl group (Scheme 9).[145]

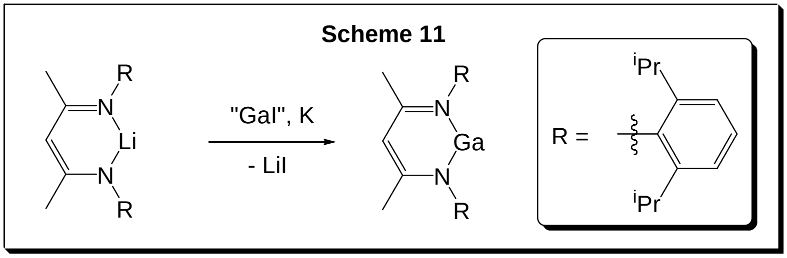


A later study centred on the reactivity of [MMeCl(L)] prepared by reaction of [LiL] (L = $[\{N(Dipp)C(Me)\}_2CH]^-$) with $MeMCl_2$ (Me = Al, Ga, In). The gallium compounds [GaClMe(L)] and $[LGaI_2]$ were reacted with various hydridic substrates to generate novel hydride and halide-substituted products (Scheme 10).[253]



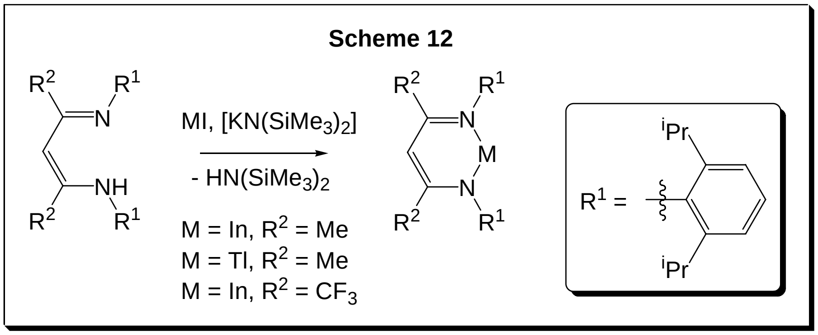
In 2000 the group of Power reported the gallium analogue of Roesky's Al(I) species, which was synthesised by reaction of the lithiated ligand with "GaI". This reaction required the presence of potassium to ensure the reduction of any $GaI_2(L)$ formed during the reaction by disproportionation of "GaI" (Scheme 11).[254]

Scheme 11



Surprisingly, despite the established and more stable nature of low valent indium chemistry, it was not until 2004 that Hill *et al.* published the indium(I) analogue of the Roesky-Power monovalent ketiminate species.[255] A one-pot synthesis from equimolar quantities of InI, $K[N(SiMe_3)_2]$ and $H(Dipp)C(Me)\}_2CH$ (Dipp = 2,6-diisopropylphenyl) at low temperature yielded the thermally stable (dec. 203-205 °C) but photolabile product (Scheme 12). A later report from the same group detailed the preparation of the respective thallium species and a 1,3-perfluorinated indium analogue (Scheme 12).[256]

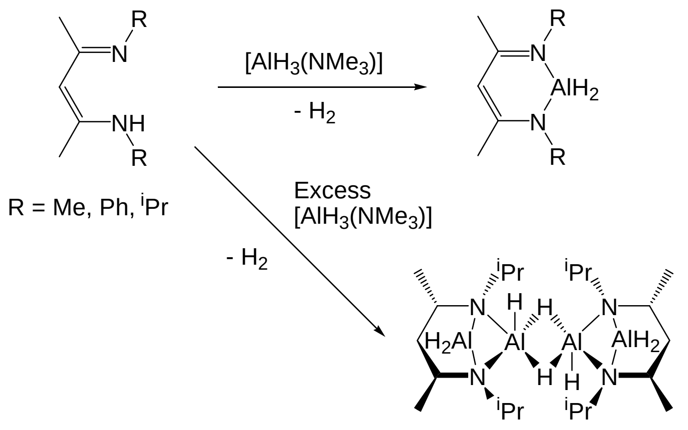
Scheme 12



4.3.2.3 Reactions of *β*-diketiminates with group 13 hydrides

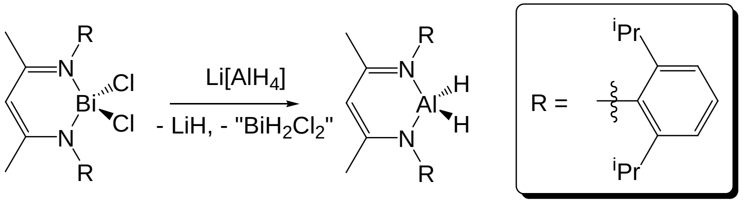
Several *β*-diketiminate supported group 13 hydride species have been prepared in recent years. The first report in 2000 by Kuhn *et al*. of a *β*-diketiminate supported aluminium hydride species was from the reaction of $[AlH_3(NMe_3)]$ with $H\{N(R)C(Me)\}_2CH$, where R = Me and Ph, ^{i}Pr. In the case of the isopropyl substituted ligand, an excess of the hydride reagent resulted in an unusual dinuclear compound via imine reduction (Scheme 13).[257]

Scheme 13



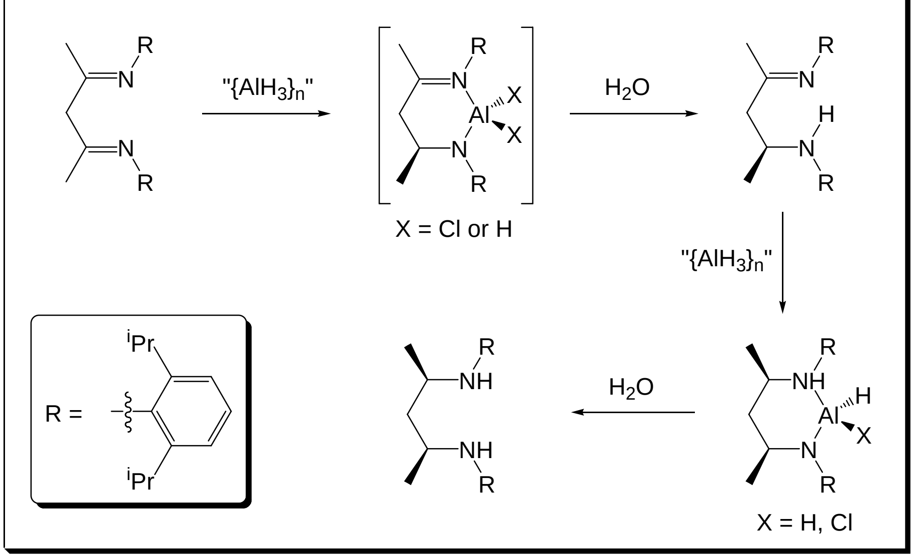
In 2001 Power reported the crystallographic study of an aluminium *β*-diketiminate dihydride species, prepared by ligand transmetallation from [$BiCl_2\{N(Dipp)C(Me)\}_2CH$] to Li[$AlH_4$] (Scheme 14).[258]

Scheme 14



This structural study was followed up by a report that focussed on the reduction of the same *β*-diketimines to 1,3-diamines by group 13 hydrides[259] (*cf*. Kuhn syntheses above). Despite the failure of Lewis base adducts of alane to reduce $H\{N(Dipp)C(Me)\}_2CH$,[259] the addition of *in situ* prepared polymeric alane to this ligand resulted in reduction of a single imine. Partial reduction was accomplished by addition of an equivalent of *in situ* prepared alane. Further addition resulted in the isolation of two interesting species as intermediates in the second reduction; a mixture of a dihydro- and a chlorohydroalumino complexes of the singly-reduced 1,3-diketimine (Scheme 15).[259]

Scheme 15



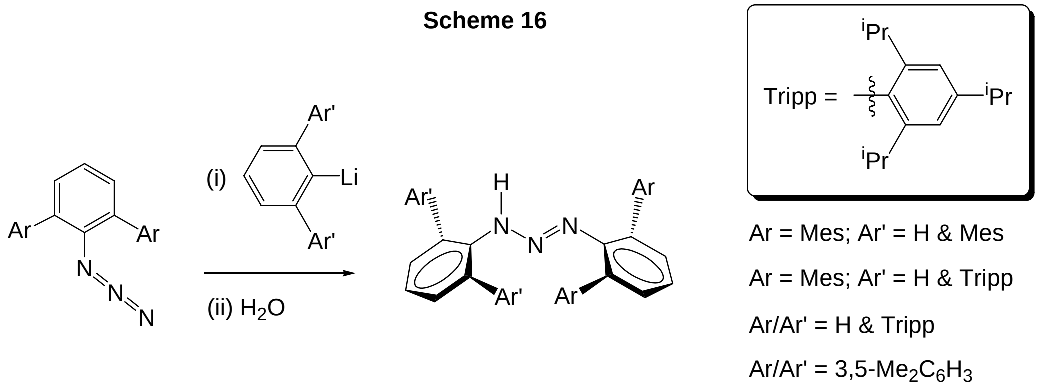
In the context of the present research, despite the success of 2,6-terphenyls as ligands in low valent group 13 chemistry, there are no reported amidinate or *β*-diketiminate ligands bearing terphenyl groups at nitrogen that could be used to marry the kinetic stabilising effects of 2,6-terphenyl substituents and amidinate-type ligands. Accordingly, the impact of these hugely influential groups on these ligand frameworks and group 13 hydrides remains unknown. The provision of Niemeyer's triazenes and the aptitude of such ligands to stabilise low valent stabilisation indicates that the application of related ligands to group 13 hydrides may be fruitful.

4.4 Triazenides in group 13 chemistry

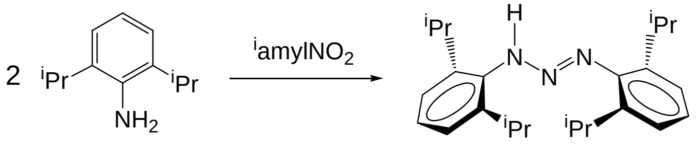
4.4.1 Preparation of triazenes

As highlighted by Niemeyer and co-workers,[225, 260] a somewhat less studied subclass of anionic dinitrogen ligands capable of chelation is the triazenide family of ligands. The pursuit of the coordination chemistry of triazenides appears to have been hampered by a lack of scalable methods for their preparation and the perceived dangers of handling organic azide compounds. Indeed, Sharpless *et al.* refer to this partly unfounded perception as "azidophobia".[261] To overcome these drawbacks, Niemeyer[262-264] and Gibson[265] have recently reported large scale syntheses of 1,3-bis(aryl)triazenides as described in Schemes 16 and 17 respectively.

Scheme 16

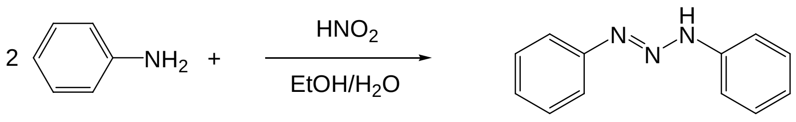


Scheme 17

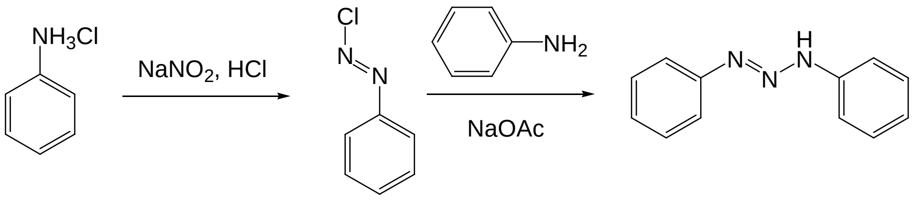


This chemistry is underpinned by work on azaheterocycles and azides that stretches back almost 150 years. According to Moore and Robinson,[266] the first recorded example of a biaryl triazene appeared in 1859,[267] however the true structure of the species was not reported at that time. In 1866, 1,3-diphenyltriazene was prepared by a one-pot synthesis using aniline and nitrous acid (Scheme 18).[268] This compound was synthesised by virtually the same method in 1943 by Hartmann and Dickey, however prior to synthesis, the authors prepared the intermediate *N*-chlorobenzenamine separately from 2-chloro-1-phenyldiazine and sodium nitrite in the presence of hydrochloric acid (Scheme 19).[269]

Scheme 18



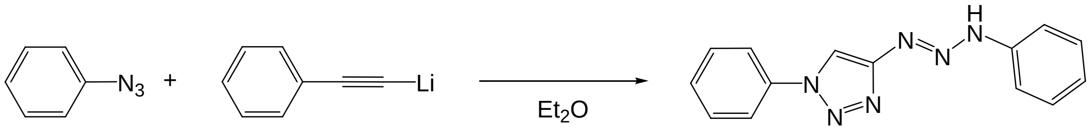
Scheme 19



This type of reaction, where a diazonium salt and aniline are combined to prepare an "N_3" compound has been used successfully over the years to prepare intermediates in heterocyclic synthesis, and it provides the basis for the Sandmeyer reaction used by Gibson.[270-274]

With regard to Niemeyer's triazene preparation, Akimova and co-workers prepared a triazole-substituted triazene species in 1968 by reaction of phenyl azide with a lithium acetylide.[275] This reaction, which incorporates an early example of the now ubiquitous Huisgen azide-alkyne 1,3-dipolar cycloaddition,[276] yields a triazenide by addition of a 1,2,3-triazolyllithium across an aryl azide, followed by quenching to yield the neutral triazene (Scheme 20).

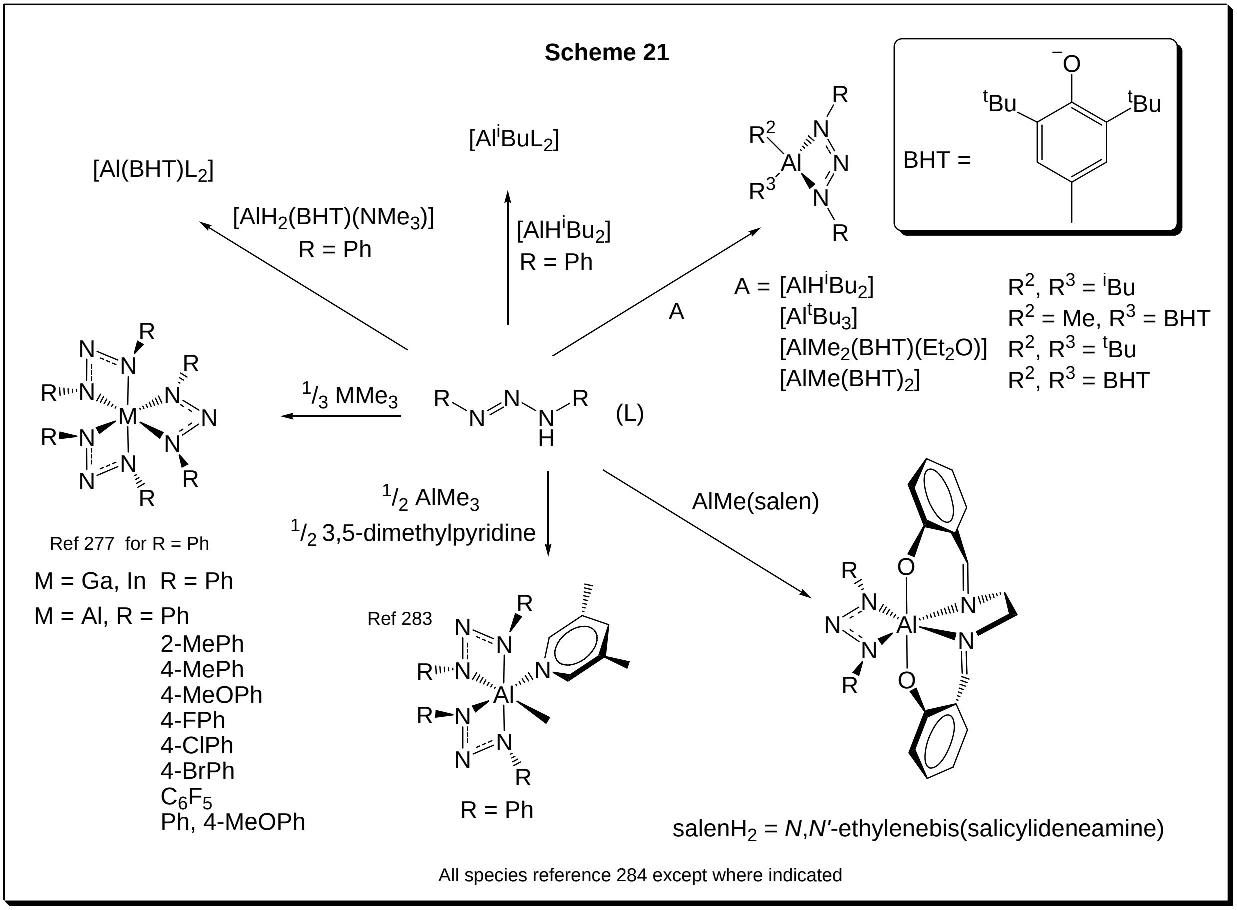
Scheme 20



4.4.2 Group 13 triazenide complexes

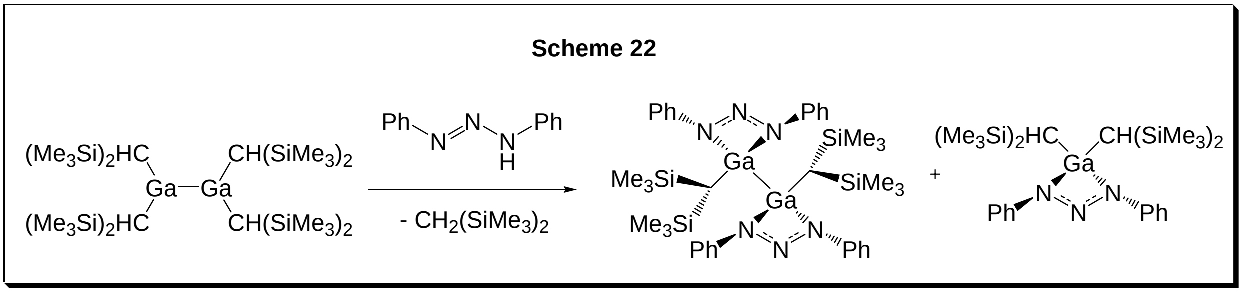
The coordination chemistry of 1,3-bis(aryl)triazenes began well over a century ago.[277-279] However, it was not until 1979 that the first group 13 triazenide was reported. This report, from the group of Deacon, detailed the preparations of the thallic homoleptic compounds [Tl(dpt)$_3$] (Hdpt = 1,3-diphenyltriazene) and [Tl(ppt)$_3$] (Hppt = 1-phenyl-3-(2′-pyridyl)triazene), both characterised by spectroscopic methods.[280] In 1986, dimeric [Tl(dpt)]$_2$ was structurally characterised by Beck and Straehle,[281] followed by the work of Barron who reported [Al(dpt)$_3$], [Ga(dpt)$_3$] and [In(dpt)$_3$] by methane elimination from the respective group 13 trimethyl reagent reacted with the neutral triazene.[282] Further reports by Barron detailed the first monomeric octahedral aluminium alkyl, [AlMe(PhNNNPh)$_2$(3,5-Me$_2$py)] (py = pyridine),[283] followed by a plethora[284] of 1,3-diaryltriazenido aluminium compounds. Barron's contribution to this area is summarised in Scheme 21. In 1997, Uhl and co-workers utilised a gallium(II) precursor to prepare two triazenide complexes, one containing Ga(II) and the other Ga(III) (Scheme 22).[285]

Scheme 21



All species reference 284 except where indicated

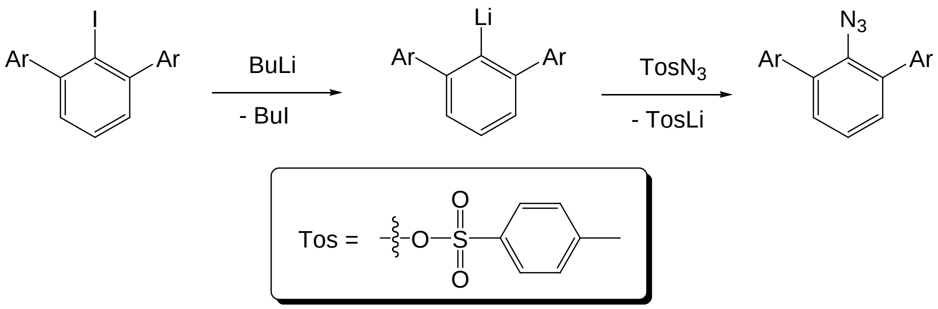
Scheme 22



4.4.3 Synthetic routes to terphenyl triazenide precursors

As outlined in Schemes 16 and 20, an efficient and scalable method for producing bi(aryl)triazenes is the reaction of an aryl azide with an aryllithium species, followed by protonation. Aryl azides can be prepared by reacting tosyl azide with a lithiated aryl species, which are in turn conveniently prepared by addition of *n*-butyllithium to aryl bromides or iodides at low temperature (Scheme 23).

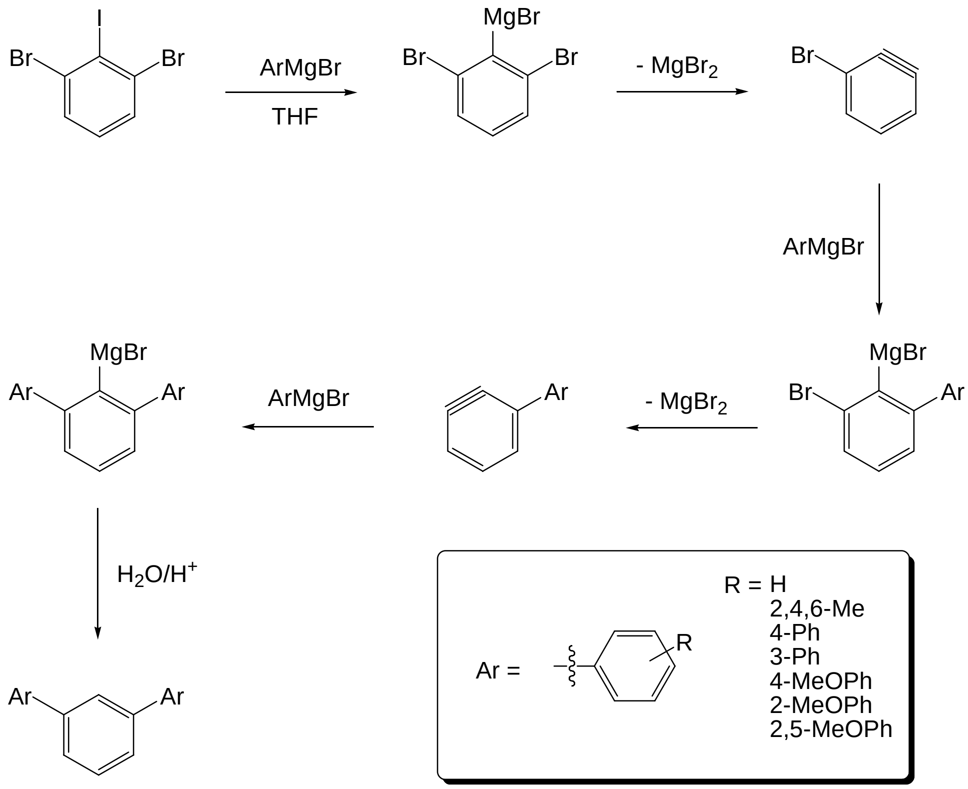
Scheme 23



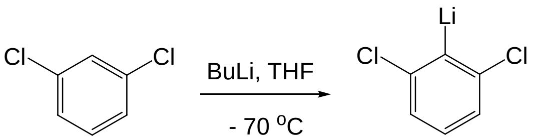
2,6-Terphenyl iodides may be prepared by a variety of methods, [286-288] however the literature benchmark for scalable syntheses is underpinned by the chemistry outlined in Scheme 24. Based on earlier reports[289, 290] of carbon-carbon bond formation by the preparation and capture of benzynes using Grignard reagents, the group of Hart reported the preparation of *m*-terphenyls using a 1,2,3-trihalobenzene and excess Grignard reagent.[291] The authors proposed that reaction of the trihalobenzene with the first equivalent of Grignard reagent generates a bromoaryne species via a metallated intermediate and subsequent loss of magnesium bromide. Further reaction with the Grignard via a similar process would afford firstly an aryl-substituted aryne, followed by a metallated 1,3-arylbenzene species. Quenching of the latter with dilute aqueous acid afforded the protonated product (Scheme 24).

Further to this, in 1988 Kress and Leanna observed that 2,6-dichlorophenyllithium could be prepared by regioselective lithiation of 1,3-dichlorobenzene using *n*-butyllithium at – 70°C in THF (Scheme 25).[286] In a later report, Saednya and Hart observed that such solutions could be reacted with aryl Grignard reagents at room temperature or reflux and quenched with iodine to yield iodo-*m*-terphenyls in good to high yields. The use of three equivalents of the Grignard reagent improved yields by 15-20%, perhaps indicating a greater reactivity to arylmagnesium species.[287] An alternative approach to these syntheses is to use excess (3-5 equivalents) of the Grignard reacted directly with 1,3-dichlorobenzene in diethyl ether, followed by an iodine quench (Scheme 26).[287] This synthesis of terphenyl iodides was used by Smith and Protasiewicz during their study of phospha-PPVs (PPV = poly(*para*-phenylenevinylene)) for use in polymeric systems.[288]

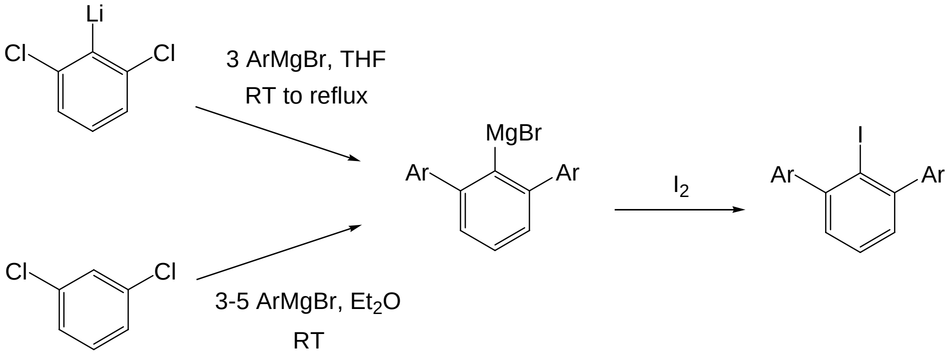
Scheme 24



Scheme 25



Scheme 26



4.5 Research proposal

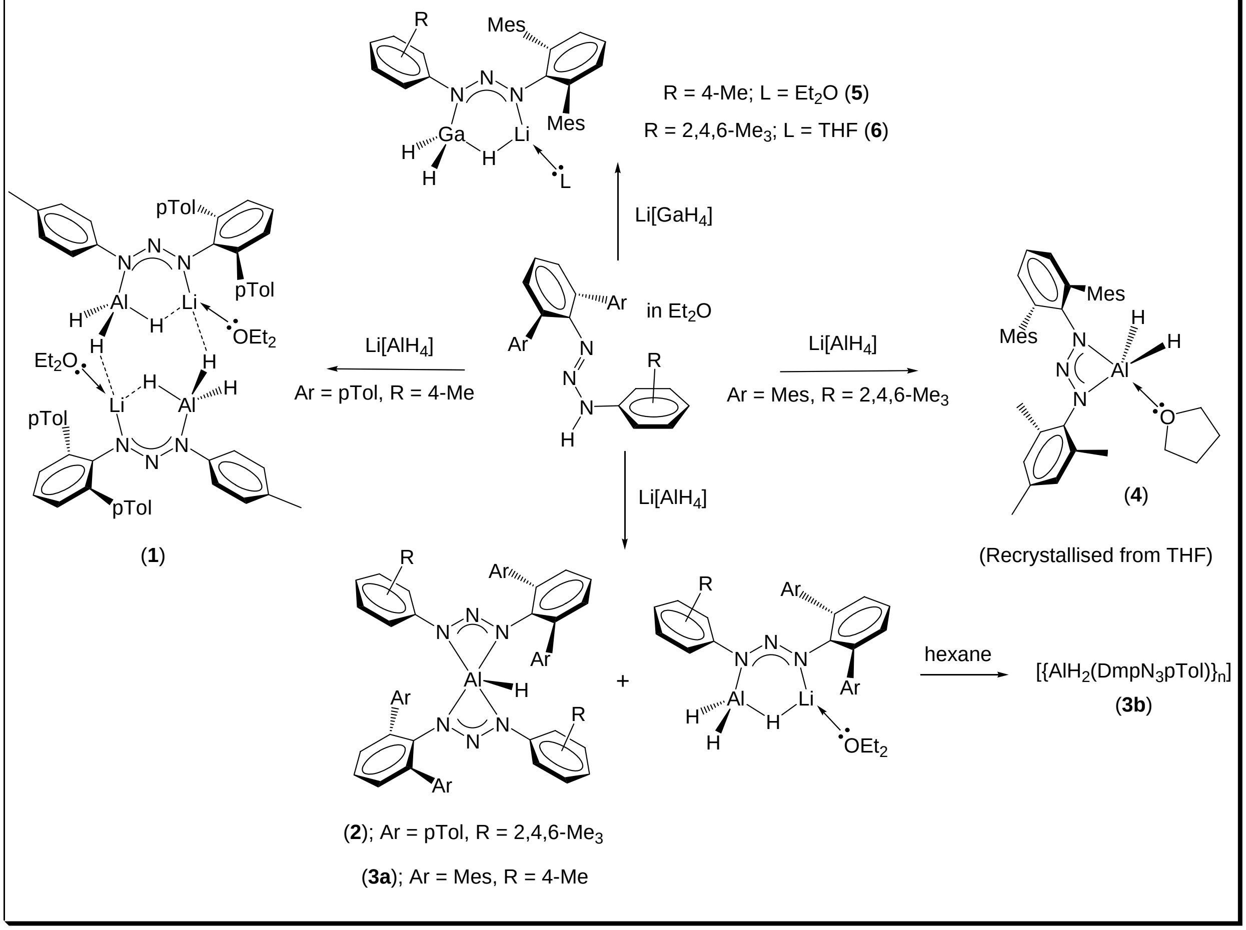
This chapter will expand on the known 2,6-terphenyl substituted triazenes and utilise them in the stabilisation of aluminium and gallium hydride species. The electronic properties of triazenides lend themselves to the stabilisation of group 13 metals, including low valent and hydride variants.[5] In the event of successful syntheses, the stability of these compounds will be investigated. To achieve these objectives, triazenes will be prepared using existing methods. In view of the aforementioned work of Niemeyer,[225] the steric properties of these ligands will also be explored further.

4.6 Results and Discussion

4.6.1 Preparation of 1-terphenyl substituted 1,3-bis(aryl)triazenes

As discussed in Section 4.4, Niemeyer and co-workers reported the large-scale preparations of several 1-terphenyl,3-biphenyltriazenes[225] and 1,3-bis(bi/terphenyl)triazenes[262] by reaction of lithiated biphenyls or a *m*-terphenyl with bi/terphenylazides followed by hydrolysis. Utilising an analogous synthetic route, several terphenyl substituted triazenes were prepared. These incorporate the terphenyl substituents Ditop (2,6-di-*p*-tolylphenyl) or Dmp (2,6-dimesitylphenyl) at one nitrogen terminus and either *para*-tolyl (pTol) or mesityl (2,4,6-$Me_3C_6H_2$; Mes) at the other (Scheme 27).

Scheme 27



All four ligand precursors have been fully characterised by infrared and NMR spectroscopies, C, H, N elemental analyses and, in the case of $DmpN_3(H)Mes$, single crystal X-ray structure determination. All four triazenes exhibit a sharp N-H stretch at *ca.* 3300-3400 cm^{-1} and strong absorptions in the NNN stretch region of the spectrum (1400-1200 cm^{-1}). For the smallest of the triazenes in this chapter, $DitopN_3(H)pTol$, several N-N stretching absorptions are observed in the region 1307-1153 cm^{-1}, while for the larger triazenes DitopN_3(H)Mes, DmpN_3(H)pTol and DmpN_3(H)Mes a single prominent strong absorption is observed at 1435, 1471 and 1457 cm^{-1} respectively. This suggests that DitopN_3(H)pTol may possess a solid-state structure different to the bulkier compounds in this chapter. In solution, all four triazenes exist as single well defined isomers, as evidenced by singular aryl environments (both terphenyl and monoaryl) in their ^{1}H and {^{1}H}^{13}C NMR spectra and a single N-H resonance at 9.18, 8.79, 9.03 and 8.43 ppm respectively. This contrasts the fluxional behaviour of DippN_3HDipp, which exists as a 7:1 ratio of isomers in solution.[265] Crystalline samples of DmpN_3(H)Mes suitable for single crystal X-ray structure determination were forthcoming during purification by recrystallisation and the molecular structure of this triazene (POV-RAY illustration, 50% thermal ellipsoids) is depicted in Figure 4.

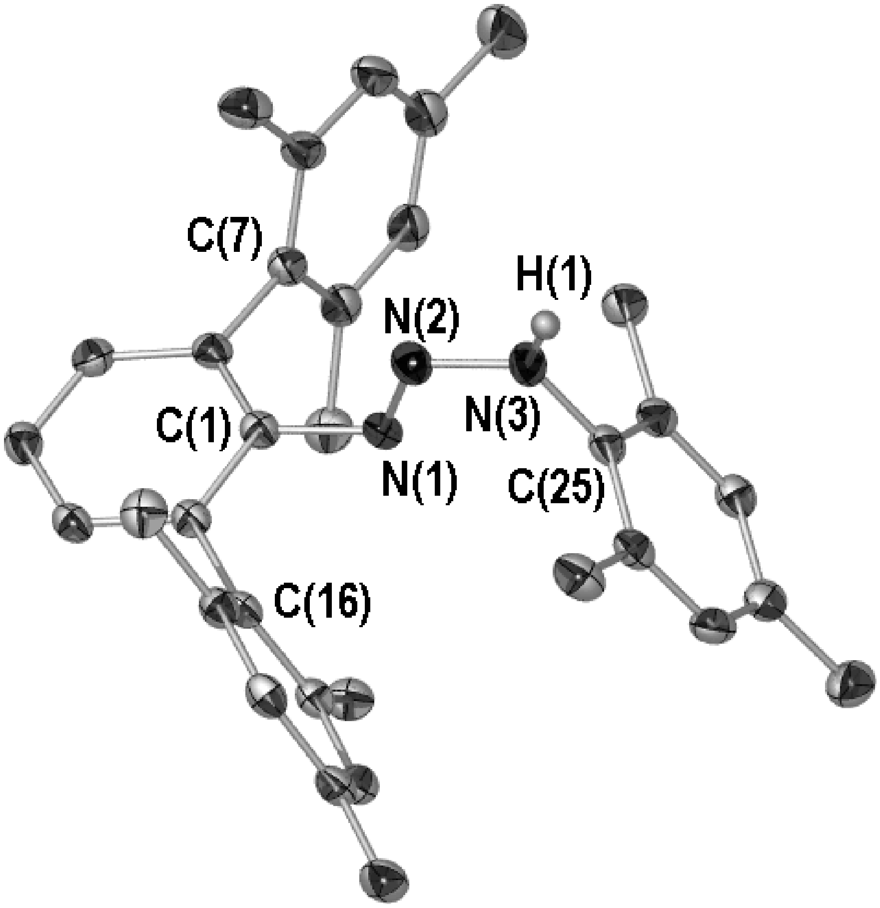


Figure 4. Molecular structure of the triazene DmpN_3(H)Mes. All hydrogen atoms excepting H(1) omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)-N(2) 1.256(2), N(2)-N(3) 1.355(3), C(1)-N(1)-N(2) 112.49(17), N(1)-N(2)-N(3) 113.35(18), N(2)-N(3)-C(25) 123.18(19).

As per the 1,3-bis(terphenyl)triazene 1,3-bis{2,6-(3,5-$Me_2C_6H_3)_2C_6H_5\}_2N_3H$,[264] DmpN$_3$(H)Mes exists as an *E-syn* isomer[292] in the solid state. The similar IR spectra of DitopN$_3$(H)Mes and DmpN$_3$(H)pTol suggest these triazenes may also adopt the same isomeric form in the solid state. The bond lengths and angles of DmpN$_3$(H)Mes are representative of discrete N-N single and double bonds across the triazene backbone (1.355(3) and 1.256(2) Å respectively), while the N-N=N angle of 113.35(18)° is greater than the mean average of 1,3-disubstituted triazenes structurally characterised (112.0°)[161] which, with the exception of the aforementioned 1,3-bis(terphenyl)triazene,[263, 264] exist as *E*-anti isomers in the solid state.[292] Furthermore, as per 1,3-bis{2,6-(3,5-$Me_2C_6H_3)_2C_6H_5\}_2N_3H$,[264] the steric crowding of DmpN$_3$(H)Mes manifests as perpendicular placement of the central 'terphenyl' aryl plane to the N$_3$ plane (torsion angle 85.6(1)°) and distortion of the trigonal pyramidal *sp*^{3} nitrogen such that the mesityl ring *ipso*-carbon sits markedly out of the N$_3$ plane (0.16(1) Å).

4.6.2 1:1 Reaction of triazenes with Li[AlH$_4$]

As described in Section 4.4, Jones and co-workers have recently prepared several *N,N'*-bis(2,6-diisopropylphenyl) amidinate ([DippNC(R)NDipp]$^-$, Dipp = 2,6-diisopropylphenyl, R = H or ^{t}Bu) complexes of aluminium, gallium and indium hydrides.[246, 247] These compounds exhibit a number of structural types and nuclearities that are consistent with the spatial requirements and bonding characteristics of the formamidinate (FIso; R = H) or pivamidinate (PIso; R = ^{t}Bu) anion used.

The smallest of the prepared triazenes, DitopN$_3$(H)pTol, was added as a dilute solution to cooled (–78 °C) Li[AlH$_4$] in diethyl ether in a 1:1 stoichiometry (Scheme 27). Gradual warming of the reaction mixture afforded a bright yellow solution that was subsequently evacuated to dryness to afford a crude aluminohydride complex (**1**) that exhibits Al-H infrared absorption bands at 1853 and 1746 cm^{-1}. The number and intensity of such absorptions are highly diagnostic of the coordination environment and symmetry at the metal centre; this includes identification of bridging and terminal M-H bonds.[247]

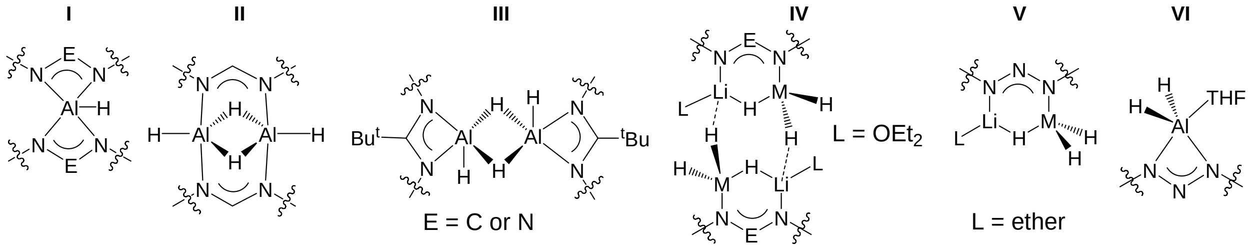
Table 1 provides a detailed overview of the known group 13 hydride complexes supported by amidinate ligands, their structure types (see key to table), melting/decomposition points and respective metal-hydride stretching frequencies. It also incorporates relevant data for the complexes in this chapter. The presence of two Al-H infrared stretching absorptions for crude **1** contrasts the single absorption of the pivamidinate complex $[\{AlH(PIso)(\mu\text{-}H)\}_2]$[247] (1845 cm^{-1}, structure type **III** Table 1) and the two close energy stretches of $[\{AlH(\mu\text{-}FIso)(\mu\text{-}H)\}_2]$[247] (1868 and 1835 cm^{-1}, structure type **II** Table 1) however, they are reminiscent of the Al-H stretching modes of structure type **IV** 'LiH' complex $[\{Li(OEt_2)(\mu\text{-}H)(\mu\text{-}FIso)AlH(\mu\text{-}H)\}_2]$[247] ($\tilde{\nu}_{Al\text{-}H}$ 1821 and 1756 cm^{-1}, Table 1) prepared by reacting *N,N'*-bis(2,6-diisopropylphenyl)formamidine (HFIso) with one equivalent of $Li[AlH_4]$ in diethyl ether. As well as being consistent with structure type **IV**, the relative terminal and bridging Al-H stretching frequencies of **1**, which are increased and decreased respectively relative to those of $[\{Li(OEt_2)(\mu\text{-}H)(\mu\text{-}FIso)AlH(\mu\text{-}H)\}_2]$, suggest reduced donation of the triazenide $DitopN_3pTol$ relative to the formamidinate FIso.[225, 260]

Compound **1** was purified by recrystallisation from hexane to afford analytically pure $[LiAlH_3(DitopN_3pTol)(Et_2O)]$. Attempts to acquire samples suitable for single crystal X-ray structure determination met with repeated failure, however, the ^1H NMR spectrum of **1** (C_6D_6) exhibits the expected resonances attributable to diethyl ether and three singlets that integrate in a 1:1:1 ratio for the *para*-methyl groups of the $DitopN_3pTol$ ligand. This is consistent with an unsymmetrical Ditop environment, wherein the 2,6-*p*-tolyl rings possess distinct chemical environments on an NMR timescale, and is consistent with structure type **IV** (Table 1). No ^1H NMR resonances for the hydride ligands of **1** were observed. This may be attributed to the likely low symmetry coordination environment of the aluminohydride functionality in **1** in tandem with the aluminium quadrupole.

Analogous reactions of $DitopN_3(H)Mes$, $DmpN_3(H)pTol$ and $DmpN_3(H)Mes$ with $Li[AlH_4]$ in a 1:1 ratio were undertaken using similar reaction conditions to **1** (Scheme 27). However, unlike **1**, it was noted that the IR spectra of the crude reaction mixtures were consistent with the presence of two or more Al-H containing species ($DitopN_3Mes$ (**2**) and $DmpN_3pTol$ (**3**)) or a differing but singular coordination environment to **1** ($DmpN_3Mes$ (**4**)). Recrystallisation of crude reaction mixtures **2-4** from diethyl ether (**2** and **3**) or THF (**4**) afforded crystalline samples that were suitable for single crystal X-ray structure determination (Figures 5-7; POV-RAY illustration, 40 % thermal ellipsoids). No attempt was made to internationally prepare the 2:1 complexes. Table

2 contains a summary of crystal measurement and refinement data for all compounds studied by single crystal X-ray diffraction in this chapter.

Table 1. Overview of the known group 13 hydride complexes supported by amidinate ligands and the complexes in this chapter. See key for ‘structure-type’ information.



Compound	IR ***v*** M-H (term.) (cm^{-1})	IR ***v*** M-H (bridg.) (cm^{-1})	m.p. (°C)	Structure
$[\{Li(OEt_2)AlH_3(FIso)\}_2]$[247]	1821 sharp s	1756 broad s	126-127	IV
$[AlH(FIso)_2]$[247]	1823 sharp s	-	231-233 (dec.)	I
$[\{AlH_2(FIso)\}_2]$[247]	1868	1835	205-207 (dec.)	II
$[\{AlH_2(PIso)\}_2]$[247]	1845 s	-	190-191 (no dec. <300)	III
$[\{Li(OEt_2)AlH_3(DitopN_3pTol)\}_2]$ (1)	1853 broad m	1746 broad m	118-122 (dec. 165)	IV^{a}
$[AlH(DitopN_3Mes)_2]$ (2)	1889 sharp s	-	258 (dec.)	I
$[Li(OEt_2)AlH_3(DmpN_3pTol)\}_n]$ (3a)	1806 s, 1777 s	1668 s	125-128	V^{a}
$[AlH(DmpN_3pTol)_2]$ (3b)	1893 sharp s	-	153-157 (dec. 170)	I
$[AlH_2(DmpN_3Mes)(THF)]$ (4)	1820 sh s, 1804 sharp s	-	125	VI
$[AlH(\mathit{i}PrNC(NMe_2)N\mathit{i}Pr)_2]$[293]	not given	-	61	I
$[AlH\{C(Ph)(NSiMe_3)_2\}_2]$[244]	1773	-	not given	I
$[\{Li(OEt_2)GaH_3(FIso)\}_2]$[246]	1879 sharp s	1769 broad s	84-86	V
$[GaH(FIso)_2]$[247]	1911 sharp s		211-213 (dec.)	I
$[Li(OEt_2)GaH_3(DmpN_3pTol)]$ (5)	1910 s, 1859 s	1719 s	106 (182 dec.)	V
$[Li(THF)GaH_3(DmpN_3Mes)]$ (6)	1917 s, 1842 s	1724 s	125	V

a) Suggested on the basis of infrared data (see selected references[246, 247] and data for compounds **5** and **6**).

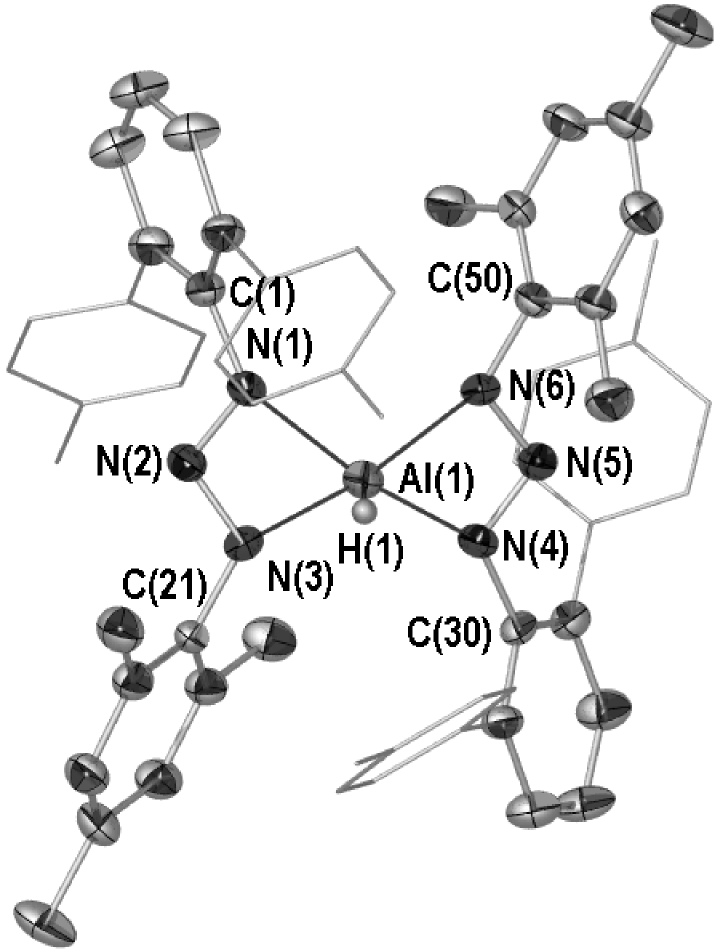


Figure 5. Molecular structure of **2**. All hydrogen atoms excepting hydride ligand H(1) omitted and 2,6-para-tolyl rings depicted as wire frames for clarity. Selected bond lengths (Å) and angles (º): Al(1)-H(1) 1.60, Al(1)-N(1) 1.987(4), Al(1)-N(3) 1.990(4), Al(1)-N(4) 1.996(4), Al(1)-N(6) 1.981(4), N(1)-N(2) 1.316(4), N(2)-N(3) 1.303(4), N(4)-N(5) 1.318(4), N(5)-N(6) 1.311(4), N(1)-Al(1)-N(3) 63.42(15), N(4)-Al(1)-N(6) 63.93(15), N(1)-N(2)-N(3) 105.9(4), N(4)-N(5)-N(6) 106.4(4).

Table 2. Summary of crystallographic data for compounds characterised by X-ray structure determination.

	DmpN$_3$(H)Mes (1)	[AlH(DitopN$_3$Mes)$_2$] (2)	[AlH(DmpN$_3$pTol)$_2$] (3b)	[AlH2(DmpN$_3$Mes)(THF)] (4)	[Li(THF)(μ-H)(μ-DmpN$_3$Mes)GaH$_2$] (6)
Mol. Formula	$C_{33}H_{37}N_3$	$C_{58}H_{57}AlN_6$	$C_{62}H_{65}AlN_6$	$C_{37}H_{46}AlN_3O$	$C_{37}H_{47}GaLiN_3O$
Mol. Weight	475.66	865.08	460.59	575.75	626.44
Temperature (K)	123(2)	223(2)	123(2)	123(2)	123(2)
Space Group	$P2_1/c$	*P-1*	*P-4*	$P2_1/n$	*P-1*
a, Å	11.5637(3)	11.8179(5)	15.1771(11)	12.1434(5)	8.6815(3)
b, Å	16.0951(4)	11.8232(4)	15.1771(11)	22.3094(10)	12.2606(4)
c, Å	14.7471(4)	20.7647(12)	11.6305(7)	12.2121(6)	17.0034(6)
α, deg	90	98.803(2)	90	90	71.8560(10)
β, deg	94.6210(10)	99.288(2)	90	94.860(2)	84.2670(10)
γ, deg	90	116.586(3)	90	90	85.6960(10)
Volume, Å^3	2735.79(12)	2475.7(2)	2679.0(3)	3296.5(3)	1709.41(10)
Z	4	2	4	4	2
D$_c$, g cm^{-3}	1.155	1.160	1.142	1.160	1.217
μ, mm^{-1}	0.067	0.085	0.082	0.094	0.836
Reflections collected	17849	18948	20930	25717	28145
Unique reflections	7533	11489	7151	9228	9855
Parameters varied	473	600	321	396	409
R(int)	0.0893	0.1060	0.0658	0.0459	0.0282
R$_1$	0.0703	0.0922	0.0621	0.0895	0.0442
wR$_2$ (all data)	0.2184	0.2704	0.1346	0.1575	0.1196

Despite the 1:1 Li[AlH_4]:triazene stoichiometries employed during the preparation of **2** and **3**, the 1:2 Al:triazenide complexes [AlH($DitopN_3Mes$)$_2$] (**2**) and [AlH($DmpN_3pTol$)$_2$] (**3b**) were isolated after recrystallisation from diethyl ether in low yield (20% and 29% respectively). The molecular structures of these compounds (Figures 5 and 6) indicate a 5-coordinate square-based pyramidal aluminium coordination environment with an apical terminal hydride ligand. The Al coordination of **3b** may also be related to a trigonal bipyramid with the $N_{terphenyl}$ donor atoms at the apical positions (trans N-Al-N angles **2**; 136.68(18) and 142.81(19)º, **3b**; 154.89(11) and 112.99(12)º).

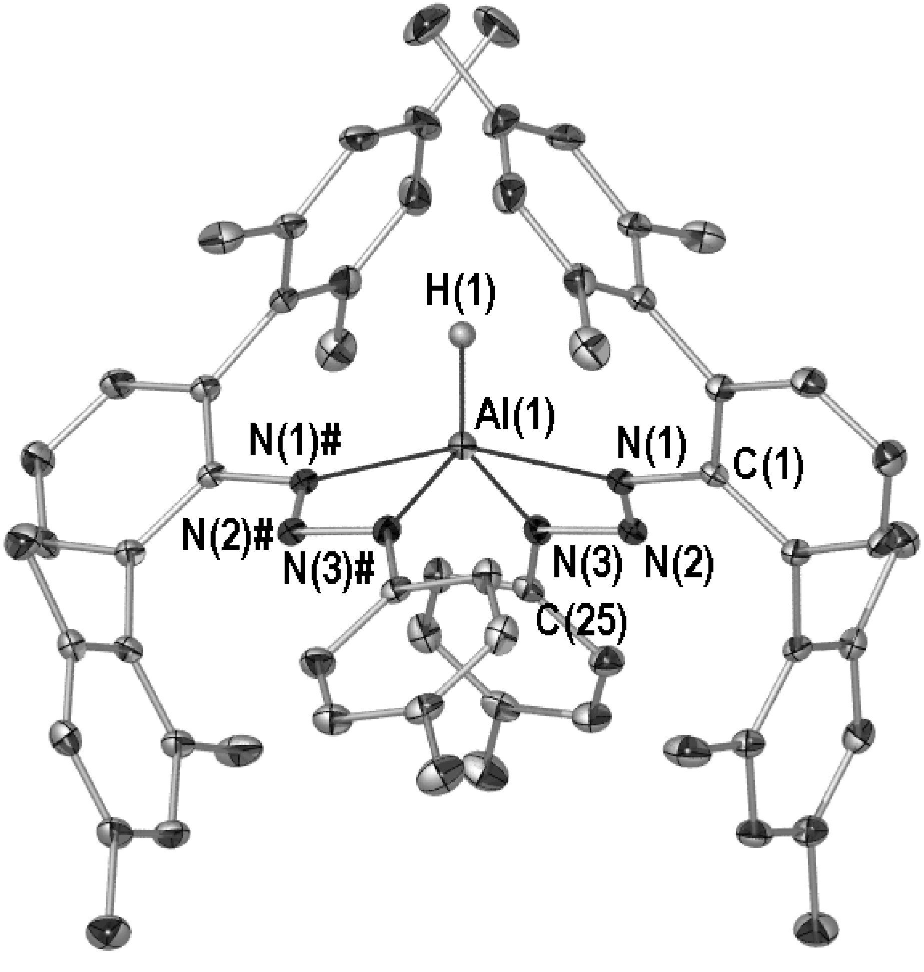


Figure 6. Molecular structure of **3b**. All hydrogen atoms excepting hydride ligand H(1) omitted for clarity. #' Atoms generated using the symmetry transformation 1-x, 2-y, z. Selected bond lengths (Å) and angles (º): Al(1)-H(1) 1.45, Al(1)-N(1) 2.0807(19), Al(1)-N(3) 1.920(2), Al(1)-N(1)# 2.0807(19), Al(1)-N(3)# 1.920(2), N(1)-N(2) 1.311(3), N(2)-N(3) 1.327(3), N(1)#-N(2)# 1.311(3), N(2)#-N(3)# 1.327(3), N(1)-Al(1)-N(3) 63.65(8), N(1)#-Al(1)-N(3)# 63.65(8), N(1)-N(2)-N(3) 106.48(17), N(1)#-N(2)#-N(3)# 106.48(17).

These coordination types (**I**, Table 1) are consistent with that exhibited by [AlH(FIso)$_2$],[247] [AlH{^{i}PrNC(NMe_2)N^{i}Pr}$_2$][293] and [AlH{$Me_3SiNC(Ph)NSiMe_3$}$_2$],[244] as are the single sharp Al-H infrared stretching absorptions of **2** and **3b** (1889 and 1893 cm^{-1}), which are placed at higher frequency relative to those of [AlH(FIso)$_2$] (1823 cm^{-1})[247] and [AlH{^{i}PrNC(NMe$_2$)N^{i}Pr}$_2$] (1773 cm^{-1}),[293] thereby demonstrating the reduced donor character of triazenide ligands relative to amidinates (see above).[225, 260]

Contrary to the isolation of bis(triazenide) complexes **2** and **3b**, recrystallisation of **4** from THF affords the THF-coordinated mono(trazenido)aluminodihydride [AlH$_2$(DmpN$_3$Mes)(THF)] (**4**) in moderate yield (43%). Like **2** and **3b** but unlike **1** compound **4** does not include lithium hydride. Its coordination environment (Figure 7) is similarly five-coordinate but, rather than square-based pyramidal, is better described as a distorted trigonal bipyramid with the terphenyl nitrogen and THF ligands occupying the apical positions. It should be noted that the monomeric composition of THF complex **4** contrasts the dimeric nature of [{AlH$_2$(FIso)}$_2$] and [{AlH$_2$(PIso)}$_2$] (Table 1, structure types **II** and **III** respectively) reported by Jones and co-workers.[247]

The hydride ligands of **2**, **3b** and **4** (Figures 5-7) were located from difference maps and refined isotropically. The asymmetric units of compounds **2** and **4** contain a single molecular unit, while that of **3b** comprises half a molecular unit with the remaining half generated by a two-fold rotation about the Al-H bond vector *cf.* Table 2. The AlN$_3$ metallocycles of the three compounds possess N-N bond lengths that indicate delocalisation of charge across the anionic donor (N-N **2**; 1.303(4)-1.318(4) Å, **3b**; 1.311(3) and 1.327(3) Å), **4**; 1.305(3) and 1.319(3) Å) and slight elongation of the Al-N$_{\text{terphenyl}}$ contact relative to its non-terphenyl counterpart in DmpN$_3$Ar (Ar = pTol and Mes respectively) complexes **3b** and **4** (**3b**; 2.0807(19) vs. 1.920(2) Å, **4**; 2.094(2) vs. 1.950(2) Å). A related elongation is not observed in **2**, wherein the Al-N bond lengths are approaching statistical equivalence (1.987(4)/1.990(4) vs. 1.996(4)/1.981(4) Å). The disparity in Al-N bonding between **2** and **3b**, i.e. Al-N 0.015(8) Å *versus* 0.161(4) Å, most likely results from the coplanarity of the *N-para*-tolyl substituents of the latter to the AlN$_3$ metallacyclic plane. This contrasts **2**, wherein the mesityl rings sit out of the AlN$_3$ plane. This observation may also explain the intense colouration of **3b**. The Al-N bond lengths of **2** and **3b** are expectedly longer overall relative to those of trigonal bipyramidal [AlH(FIso)$_2$] (equatorial Al-N 1.910(3)/1.927(3) vs. axial Al-N 2.071(3)/2.085(3) Å),[247] while the terminal Al-H bond lengths of **2** (1.60 Å), **3b** (1.45 Å) and **4** (1.52 and 1.53 Å) are in the range expected for terminal Al-H moieties.[19, 22, 165] Lastly, the N-N-N and N-Al-N angles of all three dinitrogen chelate complexes (**2**, **3b** and **4**) are remarkably consistent (**2**; 105.9(4) and 106.4(4), 63.42(15) and 63.93(15)°, **3b**; 106.48(17), 63.65(8)°, **4**; 106.54(18), 62.55(8)°) and, in the case of the former, the N-N-N angles sit between the mean average of angles reported by Barron and co-workers for four-[284] and six-coordinate[282-284, 294] 1,3-bis(aryl)triazenidoaluminium complexes (107.1 and 105.2° respectively; no reported five coordinate complexes). It is also noteworthy that, despite the significantly larger aryl groups in this chapter, the Al-N and N-N bonding contacts and N-Al-N angles within the present complexes differ minimally to those of Barron (mean average Al-N 1.99, N-N 1.32 Å, 63.9° respectively).[282-284, 294]

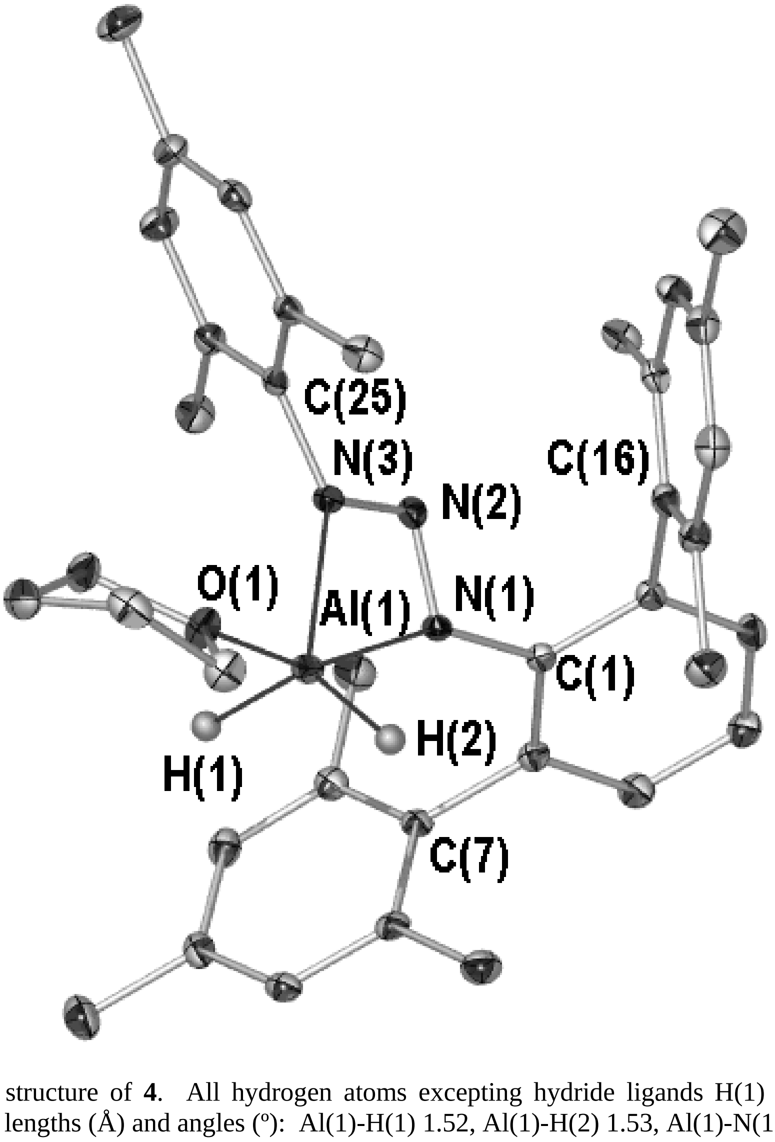


Figure 7. Molecular structure of **4**. All hydrogen atoms excepting hydride ligands H(1) and H(2) omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)-H(1) 1.52, Al(1)-H(2) 1.53, Al(1)-N(1) 2.094(2), Al(1)-N(3) 1.950(2), Al(1)-O(1) 2.0071(18), N(1)-N(2) 1.305(3), N(2)-N(3) 1.319(3), N(1)-Al(1)-N(3) 62.55(8), N(1)-N(2)-N(3) 106.54(18), O(1)-Al(1)-N(1) 153.32(8), O(1)-Al(1)-N(3) 92.74(8).

The solid-state stability of **2** is considerably greater than that of **3b** (dec. 258 Vs 170 ºC). These stabilities flank the reported decomposition temperature of [AlH(FIso)$_2$] (231-233 ºC)[247] which is, to our knowledge, the most stable amidoaluminohydride complex known. The contrasting stabilities of **2** and **3b** may be rationalised on the basis of the greater proximity of terphenyl methyl substituents to the Al-H moiety in **3b**, which may assist decomposition at high temperatures by H_2 elimination/alkylaluminium complex formation. A similar but less dramatic trend is evident for *N*-heterocyclic carbene (NHC) complexes[92, 121] of alane (AlH_3), wherein the complex [AlH_3(IMes)][131] (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) possesses a thermal stability of 257 ºC (see Chapter 2) (m.p. 246-247 ºC),[131] while the bulkier NHC complex [AlH_3(IDipp)][134] (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) decomposes at 229-234 ºC and the modestly sized NHC complex [AlH_3(I^{i}PrMe)] (I^{i}PrMe = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene) decomposes at 250 ºC.[132]

The ^{1}H NMR spectra of **2**, **3b** and **4** (C_6D_6) exhibit singular triazenide coordination environments with minimal broadening due to fluxional behaviour. Spectra of **2** and **3b** indicate distinct 2,6-aryl environments about the *N*-terphenyl group. The source of this can be seen clearly in Figures 5 and 6 in that one 2,6-aryl sits perpendicular to the primary aryl ring close to the Al-H moiety, while the other (also out of primary aryl plane) is directed below the ‘square-pyramidal’ N_4 base. The observation of these distinct chemical environments in solution suggests the solid-state structures may be maintained in solution. By contrast, despite the unique mesityl environments evidenced in the molecular structure of **4**, only one set of sharp singlet resonances attributable to the Dmp mesityl rings are observed at room temperature. This may indicate free rotation about the C-N$_{\text{terphenyl}}$ bond on an NMR timescale.

Closer inspection of the second product in crude reaction mixtures of **3**, as identified in infrared spectra of reaction mixtures *vide supra*, ruled out an analogous composition to **1**. Discounting the stretch of **3b**, the IR stretches observed ($\tilde{\nu}_{\text{Al-H}}$ 1806, 1777 and 1668 cm^{-1}) are consistent with the second product in reaction mixtures of **2** and monomeric gallium complexes prepared by reaction of the triazenes DmpN$_3$(H)pTol and DmpN$_3$(H)Mes with Li[GaH$_4$] *vide infra* (**V**, Table 1), *i.e.* [{Li(OEt$_2$)AlH$_3$(DmpN$_3$pTol)}$_n$]. However, recrystallisation of reaction mixtures of **3** from hexane (*cf.* **3b** recrystallised from diethyl ether) affords a microcrystalline powder of empirical formulation [{AlH$_2$(DmpN$_3$pTol)}$_n$]·nhexane (**3a**) by elemental analyses (28% yield, *cf.* **3b** isolated in 29% yield). This composition indicates loss of diethyl ether and lithium hydride upon recrystallisation from hexane relative to the crude product (*cf.* IR data, which contrasts the isolation of **1** after recrystallisation from the same solvent). This is borne out by the loss of Al–H stretches attributable to [{Li(OEt$_2$)AlH$_3$(DmpN$_3$pTol)}$_n$] (IR (Nujol): $\tilde{\nu}$ = 1806 (s), 1777 (s) (terminal Al–H), 1668 (bridging Al–H) cm^{-1}) in the infrared spectrum of **3a** ($\tilde{\nu}_{\text{Al-H}}$ = 1867 cm^{-1}). The single Al–H stretching absorption of **3a** is consistent with structure type **III** (Table 1). Moreover, the ^{1}H NMR spectrum of **3a** exhibits a resonance attributable to hydride ligands that integrates to two hydrogens relative to DmpN$_3$pTol, as per the sought 1:1 monotriazenide aluminium dihydride complex. Thus, despite the low temperature reaction conditions employed during the preparations of **2** and **3**, there appears to be limited selectivity for the reaction between 1:1 and 1:2 (Al:triazenide) product formation. As compounds **1** and **4** are the sole Al–H containing species observed in crude reaction mixtures for these reactions, one may conclude that the relative stoichiometries of the reactions herein are determined by the relative sizes of the triazenes employed.

4.6.3 1:1 Reaction of triazenes with Li[GaH$_4$]

The 1,3-bis(aryl)triazenide chemistry of gallium is relatively sparse compared to that of aluminium and, similarly, there are no reports of triazenide supported gallohydrides. Uhl and co-workers have reported a handful of 1,3-bis(aryl)triazenide gallium complexes prepared by the protolysis of 1,3-diphenyltriazene by alkylgalliums,[285, 295] however, as per the aluminium studies above, the studies of Jones and co-workers using the bulky amidinate 1,3-bis(diisopropylphenyl)formamidinate, or FIso,[246, 247] provide the best comparison for discussion of the bulky triazene studies herein.

The bulkiest triazenes, DmpN$_3$(H)pTol and DmpN$_3$(H)Mes, were reacted 1:1 with lithium tetrahydridogallate (using diethyl ether as solvent) at low temperature. In both cases, the reaction resulted in loss of H$_2$ at approximately –30 ºC and the formation of a bright yellow solution without precipitation. Removal of volatiles under reduced pressure gave the crude products, **5** and **6** respectively, that exhibit three prominent Ga-H stretches in their infrared spectra (*ca.* 1915, 1850 and 1720 cm^{-1}, *cf.* IR of **3a**). ^{1}H NMR spectra of crude **5** and **6** exhibit a single triazenide coordination environment and a single hydride resonance integrating to three hydrogens at *ca.* 4 ppm (see experimental section). Accordingly, both reaction mixtures were recrystallised from fresh ether (**5**; Et_2O, **6**; THF) to afford thermally robust gallohydrides (m.p. 106 and 125 ºC respectively) that analyse as [$LiGaH_3$(ether)($DmpN_3Ar$)] (**5**; Ar = pTol, **6**; Ar = Mes) by elemental microanalysis. This reaction outcome is empirically similar to the reaction of HFIso with Li[GaH_4] (1:1 stoichiometry) reported by Jones,[246] where a dimeric compound of analogous composition was obtained. However, the infrared spectra of **5** and **6**, which display three prominent bands (Table 1), differ substantially to the single bridging and terminal Ga-H stretches of [{Li(OEt_2)(μ-H)(μ-FIso)GaH(μ-H)}$_2$] (1769 and 1879 cm^{-1} respectively)[246] indicating a different structural composition in the present cases. Furthermore, the stretching absorptions observed for **5** and **6** are not similar to the single $\nu_{\text{Ga-H}}$ reported for four coordinate [GaH_2(FIso)(quinuclidine)] (1872 cm^{-1}) or five-coordinate [GaH$(FIso)_2$] (1911 cm^{-1}).[247]

Crystalline samples of compound **6** suitable for single crystal X-ray structure determination were forthcoming during recrystallisation from THF at -30 ºC. The molecular structure of **6** is illustrated in Figure 8 (POV-RAY illustration, 40% thermal ellipsoids), with salient data collection parameters compiled in Table 2. Compound **6**, and by extrapolation **5**, is a monomeric relative of structure type **IV** exhibited by its FIso relative[246] (**V** in Table 1), wherein the triazenide ligand bridges a lithium and gallium centre in conjunction with a single hydride. In the present case, the steric bulk of the terphenyl substituent, which is situated at the Ga-N terminus of the triazenide, frustrates dimer formation leading to the observed monomeric formulation. To our knowledge, compound **6** is the first triazenide bridged non-transition metal heterobimetallic complex structurally authenticated.[161]

The hydride ligands of **6** were located and refined isotropically providing Ga-H contacts of 1.50 and 1.62 Å (terminal) and 1.50 Å (bridging), and an Li-H contact of 1.94 Å. These compare well to those of [{Li(OEt_2)(μ-H)(μ-FIso)GaH(μ-H)}$_2$] (terminal 1.48 Å, Li-Ga bridging 1.54 and 1.51 Å).[246] Relative to the chelating $DmpN_3Mes$ ligand of **4**, the N-N-N angle of **6** is expectedly obtuse 115.29(13)º (**4**; 106.54(18)º) and, despite the heterobimetallic coordination, the N-N bond lengths are similar (1.3045(18) and 1.3010(18) Å). These values compare well to those of the triazenide bridged digallium complex [Ga_2{CH$(SiMe_3)_2$}$_2$(μ-O_2CCH_3)(μ-PhN_3Ph)] of Uhl (1.297(3) and 1.304(3) Å),[295] while the Ga-N contact of **6** (1.9855(14) Å) is somewhat shorter than this diligand bridged digallium species (2.064(2) and 2.060(2) Å). Lastly, one Dmp mesityl group of **6** exhibits Li-C_{aryl} distances (Li(1)-C(7) 2.499(4), Li(1)-C(8) 2.580(4) Å) that are within those accepted for Li-π-aryl contacts.[296] Similar M-π-aryl contacts have been observed in several triazenide complexes (M = *s*-block or divalent lanthanide) from Niemeyer and co-workers.[225, 260, 262, 263]

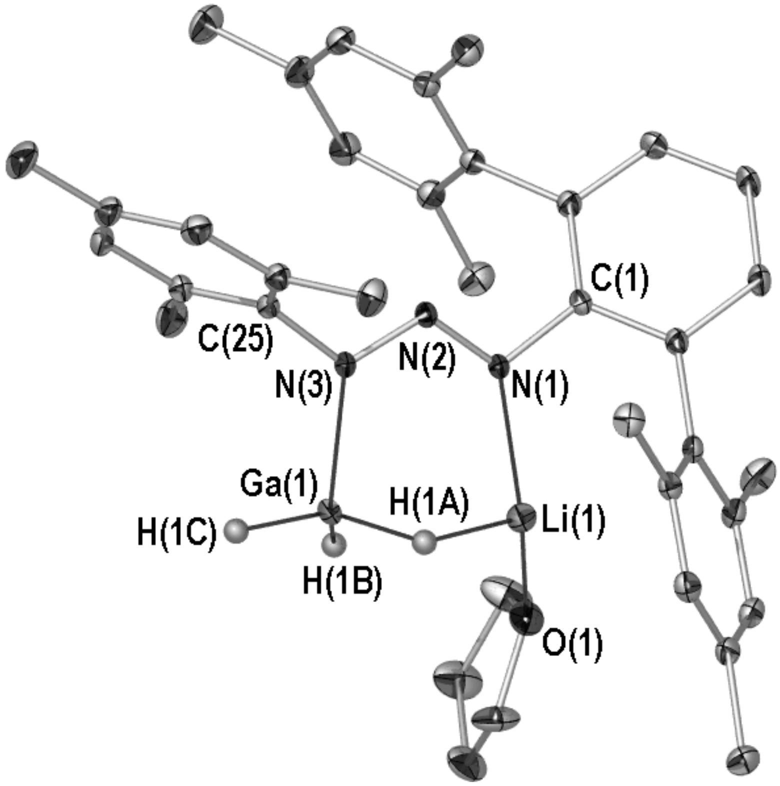


Figure 8. Molecular structure of **6**. All hydrogen atoms excepting hydride ligands H(1a), H(1b) and H(1c) omitted for clarity. Selected bond lengths (Å) and angles (º): Ga(1)-H(1a) 1.50, Ga(1)-H(1b) 1.62, Ga(1)-H(1c) 1.50, Li(1)-H(1a) 1.94, Ga(1)-N(3) 1.9855(14), Li(1)-N(1) 2.052(3), Li(1)-O(1) 1.909(3), N(1)-N(2) 1.3045(18), N(2)-N(3) 1.3010(18), N(1)-N(2)-N(3) 115.29(13), O(1)-Li(1)-N(1) 135.66(19), N(2)-N(3)-Ga(1) 126.32(10), N(2)-N(1)-Li(1) 115.29(13).

4.7 Conclusion

In summary, this chapter describes the preparation of four new triazene compounds bearing terphenyl substituents at a terminal nitrogen, and their use to prepare several alumino- and gallohydride complexes that adopt structures and compositions dependent on the bulk of the triazene used. Infrared data for these complexes corroborates the supposition that triazenides are weaker donors relative to similar amidinate ligand types. On the basis of this preliminary study, it would appear the group 13 hydride chemistry of 1,3-bis(aryl)triazenides has the potential to overlap with several areas at the frontier of fundamental studies of these elements. Studies concerning the use of 1,3-bis(aryl)triazenide supported alumino- and gallohydrides as precursors to group 13 materials and low valent species would make worthy investigations in their own right.

Experimental

General

Diethyl ether, THF and hexane were dried over sodium and freshly distilled from sodium diphenylketyl before freeze-thaw degassing prior to use. Toluene was dried over sodium and freshly distilled from potassium before freeze-thaw degassing prior to use. Lithium tetrahydridoaluminate was purified by extraction into diethyl ether. Lithium tetrahydridogallate was prepared and used *in situ* by reaction of gallium trichloride with excess lithium hydride (*ca*. 30 equivalents) at -30 ºC in diethyl ether. $DmpN_3$ was prepared according to a literature procedure[297] and $DitopN_3$ was prepared using an analogous procedure (see Chapter 5). All other materials were acquired from Sigma-Aldrich and used as received. All manipulations, excepting the work-up procedures for the $DitopN_3(H)Ar$ and $DmpN_3(H)Ar$ (Ar = Mes, pTol) ligand precursors, were performed using conventional Schlenk or glovebox techniques under an atmosphere of ultra high purity argon in flame-dried glassware. Infrared spectra were recorded as Nujol mulls using sodium chloride plates on a Nicolet Nexus FTIR spectrophotometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 300.13 MHz and 75.46 MHz respectively using a Varian 2000 spectrometer with chemical shifts referenced to the residual ^1H resonances of the *deutero*-benzene solvent (δ 7.16 and 128.39 ppm respectively). Melting points were determined in sealed glass capillaries under argon and are uncorrected. All microanalyses were conducted by the Campbell Microanalytical Laboratory, Chemistry Department, University of Otago, P.O. Box 56, Dunedin, New Zealand. Single crystal X-ray data collections were undertaken at Monash University. Further details are listed in a separate section below.

***N*-(2,6-di-*p*-tolylphenyl),*N′*-*p*-tolyltriazene, $DitopN_3(H)pTol$**

p-Tolylmagnesium bromide (1.0 M in Et_2O; 1.70 cm^3, 1.70 mmol) was added dropwise to a solution of $DitopN_3$ (0.50 g, 1.67 mmol) in THF (30 cm^3) at room temperature with stirring. After 2 hours the resultant yellow solution was quenched carefully with water (100 cm^3) at 0 ºC, separated and the aqueous layer extracted with Et_2O (3 x 100 cm^3). Washing with water (2 x 50 cm^3), drying over anhydrous $MgSO_4$ and removal of volatiles *in vacuo* gave an orange solid that was recrystallised from acetone (0.55 g, 84%) m.p. 136-138 °C. Elemental analysis calculated (%) for $C_{27}H_{25}N_3$: C 82.83, H 6.44, N 10.73; Found: C 82.76, H 6.70, N 10.82; I IR (Nujol, cm^{-1}), ν 3301 (sharp s), 1907 (w), 1866 (w), 1581 (w), 1510 (m), 1307 (s), 1298 (s), 1256 (s), 1230 (s), 1215 (s), 1178 (s), 1164 (s), 1153 (s), 1103 (m), 1077 (m), 1035 (m), 1015 (m), 958 (m), 943 (m), 932 (w), 915 (w), 890 (w), 821 (m), 790 (m), 785 (m), 731 (s), 665 (w); ^{1}H NMR (C_6D_6, 300 K): δ 2.01 (s, 3H; pTol CH_3), 2.11 (s, 6H; Ditop CH_3), 6.78-6.86 (m, 4H; pTol ArCH), 6.98 (d, 4H, $^3J_{HH}$ 8.0 Hz; Ditop 2/3 Ar'CH), 7.07 (t, 1H, $^3J_{HH}$ 6.8 Hz; Ditop 4-ArCH), 7.29 (d, 2H, $^3J_{HH}$ 6.8 Hz; Ditop 3,5-ArCH), 7.30 (d, 4H, $^3J_{HH}$ 8.0 Hz; Ditop 2/3 Ar'CH), 9.18 (br s, 1H; NH); $^{13}C\{^1H\}$ NMR (C_6D_6, 300 K): δ 21.2, 21.4 (s; DitopN_3(H)pTol CH_3), 125.2, 125.5, 126.1, 127.0, 127.5 (s; DitopN_3(H)pTol ArC), 129.7, 129.9, 130.3, 131.1 (s; DitopN_3(H)pTol ArCH), 135.4 (s; DitopN_3(H)pTol ArC), 136.9, 138.5 (s; DitopN_3(H)pTol ArCH).

N-(2,6-di-*p*-tolylphenyl),*N′*-mesityltriazene, DitopN_3(H)Mes

DitopN_3(H)Mes was prepared using an analogous method to DitopN_3(H)pTol replacing the *para*-tolyl Grignard reagent with mesitylmagnesium bromide (1.0 M in THF). The scale and work-up procedure were also conducted in an identical fashion. Yield after recrystallisation from acetone; 0.63 g, 90%, m.p. 120-121 °C. Elemental analysis calculated (%) for $C_{29}H_{29}N_3$: C 83.02, H 6.97, N 10.02; Found: C 82.54, H 7.17, N 9.78; IR (Nujol, cm^{-1}), v 3315 (sharp s), 1939 (w), 1891 (w), 1816 (w), 1788 (w), 1715 (w), 1609 (w), 1567 (w), 1513 (s), 1484 (m), 1435 (s), 1397 (s), 1306 (s), 1238 (s), 1212 (m), 1196 (s), 1109 (m), 1082 (m), 1035 (m), 968 (w), 938 (w), 917 (w), 852 (m), 842 (m), 827 (w), 815 (m), 786 (s), 768 (m), 752 (m), 672 (w), 614 (w), 604 (w); ^{1}H NMR (C_6D_6, 300 K): δ 1.86 (s, 6H; Mes *o*-CH_3), 2.05 (s, 3H; Mes *p*-CH_3), 2.14 (s, 6H; Ditop *p*-CH_3), 6.65 (s, 2H; Mes *m*-ArCH), 7.00 (d, 4H, $^3J_{HH}$ 8.1 Hz; Ditop 2/3 Ar′CH), 7.11 (t, 1H, $^3J_{HH}$ 7.5 Hz; Ditop 4-ArCH), 7.32 (d, 2H, $^3J_{HH}$ 7.5 Hz; Ditop 3,5-ArCH), 7.33 (d, 4H, $^3J_{HH}$ 8.1 Hz; Ditop 2/3 Ar′CH), 8.79 (br s, 1H; NH); $^{13}C\{^1H\}$ NMR (C_6D_6, 300 K): δ 18.7, 21.2, 21.4 (s; DitopN_3(H)Mes CH_3), 126.5, 129.5, 129.8, 130.7, 130.8 (s; DitopN_3(H)Mes ArCH), 135.5, 136.7, 137.1, 138.2 (s, DitopN_3(H)Mes ArC), no further resonances observed.

N-(2,6-dimesitylphenyl),*N′*-*p*-tolyltriazene, DmpN_3(H)pTol

p-tolylmagnesium bromide (1.0 M in Et_2O; 2.80 cm^3, 2.80 mmol) was added dropwise to a THF (20 cm^3) solution of DmpN_3 (1.00 g, 2.81 mmol) at ambient temperature. The resulting orange solution was left to stir for 24 hours whereupon water (3.0 cm^3, 0.17 mol) was added carefully over a period of five minutes. This resulted in immediate precipitation of a white solid. Further water (7.0 cm^3, 0.39 mol) and Et_2O (20 cm^3) were added and the reaction mixture stirred for several minutes. The organic phase was isolated and washed with water (3 x 30 cm^3) prior to drying over anhydrous magnesium sulfate and removal of all volatiles *in vacuo*. The resulting orange oil was dissolved in Et_2O (2 cm^3) and placed at -30 ºC overnight. $DmpN_3(H)pTol$ was isolated as a pale yellow powder (0.83 g, 66 %), m.p. 143-144 ºC. Elemental analysis calculated (%) for $C_{31}H_{33}N_3$: C 83.18, H 7.43, N 9.39; Found: C 82.87, H 7.98, N 9.14; IR (Nujol, cm^{-1}), ν 3282 (sharp s), 1933 (w), 1906 (w), 1767 (w), 1736 (w), 1655 (w), 1610 (m), 1583 (m), 1471 (s), 1392 (m), 1377 (m), 1308 (w), 1253 (m), 1224 (m), 1192 (s), 1152 (s), 1093 (s), 1035 (m), 964 (w), 945 (w), 926 (w), 854 (m), 822 (m), 801 (m), 758 (m), 742 (w), 678 (w), 640 (w), 602 (m); ^1H NMR (C_6D_6, 300 K): δ 2.01 (s, 3H; pTol CH_3), 2.13 (s, 12H; Dmp *o*-CH_3), 2.21 (s, 6H; Dmp *p*-CH_3), 6.71 (br s, 1H; Dmp 4-ArCH), 6.82-6.88 (m, 6H; Dmp 3,5-ArCH and pTol ArCH), 7.00 (s, 4H; Dmp *m*-Ar'CH), 9.03 (br s, 1H; NH); $^{13}C\{^1H\}$ NMR (C_6D_6, 300 K): δ 21.4, 21.6, 25.7 (s; $DmpN_3(H)pTol$ CH_3), 119.1, 129.5, 130.4 (s; $DmpN_3(H)pTol$ ArCH), 132.1 (s; $DmpN_3(H)pTol$ ArC), 135.9, 148.8 (s; $DmpN_3(H)pTol$ ArCH) no further resonances observed.

N-(2,6-dimesitylphenyl),N′-mesityltriazene, $DmpN_3(H)Mes$

$DmpN_3(H)Mes$ was prepared using an analogous method to $DmpN_3(H)pTol$ replacing the *para*-tolyl Grignard reagent with mesitylmagnesium bromide (1.0 M in THF). The scale and work-up procedure were also conducted in an identical fashion. Yield after recrystallisation from the minimum Et_2O (light yellow elongated hexagonal prisms) at -30 ºC; 0.86 g, 65%, m.p. 157-159 °C. Elemental analysis calculated (%) for $C_{33}H_{37}N_3$: C 83.33, H 7.84, N 8.83; Found: C 83.10, H 7.56, N 8.91; IR (Nujol, cm^{-1}), ν 3398 (sharp s), 1925 (w), 1783 (w), 1611 (w), 1573 (w), 1515 (w), 1457 (s), 1377 (s), 1260 (w), 1228 (w), 1207 (m), 1154 (m), 1113 (m), 1078 (m), 1029 (m), 847 (s), 794 (m), 762 (m), 740 (w), 718 (w); ^1H NMR (C_6D_6, 300 K): δ 1.73 (br s, 6H; Mes *o*-CH_3), 2.03 (s, 3H; Mes *p*-CH_3), 2.13 (s, 12H; Dmp *o*-CH_3), 2.20 (s, 6H; Dmp *p*-CH_3), 6.61 (s, 2H; Mes *m*-ArCH), 6.82 (s, 4H; Dmp *m*-Ar'CH), 6.98-7.07 (m, 3H; Dmp 3,4,5-ArCH), 8.43 (br s, 1H; NH); $^{13}C\{^1H\}$ NMR (C_6D_6, 300 K): δ 17.6, 20.7, 21.0, 21.2 (s; $DmpN_3(H)Mes$ CH_3), 125.5 (s; $DmpN_3(H)Mes$ ArC), 127.2, 128.2, 128.8, 129.7 (s; $DmpN_3(H)Mes$ ArCH), 130.2, 133.6, 135.3, 136.2, 136.4, 136.8, 137.5 (s; $DmpN_3(H)Mes$ ArC).

[{Li(Et_2O)(μ-H)(μ-$DitopN_3pTol$)AlH(μ-H)}$_2$] (1)

A pale yellow solution of $DitopN_3(H)pTol$ (0.52 g, 1.33 mmol) in Et_2O (20 cm^3) was added dropwise to a cooled (-78 °C) colourless solution of Li[AlH_4] (0.05 g, 1.32 mmol), also in Et_2O (10 cm^3). Warming of the solution to -30 °C resulted in a colour change to bright yellow with effervescence (H_2). The solution was warmed to ambient temperature and stirred for a further 90 minutes whereupon volatiles were removed *in vacuo* to afford an oily yellow solid. Recrystallisation from hexane afforded the product as a yellow solid (0.26 g, 39%), m.p. 118-122 °C (dec. 165 °C). Elemental analysis calculated (%) for $C_{54}H_{54}N_6Al_2Li_2$: C 75.87, H 6.37, N 9.83; Found: C 75.63, H 6.13, N 9.51; IR (Nujol, cm^{-1}), ν 1853 (br m) (terminal Al-H), 1746 (br m) (bridging Al-H); ^1H NMR (C_6D_6, 300 K): δ 1.09 (t, 12H, $^3J_{HH}$ 7.2 Hz; Et_2O CH_3), 1.98 (s, 6H; pTol CH_3), 2.03 (s, 6H; pTol CH_3), 2.07 (s, 6H; pTol CH_3), 3.18 (q, 8H, $^3J_{HH}$ 7.2 Hz; Et_2O CH_2), 6.73 (d, 4H, $^3J_{HH}$ 8.6 Hz; pTol 2/3-ArCH), 6.81 (d, 4H, $^3J_{HH}$ 8.6 Hz; pTol 2/3-ArCH), 6.91-6.97 (m, 8H; pTol 2,3-ArCH), 7.14 (obsc. by solvent resonance; Ditop 3,5-ArCH), 7.24 (t, 2H, $^3J_{HH}$ 6.9 Hz; Ditop 4-ArCH) (no hydride resonance observed); $^{13}C\{^1H\}$ NMR (C_6D_6, 300 K) vacuum dried sample: δ 21.2, 21.5 (s; DitopN_3pTol CH_3), 118.7, 119.2, 122.9, 126.5, 129.3, 129.5, 130.1, 130.2, 130.7, 131.3, 136.1, 136.4 (s; DitopN_3pTol ArC).

[AlH(DitopN_3Mes)$_2$] (2)

A pale yellow solution of DitopN_3(H)Mes (0.24 g, 0.57 mmol) in Et_2O (20 cm^3) was added dropwise to a cooled (-78 °C) colourless solution of Li[AlH_4] (0.02 g, 0.57 mmol), also in Et_2O (20 cm^3). Analogous work-up to (**1**) followed by recrystallisation from Et_2O afforded **2** as a yellow prisms (0.10 g, 20%), m.p./dec. 258 °C. IR (Nujol, cm^{-1}), ν 1889 (s sharp) (Al-H); ^1H NMR (C_6D_6, 300 K): δ 1.83 (br s, 12H; Mes *o*-CH_3), 1.89 (br s, 6H; Mes *p*-CH_3), 2.12 (br s, 6H; Ditop CH_3), 2.16 (br s, 6H; Ditop CH_3), 6.70 (br s, 4H; Mes ArCH), 6.94 (br d, 8H; pTol ArCH), 7.02 (br d, 8H; pTol ArCH), 7.11-7.27 (m, 6H; Ditop Ar'CH) (no hydride resonance observed); $^{13}C\{^1H\}$ NMR (C_6D_6, 300 K): δ 21.1, 21.4. 21.5 (s; DitopN_3Mes *o,p*-CH_3), 129.4, 130.8, 131.0, 136.4, 137.9, (s, DitopN_3Mes ArCH) 126.2, 126.4, 126.2, 127.6, 126.8, 127.3, 141.2, (s, DitopN_3Mes ArC). Samples of **2** were routinely contaminated with a low yielding co-product *cf.* **3** below. This precluded the acquisition of meaningful C, H, N microanalytical data.

[{AlH_2(DmpN_3pTol)}$_n$].nhexane (3a)

A cooled (0 °C) pale yellow solution of DmpN_3(H)pTol (0.23 g, 0.51 mmol) in Et_2O (15 cm^3) was added drop wise to a cold (0 °C) solution of Li[AlH_4] (0.02 g, 0.53 mmol), also in Et_2O (20 cm^3), resulting in an immediate colour change to bright yellow with effervescence (H_2). The stirred solution was left to warm to ambient temperature and stirred for 24 hours. Filtration and drying *in vacuo* gave a yellow oil containing **3a** contaminated with a small quantity of **3b** (< 5% by ^1H NMR), which solidified after prolonged standing. Purification of **3a** was achieved by recrystallisation from hexane to afford a solvent dependent yellow microcrystalline powder (0.08 g, 28 %), m.p. 125-128 °C. Elemental analysis calculated (%) for $C_{31}H_{34}AlN_3$+(C_6H_{14}): C 79.11, H 8.61, N 7.48; Found: C 78.98, H 8.75, N 6.49; IR (Nujol, cm^{-1}), *v* 1806 (s), 1777 (s) (terminal Al-H), 1668 (bridging Al-H); ^1H NMR (C_6D_6, 300 K) vacuum dried sample: δ 2.14 (s, 3H; *p*-Tol *p*-CH_3), 2.16 (s, 6H; Dmp *p*-CH_3), 2.36 (s, 12H; Dmp *o*-CH_3), 3.60 (br s, 2H; AlH), 6.87 (s, 4H; Dmp *m*-ArH), 6.96-7.03 (m, 4H; Dmp/*p*-Tol ArH), 7.07-7.14 (m, 3H; Dmp/*p*-Tol ArH); $^{13}C\{^1H\}$ NMR (C_6D_6, 300 K) vacuum dried sample: δ 20.8 (s; *p*-Tol *p*-CH_3), 21.2 (s; Dmp *p*-CH_3), 22.1 (s; Dmp *o*-CH_3), 121.0 (s; DmpN_3pTol ArCH), 123.7, 128.8 (s; DmpN_3pTol ArC), 129.1, 129.6, 130.9 (s; DmpN_3pTol ArCH), 133.5 (s; DmpN_3pTol ArC), 136.5 (s; DmpN_3pTol ArCH), 136.8 (s; DmpN_3pTol ArC), 137.3 (s; DmpN_3pTol ArCH), 138.5, 138.8 (s; DmpN_3pTol ArC).

[AlH(DmpN_3pTol)$_2$] (3b)

A pale yellow solution of DmpN_3(H)pTol (0.236 g, 0.53 mmol) in Et_2O (30 cm^3) was added drop wise to a cooled (-78 °C) solution of Li[AlH_4] (0.02 g, 0.53 mmol), also in Et_2O (30 cm^3). Warming of the solution to -30 °C resulted in a colour change to bright yellow with effervescence (H_2). The solution was left to warm to ambient temperature and stirred for a further 90 minutes whereupon it was filtered and dried *in vacuo* to yield crude **3b**. Recrystallisation from fresh Et_2O (10 cm^3) afforded **3b** as yellow-orange tabular crystals (0.14 g, 29 %), m.p. 153-157 °C (170 °C dec.). Elemental analysis calculated (%) for $C_{62}H_{65}AlN_6$: C 80.84, H 7.11, N 9.12; Found: C 81.01, H 6.97, N 8.89; IR (Nujol, cm^{-1}), *v* 1893 (sharp s) (Al-H); ^1H NMR (C_6D_6, 300 K): δ 1.97 (s, 3H; Dmp/*p*-Tol CH_3), 2.04 (s; 3H; Dmp/*p*-Tol CH_3), 2.08 (s, 3H; Dmp/*p*-Tol CH_3), 2.12 (s, 6H; Dmp/*p*-Tol CH_3), 2.17 (s, 6H; Dmp/*p*-Tol CH_3), 2.27 (s, 3H; Dmp/*p*-Tol CH_3), 6.26 (br d, 4H; *p*-Tol ArCH), 6.35 (br d, 4H; *p*-Tol ArCH), 6.58 (br s, 4H; Dmp *m*-ArH), 6.80-7.02 (m, 10H; Dmp ArH); $^{13}C\{^1H\}$ NMR (C_6D_6, 300 K): δ 21.4, 21.6, 25.7, 25.9, 26.0, 27.6 (s; DmpN_3Mes CH_3), 119.1, 129.5, 130.4, 132.1, 132.6, 134.1, 135.9, 139.0, (s; Dmp ArCH/ArC) no further resonances observed.

[AlH_2(DmpN_3Mes)(THF)] (4)

A yellow solution of DmpN_3(H)Mes (0.50 g, 1.05 mmol) in Et_2O (10 cm^3) was added to a cooled (0 °C) colourless solution of Li[AlH_4] (0.05 g, 1.32 mmol) in Et_2O (30 cm^3) resulting in hydrogen gas evolution and a colour change to radiant yellow. After stirring for 1 hour at ambient temperature all volatiles were removed *in vacuo* to yield crude **4** as a yellow solid that was recrystallised from THF to afford **4** as pale yellow blocks (0.26 g, 43 %), m.p. 125 °C. Elemental analysis calculated (%) for $C_{37}H_{46}AlN_3O$: C 77.18, H 8.05, N 7.30; Found: C 77.36, H 8.21, N 7.28; IR (Nujol, cm^{-1}), ν 1820 (s sh), 1804 (sharp s) (Al-H); ^1H NMR (C_6D_6, 300 K) vacuum dried sample: δ 1.98 (s, 6H; Dmp/*o*-CH_3 Mes *p*-CH_3), 2.02 (s, 3H; Mes *p*-CH_3), 2.28 (s, 6H; Dmp/*o*-CH_3 Mes *p*-CH_3), 2.34 (s, 12H; Dmp *o*-CH_3), 3.63 (br s, 2H; AlH), 6.66 (s, 2H; Mes *m*-ArH), 6.79 (m, 1H; Dmp *p*-ArH), 6.94 (s, 4H; Dmp *m*-ArH), 7.07-7.11 (m, 2H; Dmp *m*-ArH); $^{13}C\{^1H\}$ NMR (C_6D_6, 300 K) vacuum dried sample: δ 18.7, 21.0, 21.6, 23.9 (s; $DmpN_3Mes$ CH_3), 126.2, 130.3, 135.8, 136.4, 137.0 (s; $DmpN_3Mes$ ArCH) no further resonances observed.

[Li(Et$_2$O)(μ-H)(μ-DmpN$_3$pTol)GaH$_2$] (5)

A yellow solution of $DmpN_3(H)pTol$ (0.45 g, 1.01 mmol) in Et_2O (10 cm^3) was added to a cooled (-78 °C) solution of Li[GaH_4] in Et_2O (40 cm^3) that had been prepared *in situ* from the reaction of gallium trichloride (0.18 g, 1.02 mmol) with excess lithium hydride (0.30 g, 37.74 mmol) at -30 °C for 4 hours followed by filtration. The resulting pale coloured solution was warmed to ambient temperature over a period of 2 hours with a noticeable colour change to yellow at *ca.* -30 °C, accompanied by gas evolution (H_2). Stirring at ambient temperature for a further hour followed by filtration and removal of volatiles *in vacuo* afforded a yellow solid that was washed with cold (0 °C) hexane (3 x 2 cm^3) to give **5** as a fine powder (0.23 g, 38 %), m.p. 106 °C (182 °C dec.). Elemental analysis calculated (%) for $C_{35}H_{45}GaLiN_3O$: C 70.01, H 7.05, N 7.00; Found: C 70.35, H 6.98, N 6.72; IR (Nujol, cm^{-1}), ν 1910 (s), 1859 (s) (terminal Ga-H), 1719 (s) (bridging Ga-H-Li); ^1H NMR (C_6D_6, 300 K): δ 1.02 (t, 6H; Et_2O CH_3, $^3J_{HH}$ 6.90 Hz), 1.97 (s, 6H; Dmp *p*-CH_3), 2.13 (s, 3H; *p*-Tol *p*-CH_3), 2.16 (s, 12H; Dmp *o*-CH_3), 3.17 (q, 4H; Et_2O CH_2, $^3J_{HH}$ 6.90 Hz), 4.20 (br s, 3H; GaH), 6.33-6.36 (m, 4H; *p*-Tol ArH), 6.79 (s, 4H; Dmp *m*-ArH), 6.93-6.96 (m, 2H; Dmp *m*-ArH), 7.02-7.09 (m, 1H; Dmp *p*-ArH); $^{13}C\{^1H\}$ NMR (C_6D_6, 300 K): δ 20.2, 20.7, 20.8 (s; $DmpN_3pTol$ CH_3), 121.7, 129.1, 129.7, 130.5, 137.3 (s; $DmpN_3pTol$ ArCH) no Et_2O resonances or further resonances observed.

[Li(THF)(μ-H)(μ-DmpN$_3$Mes)GaH$_2$] (6)

Compound **6** was prepared using an identical procedure to that used for compound **5**. Salient details; reagents used $DmpN_3(H)Mes$ (0.50 g, 1.05 mmol) in Et_2O (7.5 cm^3), Li[GaH_4] (0.19 g of $GaCl_3$; 1.08 mmol) in Et_2O (40 cm^3) reaction observed at *ca.* -30 °C. Crystalline samples (pale yellow prisms) suitable for single crystal X-ray diffraction obtained by recrystallisation from the minimum volume of THF followed by placement at -30 °C (0.39 g, 59 %), m.p. 125 °C. Elemental analysis calculated (%) for $C_{37}H_{47}GaLiN_3O$: C 70.94, H 7.56, N 6.71; Found: C 70.86, H 7.64, N 6.78; IR (Nujol, cm^{-1}), ν 1917 (s), 1842 (s) (terminal Ga-H), 1724 (s) (bridging Ga-H-Li); ^1H NMR (C_6D_6, 300 K): δ 1.27 (m, 4H; THF CH_2), 2.07 (s, 6H; Dmp/*o*-CH_3 Mes *p*-CH_3), 2.10 (s, 12H; Dmp *o*-CH_3), 2.17 (s, 6H; Dmp/*o*-CH_3 Mes *p*-CH_3), 2.21 (s, 3H; Mes *p*-CH_3), 3.31 (m, 3H; THF OCH_2), 3.96 (br s, 3H; GaH), 6.74 (s, 4H; Dmp *m*-ArH), 6.77 (s, 2H; Mes *m*-ArH), 6.97-7.04 (m, 3H; Dmp *m*- & *p*-ArH); $^{13}C\{^1H\}$ NMR (C_6D_6, 300 K) vacuum dried sample: δ 19.1, 20.0, 21.4, 23.7 (s; $DmpN_3Mes$ CH_3), 124.2, 130.5, 133.7 (s; $DmpN_3Mes$ ArCH), 134.6, 134.9, 136.4 (s; $DmpN_3Mes$ ArC), 136.8 (s; $DmpN_3Mes$ ArCH), 137.5, 138.3, 146.2, 149.4 (s; $DmpN_3Mes$ ArC).

X-ray structure determination

Crystalline samples of $DmpN_3(H)Mes$, **2**, **3b**, **4** and **6** were mounted on glass fibres in silicone oil at – 150(2) °C (123 (2) K) with the exception of **2** (–50(2) °C 223 (2) K) due a destructive phase change below – 100 °C. A summary of crystallographic data can be found in Table 2. Hydrogen atoms were refined in calculated positions (riding model) for all compounds with the exception of hydride ligands (**2**, **3b**, **4** and **6**) and all of the hydrogen atoms of $DmpN_3(H)Mes$, which were located and refined isotropically. Data were collected using graphite monochromated $Mo_{K\alpha}$ X-ray radiation (λ = 0.71073 Å) on an Enraf-Nonius Kappa CCD diffractometer for $DmpN_3(H)Mes$ and **2**, and a Bruker X8 Apex CCD diffractometer for complexes **3b**, **4** and **6**. Data were corrected for absorption by the DENZO-SMN package ($DmpN_3(H)Mes$ and **2**),[30] or empirical methods using scalepack programs (**3b**, **4** and **6**). Structural solution and refinement was carried out using the SHELX suite of programs with the graphical interface X-seed.[164] For compound **2**, data suggest a possible new symmetry element (*n*) or space group (*C2/c*). Attempts to refine in a monoclinic space group repeatedly failed. Furthermore, no meaningful correlation matrix elements >0.5 or evidence of disorder was observed. For compound **3b**; Flack tests were ambiguous (Flack parameter = 0.3580(2190), refinement of inverted structure = 0.6321(2194)), however attempts to refine in a centrosymmetric, non chiral, space group were repeatedly unsuccessful. For compound **6**, all atoms were refined without any evidence of disorder, and no residual electron density (holes or peaks) are evident with the exception of a peak (0.61 e Å^{-3}) 0.78 Å from Ga(1), and a hole (–1.05 e Å^{-3}) 0.77 Å from Ga(1).

Chapter 5: Preparation of a super-bulky silver N-heterocyclic carbene complex and related species

5.1 Introduction

This chapter comprises a study of super-bulky terphenyl-substituted NHCs and their precursors, along with two related silver complexes. The preparation of a 1,3-bis(2,6-terphenyl)imidazolium salt and the first coordination complex containing a 1,3-bis(2,6-terphenyl)imidazol-2-ylidene NHC (IDitop) are discussed, along with the preparation of the *N*,*N'*-bis(2-phenylphenyl)imidazolium ($IBpH^+$) and imidazol-2-ylidene (IBp) congeners. The resulting complexes and their precursors have been characterised by infrared and NMR spectroscopies (^1H and $\{^1H\}^{13}C$) and, where possible, X-ray structure determination. The spatial bulk of the new bulky NHCs is discussed relative to existing bulky NHCs, using the molecular structure of their silver(I) chloride complexes as a basis for calculation.

5.2 Significance of research

The use of super bulky aryl substituents to kinetically stabilise unusual or unprecedented chemical functionalities is a common feature of contemporary organometallic chemistry.[298-300] As mentioned in Chapter 4, two landmark examples are Yoshifuji's isolation of a P=P containing compound in 1981[227] and Robinson's report of a gallium-gallium multiple bond in $Na_2[Ar^*GaGaAr^*]$[229] (Ar^* = 2,6-$Tripp_2C_6H_3$, Tripp = 2,4,6-$^iPr_3C_6H_2$) that was controversially described as a metal-metal triple bond. Compounds such as these have encouraged many research groups to incorporate super bulk into a variety of ligand classes, such as cyclopentadienyls,[301, 302] *N*,*N'*-disubstituted amidinates[17, 245, 303-307] and β-diketiminates,[249, 250, 253, 308, 309] in order to quantitatively evaluate the impact of 'steric engineering' on their chemistry.[306, 307] Beyond fundamental studies of element-element bonding, this includes the effect of bulk on catalytic systems and small molecule activation.[224] Of the aryl substituents employed, the 2,6-terphenyl based Tripp, Dipp (2,6-(2′,6′-diisopropylphenyl)$_2$phenyl) and Dmp (2,6-dimesitylphenyl, mesityl = 2,4,6-$Me_3C_6H_2$) aryls have availed themselves particularly well due to their unsurpassed spatial shielding of functions at the *ipso*-carbon.[288, 298-300, 310] This shielding is afforded by the 2,6-aryl functions, which sit orthogonal to the primary aryl plane.

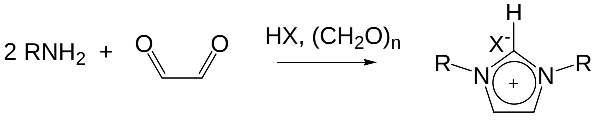
Considering the wide application of 2,6-terphenyls[298-300] it is perhaps surprising that they have not been incorporated into 1,3-disubstituted imidazol-2-ylidene *N*-heterocyclic carbenes (NHCs), one of the most studied ligand classes in modern organometallic chemistry.[92] As recently reviewed by Hahn,[121] imidazol-2-ylidenes have been successfully incorporated into dendrimer frameworks,[297] solid-state scaffolds[311] and even porphyrin based constructs,[312, 313] however, 1,3-substitution of these NHCs by 2,6-terphenyl groups has not been accomplished. To our knowledge, only 3,5-terphenyls have been applied in this regard,[314] while the most commonly utilised bulky NHC is arguably IDipp (1,3-bis(2,6-diisopropyl)phenylimidazol-2-ylidene), first prepared by Arduengo and co-workers.[315]

5.3 Synthesis of NHC precursors

5.3.1 1,3-Substituted imidazolium salts

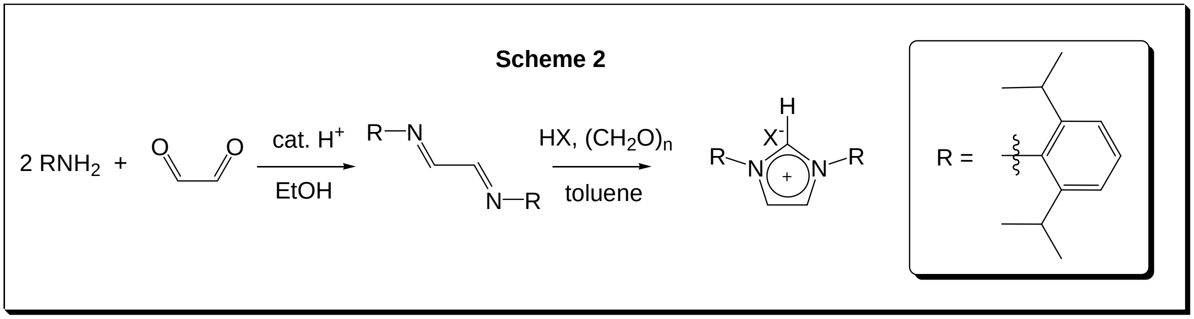
As discussed in Chapter 2, imidazol-2-ylidene NHCs are typically prepared by the deprotonation of 1,3-substituted imidazolium salts. These may be prepared by the stoichiometric combination of two equivalents of primary amine with one equivalent of α-dicarbonyl and paraformaldehyde in the presence of an acid (Scheme 1). This one-pot synthesis, presented as a patent in 1991 by Arduengo *et al.*, stated that the reagents could be added in any order without any effect on reaction outcome.[316]

Scheme 1



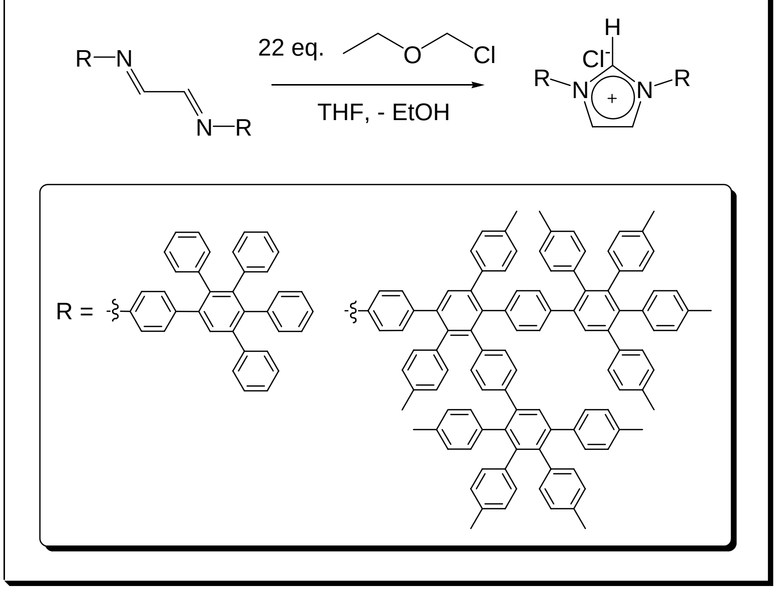
Alternatively, 1,3-substituted imidazolium salts can be accessed by a two-step process involving the treatment of an *N,N'*-disubstituted-1,4-diazabuta-2,3-diene (DAB) with alternative formylating agents. One of these methods, reported by Nolan *et al.*, involved a modification to Arduengo's method. Synthesis of IDipp could not be achieved via simultaneous combination of all the reagents, however synthesis of the diazabutadiene precursor followed by reaction with paraformaldehyde and acid afforded the desired product (Scheme 2).[317] Synthesis of DAB precursors is discussed in a later section.

Scheme 2



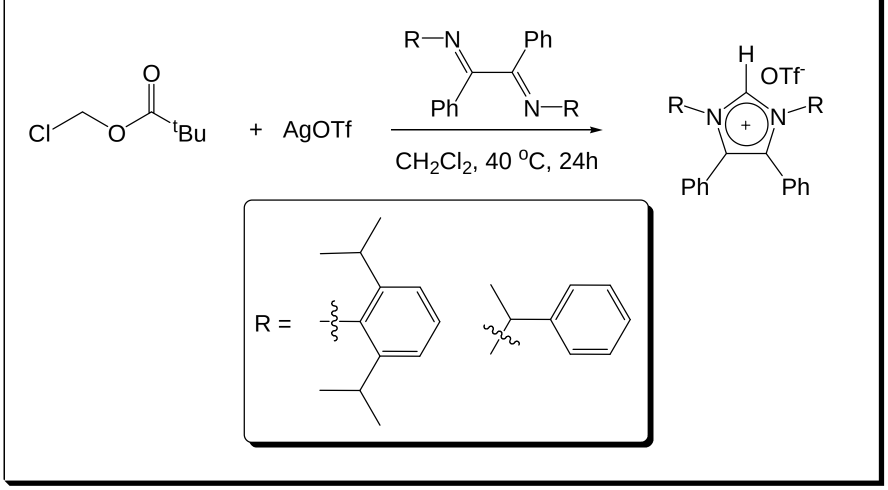
An alternative formylation method was reported in 1999 by Arduengo.[315] Treatment of $\{RN{=}CH\}_2$ (R = Mes, Dipp) in THF with an equimolar portion of chloromethylethyl ether (CME) afforded imidazolium salts in 40% and 57% yield respectively. This method was utilised in a later study by the group of Tsuji to prepare precursors for dendrimer frameworks; in this case up to 22 equivalents of CME were necessary, presumably to increase the solubility and overcome the considerable steric buttressing of the *N*-substituents. (Scheme 3).[297]

Scheme 3



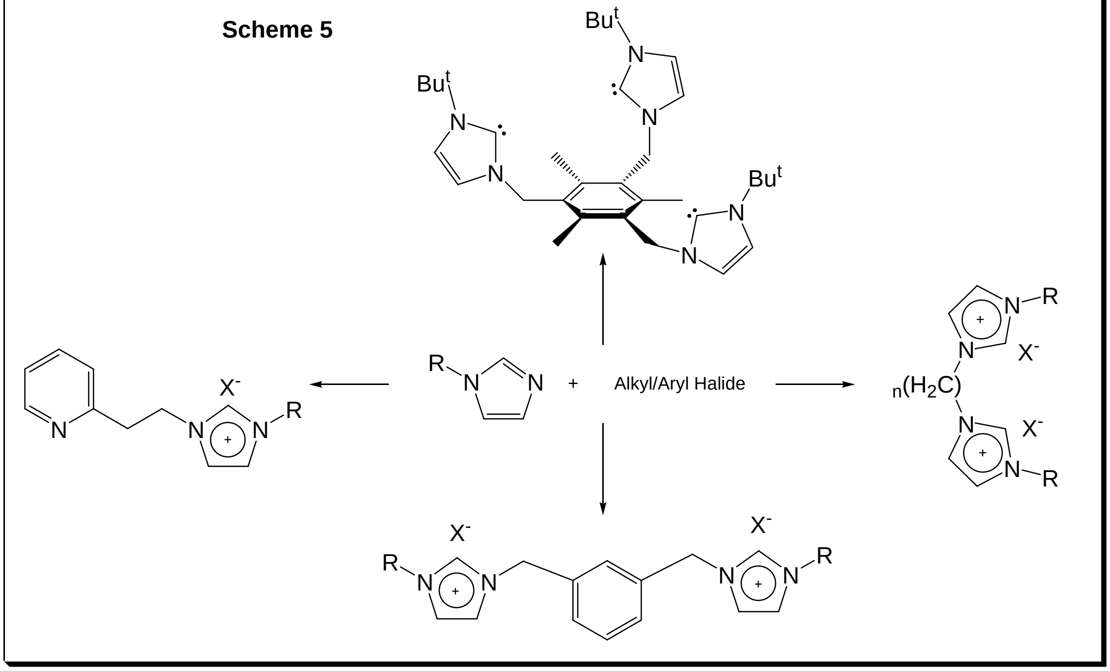
Yet another method, originally proposed by Altenhoff and Glorius in the synthesis of bisoxazoline-derived NHCs,[318] was utilised by Waymouth *et al.* to prepare two sterically encumbered imidazolium salts.[319] Treatment of silver triflate with chloromethyl pivalate generated an *in situ* formylating reagent, which on reaction with the DAB afforded the corresponding imidazolium triflate salt (Scheme 4).

Scheme 4



Imidazolium salts can also be prepared from the corresponding *N*-substituted imidazole and an alkyl or aryl halide (Scheme 5).[320, 321] This method allows for the preparation of unsymmetrical variants, which have found application in a number of areas, including precursors for ligands in Heck and Suzuki reactions.[322, 323]

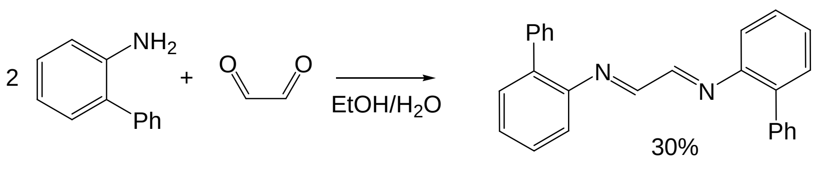
Scheme 5



5.3.2 Bulky *N,N'*-disubstituted-1,4-diazabuta-2,3-dienes (DAB)

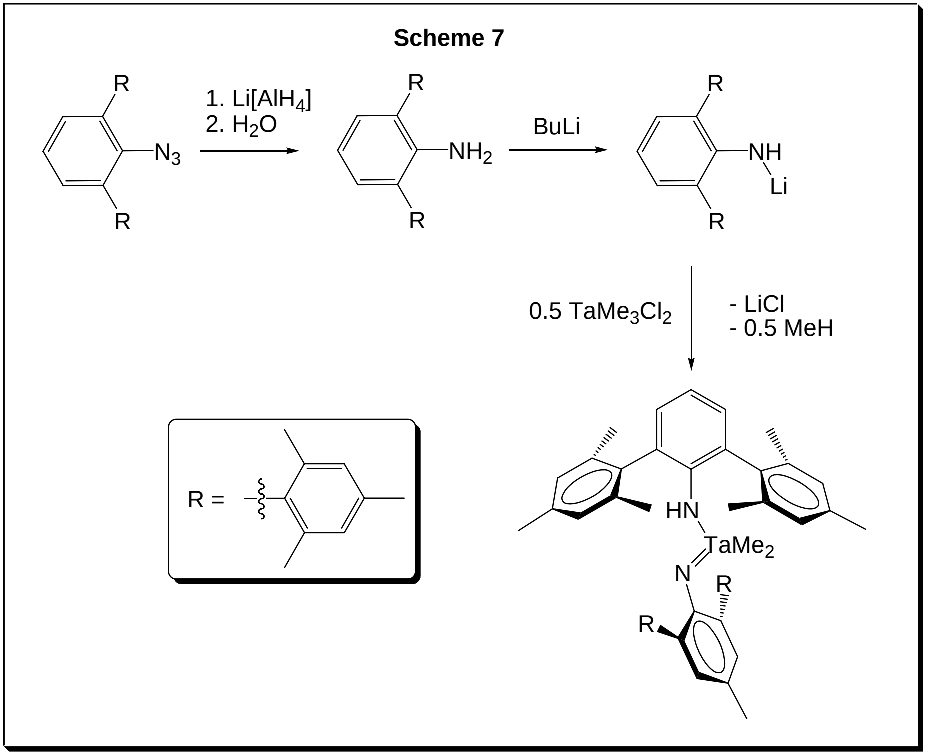
Synthesis of DAB compounds is commonly achieved by combination of two equivalents of primary amine with one equivalent of an α-dicarbonyl, a process that was first reported in 1951.[324-326] These reactions typically use an alcohol solvent, e.g. isopropyl, methyl or ethyl alcohol, in the presence of catalytic acid at room temperature.[326-328] A recent study of bulky species used acetonitrile at an elevated temperature (70 °C).[297] Murase *et al.* reported that although certain DAB products could be prepared at room temperature with catalytic acid, they were hydrolysed at elevated temperature under the same conditions.[324] A low-yielding preparation of a biphenyl-substituted DAB using ethanol-water was recently reported (Scheme 6).[329]

Scheme 6



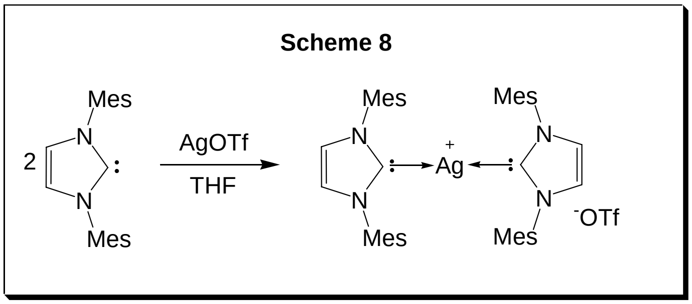
5.3.3 Preparation of bulky anilines

Bulky anilines, including terphenyl amines, can be accessed simply from the parent azide via reduction with Li[AlH_4]. Prior to this the Staudinger reaction (a mild process using a phosphine or phospite)[330] was used, however the rapid evolution of group 13 hydride reducing agents[169] has simplified this process. For example, in 2002 Gavenonis and Tilley used this method to successfully reduce the bulky terphenyl azide $DmpN_3$ (Dmp = 2,6-dimesitylphenyl) to the aniline $DmpNH_2$, prior to coordination of the amide derivative in a tantalum species (Scheme 7).[310]



5.3.4 Silver-NHC adducts

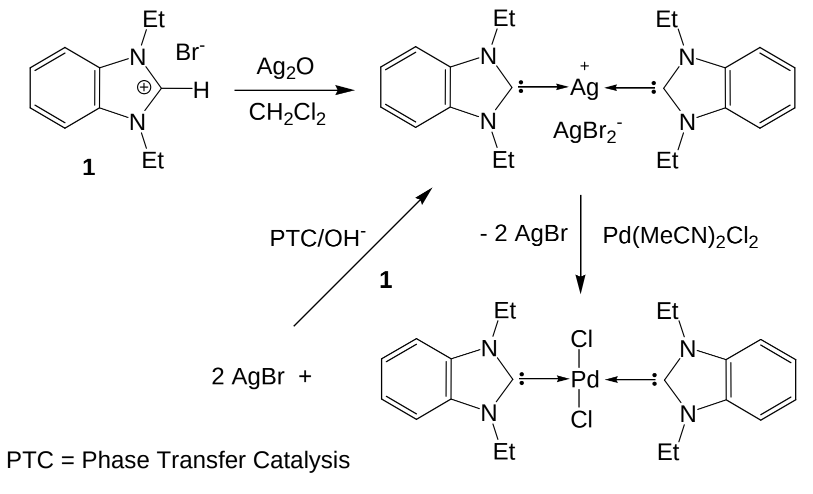
In 1993 Arduengo *et al*. reported the first silver(I)-NHC complex; addition of two equivalents of the NHC IMes to one of silver triflate yielded a bis-NHC-silver(I) triflate as a precipitate (Scheme 8).



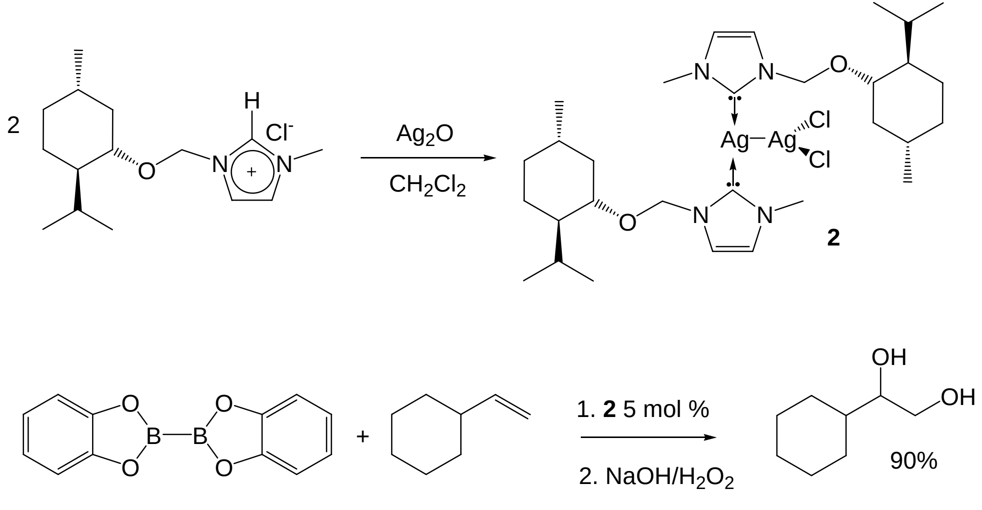
In 1998 Wang and Lin published a simple synthesis for silver(I)-NHC complexes using an imidazolium precursor and silver(I) oxide to give "AgX(NHC)" compounds, where X is the imidazolium counterion, (Scheme 9).[331] The key benefit of this method over that of Arduengo's is that a free carbene is not required. This also avoids the need for strict anaerobic conditions. In the same report the authors demonstrated that silver(I)NHC species can be used as carbene transfer reagents to form catalytic transition metal-NHC complexes, a feature that has been used to good effect by Cavell and co-workers.[322] In the Wang-Lin study, the silver oxide preparation was shown to be superior as a path to NHC complexes, as attempts to deprotonate functionalised imidazolium salts for direct reaction with palladium failed due to the presence of other acidic protons in the precursors. Subsequently, this transmetallation process has been made catalytic in silver by recycling of the AgX by-product of the reaction under basic phase transfer catalysis (PTC) conditions to re-form the active AgX(NHC) reagent (Scheme 9).[331] Although silver complexes are well known to be photosensitive, Nolan *et al.* have reported that the exclusion of light for this type of reaction is often unnecessary.[332]

The “silver” method was utilised successfully by Lee *et al.* in 2006 to synthesise similar compounds with long alkyl side-chains. These target compounds were studied for their potential as silver nanomaterials, namely in liquid-crystal applications.[333] This type of compound has also been used as a precursor to silver nanoparticles[334] and as a catalyst for organic transformations (Scheme 10).[335] Lastly, silver-NHC complexes have also been shown to have antimicrobial activity.[336]

Scheme 9



Scheme 10



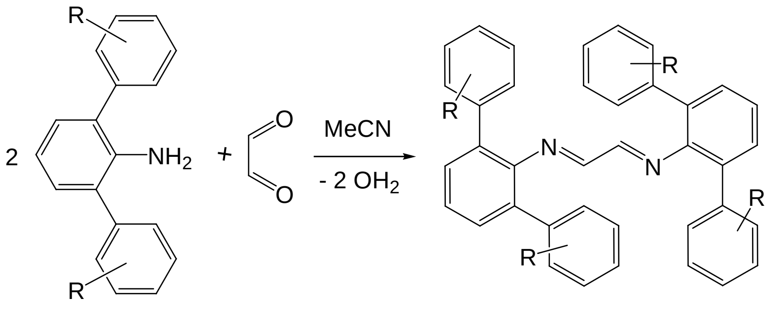
5.4 Research proposal

It is proposed that *N,N'*-bis(2,6-terphenyl)imidazol-2-ylidenes will generate metal complexes with distinct properties relative to less bulky counterparts. This chapter proposes to synthesise super-bulky NHC precursors, including their respective diazabutadienes and imidazolium salts, and utilise them in the preparation of silver-NHC complexes as a prelude to future broader studies. In the event of successful syntheses, the spatial bulk and geometry of these compounds will be investigated.

5.5 Results and discussion

The bulky NHC precursors DmpDAB (Dmp = 1,4-dimesitylphenyl; DAB = *N*,*N'*-disubstituted-1,4-diazabutadiene) and DitopDAB (Ditop = 2,6-bis(4-tolyl)phenyl) were prepared in moderate yield by condensation of the respective anilines, $DmpNH_2$ and $DitopNH_2$, with half an equivalent of glyoxal in acetonitrile (Scheme 11). Although this preparation has previously been used to access several *N*,*N'*-bis(2,6-terphenyl)-α-diketimines, which have found utility in late transition metal catalysis,[337, 338] DitopDAB and DmpDAB are the first α-dialdimines prepared by this route.

Scheme 11



R = 4-Me (**DitopDAB**)
R = 2,4,6-Me_3 (**DmpDAB**)

Both α-dialdimines exhibit *N*-arylimine symmetrical chemical environments in solution, as evidenced by ^{1}H NMR spectroscopy (C_6D_6). This suggests C_2-symmetric *E*-anti or –syn isomerism or free rotation in solution.[292] The *E-anti* structure of DitopDAB in the solid-state was determined by XRD methods (Figure 1), wherein DitopDAB crystallises in the monoclinic spacegroup $P2_1/c$ with half a molecule in the asymmetric unit. The bonding parameters of DitopDAB (C=N 1.279(3) Å, C-C 1.453(5) Å) are comparable to those of the related α-diimines Ar'N=C(Me)-C(Me)=N'Ar, where Ar' is 3- or 4-trimethylsilylphenyl, which also exist as *E*-anti isomers in the solid-state.[339] The imine functionalities of both DmpDAB and DitopDAB are evidenced by medium intensity C=N absorptions at *ca.* 1610 cm^{-1} in the IR spectra of both α-dialdimines.

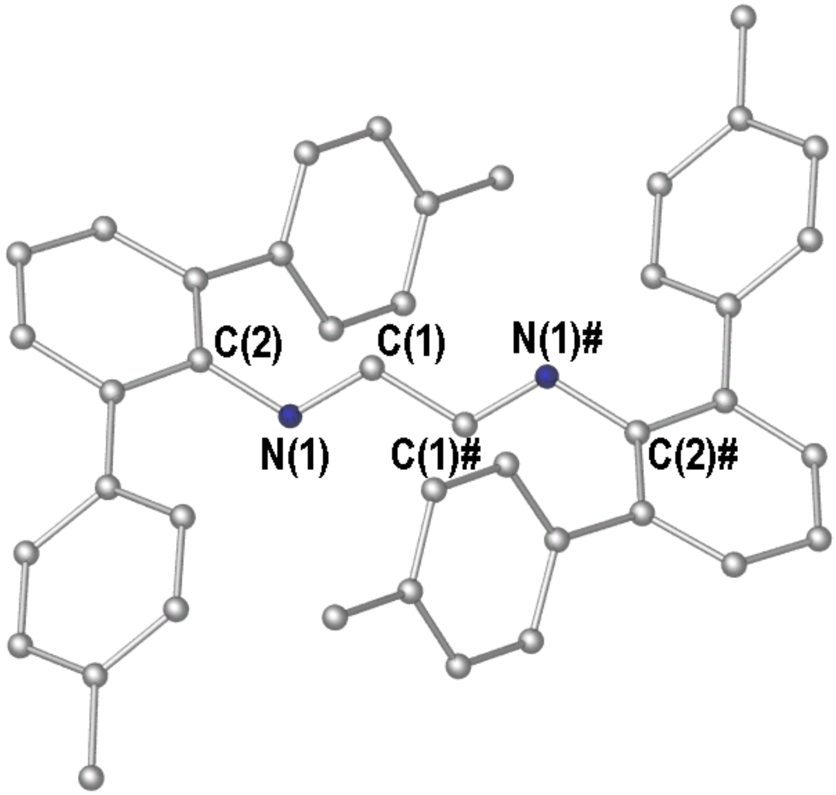
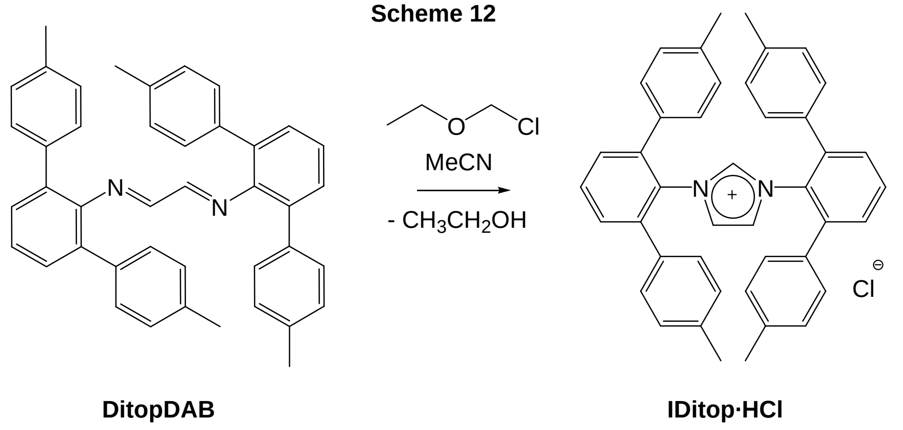


Figure 1. Molecular structure of DitopDAB (POV-RAY illustration, 10% van der Waals radii). All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (º): C(1)-N(1) 1.279(3), C(1)-C(1)# 1.453(5), N(1)-C(2) 1.421(3), C(1)-N(2)-C(2) 118.9(2), N(1)-C(1)-C(1)# 119.2(3). Symmetry transformation used to generate '#' atoms: *2-x, -y, 1-z.* , POV-RAY illustration, 10% van der Waals radii

The preparation of 1,3-bis(2,6-terphenyl)imidazolium salts from DitopDAB and DmpDAB was initially attempted using paraformaldehyde in the presence of hydrochloric acid, as per the method described by Nolan for IDipp·HCl (Scheme 2).[317] However, this led to hydrolysis of the diazabutadiene to regenerate the parent anilines as their hydrochloride salts. Reverting to Arduengo's 1999 method (Scheme 3) both were treated with chloromethylethyl ether in acetonitrile at ambient temperature.[315] This method was successfully gave IDitop·HCl (Scheme 12) but the analogous reaction of DmpDAB, even at elevated temperatures, afforded only Dmp anilinium chloride. As cyclisation of diazabutadienes to imidazolium salts necessitates an *E-syn* isomer for formylation,[292] it is reasonable to suggest that the steric buttressing of DmpDAB may prevent imidazolium formation.

Scheme 12

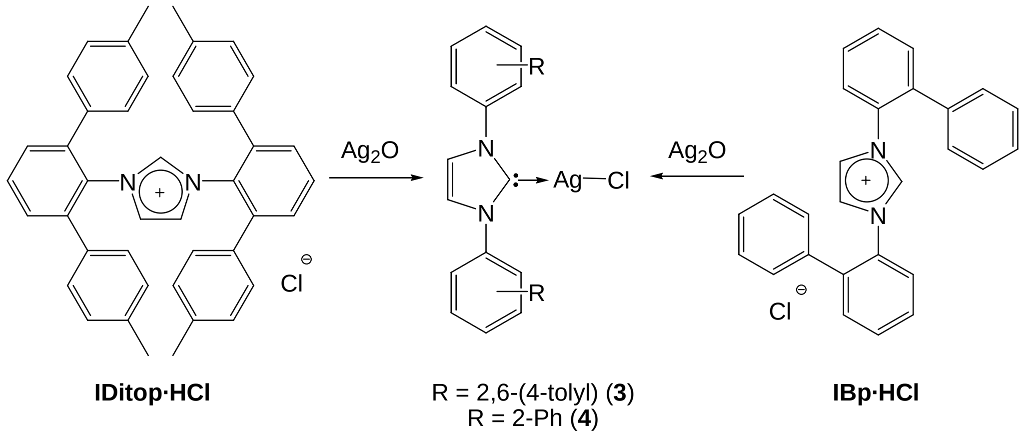


The imidazolium salt IDitop·HCl is a colourless deliquescent thermally robust solid (dec. 188 ºC without melting). As per DitopDAB, its ^{1}H NMR spectrum (d_6-DMSO) exhibits a single well-defined methyl singlet at 2.35 ppm that is indicative of symmetrical tolyl environments on an NMR timescale in solution. Attempts to obtain crystalline samples of IDitop·HCl suitable for single crystal X-ray structure determination were not successful.

NHC silver(I) coordination compounds are commonly utilised precursors for transmetallation of NHCs onto catalytically active group 8-10 metals.[92, 121] As a preliminary foray into the coordination chemistry of IDitop, a silver(I) chloride coordination complex, [AgCl(IDitop)] (**3**), was prepared by reaction of IDitop·HCl with excess silver(I) oxide in dichloromethane at 50 ºC (Scheme 13).[297, 332] In order to assess the contribution of both 2- and 6-aryl substituents on the principal *N*-aryls of IDitop, and its overall steric bulk, a silver(I) chloride complex coordinated by *N*,*N'*-bis(2-phenylphenyl)imidazol-2-ylidene (IBp), [AgCl(IBp)] (**4**), was also prepared using analogous preparative procedures.

Compounds **3** and **4** are thermally robust complexes (dec. >315 ºC) that, even on prolonged exposure to sunlight, do not reductively deposit silver. Both compounds are soluble in dichloromethane and may be isolated in analytically pure form by filtration of the Ag_2O:NHC·HCl reaction mixtures and removal of volatiles under reduced pressure. Single crystals of **3** and **4** suitable for single crystal X-ray structure determination were grown from dichloromethane-hexane solutions (Figure 3). Compound **3** crystallises with half a molecule in the asymmetric unit that lies about a two-fold axis with Ag(1), Cl(1) and C(1) on the two-fold axis. Compound **4** crystallises with one whole molecule in the asymmetric unit.

Scheme 13



The molecular structures of **3** and **4** (Figure 2) provide considerable insight into the steric bulk of coordinated NHCs bearing *N*-2,6-terphenyl and *N*-2-phenylphenyl substituents. Calculation of 'Tolman' type cone angles[340] (Figure 2) for the NHCs of **3** and **4** using the structural location of the Ag atoms calculated here indicates angles of 184.01(20)° and 131.07(5)° respectively.

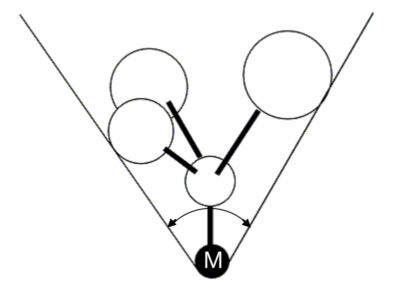


Figure 2. Diagrammatical representation of the Tolman cone angle, showing the relationship between the metal (M) and the ligand's groups.

The former angle exceeds the 155.1° angle calculated for the Ag(IDipp) unit of [AgCl(IDipp)],[332] which exhibits Ag-Cl/C bonding parameters consistent with those of **3** and **4** (Ag-Cl 2.316(17), Ag-C 2.056(6) Å).[332] The impressive cone angles of 1,3-bis(Tmt)imidazol-2-ylidene (Tmt = 3,5-bis(2,4,6-trimethyl)phenyl)[314] and 1,3-bis(4-(2',3',4',5-tetraphenylphenyl)phenyl)imidazol-2-ylidene,[297] which are both likely to exceed 180°, are likely to have a majority of their bulk placed remote to the metal coordination sphere. It is likely that this leads to minimal spatial influence at the metal. Thus, IDitop possesses the largest cone angle of any monocyclic NHC prepared to date.

The 2-phenyl placement of **4** (Figure 3) has precedent in the 1,3-bis(2-phenylphenyl)imidazolin-2-ylidene NHC of Bellemin-Laponnaz,[329] which differs to **4** in its saturation of the 4,5-hetrocyclic C-C bond. It is also relevant to the recent chiral imidazolin-2-ylidenes of Shi and co-workers[341] that utilise the asymmetric principles of Grubbs, *cf.* asymmetric olefin metathesis catalysts (chirality at 4- and 5-position of heterocycle, e.g. 4*R*,5*R*-NC(H)PhC(H)PhN),[342] to guide the 2-phenyl groups in order to achieve C_2-NHC symmetry at the coordinated metal.

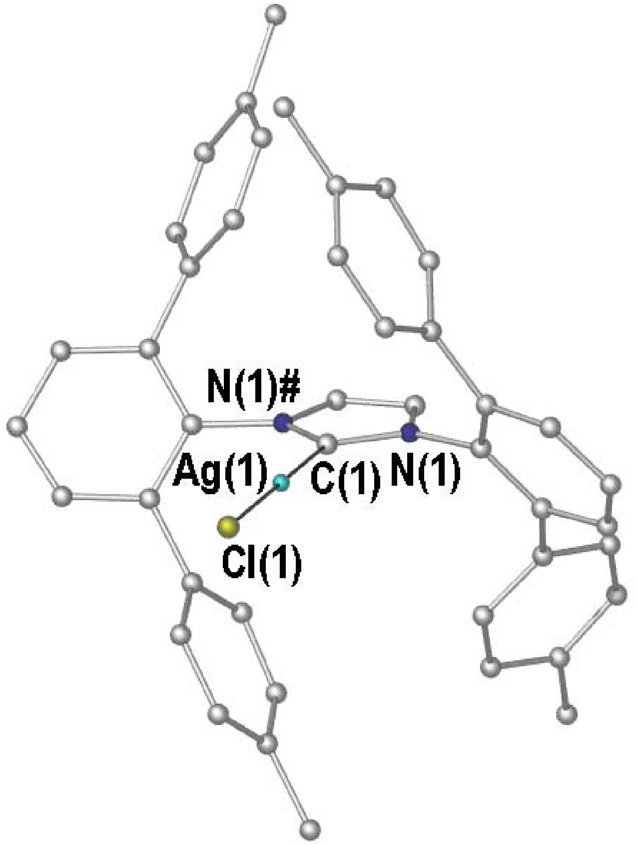


Figure 3. Molecular structure of compound **3** (POV-RAY illustration, 10% van der Waals radii). All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ag(1)-Cl(1) 2.345(2), Ag(1)-C(1) 2.062(8), 4,5-C-C 1.326(11), N(1)-C(1)-N(1)# 103.1(7), Tolman cone angle[340] formed by NHC about Ag(1) 184.01(20). Symmetry transformation used to generate '#' atoms: -*x*, *y*, ½-*z*.

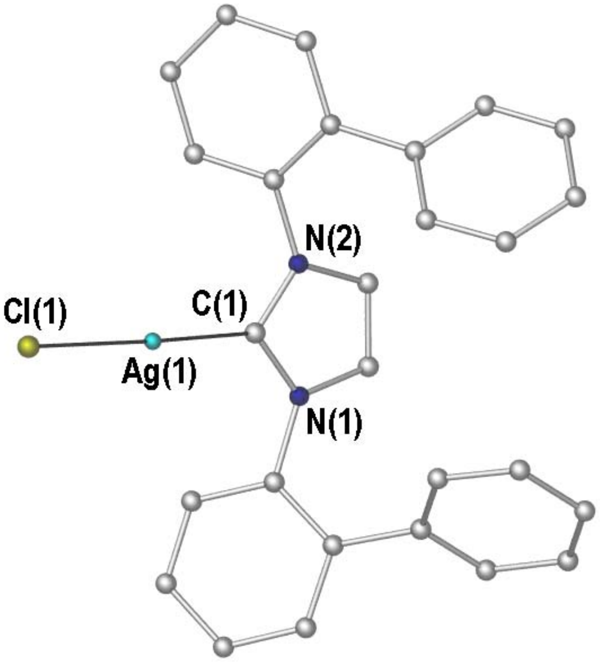
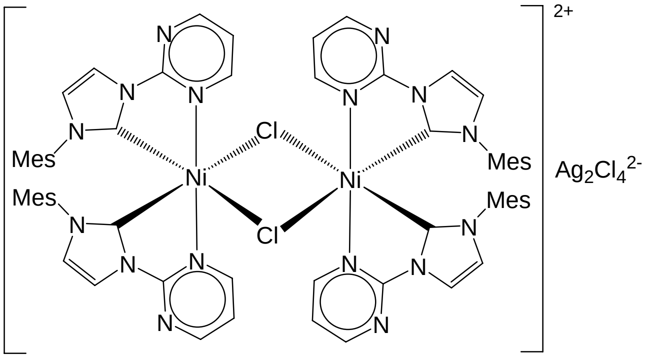


Figure 4. Molecular structure of compound **4**. All hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (º): Ag(1)-Cl(1) 2.3440(11), Ag(1)-C(1) 2.079(2), 4,5-C-C 1.343(3), N(1)-C(1)-N(2)# 103.79(18), Tolman cone angle[340] formed by NHC about Ag(1) 131.07(5).

A serendipitous product was isolated from the reaction of IBp·HCl and an inadequate quantity (0.5 equivalent) of Ag_2O in dichloromethane. Instead of the intended silver(I) chloride carbene complex, an intermediate species $[IBpH]_2[Ag_2Cl_4]$ (**5**) was isolated, featuring an Ag_2Cl_4 dianion with two IBp·H imidazolium units (Figure 4). It is proposed that the formation of **5** arose from the addition of **4** to residual IBp·HCl to afford $[Ag_2Cl_4(IBpH)_2]$ and, presumably, free IBp; a deliberate reaction was not attempted however. No additional data was recorded for **5** due to its low yield. Compound **5** crystallises in the monoclinic spacegroup C2/c with one cation, half a dianion and one molecule of dichloromethane in the asymmetric unit. The bonding parameters of the two identical imidazolium subunits (N-C-N 108.51(14)º, 4,5-C=C 1.340(3) Å) are comparable to those of 1,3-diphenylimidazolium perchlorate (109.2º and 1.33(9) Å respectively).[343] As expected, the N-C-N angle 108.51(14)º is increased relative to that of **4** (103.79(18)º) reflecting the aromaticity of the former. The Ag-Cl distances within the Ag_2Cl_4 centre (terminal 2.4039(7) , bridging 2.4258(9) and 2.8020(8)) Å are long relative to those of **3** and **4** (2.344(2) and 2.3440(11) Å respectively). These distances are comparable to those of a similar Ag_2Cl_4 subunit in the nickel complex **6**[344] (terminal 2.3312(15), bridging 2.3997(16) and 2.7500(19) Å).[344] The two Cl-Ag-Cl angles (112.9º and 152.4º) indicate that the central $[Ag_2Cl_4]^-$ subunit is composed of two weakly-associated $(AgCl_2)^-$ anions.

Compound 6



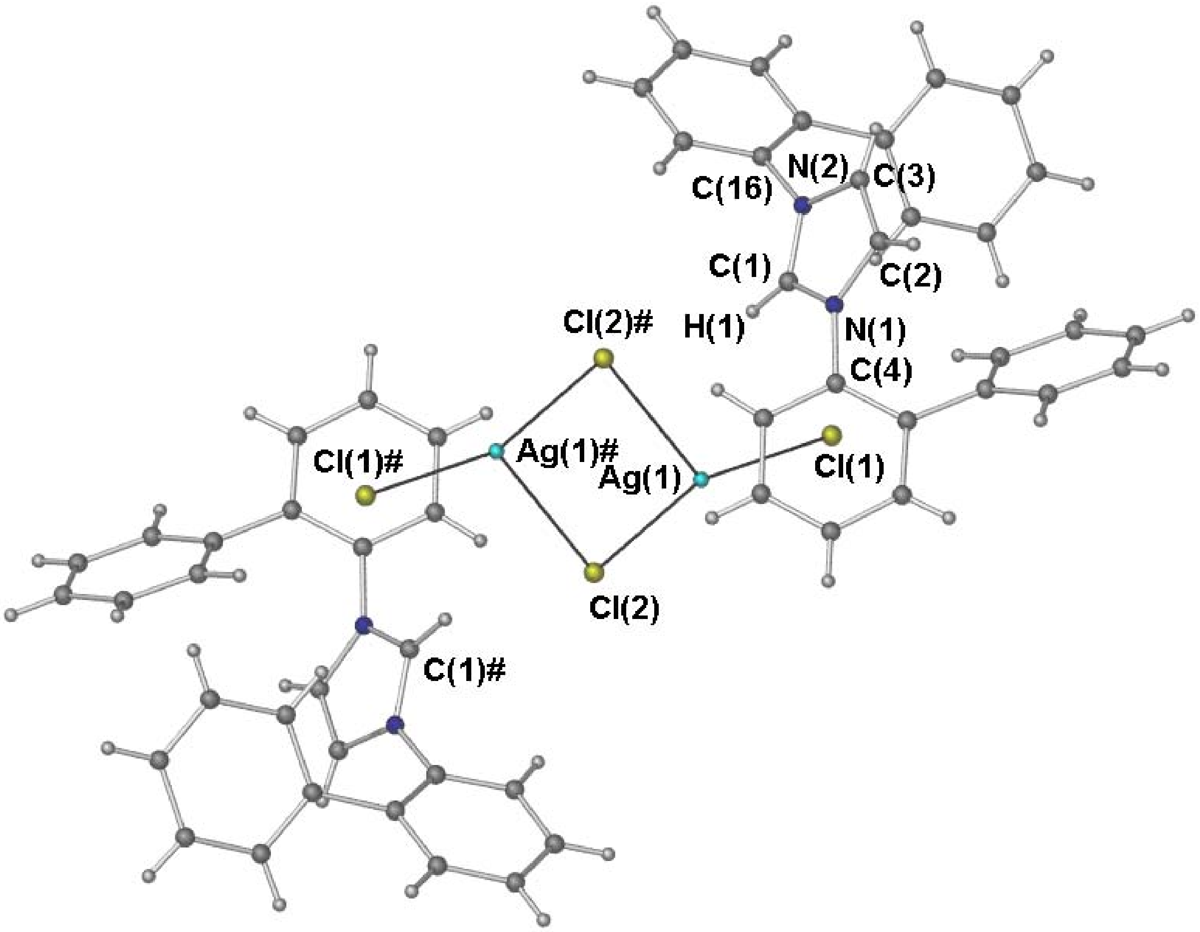


Figure 5. Structure of compound **5**. Selected bond lengths (Å) and angles (º): Ag(1)-Cl(1) 2.4039(7), Ag(1)-Cl (2) 2.4258(9), C(2)-C(3) 1.340(3), N(1)-C(1)-N(2) 108.51(14).

5.6 Conclusions

In summary, the first *N*,*N'*-bis(2,6-terphenyl) subtituted imidazol-2-ylidene; IDitop, as its silver(I) chloride complex, has been successfully prepared in readiness for use as a support ligand in NHC coordination chemistry. Attempts to undertake similar chemistry using the bulkier terphenyl Dmp were unsuccessful. Molecular structure comparison of AgCl coordinated IDitop with IBp indicates a significantly greater 'cone-angle' for the former which surpasses that of the commonly favoured 'bulky' NHC IDipp.

Experimental

General

Diethyl ether and hexane were dried over sodium and freshly distilled from sodium diphenylketyl before freeze-thaw degassing prior to use. Toluene was dried over sodium and freshly distilled from potassium before freeze-thaw degassing prior to use. Dichloromethane was dried over calcium hydride and freshly distilled prior to use. $DmpNH_2$ and $DitopNH_2$ were prepared using the procedure of Tilley and Gavenonis for the preparation of $DmpNH_2$.[310] BpDAB was made using the same procedure as that used for DitopDAB with ethanol as solvent. All other chemicals were purchased from Sigma-Aldrich and used as received. The preparations of compounds **3** and **4** were performed using conventional Schlenk techniques under an atmosphere of ultra high purity argon. Infrared spectra were recorded as Nujol mulls using sodium chloride plates on a Nicolet Nexus FTIR spectrophotometer. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded at 300.13 MHz and 75.46 MHz respectively using a Varian Gemini 2000 spectrometer with chemical shifts referenced to the residual ^{1}H resonances of the *deuterated* solvents used. Melting points were determined in glass capillaries. Mass spectrometric analyses were conducted on a Finnegan LCQMS under electronic ionisation conditions. All microanalyses were conducted by the Campbell Microanalytical Laboratory, Chemistry Department, University of Otago, P.O. Box 56, Dunedin, New Zealand.

X-ray structure determination

All single crystal X-ray structure determinations were undertaken using samples mounted on glass fibres in silicone oil. Data were collected using graphite monochromated $Mo_{K\alpha}$ X-ray radiation (λ = 0.71073 Å) at 123(2)K on a Bruker X8 Apex diffractometer. Structural solution and refinement was carried out using the SHELX suite of programs.[164]

DitopDAB

$DitopNH_2$ (3.30 g, 12.07 mmol), 40 % aqueous glyoxal (0.86 g, 6.03 mmol), and acetonitrile (20 mL) were stirred at 50 °C for three days resulting in a colour change to brown and the formation of DmpDAB as a yellow precipitate. Filtration and washing with cold methanol afforded analytically pure DmpDAB (1.81 g, 53%), m.p. 208 °C. Elemental analysis calculated (%) for $C_{42}H_{36}N_2$: C 88.69, H 6.38, N 4.93; Found: C 88.94, H 6.31, N 4.91; ^{1}H NMR (C_6D_6): δ 2.20 (s, 12H, p-CH_3), 6.98 (d, 8H, $^{3}J_{HH}$ 7.8 Hz, 2/3-Ar′CH), 7.00 (t, 2H, $^{3}J_{HH}$ 7.5 Hz, 4-ArCH), 7.14 (d, 8H, $^3J_{HH}$ 7.8 Hz, 2/3-Ar′C*H*), 7.23 (d, 4H, $^3J_{HH}$ 7.5 Hz, 3/5-ArC*H*), 7.62 (s, 2H, N=C*H*); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 21.6 (*p*-*C*H_3), 125.9, 129.3, 130.6, 133.8 (Ar*C*H), 129.5, 136.4, 137.7, 148.0 (Ar*C*), 165.5 (N=*C*); IR (Nujol, cm^{-1}), ν 1613 m, 1571 w, 1303 w, 1289 w, 1188 w, 1111 w, 1076 w, 1035 w, 1017 w, 948 w, 941 w, 846 w, 830 w, 812 m, 787 m, 764 m, 745 m, 660 w; EIMS (*m/z*) 568.3 (100% [M$^+$]).

DmpDAB

DmpNH$_2$ (1.10 g, 3.90 mmol), 40 % aqueous glyoxal (0.4 mL, 1.95 mmol), and acetonitrile (10 mL) were stirred for two days at 60 °C resulting in the precipitation of DmpDAB as a yellow solid. The product was filtered, washed with acetonitrile (10 mL) and recrystallised from ethyl acetate to afford a microcrystalline powder (0.819 g, 72%), m.p. 252-253 °C. Elemental analysis calculated (%) for $C_{50}H_{52}N_2$: C 88.19, H 7.70, N 4.11. Found: C 87.59, H 7.97, N 4.16; ^{1}H NMR (C_6D_6,): δ 1.86 (s, 24H, *o*-CH_3), 2.29 (s, 12H, *p*-CH_3), 6.81 (s, 8H, 3/5-Ar′C*H*), 6.89 (d, 4H, $^3J_{HH}$ 6.0 Hz, 3/5-ArC*H*), 6.90 (t, 2H, $^3J_{HH}$ 6.0 Hz, 4-ArC*H*) 7.13 (s, 2H, N=C*H*); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 20.8 (*o*-*C*H_3), 21.7 (*p*-*C*H_3), 126.0, 130.0, 132.5, 136.2, 136.5, 136.6, 148.0, (Ar*C*), 161.4 (N=*C*); IR (Nujol, cm^{-1}), ν 1612 m; 1574 w, 1414 m, 1290 m, 1261 m, 1192 w, 1156 w, 1096 m, 1072 m, 1029 m, 932 w, 848 s, 825 m, 803 s, 799 w, 765 s, 741 m, 659 w, 604 s; EIMS (m/z) 681.5 (25% [MH$^+$]), 703.6 (100% [MNa$^+$]).

IDitop·HCl

DitopDAB (0.57 g, 1.0 mmol) and chloromethylethyl ether (2.0 mL, 22 mmol) were stirred for 5 minutes before adding acetonitrile (3 mL). The resultant brown solution was stirred for 1 hour after which all volatiles were removed *in vacuo* to afford a brown solid. The crude product was extracted with water (10 mL), washed with diethyl ether (10 mL) and recrystallised from acetone to afford fine white needles (0.44 g, 70%), m.p. 288 °C (dec). Elemental analysis calculated (%) for $C_{43}H_{37}N_2Cl$: C 83.68, H 6.04, N 4.54; Found: C 83.15, H 6.09, N 4.36; ^{1}H NMR (*d*$_6$-DMSO): δ 2.35 (s, 12H, *p*-CH_3), 6.85 (d, 8H, $^3J_{HH}$ 8.2 Hz, 2/3-Ar′C*H*), 7.12 (d, 8H, $^3J_{HH}$ 8.2 Hz 2/3-Ar′C*H*), 7.41 (d, 4H, $^3J_{HH}$ 7.6 Hz, 4-ArC*H*), 7.49 (s, 2H, 4,5-C_2H_2), 7.68 (s, 2H, $^3J_{HH}$ 7.6 Hz, 3/5-ArC*H*), 9.41 (s, 1H, 2-C*H*); $^{13}C\{^1H\}$ NMR (*d*$_6$-DMSO): 20.8 (*C*H_3), 124.8 (4,5-C_2), 128.5, 129.2, 130.6, 131.5 (Ar*C*H), 129.3, 133.6, 137.5, 138.8 (Ar*C*), 139.1 (2-*C*); IR (Nujol, cm^{-1}), ν 1512 m, 1402 m, 1309 m, 1243 s, 1202 s, 1107 m, 1088 m, 1036 m, 1019 m, 954 w, 937 w, 924 w, 851 m, 841 m, 814 s, 790 s, 768 m, 749 m, 670 w, 616 w.

IBp·HCl

BpDAB (1.08 g, 3.0 mmol) and chloromethylethyl ether (4.0 mL, 44 mmol) were stirred for 2 minutes before adding acetonitrile (10 mL). The resultant brown solution was stirred for 1 hour, after which the volatiles were removed *in vacuo* to afford a brown solid. A diethyl ether (30 mL) or the crude product was extracted into water (30 mL) and dried under reduced pressure to give the title compound as a brown solid that was washed with toluene (5 mL) (0.78 g, 64%), m.p. 140-143 °C. Elemental analysis calculated (%) for $C_{27}H_{21}N_2Cl$: C 79.30, H 5.18, N 6.85; Found: C 79.37, H 5.53, N 6.37; ^{1}H NMR (d_6-DMSO): δ 7.20 (d, 4H, $^3J_{HH}$ 6.0 Hz, 2/6-Ar’C*H*), 7.42 (coincident dd and t, 6H, 3,4,5-Ar’C*H*), 7.62 (coincident d and s, 4H, 3-ArC*H* and 4,5-C_2H_2), 7.69 (dd, 2H, $^3J_{HH}$ 7.8 Hz, 7.8 Hz, 4-ArC*H*), 7.74 (dd, 2H, $^3J_{HH}$ 7.8 Hz, 7.8 Hz, 5-ArC*H*), 7.75 (d, 2H, $^3J_{HH}$ 7.8 Hz, 6-ArC*H*), 9.91 (s, 1H, 2-C*H*); ^{13}C{^{1}H} NMR (d_6-DMSO): δ 124.1 (4,5-C_2), 127.2, 128.4, 128.6, 128.8, 129.1, 131.2, 131.5, 131.3, 136.1, 137.3 (Ar*C*), 138.2 (2-*C*); IR (Nujol, cm^{-1}), v 1662 w, 1596 w, 1538 m, 1338 m, 1266 m, 1224 m, 1159 m, 1118 m, 1069 m, 1009 w, 918 w, 763 s, 734 s, 702 s, 682 m, 654 m, 610 m.

[AgCl(IDitop)] (3)

IDitop·HCl (0.46 g, 0.74 mmol) and Ag_2O (0.18 g, 0.74 mmol) were stirred under vacuum for 30 minutes before addition of dichloromethane (50 mL). The resulting slurry was stirred for 20 hours to afford a pale brown solution. Filtration, followed by removal of volatiles under reduced pressure, afforded the title compound as a pale brown solid that was subsequently recrystallised from dichloromethane-hexane as colourless plates (0.40 g, 73%), m.p. >315 °C. Elemental analysis calculated (%) for $C_{44}H_{38}AgCl_3N_2$ (NB: +CH_2Cl_2): C 65.32, H 4.73, N 3.46; Found: C 65.97, H 4.64, N 3.79; ^{1}H NMR (CD_2Cl_2): δ 2.35 (s, 12H, *p*-C*H*$_3$), 6.33 (s, 2H, 4,5-$C_2\mathit{H}_2$), 6.92 (d, 8H, $^3J_{HH}$ 8.2 Hz, 2/3-Ar’C*H*), 7.19 (d, 8H, $^3J_{HH}$ 8.2 Hz, 2/3-Ar’C*H*), 7.33 (d, 4H, $^3J_{HH}$ 7.2 Hz, 3/5-ArC*H*), 7.48 (t, 2H, $^3J_{HH}$ 7.2 Hz, 4-ArC*H*); ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 21.0 (*p*-*C*H$_3$), 122.9 (4,5-C_2), 128.8, 129.3, 131.7, 137.5 (Ar*C*H), 128.6, 130.0, 136.0, 139.2 (Ar*C*); IR (Nujol, cm^{-1}), v 1944 w, 1890 m, 1831 w, 1781 w, 1736 w, 1642 w, 1609 w, 1566 w, 1512 s, 1470 s, 1449 s, 1402 s, 1309 m, 1243 s, 1206 s, 1203 s, 1197 m, 1107 m, 1088 m, 1036 m, 1019 w, 954 w, 937 w, 924 w, 851 m, 841 m, 815 s, 791 s, 768 m, 749 m, 670 w, 616 w; EIMS (*m/z*) 581.4 (100% IDitopH$^+$).

[AgCl(IBp)]·CH_2Cl_2 (4)

IBp·HCl (0.82 g, 2.0 mmol) and Ag_2O (0.46 g, 2.0 mmol) were reacted and worked up in an identical fashion to **1**. Recrystallisation from dichloromethane/hexane afforded **2** as small colourless plates (0.64 g, 62%), m.p. 135-137 °C, dec. >315 °C. Elemental analysis calculated (%) for $C_{28}H_{22}AgCl_3N_2$: C 55.98, H 3.69, N 4.66; Found: C 55.41, H 3.70, N 4.69; ^1H NMR (CD_2Cl_2): δ 6.79 (s, 2H, 4,5-C_2H_2), 7.19 (br d, 4H, 2/6- or 3/5-Ar'C*H*), 7.36 (m, 6H, coincident 2/6- or 3/5-Ar'C*H* and ArC*H*), 7.46 (br d, 2H, 3- or 6-ArC*H*), 7.54 (m, 4H, coincident 3- or 6-ArC*H* and 4- or 5-ArC*H*), 7.59 (br t, 2H, 4- or 5-ArC*H*); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 123.7 (4,5-C_2), 128.1, 128.4, 129.3, 129.4, 129.6, 130.4, 132.1 (Ar*C*H), 137.9, 138.4, 138.8 (s, Ar*C*); IR (Nujol, cm^{-1}), ν 1978 w, 1958 w, 1938 w, 1922 w, 1893 w, 1815 w, 1769 w, 1746 w, 1731 w, 1704 w, 1698 w, 1681 w, 1660 w, 1651 w, 1633 w, 1606 w, 1583 w, 1564 w, 1557 w, 1538 w, 1503 m, 1407 m, 1352 m, 1339 m, 1279 m, 1264 s, 1224 w, 1185 w, 1166 w, 1152 w, 1115 w, 1090 w, 1073 w, 1049 w, 1031 w, 996 w, 979 w, 968 w, 945 m, 925 w, 892 w, 871 w, 831 w, 761 s, 749 m, 725 s, 702 s, 686 m, 661 w, 611 m; EIMS (*m/z*) 373.4 (100% $IBpH^+$), 852.3 (24% $Ag(IBp)_2^+$).

[$Ag_2Cl_4(IBpH)_2$] (5)

Reaction conditions were similar to that for compound **4** but with the reduction of the silver oxide to half an equivalent. The reaction was stirred for 20 hours to afford a pale brown solution. Filtration was followed by removal of volatiles under reduced pressure, and the resultant light-brown solid was recrystallised from dichloromethane to afford colourless plates.

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Appendix 1

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