Aryl-NHC group 13 trimethyl complexes : structural, stability and bonding insights

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**DIVISION OF CHEMISTRY AND BIOLOGICAL CHEMISTRY
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Aryl-NHC Group 13 Trimethyl Complexes: Structural, Stability and Bonding Insights

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Abbreviations

Å	angstrom
δ	NMR chemical shift (ppm)
τ	irreducible representations
A	abnormal
ACN	acetonitrile
BIAN	bis(imino)acenaphthene
BSE	bond snapping energy
Bu	butyl
C ₅ Me ₅	pentamethylcyclopentadienyl
CIF	crystallographic information file
Cod	cyclooctadiene
CSOV	constrained space orbital variation
Cy	cyclohexyl
CAAC	cyclic(alkyl)(amino) carbenes
D	doublet
DCM	dichloromethane
DFT	density functional theory
Dipp	2,6-diisopropylphenyl
diMe-MDI	1,3-dimethyl-2-methylene-2,3-dihydro-1 <i>H</i> -imidazole
DMSO	dimethylsulfoxide
EtIBu [†]	1,2-ethylene-3,3'-di-tert-butyl-diimidazole-2,2'-diylidene
EDA	bond energy decomposition analysis
E _{diss}	dissociation energy
ESI	electrospray ionisation
ΔE_{elstat}	electrostatic interaction
ΔE_{int}	orbital interaction
ΔE_{Pauli}	pauli repulsion
ΔE_0	steric interaction
$E_{1/2}$	redox potential
Eqn	equation
Et	ethyl
Et ₂ O	diethyl ether
EtOAc	ethyl acetate
FLPs	frustrated lewis pairs
FTIR	fourier transformed infrared spectroscopy

HOMO	highest occupied molecular orbital
HOAc	acetic acid
HRMS	high resolution mass spectroscopy
Hz	hertz
IMe	1,3-di(methyl)imidazol-2-ylidene
IBox	bisoxazoline-based N-heterocyclic carbene
liPrMe	1,3-diisopropyl-4,5-dimethylimidazoylidene
iPr	<i>iso</i> -propyl
IPr	1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene
IMes	1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
IAd	1,3-diadamantylimidazol-2-ylidene
ItBu	1,3-di- <i>tert</i> -butylimidazol-2-ylidene
IR	infrared spectroscopy
<i>J</i>	<i>J</i> -coupling
LA	<i>rac</i> -lactide
LiHMDS	lithium bis(trimethylsilyl)amide
LUMO	lowest unoccupied molecular orbital
M	Molarity
m	Multiplet
M.p	melting point
Me	methyl
MeOH	methanol
Mes	2,4,6-trimethylphenyl
NaHMDS	sodium bis(trimethylsilyl)amide
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance
<i>N</i>	normal
<i>o</i>	ortho
<i>P</i>	para
Ph	phenyl
PHC	P-heterocyclic carbene
PLA	polylactide
Ppm	parts per million
Q	quintet
Quin	quinuclidine
RBF	round-bottomed flask

ROP	ring-opening polymerisation
S	singlet
Sat.	saturated
SIMes	1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene
SIPr	1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene
sNHC	saturated N-heterocyclic carbene
SItBu	1,3-di- <i>tert</i> -butylimidazolin-2-ylidene
t-Bu	<i>tert</i> -butyl
TEP	Tolman electronic parameter
THF	tetrahydrofuran
TMSCl	trimethylsilyl chloride
TM	transition metal
uNHC	unsaturated N-heterocyclic carbene
Unsat.	unsaturated
% V_{Bur}	percent buried volume

Abstract

This first aim of this thesis was to synthesize a series of new N-heterocyclic carbene group 13 metal complexes. The synthesis of the new compounds was achieved using group 13 trimethyl complexes and NHC starting materials. The species produced comprises of aluminium, gallium and indium group 13 metals. Furthermore, reactivity studies have also been carried out on the obtained NHC species with a series of electrophiles. All the structures synthesized have been fully characterized by single crystal X-ray studies, multi-nuclear NMR, IR and mass spectrometry.

The second aim of this thesis was to investigate the origin of the range of stability displayed by the newly synthesised complexes. These differences have been assessed using percent buried volume, $\% V_{\text{Bur}}$, topographic steric maps, dissociation energy, E_{diss} , and calculated bond snapping energy (BSE) decomposition analysis of the M-NHC bonds (M = Al, Ga and In). The results obtained indicated that the differences in stability observed are mainly attributed to small differences in the steric demands of the NHC ligands.

Finally, preliminary investigations to evaluate applicability and efficiency of solvent-free mechanochemical techniques for the synthesis of main group NHC complexes have been carried out. The rapid and high yielding syntheses of NHC gallium and indium trichlorido complexes highlight the potential of this technique.

Introduction

1. Introduction

1.1 N-heterocyclic Carbene (NHC)

Generally speaking, N-heterocyclic carbenes are divalent species, in which the carbenic centre is bonded to at least one nitrogen atom within the heterocycle.¹ Wanzlick² was the first to demonstrate their existence, closely followed by Öfele³ and Lappert,⁴ who highlighted their usability as ligands in organometallic chemistry. However, it was only the discoveries by Bertrand and co-workers on the first stable (phosphine)(silyl) carbene **1**⁵ and, more importantly, the Arduengo carbene **2**⁶ depicted in Figure 1.1 that truly paved the way towards the use of NHCs extensively in the field.

Figure 1.1

1.1.1 Electronic Properties

Currently, the majority of the NHCs reported in the literature belong to the family of 5-membered nitrogen heterocycles. Nevertheless, heterocyclic NHCs of differing sizes and substitution patterns have been reported, alongside observations that variations of these types can exert profound effects on the final steric and electronic properties of the carbene moieties. The structural features of the Arduengo carbene provide a classical representation to explain the overall electronic and steric contributions to the stability of the carbene centre C².

Figure 1.2: Illustration of the σ -withdrawing and the π -donating effects of the nitrogen atoms in stabilising the singlet carbene.

As shown in Figure 1.2, the carbene centre exhibits a singlet ground state configuration where the highest occupied molecular orbital (HOMO) contains a formally sp^2 -hybridized lone pair, and the lowest occupied molecular orbital (LUMO) possesses an empty p-orbital.

The adjacent nitrogen atoms play an important role in stabilizing the overall structure. On one hand, the inductive σ electron-withdrawing effect stabilizes the σ non-bonding orbital by increasing its s-character whilst the p_x orbital remains unchanged. On the other hand, the mesomeric effect comprises the interaction of the carbon orbitals and the p or π orbitals of the substituents. The cyclic nature of the NHCs also helps to force the carbene carbon into a bent, sp^2 -like arrangement, favouring the singlet state configuration.⁷

Figure 1.3: Structures of the various classes of NHCs that have been reported.

These general features of carbene stabilization apply to all classes of the NHCs, although the relative effects vary within the various classes of NHC compounds. The Arduengo carbene **2** (IAd) is kinetically stabilized by the large adamantyl groups on the nitrogen atoms, sterically preventing dimerization (Wanzlick equilibrium).⁸ However, this steric proximity demand can be reduced with NHCs deriving from heteroaromatic compounds, as additional stability is provided from their partial aromaticity. This partial aromaticity effect has been calculated with model imidazol-2-ylidenes to be around 25 kcal mol⁻¹,⁹ hence, the simple methyl substituted NHC 1,3-di(methyl)imidazol-2-ylidene (IMe) is observed in solution. Consequently, various NHCs benefit from partial aromaticity; however, this is not a prerequisite as many stable NHCs have been successfully synthesized without contributions from this effect, with the first example, 1,3-di(mesityl)imidazolin-2-ylidene (SIMes, type **B** in Figure 1.3), being reported by Arduengo *et. al.* in 1995.¹⁰

As previously alluded, 5-membered nitrogen heterocycles are the most common form of NHCs, however, variants containing smaller or larger ring sizes have been reported (types **I** and **J** in Figure 1.3).¹¹ It is also not necessary for the NHC to possess two nitrogen atoms adjacent to its carbene center, indeed, other heteroatoms such as sulphur (**C**) and oxygen (**D**),¹² or even a single nitrogen substituent within the heterocycle (e.g., the cyclic(alkyl)(amino) carbenes (CAAC), type **G** in Figure 1.3) has been reported, with the latter compounds receiving considerable attention due to their intrinsically strong donor properties.¹³

Lastly, the generation of a carbene centre at an alternative positions rather than C2, stabilized by a single nitrogen atom is possible. These carbene species termed ‘mesoionic’ or ‘abnormal’ (type **H**, in Figure 1.3) are generally more electron-donating in character and display very different properties than their ‘normal’ carbene counterparts.⁷

Figure 1.4: Structural modifications applied on NHC.

The NHC electronic properties can be modified or tuned by altering various structural parameters on the NHC backbone. The ease at which starting material may be simply modulated in addition to the wide range of applicable synthetic routes result in a myriad of potential structural derivatives. This has led to NHCs becoming a very attractive system for use in the fields of synthetic chemistry and catalysis.^{7, 14} As shown in Figure 1.4 for 5-membered NHC species, the substituents adjacent to the carbene center have the largest steric influence on the carbene environment (since they are closest to the C_{carbene}), while the class of the heterocycle and the ring backbone mainly exhibit effects over its electronic properties.^{7, 15}

The most widely implemented assessment tool to describe the electronic properties of NHC ligands is the Tolman electronic parameter (TEP). Originally, the TEP was designed to evaluate the electron-donating properties of phosphines,¹⁶ but this method was also adopted for the description of NHC species.¹⁷ The evaluation of the donating ability of a ligand (L) is carried out by measuring the infrared stretching frequencies of the carbonyl ligands on transition metal carbonyl complexes. If the ligand is a strong electron donor, the metal centre will become more electron-rich and, hence, increase the π -backbonding ability from the

metal center to the carbonyl ligands. This effect weakens the C-O bond resulting in a reduction of its infrared stretching frequency. There are noticeable variations of the NHC TEP values making this parameter very useful in general. However, this method is dependent on the resolution of the infrared spectrometer (NHCs TEP values only span about 10 cm^{-1}), and the values are also highly dependent on the solvent used during the measurement.^{7, 17} This has led to the development of alternative methods, such as ^{13}C NMR, pK_a and the redox potential $E_{1/2}$ by cyclic voltammetry on different metals, in attempts to increase the accuracy of measurement of the electronic properties of the NHCs.^{15, 18, 19, 20}

1.1.2 Steric Properties

As with tertiary phosphines, the steric properties of the NHC ligands do determine the chemical properties of the metals. However, the NHC ligands possess a local C_2 symmetry axis, as compared to the phosphines which have a local C_3 symmetry axis. Hence, the common tool to describe the steric properties in phosphines, the Tolman cone angle, is not recognized as representative for NHC ligands and an alternative standard descriptor model is therefore necessary.

Figure 1.5: Description of the $\%V_{\text{Bur}}$, the percentage of space of the sphere occupied by the ligand upon coordination to the metal at the centre of the sphere.

The current standard parameter, the percent buried volume, $\%V_{\text{Bur}}$, is a measure of the space of the first coordination sphere of the metal center occupied by the NHC ligand, as seen in Figure 1.5. Luigi Cavallo *et al.* reported an extended set of $\%V_{\text{Bur}}$ values of the NHCs, calculated from DFT-optimized geometries of $(\text{NHC})\text{Ir}(\text{CO})_2\text{Cl}$ complexes (Table 1.1).²¹

Figure 1.6

Table 1.1: % V_{Bur} values of DFT-optimized geometries of (NHC)Ir(CO)₂Cl complexes

NHC	Unsaturated	Saturated	Aromatic
1	18.8	19.0	18.9
2	24.9	25.4	25.1
3	26.0	25.9	26.4
4	31.1	31.8	30.4
5	35.5	36.2	38.9
6	36.1	36.6	40.8
7	30.5	31.6	30.2
8	30.5	32.4	30.2
9	31.3	32.3	30.9
10	31.6	32.7	31.2
11	33.6	35.7	31.9

One of the major advantages of the % V_{Bur} model is its generality, since it allows the assignment and comparison of the steric parameters of tertiary phosphines and NHCs on the same scale. Thus, the % V_{Bur} ¹ of the two most common tertiary phosphines, PPh₃ (30.5%) and the bulkier PCy₃ (35.3%), reflected that the PPh₃ has a moderate steric volume, whereas PCy₃ has a steric volume comparable to that of Dipp or SIPr N-heterocyclic carbene.¹⁵

¹ obtained from the optimized structure of Ni(CO)₃(PR₃) -

1.2 Group 13 Elements

As Group 13 is descended, a general trend is observed upon the transition from non-metallic to metallic character. Boron is typically regarded as a non-metal, whereas the remainder of the group are classified as metals. This is illustrated by the much higher ionization energy of boron as compared to the other elements. However, proceeding down the group, the trend of increasing ionization energy is disobeyed by Gallium, which displays a higher than expected corresponding ionization energy (see Table 1.2). This irregularity can be justified due to the electronic structure of gallium atoms. Gallium has a filled set of d-orbitals preceding its p-orbitals and their poor shielding of the d-orbitals termed “*d block contraction*” results in a higher effective nuclear charge of the valence electrons on gallium. A similar effect is also observed in the case of thallium, as it has a filled f orbital preceding its valence orbitals and in this instance is termed “*f block contraction*”.^{22, 23}

Table 1.2: Electron configuration, covalent radius and selected properties of the Group 13 elements.

Element	Electron Configuration	Electronegativity	Covalent Radius	1 st Ionization Energy/kJ mol ⁻¹	2 nd Ionization Energy/kJ mol ⁻¹	3 rd Ionization Energy/kJ mol ⁻¹
B	[He]2s ² 2p ¹	2.0	0.80	800.6	2,427.00	3,660.00
Al	[Ne]3s ² 3p ¹	1.5	1.25	577.4	1,816.00	2,744.60
Ga	[Ar]3d ¹⁰ 4s ² 4p ¹	1.6	1.25	578.3	1,979.00	2,963.00
In	[Kr]4d ¹⁰ 5s ² 5p ¹	1.7	1.50	558.3	1,820.60	2,704.00
Tl	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹	1.8	1.55	589.3	1,971.00	2,878.00

In most cases, the +3 oxidation state is the most stable oxidation state for Group 13 elements. However, the heaviest element thallium is preferentially found in the lower +1 oxidation state and the +3 state is oxidizing. The preference of the +1 oxidation state is due to the *inert pair effect*, in which the shielding and relativistic effects of the orbitals are responsible for the reluctance of the electrons in the s-orbital to take part in bonding.^{22, 23}

1.3 Group 13 Metal Carbene Complexes

In general, the NHCs are considered as Lewis bases due to their unshared electrons at the carbenic carbon, and Group 13 metal complexes are in term Lewis acids, due to their electron acceptor properties. For this reason, allowing the ‘Lewis base center’ to interact with the ‘Lewis acid’ (R[X]₃M) should form a stable Lewis acid-base adduct (Scheme 1.1). Hence, the strong σ -donating properties of N-heterocyclic carbenes (NHC) in stabilizing trivalent group 13 compounds have been established with the isolation of several aluminium, gallium, indium and thallium compounds.

Scheme 1.1: General scheme for the syntheses of NHC Group 13 Lewis acid-base adducts.

The synthesis of such compounds has been performed by the direct addition of the imidazol-ylidene, (a Lewis base) to the metal halides or hydrides (a Lewis acid) in non-polar solvent (pentane, toluene, *etc.*) under an anaerobic atmosphere to form a Lewis acid-base adduct. Based on the general synthetic procedure shown above, only 5-membered, NHC-stabilized, group 13 +3 oxidation state metal complexes will be discussed in this introduction. Other NHC-stabilized, low valent group 13 complexes, or those larger than 5 membered imidazole-ylidene will not be extensively reviewed.

1.3.1 Aluminium Carbene Complexes

1.3.1a NHC•AlH₃

Arduengo *et al.* were the first to isolate an alane adduct of an imidazole-2-ylidene (Figure 1.7, complex **3**).²⁴ This compound was synthesized after the group was able to isolate the free carbene IMes.²⁵ Complex **3** was obtained by the equimolar reaction of IMes (Lewis base) with AlH₃•NMe₃ (Lewis acid) in toluene.

Figure 1.7

The resulting compound was surprisingly stable, with a relatively high melting point of 246 – 247 °C, as compared to the starting material AlH₃•NMe₃, which decomposes above 100 °C. An additional and important attribute of complex **3** is related to the ¹³C NMR of the alane adduct (δ 173.3 ppm), which exhibits substantially upfield chemical shifts as compared to the free carbene (δ 219.7 ppm), reflecting the electron donating properties of the carbene towards the aluminium centre. Moreover, the ²⁷Al NMR shows a peak at δ 107 ppm that is a

typical 4-coordinate aluminium species.²⁴ Taken together, along with single crystal X-ray crystallographic studies, these characteristics have formed the basis for future reporting of similar structures.

Jones *et al.*^{26, 27} synthesized various carbene derivatives of AlH_3 using $\text{AlH}_3 \cdot \text{NMe}_3$ as the aluminium source. The carbene derivatives were treated with LiAlH_4 in ether. **4** was synthesized in low yields (30%) compared to when utilizing $\text{AlH}_3 \cdot \text{NMe}_3$ as the Al source (64%),²⁶ although **5** was obtained in high yields (74%) and is thermally robust with a melting point of 229°C ²⁷ compared to **3**.²⁴

Figure 1.8

Attempts made to synthesize chelating NHC group 13 trihydride complexes using the bidentate bis-carbene ligand, 1,2-ethylene-3,3'-di-tert-butyl-diimidazole-2,2'-diylidene (EtIBu^t), resulted only in formation of the monodentate adducts (ratio of EtIBu^t to $\text{MH}_3 \cdot \text{NMe}_3$ is 1:2) (Scheme 1.2). Interestingly, applying the ratio of 1:1 EtIBu^t to the metal trihydrides also leads to the same products with recovery of the ligand. The monodentate ligand complexes formed, **6** and **8**, have been used in attempts to further react with excess EtIBu^t however no reaction occurs. Furthermore, when the In complex **8**, was reacted with excess PEt_3 , only decomposition into indium metal, PEt_3 and the free ligand was observed. These observations have lead to the conclusion that the NHCs are strong donor ligands and they electronically satisfy the metal hydride centres, thus preventing the formation of hypervalent compounds (coordination number 5 or more).²⁸

Scheme 1.2: Syntheses of bis-carbene group 13 trihydrides complexes. M= Al (**6**), Ga (**7**), In (**8**). Additions of reactants were conducted at -50 - -78°C for the various complexes respectively and allowed to stir for 15 mins before warming up and stirred overnight.²⁸

1.3.1b NHC•AlMe₃

Robinson *et al.* were the first to report trimethylaluminium and gallium NHC complexes **9** and **10**. These complexes were synthesized by the slow addition of AlMe₃/GaMe₃ into a solution of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene in hexane. Colourless crystals were grown in high yields (~90%).²⁹

Figure 1.9

After their syntheses, trimethylaluminium NHC species were not extensively explored until recently, with the synthesis and structural studies on the NHC amino-linked carbene (see Scheme 1.3). The synthetic route to NHC **11** poses solubility problems in organic solvents, since its salt structure precursor **11a** contains two cationic groups, making it hard to work with strong organic bases. This insolubility issue was rectified by removal of the HBr with an excess of NaOH, to afford the amine imidazolium bromide salt. With enhanced solubility, the salt can then be easily deprotonated by NaHMDS or LiHMDS to afford carbene **11**, which can readily bind to AlMe₃ and AlEt₃, affording the trimethylaluminium and triethylaluminium complexes **12** and **13**, respectively (Scheme 1.3).³⁰

Scheme 1.3: Synthesis of amino-linked NHC trimethyl- and triethylaluminium complex **12** and **13**. Reactions i and ii are carried out at 1:1 equivalent of carbene with LiHMDS/NaHMDS in THF at -20 °C.³⁰

It was previously reported in the literature that catalytic amounts of imidazolium salts or NHCs in the presence of triethylaluminium catalysed the ring opening of epoxides and resulted in high yield synthesis of alcohols. Hence, the reactivity of complex **12** was tested by reacting with an electrophile. The reaction resulted in an insertion of the carbonyl moiety of the benzaldehyde into the Al-carbene bond, and generation of zwitterionic species **14** (Scheme 1.4). It was initially postulated that the amino-linked pendant arm was a directing group that mediated the insertion process of the electrophile although no reactivity studies have been conducted on the Al-carbene bond. In order to test their hypothesis, *Ong et al.* synthesised the analogous IMes trimethylaluminium complex (**15**) and carried out the same insertion reaction. Similar observations were reported for complex **15**, which resulted in the zwitterionic species **16**, hence failing to support the hypothesis of the active role of the amino side arm in the insertion reaction.³⁰ Complex **12** was further subjected to various other electrophiles (isocyanates and dicarboimide) and similar insertion reactions occurred; therefore, no difference in reactivity was observed between the two species (**12** and **15**).³¹

Scheme 1.4: Reactivity studies of trimethylaluminium complexes **12** and **15** to electrophiles. All reactivity studies were conducted at room temperature.³⁰

Complex **12** has been further utilised as a Lewis acid component, to form a bimetallic Ni-Al complex **17** for the C-H activation of pyridine and quinoline. The isolation of Complex **17** is of significance as it is the first structurally isolated example of a C-H activation intermediate, showing the synergistic effect of the Ni-Al interaction (Figure 1.10). The bimetallic Ni-Al complex formed is able to catalyse the alkenylation of various nitrogen heterocycles. Whilst 4-octyne results in only selective *meta*- and *para*- products, no *ortho*- selectivity was

observed which is commonly the case for directing functional groups, hence it can be stated that the complex is highly regioselective. The catalytic reaction was predominantly conducted by the addition of ligand **11**, trimethylaluminium and $\text{Ni}(\text{cod})_2$ together *in-situ*, without the need for the preparation of complex **12** or **17**, even though both species catalyze the reaction, and themselves show good reactivity (Scheme 1.5).³²

Figure 1.10: X-ray crystal structure of bimetallic Ni-Al complex **17**.³²

Scheme 1.5: General synthetic scheme for the alkenylation of nitrogen heterocycles. Reactions were carried out using 1 equiv of the heterocycles with 2 equiv of the 4-octyne and the ratio of para and meta substituted products were determined from ^1H NMR.³²

Sterically bulky NHC $\text{t}^{\text{t}}\text{Bu}$ have also been used to synthesize a series of Lewis acid-base adduct $\text{t}^{\text{t}}\text{Bu}\cdot\text{AlMe}_3$ (**18**), $\text{t}^{\text{t}}\text{Bu}\cdot\text{AlCl}_3$, (**19**), $\text{t}^{\text{t}}\text{Bu}\cdot\text{GaMe}_3$ (**20**), and $\text{t}^{\text{t}}\text{Bu}\cdot\text{InMe}$ (**21**).^{33,34} These complexes are extremely air-sensitive colourless solids, and the crystal structures obtained for **18**³³ and **19**³⁴ indicate that the $\text{Al}-\text{C}_{\text{carbene}}$ bond distances of the complexes are the longest to date, as compared to other NHC trimethylaluminium complexes (*cf.* 2.124(6) Å, 2.074(2) Å, 2.097(2) Å, 2.162(2) Å for **9** (IPrMe),²⁹ **12** (amino-linked bidentate NHC),³⁰ **15** (IMes)³⁰ and **18** ($\text{t}^{\text{t}}\text{Bu}$)³³, respectively), and for other trichloroaluminium complexes (*cf.* 2.057(2) Å, 2.006(3) Å, 2.009(5) Å for **19** ($\text{t}^{\text{t}}\text{Bu}$),³³ **34** (IMes)^{42b} and **38** (IMe)^{42a}, respectively). The presence of several short contacts of the aluminium atom and the corresponding hydrogen on the *tert*-butyl groups suggest that there are substantial steric clashes between the $\text{t}^{\text{t}}\text{Bu}$ groups and the AlMe_3 and AlCl_3 moiety of **18** and **19** (Figure 1.11).^{33, 34}

Scheme 1.6: Isomerisation of ItBu•MR₃ (**18-21**) to the 'abnormal' ItBu•MR₃ (**22-25**).^{33, 34}

The strong steric repulsion resulted in complexes **18-21** being unstable in solution (such as DCM, toluene and THF); and the normal adducts isomerised to the 'abnormal' NHC-MR₃ adducts **22-25** in THF or toluene (Scheme 1.6). This isomerisation process was attributed to reduced steric congestion experienced by the MR₃ moiety upon bonding at the 4-position of the imidazole ring.^{33, 34} Calculations performed on the normal (*n20* and *n21*) and abnormal (*a20* and *a21*) model complexes of **20** and **21** showed that their abnormal counterparts were more greatly stabilized as compared to their normal carbene complexes (Gibbs free energy for -5.89 kcal mol⁻¹ for Ga model *n20* vs. *a21* and -1.40 kcal mol⁻¹ for In model *n20* vs. *a21*).³⁴

Figure 1.11: X-ray crystal structure of ItBu•AlMe₃ (**18**) and the 'abnormal' ItBu•AlMe₃ (**22**).³³

1.3.1c NHC•AlR₃

The first structurally characterized NHC aluminium alkynyl complex was the IMe aluminium ethynyl compound **26** reported by Roesky *et. al.*. Its synthesis was carried out by reacting aluminium halides with three equivalents of the LiC≡C^tBu stabilized by the IMe.³⁵ Stabilized aluminium alkynyl complexes are useful as the alkynyl groups can be functionalized for the preparation of new materials such as aluminium hydride clusters for surface chemistry studies.³⁶

Figure 1.12

The corresponding NHC trimethylaluminium counterparts, the NHC tributylaluminium and triethylaluminium complexes, **27** and **28**, have also been structurally characterized. The formation of complex **27** was unanticipated as originally the NHC IPr was utilized in the stabilization of a bis-alkyl magnesium species ${}^n\text{Bu}_2\text{Mg}$ for structural studies. NMR studies suggested that complex **27** had been obtained rather than NHC magnesium complexes. In order to confirm the identity of structure **27**, direct reaction of the IPr with tributylaluminium was conducted, and the results further corroborating its formation. On inspection of commercially purchased ${}^n\text{Bu}_2\text{Mg}$, it was found to contain approximately 5-10% of triethylaluminium as a stabilizing agent. Hence, apparent alkyl exchange between the magnesium and aluminium occurred during this reaction, with larger charge-density of the aluminium favouring the formation of the NHC aluminium complex **27**.³⁷

In complex **28**, two equivalents of triethylaluminium were used to stabilize the carbene centre of an anionic N-heterocyclic dicarbene manganese complex. The obtained bimetallic complex is the first reported example of a transition metal complex containing an anionic NHC dicarbene ligand (seen in Figure 1.13).³⁸

Figure 1.13: X-ray crystal structure of anionic dicarbene Mn-Al bimetallic complex **28**.³⁸

Another noteworthy complex **29**, was obtained from the reaction of the sterically encumbered alane $\text{Al}(\text{C}_6\text{F}_5)_3$ with the bulky IMes carbene.³⁹ The resulting structure was unexpected, since sterically bulky Lewis acid and bases generally do not form classical acid/base adducts but rather ‘frustrated Lewis pairs’ (FLPs).⁴⁰ Nevertheless, the apparent reactivity for **29** is comparable to typical FLP systems and was able to catalyze polymerization reactions with both high reactivity and selectivity. Furthermore, the bulkier ItBu analogue has also been observed in solution using ^1H NMR spectroscopy; however, no structural data was reported.³⁹

Figure 1.14: X-ray crystal structure of the sterically bulky IMes• $\text{Al}(\text{C}_6\text{F}_5)_3$ bimetallic complex **29**.³⁹

More recently, the classical IMes carbene has been used to stabilise a series of monomeric group 13 phosphine compounds (Scheme 1.7). The IMes carbene was selected due to its good electron donating properties and its high steric bulk. The high steric demand of the IMes carbene prevents its dimerization or polymerization. All the monomeric NHC group 13 phosphine complexes obtained are the first examples of their kind to be structurally characterized.⁴¹

Scheme 1.7: Syntheses of a series of monomeric NHC group 13 phosphine complexes. Reactions were conducted at 50 – 70 °C overnight for the various Al and Ga complexes, as for In complex **33**, the addition was carried out at -30 °C and stirred overnight at RT. Solvent used for the reactions were heptane or toluene respectively.⁴¹

1.3.1d NHC•AlX₃

A series of NHC aluminium halide complexes were synthesized using the general procedure described in Scheme 1.1. Hence, reaction of a slight excess of AlX₃ with selected free NHCs produced compounds **19** and **34 - 38**.^{34, 42}

Figure 1.15: No bromido complexes have been reported yet, however, the same reactivity pattern previously seen for the chlorido and iodido compounds would be expected.

1.3.1e NHC•AlX_nH_{3-n} (n = 1 or 2)

In terms of mixed hydride-halide NHC complexes, Cole *et. al.* synthesized a set of mixed chloro- and bromo-NHC alanes using tertiary amine substituted mixed alane halide species (see Scheme 1.8). Since there is an increased Lewis acidity at the metal centres, due to the presence of halide substituents, these complexes were expected to display hypervalent aluminium atoms, however, no 5-coordinate aluminium species were isolated. This was attributed to the characteristic high electron donating properties and high spatial steric demands of IMes, thus preventing hypervalency.⁴³

Scheme 1.8: Syntheses of NHC mixed chloro- and bromo alanes complex **39** and **40**.⁴³

Complexes **39** and **40** exhibit remarkable thermal stability displaying decomposition temperatures of 268 °C and 320 °C, respectively. In particular complex **40**, exhibits a much higher decomposition temperature as compared to IMes•AlH₃ (256 °C) synthesized by Arduengo (**3**). Such thermal stability was credited to the presence of chlorido ligands within the complexes; and it was hypothesized that substitution of one or more of the hydrido ligands with the more electronegative halido ligands (σ -electron withdrawing effect) would strengthen the M-H bond by increasing the Lewis acidity of the metal centre and, hence, the overall stability of the complex.⁴³

Scheme 1.9: Syntheses of complex **41**, **42** and **43** showing the hydrido bromido ligand exchange.⁴⁴

Cole *et al* also utilized quinuclidine aluminium and gallium hydride complexes Quin•AlH₃ and Quin•GaH₃, for the synthesis of IMes•AlBr₂H (**42**) and IMes•GaBr₂H (**43**), respectively. In reaction of Quin•AlH₃ with IMesBr instead of the targeted IMesBr•AlH₃ complex, a hydrido-

bromido ligand exchange process occurred to yield $\text{IMes}\cdot\text{AlBr}_2\text{H}$ (**42**). As for gallium, the complex $\text{IMesBr}\cdot\text{GaH}_3$ (**41**), a presumed intermediate, was isolated. Complex **41** isomerized into $\text{IMes}\cdot\text{GaBr}_2\text{H}$ (**43**) upon heating. In order to understand the mechanism involved in the formation of complexes **42** and **43**, deuterated and low VT NMR spectroscopic studies were carried out; although unfortunately no long-lived intermediates were observed.⁴⁴

1.3.1f Chelating NHC Al complexes

Aluminium complexes containing bidentate and tridentate NHC ligands have also been synthesized. For example, the chelating dimethylaluminium complex **44** has been synthesized by heating **12** in toluene at 110 °C to achieve demethylation in addition to deprotonation of the NH group (Scheme 1.10). Similarly to complex **12**, compound **44** features a distorted tetrahedral geometry at the aluminium centre. Furthermore, **44** displays a six-membered metallacyclic backbone in a half-chair conformation due to coordination of both the carbene and the amide to the metal centre (Figure 1.16).³¹

Scheme 1.10: Synthesis of chelating dimethylaluminium complex **44** from complex **12**.³¹

Figure 1.16: X-ray crystal structure of the chelating dimethylaluminium complex **44**.³¹

Similarly, attempts have been made to obtain the analogous metallacyclic arrangement of complex **13** (Its structure can found in Scheme 1.3), however, no coordination has been obtained. It was postulated that the chelating formation was unfavourable due to insufficient space around the aluminium centre for the amino pendant arm to approach. The steric hindrance around the aluminium center was attributed to steric crowding between the ethyl and tert-butyl groups attached to the aluminium and the amino pendant arm, respectively.³¹

In a similar manner to complex **12** (see Scheme 1.3), complex **44** was subjected to reactions with electrophiles (isocyanates) to explore whether with the bidentate ligand, the stability of the Al-carbene bond would increase and reduce its susceptibility to electrophilic attack. An analogous insertion reaction to that observed for complex **12** took place. However, the unexpected double insertion of two isocyanates groups to both the Al-carbene bond and the Al-amide bond resulted in the formation of the 8-membered metallacyclic complex **45**.³¹

Scheme 1.11: Reactivity studies of complex **44** to electrophiles.³¹

Anionic tethered N-heterocyclic carbenes have been used extensively as ligands for the stabilization of transition metals and lanthanides alike, and these ligands have also been applied to group 13 metals.⁴⁵ An example of such ligand is shown in the chiral imidazolium sulfonate compound **46**, having been applied in the synthesis of dimethylaluminum complex **47**. Compared to the synthesis of **44**, that of **47** was complex, as simple addition of the chiral NHC did not result the formation of the chelating product (no complex formation after 24 hrs in THF at 22 °C). Instead, in order to access the desired product, a ligand exchange between the NHC-Zn(II) complex and trimethylaluminum was required (Scheme 1.12). Such exchange was attributed to the trimethylaluminum not being basic enough for the deprotonation of the proton on C2 to allow the formation of metallacyclic complex **47**.⁴⁶

Scheme 1.12: Synthesis of chelating NHC dimethylaluminium sulfonate complex **47** from ligand exchange with the NHC Zn(II) complex. Ratio of NHC Zn(II) complex with Al complex **47** is 55:45 with 3.0 equiv of AlMe_3 . Ratio increases for complex **47** with 10 equiv of AlMe_3 to 25:75 NHC Zn(II) complex and Al complex **41** respectively.⁴⁶

Another anionic tethered NHC ligand, the NHC bis-phenolate **48**, has also been employed in the synthesis of a series of aluminium chelates (**49-52**) (Scheme 1.13). The ligand system has its advantage in its ability to stabilize the chelating aluminium complexes. It not only contains a strong σ -donor NHC, but also the anionic tethered phenolate arms, which aid in binding to the metal centre due to the oxophilicity of the aluminium.⁴⁷

Scheme 1.13: Synthesis of a series of chelating NHC bis-phenolate complexes.⁴⁷

1.3.2 Gallium Carbene Complexes

1.3.2a NHC•GaH₃, NHC•GaX_nH_{3-n} (n = 1 or 2) and NHC•GaH_nR_{3-n} (n = 0, 1)

The gallane NHC complexes were synthesized in a similar manner to their alane counterparts. Their general synthetic procedures are summarized below. (Scheme 1.14).^{26,}

28, 48

Scheme 1.14: Summary of the various gallane NHC complexes that have been reported.^{26, 28, 48}

As for the synthesis of mixed gallane halide NHC complexes [NHC•GaX_nH_{3-n} (n = 1 or 2)], rather than using tertiary amine substituted mixed gallane halide species in their synthesis as reported for their Al counterparts (*vide supra*),⁴³ the majority of reactions have been carried out using stoichiometric ratios of NHC gallium hydride (**41** and **56**) and gallium halide (**60**) complexes to enable the exchange (Scheme 1.15).^{48, 49} Alternative reagents have also been applied for the exchange for the NHC gallium halides to the hydrido ligands and their synthetic methods are summarized in Scheme 1.15.

Scheme 1.15: Summary of the syntheses for the mixed gallane halide complexes reported.^{48, 49}

Only two gallane alkyl complexes ($\text{NHC}\cdot\text{GaH}_n\text{R}_{3-n}$), **63** ($n = 1$) and **64** ($n = 0$) respectively, have previously been reported. The synthesis of complex **63** was unexpected since the proposed synthetic route was designed as a facile lewis acid-base adduct formation between the IMe NHC and the $\text{Ga}(\text{C}_5\text{Me}_5)_3$ as illustrated in Scheme 1.16. However, the reaction resulted in the formation of a gallium metal hydride complex. A plausible mechanism for the formation of complex **63** involves the initial displacement of a $[\text{C}_5\text{Me}_5]^-$ anion and the formation of a carbene adduct of the decamethylgalloccenium cation. The resulting cation becomes unstable and undergoes a reaction with the $[\text{C}_5\text{Me}_5]^-$ anion to give complex **63** and tetramethylfulvene *via* hydrido transfer (Scheme 1.16).⁵⁰

Scheme 1.16: Proposed scheme for the synthesis of complex **63** via hydrido transfer.⁵⁰

Complex **64** was synthesized by reacting equimolar amounts of IPr with trimethylsilylmethylgallium(III) (GaR_3) [$\text{R} = \text{CH}_2\text{SiMe}_3$] at room temperature to afford the Lewis acid-base adduct. This complex was used to study the thermally-induced rearrangement process to abnormal counterpart **65** as seen in Scheme 1.17.⁵¹

Scheme 1.17: Synthesis of complex **64** and their rearrangement to its abnormal counterpart **65**. When the solvent was C_6D_6 , the time taken for the isomerisation process is 10 h; for THF, it was 1 h.⁵¹

1.3.2b $\text{GaMe}_3 \cdot \text{NHC}$ and $\text{GaX}_n\text{Me}_{3-n} \cdot \text{NHC}$ ($n = 1$)

Currently, five trimethylgallium complexes (**10**,²⁹ **20**,³⁴ **66a** (IMes),⁵² **66b** (SiMes)⁵² and **67** (SIPr)⁵²), and four heteroleptic dimethylgallium complex (**68a** (IMes),⁵² **68b** (SiMes),⁵³ **70a** (IMes)⁵² and **70b** (SiMes)⁵²) have been synthesized and structurally characterized (with the exception of **20**). Complexes **10** and **67** were synthesized using the same protocol as that previously reported in the synthesis of the trimethylaluminium counterpart complex **9** (*vide supra*).²⁹ However, the synthesis of complexes **66a** and **66b** was carried out using an alternative synthetic route involving the reaction of alkoxy NHC dimethylgallium complexes **68a** and **68b**, and trimethyl gallium in a 1:1 ratio to produce complexes **66a** and **66b** (IMes and SiMes, respectively) and a dimeric dialkylgallium byproduct **69** (Scheme 1.18).⁵²

Scheme 1.18: Synthesis of complexes **66a** and **66b** (IMes and SiMes, respectively) from an alkoxy dimethylgallium complexes **68**.⁵²

Heteroleptic dimethylgallium complexes **68a/b** and **70a/b**, were synthesized by reacting the dialkylgallium byproduct **69** with the IMes/SIMes NHC (Scheme 1.19). X-ray crystal

structures have been reported for complexes **68a** (IMes), **70a** (IMes) and **70b** (SIMes) which feature a distorted tetrahedral geometry at the Ga centre, in parallel to the majority of complexes reported for group 13. As for complex **68b** (SIMes), no X-ray crystal structure has been reported, however formation of the complex has been confirmed through ^1H and ^{13}C NMR. All four complexes (**68a/b** and **70a/b**) have been used for catalytic functions and have reported to catalyse polymerization reactions of *L*-lactide and *rac*-lactide with high conversion rates and selectivities.^{52, 53}

Scheme 1.19: Synthesis of complexes **68a/b** and **70a/b** from dimeric dialkylgallium by-product **69** with different ratio of the IMes / SIMes NHC. All reactions were conducted at room temperature.^{52, 53}

1.3.2c NHC•GaX₃

The vast majority of reported NHC gallium complexes have concentrated on the gallium halides. As described in Scheme 1.1, these NHC gallium complexes were attained by mixing the various carbenes together with the gallium halides to form the Lewis acid-base adducts. The complexes that have been previously reported in the literature are summarized in Scheme 1.20.^{42b, 49, 54}

Scheme 1.20: Summary of the NHC gallium halide complexes that have been reported.^{42b, 49, 54}

As previously illustrated in Scheme 1.15, complex **60** has been used for the redistribution of hydrido and bromido ligands around gallium to generate mixed NHC gallane halide

complexes of the general formula $[\text{NHC}\cdot\text{GaX}_n\text{H}_{3-n}]$ ($n = 1$ or 2) by reaction with NHC gallium hydrides or other hydride reagents such as silane and $^n\text{BuLi}$.

The NHC gallium halide complexes (**71**, **73**, **76** - **78**) synthesized by Gandon *et. al.* have been used to catalyse a one pot cycloisomerization/Friedel-Craft type tandem reaction with AgSbF_6 as an additive (Scheme 1.21). The advantages of using NHC gallium halide complexes for catalysis over their respective gallium salts, is their enhanced air and moisture resistance to decomposition. Therefore, these reactions are less cumbersome; avoid energy- and time-intensive extensive drying of solvents, and significantly reduce catalyst decomposition. Reported screening with NHC gallium complexes and the gallium salts have also demonstrated reduced requirements in catalyst loading for the studied NHC gallium complexes and higher yields compared to the direct use of gallium salts.^{54a}

Scheme 1.21: General synthetic scheme of the cycloisomerisation/Friedel-Crafts tandem reaction catalysed by *in-situ* generated cationic gallium (III) dihalides.^{54a}

Gallium trihalide complexes have been further employed to synthesize a series of cationic NHC gallium complexes bearing electron-rich nitriles (Scheme 1.22). These cationic NHC gallium complexes are desirable due to the avoidance of silver additive use, which are to some extent moisture and light sensitive. The cationic NHC gallium complexes display identical catalytic function as the NHC gallium trihalide complexes with the silver additive, however their reactivity was lower in comparison to the latter, even with the addition of AgSbF_6 .^{54a}

- 79** $\text{R} = \text{Mes}$, $\text{R}^1 = \text{H}$, $\text{R}^2 = 2,4,6\text{-(MeO)}_3\text{-C}_6\text{H}_2$
80 $\text{R} = \text{Mes(S)}$, $\text{R}^1 = 2\text{H}$, $\text{R}^2 = \text{C}_6\text{H}_5$
81 $\text{R} = \text{Dipp}$, $\text{R}^1 = \text{Me}$, $\text{R}^2 = 2,4,6\text{-F}_3\text{-C}_6\text{H}_2$
82 $\text{R} = \text{Dipp(S)}$, $\text{R}^1 = 2\text{H}$, $\text{R}^2 = \text{C}_6\text{F}_5$

Scheme 1.22: General synthetic route for the syntheses of cationic NHC gallium complexes **79-82**.^{54a}

In order to further understand the effect of silver additives on the activity of the NHC gallium complexes, reactions using a series of silver salts have been studied. It is known that the active catalytic species is $[L\cdot\text{GaCl}_2]^+$, since neither the NHC gallium complex or the AgSbF_6 catalyse the transformation alone. Hence, the active catalytic species are obtained by chloride abstraction by the silver additive AgSbF_6 . However, when alternative silver additives were used, namely AgPF_6 or AgBF_4 , no reactivity was observed. It was only when single crystal X-ray structures following the reaction of the NHC gallium halide complexes with the silver salts were obtained; in combination with extensive DFT calculations, that it became clear that AgPF_6 and AgBF_4 favour the formation of the NHC gallium fluoride complexes (**83**), which are inactive for the catalytic transformation (Scheme 1.23).⁵⁵

Scheme 1.23: Formation of NHC gallium trifluoride complex through the addition of AgBF_4 . X-ray crystal structure was obtained for this complex.⁵⁵

It was observed that in certain cases, direct reaction of NHC with gallium halides leads to the formation of ion pairs $[\text{GaX}_2(\text{NHC})_2][\text{GaX}_4]$, rather than to neutral molecular adducts $\text{NHC}\cdot\text{GaX}_3$. Therefore, to gain insight regarding their preferential formation, a series of NHCs were reacted with Ga halides to prepare the ion pairs **84** and **85**, and neutral molecular complexes **75**, **86** and **87**.^{54c}

Figure 1.17

As expected, reaction of ^HIme carbene with gallium trichloride forms the neutral Lewis acid-base adduct complex **75**. However, when the reaction was conducted with 1,3-dimethyl-2-methylene-2,3-dihydro-1*H*-imidazole (diMe-MDI) or the IBoxMe₄ carbene with gallium trichloride, both compounds resulted in the ion pair complexes **84** and **85**. Whilst the IBoxMe₄ carbene is sterically bulkier compared to the ^HIme carbene, diMe-MDI is structurally similar to the ^HIme carbene, and hence sterics do not play a significant part in the formation of the ion-pair. In addition, when reactions were carried out with the IBoxMe₄ carbene with gallium tribromide and gallium triiodide, the neutral molecular IBoxMe₄•GaBr₃ (**86**) and IBoxMe₄•GaI₃ (**87**) were obtained respectively, without any indication of ion pair formation. Hence, the formations of respective complexes are dependent on the nature of the halide.^{54c}

DFT calculations elucidated that in all cases, the dinuclear intermediate $\text{LGaCl}_2(\mu\text{-Cl})\text{GaCl}_3$ (**88**) was present prior to product formation. As seen in Figure 1.18, once **88** is formed, after the first nucleophilic attack, Ga¹ remains as the most accessible centre for subsequent nucleophilic addition; whereas Ga² is more sterically hindered due to the presence of the first diMe-MDI ligand. If the second nucleophilic attack occurs at Ga², an ion pair will be formed, $[\text{L}_2\text{GaCl}_2][\text{GaCl}_4]$. In contrast, if the second addition occurs at Ga¹, a molecular adduct will be formed $[\text{LGaCl}_3]$. After optimizing the structural intermediates with a wide range of ligands, it was concluded that the high nucleophilic nature of diMe-MDI causes the Ga²-Cl¹ bond to be strongly polarized, which enhanced steric protection on the Ga¹ atom favouring the ion pair formation instead of the expected LGaCl_3 .^{54c}

Figure 1.18: Proposed mechanism based on computational calculation of the exothermic formation of the intermediate **88** from the reaction of the carbene ligand with gallium chloride.^{54c}

As for the IBoxMe₄ ligand, its nucleophilicity has been shown to be intermediate, falling between the ^HIme and the diMe-MDI (increase nucleophilicity: $^H\text{Ime} < \text{IBoxMe}_4 < \text{diMe-MDI}$), and since Cl is more electronegative than Br and I, the Ga-Cl bond is more polarized compared to Ga-Br and Ga-I, thus favouring the formation of an ion pair in the case of gallium chloride, and neutral molecular adducts for the gallium bromide and iodide.^{54c}

A series of cyclic amino carbene (CAAC) gallium trihalide complexes (**89** – **91**) have been synthesized and structurally characterized. These CAAC carbenes are generally more electron donating compared to the NHC carbenes,⁵⁷ but through comparison of the TEP values of the ligands coordinated to gallium, and also the structural parameters of the complexes, the NHC carbenes prove comparable to CAAC carbenes, with no distinct differences in electron donating properties to the gallium being observed (Table 1.3).⁵⁶

Figure 1.19

Table 1.3: TEP values, $C_{\text{NHC}}\text{-Ga}$ and average Ga-X bond lengths (Å) of selected NHC•GaX₃ adducts.

Complexes	TEP (cm ⁻¹) ^a	$C_{\text{NHC}}\text{-Ga}$ (Å)	Ga-X (aver. Å)
73	2050.5	2.016(2)	2.176
74	2049.6	2.011(4)	2.199
77	2051.5	2.025(2)	2.169
89	2050.0	2.039(2)	2.180
90	2049.0	2.036(1)	2.180
91	2046.3	2.064(5)	2.188

^aTEP values are obtained from the optimized structure of LNi(CO)_3 complexes at the mPW1PW91/6-311+G(2d) (Ni)/6-311+G(d,p) (other atoms) level of theory (TEP = ν_{CO} (A1)*0.9541).^{54a, 54b, 56}

Similarly to complex **28**, gallium trichloride has been used to stabilize an abnormal carbene centre to obtain an abnormal carbene gallium complex **92**. The complex was synthesized by a boron-stabilized NHC, which was lithiated to generate a carbene centre at C4, thus allowing nucleophilic attack on the carbene centre to the gallium trichloride. The dissociation of BET_3 was attributed to the steric repulsion of the Dipp substituents following binding of the gallium halides, which forces the Dipp substituent closer toward BET_3 . Subsequently, the dissociation of BET_3 generated an anionic C2 carbene centre, thus solvent-mediated protonation generated the neutral complex **92** (Scheme 1.24).⁵⁸

Scheme 1.24: Synthetic route for the synthesis of abnormal gallium complexes **92** and the normal NHC gallium complexes **93**.⁵⁸

The reaction showed dependency on the boron atom position on the NHC. When the boron atom was isomerised to the abnormal position, the addition of the gallium trichloride resulted in its attachment to the C2 position rather than the C4 position (**93**). The reaction also resulted in the formation of diethylborane *via* the elimination of ethyllithium, however no explanation was given in regards to the formation of complex **93** (Scheme 1.24).⁵⁸

1.3.2d Chelating NHC Ga complexes

A series of chelating NHC gallium complexes bearing aryl/alkoxide bidentate ligands have been synthesized and structurally characterized (**94** - **98**). These ligands are attractive for the stabilization of metal complexes because the tethered anionic oxygen can covalently bond to the hard, electropositive metal centre, which allows the NHC to bond more strongly to the metal, resulting a highly stable chelate complex. As illustrated above, similar ligands have also been applied in the synthesis of the chelating Al complexes (**47**, **49** - **52**) (*vide supra*).^{46, 47}

Figure 1.20

Similarly to their chelating Al complex analogues, Ga complexes are typically 4-coordinated, showing distorted tetrahedral geometry at the Ga centre and Ga-C_{carbene} bond distances comparable to their monodentate ligand complexes.⁵²

1.3.3 Indium Carbene Complexes

1.3.3a $\text{InH}_3\cdot\text{NHC}$, $\text{InX}_n\text{H}_{3-n}\cdot\text{NHC}$ ($n = 1$ or 2)

The indane NHC complexes have been synthesized in a similar manner to their alane and gallane counterparts, and their general procedures are summarized below. (Scheme 1.25).^{26,}

28, 59, 60

Scheme 1.25: Summary of the various indane NHC complexes that have been reported.^{26, 28, 59, 60}

For the synthesis of mixed indane halide NHC complexes $[\text{InX}_n\text{H}_{3-n}\cdot\text{NHC}]$ ($n = 1$), two different methods have been applied, either by first generating the mixed $\text{InH}_2\text{Cl}(\text{NMe}_3)_n$ *in-situ* by reaction of excess NMe_3HCl with LiInH_4 , followed by the addition of the IMes carbene, or by reacting $\text{IMes}\cdot\text{InH}_3$ (**100**) with quinuclidine $\cdot\text{HCl}$ (Scheme 1.26).⁶⁰

Scheme 1.26: Synthetic route for the synthesis of mixed indane halide NHC complex **101**.⁶⁰

Similarly to their alane and gallane counterparts, the presence of the chlorido ligand results in an enhanced stability of complex **101** compared to the indane NHC complex **100**. This was indicated by the increase in the melting point of complex **101** as compared to complex **100** ($119\text{ }^\circ\text{C}$ vs. $115\text{ }^\circ\text{C}$, respectively). Furthermore, a downfield shift of the In hydrido ligands (δ_{H} 6.25 and 5.20 of complex **101** and **100**, respectively), followed by a higher frequency of the IR stretching modes of the In-H bonds (IR stretching frequency of complex **101** is 1737 cm^{-1} (Nujol), and 1650 cm^{-1} (Nujol) or 1640 cm^{-1} (toluene solution) for complex **100**) was observed respectively.⁶⁰

1.3.3b $\text{InX}_n\text{Me}_{3-n}\cdot\text{NHC}$ ($n = 1$ or 2)

Notably, only one trimethylindium NHC complex has been synthesized to date, which is the $\text{ItBu}\cdot\text{InMe}_3$ complex **21** (*vide supra*). The only other alkyl indium complexes previously synthesized were a series of mixed halido methylindium complexes reported by Frost *et al.*⁶¹ These compounds were synthesized reacting one equivalent of InMe_3 with the imidazolium salt $[\text{IMesH}]\text{Cl}$, followed by further reaction with TMS-OTf and HOTf to afford the triflate compounds (Scheme 1.27).

Scheme 1.27: Synthesis of mixed halide methylindium complexes IMesInMe₂Cl (**102**), IMesInMe₂OTf (**103**) and IMesInMeOTf₂ (**104**).⁶¹

Unlike the previously discussed group 13 NHC complexes, complexes **102** – **104** do not adopt a distorted tetrahedral geometry at the indium centre. Albeit complex **102** indium centre is four-coordinate, the chlorido ligand lies orthogonal to the carbene plate, due to a weak carbene chloride interaction. As for complex **103** and **104**, the indium centre is five-coordinate owing to an additional interaction with the neighbouring triflate of the adjacent indium molecule in the lattice, hence promoting a trigonal bipyramidal geometry.⁶¹

1.3.3c InX₃•NHC and Chelating NHC In halide complexes

Equivalent to their gallium NHC complexes, the majority of NHC indium complexes reported have been indium halide species. Complexes reported in the literature have been shown to be similar to their Al and Ga NHC counterparts, and their synthetic routes are summarized below (Scheme 1.28).^{27, 62, 63}

Scheme 1.28: Summary of the NHC indium halide complexes that have been reported.^{27, 62, 63}

As for the synthesis of the IMes•InCl₃ complex (**109**), it was obtained by the thermal decomposition of the IMes•InH₃ (**100**) in dichloromethane. No crystal structure was obtained for this complex but spectroscopic evidence indicated the presence of the complex formation.

Scheme 1.29: Thermal decomposition of $\text{IMes}\cdot\text{InH}_3$ resulting in the formation of $\text{IMes}\cdot\text{InCl}_3$ (**109**).⁶⁰

In addition, indium has the tendency to form complexes with higher coordination numbers than its lighter congeners due to their lower electronegativity. Hence, the reaction of two equivalents of the NHCs with the indium halide complexes resulted in the formation of five coordinate bis-carbene indium halide complexes **110** and **111** (Scheme 1.30).⁶²

Scheme 1.30: Synthetic route for the synthesis of bidentate NHC halide complexes.^{27, 62}

The reaction was further extended using a bidentate ligand EtIBu^t to synthesize a five coordinate indium and thallium complex **112** and **113**, respectively. However, when the reaction was conducted with Al and Ga, only the bis-imidazolium dichloride compound **114** was obtained, even after rigorous efforts to exclude moisture (Scheme 1.30). The mechanism underlying the formation of **114** is not known, although presumably the acidic protons on the imidazolium originated from the solvent, and the chlorides from the AlCl_3 fragment. As previously mentioned, the ligand EtIBu^t was also applied onto Group 13 metal hydride in an attempt to synthesize a series of chelating NHC metal hydride complexes, but only the monodentate ligand complexes **6-8** were obtained (Scheme 1.2). This was attributed to the fact that the metal hydrides are less Lewis acidic as compared to their halido counterparts (*vide supra*).²⁷

Scheme 1.31: General synthetic scheme of the cationic cyclization reaction catalysed by *in-situ* generated cationic indium complex InI_2^+ .⁶⁴

Indium salts such as InBr_3 and InI_3 have shown to exhibit strong affinity for alkynes and initiate elegant cationic polycyclizations that yield complex chiral polycycles.⁶⁴ These cascade polycyclic reactions were even further enhanced when catalytic amounts of InI_3 and AgX ($\text{X} = \text{SbF}_6$ or $\text{B}[\text{C}_6\text{H}_3-3,5-(\text{CF}_3)_2]_4$) were employed (Scheme 1.31). Based on elementary investigation by Corey *et. al.*, it was postulated that the InI_3 and AgY generated the InI_2^+ cations, somewhat explaining the higher activity observed when employing both components, as InI_2^+ has two vacant p-orbitals that allow coordination of the orthogonal π -orbitals of the alkyne in a crisscrossed geometry, thus initiating the cascade reaction. Attempts to isolate the $[\text{InI}_2^+][\text{Y}]$ cations failed, as the cationic species proved too hard to be separated from the AgY , as the cation is weakly soluble in the dichloromethane solvent.^{64c}

As previously mentioned, Gandon *et. al.* reported a series of NHC-stabilized, Ga halide complexes $\text{NHC}\cdot\text{GaCl}_3$ (**71**, **73**, **76** - **78**, with AgSbF_6 additive) and cationic complexes $\text{NHC}\cdot\text{GaCl}_2^+$ (**79** - **82**), and they have been used to carry out a series of one-pot cycloisomerization/Friedel-Craft type tandem reactions. Advantages of these NHC gallium complexes include relative stability as compared to the respective gallium salts. In addition, the $\text{NHC}\cdot\text{GaCl}_2^+$ was found to be more active than GaCl_3 toward alkynes, even though the complex display only one vacant orbital (*vide supra*).^{54a} Therefore, a similar reaction was applied on the InBr_3 in order to isolate out a cationic NHC indium complex and evaluate its π -acidity.

Scheme 1.32: Synthetic route for the synthesis of cationic indium NHC complex **115**.⁶³

Figure 1.21: X-ray crystal structure of the cationic indium NHC complex $[\text{IPr}\cdot\text{InBr}_2][\text{SbF}_6]$ **115**.⁶³

They reported the synthesis of a cationic NHC indium bromide complex by reacting the bench-stable $\text{IPr}\cdot\text{InBr}_3$ complex **105** with AgSbF_6 (1 equiv) to generate the cationic complex $[\text{IPr}\cdot\text{InBr}_2][\text{SbF}_6]$ **115** (Scheme 1.32), which could also be represented as a fluorine-bridged species $[\text{IPr}\cdot\text{InBr}_2(\mu\text{-F})\text{SbF}_5]$, as highlighted by the X-ray crystal structure obtained by slow evaporation of deuterated DCM solvent (Figure 1.21). This cationic complex is a rare species of type $(\kappa^1\text{-L})_n\cdot\text{InX}_2^+$ having mono-coordinating ligands with only two InX_2^+ ions having been structurally characterized. Furthermore, the majority of compounds display $\kappa^2\text{-L}$ bidentate ligands having 8- or 12- electron species ($(\kappa^2\text{-L})\cdot\text{InX}_2^+$ or $(\kappa^2\text{-L})_2\cdot\text{InX}_2^+$), hence the 6 electron cationic NHC indium bromide complex **115** can be expected to show interesting Lewis acid properties due to its unsaturated character.⁶³

Complex **105** with AgSbF_6 and complex **115** have been used to carry out a cationic cascade reaction with the activation of the alkyne of the arenyne to give **A**, followed by the activation of the alkene moiety of **A** to give the tandem product **B**. As shown in Table 1.4, comparing complex **105** (with AgSbF_6) and complex **115** with the InCl_3 and InBr_3 salts, the isolable yields obtained (with product **B** as the major component) were comparable to the indium salts. In addition, when carrying out the synthesis by replacing the anisole with 1,2-dimethoxybenzene or 1-(phenylsulfonyl)indole, complex **105** was obtained in greater yields as compared to the InBr_3 salt. Therefore, the cationic NHC indium complexes prove to be powerful π -Lewis acids even though displaying only a single vacant site as compared to the InBr_2^+ .⁶³

Scheme 1.33

Table 1.4: Cationic cascade reaction with the activation of the alkyne of the arenynes to give A, followed by the activation of the alkene moiety of A to give the tandem product B.

Entry	[In]	Ar-H	t (h)	A : B ^b (% conv.)	Yield of B (%)
1	InBr ₃	Anisole	6	18/81	65 ^d
2	105	Anisole	6	20/80	62 ^d
3	115 ^a	Anisole	6	29/71	68 ^d
4	InBr ₃	1,2-Dimethoxybenzene	24	- ^c	45 ^b
5	105	1,2-Dimethoxybenzene	2	- ^c	82 ^b
6	InBr ₃	1-(Phenylsulfonyl)indole	24	- ^c	69 ^b
7	105	1-(Phenylsulfonyl)indole	16	- ^c	83 ^b

^a No AgSbF₆ was added. ^b Values determined by GC. ^c No values reported. ^d Isolated yields.⁶¹

During investigation into the use of cationic indium species as catalysts, the presence of HSbF₆ was observed in crystals grown from solution of reaction (3) shown in Scheme 1.34. This discovery is significant since superacid systems such as HF/MF₅ (M = As, Sb) have been used as reagents, reaction media, or catalysts, but the free acid HMF₆ species have remained elusive. Moreover, X-ray structural analysis of the majority of superacid HF/SbF₅ revealed the existence of [H₂F]⁺[Sb₂F₁₁]⁻ and [H₃F₂]⁺[Sb₂F₁₁]⁻.⁶⁵ It was only recently that Kornath *et. al.* detected the free acid HAsF₆ in the crystal structure of [(CH₃)₂NH₂][AsF₆]•HAsF₆. Therefore, further investigations were conducted to identify the free acid HSbF₆.^{65b}

Scheme 1.34: Equation 1 and 2 was the proposed route for the generation of HSbF_6 , and 3 and 4 is the isolation of complex **116** and **117**.^{65a}

In order to explain the formation of the free acid, it was proposed that anion metathesis of $\text{IPr}\cdot\text{InBr}_3$ (**105**) and AgSbF_6 resulted in the formation of the species $[\text{IPr}\cdot\text{InBr}_{3-x}][\text{SbF}_6]_x$ ($x = 1, 2$ or 3), followed by the reaction with adventitious water in the reaction mixture or hygroscopic silver salt to give the corresponding indium hydroxide $[\text{IPr}\cdot\text{InBr}_{3-x}(\text{OH})][\text{SbF}_6]_{x-1}$ ($x = 1, 2$ or 3) and HSbF_6 (Scheme 1.34, eq 1 & 2). The free acid did not co-crystallize with the $[\text{IPr}\cdot\text{InBr}_{3-x}][\text{SbF}_6]_x$ species or with the indium hydroxide, but instead with the pre-metathetic species complex **116**, with the Ag^+ coordinated to Br (Scheme 1.34, eq 3). Nevertheless, it was believed that adventitious water present in the reaction mixture prompted the formation of HSbF_6 as the reaction of $\text{IPr}\cdot\text{InBr}_3$ with AgSbF_6 (1 equiv) produced AgBr precipitate, hence confirming that anion metathesis occurred and complex **116** was formed as the side product. When the reaction was heated to 60°C , the indium hydroxide complex **117** was obtained (Scheme 1.34, eq 4). X-ray crystal structures of both complexes were attained through slow evaporation of DCE solvent. Complex **116** displayed the presence of HSbF_6 in the crystal structure, and represents the first evidence of the existence of the superacid.^{65a}

Figure 1.22: X-ray crystal structures complex **116**• $(\text{HSbF}_6)_2$ and indium hydroxide complex **117**.⁶⁵

1.3.4 Thallium Carbene Complexes

Scheme 1.35: Synthetic route for the synthesis of bis-carbene thallium complex **121**.⁶⁶

The only reported thallium NHC complexes in the literature are the thallium halides. These complexes have been synthesized by treating TiX_3 with the IMes or IMesBr in THF. As thallium preferentially exists in the +1 oxidation state, and Ti(III) has strong oxidizing nature, it was surprising that none of the carbenes have been oxidized as compared with phosphine analogues. In addition, and in like to the indium complexes, a bis-carbene thallium complex was synthesized with the reaction of complex **118** with IMe (Scheme 1.35). Attempts were made to crystallize the bis-carbene complex however only microcrystalline powder was able to be obtained. Furthermore, the reaction was carried out with complex **118** and IMes, but the reaction failed to proceed. Subsequently it was concluded that the bulkiness of IMes prohibited this reaction from taking place.⁶⁶

Trimethylaluminium NHC Species

Summary

This chapter describes the synthesis and characterization of new aryl substituted N-heterocyclic carbene (NHC) trimethylaluminium complexes - IMes•AlMe₃ (**122**), SIMes•AlMe₃ (**123**), IPr•AlMe₃ (**124**) and SIPr•AlMe₃ (**125**) - and studies on their differential stability with respect of the nature of the NHC ligand used. The differences in stability were evaluated by detailed study of their topographic steric maps, buried volume (% V_{Bur}) and dissociation energies (E_{diss}). Due to their differential stability, the reactivity of these NHC•AlMe₃ complexes are further examined by reacting them with a series of electrophiles, which resulted in a series of metal free betaine adducts (**132-134**) that differ from previous reports in the literature. Interestingly, these betaine adducts have been previously applied to stabilize metal nanoparticles. Therefore, the betaine adducts produced have been reacted with metal salts using mechanochemical methodologies to cleave a C-C bond and the synthesis of a NHC copper complex **144**.

2.1 Introduction

It has been clearly demonstrated that N-heterocyclic carbenes are excellent Lewis bases to stabilize many group 13 complexes, as summarized in the extensive introduction (Chapter 1). However, their properties and reactivities have not been extensively studied as compared to their transition metal counterparts. In addition to demonstrating catalytic capabilities, these species have exhibited potential in a wide range of applications. For example, the IMes carbene has been used to synthesize a neutral Ga_6 octahedron cluster;⁶⁷ sterically demanding carbenes, such as IPr and ItBu, have been used to stabilize double and triple bonded B-B species;⁶⁸ and frustrated Lewis pair (FLP) systems have been successfully used in small molecule activation (H_2 , NHRR').⁴⁰ Therefore, further in-depth investigations in terms of the properties and reactivities of these systems constitutes an exciting area for synthetic chemists.

Figure 2.1

Within the current chapter, the discussion will concentrate on trimethylaluminium complexes, as the majority of previously reported NHC-aluminium complexes comprise of alane, alkyl and halido species ($\text{AlX}_n\text{H}(\text{R})_{3-n}$, $n = 0, 1, 2$). Prior to commencing the studies in this thesis, only four monodentate (**9**, **12**, **15**, **18**),^{29, 30, 33} and three bidentate ligands (**44**, **47**) and one tridentate ligand (**50**) trimethylaluminium complexes had been synthesized and fully characterized.^{31, 46, 47} Furthermore, there are only a few known examples of saturated NHC

stabilised group 13 complexes that have been fully characterized. Herein, this chapter will report the synthesis, characterization, theoretical and reactivity studies on the series of the NHC trimethylaluminium complexes.

2.2 Results and Discussion

2.2.1 Synthesis of trimethylaluminium complexes **122** - **125**

The general synthetic methodology is described in Scheme 2.1. Treatment of one equivalent of the N-heterocyclic (IMes, SIMes, IPr and SIPr) with trimethylaluminium (1M in toluene) resulted in the isolation of the Lewis acid-base adducts: IMes•AlMe₃ (**122**), SIMes•AlMe₃ (**123**), IPr•AlMe₃ (**124**) and SIPr•AlMe₃ (**125**) (Figure 2.2). An analogous complex of **122**, complex **15**, was previously reported by Ong *et. al.* utilising the same synthetic route as Scheme 2.1 and has been included in this report to maintain the rigour of the studies.³⁰

Scheme 2.1: General synthetic route for the syntheses of the NHC trimethylaluminium adducts (**122** - **125**).

Figure 2.2

Compounds **122** - **125** are highly air and moisture sensitive. During the isolation and characterization of these compounds, traces of decomposition were consistently observed in the ¹H and ¹³C NMR spectra (*vide infra*), with the main decomposition product consistent with their parent imidazolylienes. This was especially dominant in complexes **124** and **125**

in which solid-state samples stored under argon decomposed at room temperature to the imidazolylidene and imidazolinylidene, respectively, and other unidentified side-products. Figure 2.3 shows the ^1H NMR spectrum of the acceleration of the decomposition of selected complex **125** at 60°C , which indicated the increase presence of the imidazolinylidene SIPr as the decomposition proceeded. Surprisingly, no signs of decomposition were observed for complexes **122** and **123** in solid-state stored under argon over a long periods of time.

Figure 2.3: ^1H NMR spectra showing the decomposition of $\text{SIPr}\bullet\text{AlMe}_3$ (**125**) conducted at 60°C for 1 month. Red represents our complex; blue represents the carbene.

2.2.2 Spectroscopic studies of trimethylaluminium complexes **122** - **125**

The identities of complexes **122** - **125** were confirmed through various spectroscopic studies. The ^1H and ^{13}C NMR spectra display singlets within the range of δ_{H} -0.78 to -0.91 and δ_{C} -7 ppm respectively, which are indicative of the presence of the methyl groups on the aluminium centre. This was further confirmed by the IR spectra, which displayed a relatively strong stretching signals at around 620 cm^{-1} , representing the Al-C stretching mode.⁶⁹ Furthermore, the ^{13}C NMR indicated an upfield shift of the $\text{C}_{\text{carbene}}$ signal which is consistent with the formation of a metal-carbene bond (Table 2.1).

Table 2.1: ^1H and ^{13}C NMR chemical shifts for complexes **122** - **125**.

Complexes	^1H [AlMe ₃] ^a (ppm)	^{13}C [Al-C _{carbene}] ^a (ppm)	^{13}C [C _{carbene}] ^b (ppm)
122	-0.78	178.5	219.4
123	-0.86	202.3	243.8
124	-0.86	181.1	220.4
125	-0.91	205.3	244.0

^a ^1H and ^{13}C NMR chemical shifts were obtained in C₆D₆. ^b ^{13}C NMR chemical shift was obtained from ref. 70 in C₆D₆.

Theoretical calculations performed on the optimized geometries of the complexes **122** - **125** (optimized using PBE0/6-311G(d,p) model chemistry), and the calculated ^1H and ^{13}C NMR spectra using B972/6-311+G(2d,p) were consistent with the experimental data obtained (Table 2.2), further supporting the proposed structures.

Figure 2.4**Table 2.2:** Theoretical and experimental ^1H and ^{13}C NMR chemical shifts for complexes **122** - **125**.

Complex	H ₄ , H ₅ calculated shifts	H ₄ , H ₅ relative shifts ^a (ppm)	H ₄ , H ₅ experimental shifts ^b (ppm)	C ₁ calculated shifts	C ₁ relative shift ^a (ppm)	C ₁ experimental shift ^b (ppm)
122	24.7978	7.05	5.96	5.9648	181.7	178.5
123	27.9631	3.89	3.00	-18.5234	206.1	202.3
124	24.6442	7.21	6.45	3.2347	190.8	181.1
125	27.8453	4.01	3.45	-22.1060	209.7	205.1

^a The calculated TMS for ^1H and ^{13}C NMR chemical shift, 31.85 and 187.61 respectively, are used as the reference. ^b ^1H and ^{13}C NMR chemical shifts were obtained in C₆D₆.

2.2.3 Crystallographic studies of trimethylaluminium complexes **122** - **125**

Single-crystal X-ray structures of complexes **122** - **125** are shown in Figures 2.5 and 2.6. Complex **123** and **124** crystallized as two crystallographically independent but chemically equivalent molecules; hence only one molecule will be described herein.

Figure 2.5: Molecular structure of complex **122** (IMes•AlMe₃) and **123** (SIMes•AlMe₃) left and right, respectively. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] for **122**: Al(1)-C(1) 2.098(2), Al(1)-C(4) 1.978(2), Al(1)-C(5) 1.991(1), C(1)-N(1) 1.365(2), C(1)-N(2) 1.364(2), C(2)-N(1) 1.385(2), C(3)-N(2) 1.382(2), C(2)-C(3) 1.353(2), C(4)-Al(1)-C(5) 110.8(1), C(4)-Al(1)-C(1) 108.7(1), C(5)-Al(1)-C(5A) 114.4(1), C(5)-Al(1)-C(1) 105.8(1), N(1)-C(1)-N(2) 103.5(1). Selected bond lengths [Å] and angles [°] for **123**: Al(1)-C(1) 2.112(6), Al(1)-C(4) 1.984(6), Al(1)-C(5) 1.994(7), Al(1)-C(6) 1.983(6), C(1)-N(1) 1.341(7), C(1)-N(2) 1.343(7), C(2)-N(1) 1.477(7), C(3)-N(2) 1.474(7), C(2)-C(3) 1.534(8), C(4)-Al(1)-C(5) 110.7(3), C(4)-Al(1)-C(1) 105.7(3), C(4)-Al(1)-C(6) 112.3(3), C(5)-Al(1)-C(6) 111.8(3), C(5)-Al(1)-C(1) 107.6(3), C(6)-Al(1)-C(1) 108.4(2), N(1)-C(1)-N(2) 107.3(5).

Figure 2.6: Molecular structure of complex **124** (IPr•AlMe₃) and **125** (SIPr•AlMe₃) left and right, respectively. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°] for **124**: Al(1)-C(1) 2.103(3), Al(1)-C(4) 1.992(3), Al(1)-C(5) 1.994(3), Al(1)-C(6) 1.994(3), C(1)-N(1) 1.370(4), C(1)-N(2) 1.370(4), C(2)-N(1) 1.387(4), C(3)-N(2) 1.385(4), C(2)-C(3) 1.351(4), C(4)-Al(1)-C(5) 111.5(1), C(4)-Al(1)-C(1) 109.6(1), C(4)-Al(1)-C(6) 111.3(1), C(5)-Al(1)-C(6) 113.6(1), C(5)-Al(1)-C(1) 104.7(1), C(6)-Al(1)-C(1) 105.7(1), N(1)-C(1)-N(2) 103.1(2). Selected bond lengths [Å] and angles [°] for **125**: Al(1)-C(1) 2.127(2), Al(1)-C(4) 1.986(3), Al(1)-C(5) 1.992(2), Al(1)-C(6) 1.980(2), C(1)-N(1) 1.346(2), C(1)-N(2) 1.345(2), C(2)-N(1) 1.477(2), C(3)-N(2) 1.483(2), C(2)-C(3) 1.521(3), C(4)-Al(1)-C(5) 109.4(1), C(4)-Al(1)-C(1) 100.7(1), C(4)-Al(1)-C(6) 114.0(1), C(5)-Al(1)-C(6) 111.5(1), C(5)-Al(1)-C(1) 110.9(1), C(6)-Al(1)-C(1) 109.5(1), N(1)-C(1)-N(2) 107.1(1).

Complexes **122** - **125** adopted a distorted tetrahedral geometry at the aluminium centre, which is consistent with the majority of complexes previously reported in the literature (see Chapter 1). The Al-C_{carbene} bond lengths of the complexes **122** - **125** were also consistent with the reported trimethylaluminium complexes (Table 2.3).

It was noted that the Al-C_{carbene} bond length of SIPr (**125**) was similar to the less sterically bulky IPrMe (**9**) (see Table 2.3). NMR spectroscopic studies conducted by Huynh *et. al.* using their own state-of-the-art NHC-NMR spectroscopic probe,¹⁸ combined with calculated pK_a values for a wide range of NHC species by O'Donoghue *et. al.*⁷¹ indicated that saturated NHCs are marginally more basic (σ donor) as compared to their unsaturated counterparts (SIPr ~ SIMes > IPr > IMes). This was further corroborated by the ¹H NMR chemical shifts observed pertaining to the methyl groups coordinated to the aluminium centres in complexes **122** - **125**. These complexes also showed slight bond lengthening when comparing saturated versus unsaturated counterparts (2.098(2) Å vs. 2.112(6) Å for complexes **122** and **123**, and 2.103(3) Å and 2.127(2) Å for complexes **124** and **125**). However, clear bond lengthening is only observed between **124** and **125** (Table 2.3), since the difference between **122** and **123** could be attributed to statistical error range (3 σ). Furthermore, all distances are shorter than those found in complex **18**, which has the longest Al-C_{carbene} bond length reported to date. This was attributed to the steric repulsion between the t-butyl groups and the methyl groups on the aluminium centre which causes the decomposition (in DCM) or the isomerization to an abnormal carbene (in THF or toluene) (Chapter 1).³³

Table 2.3: Al-C_{carbene} bond lengths of selected NHC aluminium complexes.

Entry	Complex	Al-C _{carbene} [Å]
1	IMes•AlMe ₃ (122)	2.098(2)
2	SIMes•AlMe ₃ (123)	2.112(6)
3	IPr•AlMe ₃ (124)	2.103(3)
4	SIPr•AlMe ₃ (125)	2.127(2)
5	IPrMe•AlMe ₃ (9)	2.124(6)
6	IMes•AlMe ₃ (15)	2.097(2)
7	ItBu•AlMe ₃ (18)	2.162(2)
8	12	2.074(2)
9	44	2.059(2)
10	47	2.078(3)
11	50	2.032(2)

2.2.4 Lewis acid-base properties of trimethylaluminium complexes **122** - **125**

N-Heterocyclic carbenes are often compared with commonly used phosphine counterparts to assess their relative donating abilities (Lewis basicity) when used as ligands to metal centres. Therefore, complexes **122** - **125** were evaluated with selected phosphine-Al complexes for their assessment.

Table 2.4: Average bond length (Al-Me), bond angles (C-Al-C) and ^1H NMR of selected NHC and phosphine AlMe_3 complexes.

Complex	Al-Me ^a [Å]	C-Al-C ^a [°]	^1H [AlMe_3] ^b (ppm)
IMes• AlMe_3 (122)	1.985	112.6	-0.78
SiMes• AlMe_3 (123)	1.987	111.6	-0.86
IPr• AlMe_3 (124)	1.993	112.1	-0.86
SiPr• AlMe_3 (125)	1.986	111.7	-0.91
IMes• AlMe_3 (15) ³⁰	1.983	123.2	-0.75
ItBu• AlMe_3 (18) ³³	2.000	109.5	-0.73 ^c
AlMe_3 ⁷⁰	1.956	123.3	-0.35
$\text{Me}_3\text{P} \bullet \text{AlMe}_3$ ⁶⁹	1.973	117.1	-0.41
$\text{Ph}_3\text{P} \bullet \text{AlMe}_3$ ^{69, 71}	1.981	116.6	-0.09
(o-tolyl) ₃ P• AlMe_3 ⁶⁹	1.874	113.9	-0.31

^a Average values were taken for both bond lengths and bond angles. ^b ^1H NMR was obtained in C_6D_6 unless otherwise stated. ^c ^1H NMR was obtained in CD_2Cl_2 .

Barron *et al.* reported that in the case of trimethylaluminium, the Al-C bond length should increase and the C-Al-C angles should decrease upon coordination of the phosphines to the aluminium centre, due to the increase in p-character on the Al-C bond on changing from planar to tetrahedral geometries.⁷² These observations were seen on the Al-NHC complexes, with the increase in bond length (*cf.* 1.956 Å for AlMe_3 , and 1.985 Å, 1.987 Å, 1.993 Å and 1.986 Å for complexes **122** - **125** respectively) as well as a decrease in C-Al-C bond angles (*ca.* 120° for AlMe_3 , and respective average angles of 112.6°, 111.6°, 112.1° and 111.7° for complexes **122** - **125**) upon binding of the NHC to the aluminium. In addition, there was a greater distortion from planarity for the NHC aluminium complexes as compared to their phosphine counterparts (Table 2.5), which showed the greater electron donating ability of the NHC ligands as compared to the phosphine ligands.

As the NHC trihydride and trihalide aluminium complexes have been extensively discussed in the literature, it will be appropriate to use these as a basis of comparison for the newly synthesized trimethylaluminium species, to gain a better understanding of their properties. In terms of Lewis acid character, it was found that for complexes **122** - **125** the trimethylaluminium moiety was a poorer Lewis acid as compared to hydrido and halido species, with the Lewis acid trend ranging from trihalides being the most Lewis acidic, followed by trihydrides to trimethylaluminium being the least acidic ($\text{AlMe}_3 < \text{AlH}_3 < \text{AlX}_3$). This was evident by the shortening of the aluminium carbene bond distances for the IMes and IPr complexes: Al-C_{carbene} bond distances for IMes• AlMe_3 (**122**) is 2.098(2) Å, IMes• AlH_3

(**3**)²⁴ is 2.034(3) Å and IMes•AlCl₃ (**34**)^{42b} is 2.017(2) Å; IPr•AlMe₃ (**124**) is 2.103(6) Å, IPr•AlH₃ (**5**)²⁴ is 2.056(2) Å and IPr•AlI₃ (**37**)^{42c} is 2.031(2) Å. Similar tendencies are observed for the NHC mixed allane and gallane halide complexes, where the number of electronegative atoms increases and the bond distances shorten as summarised in Table 2.6.

Table 2.6: Al-C_{carbene} bond length of selected mixed NHC allane and gallane complexes.^{43, 48}

Entry	Complex	Al-C _{carbene} [Å]
1	IMes•AlH ₃ (3) ^{25, 43}	2.034(3)
2	IMes•AlH ₂ Cl (39) ⁴³	2.039(2)
3	IMes•AlHCl ₂ (40) ⁴³	2.020(7)
4	IMes•AlCl ₃ (34) ⁴³	2.017(2)
5	IMes•GaH ₂ Cl (57) ⁴⁸	2.030(3)
6	IMes•GaHCl ₂ (58) ⁴⁸	2.005(6)
7	IMes•GaCl ₃ (75) ⁴⁸	1.954(4)

Further evidence was afforded by indium and thallium complexes, with differences in the observed Lewis acidity between hydrido and halido ligands. During the synthesis of bis-NHC (*i.e.*, NHC-(CH₂)₂-NHC) complexes, it was noted that for group 13 complexes, the hydrido species were only able to form monodentate tetra-coordinate or bimetallic conformation (*i.e.*, R₃E←NHC-(CH₂)₂-NHC→ER₃). In contrast, the halido compounds showed monometallic pentacoordinate indium and thallium complexes containing a bidentate bis-NHC moiety, suggesting the higher Lewis acidity of the latter.²⁸ In addition, the relative Lewis acidity can also be assessed using ¹³C NMR spectroscopy – noteworthy to highlight is that many Al-C_{carbene} chemical shifts have not been reported in the literature due to the quadrupolar nature of the aluminium metal centre to which they are attached. Nevertheless, based on the chemical shift observed for our complexes **122** - **125** (Table 2.1), in conjunction with the previously reported chemical shifts for IMes•AlH₃ (**3**),²⁴ IMes•AlI₃ (**36**)^{42c} and IPr•AlI₃ (**37**)^{42c} (¹³C NMR signals of Al-C_{carbene}: δ_C 175.3 for IMes•AlH₃ (**3**),²⁴ δ_C 153.9 for IMes•AlI₃ (**36**)^{42c} and δ_C 153.3 for IPr•AlI₃ (**37**)^{42c}) it further confirms that the trimethylaluminium moiety is a poorer electron acceptor as compared to AlH₃ and AlX₃.

2.2.5 Stability studies of trimethylaluminium complexes **122** - **125**

It was previously reported that the *tert*-butyl NHC trimethylaluminium and trichloroaluminium complexes, ItBu•AlMe₃ (**18**) and ItBu•AlCl₃ (**19**) respectively, isomerised to their ‘abnormal’ isomeric form in either THF or toluene due to steric factors (Chapter 1).^{33, 34} A standard parameter designed to quantify the steric properties of N-Heterocyclic carbenes, the percent buried volume %V_{Bur} (Chapter 1), was used to compare complexes **122** - **125** with other NHC•AlR₃ species previously reported in the literature (Table 2.7). The %V_{Bur} for each

complex was calculated using the Al-NHC bond distance fixed at the experimental value obtained by X-ray diffraction studies, and also at 2.0 Å, in order to provide a point of comparison independent of the Al-NHC distances.

Table 2.7: Al-C_{carbene} bond lengths, %V_{Bur} and dissociation energies for selected NHC Al complexes.

Entry	Complex	Al-C _{carbene} [Å]	%V _{Bur}	%V _{Bur}	E _{diss} ^a (kJmol ⁻¹)
			R = X-ray	R = 2.0 Å	
1	IMes•AlMe ₃ (122)	2.098(2)	31.7	33.7	114.47
2	SIMes•AlMe ₃ (123)	2.112(6)	32.0	34.1	104.76
3	IPr•AlMe ₃ (124)	2.103(3)	34.2	36.2	97.14
4	SIPr•AlMe ₃ (125)	2.127(2)	36.1	38.5	79.82
5	liPrMe•AlMe ₃ (9) ²⁹	2.124(6)	25.5	27.2	132.59
6	ItBu•AlMe ₃ (18) ³³	2.162(2)	34.3	36.9	59.33
7	IMes•AlMe ₃ (15) ³⁰	2.097(2)	31.8	33.6	114.47
8	IMes•Al(C ₆ F ₅) ₃ (29) ³⁹	2.061(3)	31.2	32.7	157.79
9	IMe•Al(C≡CtBu) ₃ (27) ³⁵	2.051(2)	25.3	25.9	161.73
10	IPr•Al((CH ₂) ₃ CH ₃) ₃ (28) ³⁷	2.118(2)	32.6	34.9	85.85
11 ^a	SItBu•AlMe ₃	2.229	33.3	37.6	38.59

^a Values were obtained using DFT calculations with the PBE0/6-311G(d,p) basis set.

Calculations revealed that the order of magnitude of %V_{Bur} of the ligands in each new NHC complexes was **125** > **124** > **123** > **122**. In addition, to provide a meaningful assessment of the steric influence of the NHC moiety on the overall stability of the NHC-AlMe₃ complexes, %V_{Bur} values for the ligands of the literature reported trimethylaluminium complexes were included. With the inclusion of previously reported complexes (*i.e.*, **9**, **15** and **18**) the more complete trend becomes **125** > **18** > **124** > **123** > **122** ≈ **15** > **9**. This highlights that the ItBu NHC of ItBu•AlMe₃ (**18**) occupies a larger volume than complexes **122** and **123**, and its value is comparable to that of **124** and surprisingly lower than that of **125** (Table 2.7). As the %V_{Bur} for ligand of compound **124** is larger than that of **122** and **123**, and no decomposition was observed for the latter complexes, the onset of decomposition may be attributed to the larger volume occupied by the isopropylphenyl groups as compared to their mesityl counterparts. The lower stability of complexes **124** (%V_{Bur} = 36.2%, comparable to **18**) and **125** (%V_{Bur} = 38.5%, greater than **18**) were further rationalized by Dagorne *et. al.* using the congested nature of the ItBu NHC present.³³

To gain insight at the molecular level into the steric impact of the different NHCs on the trimethylaluminium, topographic steric maps for complexes **122** - **125**, **9**, **18** and **15** were calculated (see Appendix 1). A comparative analysis of the topographic maps of complex

123 and **125**, as representatives of a stable and of an unstable system, can therefore be performed (Figure 2.8).

Figure 2.8: Topographic steric maps of the SIMes and SIPr ligands in **123** and **125**. The iso-contour curves of the steric maps are in Å. The maps have been obtained starting from the crystallographic data of the Al-NHC complexes (CIF), with the Al- C_{carbene} distance fixed at 2.0 Å. The xz plane is the mean plane of the NHC ring, whereas the yz plane is the plane orthogonal to the mean plane of the NHC ring, and passing through the C_{carbene} atom of the NHC ring.

The steric contour maps revealed that the distribution of the steric bulk of the SIMes ligand in **123** is quite symmetrical around the metal centre, with large grooves between the two mesityl rings. As for complex **125**, the increased steric hindrance largely concentrates around the *ortho* isopropyl groups, blocking the grooves between the two N-substituents. Therefore, the difference in the nature of the distribution of the NHC ligands around the metal centre (similarly found for complex **122** and **124**, see Appendix 1) helps to explain the lower stability observed for complexes **124** and **125** as compared to **122** and **123**.

At this stage, it is also worth performing a comparative analysis of the topographic steric map of ItBu (**18**) with that of complex **125**, since the former complex is the only reported unstable $\text{NHC} \cdot \text{AlMe}_3$ complex (Figure 2.9). The topographic steric map of ItBu displayed the two top quadrants being slightly more sterically hindered, but its topographical asymmetry is lower as compared to SIPr (**125**), where the distribution of the steric bulk is much more greatly localized into the top left and top right quadrants. The difference is even more evident upon review of the $\%V_{\text{Bur}}$ representation of each single quadrant, i.e. 39.6 – 40.2% for ItBu (**18**) vs. 43.1 – 50.7% for SIPr (**125**). From these calculations, the greater localization of the ligand steric hindrance into one or two quadrants around the metal center may help to explain the lower stability observed for these complexes, in this case of **18** as compared to **125**.

Figure 2.9: Topographic steric maps of the ItBu and SIPr ligands in **18** and **125**. The iso-contour curves of the steric maps are in Å. The maps have been obtained starting from the crystallographic data of the Al-NHC complexes (CIF), with the Al-C_{carbene} distance fixed at 2.0 Å. The xz plane is the mean plane of the NHC ring, whereas the yz plane is the plane orthogonal to the mean plane of the NHC ring, and passing through the C_{carbene} atom of the NHC ring.

In addition to the use of %V_{Bur} and topographic steric maps to evaluate the complexes stability, bond dissociation energies have also been calculated to further rationalize the stability differences observed. As the dissociation energy were calculated using DFT optimized structures (PBE0/6-311G(d,p) model chemistry), the Al-C_{carbene} bond length will be an appropriate structural parameter on which to base a comparison between the calculated and experimental values for the DFT analysis.

Figure 2.10: A plot of DFT calculated vs. experimental Al-C_{carbene} bond lengths of entries 1-10 from Table 2.7.

The plot above (Figure 2.10) revealed a direct relationship between the experimental and the calculated Al-C_{carbene} bond distances ($R^2 = 0.919$). On average, the calculated Al-C_{carbene} bond length is observed to be 3.5 pm longer than the experimentally determined structures. Nevertheless, an overall good structural agreement was achieved between the experimental and calculated structural parameters enabling meaningful insights into the dissociation energies of the complexes.

From Table 2.8, the DFT calculated dissociation energy shows that the bond dissociation energy of complexes **122** - **125** decreases with increasing steric bulkiness of the NHC: **122** >

123 > 124 > 125, which further corroborated the observation that complexes **122** and **123** were less susceptible to dissociation as compared to **124** and **125**. With the inclusion of the dissociation energy calculated for the rest of the trimethylaluminium counterparts, the order is: **9 > 122 $\approx$ 15 > 123 > 124 > 125 > 18** (Table 2.8). It is worth noting that there is a discrepancy between complex **125** and complex **18**; with the % V_{Bur} calculated for NHC ligands for complex **125** being higher than that for complex **18**, however the dissociation energy calculated for complex **125** is higher than for complex **18** (% V_{Bur} **18** > % V_{Bur} **125**; E_{diss} **18** < E_{diss} **125**). This difference may be explained by considering the differing electronic properties of the SIPr and ItBu moieties. On the one hand, saturated NHCs contribute to an increase in donor ability as compared to their unsaturated counterparts (sNHC > uNHC). On the other hand, the presence of electron withdrawing aryl N-substituents in the NHC imparts a decrease in the electron donor ability of the NHC (alkyl-NHC > aryl-NHC). The opposing electronic effects present in both SIPr and ItBu (i.e., the electron donating effect of the sp^3 backbone and withdrawing effects of the aryl groups in SIPr vs. the less donating sp^2 backbone combined with more donating alkyl groups in ItBu) make the relative NHC→aluminium donation properties difficult to predict.¹⁸ However, experimental evidence may suggest that the SIPr moiety is a better donor ligand in **125** as compared to the ItBu ligand in **18**; the ^1H NMR chemical shift of the methyl groups in **125** (δ_{H} -0.91) is more upfield shifted as compared to those found in complex **18** (δ_{H} -0.73), and the NMR chemical shifts were further supported by the ^{11}B NMR studies on NHC•BX₃ complexes, where the chemical shift for the ItBu•BCl₃ displays a more downfield shift as compared to its IPr analogue.⁷⁵ Nevertheless, the overall stability of these complexes is a concomitant balance between the electronic and steric properties of the NHC moieties present.

On further inspection of Table 2.8, it is observed that the calculated % V_{Bur} for all the ligands of stable complexes falls within or below 34%, whereas **18**, **124** and **125** have % V_{Bur} values exceeding 36%. Therefore, the difference observed between the stable and the unstable complexes of their % V_{Bur} is only 2–4% (Table 2.8). The observed differences in % V_{Bur} between **122** and **125** ligands are concentrated in small areas (as shown by the topographic maps in Appendix 1), but they exhibit profound effects on the stability and dissociation energies of these complexes (the asymmetry underlined by the maps adds value to this 2–4%).

Table 2.8: % V_{Bur} and dissociation energies for selected NHC Al complexes in increasing order of stability.

Complex	% V_{Bur}	% V_{Bur}	E_{diss}^a (kJ mol ⁻¹)	Overall Stability
	R = X-ray	R = 2.0 Å		
SlitBu•AlMe ₃	33.3	37.6	38.59	Unstable
ItBu•AlMe ₃ (18)	34.3	36.9	59.33	
SiPr•AlMe ₃ (125)	36.1	38.5	79.82	
IPr•AlMe ₃ (124)	34.2	36.2	97.14	
SiMes•AlMe ₃ (123)	32.0	34.1	104.76	Stable
IMes•AlMe ₃ (122)	31.7	33.7	114.47	
IMes•AlMe ₃ (15)	31.8	33.6	114.47	
IPrMe•AlMe ₃ (9)	25.5	27.2	132.59	

^a Values were obtained using DFT calculations with the PBE0/6-311G(d,p) basis set.

A plot of the calculated % V_{Bur} (R = 2.0 Å) *versus* the calculated dissociation energy E_{diss} for all the crystallographically characterized structures was performed (Figure 2.11), which shows a linear correlation can be established between the steric bulk of the NHC ligand and the dissociation energy of these complexes ($R^2 = 0.7057$); wherein the steric bulk of the NHC ligand increases, the dissociation energy decreases.

Figure 2.11: A plot of calculated % V_{Bur} vs. DFT calculated dissociation energy E_{diss} of NHC trimethylaluminium complexes.

Synthesis of SlitBu•AlMe₃ (the saturated counterpart of **18**) was carried out in order to test the proposed stability threshold of % V_{Bur} of 36%, and also ideally, to complete the series of trimethylaluminium complexes.⁷⁶ Unfortunately, all synthetic attempts proved futile, resulting in the formation of complex mixtures of products only. The slurry obtained in the reaction mixture was also insoluble in most aprotic solvents (pentane, hexane, ether, THF, benzene, and toluene), which made the isolation of any viable product unsuccessful. However, for comparison with other trimethylaluminium complexes, the optimised geometry for SlitBu•AlMe₃ was calculated using DFT methods. Table 2.7 and 2.8 shows the calculated

$\% V_{\text{Bur}}$ of the ligand SItBu and dissociation energy of complex SItBu•AlMe₃ and from the theoretical values obtained, and in light of the comparison to other NHC trimethylaluminium complexes, its value falls within the range observed for the unstable complexes ($\% V_{\text{Bur}} = 37.6\%$, $E_{\text{diss}} = 38.59 \text{ kJ mol}^{-1}$). This could partially explain the difficulties encountered during the attempted synthesis described herein.

2.2.6 By-product obtained from SIPr•AlMe₃ (**125**)

As discussed previously, compounds **124** and **125** were shown to be susceptible towards the formation of the imidazolyidenes and other unidentified decomposition products. In order to shed light on the decomposition process, efforts were made to isolate and identify some of the side-products. Previous observation of the decomposition process showed that the decomposition rate was temperature dependent. Hence, the reaction mixture initially used to produce complex **125** at room temperature, was refluxed overnight instead.

Figure 2.12: Molecular structure of complex **126**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except for H(4) and H(29), are omitted for clarity. C(1)-N(1) 1.319(4), C(1)-N(2) 1.320(4), C(1)-C(4) 1.483(4), C(2)-N(1) 1.488(2), C(3)-N(2) 1.471(4), C(2)-C(3) 1.539(4), C(2)-H(2) 0.991, C(3)-H(3) 0.990, C(4)-H(4) 0.980, C(29)-O(1) 1.266(4), C(29)-O(2) 1.219(4), C(29)-H(29) 0.950, N(1)-C(1)-N(2) 111.9(3), N(1)-C(1)-C(4) 124.3(3), N(2)-C(1)-C(4) 123.7(3), N(1)-C(2)-C(3) 102.4(2), N(2)-C(3)-C(2) 102.8(2), C(1)-C(4)-H(4) 109.4, O(1)-C(29)-O(2) 127.1(3), O(1)-C(29)-H(29) 116.5, O(2)-C(29)-H(29) 116.4.

Crystalline solids from this reaction proved to be remarkably air and moisture sensitive, and difficult to separate from the complex mixture of products obtained from the reaction. However, solid **126** was obtained when the reaction mixture was extracted in THF. Suitable single crystals for X-ray diffraction studies were grown in a THF–hexane mixture (Figure 2.12).

Complex **126** crystallized out of solution as a methylated imidazolium salt containing a formate counter ion and an acetic acid molecule in the crystal lattice (1:1:1 ratio). Even though reactions were conducted under strict inert atmosphere conditions, presumably traces of water, oxygen or carbon dioxide were present in the reaction medium. Due to the presence of these impurities, the isolated product could be considered closely related to the

reaction proposed by Rogers *et. al.* in describing the generation of carboxylate zwitterion species with acetate ionic liquids (**127** and **128**) since both the products have close structural similarities (*vide infra*).⁷⁷ Further mechanistic and reactivity studies on complexes **122** - **125** are being conducted in order to rationalize the formation of **126**.

2.2.7 Reactivity studies on Complexes **122** - **125**

The solid state structure of **128** (Figure 2.13) resembles that of complex **126** which may suggest that **122** - **125** have similar reactivity as the ionic liquid **127** (Eqn 1, Scheme 2.2). Therefore, reactions were carried out by bubbling CO₂ (dried using a drying column) over *in-situ* generated of the NHC trimethylaluminium complexes **122** - **125**, to observe whether similar reactivity had occurred as according to the proposed reaction by Rogers *et.al.* (Scheme 2.2, Eqn 1)

Figure 2.13: Molecular structure of complex **128**, [C₂mim][H(OAc)₂][C₂mim⁺-COO⁻]. C₂mim: 1-ethyl-3-methylimidazolium salt, C₂mim⁺-COO⁻: 1-ethyl-3-methylimidazolium-2-carboxylate.⁷⁷

Scheme 2.2: Proposed reaction scheme of the reaction of CO₂ and the ionic liquid **127**, and complexes **122** – **125**.⁷⁷

This bubbling of CO₂ resulted in the precipitation of white solid and a yellow oily substance from all reactions. Significant difficulties were faced in separating the two substances due to the sparing solubility of both substances, which made it difficult to isolate any useful products. Nevertheless, for SiPr•AlMe₃ (**125**) complex, the bubbling of the CO₂ resulted in suitable single crystals (**132**) formed on the side of the glasswares for X-ray diffraction studies (Figure 2.14). For all other complexes (**122** – **124**), no single crystals were obtained after repeated attempts at re-synthesis and purification.

Surprisingly, compound **132** did not retain the trimethylaluminium as compared to the other complexes when exposed to electrophiles (**14**, **16**, **45**).^{30, 31} As previously mentioned, SiPr•AlMe₃ undergoes decomposition to give the imidazolidinylidene as the major side product (*vide supra*). Therefore, the formation of compound **132** was most probably due to the instability of **125**, which resulted in the release of the SiPr ligand, and reacted with the CO₂ to form the carboxylate compound. Compound **132** structure was similar to the ones reported by Louie *et. al.* (IPrCO₂ and SiPrCO₂),⁷⁸ and unfortunately due to the sensitivity and instability of the crystals, no further analysis could be conducted.

Figure 2.14: Molecular structure of complex **132**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for **132**: C(1)-C(2) 1.515(5), C(1)-O(1) 1.243(5), C(1)-O(2) 1.240(5), C(2)-N(1) 1.328(5), C(2)-N(2) 1.324(4), C(3)-N(1) 1.479(4), C(3)-C(4) 1.519(5), C(4)-N(2) 1.475(4), N(1)-C(5) 1.445(5), N(2)-C(17) 1.446(4), O(1)-C(1)-O(2) 130.9(4), O(1)-C(1)-C(2) 113.2(4), O(2)-C(1)-C(2) 115.9(3), N(1)-C(2)-N(2) 111.2(3), N(1)-C(3)-C(4) 102.7(3), N(2)-C(4)-C(3) 102.9(3), C(2)-N(1)-C(3) 110.9(3), C(2)-N(2)-C(4) 111.1(3), C(5)-N(1)-C(3) 119.0(3), C(17)-N(2)-C(4) 122.1(3).

Comparing the crystal structure of **132** to the rest of the NHC carboxyl compounds, the carboxylate bond lengths are near equivalent to each other (C-O bond distances: 1.243(5) Å and 1.240(5) Å for **122**, 1.225(4) Å and 1.221(4) Å for IPrCO₂, and 1.237(2) Å and 1.234(2) Å for SiPrCO₂), which indicated an even distribution of the negative charge between the central C atom and the two oxygen atoms. The two C-N bond distances were also similar to one other (C-N bond distance: 1.328(5) Å and 1.324(4) Å), implying the positive charge was evenly distributed among the N-C-N scaffold. Lastly, the carboxylate group lay perpendicular to the plane of the imidazole ring, hence suggesting that no delocalization occurred between

the carboxylate charge and the imidazole ring. Similar observations of absent delocalization were also made for the IPrCO₂ and the SIPrCO₂ compounds.⁷⁸

Alternatives to the use of CO₂ as an electrophile, other variants of electrophiles such as carbon disulphide and carbodiimide have also been applied to complexes **122** – **125** to test the reactivity of the NHC•AlMe₃ complexes, as previously applied to other NHC aluminium complexes reported by Ong *et. al.*^{30, 31} Reactions carried out with carbon disulphide did not yield any conclusive results even following repeated attempts. However, when reactions were carried out with the carbodiimides (bis(2,6-diisopropylphenyl)carbodiimide), new compounds **133** and **134** were obtained (Figure 2.15 and 2.16).

Figure 2.15: Molecular structure of compound **133**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. C(1)-N(1) 1.343(5), C(1)-N(2) 1.333(5), C(1)-C(22) 1.508(6), C(2)-N(1) 1.402(6), C(3)-N(2) 1.387(6), C(2)-C(3) 1.329(7), N(1)-C(4) 1.457(5), N(2)-C(13) 1.454(5), C(22)-N(3) 1.318(6), C(22)-N(4) 1.321(6), N(3)-C(35) 1.415(6), N(4)-C(23) 1.409(6), N(1)-C(1)-N(2) 106.5(4), N(1)-C(2)-C(3) 106.2(4), N(2)-C(3)-C(2) 107.8(4), C(1)-N(1)-C(2) 109.7(4), C(1)-N(1)-C(4) 129.6(4), C(1)-N(2)-C(3) 109.8(4), C(1)-N(2)-C(13) 130.5(4), N(3)-C(22)-N(4) 141.4(4), C(22)-N(3)-C(35) 124.7(4), C(22)-N(4)-C(23) 126.6(4).

Figure 2.16: Molecular structure of compound **134**. Due to twinning of the crystal, structure cannot be resolved entirely, therefore no bond lengths [Å] and angles [°] are reported.

Similarly to compound **132**, no retention of trimethylaluminium was observed for compound **133** and **134** even though this feature was observed for the other trimethylaluminium complexes (**14**, **16**, **45**).^{30, 31} The IMes•AlMe₃ (**122**) and SIMes•AlMe₃ (**123**) are considered highly stable as compared to their isopropylphenyl counterparts and no decomposition was observed during liquid or solid state (*vide supra*), the reaction still resulted in the generation of the free carbene. In addition, when the reaction was conducted with IPr•AlMe₃ (**124**) or SIPr•AlMe₃ (**125**) with the bis(2,6-diisopropylphenyl)carbodiimide, based on NMR analysis, the reaction did not proceed and only the NHC trimethylaluminium complexes and the carbodiimide were present. Therefore, from these observations, it may be concluded that the presence of the trimethylaluminium adduct increases the steric interactions between the complexes and the carbodiimide, which resulted in the release of the trimethylaluminium adduct. As for the IPr•AlMe₃ (**124**) and SIPr•AlMe₃ (**125**) counterparts, there may be substantial steric interaction between the isopropylphenyl groups on the NHC and on the carbodiimide, which lead to unfavourable conditions for the release of the trimethylaluminium adduct and hence no reaction proceeded.

Scheme 2.3: Compounds **135** and **136** reported by Kuhn *et. al.* and Chaudret *et. al.* respectively.^{79, 80} SIMes family undergoing [3+2] cycloelimination to give the corresponding carbodiimide trapped by the SIMes carbene (**137-140**).⁸¹

Compounds **133** and **134** represent the betaine adducts of N-Heterocyclic carbenes. Kuhn *et. al.* were the first to report compounds of this type by reacting 1,3-diisopropyl-4,5-dimethylimidazoylidene (IIPrMe) with N,N'-diisopropylcarbodiimide (**135**).⁷⁹ Only recently these betaine adducts were expanded, in a report by Chaudret *et. al.* that described utilization of the betaine compound (**136**) in stabilization of very small ruthenium

nanoparticles.⁸⁰ More importantly, it was reported by Johnson *et. al.* that the imidazolidinylidene SIMes family undergoes a concerted [3+2] cycloelimination by heating to give ethylene and the corresponding bis-(2,4,6-trimethylphenyl)carbodiimide, in which the carbodiimide was trapped by a second NHC in nearly quantitatively yield to give the corresponding betaine adducts (**137 – 140**). With the SIMes protected with CO₂, similar cycloelimination proceeded to obtain the betaine adduct (**137**).⁸¹ Such instability of the NHCs may offer some explanation of some of the decompositions that were observed in the trimethylaluminium complexes, especially the SIPr ligand, which may undergo similar cycloelimination to give the corresponding carbodiimide. However, based on ¹H NMR analysis, no such carbodiimide was observed during the decomposition of the SIPr•AlMe₃ complex (**125**) and only the SIPr ligand and other unidentifiable by-products were identified. Since these betaine adducts can serve as Lewis base ligands towards the stabilization of metal complexes, further extension of the series of betaine adducts was conducted, by reacting a series of NHCs to 1,3-di-p-tolylcarbodiimide (**141 – 143**, Scheme 2.4).⁸¹ Comparing the single crystal X-ray structures of the betaine adducts that crystallized (**133**, **137 – 143**), all compounds share similar structural similarities: the central C-C bond lengths of the NHCs carbodiimide fall within the range of 1.50 – 1.51 Å, the carbodiimide C-N bond lengths are in the range of 1.31 – 1.32 Å, the carbodiimide N-C=N bond angles are in the range of 139.0 – 141.6°, and the NHC N-C=N bond angles are in the range of 106.5 – 108.4° for imidazolylidene and 111.0 – 112.0° for imidazolynylidene (Table 2.9).⁸¹ Interestingly, even though compound **135** exhibits a similar C-C bond length between the NHC and the carbodiimide (1.516(2) Å) when comparing to the rest of the betaine adducts, its carbodiimide N-C=N bond angle is 10° smaller than the rest of the reported betaine adducts.⁷⁹ Whilst this bond angle difference is not huge, it was attributed to the large steric bulk of the aryl substituents on both the NHC and carbodiimide (**133**, **137 – 143**), as compared to the Me and ⁱPr groups in the NHC and carbodiimide in compound **135**. This was further supported by the dihedral angle between the NHC and the carbodiimide; compound **135** having the largest dihedral angle of 85.6° between the NHC and the carbodiimide due to the presence of less sterically bulky Me and ⁱPr groups, however, at 47.0°, the dihedral angle for compound **133** represents the smallest of the compounds, due to the large steric bulk between the Mes and the Dipp groups.^{79, 81} Lastly, by following the reaction scheme of Kuhn and Johnson *et. al.*, attempts were also made to react the IMes, SIMes, IPr and SIPr carbene with the N,N'-diisopropylcarbodiimide, however, no betaine adducts were observed. The reaction was also conducted by Johnson *et. al.*, and similar outcome occurred. Based on these results it was suggested that the aryl substituents in the carbodiimide portion of the NHC-carbodiimide provided enhanced stability likely through the

delocalization of the amidinate negative charge and the greater electronegativity of the sp^2 vs. sp^3 hybridized carbon.⁸¹

Scheme 2.4: Synthesis of compounds **141** – **143** by reacting a series of NHCs with the 1,3-di-p-tolylcarbodiimide.⁸¹

Spectroscopic analysis also confirms the formation of the betaine adducts. For all compounds, there was an upfield shift of the ^{13}C NMR signal pertaining to the carbene carbon, and a downfield shift of the N-C-N carbodiimide carbon signal (Table 2.9), further verifying the formation.^{79, 80, 81}

Table 2.9: Bond distances, bond angles, dihedral angle of the NHC and the carbodiimide and ^{13}C NMR of the selected compounds.

Complex	C ₁ – C ₂ [Å]	C ₂ – N ₃ & C ₂ – N ₄ [Å]	N ₁ -C ₁ -N ₂ [°]	N ₃ -C ₂ -N ₄ [°]	Dihedral angle [°]	^{13}C NMR of C ₁ (ppm) ^b
133	1.508(6)	1.318(6) 1.321(6)	106.5(4)	141.4(4)	47.0	150.1 ^c
135	1.516(2)	1.319(2) 1.308(3)	108.4(2)	130.4(2)	85.6	148.8 ^c
137	1.501(2)	1.323(2) 1.324(2)	111.3(1)	139.9(2)	66.3	165.5
138	1.505(1)	1.325(1) 1.322(1)	111.2(1)	140.0(1)	63.8	165.6
139	1.509 ^a	1.319 ^a 1.319 ^a	111.0 ^a	140.1 ^a	67.0	165.8
140	1.511(1)	1.317(1) 1.325(1)	111.0(1)	139.6(1)	84.7	165.7
141	1.502(1)	1.311(1) 1.325(1)	112.0(1)	139.0(1)	67.2	165.5
142	1.500(2)	1.324(1) 1.321(2)	107.5(1)	138.4(1)	71.9	149.8
143	1.498(1)	1.315(1) 1.321(2)	107.4(1)	141.6(1)	76.5	150.6

^a No estimated standard deviations were reported for complex **139**.^{79, 80, 81} ^b ^{13}C NMR was obtained in CD_2Cl_2 unless stated otherwise. ^c ^{13}C NMR was obtained in C_6D_6 .

Rather than utilizing traditional solution method synthesis, solvent-free synthesis of the type, mechanochemistry (*vide infra*), was applied to complex **133** with a series of metal complexes (AlCl_3 , GaCl_3 , InCl_3 , SnCl_2 , CuCl) in hope of obtaining a new series of NHC amidinate metal complexes. The majority of the solid-state reactions did not yield any positive results, except for the CuCl complex, in which crystallization from DCM solvent yielded the $\text{IMes}\cdot\text{CuCl}$ complex (**144**) instead, with no carbodiimide attached. Previously, it was mentioned that the imidazolidinylidene SIMes family of compound undergoes a concerted [3+2] cycloelimination by heating to give ethylene and the corresponding bis-(2,4,6-trimethylphenyl)carbodiimide, and the carbodiimide was trapped by a second NHC to give the betaine adducts. Therefore, it is plausible that the reaction of the betaine adducts is reversible which resulted in complex **133** releasing the NHC and the carbodiimide and the NHC react with the CuCl to give complex **144**.⁸¹ This is interesting as this reversibility is only observed mechanochemically and not in solvent-based synthesis. Hence, future work will focus on conducting mechanochemical reactions applied to the various betaine adducts with a series of other transition metals to observe whether such reversibility exists. Complex **144** was synthesized by a student working under my supervision from Warwick University, and unfortunately due to time constraints of that attachment, no further analysis of the copper complex **144** could be conducted.

Figure 2.17: Molecular structure of compound **144**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. C(1)-N(1) 1.355(4), C(1)-Cu(1) 1.876(5), Cu(1)-Cl(1) 2.098(1), C(2)-N(1) 1.379(4), C(2)-C(2A) 1.361(6), N(1)-C(3) 1.438(3), N(1)-C(1)-N(1A) 104.6(4), N(1)-C(1)-Cu(1) 127.7(2), N(1)-C(2)-C(2A) 106.5(2), C(1)-Cu(1)-Cl(1) 180.0, C(1)-N(1)-C(2) 111.2(3), C(1)-N(1)-C(3) 122.0(3), C(2)-N(1)-C(3) 126.8(2).

2.3 Conclusions

This chapter discusses the synthesis and characterization of a series of new aryl N-substituted N-heterocyclic carbene trimethylaluminium species. From observations of the synthesis of these complexes, it is determined that the steric bulk of the NHCs used contributed to differing stability of the complexes. The studies demonstrated that the mesityl substituted NHC complexes (**122** - **123**) were more robust as compared to their isopropylphenyl counterparts (**124** - **125**). In addition, by comparing the steric bulk with other previously characterized NHC trimethylaluminium complexes, small variation of 2-4% in steric differences of the percent buried volume ($\% V_{\text{Bur}}$) have a profound effect on the overall stability of the complex formed. The results indicated that all the reported stable NHC•AlMe₃ complexes have ligands fall within or below a $\% V_{\text{Bur}}$ of 34%, and the unstable complexes ligands were with higher values than 36%, and were illustrated by the new complexes **124** and **125**, and the previously reported complex **18**. Reactivity studies have also been conducted on these new NHC trimethylaluminium complexes, and by reacting the new complexes with electrophiles, it was observed that no trimethylaluminium was coordinated following the reactions, as reported in the literature, stable betaine adducts were obtained instead (**132** - **134**). As it has been previously reported that betaine adducts serve as Lewis bases in their abilities to stabilise very small ruthenium nanoparticles⁸⁰, adduct **133** was applied to a series of metal complexes utilizing a mechanochemical approach, in the hope of obtaining a new series of NHC amidinate metal complexes. However, from the series of reactions, only a NHC copper complex **144** could be isolated and structurally characterized. From the observation of the formation of complex **144**, it was postulated that the reactions of the betaine adducts were reversible which resulted in complex **133** releasing the NHC and the carbodiimide, with the NHC reacted with the CuCl to give complex **144**. Future work requires further mechanochemical reactions to be conducted on these series of betaine adducts to transition metals in order to investigate reversibility, as no such reversibility was observed in solvent-based reactions.

Trimethylgallium and Indium NHC Species

Summary

This chapter describes the synthesis and characterisation of new aryl substituted N-heterocyclic carbene (NHC) trimethylgallium and indium complexes, IMes•GaMe₃ (**145**), SIMes•GaMe₃ (**146**), IPr•GaMe₃ (**147**), SIPr•GaMe₃ (**148**), IMes•InMe₃ (**149**), SIMes•InMe₃ (**150**), IPr•InMe₃ (**151**) and SIPr•InMe₃ (**152**). Their different stabilities depending on the nature of the NHC ligands on the trimethylgallium and indium complexes were explored. Similarly to the NHC aluminium counterparts, the differences in stability of the ligands were demonstrated by the analyses of the topographic steric maps, their calculated percent buried volume, %V_{Bur}, and dissociation energies, E_{diss}. In addition, bonding studies were conducted with a series of group 13 metal complexes, in order to rationalize the observed differences in bonding between saturated and unsaturated carbenes, group 13 and transition metals and, NHC and PHC (P-heterocyclic carbene) complexes. Our studies were able to quantify specific contributing factors of the ligands on the stability of the resulting complexes.

3.1 Introduction

Employing Arduengo carbenes as highly nucleophilic bases to stabilise transition metal complexes for organic synthesis have been extensively explored over the last three decades.^{15, 82} Conversely, in the case of N-heterocyclic carbene group 13 metal complexes, only a limited range of compounds have been applied during organic synthesis.⁸³ Nevertheless, these compounds do exhibit excellent catalytic activity in certain organic synthesis. For example, complex $\text{SiMes}\cdot\text{GaMe}_2\text{OMe}$ (**70**) exhibits a controlled and iso-selective ring opening polymerisation reactions (ROP) of *rac*-lactide (LA) with chain-length-controlled isotactic PLA with good conversions and polydispersity.⁵³ In addition, slight modifications within the NHC group 13 complexes can result in drastic changes in their reactivity towards organic transformations. This is illustrated by the greater yields and selectivity displayed by $\text{IMes}\cdot\text{AlH}_2\text{Cl}$ (**39**) over $\text{IMes}\cdot\text{AlHCl}_2$ (**40**) in hydroalumination reactions on carbonyl or epoxide containing substrates. This was attributed to the strengthening of the Al-H bond and increased steric bulk of the latter resulting in poorer catalytic activity. Moreover, $\text{IMes}\cdot\text{AlH}_2\text{Cl}$ (**39**) mediates the ring-opening of styrene oxide into the primary alcohol derivatives 1-phenylethan-1-ol and 2-phenylethan-1-ol (ratio 29:71); whereas no reaction is observed for $\text{IMes}\cdot\text{AlHCl}_2$ (**40**).⁴³ More recently, Hevia *et al.*⁵¹ described the structure, stability and isomerization reactions between normal (*n*) and abnormal (*a*) NHC-gallium alkyl complexes; followed by studies by Dagorne *et al.*³⁴ into the normal-to-abnormal NHC rearrangement and small molecule activation on the aluminium, gallium and indium triad. These studies highlight the importance of steric and electronic factors on the stability, and hence accessibility and stability of both normal and abnormal NHC main group complexes.

Therefore, the synthesis, characterisation and reactivity studies of new NHC Group 13 complexes still remains as an exciting area for main group chemists. On the previous chapter, it was reported that in a series of NHC trimethylaluminium complexes (**122** - **125**), small differences in their steric properties have a profound effect on their stability (Figure 3.1).⁸⁴ Therefore, these findings prompted us to find out more about the stability and reactivity of their heavier counterparts. Herein, this chapter will report the synthesis, characterization and stability studies of a series of aromatic N-substituted NHC trimethylgallium and indium complexes. In addition, extensive DFT calculations have been performed on the metal series of NHC Group 13 complexes to understand their bonding contributions to stability, as well as their differences in bonding in comparison with NHC transition metal and PHC complexes.

Scheme 3.1: Synthetic route for the syntheses of the NHC trimethyl-Group 13 complexes (**122 - 125**, **145 - 152**).⁸⁴

3.2 Results and Discussion

3.2.1 Synthesis of trimethylgallium and indium complexes **145 - 152**

The general synthetic route for the syntheses of these complexes is the formation of a Lewis acid-base adducts (Scheme 3.1).^{30, 83} Hence, treatment of 1 equivalent of carbene (IMes, SIMes, IPr and SIPr) with trimethylgallium⁸⁵ and indium, generated *in-situ*,⁸⁶ resulted in the isolation of their respective complexes IMes•GaMe₃ (**145**), SIMes•GaMe₃ (**146**), IPr•GaMe₃ (**147**), SIPr•GaMe₃ (**148**), IMes•InMe₃ (**149**), SIMes•InMe₃ (**150**), IPr•InMe₃ (**151**), SIPr•InMe₃ (**152**). All the compounds were crystallised in ether or toluene at room temperature or at 0°C.

Figure 3.1

All compounds are highly air- and moisture-sensitive; traces of decomposition were consistently observed during their characterization, making their characterization tedious and all attempts of elemental analyses unsuccessful. Moreover, this was also observed for **148**

and **152** in the solid state, where argon-gas-stored samples slowly decomposed at room temperature.

3.2.2 Spectroscopic studies of trimethylgallium and indium complexes **145** - **152**

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra obtained for complexes **145** - **152** are consistent with their low temperature X-ray crystallographic analysis. The ^1H NMR spectra for the gallium and indium complexes display singlets at δ_{H} -0.56 to -0.60, and at δ_{H} -0.52 to -0.62 respectively, which is indicative of the presence of the methyl groups on the metal centre. This is further corroborated by the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra which display singlets at δ_{C} -5.2 to -6.1 and δ_{C} -9.6 to -11 for gallium and indium complexes, respectively. Moreover, the IR spectra of **145** - **148** show a relatively strong stretching signal at around 524 cm^{-1} , representing the Ga-C stretching mode, and consistent with the presence of the methyl groups on the metal centre.⁸⁷ Unfortunately, in case of indium analogues, no suitable IR stretching signal was clearly observed since the In-Me range fall within a high noise background region (*i.e.*, $\sim 400\text{ cm}^{-1}$).⁸⁷ Additionally, an upfield shift of the $\text{C}_{\text{carbene}}$ signals further confirmed the formation of the complexes (Table 3.1).^{70, 83} Unfortunately, no $\text{C}_{\text{carbene}}$ signal was obtained for complex **149** due to the high quadrupole moment of the indium centre.^{29, 49, 50, 52, 59, 60, 83, 88}

Table 3.1: ^1H and ^{13}C NMR chemical shifts for complexes **145**-**152**.

Complexes	^1H [MMe_3] ^a (ppm)	^{13}C [$\text{M-C}_{\text{carbene}}$] ^a (ppm)	^{13}C [$\text{C}_{\text{carbene}}$] ^b (ppm)
145	-0.56	181.7	219.4
146	-0.60	206.1	243.8
147	-0.59	184.5	220.4
148	-0.58	209.0	244.0
149	-0.52	-	219.4
150	-0.58	209.3	243.8
151	-0.60	186.8	220.4
152	-0.62	211.7	244.0

^a ^1H and ^{13}C NMR chemical shifts were obtained in C_6D_6 . ^b ^{13}C NMR chemical shift was obtained from ref. 70 in C_6D_6 .

3.2.3 Crystallographic studies of trimethylgallium and indium complexes **145** - **152**

Single-crystal X-ray structures of complexes **145** - **152** are shown in Figures 3.2 – 3.5. Complexes **146** - **150** crystallised out as two crystallographically independent but chemically equivalent molecules, hence only one molecule will be described herein. In addition, the complexes **150** and **152** are the first structurally characterized indium complexes containing saturated NHC moieties.

Figure 3.2: Molecular structure of complex IMes•GaMe₃ (**145**) and IMes•InMe₃ (**149**), left and right, respectively. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°) for **145**: Ga(1)-C(1) 2.111(2), Ga(1)-C(2) 1.987(3), Ga(1)-C(3) 1.996(2), N(1)-C(1) 1.357(3), N(1)-C(6) 1.381(3), N(2)-C(1) 1.362(3), N(2)-C(5) 1.384(3), C(5)-C(6) 1.334(4), C(1)-Ga(1)-C(2) 108.8(1), C(1)-Ga(1)-C(3) 105.8(1), C(2)-Ga(1)-C(3) 111.1(1), C(3)-N(1)-C(3A) 114.0(2), N(1)-C(1)-N(2) 103.6(2). Selected bond lengths (Å) and angles (°) for **149**: In(1)-C(1) 2.304(8), In(1)-C(2) 2.186(9), In(1)-C(3) 2.175(8), In(1)-C(4) 2.190(8), N(1)-C(1) 1.359(1), N(1)-C(5) 1.369(1), N(2)-C(1) 1.349(1), N(2)-C(6) 1.386(1), C(5)-C(6) 1.336(1), C(1)-In(1)-C(2) 105.5(3), C(1)-In(1)-C(3) 105.2(3), C(1)-In(1)-C(4) 104.3(3), C(2)-In(1)-C(3) 114.7(3), C(2)-In(1)-C(4) 111.0(4), C(3)-In(1)-C(4) 114.9(4), N(1)-C(1)-N(2) 103.9(6).

Figure 3.3: Molecular structure of complex SiMes•GaMe₃ (**146**) and SiMes•InMe₃ (**150**), left and right, respectively. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°) for **146**: Ga(1)-C(1) 2.124(5), Ga(1)-C(2) 2.000(6), Ga(1)-C(3) 2.018(6), Ga(1)-C(4) 2.028(6), N(1)-C(1) 1.346(7), N(1)-C(5) 1.480(7), N(2)-C(1) 1.339(7), N(2)-C(6) 1.499(7), C(5)-C(6) 1.535(8), C(1)-Ga(1)-C(2) 105.0(2), C(1)-Ga(1)-C(3) 110.8(2), C(1)-Ga(1)-C(4) 106.8(2), C(2)-Ga(1)-C(3) 112.5(2), C(2)-Ga(1)-C(4) 113.1(2), C(3)-Ga(1)-C(4) 108.5(3), N(1)-C(1)-N(2) 107.8(5). Selected bond lengths (Å) and angles (°) for **150**: In(1)-C(1) 2.316(8), In(1)-C(2) 2.216(9), In(1)-C(3) 2.199(9), In(1)-C(4) 2.183(8), N(1)-C(1) 1.346(10), N(1)-C(5) 1.478(11), N(2)-C(1) 1.331(10), N(2)-C(6) 1.491(10), C(5)-C(6) 1.535(11), C(1)-In(1)-C(2) 105.9(3), C(1)-In(1)-C(3) 109.2(3), C(1)-In(1)-C(4) 101.8(3), C(2)-In(1)-C(3) 109.7(4), C(2)-In(1)-C(4) 114.1(3), C(3)-In(1)-C(4) 115.3(3), N(1)-C(1)-N(2) 107.4(7).

Figure 3.4: Molecular structure of complex $\text{IPr}\cdot\text{GaMe}_3$ (**147**) and $\text{IPr}\cdot\text{InMe}_3$ (**151**), left and right, respectively. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) for **147**: Ga(1)-C(1) 2.105(4), Ga(1)-C(2) 2.013(4), Ga(1)-C(3) 2.006(4), Ga(1)-C(4) 1.994(4), N(1)-C(1) 1.356(4), N(1)-C(5) 1.388(5), N(2)-C(1) 1.351(4), N(2)-C(6) 1.386(5), C(5)-C(6) 1.332(5), C(1)-Ga(1)-C(2) 101.3(1), C(1)-Ga(1)-C(3) 110.7(1), C(1)-Ga(1)-C(4) 108.4(2), C(2)-Ga(1)-C(3) 115.3(2), C(2)-Ga(1)-C(4) 112.4(2), C(3)-Ga(1)-C(4) 108.3(2), N(1)-C(1)-N(2) 103.6(3). Selected bond lengths (Å) and angles ($^\circ$) for **151**: In(1)-C(1) 2.309(2), In(1)-C(2) 2.183(2), In(1)-C(3) 2.192(2), In(1)-C(4) 2.202(2), N(1)-C(1) 1.353(2), N(1)-C(6) 1.388(2), N(2)-C(1) 1.361(2), N(2)-C(5) 1.384(2), C(5)-C(6) 1.342(2), C(1)-In(1)-C(2) 106.8(1), C(1)-In(1)-C(3) 108.6(1), C(1)-In(1)-C(4) 101.3(1), C(2)-In(1)-C(3) 111.4(1), C(2)-In(1)-C(4) 114.5(1), C(3)-In(1)-C(4) 113.3(1), N(1)-C(1)-N(2) 103.7(1).

Figure 3.5: Molecular structure of complex $\text{SiPr}\cdot\text{GaMe}_3$ (**148**) and $\text{SiPr}\cdot\text{InMe}_3$ (**152**), left and right, respectively. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) for **148**: Ga(1)-C(1) 2.137(2), Ga(1)-C(2) 2.010(2), Ga(1)-C(3) 2.010(2), Ga(1)-C(4) 1.991(2), N(1)-C(1) 1.343(2), N(1)-C(5) 1.487(2), N(2)-C(1) 1.343(2), N(2)-C(6) 1.482(2), C(5)-C(6) 1.532(3), C(1)-Ga(1)-C(2) 100.0(1), C(1)-Ga(1)-C(3) 111.2(1), C(1)-Ga(1)-C(4) 107.5(1), C(2)-Ga(1)-C(3) 110.4(1), C(2)-Ga(1)-C(4) 115.1(1), C(3)-Ga(1)-C(4) 112.1(1), N(1)-C(1)-N(2) 108.1(2). Selected bond lengths (Å) and angles ($^\circ$) for **152**: In(1)-C(1) 2.342(2), In(1)-C(2) 2.200(2), In(1)-C(3) 2.178(2), In(1)-C(4) 2.196(2), N(1)-C(1) 1.339(2), N(1)-C(5) 1.481(2), N(2)-C(1) 1.340(2), N(2)-C(6) 1.484(2), C(5)-C(6) 1.528(3), C(1)-In(1)-C(2) 99.6(1), C(1)-In(1)-C(3) 104.8(1), C(1)-In(1)-C(4) 108.5(1), C(2)-In(1)-C(3) 119.1(1), C(2)-In(1)-C(4) 109.8(1), C(3)-In(1)-C(4) 113.5(1), N(1)-C(1)-N(2) 108.3(2).

Previously reported gallium and indium NHC complexes were mostly heteroleptic species.⁵² Furthermore, only five trimethylgallium and one trimethylindium complexes were characterized prior to our studies (*i.e.*, **10**, **20**, **66a**, **66b**, **67** and **21**).^{29, 34, 52} In general, these complexes adopt a distorted tetrahedral geometry at the metal centre, with the exception of In complexes **102**, **103** and **104**.⁵⁹ For complex **102**, albeit the indium centre is four

coordinate, it does not adopt a distorted tetrahedral geometry due to the weak carbene chloride interaction, causing the chloride to lie orthogonal to the carbene plane.⁵⁹ As for **103** and **104**, the indium centre is five coordinate due to additional interaction with the neighbouring triflate of the adjacent indium molecule, hence adopting a pentacoordinate trigonal bipyramidal geometry.⁵⁹

Figure 3.6

Figure 3.7

Compounds **145** - **152** adopt a distorted tetrahedral geometry at the Ga and In centres, with M-C_{carbene} bond lengths ranging from 2.111 – 2.137 Å, and 2.301 – 2.342 Å, respectively. In the case of compounds **145** - **148** the bond lengths are consistent with the previously reported trimethylgallium complexes (*cf.* 2.130(2) Å, 2.105(2) Å, 2.121(3) Å, 2.132(3) Å for **10**, **66a**, **66b** and **67**, respectively) (see Table 3.2).^{29, 52} In accordance with what was previously observed for the trimethylaluminium counterparts, where the M-C_{carbene} bond distance in SiPr•AlMe₃ (**125**) was similar to that of the less sterically bulky liPrMe•AlMe₃ (**10**) (2.127(2) and 2.124(6) Å, respectively) (Chapter 2).^{29, 84} The Ga-C_{carbene} bond distance in **148** is comparable to that of liPrMe•GaMe₃ (**10**) (2.137(2) and 2.13(2) Å, respectively).²⁹ Slight bond lengthening of the M-C_{carbene} bond distances was also observed going from **146**, **148**, **150** and **152** with respect to **145**, **147**, **149** and **151** (saturated NHCs vs. unsaturated NHCs) (Table 3.2), which is consistent with Yates, Huynh and Plenio previous observations where saturated NHCs were shown to be marginally more basic as compared to their

unsaturated counterparts for group 13 elements (decreasing σ -donor strength (SIPr ~ SIMes > IPr > IMes)).^{18, 19, 20}

Table 3.2: Ga-C_{carbene} and In-C_{carbene} bond lengths of selected NHC gallium and indium complexes.^{29, 52, 59, 84}

Entries	Complexes	M-C _(carbene) [Å]
1	IMes•GaMe ₃ (145)	2.111(2)
2	SIMes•GaMe ₃ (146)	2.124(5)
3	IPr•GaMe ₃ (147)	2.105(4)
4	SIPr•GaMe ₃ (148)	2.137(2)
5	IMes•InMe ₃ (149)	2.304(7)
6	SIMes•InMe ₃ (150)	2.316(8)
7	IPr•InMe ₃ (151)	2.309(2)
8	SIPr•InMe ₃ (152)	2.342(2)
9	IMes•AlMe ₃ (122)	2.098(2)
10	SIMes•AlMe ₃ (123)	2.112(6)
11	IPr•AlMe ₃ (124)	2.103(3)
12	SIPr•AlMe ₃ (125)	2.127(2)
13	liPrMe•GaMe ₃ (10)	2.130(2)
14	IMes•GaMe ₃ (66a)	2.105(2)
15	SIMes•GaMe ₃ (66b)	2.121(3)
16	SIPr•GaMe ₃ (67)	2.132(3)
17	IMes•GaMe ₂ OMe (70a)	2.089(2)
18	SIMes•GaMe ₂ OMe (70b)	2.101(1)
19	IMes•InMe ₂ Cl (102)	2.267(2)
20	IMes•InMe ₂ OTf (103)	2.264(2)
21	IMes•InMe(OTf) ₂ (104)	2.183(2)

3.2.4 Lewis acid-base properties of trimethylgallium and indium complexes **145 - 152**

The majority of previously reported NHC-gallium and -indium complexes comprise of halido and hydrido derivatives (NHC·MH_{3-n}Cl_n; M = Ga and In; n = 1, 2).^{83, 88} The reported chlorogallane complexes IMes·GaH₂Cl (**57**) and IMes·GaHCl₂ (**58**) showed that the Lewis acidity of the metal centre increases with an increasing number of electron withdrawing groups (*i.e.*, chlorido ligands). The increase in Lewis acidity results in the shortening of the Ga-C_{carbene} bond length and the strengthening of the gallium hydride bond (Table 3.3, entries 9 and 10).⁴⁸ The same effect was also observed for lighter counterparts, IMes·AlH₂Cl (**39**) and IMes·AlHCl₂ (**40**), which resulted in significantly different catalytic activity for the hydroalumination reactions (*vide supra*).⁴³ With the inclusion of the herein reported trimethylgallium and indium complexes, a comparison can be established with the other metal halides and hydrides complexes. In the case for the gallium complexes **145 - 148**, the trimethylgallium moiety is a poorer Lewis acid as compared to the hydrido and halido

ligands. This is evident from the Ga-C_{carbene} bond distances reported for the IMes, SIMes and IPr compounds (see Table 3.3, entries 1-3, 9-13). The IMes•GaH₃ (**56**) has been synthesized but no suitable crystal data was obtained as reported by Jones *et. al.*⁶⁰ In the case of indium complexes, similar trend can be established as with the gallium (Lewis acid strength in increasing order: MMe₃ < MH₃ < MX₃), the reported In-C_{carbene} bond distances are shown in Table 3.3 (entries 5 and 7, 14 - 18).^{27, 59, 60}

In general, the majority of reported NHCs gallium and indium complexes do not have M-C_{carbene} peak in their ¹³C{¹H} NMR spectra. This is attributed to the quadrupolar moment of the metal centre attached to the carbenic carbon. Hence, only two gallium and indium NHCs complexes, IMes•GaH₂Cl (**57**) and IMes•InMe₂Cl (**102**), had their C_{carbene} signals reported (δ_C 172.5 and 177.5, respectively).^{48, 60} Nevertheless, by comparing the ¹³C{¹H} NMR signal of the IMes•GaH₂Cl (**57**) and IMes•InMe₂Cl (**102**) with the newly synthesized complexes **145** - **152**, the signal obtained was relatively downfield as compared to gallium and indium complex **145** - **152** (Tables 3.1). This is unsurprising, since the chloride ligand on the metal exerts a strong electron withdrawing effect. These observations further corroborate that the MMe₃ are poorer electron acceptor as compared to the MH₃ and MX₃.

Table 3.3: Ga-C_{carbene} and In-C_{carbene} bond lengths of complexes **145** - **152** and selected mixed NHC gallium and indium complexes.^{27, 48, 59, 60,}

Entries	Complexes	M-C _(carbene) [Å]
1	IMes•GaMe ₃ (145)	2.111(2)
2	SIMes•GaMe ₃ (146)	2.124(5)
3	IPr•GaMe ₃ (147)	2.105(4)
4	SIPr•GaMe ₃ (148)	2.137(2)
5	IMes•InMe ₃ (149)	2.304(7)
6	SIMes•InMe ₃ (150)	2.316(8)
7	IPr•InMe ₃ (151)	2.309(2)
8	SIPr•InMe ₃ (152)	2.342(2)
9	IMes•GaClH ₂ (57)	2.030(3)
10	IMes•GaCl ₂ H (58)	2.005(6)
11	IMes•GaCl ₃ (75)	1.954(4)
12	IPr•GaH ₃ (55)	2.055(1)
13	IPr•GaCl ₃ (73)	2.016(2)
14	IMes•InH ₃ (100)	2.253(5)
15	IMes•InH ₂ Cl (101)	2.244(6)
16	IMes•InBr ₃ (106)	2.195(5)
17	IMes•InMe ₂ Cl (102)	2.267(2)
18	IPr•InBr ₃ (105)	2.212(8)

Jones *et al.* also demonstrated the difference in Lewis acidity between indium halides and hydrides by showing that indium halides tend to form chelating complexes or 2:1 adducts, whereas complexes containing hydrido ligands only form monomeric species.²⁸ Since the trimethylindium is expected to be a poorer Lewis acid, it is expected to only form monomeric species. Therefore, and in order to verify our observation, two equivalents of the IMes carbene were reacted with trimethylindium under various conditions. However, despite several attempts, no pentacoordinate trigonal bipyramidal adducts were able to be isolated which supported our initial postulation.

3.2.5 Stability studies of trimethylgallium and indium complexes 145 - 152

Previously it was observed for trimethylaluminium counterparts **122** - **125**, that complexes **124** and **125** decompose to their respective imidazolylidene and imidazolinylidene and other side products, whereas no decomposition was observed for **122** and **123**. The differential stability observed was attributed to small subtle variations in percent buried volume, % V_{Bur} , occupied by the NHC groups (IPr and SiPr) present on **124** and **125**, as compared to the ones present in **122** and **123** (IMes and SIMes).²¹

In addition, it was also reported by Hevia *et al.*⁵¹ and Dagorne *et al.*³⁴ that bulky NHC group 13 complexes, such as IPrGa•(CH₂SiMe₃)₃, ItBu•GaMe₃ (**20**) and ItBu•InMe₃ (**21**), isomerized to their respective abnormal NHC counterparts, with the latter two complexes unable to be structurally characterized due to its rapid isomerization to their abnormal carbene complexes (Chapter 1).³⁴ Calculations performed on the normal (*n20* and *n21*) and abnormal (*a20* and *a21*) model complexes of **20** and **21** showed that their abnormal counterparts were more stabilized as compared to their normal carbene complexes (Gibbs free energy for -5.89 kcal mol⁻¹ for Ga model *n20* vs. *a20* and -1.40 kcal mol⁻¹ for In model *n21* vs. *a21*).³⁴ As for Hevia *et al.*, they proposed a mechanism utilizing the IPrGa•(CH₂SiMe₃)₃ complex as model (see Scheme 3.2).

Scheme 3.2: Proposed mechanism for the isomerization of $\text{IPrGa}\cdot(\text{CH}_2\text{SiMe}_3)_3$ to its abnormal counterpart.⁵¹

The generation of the free carbene IPr and the abnormal NHC gallium complex (Scheme 3.2), is consistent with some of the experimental observations on our Al complexes **124** and **125**, where the generation of the free carbenes alongside other by products were detected; however, no abnormal NHC species were observed during our studies.⁵¹

In the case of the Ga and In counterparts, compounds **145** - **152** are relatively more stable than their lighter aluminium analogues since decomposition was only observed for compounds **149** and **152** (in C_6D_6) (*vide infra*). However, signals indicating the formation of abnormal species were not observed during out ^1H NMR spectroscopic studies. In order to compare the group traits of the complexes, the percent buried volume, $\% V_{\text{Bur}}$, was used to compare the ligands in the gallium and indium complexes (**145** - **152**).²¹ Following the same procedure previously used for the stability studies on the Al complexes, the $\% V_{\text{Bur}}$ was calculated with the M-NHC distance fixed at $2.0 \text{ \AA}$, in order to have a comparison of the various NHCs not biased by different M-NHC distances (Table 3.4).

Table 3.4: Ga-C_{carbene} and In-C_{carbene} bond lengths, %V_{Bur}, and dissociation energies E_{diss} of complexes **145** - **152** and selected mixed NHC gallium and indium complexes.

Entries	Complexes	M-C _{carbene}	M-C _{carbene}	%V _{Bur}	E _{diss}
		[Å] X-ray	[Å] DFT	R= 2.0 Å	(kJ mol ⁻¹)
1	IMes•GaMe ₃ (145)	2.111(2)	2.201	32.7	78.8
2	SIMes•GaMe ₃ (146)	2.124(5)	2.231	33.9	71.2
3	IPr•GaMe ₃ (147)	2.105(4)	2.213	34.3	70.2
4	SIPr•GaMe ₃ (148)	2.137(2)	2.233	35.6	52.9
5	IMes•InMe ₃ (149)	2.301(8)	2.428	33.3	76.8
6	SIMes•InMe ₃ (150)	2.301(8)	2.453	34.4	69.8
7	IPr•InMe ₃ (151)	2.309(2)	2.446	35.1	67.0
8	SIPr•InMe ₃ (152)	2.342(2)	2.478	36.2	50.6
9	IMes•AlMe ₃ (122)	2.098(2)	2.162	32.8	107.9
10	SIMes•AlMe ₃ (123)	2.112(6)	2.188	33.8	99.0
11	IPr•AlMe ₃ (124)	2.103(3)	2.164	34.3	98.2
12	SIPr•AlMe ₃ (125)	2.127(2)	2.190	35.5	79.9
13	IPrMe•GaMe ₃ (10)	2.130(2)	2.165	27.8	90.5
14	IPrBu•GaMe ₃ (20)	-	2.316	36.7	34.2
15	IPrBu•InMe ₃ (21)	-	2.558	37.5	20.2
16	IPrGa•(CH ₂ SiMe ₃) ₃	2.196(2)	2.301	31.6	26.4

%V_{Bur} Me groups on IPr-GaR₃ = 48.7
%V_{Bur} CH₂SiMe₃ groups on IPr-GaR₃ = 64.5

Calculations performed on the complexes showed that the volume of the NHCs increases gradually from **145** - **148** for the gallium complexes (**145** > **146** > **147** > **148**) and **149** - **152** for the indium complexes (**149** > **150** > **151** > **152**). Similar trend was observed on the Al complexes (**122** > **123** > **124** > **125**) (Table 3.4), which is in agreement with their calculated dissociation energies. The similar stability trend observed for **148** and **152** can be attributed to the larger volume occupied by isopropylphenyl groups as compared to the mesityl groups (*vide supra*). In addition, comparison of the %V_{Bur} of the ligands between complexes **148** and **152** and their hypothetical (DFT calculated) ItBu analogues **20** and **21** (Ga and In respectively), showed a comparable %V_{Bur} values (*cf.* 35.6%, 36.2%, 36.7% and 37.5% for **148**, **152**, **20** and **21** respectively). These values support the slightly higher stability in their normal NHC form as compared to their ItBu analogues. However, all attempts to isolate metallic containing species produced during the observed decay of **148** and **152** were unsuccessful. Moreover, the facile isomerization to aNHC complex of the previously reported IPr•Ga(CH₂SiMe₃)₃⁵¹ in comparison to **147** can be attributed to the higher steric congestions imposed by the CH₂SiMe₃ vs. Me₃ groups (%V_{Bur} 64.5% and 48.7% for CH₂SiMe₃ and Me

groups respectively). This is further illustrated by the longer Ga-C_{carbene} bond distance and lower calculated dissociation energy when compared to those of **147** (cf., 2.213 vs. 2.301 Å and 70.2 vs. 26.4 kJ·mol⁻¹, respectively).

Comparative analysis of the topographic maps of complex **150** and **152** (a stable vs. an unstable system) showed that the distribution of the steric bulk of the ligand in **150** is symmetrical around the metal, whereas for **152** high steric hindrance localized around the bulkier ortho isopropyl group was clearly observed on the steric contour map (see Figure 3.10). The spatial distribution of the NHC ligand around the indium centre in **152** is clearly correlated to its reduced stability compared to the indium complex **150**.

Figure 3.8: Topographic steric maps of the SIMes and SIPr ligands in **150** and **152**. The iso-contour curves of the steric maps are in Å. The maps have been obtained starting from the crystallographic data of the Al-NHC complexes (CIF), with the Al-C_{carbene} distance fixed at 2.0 Å. The xz plane is the mean plane of the NHC ring, whereas the yz plane is the plane orthogonal to the mean plane of the NHC ring, and passing through the C_{carbene} atom of the NHC ring.

3.2.6 Bonding studies of the NHCs Group 13 complexes **122 - 125, 145 - 152**

To gain a better understanding of the nature of M-NHC bonds with M = Al, Ga and In, a *bond snapping energy* (**BSE**) analysis was performed.⁸⁹ The BSE is the energy required for the dissociation of the M-L bond. The bonding energy is analyzed based on the interaction of two fragments that both possess the local equilibrium geometry of the final molecule and which both have an electronic structure suitable for bond formation. In these calculations the geometry of the metal fragment [M] – in this case MMe₃ – was fixed, and the heterolytic BSE for **145 - 152** were calculated, which involves fragmenting the complex into neutral [M] and NHC fragments. Although BSE does not always correlate with bond dissociation enthalpies (since reorganization and relaxation of the fragments are not considered). BSE is closely related to bond enthalpy terms and can be a good approximation to bond strength values.

In addition, BSE can be decomposed into two main components, namely *steric interaction* (ΔE_0) and *orbital interaction* (ΔE_{int}) (Eqn 1).⁸⁹

$$BSE = -[\Delta E_0 + \Delta E_{int}]$$

The steric interaction term ΔE_0 can further be split into an electrostatic interaction term ΔE_{elstat} and a Pauli repulsion term ΔE_{Pauli} , which is directly related to the two-orbital electron interactions between occupied orbitals on both interacting fragments (Eqn 2):⁸⁹

$$\Delta E_0 = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}}$$

Whereas ΔE_{elstat} constitutes a stabilizing contribution to BSE, ΔE_{Pauli} constitutes a destabilizing contribution, and it is the relative size of electrostatic interaction and Pauli repulsion that determines the overall character of the steric interaction term.

The total orbital interaction energy ΔE_{int} can further be broken down into contributions from different orbital interactions within the various irreducible representations τ of the overall symmetry group of the system (Eqn 3):⁸⁹

$$\Delta E_{\text{int}} = \sum_{\tau} \Delta E_{\text{int}}^{\tau}$$

All the molecules studied in the present work have been optimized with a C_s imposed symmetry, where the NHC ligands are located in the σ_{xy} mirror plane of the molecule. Therefore, the A' contributions to the orbital interaction energy are associated with σ -bonding and the A'' contributions represent π -interactions.

The A'' contribution of the orbital interaction energy is further divided into NHC $\rightarrow$ M π -donation, $\Delta E_{\text{int}}^{\pi} \text{C} \rightarrow \text{M}$, and M $\rightarrow$ NHC π -backdonation, $\Delta E_{\text{int}}^{\pi} \text{M} \rightarrow \text{C}$. In order to estimate these two interactions, additional constrained space orbital variation (CSOV) calculations were performed.⁸⁹ In particular, to assess the contribution of π -donation, the bond decomposition analysis was performed by considering the interaction of a [M] fragment and an NHC ligand, but now excluding the set of virtual A'' orbitals of the NHC fragment from the variational space. In this way, the A'' contribution of the orbital interaction energy is associated only with the NHC $\rightarrow$ [M] A'' donation, or π -donation. Similarly, the level of π -backdonation was determined explicitly excluding all virtual A'' orbitals on the [TM] fragment.

Since the energy decomposition analysis (EDA) is performed on the intrinsic strength of the M-NHC bond, which is independent on the environment that may stabilize the two fragments, the EDA is performed in the gas-phase. One NHC ligand was selected, namely IMes, as the focus of comparison between the three metals (see Table 3.5).

Table 3.5: BSE-decomposition (in kJ mol⁻¹) of M-IMes bond for Al, Ga and In as metal

	Complexes		
	122 (Al)	145 (Ga)	149 (In)
ΔE_{elstat}	-321.4	-334.7	-287.6
ΔE_{Pauli}	331.4	380.4	308.0
ΔE^0	10.0	45.7	20.3
ΔE_{int}	-175.4	-180.8	-135.5
$\sigma - \Delta E_{\text{int}}$	-151.3 (86.3%)	-161.4 (89.3%)	-119.8 (88.5%)
$\pi - \Delta E_{\text{int}}$	-24.1 (13.7%)	-19.4 (10.7%)	-15.6 (11.5%)
$\Delta E_{\text{int}}^{\pi} \text{ c} \rightarrow \text{M}$	-8.5	-7.3	-5.5
$\Delta E_{\text{int}}^{\pi} \text{ M} \rightarrow \text{c}$	-18.1	-14.3	-11.4
BSE	165.3	135.1	115.2

The data reported in Table 3.5 suggest that the greater strength of the Al–IMes bond with respect to that of the Ga–IMes is mainly attributable to the steric term (ΔE_0). In fact, the steric term of the Pauli contribution destabilizes the Ga system more than the electrostatic term is able to stabilize, with the $\Delta(\Delta E_{\text{Pauli}}(\text{Ga}) - \Delta E_{\text{Pauli}}(\text{Al}))$ being almost 3.5 times larger with respect to the $\Delta(\Delta E_{\text{elstat}}(\text{Ga}) - \Delta E_{\text{elstat}}(\text{Al}))$. As a result, the steric term disfavors the Ga–IMes bond by 45.7 kJ mol⁻¹. A detailed orbital analysis shows that the greater ΔE_{Pauli} term for Ga–IMes system is related to interactions between occupied orbitals on the NHC and occupied 3d orbitals on the Ga atom. The repulsion term decreases for Al since there are no d-electrons. Intuitively, the orbital interaction is mainly constituted by the σ term and is larger in magnitude for the Ga–IMes system. For the π term, the main difference is in the M→C interaction, *i.e.* almost 4 kJ mol⁻¹ stronger for Al.

In a comparison of Ga vs. In, the steric term again unfavors the Ga system: the Pauli term gives the greatest contribution, $\Delta(\Delta E_{\text{Pauli}}(\text{Ga}) - \Delta E_{\text{Pauli}}(\text{In}))$ 1.5 times greater with respect to the $\Delta(\Delta E_{\text{elstat}}(\text{Ga}) - \Delta E_{\text{elstat}}(\text{In}))$. The orbital interaction is much greater for the Ga–IMes bond, both at σ and π level, compensating the unfavored steric term. For completeness, it is worth noting that the greater energy observed for the Al–NHC bond with respect to that of Ga–NHC reflects the larger dissociation energy calculated for Al compounds with respect to Ga (see last column in Table 3.4). With regard to the Ga/In trend, the dissociation energies reported are almost the same (varying less than 4.0 kJ mol⁻¹) in agreement with the smaller difference calculated, reported in Table 3.5, for the strength of the Ga/In–NHC bonds (*i.e.* 20 kJ mol⁻¹ and 30 kJ mol⁻¹ for Al and Ga, respectively).

As observed in the ¹H and ¹³C NMR, in which a downfield shift of the ¹³C NMR signal of the carbene C atom and the upfield shift of the ¹H NMR signal of the hydrogen atoms on the Me groups on Al, in the case of the SIMes•AlMe₃ complex as compared to the IMes•AlMe, a

DFT-NMR analysis was performed to better decipher these shifts. The chemical shielding calculated, σ_C , is -3.9 and -24.3 ppm for the carbene atom of IMes and SIMes system, respectively. Decomposing the isotropic chemical shielding σ_C into dia- and paramagnetic terms, $\sigma_C = \sigma_d + \sigma_p$, indicates that the change in σ_C is due to the paramagnetic term σ_p , that varies by almost 21 ppm downfield from IMes to SIMes. Based on literature considerations,⁹⁰ which indicated that the carbene chemical shift in NHCs is connected to transitions between the filled M-NHC σ bond and the empty π orbital of the carbene, the energy gap between the HOMO and the LUMO on the NHC was focused. This energy gap calculated decreases by almost 0.2 eV moving from IMes to SIMes due to a decreased stability of the HOMO orbital on the SIMes NHC. The smaller energy gap involved results in a stronger magnetic coupling and accounts for the higher paramagnetic shielding (downfield shift) in Al-SIMes respect to Al-IMes.

As for the ^1H NMR analysis, the observed and calculated upfield shift of the methyl hydrogens on Al in case of the SIMes ligand system is related to reduced back-donation $[\text{Al}] \rightarrow \text{NHC} (\pi^*)$ that results from a smaller π orbital overlap, probably as consequence of the slightly elongated Al-SIMes distance. As result of this decreased $[\text{Al}] \rightarrow \text{NHC}$ back-donation, the electron density is pushed towards the other ligands on the Al center, *i.e.* the methyl groups, leading to an upfield shift of the H atoms.^{91, 92}

Overall, the EDA results highlighted that the interactions between occupied orbitals on the NHC and occupied 3d orbitals on the Ga destabilize the Ga system with respect to the Al and the In one. However, the orbital interaction is stronger for Ga than for In, making the overall trend of the M-NHC strength equal to $\text{Al} > \text{Ga} > \text{In}$. As for the orbital interaction, it is mainly constituted by the σ term, with a small π term consisting mostly in a back-donation from the metal fragment to the NHC.

As a final remark, a comparison with the BSE decomposition analysis were performed on a TM-NHC and a TM-PHC complex, *i.e.* IMes-Pd-IMes and IMes(P)-Pd-(P)IMes, to highlight the main differences between transition metal and group 13 M-NHC (Me_3Al -IMes as case in point) bonds (Table 3.6).

Table 3.6: BSE-decomposition (in kJ/mol) of Al-IMes, Pd-IMes and Pd-(P)IMes

	Complexes		
	Al - IMes	Pd - IMes	Pd - (P)IMes
ΔE_{elstat}	-321.4	-589.4	-537.3
ΔE_{Pauli}	331.4	578.3	550.6
ΔE^0	10.0	-11.1	13.3
$\sigma - \Delta E_{\text{int}}$	-151.3	-129.0	-143.2
$\pi - \Delta E_{\text{int}}$	-24.1	-53.8	-53.5
$\Delta E_{\text{int}}^{\pi} \text{ C} \rightarrow \text{M}$	-8.5	-5.8	-5.6
$\Delta E_{\text{int}}^{\pi} \text{ M} \rightarrow \text{C}$	-18.1	-50.6	-49.6
ΔE_{int}	-175.4	-182.7	-196.7
BSE	165.3	193.8	183.2

The increased bond strength of the Pd-NHC bond (almost 30.0 kJ mol⁻¹) with respect to that of Al-NHC is largely attributed to the steric term (20.0 kJ mol⁻¹) rather than to the orbital interaction (10 kJ mol⁻¹). For the latter contribution, despite a smaller σ term in the Pd-NHC bond, a more than double π term is found due to π -backdonation. For the Pd-PHC system, the considered bond bears a greater resemblance to that of Al-NHC for the steric and σ terms, however, as expected, the same meaningful π -backdonation term as Pd-PHC is found. Overall, the substitution of N atoms with P ones leads to a stronger orbital contribution (σ term) to the M-NHC bond but disfavors the steric term (mainly Pauli term) to the M-NHC bond.

3.2.7 By-product obtained from SIPr•InMe₃ (**152**)

As the generation of the indium complexes **150** and **151** were performed at room temperature, similar procedure was also followed for **149** and **152**, but instead by-products were observed and only the desired compounds were obtained at 0 °C. For complex **149**, indium metal was deposited when reactions were conducted at room temperature. As for complex **152**, a formamide derivative **153** was obtained instead. This reaction was reported by Günay *et al.* on palladacycle acetate dimer to be favoured by the presence of water due to the presence of the aldehyde and NH group on **153**.⁹³ Therefore, the reaction was performed again by first obtaining complex **152** at 0 °C, followed by the addition of stoichiometric amount of water, and the expected product **153** was obtained. Currently we are studying the mechanism of the reaction to see whether indium plays a part in the reaction. Another postulation is the NHC SIPr was dissociated from the indium complex **152** followed by insertion of the water which resulted in the cleavage of the ring, since dissociation of saturated NHCs were shown to react with water to give the expected formamide

derivative.^{93, 94} In addition, such conclusion was expected since dissociation of the imidazolylidene was observed for the Al complexes **124** and **125**.

Figure 3.9: Molecular structure of complex **153**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except for H(13), are omitted for clarity.

3.3 Conclusion

In conclusion, the presented work describes the synthesis and characterization of series of new aromatic *N*-substituted NHC trimethylgallium and indium species. Similarly to their aluminium counterparts, these complexes showed different stabilities, which is attributed to differences in steric bulk of the NHC used, with the mesityl group (**145 - 146** and **149 - 150**) being more robust as compared to their isopropylphenyl counterparts (**147 - 148** and **151 - 152**). From the detailed computational energy (BSE) decomposition analysis performed the different strength of the M-NHC bond for the three metals has been rationalized. Moreover, the comparison with a Pd-NHC system highlighted the increased electrostatic interaction together with the increased [M]→NHC back-bonding orbital term as the main differences moving from group 13 to transition metals NHC complexes. Additionally, compound **152** seems to be more susceptible to decomposition and in the presence of water a formamide derivative **153** is obtained. Currently, mechanistic studies are undergoing to understand further the reactivity and stability of these trimethylindium complexes and rationalize the formulation of the **153**.

Mechanochemical Methodologies in NHC Main Group Complexes

Summary

This chapter discusses the use of the solvent-free mechanochemistry techniques, and its implementation in the synthesis of main group complexes IMes•AlCl₃ (**160**), IMes•GaCl₃ (**161**) and IMes•InCl₃ (**162**). These reactions have proven that mechanochemical synthesis, in addition to the numerous environmental advantages associated with being more inherently 'green' compared to traditional approaches, is a more practical method in obtaining these unstable complexes, with decomposition to the imidazolium salt only being observed in the case of prolonged exposure to chlorinated solvents during NMR analysis. Consequently, mechanochemical reactions allow faster reaction times and higher yields as compared to solvent-based syntheses. Finally, mechanochemical reactions performed on reactions of the betaine adduct **133** and bidentate ligands **163** and **164** towards the synthesis of new metal complexes have highlighted differences in complex reactivity and some of the limitations of mechanochemistry.

4.1 Introduction

Solvent-free synthesis is gaining increasing attention as a selective and greener alternative synthetic approach compared to more traditional solvent-based methods. This is not surprising, as solvent-based reactions dominate the synthetic chemistry for very sound reasons. Solvents help to mix the reagents together and allow them to interact; they affect the rates of reactions which in turn, will affect the distribution of products in reactions; they aid to disperse heat during reactions which allows equal dispersion of heat for reactions to take place. More importantly, solvents are frequently used to extract, separate and purify products after the completion of reactions. Therefore, it does not seem that solvent-free synthesis is a totally viable 'green' approach to synthesis.⁹⁵

Despite the limitations, solvent-free synthesis does hold great advantages as compared to solvent-based reactions, and the greatest advantage is that solvent-free synthesis may demonstrate different reactivity as compared to reactions conducted in solvent, as it has been extensively reviewed by many authors, covering areas from organic chemistry,^{96, 98} inorganic and coordination chemistry,^{95, 97, 99} and catalysis.¹⁰⁰ Therefore, in this chapter, application of solvent-free synthesis in the form of mechanochemistry is applied to reactions in main group metals, and their feasibility in these reactions will be discussed.

Mechanochemistry is predominantly a solid-state process, in which the reactions are carried out by mechanical energy, either through grinding, shearing, milling, impacting, shaking, rubbing or rolling. Other than the main advantage that has been mentioned previously in which applying mechanochemistry may exhibit different reactivities as compared to solvent-based reactions, the general advantages of mechanochemical reactions include the following: **(i)** no or minimal solvent is utilised during the reaction, therefore requires no additional process to collect, purify or recycle the solvents; **(ii)** compounds formed are usually sufficiently pure, hence purification methods using chromatography or recrystallization can be bypassed; **(iii)** subsequent solvent-free reactions can be carried out in high-yielding systems; **(iv)** reactions usually have faster reaction times as compared to solvent-based reactions; **(v)** specialized equipment is mostly avoided; **(vi)** significantly lower energy usage; **(vii)** for organic reactions, functional group protection-deprotection can be avoided; **(viii)** multi-step one pot process can be carried out; **(ix)** several different compounds may exist in solution, which may result in different products in solid or liquid state, and it is observed that these problems can be overcome by solvent-free synthesis. Moreover, there may be lower processing costs associated with establishing industrial processes, as use of solvents are avoided. Hence, reducing capital outlay for equipment in

addition to considerable batch-size reduction, resulting in an all-round more environmentally friendly route.^{96, 98, 99, 100, 101}

Nevertheless, there is controversy surrounding the mechanistic aspects of mechanochemistry, especially whether mechanical action itself is the one carrying out the reaction, or is the result of thermochemical processes in which the grinding results in the generation of heat through friction.⁹⁵ This issue was quickly addressed by the earliest work in the 19th century from M. Carey Lea, who showed that these two processes can be distinguished by simply grinding silver halides, which decomposes to form the elemental silver, but only melting was observed when the silver halides are heated.⁹⁵ Currently, many models have been developed to discuss the mechanism of mechanochemistry, with E. Boldyreva giving an extensive review on the effects of mechanical action on the structures of solid and solid mixtures.¹⁰² In addition, infrared spectroscopy (IR), X-ray powder diffraction and solid state NMR have been used to identify and record the observations of mechanochemical reactions (either the end of the mechanical action or *in-situ* monitoring).⁹⁵ Still, more research should be carried out in understanding the mechanistic approach of mechanochemistry on the reagents, and a deep understanding of the mechanisms may allow fine tuning and control of the solid-state reactions.¹⁰²

Currently, mechanochemistry has been the approach that has been adopted to generate a range of main group coordination complexes. A review by James *et. al.* and Hanusa *et. al.* summarized the use of this technique in the synthesis of various transition metal complexes, including that of mononuclear complexes, coordination clusters, coordination cages, and 1-, 2- and 3-dimensional coordination polymers.^{95, 99} However, in the case of main group inorganic systems, only four such mechanochemical syntheses have been reported; an bis(*n*-propyl-tetramethylcyclopentadienyl)strontium (**154**),¹⁰³ two aluminium triallyl complexes [1,3-(SiMe₃)₂C₃H₃]₃Al (**155**) and Al[COPh₂-2,4-(SiMe₃)₂C₃H₃]₃ (**156**),¹⁰⁴ and bis(imino)acenaphthene (BIAN) In complexes (**157** - **158**) (Figure 5.1).¹⁰⁵ Hence in this chapter, mechanochemical synthesis was applied towards the IMes (1,3-Bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene) and anionic tethered N-heterocyclic carbene ligands (**163** - **164**)⁴⁵ with Group 13 metal halides (AlCl₃, GaCl₃ and InCl₃), and their synthetic routes are compared with their solvent-based equivalents to better understand the efficiency of the process, as well as to obtain full characterization of the compounds allowing stability studies to be performed.

Figure 4.1

4.2 Results and Discussion

4.2.1 Attempted solvent-based synthesis of IMes Group 13 chloro complexes (**160 - 162**).

It was previously reported by Buchmeiser *et. al.*,^{42b} Nolan *et. al.*^{54b} and Jones *et. al.*²⁷ that the N-heterocyclic carbene group 13 halide complexes have been synthesized directly utilizing equimolar amounts of free carbene and trichloro group 13 metals. In a standard 'wet method', the NHC and the group 13 halides were weighed in separate Schlenk flasks in a glovebox, followed by the addition of a non-polar solvent (such as ether, benzene, pentane, THF, DCM and chloroform) to dissolve the carbene and the addition of the group 13 halides. All volatiles were then either evaporated or filtered and the product recrystallized from DCM and ether, as is usually required for reactions of this type.

All our attempts to synthesised the NHC halide complexes utilising Al and In did not result in the reported complexes, but proceeded to give the imidazolium chloride as the major product

(other than for gallium trichloride which resulted in complexation of the NHC) (Scheme 4.1). This observation is in agreement with Dagorne *et. al.* in which the complex $\text{ItBu} \bullet \text{AlCl}_3$ (**19**) slowly decomposes in DCM (room temperature) to give the imidazolium salt $[\text{ItBu-H}][\text{AlCl}_4]$.³⁴ As it has been reported by Kuhn *et. al.* that the chloride anion may originate from the solvent itself as the reaction of 1,2-dichloroethane with NHCs give rise to 2-chloro-1,3-disubstituted imidazolium chloride salts,¹⁰⁶ alternative solvents were used for the synthesis of the complexes and, in particular, chlorinated solvents were avoided altogether. Reactions were refluxed to check whether harsher reaction conditions would drive the reactions towards the desired metal complexes. However, the formation of imidazolium salt prevailed in all reactions for the aluminium- and indium trichloride complexes. Recrystallization in the absence of chlorinated solvents proved troublesome due to insolubility of the complexes. Nonetheless, it was noted that even recrystallizations from THF could not avoid the salt formation.

Scheme 4.1: Solvent syntheses of NHC Group 13 trichloro complexes using non-polar solvents (ether, benzene, pentane, THF, DCM and chloroform).

Despite extensive efforts to strictly exclude moisture from the reactions, the imidazolium salt was still produced in both cases (AlCl_3 and InCl_3), it was concluded that the acidic imidazolium proton originated from the solvent and the chloride anion from the group 13 chlorido fragment itself,^{106, 107} as described by Jones *et al.* for the syntheses of chelating bis-carbene, Et^tBu with AlCl_3 and GaCl_3 (Scheme 4.2).²⁸

Scheme 4.2: The attempted synthesis of chelating bis-carbene, Et^tBu with AlCl_3 and GaCl_3 .²⁸

4.2.2 Mechanochemical synthesis of IMes Group 13 chloro complexes (**160** - **162**).

As solvent based reactions were unsuccessful to synthesize the series of NHC Group 13 trichloro complexes, mechanochemical synthesis was applied. This technique was chosen as minimal or no solvent was required, thus avoiding the presence of acidic protons generated from the solvent. In addition, it was reported that mechanochemical synthesis usually requires a shorter reaction time as compared to the latter technique. Therefore, a series of reactions were carried out by weighing equal equivalents of the carbene IMes and the group 13 trichloro complexes in a grinder jar equipped with a 7 mm or 10 mm milling ball, with reactions being milled for 90 minutes at a frequency of 30 Hz (Scheme 4.3).

Scheme 4.3: Mechanochemical synthesis of IMes with MCl_3 (**160** - **162**). Reaction conditions: 7 mm or 10 mm milling ball, 30 Hz, 90 minutes.

The advantage of carrying out mechanochemical synthesis was that the reaction can be monitored after each mechanical cycle to see whether the reaction has reached to completion. Initial spectroscopic analysis indicated that all reactions were completed within 90 minutes, with the reactions for aluminium and indium chlorides completed less than half the time that is required for solvent-based synthesis (solvent-based synthesis for $\text{IMes}\cdot\text{AlCl}_3$ ^{42b} and $\text{IMes}\cdot\text{InCl}_3$ ²⁷ is 3 hrs respectively). In addition, as reported by Nolan *et. al.*, the $\text{IMes}\cdot\text{GaCl}_3$ (**75**) is stable in air and moisture.^{54b} Therefore, after the milling, complex **161** was immediately exposed to air and as expected, no decomposition of the complex was observed. Comparing to the other IMes group 13 trichloro complexes, complex **161** is the most stable of the synthesized triad, with decomposition being observed for both the $\text{IMes}\cdot\text{AlCl}_3$ (**160**) and $\text{IMes}\cdot\text{InCl}_3$ (**162**) during the spectroscopic analysis, even with extensive drying of the deuterated solvent (*vide infra*).

In addition, it has been reported that bis-carbene complexes of indium and thallium were obtained by addition of 2 equivalents of carbene with the group 13 metal halide complexes (**110**, **111** and **121**) (Figure 4.2). Therefore, mechanochemical reactions were carried out using two equivalents of the IMes carbene with the group 13 metal trichloro complexes but no bis-carbene complexes were obtained and only the imidazolium salt, $\text{IMes}[\text{HCl}]$ was identifiable as a final

product of the reaction. As previously mentioned, mechanochemical synthesis may result in different reactivities as compared to solvent-based synthesis and this example clearly illustrates the differences.⁹⁵ Therefore, further studies are currently underway to understand the mechanism of these reactions,.

Figure 4.2

4.2.3 Spectroscopic studies of the mechanochemical synthesized complexes **160 - 162**

As previously mentioned, initial ^1H NMR studies showed that mechanochemical synthesis was successful in producing all the NHC Group 13 trichloro complexes (Table 4.1). As observed from the spectrums, a downfield shift was observed for the imidazolylidene protons (H4 and H5) on the imidazoles which indicated that complexation has occurred for all metal complexes. As for ^{13}C NMR, no carbenic carbon peak can be obtained from all complexes and this was attributed to the quadrupolar moment of the metal centre attached to the carbonic carbon.^{83, 88}

Figure 4.3

Table 4.1: Experimental ^1H chemical shifts for selected Al, Ga and In complexes

Complexes	^1H [H(4)-H(5)] ^a (ppm)
IMes (C_6D_6) ⁷⁰	6.48
IMes•AlCl ₃ (160)	7.20
IMes•GaCl ₃ (161)	7.19
IMes•InCl ₃ (162)	7.34
IMes•AlCl ₃ (34) ^{42b}	7.21
IMes•GaCl ₃ (75) ^{54b}	5.78
IMes•InCl ₃ (109) ⁶⁰	7.40

^a All NMRs are taken in CDCl₃ other than IMes.

As previously discussed, chlorinated solvents are known to result in the decomposition of the NHC trichloro complexes (*vide supra*). Therefore, alternative deuterated solvents were used in attempts to dissolve the complexes for NMR analysis. Unfortunately, dissolution of the complexes in all deuterated solvents proved impossible. Since only chlorinated solvents are able to achieve dissolution, the majority of analyses were performed using CDCl_3 . Nevertheless, this resulted in observable decomposition for the complexes **160** and **162** (Figure 4.4), over time into imidazolium salt (IMes[HCl]). Hence, no ^{13}C NMR analysis was achieved due to the inherent instability of the complexes. Solid state NMR was also attempted, however, during the analysis period decomposition into the imidazolium salt was again observed due to the instability of the complexes. As for IMes•GaCl₃, all analysis were obtained straightforwardly, in line with previous reports detailing its stability in both air and moisture.^{54b}

Figure 4.4: ^1H NMR of complex **160** showing its onset to the decomposition to their imidazolium salt **159**. Red represents complex 159, blue represents the imidazolium salt **159**.

4.2.4 Crystallographic studies of IMes Group 13 trichloro complexes **161** - **162**

Single-crystal X-ray structures of complexes **161** - **162** are shown in Figures 4.5. Complex **161** and **162** crystallized out in solution as two crystallographically independent, yet chemically equivalent molecules; hence only one molecule will be described herein. As for complex **160**, various solvents were used in attempts to crystallize the structure, with only the imidazolium salt being obtainable. Furthermore, temperature controlled sublimation was performed with the aim of purifying the complex **160** and allowing the growth of single

crystals. However, only decomposition products were observed for the complex **160**, and no viable by-products could be identified by NMR.

Figure 4.5: Molecular structure of complex IMes•GaCl₃ (**161**) and IMes•InCl₃ (**162**), left and right, respectively. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°) for **161**: Ga(1)-C(1) 2.009(9), Ga(1)-Cl(1) 2.190(3), Ga(1)-Cl(2) 2.168(3), Ga(1)-Cl(3) 2.165(3), N(1)-C(1) 1.340(1), N(1)-C(2) 1.400(1), N(2)-C(1) 1.360(1), N(2)-C(3) 1.348(1), C(2)-C(3) 1.325(2), C(1)-Ga(1)-Cl(1) 104.4(2), C(1)-Ga(1)-Cl(2) 113.6(3), C(1)-Ga(1)-Cl(3) 113.4(3), Cl(1)-Ga(1)-Cl(2) 107.8(1), Cl(1)-Ga(1)-Cl(3) 109.7(2), Cl(2)-Ga(1)-Cl(3) 107.7(1), N(1)-C(1)-N(2) 105.3(7). Selected bond lengths (Å) and angles (°) for **162**: In(1)-C(1) 2.193(5), In(1)-Cl(1) 2.353(2), In(1)-Cl(2) 2.359(1), In(1)-Cl(3) 2.362(1), N(1)-C(1) 1.352(6), N(1)-C(2) 1.383(6), N(2)-C(1) 1.346(6), N(2)-C(3) 1.385(6), C(2)-C(3) 1.340(7), C(1)-In(1)-Cl(1) 108.6(1), C(1)-In(1)-Cl(2) 112.0(1), C(1)-In(1)-Cl(3) 111.0(1), Cl(1)-In(1)-Cl(2) 107.6(1), Cl(1)-In(1)-Cl(3) 109.7(1), Cl(2)-In(1)-Cl(3) 107.9(1), N(1)-C(1)-N(2) 106.5(4).

As shown in Figures 4.5, **161** - **162** adopted a distorted tetrahedral geometry at the metal centre, consistent with the majority of complexes described in previously reported literature (see Chapter 1). The M-C_{carbene} bond lengths of the complexes **161** - **162** were consistent with the reported group 13 trichloro complexes (2.009(9) Å vs. 1.954(4) Å for complexes **161**^{54b} and **75**^{54b}). In addition, product yields are greater than for the majority of the solvent syntheses (Table 4.2), with the avoidance of solvent purification reducing the tendency for decomposition. Hence, mechanochemical synthesis has been shown to be a strong alternative to traditional solvent-based methods for the synthesis of these complexes, as demonstrated by these reactions in this case.

Table 4.2: Ga-C_{carbene} and In-C_{carbene} bond lengths of selected NHC gallium and indium complexes.

Complexes	M-C _(carbene) [Å]	Yield (%)
Imes•GaCl ₃ (161)	2.009(9)	96
Imes•InCl ₃ (162)	2.193(5)	95
IMes•GaCl ₃ (75) ^{54b}	1.954(4)	87
IMes•InCl ₃ (109) ⁶⁰	^a	67

^a No crystal structures were obtained.

4.3 Reversible reaction being observed through mechanochemical synthesis

As previously discussed in Chapter 2, a mechanochemical approach was also applied to the betaine adduct **133** with other metal complexes (AlCl_3 , GaCl_3 , InCl_3 , SnCl_2 , CuCl) in the hope of generating new NHC amidinate metal complexes. However, no new betaine metal complexes have been obtained, instead the NHC IMes•CuCl complex (**144**) was obtained.

Scheme 4.4: Postulated reaction pathway to complex **144** by mechanochemical synthesis of complex **133** with CuCl .⁸¹

As mentioned previously, the imidazolidinylidene SIMes family undergoes a concerted [3+2] cycloelimination reaction upon heating to give ethylene and the corresponding bis-(2,4,6-trimethylphenyl)carbodiimide, and the carbodiimide was trapped by a second NHC to give the betaine adducts (Chapter 2). Therefore, it was postulated that the reaction of the betaine adducts would be reversible resulting in complex **133** releasing the NHC and the carbodiimide and the NHC reacting with CuCl to yield complex **144**.⁸¹ This is interesting since this reversibility is only observed mechanochemically and not for solvent-based synthesis. Therefore, as illustrated in Scheme 4.4, mechanochemical routes potentially proceed *via* alternative reaction pathways compared to solvent-based approaches. Further studies will be carried out in order to elucidate the mechanisms underpinning these reactions.

Lastly, mechanochemistry has also been applied to the synthesis of the betaine adducts **133** and **134**, by adding equivalent amounts of the IMes or SIMes carbene with the Dipp carbodiimide (Chapter 2). Similar to our previous observations, yields obtained for the mechanochemical reactions were significantly greater than those resulting from solvent-based syntheses (92% vs. 72% for mechanochemical synthesis and solvent-based synthesis for complex **133**; and 95% vs. 83% for mechanochemical synthesis and solvent-based synthesis for complex **134**), along with vastly reduced reaction times for the mechanochemical routes (90 mins vs. overnight). Therefore, mechanochemistry has further been demonstrated to be a far more straightforward and efficient method for the synthesis of organic ligands also.

4.4 Synthesis of chelating Group 13 complexes utilising mechanochemistry

Anionic tethered N-heterocyclic carbenes have been extensively discussed by Arnold *et al.*⁴⁵ to be excellent ligands for the stabilization of metal complexes, especially so for electropositive metal centres. Superior stabilizing properties are due to the presence of an anionic tether which allows the functionalized NHCs to covalently bond to the hard, electropositive metal centre. If displaced, the NHC positioned itself in close proximity to the metal.^{45, 108} Therefore, due to favourable functionality, these ligands have been applied to trimethylaluminium and -gallium to synthesize a series of chelating NHC complexes (Chapter 1, **44** - **45**,³¹ **47**,⁴⁶ **49** - **52**,⁴⁷ **94** - **98**⁵²).

With this in mind, two new NHC bidentate ligands, **163** and **164**, have been synthesized by reacting the epoxide with imidazole in acetonitrile, followed by the addition of ethyl iodide to yield the imidazolium iodide, a procedure adopted from Arnold *et al.* (Scheme 4.5).¹⁰⁸ The two ligands were crystallized from DCM or ACN solvents and their single-crystal X-ray structures are shown below (Figure 4.6).

Scheme 4.5: Synthetic route for the synthesis of bidentate ligands **163** and **164**.¹⁰⁸

Figure 4.6: Molecular structure of complex **163** and **164**, left and right, respectively. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°) for **163**: C(1)-N(1) 1.330(4), C(1)-N(2) 1.333(4), N(1)-C(2) 1.379(4), N(1)-C(4) 1.474(3), N(2)-C(3) 1.376(4), N(2)-C(8) 1.481(4), C(2)-C(3) 1.352(4), C(4)-C(5) 1.532(4), C(5)-O(1) 1.438(3), N(1)-C(1)-N(2) 108.3(2), C(1)-N(1)-C(2) 108.8(2), C(1)-N(1)-C(4) 125.5(2), C(1)-N(2)-C(3) 108.9(2), C(1)-N(2)-C(8) 124.9(3), N(1)-C(2)-C(3) 107.1(3), N(1)-C(4)-C(5) 113.5(2), N(2)-C(3)-C(2) 107.0(3), C(4)-C(5)-O(1) 109.4(2). Selected bond lengths (Å) and angles (°) for **164**: N(1)-C(2) 1.483(5), N(1)-C(3) 1.327(4), N(1)-C(4) 1.370(5), N(2)-C(3) 1.331(4), N(2)-C(5) 1.372(4), N(2)-C(6) 1.455(4), C(4)-C(5) 1.341(4), C(6)-C(7) 1.528(5), C(7)-C(8) 1.525(4), C(7)-O(1) 1.403(5), C(2)-N(1)-C(3) 126.8(3), C(3)-N(1)-C(4) 108.9(3), C(3)-N(2)-C(5) 108.8(3), C(3)-N(2)-C(6) 125.5(3), N(1)-C(4)-C(5) 107.3(3), N(2)-C(5)-C(4) 107.1(3), N(2)-C(6)-C(7) 112.0(2), C(6)-C(7)-C(8) 108.5(3), C(6)-C(7)-O(1) 108.5(3), C(8)-C(7)-O(1) 113.3(3).

4.5 Conclusion

This chapter highlights the utility of a solvent-free, mechanochemical approach for the straightforward and relatively environmentally benign synthesis of main group complexes IMes•AlCl₃ (**160**), IMes•GaCl₃ (**161**) and IMes•InCl₃ (**162**). It is observed that mechanochemical reactions proceed with significantly faster reaction times and greater, cleaner product yields as compared to solvent-based reactions for the NHC group 13 complexes. Furthermore, it allows initial analysis of the product formation using NMR without the hassle of removing solvents as compared to solvent-based synthesis. To highlight further, the complexes are shown to be more stable, with decomposition to the imidazolium salt only being observed following prolonged exposure to chlorinated solvents during NMR analysis. In solvent-based reactions, complexes **160** and **161** are shown to be unstable, easily decomposing to the corresponding imidazolium salt (**159**) even in non-chlorinated solvents. Lastly, mechanochemical reactions have also been performed for reactions of the betaine adduct **133** and bidentate ligands **163** and **164** towards the synthesis of new metal complexes, with the betaine adduct **133** generating the copper complex **144** instead. This suggests that mechanochemical synthesis provides a different mechanistic approach to reactivity as compared to solvent-based reactions. Limitations are also demonstrated for mechanochemical synthesis, and the generation of new NHC chelating metal complexes did not proceed as expected and it was rationalized by the consideration that lithiated ligands are unstable at the high temperatures generated through friction during the milling process.

Experimental Section

5.1 Inert-Atmosphere Techniques

The N-heterocyclic carbenes (NHC) complexes are essentially air- and moisture-sensitive. Hence, care must be taken to prevent the exposure of these complexes to air and moisture. Consequently, standard inert-atmosphere techniques are employed for the analysis, synthesis and isolation of all the complexes.

5.1.1 Vacuum and Schlenk Line

Argon from the cylinders was first flushed through phosphorus pentoxide and molecular sieves prior to use. All glassware was pre-dried overnight at 180 °C prior to be used. All reactions were done under an atmosphere of dry argon maintained at positive pressure, on a vacuum line which allowed evacuation of the air from the reaction vessel (Figure 5.1), and then recharging with nitrogen or purging of the apparatus with a flow of argon if necessary. Most reactions were done using Schlenk tubes which have a tap allowing connection to the vacuum line. Larger-scale reactions required the use of larger reaction vessels, normally round-bottomed flasks fitted with tap adaptors to enable attachment to a vacuum line. All solvents and liquid reagents were filled under argon and transferred via septum and dry syringes, and all solids reagents weighed in aerobic atmosphere were evacuated at least 3-5 times prior to reaction.

Figure 5.1: Schematic representation of the vacuum and schlenk line when performing inert atmospheric reactions.

5.1.2 Glove box

Handling of air- and moisture-sensitive reagents and products were carried out in an argon-filled glove box ("Innovative Technology Inc", System One). Prior to transporting reagents and products into the glove box, glassware must be evacuated (under vacuum) before placing them into the antechambers. Antechambers were evacuated 4 times (10 min for small port, 15 mins for big port) and refilled with argon between evacuations to ensure the internal inert-atmosphere of the box was maintained. The blower constantly recirculate the atmosphere in the glove box through two purifying columns; one containing molecular sieves to remove moisture, and the other containing a copper catalyst to remove oxygen. The glove

box was also fitted with a moisture and oxygen analyser to monitor the atmosphere of the glove box; with typical values of 0.54 ppm for moisture and 0.1-15 ppm for oxygen. Typical procedures being carried out in the glove box involved weighing, storing reagents/products, and preparing samples for analysis. Reforming of the glove box is also periodically carried out to ensure that the inert atmosphere is preserved.

Figure 5.2: Schematic representation of the glove box.

5.1.3 Starting Material and Solvent

Anhydrous solvents (THF, ether, hexane, toluene, and difluorobenzene, C_6D_6 , $CDCl_3$, CD_2Cl_2 .) were distilled from appropriate drying agents (Na/benzophenone, CaH_2 , P_2O_5) and degassed prior to use by purging with dry argon and kept over molecular sieves.¹⁰⁹ Starting materials were synthesized as described below or were obtained commercially (Sigma-Alrich, Strem, Alfa Aesar). Aluminium trichloride and gallium trichloride were sublimed prior to use.¹⁰⁹ 1 M trimethylaluminium in toluene was prepared from the neat solution. NaH was washed with hexane to remove the oil suspension before use.

5.2 Analytical Instruments and Procedures

5.2.1 NMR Spectroscopy

Samples, which were stable in aerobic condition were prepared by taking approximately 20 mg of the compound and dissolving them in deuterated solvent ($\sim 0.6\text{ cm}^3$), before transferring to a thin-walled NMR tube (Wilmad, 528-PP). Air- and moisture sensitive samples were prepared in the glove box and dissolved in dry deuterated solvent before transferring to J. Young NMR tube. Dried deuterated solvents were distilled from appropriate drying agents (Na / benzophenone, CaH_2 or molecular sieves) and stored either in potassium mirror or molecular sieves. NMR spectra were collected using a Bruker AV 300, 400 or 500 spectrometers, with the 1H and ^{13}C NMR chemical shifts internally referenced to the residual solvent used. For 1H NMR spectroscopy, a CHD_2 -quintet at δ 2.05 ppm for acetone- d_6 , a CHD_2 -quintet at δ 2.50 ppm for DMSO, a singlet at δ 7.16 ppm for C_6D_6 , a

singlet at δ 7.26 ppm for CDCl_3 , and a triplet at δ 5.32 ppm for CD_2Cl_2 . For ^{13}C NMR spectroscopy, a triplet at δ 128 ppm for C_6D_6 , a triplet at δ 77 ppm for CDCl_3 , and a quintet at δ 53.8 ppm for CD_2Cl_2 . In addition, all NMR spectroscopic analyses were performed at room temperature (300 K) unless otherwise stated.

5.2.2 Melting Point Determination

As samples are air- and moisture-sensitive, their preparation was conducted in the glove box. The samples were placed in glass capillary tubes, which were then sealed with grease before their removal from the glove box. Melting points were determined on an SRS-Optimelt MPA-100 apparatus and were uncorrected.

5.2.3 Infrared Spectroscopy

Sample preparations were all carried out in the glove box. Small amount of samples was added to nujol oil and mixed evenly to form a nujol mull, the mull was then smeared onto sodium chloride plates. After which, the plates were immediately transferred to the spectrometer (Shimadzu IR Prestige-21 FTIR spectrometer) for analysis; with the samples protected against air and moisture due to the nujol oil and being sandwiched between the plates.

5.2.4 High-Resolution Mass Spectroscopy

All samples required for analysis were prepared in the glove box. Samples were dissolved in anhydrous acetonitrile (distilled over CaH_2 and stored under molecular sieves) and diluted to appropriate concentration in 1.5 mL glass vial. Glass vials were then sealed tightly and transferred immediately to the spectrometer (Water Q-ToF Premier) for analysis (electrospray ionisation (ESI) mode).

5.2.5 Single crystal X-ray Diffraction Studies

Two different crystal structure machines (Bruker X8 CCD Diffractometer & Bruker Kappa CCD Diffractometer) were used for the structure determination of crystals. The crystals were grown in Schlenk tubes under argon in various temperature ranging from room temperature (+25 °C), to refrigerator temperature (+2 °C) and freezer temperature (-23 °C). Crystals grown should be ideally no greater in dimensions than 0.5 x 0.5 x 0.5 mm, and they were mount onto the X-ray machine utilizing the 'oil drop mounting technique' developed by Prof. D. Stalke at Göttingen University, Germany. This technique involves extracting the crystals out from the Schlenk tube with the spatula and immediately coating them in inert perfluorinated polyether oil (Fomblin® Y). Since the crystals were air/moisture-sensitive, such technique would prevent the crystals from being hydrolyzed by the atmosphere during

mounting and data collection. Following which, the oil-coated crystals were examined under a microscope and a suitable single crystal would be selected and mounted onto a small quartz fiber attached to the diffractometer goniometer head. Once attached, a cooled dry nitrogen gas stream was applied which froze the oil around the crystals, fixing its orientation and preventing hydrolysis and oxidation. The X-ray diffraction intensity data of the mounted crystals were collected at 103 K, employing Mo K α radiation ($\lambda = 0.71073$ Å), with the SMART suite of programs.¹¹⁰ All data were processed and corrected for Lorentz and polarization effects with SAINT and for absorption effects with SADABS.¹¹¹ Structural solution and refinement were carried out with the SHELXTL suite of programs.¹¹²

5.3 Preparation of Starting Materials

- **Synthesis of 1,4-Bis-(2,4,6-trimethylphenyl)-1,4-diaza-butadiene**

A solution of glyoxal (10 g, 40% in water, 172 mmol) in MeOH (40 mL) was added with vigorous stirring to a warmed (50 °C) solution of 2,4,6-trimethylaniline (48.3 mL, 344 mmol) and HOAc (0.3 mL) in MeOH (40 mL). A slightly exothermic reaction commenced and the product started to crystallise after 15 mins. The mixture was stirred for 10 h at room temperature, and the resulting suspension was filtered with the solid product washed with MeOH, until the washing phase remained bright yellow. The product was pre-dried by suction over filter, then dried to a constant weight under high vacuum.¹¹³ Yield: 84%. ¹H NMR (300 MHz, δ /ppm, CDCl₃): 2.51 (s, 12H, *o*-Ph(CH₃)), 2.64 (s, 6H, *p*-Ph(CH₃)), 7.25 (s, 4H, C₆H₂), 8.45 (s, 2H, NCH).

- **Synthesis of 1,4-Bis-(2,6-diisopropylphenyl)-1,4-diaza-butadiene**

Analogous procedure was adopted as above which yielded a yellow solid.¹¹³ (Glyoxal - 172 mmol, 2,6-diisopropylaniline – 344 mmol). Yield: 82%. ¹H NMR (300 MHz, δ /ppm, CDCl₃): 1.27-1.30 (d, 24H, $J_{H-H} = 6.9$ Hz, CH(CH₃)₂), 2.97-3.07 (q, 4H, $J_{H-H} = 6.9$ Hz, CH(CH₃)₂), 7.22-7.29 (m, 6H, C₆H₃), 8.18 (s, 2H, NCH).

- **Synthesis of N,N'-Bis-(2,4,6-trimethylphenylamino)ethane dihydrochloride**

A solution of 1,4-Bis-(2,4,6-trimethylphenyl)-1,4-diaza-butadiene (10 g, 34.2 mmol) in 200 mL THF was cooled to 0 °C and sodium borohydride (5.304 g, 140 mmol) in spatula portions were added slowly over a period of 20 minutes. The mixture was allowed to warm up to room temperature and stirred for 16 h, followed by refluxing for 2 h. The mixture was then cooled to 0 °C, and 100 mL of ice water was added to the cooled mixture. After which, 100 mL of 3 M hydrochloric acid was added slowly to the cooled mixture till the mixture changed from yellow to off white with the precipitation of off white solids. The solids were then collected by filtration and dried in a well-ventilated oven at 80 °C.^{70b} Yield: 70%. ¹H NMR (300 MHz, δ /ppm, DMSO): 2.22 (s, 6H, *p*-Ph(CH₃)), 2.38 (s, 12H, *o*-Ph(CH₃)), 3.47 (s, 4H, NCH₂), 6.93 (s, 4H, C₆H₂).

- **Synthesis of N,N'-Bis-(2,6-diisopropylphenylamino)ethane dihydrochloride**

Analogous procedure was adopted as above which yielded off white solids.^{70b} (1,4-Bis-(2,6-diisopropylphenyl)-1,4-diaza-butadiene – 26.3 mmol, sodium borohydride – 112 mmol). Yield: 70%. ¹H NMR (300 MHz, δ /ppm, DMSO): 1.15-1.18 (d, 24H, $J_{H-H} = 6.6$

Hz, $\text{CH}(\text{CH}_3)_2$), 3.29-3.38 (q, 4H, $J_{\text{H-H}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 3.74 (s, 4H, NCH_2), 7.18-7.22 (m, 6H, C_6H_3).

- **Synthesis of 1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride (IMes•HCl)**

A 250 mL RBF containing EtOAc (100 mL) was heated to 70 °C in an oil bath. 1,4-Bis-(2,4,6-trimethylphenyl)-1,4-diaza-butadiene (6.343 g, 21.7 mmol) and paraformaldehyde (0.664 g, 22.1 mmol) were added and the walls were washed with EtOAc. A solution of TMSCl (2.75 mL, 21.7 mmol) in EtOAc (20 mL) was added dropwise over 20 min with vigorous stirring and the resulting suspension was stirred for 2 h at 70 °C. After cooling in an ice-bath while stirring, the suspension was filtered and the solids were washed with EtOAc and ether. The solids were dried in an open-dish in a well-ventilated oven at 100 °C to give an off-white powder.¹¹³ Yield: 75%. ¹H NMR (400 MHz, δ /ppm, CD_2Cl_2): 2.20 (s, 12H, *o*-Ph(CH_3)), 2.38 (s, 6H, *p*-Ph(CH_3)), 7.10 (s, 4H, C_6H_2), 7.52 (s, 2H, NCH), 11.15 (s, 1H, $\text{NC}(\text{HCl})\text{N}$).

- **Synthesis of 1,3-Bis-(2,6-diisopropylphenyl)imidazolium chloride (IPr•HCl)**

Same procedure was adopted as above which yielded off-white solids.¹¹³ (1,4-Bis-(2,6-diisopropylphenyl)-1,4-diaza-butadiene – 26.6 mmol, paraformaldehyde – 26.6 mmol, TMSCl – 26.6 mmol). Yield: 76%. ¹H NMR (300 MHz, δ /ppm, CD_2Cl_2): 1.25-1.29 (dd, 24H, $J_{\text{H-H}} = 5.7$ Hz, $\text{CH}(\text{CH}_3)_2$), 2.39-2.48 (q, 4H, $J_{\text{H-H}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 7.38-7.41 (m, 4H, *m*- C_6H_3), 7.60-7.65 (m, 2H, *p*- C_6H_3), 7.77-7.78 (s, 2H, NCH), 11.14 (s, 1H, $\text{NC}(\text{HCl})\text{N}$).

- **Synthesis of 1,3-Bis-(2,4,6-trimethylphenyl)imidazolinium chloride (SIMes•HCl)**

A 250 mL RBF was charged with N,N'-Bis-(2,4,6-trimethylphenylamino)ethane dihydrochloride (5.330 g, 14.4 mmol), 48 mL of triethylorthoformate, and 2 drops of 96% formic acid. The mixture was allowed to reflux for 45 h and subsequently cooled to room temperature with the precipitation of new solids. The solids were collected by filtration and dried in a well-ventilated oven at 80 °C. Consequently, the solids collected required purification by crystallisation to obtain the desired product.^{70b} Yield: 83%. ¹H NMR (400 MHz, δ /ppm, CDCl_3): 2.27 (s, 6H, *p*-Ph(CH_3)), 2.37 (s, 12H, *o*-Ph(CH_3)), 4.56 (s, 4H, NCH_2), 6.93 (s, 4H, C_6H_2), 9.36 (s, 1H, $\text{NC}(\text{HCl})\text{N}$).

- **Synthesis of 1,3-Bis-(2,6-diisopropylphenyl)imidazolinium chloride (SIPr•HCl)**

Analogous procedure was adopted as above which yielded off white solids.^{70b} (N,N'-Bis-(2,6-diisopropylphenylamino)ethane dihydrochloride – 12.4 mmol, triethylorthoformate –

60 ml). Yield: 61%. ^1H NMR (400 MHz, δ /ppm, CDCl_3): 1.24-1.26 (d, 12H, $J_{\text{H-H}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.38-1.39 (d, 12H, $J_{\text{H-H}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 2.98-3.04 (q, 4H, $J_{\text{H-H}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 4.82 (s, 4H, NCH_2), , 7.26-7.28 (m, 4H, $m\text{-C}_6\text{H}_3$), 7.45-7.49 (m, 2H, $p\text{-C}_6\text{H}_3$), 8.48 (s, 1H, $\text{NC}(\text{HCl})\text{N}$).

- **Synthesis of 1,3-Bis-(2,4,6-trimethylphenyl)-imidazolium tetrafluoroborate (IMes•HBF₄)**

A water solution of excess NaBF_4 (3.004 g, 27.4 mmol in 100 mL of H_2O) was added to IMes•HCl (5.393 g, 15.8 mmol) dissolved in acetone or acetonitrile (200 mL). The mixture was stirred for 15-20 min and the organic solvent was removed in vacuo. The residue left was dissolved in DCM and washed several times with water. The organic solvent was subsequently collected and dried over MgSO_4 . After filtering and removing the MgSO_4 , ether was added to precipitate the product and filtered to give an off-white powder.¹¹ Yield: 86%. ^1H NMR (300 MHz, δ /ppm, CDCl_3): 2.13 (s, 12H, $o\text{-Ph}(\text{CH}_3)$), 2.36 (s, 6H, $p\text{-Ph}(\text{CH}_3)$), 7.05 (s, 4H, C_6H_2), 7.56 (s, 2H, NCH), 8.90 (s, 1H, $\text{NC}(\text{HBF}_4)\text{N}$).

- **Synthesis of 1,3-Bis-(2,6-diisopropylphenyl)-imidazolium tetrafluoroborate (IPr•HBF₄)**

Same procedure was adopted as above which yielded off-white solids.¹¹ (IPr•HCl– 10.3 mmol, NaBF_4 – 18.6 mmol). Yield: 86%. ^1H NMR (300 MHz, δ /ppm, CDCl_3): 1.21-1.23 (d, 12H, $J_{\text{H-H}} = 6.9$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.29-1.31 (d, 12H, $J_{\text{H-H}} = 6.6$ Hz, $\text{CH}(\text{CH}_3)_2$), 2.39-2.48 (q, 4H, $J_{\text{H-H}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 7.36-7.38 (m, 4H, $m\text{-C}_6\text{H}_3$), 7.57-7.63 (m, 2H, $p\text{-C}_6\text{H}_3$), 7.83 (s, 2H, NCH), 8.70 (s, 1H, $\text{NC}(\text{HBF}_4)\text{N}$).

- **Synthesis of 1,3-Bis-(2,4,6-trimethylphenyl)-imidazolinium tetrafluoroborate (SIMes•HBF₄)**

Same procedure was adopted as above which yielded off-white solids.¹¹ (SIMes•HCl– 10.3 mmol, NaBF_4 – 18.5 mmol). Yield: 66%. ^1H NMR (400 MHz, δ /ppm, CD_2Cl_2): 2.34 (s, 6H, $p\text{-Ph}(\text{CH}_3)$), 2.36 (s, 12H, $o\text{-Ph}(\text{CH}_3)$), 4.49 (s, 4H, NCH_2), 7.06 (s, 4H, C_6H_2), 7.95 (s, 1H, $\text{NC}(\text{HBF}_4)\text{N}$).

- **Synthesis of 1,3-Bis-(2,6-diisopropylphenyl)-imidazolinium tetrafluoroborate (SIPr•HBF₄)**

Same procedure was adopted as above which yielded off-white solids.¹¹ (SIPr•HCl– 8.08 mmol, NaBF_4 – 14.5 mmol). Yield: 82%. ^1H NMR (400 MHz, δ /ppm, CD_2Cl_2): 1.26-1.27 (d, 12H, $J_{\text{H-H}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.41-1.42 (d, 12H, $J_{\text{H-H}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$),

2.96-3.03 (q, 4H, $J_{H-H} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 4.59 (s, 4H, NCH_2), 7.34-7.36 (m, 4H, $m\text{-C}_6\text{H}_3$), 7.52-7.56 (m, 2H, $p\text{-C}_6\text{H}_3$), 7.83 (s, 1H, $\text{NC}(\text{HBF}_4)\text{N}$).

- **Synthesis of 1,3-Bis-(2,4,6-trimethylphenyl)-imidazolylidene (IMes).**

In a reaction tube, IMes•HBF₄ (5.311 g, 13.5 mmol) was evacuated for 3-5 times to remove any moisture and oxygen before the reaction proceeded. After the pre-dried and argon re-filling steps, THF (70 mL) was added to the compound and NaH in THF (0.650 g, 27.1 mmol) was transferred slowly into the suspension. KO^tBu (tip of spatula) in THF was then added into the mixture and allowed to stir overnight. The mixture was filtered and the solids washed with THF. The filtrate was vacuumed to a saturated solution and pentane was added to precipitate orange-brown solids. The orange-brown solids were collected and dried under vacuum and stored in the glovebox.^{70a} Yield: 67%. ¹H NMR (500 MHz, δ /ppm, C₆D₆): 2.16 (s, 18H, Ph(CH₃)), 6.48 (s, 2H, NCH), 6.81 (s, 4H, C₆H₂). ¹³C{¹H} NMR (125 MHz, δ /ppm, C₆D₆): 219.4, 139.3, 137.2, 135.4, 129.1, 120.5, 21.0, 18.0.

- **Synthesis of 1,3-Bis-(2,6-diisopropylphenyl)-imidazolylidene (IPr)**

Same procedure was adopted as above which yielded off-white solids.^{70a} (IPr•HCl – 14.9 mmol, NaH – 29.7 mmol, KO^tBu – tip of spatula). Yield: 86%. ¹H NMR (500 MHz, δ /ppm, C₆D₆): 1.18-1.20 (d, 12H, $J_{H-H} = 7.0$ Hz, CH(CH₃)₂), 1.29-1.30 (d, 12H, $J_{H-H} = 6.5$ Hz, CH(CH₃)₂), 2.93-2.99 (q, 4H, $J_{H-H} = 6.6$ Hz, CH(CH₃)₂), 6.61 (s, 2H, NCH), 7.16-7.19 (m, 4H, $m\text{-C}_6\text{H}_3$), 7.28-7.31 (m, 2H, $p\text{-C}_6\text{H}_3$). ¹³C{¹H} NMR (100 MHz, δ /ppm, C₆D₆): 220.4, 146.2, 138.9, 129.0, 123.6, 121.5, 28.7, 24.8, 23.6.

- **Synthesis of 1,3-Bis-(2,4,6-trimethylphenyl)-imidazolinylidene (SIMes)**

Same procedure was adopted as above which yielded brown solids.^{70a} (SIMes•HBF₄ – 10.6 mmol, NaH – 21.1 mmol, KO^tBu – tip of spatula). Yield: 52%. ¹H NMR (400 MHz, δ /ppm, C₆D₆): 2.17 (s, 6H, $p\text{-Ph}(\text{CH}_3)$), 2.31 (s, 12H, $o\text{-Ph}(\text{CH}_3)$), 3.28 (s, 4H, NCH₂), 6.84 (s, 4H, C₆H₂). ¹³C NMR (125 MHz, δ /ppm, C₆D₆): 243.6, 139.7, 136.8, 135.9, 129.4, 50.4, 21.0, 18.1.

- **Synthesis of 1,3-Bis-(2,6-diisopropylphenyl)-imidazolinylidene (SIPr)**

Same procedure was adopted as above which yielded brown solids.^{70a} (SIMes•HBF₄ – 10.6 mmol, NaH – 21.1 mmol, KO^tBu – tip of spatula). Yield: 82%. ¹H NMR (400 MHz, δ /ppm, C₆D₆): 1.29-1.30 (d, 12H, $J_{H-H} = 7.2$ Hz, CH(CH₃)₂), 1.33-1.35 (d, 12H, $J_{H-H} = 6.8$ Hz, CH(CH₃)₂), 3.26-3.32 (q, 4H, $J_{H-H} = 6.9$ Hz, CH(CH₃)₂), 3.38 (s, 4H, NCH₂), 7.16-

7.18 (m, 4H, *m*-C₆H₃), 7.25-7.29 (m, 2H, *p*-C₆H₃). ¹³C{¹H} NMR (100 MHz, δ/ppm, C₆D₆): 244.2, 147.4, 139.4, 128.2, 124.0, 53.7, 28.9, 25.4, 23.6.

- **Synthesis of Trimethylgallium (GaMe₃)**

Gallium trichloride (5 g, 28.4 mmol) dissolved in 5 mL of degassed toluene was added dropwise with degassed triethylamine (4.44 g, 43.9 mmol) and neat trimethylaluminium (3.16 g, 43.9 mmol). After the addition, the reaction was stirred overnight and the solution obtained was distilled at atmospheric pressure at 56 °C to obtain the neat trimethylgallium.⁸⁵ The neat trimethylgallium was then diluted in toluene to give 0.702 M. ¹H NMR (400 MHz, δ/ppm, C₆D₆): -0.14 (s, 9H, GaMe₃).

- **Synthesis of Trimethylindium (InMe₃, *in-situ*)**

A 100 mL Schlenk tube was charged with indium trichloride (0.221 g, 1 mmol) dissolved in ether (10 mL). The mixture was then cooled to -78 °C and MeLi (1 mL, 3 M in dimethoxyethane) was slowly added. The mixture was then warmed up to room temperature and the precipitate formed was filtered off through Celite⁸⁶ and the filtrate was directly added to the carbene.

5.4 Synthesis of New Compounds

5.4.1 Synthesis of new Trimethylaluminium compounds

- Synthesis of IMes→AlMe₃ (122)**

In a reaction tube equipped with a stirring bar, IMes (0.304 g, 1.0 mmol) was dissolved in toluene to give a clear yellow solution. Then, trimethylaluminium (AlMe₃) (1.0 mL, 1.0 mmol, 1 M in toluene) was added and the solution immediately turned to dark yellow. The reaction was stirred overnight and volatiles were evaporated to dryness. Ether was then added to make a saturated solution. Colourless crystals were grown at room temperature. Yield: 64 %. M.p.: 227 – 231 °C. ¹H NMR (400 MHz, δ/ppm, C₆D₆): -0.78 (s, 9H, AlCH₃), 2.03 (s, 12H, *o*-Ph(CH₃)), 2.08 (s, 6H, *p*-Ph(CH₃)), 5.96 (s, 2H, NCH), 6.75 (s, 4H, C₆H₂). ¹³C{¹H} NMR (100 MHz, δ/ppm, C₆D₆): -7.6 (AlMe₃, broad), 17.6 (ArMe), 21.0 (ArMe), 122.5 (NCH), 129.3 (Ar), 135.3 (Ar), 135.5 (Ar), 139.4 (Ar), 178.5 (C_{carbene}, weak). IR (Nujol, cm⁻¹): $\tilde{\nu}$ = 615 (ν Al–C stretch; m). HRMS: calcd for C₂₄H₃₃AlN₂ [*M* + H]⁺: 377.2537; found 377.2538.

Crystal Structure Data:

- Empirical formula	C ₂₄ H ₃₃ AlN ₂	- Volume [Å ³]	2268.11(15)
- Formula weight	376.50	- <i>Z</i>	4
- Temperature [K]	103(2)	- Calculated Density	
- Wavelength [Å]	0.71073	[g/cm ³]	1.103
- Crystals system	Orthorhombic	- μ , Abs. coeff. [mm ⁻¹]	0.1
- Space Group	Pnma	- F(000)	816
- Unit cell dimensions, cell		- Crystal size [mm]	0.40 x 0.40 x 0.38
Length [Å]	<i>a</i> = 22.9414(9)	- 2 θ range [°]	1.77 to 37.04
	<i>b</i> = 12.2109(5)	- Reflections collected	27611
	<i>c</i> = 8.0965(3)	- Indep. Refl. (<i>R</i> _{int})	5968 (0.0965)
Angles [°]	α = 90	- Larg. diff. Peak and hole	
	β = 90	[eÅ ⁻³]	0.499, -0.341
	γ = 90	- <i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0552, 0.1339
		- <i>R</i> 1, <i>wR</i> 2 (all data)	0.1098, 0.1608

• **Synthesis of SIMes→AlMe₃ (123)**

In a reaction tube equipped with a stirring bar, SIMes (0.306 g, 1 mmol) was dissolved in toluene to give a yellow solution. Then, trimethylaluminium (AlMe₃) (1 mL, 1 mmol, 1 M in toluene) was added and the solution slowly turned dirty green. The reaction was stirred overnight and all volatiles were evaporated under vacuo. Ether was then added to dissolve the solids and the solution was kept in the fridge (+2 °C) to yield colourless crystals. Yield: 67%. M.p.: 234 – 238 °C. ¹H NMR (400 MHz, δ/ppm, C₆D₆): -0.86 (s, 9H, AlCH₃), 2.08 (s, 6H, *p*-Ph(CH₃)), 2.21 (s, 12H, *o*-Ph(CH₃)), 3.00 (s, 4H, NCH₂), 6.76 (s, 4H, C₆H₂). ¹³C{¹H} NMR (100 MHz, δ/ppm, C₆D₆): -7.6 (AlMe₃, broad), 18.0 (ArMe), 21.0 (ArMe), 51.0 (NCH), 129.7 (Ar), 135.4 (Ar), 136.1 (Ar), 138.6 (Ar), 202.3 (C_{carbene}, weak). IR (Nujol, cm⁻¹): $\tilde{\nu}$ = 627 (ν Al–C stretch; m). HRMS: calcd for C₂₄H₃₅AlN₂ [*M* + H]⁺: 379.2694; found 379.2687.

Crystal structure data:

- Empirical formula	C ₂₄ H ₃₅ AlN ₂	- Volume [Å ³]	4703.6(8)
- Formula weight	378.52	- Z	8
- Temperature [K]	103(2)	- Calculated Density	
- Wavelength [Å]	0.71073	[g/cm ³]	1.069
- Crystals system	Orthorhombic	- μ, Abs. coeff. [mm ⁻¹]	0.096
- Space Group	Pca21	- F(000)	1648
- Unit cell dimensions, cell		- Crystal size [mm]	0.12 x 0.22 x 0.28
Length [Å]	<i>a</i> = 17.7329(18)	- 2θ range [°]	1.23 to 27.06
	<i>b</i> = 16.5921(14)	- Reflections collected	36156
	<i>c</i> = 15.9863(16)	- Indep. Refl. (<i>R</i> _{int})	10236 (0.1161)
Angles [°]	α = 90	- Larg. diff. Peak and hole	
	β = 90	[eÅ ⁻³]	0.276, -0.305
	γ = 90	- <i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0644, 0.1273
		- <i>R</i> 1, <i>wR</i> 2 (all data)	0.1230, 0.1521

• **Synthesis of IPr→AlMe₃ (124)**

In a reaction tube equipped with a stirring bar, IPr (0.389 g, 1 mmol) was dissolved in toluene to give a clear solution. Then, trimethylaluminium (AlMe₃) (1 mL, 1 mmol, 1 M in toluene) was added. The reaction was stirred overnight and volatiles were evaporated under vacuo to give a saturated solution. Colourless crystals were grown at room and refrigerated temperature (+2 °C). Yield: 62%. M.p.: 211 – 213 °C. ¹H NMR (400 MHz, δ/ppm, C₆D₆): –0.86 (s, 9H, AlCH₃), 0.98–1.00 (d, 12H, J_{H-H} = 6.8 Hz, CH(CH₃)₂), 1.39–1.40 (d, 12H, J_{H-H} = 6.8 Hz, CH(CH₃)₂), 2.74–2.81 (p, 4H, J_{H-H} = 6.8 Hz, CH(CH₃)₂), 6.45 (s, 2H, NCH₂), 7.10–7.12 (m, 4H, *m*-C₆H₃), 7.21–7.25 (m, 2H, *p*-C₆H₃). ¹³C{¹H} NMR (100 MHz, δ/ppm, C₆D₆): –7.5 (AlMe₃, broad), 22.6 (CH(CH₃)₂), 25.7 (CH(CH₃)₂), 28.7 (CH(CH₃)₂), 123.9 (Ar), 124.0 (NCH), 130.5 (Ar), 135.3 (Ar), 145.8 (Ar), 181.1 (C_{carbene}, weak). IR (Nujol, cm^{–1}): $\tilde{\nu}$ = 615 (ν Al–C stretch; m). HRMS: calcd for C₃₀H₄₅AlN₂ [*M* + *H*]⁺: 461.3476; found 461.3490.

Crystal structure data:

- Empirical formula	C ₃₀ H ₄₅ AlN ₂	- Volume [Å ³]	5837.9(7)
- Formula weight	460.66	- <i>Z</i>	8
- Temperature [K]	103(2)	- Calculated Density	
- Wavelength [Å]	0.71073	[g/cm ³]	1.048
- Crystals system	Monoclinic	- μ , Abs. coeff. [mm ^{–1}]	0.088
- Space Group	P121/c1	- F(000)	2016
- Unit cell dimensions, cell		- Crystal size [mm]	0.18 x 0.22 x 0.26
Length [Å]	<i>a</i> = 16.6982(12)	- 2 θ range [°]	1.54 to 28.78
	<i>b</i> = 19.5345(14)	- Reflections collected	56158
	<i>c</i> = 19.2491(14)	- Indep. Refl. (<i>R</i> _{int})	15123 (0.1360)
Angles [°]	α = 90	- Larg. diff. Peak and hole	
	β = 111.602(3)	[eÅ ^{–3}]	0.677, -0.677
	γ = 90	- <i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>))	0.0771, 0.1611
		- <i>R</i> 1, <i>wR</i> 2 (all data)	0.1898, 0.2292

• **Synthesis of SIPr→AlMe₃ (125)**

In a reaction tube equipped with a stirring bar, SIPr (0.391 g, 1 mmol) was dissolved in toluene to give a clear solution. Then, trimethylaluminium (AlMe₃) (1 mL, 1 mmol, 1 M in toluene) was added. The reaction was stirred overnight and volatiles were evaporated under vacuo to give a saturated solution. Colourless crystals were grown at room and refrigerated temperature (+2 °C). Yield: 51%. M.p.: 194 – 204 °C. ¹H NMR (400 MHz, δ/ppm, C₆D₆): -0.91 (s, 9H, AlCH₃), 1.09–1.11 (d, 12H, J_{H-H} = 6.8 Hz, CH(CH₃)₂), 1.45–1.46 (d, 12H, J_{H-H} = 6.8 Hz, CH(CH₃)₂), 3.23–3.30 (m, 4H, CH(CH₃)₂), 3.45 (s, 4H, NCH₂), 7.08–7.10 (m, 2H, *p*-C₆H₃), 7.16–7.17 (m, 2H, *m*-C₆H₃), 7.19–7.21 (m, 2H, *m*-C₆H₃). ¹³C{¹H} NMR (100 MHz, δ/ppm, C₆D₆): -7.1 (AlMe₃, broad), 23.6 (CH(CH₃)₂), 26.2 (CH(CH₃)₂), 28.8 (CH(CH₃)₂), 54.1 (NCH), 124.7 (Ar), 129.9 (Ar), 135.7 (Ar), 146.8 (Ar), 205.2 (C_{carbene}, weak). IR (Nujol, cm⁻¹): $\tilde{\nu}$ = 617 (ν Al–C stretch; m). HRMS: calcd for C₃₀H₄₇AlN₂ [M + H]⁺: 463.3633; found 463.3611.

Crystal structure data:

- Empirical formula	C ₃₀ H ₄₇ AlN ₂	- Volume [Å ³]	2867.5(3)
- Formula weight	462.67	- Z	4
- Temperature [K]	103(2)	- Calculated Density	
- Wavelength [Å]	0.71073	[g/cm ³]	1.072
- Crystals system	Monoclinic	- μ, Abs. coeff. [mm ⁻¹]	0.090
- Space Group	P121/c1	- F(000)	1016
- Unit cell dimensions, cell		- Crystal size [mm]	0.30 x 0.31 x 0.32
Length [Å]	<i>a</i> = 17.8289(13)	- 2θ range [°]	2.33 to 30.51
	<i>b</i> = 10.1831(7)	- Reflections collected	19383
	<i>c</i> = 16.5889(10)	- Indep. Refl. (<i>R</i> _{int})	8679 (0.0644)
Angles [°]	α = 90	- Larg. diff. Peak and hole	
	β = 107.807(2)	[eÅ ⁻³]	0.481, -0.560
	γ = 90	- <i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0635, 0.1510
		- <i>R</i> 1, <i>wR</i> 2 (all data)	0.1204, 0.1937

5.4.2 Synthesis of Trimethylaluminium By-products

- Synthesis of 1,3-Bis(2,6-diisopropylphenyl)-2-methylimidazolium formate (125)**

In a reaction tube equipped with a stirring bar, SIPr (0.391 g, 1 mmol) was dissolved in toluene to give a clear solution. Then, trimethylaluminium (AlMe_3) (1 mL, 1 mmol, 1 M in toluene) was added. The reaction was refluxed overnight and volatiles were evaporated to dryness. THF was added to yield a saturated solution and colourless crystals were extracted from the THF/hexane solution at room temperature. No NMRs were obtained as the crystalline solids proved to be remarkably air and moisture sensitive, and they were difficult to separate from the complex mixture of products obtained from the reflux reaction.

Crystal structure data:

- Empirical formula	$\text{C}_{15}\text{H}_{22.25}\text{NO}_2$	- Volume [$\text{\AA}^3$]	2894.6(10)
- Formula weight	248.59	- Z	8
- Temperature [K]	103(2)	- Calculated Density	
- Wavelength [$\text{\AA}$]	0.71073	[g/cm^3]	1.141
- Crystals system	Monoclinic	- μ , Abs. coeff. [mm^{-1}]	0.075
- Space Group	P121/c1	- F(000)	1082
- Unit cell dimensions, cell		- Crystal size [mm]	0.10 x 0.12 x 0.36
Length [$\text{\AA}$]	$a = 10.653(2)$	- 2θ range [$^\circ$]	2.66 to 28.32
	$b = 17.656(3)$	- Reflections collected	22109
	$c = 15.577(3)$	- Indep. Refl. (R_{int})	7192 (0.1091)
Angles [$^\circ$]	$\alpha = 90$	- Larg. diff. Peak and hole	
	$\beta = 98.900(6)$	[$\text{e}\text{\AA}^{-3}$]	0.352, -0.378
	$\gamma = 90$	- $R1$, $wR2$ ($I > 2\sigma(I)$)	0.0775, 0.1758
		- $R1$, $wR2$ (all data)	0.1706, 0.2137

- **Synthesis of 1,3-Bis(2,6-diisopropylphenyl)-imidazolinium carboxylates (132)**

SIPr•AlMe₃ (**124**) was generated *in-situ*. In a reaction tube equipped with a stirring bar, SIPr (0.391 g, 1 mmol) was dissolved in toluene to give a clear solution. Then, trimethylaluminium (AlMe₃) (1 mL, 1 mmol, 1 M in toluene) was added. The reaction was stirred overnight, after which CO₂ was bubbled in into the reaction solution with immediate formation of white precipitate. The reaction was bubbled for 45 minutes and tiny single crystals were formed from the side of the glass. Attempts were made to isolate out the single crystals for NMR but the crystals were always coated with white precipitate, hence no clean NMR can be obtained.

Crystal structure data:

- Empirical formula	C ₂₈ H ₃₈ N ₂ O ₂	- Volume [Å ³]	2508.5(18)
- Formula weight	434.60	- Z	4
- Temperature [K]	103(2)	- Calculated Density	
- Wavelength [Å]	0.71073	[g/cm ³]	1.151
- Crystals system	Monoclinic	- μ, Abs. coeff. [mm ⁻¹]	0.072
- Space Group	P121/c1	- F(000)	944
- Unit cell dimensions, cell		- Crystal size [mm]	0.18 x 0.20 x 0.42
Length [Å]	a = 12.342(5)	- 2θ range [°]	2.62 to 25.52
	b = 15.533(7)	- Reflections collected	32863
	c = 13.384(5)	- Indep. Refl. (R _{int})	4646 (0.2297)
Angles [°]	α = 90	- Larg. diff. Peak and hole	
	β = 102.133(9)	[eÅ ⁻³]	0.333, -0.272
	γ = 90	- R1, wR2 (I>2σ(I))	0.0822, 0.1498
		- R1, wR2 (all data)	0.1918, 0.1947

- **Synthesis of IMes imidazolium-2-amidinate (Dipp) (133)**

“Wet” synthesis: IMes•AlMe₃ (**121**) was generated *in-situ*. In a reaction tube equipped with a stirring bar, IMes (0.304 g, 1 mmol) was dissolved in toluene to give a clear solution. Then, trimethylaluminium (AlMe₃) (1 mL, 1 mmol, 1 M in toluene) was added. The reaction was stirred overnight, after which the Dipp carbodiimide (0.363 g, 1 mmol) was added into the reaction solution, and the solution turned orange. The reaction was stirred overnight, and the mixture was then filtered through Celite. The filtrate was evaporated under vacuum and yellow crystals were obtained in the freezer (-21 °C). Yield: 72% ¹H NMR: (300 MHz, δ/ppm, C₆D₆): δ 0.78 – 0.80 (d, 12H, *J*_{H-H} = 6.9 Hz, CH(CH₃)₂), 1.00 – 1.02 (d, 12H, *J*_{H-H} = 6.0 Hz, CH(CH₃)₂), 2.01 (s, 6H, *p*-Ph(CH₃)), 2.29 (s, 12H, *o*-Ph(CH₃)), 3.26 – 3.35 (q, 4H, *J*_{H-H} = 6.8 Hz, CH(CH₃)₂), 5.59 (s, 2H, NCH), 6.67 (s, 4H, *m*-C₆H₂), 6.93 - 6.95 (d, 4H, *J*_{H-H} = 6.0 Hz, *m*-C₆H₃), 7.14 (s, 2H, *p*-C₆H₃) ¹³C{¹H} NMR: (100 MHz, δ/ppm, C₆D₆): δ 18.2, 20.8, 22.5, 26.1, 28.4, 119.7, 120.2, 121.9, 128.5, 129.3, 129.5, 135.5, 139.8, 140.1, 146.1, 150.1.

Mechanochemical synthesis: In a grinder jar equipped with a 10 mm steel ball, IMes•AlMe₃ (**122**, 0.377 g, 1 mmol) and Dipp carbodiimide (0.363 g, 1 mmol) were weighed into the jar and was milled for 90 mins. Product was immediately obtained and ¹H NMR was run to confirm the formation of the product. Yield: 92%.

Crystal structure data:

- Empirical formula	C ₅₀ H ₆₈ N ₄ O	- Volume [Å ³]	4475.1(4)
- Formula weight	741.08	- Z	4
- Temperature [K]	103(2)	- Calculated Density	
- Wavelength [Å]	0.71073	[g/cm ³]	1.100
- Crystals system	Orthorhombic	- μ , Abs. coeff. [mm ⁻¹]	0.065
- Space Group	P 212121	- F(000)	1616
- Unit cell dimensions, cell		- Crystal size [mm]	0.12 x 0.28 x 0.32
Length [Å]	$a = 26.4570(13)$	- 2 θ range [°]	1.56 to 29.61
	$b = 11.2445(6)$	- Reflections collected	47300
	$c = 15.0426(8)$	- Indep. Refl. (R_{int})	12566 (0.0559)
Angles [°]	$\alpha = 90$	- Larg. diff. Peak and hole	
	$\beta = 90$	[eÅ ⁻³]	0.299, -0.367
	$\gamma = 90$	- $R1$, $wR2$ ($I > 2\sigma(I)$)	0.0878, 0.1978
		- $R1$, $wR2$ (all data)	0.1153, 0.2106

- **Synthesis of SIMes imidazolium-2-amidinate (Dipp) (134)**

“Wet” synthesis: SIMes•AlMe₃ (**123**) was generated *in-situ*. In a reaction tube equipped with a stirring bar, SIMes (0.306 g, 1 mmol) was dissolved in toluene to give a clear solution. Then, trimethylaluminium (AlMe₃) (1 mL, 1 mmol, 1 M in toluene) was added. The reaction was stirred overnight, after which the Dipp carbodiimide (0.363 g, 1 mmol) was added into the reaction solution, and the solution turned orange. The reaction was stirred overnight, and the mixture was then filtered through Celite. The filtrate was evaporated under vacuum and yellow crystals were obtained in the freezer (-21 °C). Yield: 83%. ¹H NMR: (300 MHz, δ/ppm, C₆D₆): 0.79 – 0.82 (d, 12H, *J*_{H-H} = 6.9 Hz, CH(CH₃)₂), 0.96 – 0.98 (d, 12H, *J*_{H-H} = 6 Hz, CH(CH₃)₂), 2.00 (s, 6H, *p*-Ph(CH₃)), 2.49 (s, 12H, *o*-Ph(CH₃)), 3.06 (s, 4H, NCH₂), 3.20 – 3.29 (q, 4H, *J*_{H-H} = 6.8 Hz, CH(CH₃)₂), 6.68 (s, 4H, *m*-C₆H₂), 6.93 – 6.96 (d, 4H, *J*_{H-H} = 7.2 Hz, *m*-C₆H₃), 7.13 (s, 2H, *p*-C₆H₃) ¹³C{¹H} NMR: (75 MHz, δ/ppm, C₆D₆): 18.3, 20.8, 22.7, 26.2, 28.3, 48.9, 120.2, 122.1, 128.5, 129.7, 130.0, 136.2, 139.0, 140.2, 145.6, 165.5.

Mechanochemical synthesis: In a grinder jar equipped with a 10 mm steel ball, SIMes•AlMe₃ (**123**, 0.379 g, 1 mmol) and Dipp carbodiimide (0.363 g, 1 mmol) were weighed into the jar and was milled for 90 mins. Product was immediately obtained and ¹H NMR was run to confirm the formation of the product. Yield: 95%.

No suitable X-ray crystallographic data could be obtained due to twinning

5.4.3 Synthesis of New Trimethylgallium Compounds

- **Synthesis of IMes→GaMe₃ (145)**

In a reaction tube equipped with a stirring bar, IMes (0.304 g, 1.0 mmol) was dissolved in toluene to give a clear yellow solution. Then, trimethylgallium (GaMe₃) (1.45 mL, 1.0 mmol, 0.702 M in toluene) was added and the solution immediately turned to dark orange. The reaction was stirred overnight and volatiles were evaporated to dryness. Ether was then added and the mixture was filtered through Celite to give a clear solution. The ether solution was then evaporated to yield a saturated solution. Colourless crystals were grown at room temperature. Yield: 37%. M.p.: 196 – 199 °C. ¹H NMR (400 MHz, δ/ppm, C₆D₆): –0.56 (s, 9H, GaCH₃), 2.01 (s, 12H, *o*-Ph(CH₃)), 2.09 (s, 6H, *p*-Ph(CH₃)), 6.02 (s, 2H, NCH), 6.76 (s, 4H, C₆H₂). ¹³C{¹H} NMR (100 MHz, δ/ppm, C₆D₆): –6.1 (GaMe₃, broad), 17.6 (ArMe), 21.0 (ArMe), 122.5 (NCH), 129.3 (Ar), 135.4 (Ar), 135.6 (Ar), 139.3 (Ar), 181.7 (C_{carbene}, weak). IR (Nujol, cm^{–1}): $\tilde{\nu}$ = 525 (ν Ga–C stretch; m). HRMS: calcd for C₂₄H₃₃GaN₂ [*M* + H]⁺: 419.1978; found 419.1992.

Crystal structure data:

- Empirical formula	C ₂₄ H ₃₃ GaN ₂	- Volume [Å ³]	2439.27(14)
- Formula weight	419.24	- <i>Z</i>	4
- Temperature [K]	296(2)	- Calculated Density	
- Wavelength [Å]	0.71073	[g/cm ³]	1.185
- Crystal system	Orthorhombic	- μ , Abs. coeff. [mm ^{–1}]	1.181
- Space Group	Pnma	- F(000)	888
- Unit cell dimensions, cell		- Crystal size [mm]	0.18 x 0.20 x 0.28
Length [Å]	<i>a</i> = 23.0884(8)	- 2 θ range [°]	2.63 to 29.13
	<i>b</i> = 12.3990(4)	- Reflections collected	43057
	<i>c</i> = 8.2064(3)	- Indep. Refl. (<i>R</i> _{int})	3305 (0.0578)
Angles [°]	α = 90	- Larg. diff. Peak and hole	
	β = 90	[eÅ ^{–3}]	0.228, –0.283
	γ = 90	- <i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>))	0.0339, 0.0774
		- <i>R</i> 1, <i>wR</i> 2 (all data)	0.0645, 0.0908

• **Synthesis of SIMes→GaMe₃ (146)**

In a reaction tube equipped with a stirring bar, SIMes (0.306 g, 1 mmol) was dissolved in toluene to give a yellow solution. Then, trimethylgallium (GaMe₃) (1.45 mL, 1 mmol, 0.702 M in toluene) was added and the solution slowly turned dirty yellow. The reaction was stirred overnight and mixture was filtered through Celite to obtain a clear solution. The solution was then evaporated to yield a saturated solution. Colourless crystals were grown at room temperature. Yield: 53%. M.p.: 201 – 205 °C. ¹H NMR (400 MHz, δ/ppm, C₆D₆): -0.60 (s, 9H, GaCH₃), 2.08 (s, 6H, *p*-Ph(CH₃)), 2.21 (s, 12H, *o*-Ph(CH₃)), 3.02 (s, 4H, NCH₂), 6.77 (s, 4H, C₆H₂). ¹³C{¹H} NMR (100 MHz, δ/ppm, C₆D₆): -5.9 (GaMe₃, broad), 17.9 (ArMe), 21.0 (ArMe), 50.9 (NCH), 129.7 (Ar), 135.6 (Ar), 136.1 (Ar), 138.4 (Ar), 206.1 (C_{carbene}, weak). IR (Nujol, cm⁻¹): $\tilde{\nu}$ = 525 (ν Ga–C stretch; s). HRMS: calcd for C₂₄H₃₅GaN₂ [*M* + H]⁺: 421.2134; found 421.2140.

Crystal structure data:

- Empirical formula	C ₂₄ H ₃₅ GaN ₂	- Volume [Å ³]	4653.5(4)
- Formula weight	421.26	- <i>Z</i>	8
- Temperature [K]	103(2)	- Calculated Density	
- Wavelength [Å]	0.71073	[g/cm ³]	1.203
- Crystals system	Orthorhombic	- μ, Abs. coeff. [mm ⁻¹]	1.193
- Space Group	Pca21	- F(000)	1792
- Unit cell dimensions, cell		- Crystal size [mm]	0.18 x 0.20 x 0.38
Length [Å]	<i>a</i> = 17.6361(8)	- 2θ range [°]	1.23 to 29.66
	<i>b</i> = 16.5723(7)	- Reflections collected	63402
	<i>c</i> = 15.9218(8)	- Indep. Refl. (<i>R</i> _{int})	13086 (0.0860)
Angles [°]	α = 90	- Larg. diff. Peak and hole	
	β = 90	[eÅ ⁻³]	0.751, -0.637
	γ = 90	- <i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0440, 0.1034
		- <i>R</i> 1, <i>wR</i> 2 (all data)	0.0744, 0.1440

• **Synthesis of IPr→GaMe₃ (147)**

In a reaction tube equipped with a stirring bar, IPr (0.389 g, 1 mmol) was dissolved in toluene to give a clear solution. Then, trimethylgallium (GaMe₃) (1.45 mL, 1 mmol, 0.702 M in toluene) was added and the solution slowly turned light yellow. The reaction was stirred overnight and mixture was filtered through Celite to obtain a clear solution. The solution was then evaporated to yield a saturated solution. Colourless crystals were grown at room temperature. Yield: 35%. M.p.: 167 – 172 °C. ¹H NMR (400 MHz, δ/ppm, C₆D₆): –0.59 (s, 9H, GaCH₃), 0.99–1.00 (d, 12H, J_{H-H} = 6.8 Hz, CH(CH₃)₂), 1.38–1.40 (d, 12H, J_{H-H} = 6.8 Hz, CH(CH₃)₂), 2.75–2.82 (p, 4H, J_{H-H} = 6.8 Hz, CH(CH₃)₂), 6.46 (s, 2H, NCH₂), 7.11–7.13 (m, 4H, *m*-C₆H₃), 7.22–7.26 (m, 2H, *p*-C₆H₃). ¹³C{¹H} NMR (100 MHz, δ/ppm, C₆D₆): –5.6 (GaMe₃, broad), 22.8 (CH(CH₃)₂), 25.8 (CH(CH₃)₂), 28.8 (CH(CH₃)₂), 124.1 (Ar), 124.2 (NCH), 130.6 (Ar), 135.6 (Ar), 145.8 (Ar), 184.3 (C_{carbene}, weak). IR (Nujol, cm^{–1}): $\tilde{\nu}$ = 525 (ν Ga–C stretch; m). HRMS: calcd for C₃₀H₄₅GaN₂ [*M* + H]⁺: 503.2917; found 503.2930.

Crystal structure data:

- Empirical formula	C ₃₀ H ₄₅ GaN ₂	- Volume [Å ³]	5803.9(5)
- Formula weight	503.40	- Z	8
- Temperature [K]	103(2)	- Calculated Density	
- Wavelength [Å]	0.71073	[g/cm ³]	1.152
- Crystals system	Monoclinic	- μ , Abs. coeff. [mm ^{–1}]	0.967
- Space Group	P121/c1	- F(000)	2160
- Unit cell dimensions, cell		- Crystal size [mm]	0.18 x 0.20 x 0.24
Length [Å]	<i>a</i> = 16.6315(8)	- 2 θ range [°]	1.31 to 27.75
	<i>b</i> = 19.4897(10)	- Reflections collected	84170
	<i>c</i> = 19.2354(10)	- Indep. Refl. (<i>R</i> _{int})	13658 (0.1122)
Angles [°]	α = 90	- Larg. diff. Peak and hole	
	β = 111.4316(16)	[eÅ ^{–3}]	1.103, –1.091
	γ = 90	- <i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>))	0.0530, 0.1319
		- <i>R</i> 1, <i>wR</i> 2 (all data)	0.1061, 0.1875

• **Synthesis of SIPr→GaMe₃ (148)**

In a reaction tube equipped with a stirring bar, SIPr (0.391 g, 1 mmol) was dissolved in toluene to give a clear solution. Then, trimethylgallium (GaMe₃) (1.45 mL, 1 mmol, 0.702 M in toluene) was added and the solution slowly turned light yellow. The reaction was stirred overnight and mixture was filtered through Celite to obtain a clear solution. The solution was then evaporated to yield a saturated solution. Colourless crystals were grown at room temperature. Yield: 39%. M.p.: 207 – 210 °C. ¹H NMR (400 MHz, δ/ppm, C₆D₆): –0.58 (s, 9H, GaCH₃), 1.15–1.17 (d, 12H, J_{H-H} = 6.8 Hz, CH(CH₃)₂), 1.50–1.51 (d, 12H, J_{H-H} = 6.8 Hz, CH(CH₃)₂), 3.28–3.35 (p, 4H, J_{H-H} = 6.7 Hz, CH(CH₃)₂), 3.50 (s, 4H, NCH₂), 7.14–7.16 (m, 2H, *p*-C₆H₃), 7.21–7.27 (m, 4H, *m*-C₆H₃). ¹³C{¹H} NMR (100 MHz, δ/ppm, C₆D₆): –5.2 (GaMe₃, broad), 23.7 (CH(CH₃)₂), 26.1 (CH(CH₃)₂), 28.8 (CH(CH₃)₂), 54.0 (NCH), 124.6 (Ar), 129.8 (Ar), 135.8 (Ar), 146.8 (Ar), 209.0 (C_{carbene}, weak). IR (Nujol, cm^{–1}): $\tilde{\nu}$ = 521 (ν Ga–C stretch; m). HRMS: calcd for C₃₀H₄₇GaN₂ [*M* + H]⁺: 505.3073; found 505.3090.

Crystal structure data:

- Empirical formula	C ₃₀ H ₄₇ GaN ₂	- Volume [Å ³]	2831.7(2)
- Formula weight	505.41	- <i>Z</i>	4
- Temperature [K]	103(2)	- Calculated Density	
- Wavelength [Å]	0.71073	[g/cm ³]	1.186
- Crystals system	Triclinic	- μ, Abs. coeff. [mm ^{–1}]	0.991
- Space Group	P-1	- F(000)	1088
- Unit cell dimensions, cell		- Crystal size [mm]	0.22 x 0.36 x 0.42
Length [Å]	<i>a</i> = 9.9188(4)	- 2θ range [°]	1.18 to 29.60
	<i>b</i> = 16.6053(7)	- Reflections collected	85651
	<i>c</i> = 17.9050(8)	- Indep. Refl. (<i>R</i> _{int})	15861 (0.0689)
Angles [°]	α = 83.4019(14)	- Larg. diff. Peak and hole	
	β = 75.2437(14)	[eÅ ^{–3}]	0.662, –0.775
	γ = 89.8823(14)	- <i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0378, 0.1056
		- <i>R</i> 1, <i>wR</i> 2 (all data)	0.0624, 0.1395

5.4.4 Synthesis of New Trimethylindium Compounds

- **Synthesis of IMes→InMe₃ (149)**

In a reaction tube equipped with a stirring bar, IMes (0.304 g, 1.0 mmol) was dissolved in ether to give a clear yellow solution. Then, *in-situ* generated trimethylindium (InMe₃) (1.0 mmol) was added to the reaction mixture at 0 °C and was allowed to stir overnight maintaining at 0 °C. The resulting mixture was filtered through Celite to give a clear solution and the solution was concentrated. Colourless crystals were grown at refrigerated temperature (+2 °C). Yield: 34%. M.p.: 172 – 179 °C. ¹H NMR (400 MHz, δ/ppm, C₆D₆): –0.52 (s, 9H, InCH₃), 1.99 (s, 12H, *o*-Ph(CH₃)), 2.09 (s, 6H, *p*-Ph(CH₃)), 6.03 (s, 2H, NCH), 6.77 (s, 4H, C₆H₂). ¹³C{¹H} NMR (100 MHz, δ/ppm, C₆D₆): –11.0 (GaMe₃, broad), 17.6 (ArMe), 21.0 (ArMe), 122.5 (NCH), 129.4 (Ar), 135.3 (Ar), 135.6 (Ar), 139.4 (Ar), 181.7. HRMS: calcd for C₂₄H₃₃InN₂ [*M* + H]⁺: 465.1761; found 465.1757.

Crystal structure data:

- Empirical formula	C ₂₄ H ₃₃ InN ₂	- Volume [Å ³]	4721.7(2)
- Formula weight	464.34	- Z	8
- Temperature [K]	103(2)	- Calculated Density	
- Wavelength [Å]	0.71073	[g/cm ³]	1.306
- Crystals system	Orthorhombic	- μ, Abs. coeff. [mm ⁻¹]	1.011
- Space Group	Pca21	- F(000)	1920
- Unit cell dimensions, cell		- Crystal size [mm]	0.14 x 0.18 x 0.24
Length [Å]	<i>a</i> = 17.7812(5)	- 2θ range [°]	1.24 to 31.04
	<i>b</i> = 16.4794(5)	- Reflections collected	32360
	<i>c</i> = 16.1136(4)	- Indep. Refl. (<i>R</i> _{int})	13758 (0.0395)
Angles [°]	α = 90	- Larg. diff. Peak and hole	
	β = 90	[eÅ ⁻³]	1.479, -1.971
	γ = 90	- <i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0466, 0.1175
		- <i>R</i> 1, <i>wR</i> 2 (all data)	0.0842, 0.1681

• **Synthesis of SIMes→InMe₃ (150)**

In a reaction tube equipped with a stirring bar, SIMes (0.306 g, 1 mmol) was dissolved in ether to give a clear yellow solution. Then, *in-situ* generated trimethylindium (InMe₃) (1.0 mmol) was added to the reaction mixture at room temperature and was allowed to stir overnight. The resulting mixture was filtered through Celite to give a clear solution and the solution was concentrated. Colourless crystals were grown at room temperature. Yield: 60%. M.p.: 213 – 216 °C. ¹H NMR (400 MHz, δ/ppm, C₆D₆): –0.58 (s, 9H, InCH₃), 2.09 (s, 6H, *p*-Ph(CH₃)), 2.19 (s, 12H, *o*-Ph(CH₃)), 3.01 (s, 4H, NCH₂), 6.78 (s, 4H, C₆H₂). ¹³C{¹H} NMR (100 MHz, δ/ppm, C₆D₆): –10.7 (GaMe₃, broad), 17.9 (ArMe), 21.0 (ArMe), 50.9 (NCH), 129.9 (Ar), 135.5 (Ar), 136.1 (Ar), 138.5 (Ar), 209.3 (C_{carbene}, weak). HRMS: calcd for C₂₄H₃₅InN₂ [*M* + H]⁺: 467.1917; found 467.1923.

Crystal structure data:

- Empirical formula	C ₂₄ H ₃₅ InN ₂	- Volume [Å ³]	4738.5(3)
- Formula weight	466.36	- <i>Z</i>	8
- Temperature [K]	103(2)	- Calculated Density	
- Wavelength [Å]	0.71073	[g/cm ³]	1.307
- Crystals system	Orthorhombic	- μ , Abs. coeff. [mm ⁻¹]	1.007
- Space Group	Pca21	- F(000)	1936
- Unit cell dimensions, cell		- Crystal size [mm]	0.12 x 0.24 x 0.28
Length [Å]	<i>a</i> = 17.7466(7)	- 2 θ range [°]	1.69 to 26.00
	<i>b</i> = 16.5100(6)	- Reflections collected	23919
	<i>c</i> = 16.1725(5)	- Indep. Refl. (<i>R</i> _{int})	9282 (0.0528)
Angles [°]	α = 90	- Larg. diff. Peak and hole	
	β = 90	[eÅ ⁻³]	1.403, -0.467
	γ = 90	- <i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>))	0.0376, 0.0884
		- <i>R</i> 1, <i>wR</i> 2 (all data)	0.0474, 0.1125

• **Synthesis of IPr→InMe₃ (151)**

In a reaction tube equipped with a stirring bar, IPr (0.389 g, 1 mmol) was dissolved in ether to give a clear yellow solution. Then, *in-situ* generated trimethylindium (InMe₃) (1.0 mmol) was added to the reaction mixture at room temperature and was allowed to stir overnight. The resulting mixture was filtered through Celite to give a clear solution and the solution was concentrated. Colourless crystals were grown at room temperature. Yield: 63%. M.p.: 148 – 153 °C. ¹H NMR (400 MHz, δ/ppm, C₆D₆): -0.60 (s, 9H, GaCH₃), 0.99–1.01 (d, 12H, J_{H-H} = 6.8 Hz, CH(CH₃)₂), 1.36–1.38 (d, 12H, J_{H-H} = 6.8 Hz, CH(CH₃)₂), 2.72–2.79 (p, 4H, J_{H-H} = 6.9 Hz, CH(CH₃)₂), 6.48 (s, 2H, NCH₂), 7.11–7.13 (m, 4H, *m*-C₆H₃), 7.23–7.26 (m, 2H, *p*-C₆H₃). ¹³C{¹H} NMR (100 MHz, δ/ppm, C₆D₆): -10.3 (InMe₃, broad), 23.1 (CH(CH₃)₂), 25.6 (CH(CH₃)₂), 28.8 (CH(CH₃)₂), 124.2 (Ar), 124.2 (NCH), 130.6 (Ar), 135.6 (Ar), 145.8 (Ar), 186.8 (C_{carbene}, weak). HRMS: calcd for C₃₀H₄₅InN₂ [*M* + H]⁺: 549.2700; found 549.2704.

Crystal structure data:

- Empirical formula	C ₃₀ H ₄₅ InN ₂	- Volume [Å ³]	2949.3(3)
- Formula weight	548.50	- Z	4
- Temperature [K]	103(2)	- Calculated Density	
- Wavelength [Å]	0.71073	[g/cm ³]	1.235
- Crystals system	Monoclinic	- μ, Abs. coeff. [mm ⁻¹]	0.819
- Space Group	P121/n1	- F(000)	1152
- Unit cell dimensions, cell		- Crystal size [mm]	0.39 x 0.40 x 0.42
Length [Å]	<i>a</i> = 10.3930(6)	- 2θ range [°]	2.78 to 31.07
	<i>b</i> = 19.4217(9)	- Reflections collected	40592
	<i>c</i> = 14.7592(7)	- Indep. Refl. (<i>R</i> _{int})	9429 (0.0436)
Angles [°]	α = 90	- Larg. diff. Peak and hole	
	β = 98.1212(17)	[eÅ ⁻³]	0.586, -0.719
	γ = 90	- <i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0290, 0.0636
		- <i>R</i> 1, <i>wR</i> 2 (all data)	0.0403, 0.0681

• **Synthesis of SIPr→InMe₃ (152)**

In a reaction tube equipped with a stirring bar, SIPr (0.390 g, 1 mmol) was dissolved in ether to give a clear yellow solution. Then, *in-situ* generated trimethylindium (InMe₃) (1.0 mmol) was added to the reaction mixture at 0 °C and was allowed to stir 30 minutes. Subsequently, colourless crystals were formed. The resulting solution was then extracted to isolate the crystals and concentrated to yield more crystals. Colourless crystals were grown at refrigerated temperature (+2 °C). Yield: 36%. M.p.: 194 – 200 °C. ¹H NMR (400 MHz, δ/ppm, C₆D₆): -0.62 (s, 9H, InCH₃), 1.10–1.11 (d, 12H, J_{H-H} = 6.8 Hz, CH(CH₃)₂), 1.43–1.45 (d, 12H, J_{H-H} = 6.8 Hz, CH(CH₃)₂), 3.19–3.26 (p, 4H, J_{H-H} = 6.8 Hz, CH(CH₃)₂), 3.42 (s, 4H, NCH₂), 7.10–7.12 (m, 4H, *m*-C₆H₃), 7.19–7.23 (m, 2H, *p*-C₆H₃). ¹³C{¹H} NMR (100 MHz, δ/ppm, C₆D₆): -9.6 (InMe₃, broad), 23.9 (CH(CH₃)₂), 25.9 (CH(CH₃)₂), 28.8 (CH(CH₃)₂), 54.1 (NCH), 124.7 (Ar), 129.9 (Ar), 135.7 (Ar), 146.8 (Ar), 211.7 (C_{carbene}, weak). HRMS: calcd for C₃₀H₄₇InN₂ [*M* + H]⁺: 551.2856; found 551.2878.

Crystal structure data:

- Empirical formula	C ₃₀ H ₄₇ InN ₂	- Volume [Å ³]	5771.0(3)
- Formula weight	550.51	- <i>Z</i>	8
- Temperature [K]	133(2)	- Calculated Density	
- Wavelength [Å]	0.71073	[g/cm ³]	1.267
- Crystals system	Monoclinic	- μ , Abs. coeff. [mm ⁻¹]	0.838
- Space Group	C12/c1	- F(000)	2320
- Unit cell dimensions, cell		- Crystal size [mm]	0.10 x 0.38 x 0.42
Length [Å]	<i>a</i> = 34.7678(11)	- 2 θ range [°]	1.18 to 31.11
	<i>b</i> = 9.9342(2)	- Reflections collected	37529
	<i>c</i> = 16.8380(5)	- Indep. Refl. (<i>R</i> _{int})	9263 (0.0484)
Angles [°]	α = 90	- Larg. diff. Peak and hole	
	β = 97.1092(12)	[eÅ ⁻³]	0.661, -0.699
	γ = 90	- <i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>))	0.0318, 0.0733
		- <i>R</i> 1, <i>wR</i> 2 (all data)	0.0459, 0.0848

5.4.2 Synthesis of Trimethylindium By-product (153)

Method 1: In a reaction tube equipped with a stirring bar, SIPr (0.390 g, 1 mmol) was dissolved in ether to give a clear yellow solution. Then, *in-situ* generated trimethylindium (InMe_3) (1.0 mmol) was added to the reaction mixture at room temperature and was allowed to stir overnight. The resulting mixture was filtered through Celite to give a clear solution and the solution was concentrated. Colourless crystals were grown at 0 °C.

Method 2: In a reaction tube equipped with a stirring bar, SIPr (0.390 g, 1 mmol) was dissolved in ether to give a clear yellow solution. Then, *in-situ* generated trimethylindium (InMe_3) (1.0 mmol) was added to the reaction mixture at 0 °C and was allowed to stir for 30 minutes till colourless crystals were formed. Subsequently, stoichiometric amount of water (0.018 mL, 1 mmol) was added to the reaction and was allowed to stir overnight at 0 °C. The resulting mixture was filtered through Celite to give a clear solution and the solution was concentrated. Colourless crystals were grown at room temperature. Yield: 8%. M.p: 139 – 142 °C. ^1H NMR (400 MHz, δ/ppm , C_6D_6): δ = 0.94-0.96 (d, 6H, $J_{\text{H-H}}$ = 6.8 Hz, $\text{CH}(\text{CH}_3)_2$), 1.06-1.07 (d, 6H, $J_{\text{H-H}}$ = 6.8 Hz, $\text{CH}(\text{CH}_3)_2$), 1.22-1.24 (d, 12H, $J_{\text{H-H}}$ = 6.8 Hz, $\text{CH}(\text{CH}_3)_2$), 3.01-3.08 (p, 2H, $J_{\text{H-H}}$ = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$), 3.15-3.20 (q, 2H, $J_{\text{H-H}}$ = 6.9 Hz, NHCH_2), 3.35-3.42 (p, 2H, $J_{\text{H-H}}$ = 6.9 Hz, $\text{CH}(\text{CH}_3)_2$), 3.60-3.64 (t, 1H, $J_{\text{H-H}}$ = 6.8 Hz, NHCH_2), 3.83-3.87 (t, 2H, $J_{\text{H-H}}$ = 6.8 Hz, NHCH_2), 6.94-6.96 (m, 2H, $p\text{-C}_6\text{H}_3$), 7.07-7.16 (m, 4H, $m\text{-C}_6\text{H}_3$), 8.23 (s, 1H, NCHO). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, δ/ppm , C_6D_6): δ = 23.5 ($\text{CH}(\text{CH}_3)_2$), 24.3 ($\text{CH}(\text{CH}_3)_2$), 24.5 ($\text{CH}(\text{CH}_3)_2$), 25.3 ($\text{CH}(\text{CH}_3)_2$), 28.1 ($\text{CH}(\text{CH}_3)_2$), 28.5 ($\text{CH}(\text{CH}_3)_2$), 49.3 (NCH_2), 49.9 (NCH_2), 123.9 (Ar), 124.2 (Ar), 124.6 (Ar), 129.6 (Ar), 136.5 (Ar), 142.5 (Ar), 143.9 (Ar), 148.0 (Ar), 163.5 (CHO). HRMS: calcd for $\text{C}_{27}\text{H}_{41}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 409.3219; found 409.3215.

Crystal structure data:

- Empirical formula	C ₂₇ H ₄₀ N ₂ O	- Volume [Å ³]	5028.2(4)
- Formula weight	408.61	- Z	8
- Temperature [K]	133(2)	- Calculated Density	
- Wavelength [Å]	0.71073	[g/cm ³]	1.080
- Crystals system	Orthorhombic	- μ , Abs. coeff. [mm ⁻¹]	0.065
- Space Group	Pbca	- F(000)	1792
- Unit cell dimensions, cell		- Crystal size [mm]	0.18 x 0.20 x 0.28
Length [Å]	$a = 19.1039(10)$	- 2 θ range [°]	2.22 to 28.31
	$b = 11.8737(6)$	- Reflections collected	38455
	$c = 22.1669(10)$	- Indep. Refl. (R_{int})	6241 (0.0804)
Angles [°]	$\alpha = 90$	- Larg. diff. Peak and hole	
	$\beta = 90$	[eÅ ⁻³]	0.212, -0.273
	$\gamma = 90$	- $R1, wR2$ ($I > 2\sigma(I)$)	0.0518, 0.1218
		- $R1, wR2$ (all data)	0.1163, 0.1504

5.5 Mechanochemical Syntheses of Compounds

5.5.1 Synthesis of IMes $\rightarrow$ MCl₃

- **Synthesis of IMes $\rightarrow$ AlCl₃ (160)**

In a grinder jar equipped with a 7 or 10 mm steel ball, IMes (0.306 g, 1 mmol) and aluminium chloride (0.133 g, 1 mmol) were weighed into the jar and was milled for 90 mins. Product was immediately obtained and ¹H NMR was run to confirm the formation of the product. Yield: 89% (non isolated yield). ¹H NMR (400 MHz, δ/ppm, CDCl₃): 2.13 (s, 12H, *o*-Ph(CH₃)), 2.36 (s, 6H, *p*-Ph(CH₃)), 7.02 (s, 4H, C₆H₂), 7.06 (s, 2H, NCH). ¹³C{¹H} NMR cannot be run as the sample gradually decompose to the imidazolium chloride.

• **Synthesis of IMes→GaCl₃ (161)**

In a grinder jar equipped with a 7 or 10 mm steel ball, IMes (0.306 g, 1 mmol) and gallium chloride (0.176 g, 1 mmol) were weighed into the jar and was milled for 90 mins. Product was immediately obtained and ¹H NMR was run to confirm the formation of the product. Yield: 96% (non isolated yield). ¹H NMR (400 MHz, δ/ppm, CDCl₃): 2.08 (s, 12H, *o*-Ph(CH₃)), 2.30 (s, 6H, *p*-Ph(CH₃)), 6.97 (s, 4H, C₆H₂), 7.19 (s, 2H, NCH). ¹³C{¹H} NMR (100 MHz, δ/ppm, C₆D₆): 17.6 (ArMe), 21.0 (ArMe), 124.8 (NCH), 129.5 (Ar), 132.5 (Ar), 135.1 (Ar), 140.9 (Ar), 165.0.

Crystal structure data:

- Empirical formula	C ₂₁ H ₂₄ Cl ₃ GaN ₂	- Volume [Å ³]	4587.6(7)
- Formula weight	480.49	- Z	8
- Temperature [K]	153(2)	- Calculated Density	
- Wavelength [Å]	0.71073	[g/cm ³]	1.391
- Crystals system	Orthorhombic	- μ, Abs. coeff. [mm ⁻¹]	1.557
- Space Group	Pca 21	- F(000)	1968
- Unit cell dimensions, cell		- Crystal size [mm]	0.24 x 0.26 x 0.30
Length [Å]	<i>a</i> = 17.0778(15)	- 2θ range [°]	1.21 to 29.61
	<i>b</i> = 33.810(3)	- Reflections collected	73772
	<i>c</i> = 7.9453(7)	- Indep. Refl. (<i>R</i> _{int})	12861 (0.0530)
Angles [°]	α = 90	- Larg. diff. Peak and hole	
	β = 90	[eÅ ⁻³]	2.058, -2.085
	γ = 90	- <i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0673, 0.1778
		- <i>R</i> 1, <i>wR</i> 2 (all data)	0.0820, 0.1901

• **Synthesis of IMes→InCl₃ (162)**

In a grinder jar equipped with a 7 or 10 mm steel ball, IMes (0.306 g, 1 mmol) and indium chloride (0.221 g, 1 mmol) were weighed into the jar and was milled for 90 mins. Product was immediately obtained and ¹H NMR was run to confirm the formation of the product. Yield: 95% (non isolated yield), 74% (isolated yield)). ¹H NMR (400 MHz, δ/ppm, CDCl₃): 2.14 (s, 12H, *o*-Ph(CH₃)), 2.37 (s, 6H, *p*-Ph(CH₃)), 7.06 (s, 4H, C₆H₂), 7.37 (s, 2H, NCH). ¹³C{¹H} NMR cannot be run as the sample gradually decompose to the imidazolium chloride.

Crystal structure data:

- Empirical formula	C ₂₁ H ₂₄ Cl ₃ InN ₂	- Volume [Å ³]	4668.5(10)
- Formula weight	525.59	- Z	8
- Temperature [K]	103(2)	- Calculated Density	
- Wavelength [Å]	0.71073	[g/cm ³]	1.496
- Crystals system	Orthorhombic	- μ, Abs. coeff. [mm ⁻¹]	1.364
- Space Group	Pca 21	- F(000)	2112
- Unit cell dimensions, cell		- Crystal size [mm]	0.22 x 0.28 x 0.38
Length [Å]	<i>a</i> = 16.360(2)	- 2θ range [°]	1.23 to 31.15
	<i>b</i> = 16.581(2)	- Reflections collected	67822
	<i>c</i> = 17.210(2)	- Indep. Refl. (<i>R</i> _{int})	13702 (0.0772)
Angles [°]	α = 90	- Larg. diff. Peak and hole	
	β = 90	[eÅ ⁻³]	0.551, -0.655
	γ = 90	- <i>R</i> 1, <i>wR</i> 2 (<i>I</i> >2σ(<i>I</i>))	0.0386, 0.0689
		- <i>R</i> 1, <i>wR</i> 2 (all data)	0.0563, 0.0767

5.5.2 Synthesis of Bidentate Ligands for Mechanochemical Synthesis

- Synthesis of 3-ethyl-1-(2-hydroxy-2-methylpropyl)-1H-imidazol-3-ium iodide**

In a high pressured reaction tube equipped with a stirring bar, imidazole (3 g, 45 mmol) and the epoxide, 2,2-dimethyloxirane (3.24 g, 45 mmol, 1 equiv) was weighed into the tube and the resulting mixture was allowed to stir at 50 °C for 12 h. Acetonitrile (10 mL) and the alkyl halide iodoethane (7.02 g, 45 mmol, 1 equiv) were then added to the mixture and stirred an additional 2 h at 80 °C. The solvent was then removed to yield the product, and the product was recrystallized to give brownish white crystals. Yield: 80%. ^1H NMR (400 MHz, δ /ppm, Acetone- d_6): 1.25 (s, 6H, $\text{CH}_2\text{C}(\text{CH}_3)_2$), 1.57 – 1.60 (t, 3H, $J_{\text{H-H}} = 7.2$ Hz, $\text{CH}_2(\text{CH}_3)$), 4.39 (s, 1H, OH), 4.45 – 4.51 (q, 2H, $J_{\text{H-H}} = 7.3$ Hz, $\text{CH}_2(\text{CH}_3)$), 4.53 (s, 2H, NCH₂), 7.91 (s, 1H, NCH), 7.92 (s, 1H, NCH), 9.51 (s, 1H, NCHN). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, δ /ppm, C_6D_6): 15.6 ($\text{CH}_2(\text{CH}_3)$), 27.0 ($\text{CH}_2(\text{CH}_3)_2$), 45.6 ($\text{CH}_2(\text{CH}_3)$), 59.5 ($\text{CH}_2\text{C}(\text{CH}_3)_2$), 69.7 ($\text{CH}_2\text{C}(\text{CH}_3)_2$), 122.0 (NCH), 124.9 (NCH), 137.3 (NCHN).

Crystal Structure Data:

- Empirical formula	$\text{C}_{18}\text{H}_{34}\text{I}_2\text{N}_2\text{O}_2$	- Volume [$\text{\AA}^3$]	1184.52(5)
- Formula weight	592.29	- Z	2
- Temperature [K]	103(2)	- Calculated Density	
- Wavelength [$\text{\AA}$]	0.71073	[g/cm^3]	1.661
- Crystals system	Orthorhombic	- μ , Abs. coeff. [mm^{-1}]	2.673
- Space Group	Pna 2(1)	- F(000)	584
- Unit cell dimensions, cell		- Crystal size [mm]	0.40 x 0.22 x 0.20
Length [$\text{\AA}$]	$a = 15.7708(4)$	- 2θ range [$^\circ$]	2.93 to 34.97
	$b = 7.7426(2)$	- Reflections collected	9780
	$c = 9.7007(2)$	- Indep. Refl. (R_{int})	5007 (0.0155)
Angles [$^\circ$]	$\alpha = 90$	- Larg. diff. Peak and hole	
	$\beta = 90$	[$\text{e}\text{\AA}^{-3}$]	0.772, -0.528
	$\gamma = 90$	- $R1$, $wR2$ ($I > 2\sigma(I)$)	0.0195, 0.0585
		- $R1$, $wR2$ (all data)	0.0217, 0.0594

• **Synthesis of 3-ethyl-1-(2-hydroxy-2-phenylethyl)-1H-imidazol-3-ium iodide**

In a high pressured reaction tube equipped with a stirring bar, imidazole (3 g, 45 mmol) and the epoxide, 2-phenyloxirane (5.41 g, 45 mmol, 1 equiv) was weighed into the tube and the resulting mixture was allowed to stir at 50 °C for 12 h. Acetonitrile (10 mL) and the alkyl halide iodoethane (7.02 g, 45 mmol, 1 equiv) were then added to the mixture and stirred an additional 2 h at 80 °C. The solvent was then removed to yield the product, and the product was recrystallized to give brownish white crystals. Yield: 72%. ¹H NMR (400 MHz, δ/ppm, DMSO): 1.38 – 1.42 (t, 3H, *J*_{H-H} = 7.2 Hz, CH₂(CH₃)), 4.20 – 4.25 (q, 2H, *J*_{H-H} = 7.4 Hz, CH₂(CH₃)), 4.41 – 4.45 (dd, 2H, *J*_{H-H} = 3.2, 13.6 Hz, NCH₂), 4.97 – 5.01 (m, 1H, CHOH), 5.94 (s, 1H, OH), 7.29 – 7.33 (m, 2H, ArH), 7.36 – 7.43 (m, 3H, ArH), 7.74 (s, 1H, NCH), 7.81 (s, 1H, NCH), 9.17 (s, 1H, NCHN). ¹³C{¹H} NMR (100 MHz, δ/ppm, DMSO): 15.2 (CH₂(CH₃)), 44.1 (CH₂(CH₃)), 55.7 (NCH₂), 70.4 (NCH₂CHOH), 121.5 (NCH), 123.1 (Ar), 125.8 (Ar), 127.7 (NCH), 128.2 (Ar), 136.1 (Ar), 141.1 (NCHN).

Crystal Structure Data:

- Empirical formula	C ₁₃ H ₁₇ I ₂ N ₂ O	- Volume [Å ³]	686.70(6)
- Formula weight	344.19	- Z	2
- Temperature [K]	103(2)	- Calculated Density	
- Wavelength [Å]	0.71073	[g/cm ³]	1.665
- Crystals system	Monoclinic	- μ, Abs. coeff. [mm ⁻¹]	2.319
- Space Group	P 2(1)	- F(000)	340
- Unit cell dimensions, cell		- Crystal size [mm]	0.40 x 0.40 x 0.34
Length [Å]	<i>a</i> = 7.8327(4)	- 2θ range [°]	2.74 to 29.27
	<i>b</i> = 11.8102(6)	- Reflections collected	7059
	<i>c</i> = 8.3272(4)	- Indep. Refl. (<i>R</i> _{int})	3473 (0.0224)
Angles [°]	α = 90	- Larg. diff. Peak and hole	
	β = 116.9450(10)	[eÅ ⁻³]	1.255, -0.506
	γ = 90	- <i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0237, 0.0583
		- <i>R</i> 1, <i>wR</i> 2 (all data)	0.0249, 0.0588

References

References

1. L. Benhamou, E. Chardon, G. Lavigne and S. Bellemin-Laponnaz, V. César, *Chem. Rev.* **2011**, *111*, 2705.
2. (a) H. W. Wanzlick, *Angew. Chem. Int. Engl.*, **1962**, *1*, 75; (b) H. W. Wanzlick and H. J. Schönherr, *Angew. Chem. Int. Engl.*, **1968**, *7*, 141
3. K. Öfele and M. Herberhold, *Angew. Chem. Int. Ed.*, **1970**, *9*, 739
4. M. F. Lappert, D. J. Cardin and B. Cetinkaya, *Chem. Rev.*, **1972**, *111*, 545
5. A. Igau, H. Grutzmacher, A. Baceiredo, G. Bertrand and V. César, *J. Am. Chem. Soc.*, **1988**, *110*, 6463
6. A. J. Arduengo, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, **1991**, *113*, 361
7. M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, **2014**, *510*, 485
8. R. W. Alder, M. E. Blake, L. Chaker, J. N. Harvey, F. Paolini and J. Schütz, *Angew. Chem. Int. Ed.*, **2004**, *43*, 5896
9. C. Heinemann, T. Müller, Y. Apeloig and H. Schwarz, *J. Am. Chem. Soc.*, **1996**, *118*, 2023
10. A. J. Arduengo, J. R. Goerlich and W. J. Marshall, *J. Am. Chem. Soc.*, **1995**, *117*, 11027
11. M. Iglesias, D. J. Beetstra, J. C. Knight, L.-L. Ooi, A. Stasch, S. Coles, L. Male, M. B. Hursthouse, K. J. Cavell, A. Dervisi and I. A. Fallis, *Organometallics*, **2008**, *27*, 3279
12. M. Melaimi, M. Soleilhavoup and G. Bertrand, *Angew. Chem. Int. Ed.*, **2010**, *49*, 8810
13. V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu and G. Bertrand, *Angew. Chem. Int. Ed.*, **2005**, *44*, 5705
14. L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Laponnaz and V. César, *Chem. Rev.*, **2011**, *111*, 2705
15. Cavallo L., Cazin C. S. J. and Forster S., *N-heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis*, Springer Science + Business Media B. V., **2011**, vol 32, p 1
16. C. A. Tolman, *Chem. Rev.*, **1977**, *77*, 313
17. D. J. Nelson and S. P. Nolan, *Chem. Soc. Rev.*, **2013**, *42*, 6723
18. H. V. Huynh, Y. Han, R. Jothibas and J. A. Yang, *Organometallics*, **2009**, *28*, 5395
19. A. M. Magill, K. J. Cavell and B. F. Yates, *J. Am. Chem. Soc.*, **2004**, *126*, 8717
20. S. Leuthäusser, D. Schwarz and H. Plenio, *Chem. Eur. J.*, **2007**, *13*, 7195
21. (a) A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano and L. Cavallo, *Eur. J. Inorg. Chem.*, **2009**, 1759; (b) H. Clavier and S. P. Nolan, *Chem. Commun.*, **2010**, *46*, 841
22. Massey A. G., *Main Group Chemistry*, 2nd Ed.; John Wiley and Sons, **2000**.

23. William H., *Main Group Chemistry, Tutorial Chemistry Textbook*, 1st Ed., Royal Society of Chemistry, **2000**, p 57
24. A. J. Arduengo, H. V. R. Dias, J. C. Calabrese and F. Davidson, *J. Am. Chem. Soc.*, **1992**, 114, 9725
25. A. J. Arduengo, H. V. R. Dias, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.* **1992**, 114, 5530
26. M. D. Francis, D. E. Hibbs, M. B. Hursthouse, C. Jones and N. A. Smithies, *J. Chem. Soc., Dalton. Trans.* **1998**, 3249
27. R. J. Baker, A. J. Davies, C. Jones and M. Kloth, *J. Organometallic. Chem.* **2002**, 656, 203
28. R. J. Baker, M. L. Cole, C. Jones and M. F. Mahon, *J. Chem. Soc., Dalton. Trans.*, **2002**, 1992
29. X. W. Li, J. Su and G. H. Robinson, *Chem. Commun.*, **1996**, 2683
30. W.-C. Shih, C.-H. Wang, Y.-T. Chang, G. P. A. Yap and T.-G. Ong, *Organometallics*, **2009**, 28, 1060
31. C.-C. Tsai, Y.-T. Chang, J.-H. Tsai, T. Jurca, G. P. A. Yap and T.-G. Ong, *Organometallics*, **2012**, 31, 637
32. C.-C. Tsai, W.-C. Shih, C.-H. Fang, C.-Y. Li, T.-G. Ong and G. P. A. Yap, *J. Am. Chem. Soc.*, **2010**, 132, 11887
33. A. L. Schmitt, G. Schnee, R. Welter and S. Dagorne, *Chem. Commun.*, **2010**, 46, 2480
34. G. Schnee, O. N. Faza, D. Specklin, B. Jacques, L. Karmazin, R. Welter, C. S and López, S. Dagorne, *Chem. Eur. J.*, **2015**, 21, 17959
35. M. Schiefer, N. D. Reddy, H.-J. Ahn, A. Stasch, H. W. Roesky, A. C. Schlicker, H.-G. Schmidt, M. Noltemeyer and D. Vidovic, *Inorg. Chem.*, **2003**, 42, 4970
36. A. Stasch, M. Ferbinteanu, J. Prust, W. Zheng, F. Cimpoesu, H. W. Roesky, J. Magull, H.-G. Schmidt and M. Noltemeyer, *J. Am. Chem. Soc.*, **2002**, 124, 5441
37. A. R. Kennedy, R. E. Mulvey and S. D. Robertson, *Dalton. Trans.*, **2010**, 39, 9091
38. R. A. Musgrave, R. S. P. Turbervill, M. Irwin and J. M. Goicoechea, *Angew. Chem. Int. Ed.*, **2012**, 51, 10832
39. Y. Zhang, G. M. Miyake and E. Y.-X. Chen, *Angew. Chem. Int. Ed.*, **2010**, 49, 10158
40. (a) D. W. Stephan, *Dalton. Trans.*, **2009**, 3129; b) P. A. Chase and D. W. Stephan, *Angew. Chem. Int. Ed.*, **2008**, 47, 7433; c) D. Holschumacher, T. Bannenberg, C. G. Hrib, P. G. Jones and M. Tamm, *Angew. Chem. Int. Ed.*, **2008**, 47, 7428
41. M. Kapitein and C. v. Hänisch, *Eur. J. Inorg. Chem.*, **2015**, 837
42. (a) A. Stasch, S. Singh, H. W. Roesky, M. Noltemeyer and H. G. Schmidt, *Eur. J. Inorg. Chem.*, **2004**, 4052; (b) B. Bantu, G. M. Pawar, K. Wurst, U. Decker, A. M.

- Schmidt and M. R. Buchmeiser, *Eur. J. Inorg. Chem.*, **2009**, 1970; (c) R. S. Ghadwal, H. W. Roesky, R. H. Irmer and P. G. Jones, *Z. Anorg. Allg. Chem.*, **2009**, 635, 431
43. S. G. Alexander, M. L. Cole and C. M. Forsyth, *Chem. Eur. J.*, **2009**, 15, 9201
 44. S. G. Alexander, M. L. Cole, S. K. Furfari and M. Kloth, *Dalton. Trans.*, **2009**, 2909
 45. S. T. Liddle, I. S. Edworthy and P. L. Arnold, *Chem. Soc. Rev.*, **2007**, 36, 1732
 46. Y. Lee, B. Li and A. H. Hoveyda, *J. Am. Chem. Soc.*, **2009**, 131, 11625
 47. C. Romain, C. Fliedel, S. Bellemin-Laponnaz and S. Dagorne, *Organometallics*, **2014**, 33, 5730
 48. M. L. Cole, S. K. Furfari and M. Kloth, *J. Organometallic. Chem.*, **2009**, 694, 2934
 49. G. E. Ball, M. L. Cole and A. I. McKay, *Dalton. Trans.*, **2012**, 41, 946
 50. J. D. Gorden, C. L.B. Macdonald and A. H. Cowley, *J. Organometallic. Chem.*, **2002**, 643-644, 487
 51. M. Uzelac, A. Hernán-Gómez, D. R. Armstrong, A. R. Kennedy and E. Hevia, *Chem. Sci.*, **2015**, 6, 5719
 52. a) P. Horeglad, M. Cybularczyk, B. Trzaskowski, G. Z. Żukowska, M. Dranka and J. Zachara, *Organometallics*, **2015**, 34, 3480; b) P. Horeglad, O. Abilalimov, G. Szczepaniak, A. M. Dabrowska, M. Dranka and J. Zachara, *Organometallics*, **2014**, 33, 100
 53. P. Horeglad, G. Szczepaniak, M. Dranka and J. Zachara, *Chem. Commun.*, **2012**, 48, 1171
 54. a) S. Tang, J. Monot, A. El-Hellani, B. Michelet, R. Guillot, C. Bour and V. Gandon, *Chem. Eur. J.*, **2012**, 18, 10239; b) N. Marion, E. C. Escudero-Adán, J. Benet-Buchholz, E. D. Stevens, L. Fensterbank, M. Malacria and S. P. Nolan, *Organometallics*, **2007**, 26, 3256; c) A. El-Hellani, J. Monot, R. Guillot, C. Bour and V. Gandon, *Inorg. Chem.*, **2013**, 52, 506
 55. C. Bour, J. Monot, S. Tang, R. Guillot, J. Farjon and V. Gandon, *Organometallics*, **2014**, 33, 594
 56. A. El-Hellani, J. Monot, S. Tang, R. Guillot, C. Bour and V. Gandon, *Inorg. Chem.*, **2013**, 52, 11493
 57. V. Lavallo, Y. Canac, C. Präsang, B. Donnadieu and G. Bertrand, *Angew. Chem. Int. Ed.*, **2005**, 44, 5705
 58. M. Chen, Y. Wang, R. J. Gilliard, Jr., P. Wei, N. A. Schwartz and G. H. Robinson, *Dalton Trans.*, **2014**, 43, 14211
 59. D. E. Hibbs, M. B. Hursthouse and C. Jones, N. A. Smithies, *Chem. Commun.*, **1998**, 869
 60. C. D. Abernethy, M. L. Cole and C. Jones, *Organometallic*, **2000**, 19, 4852

61. J. H. Cotgreave, D. Colclough, G. Kociok-Köhn, G. Ruggiero, C. G. Frost and A. S. Weller, *Dalton Trans*, **2004**, 1519
62. S. J. Black, D. E. Hibbs, M. B. Hursthouse, C. Jones, K. M. A. Malik and N. A. Smithies, *J. Chem. Soc., Dalton. Trans.*, **1997**, 4313
63. B. Michelet, J. -R. Colard-Ilté, G. Thiery, R. Guillot, C. Bour and V. Gandon, *Chem. Commun.*, **2015**, 51, 7401
64. a) W.-W. Qiu, K. Surendra, L. Yin and E. J. Corey, *Org. Lett*, **2011**, 21, 5893; b) K. Surendra, W.-W. Qiu and E. J. Corey, *J. Am. Chem. Soc.*, **2011**, 133, 9724; c) K. Surendra and E. J. Corey, *J. Am. Chem. Soc.*, **2014**, 136, 10918
65. a) C. Bour, R. Guillot and V. Gandon, *Chem. Eur. J.*, **2015**, 21, 6066; b) J. Axhausen, K. Lux and A. Kornath, *Angew. Chem. Int. Ed.*, **2014**, 53, 3720
66. M. L. Cole, A. J. Davis and C. Jones, *J. Chem. Soc., Dalton. Trans.*, **2001**, 2451
67. B. Quillian, P. Wei, C. S. Wannere, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, **2009**, 131, 3168
68. a) Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, **2007**, 129, 12412; b) H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki and V. Vargas, *Science*, **2012**, 336, 1420
69. G. Davidson, in *Spectroscopic Properties of Inorganic and Organometallic Compounds*, ed. G. Davidson and E. A. V. Ebsworth, Royal Society of Chemistry, UK, **1990**, vol. 23, p. 227.
70. a) X. Bantreil and S. P. Nolan, *Nat. Protocols*, **2011**, 6, 69; b) A. J. Arduengo, R. Krafczyk and R. Schmutzler, *Tetrahedron*, **1999**, 55, 14523.
71. E. M. Higgins, J. A. Sherwood, A. G. Lindsay, J. Armstrong, R. S. Massey, R. W. Alder and A. C. O'Donoghue, *Chem. Commun.*, **2011**, 47, 1559
72. J. C. Huffman and W. E. Streib, *Chem. Commun.*, **1971**, 911
73. a) V. V. Shatunov, A. A. Korlyukov, A. V. Lebedev, V. D. Sheludyakow, B. I. Kozyrkin and V. Y. Orlov, *J. Organomet. Chem.*, **2011**, 696, 2238 b) M. Kessler, C. Knapp and A. Zogaj, *Organometallic*, **2011**, 30, 3786; c) N. W. Mitzel and C. Lustig, *Z. Naturforsch., B: Chem. Sci*, **2004**, 59, 1532; d) A. Kuczkowski, S. Schulz and M. Nieger, *Eur. J. Inorg. Chem.*, **2001**, 2605; e) J. A. Burns, W. T. Pennington and G. H. Robinson, *Organometallics*, **1995**, 14, 1533; f) J. B. Hill, S. J. Eng, W. T. Pennington and G. H. Robinson, *J. Organomet. Chem.*, **1993**, 445, 11; g) A. M. Bradford, D. C. Bradley, M. B. Hursthouse and M. Motevalli, *Organometallics*, **1992**, 11, 111; h) D. A. Wierda and A. R. Barron, *Polyhedron*, **1989**, 8, 831; i) D. C. Bradley, H. Chudzynska, M. M. Faktor, D. M. Frigo, M. B. Hursthouse, B. Hussain and L. M. Smith,

- Polyhedron*, **1988**, 14, 1289; j) H. Krause, K. Sille, H.-D. Hausen and J. Weidlein, *J. Organomet. Chem.*, **1982**, 235, 253;
74. A. R. Barron, *J. Chem. Soc., Dalton. Trans.*, **1988**, 3047
 75. S. Muthaiah, D. C. H. Do, R. Ganguly and D. Vidović, *Organometallic*, **2013**, 32, 6718
 76. K. Arentsen, S. Caddick and F. G. N. Cloke, *Tetrahedron*, **2005**, 61, 9710
 77. a) G. Gurau, H. Rodríguez, S. P. Kelly, P. Janiczek, R. S. Kalb and R. D. Rogers, *Angew. Chem. Int. Ed.*, **2011**, 50, 12024; b) H. Rodríguez, G. Gurau, J. D. Holbrey and R. D. Rogers, *Chem. Commun.*, **2011**, 47, 3222
 78. a) H. A. Duong, T. N. Tekavec, A. M. Arif, and J. Louie, *Chem. Commun.*, **2004**, 112; b) B. R. V. Ausdall, J. L. Glass, K. M. Wiggins, A. M. Aarif and J. Louie, *J. Org. Chem.*, **2009**, 74, 7935
 79. a) L. Delaude, *Eur. J. Inorg. Chem.*, **2009**, 1681; b) N. Kuhn, M. Steimann, G. Weyers and G. Henkel, *Z. Naturforsch.*, **1999**, 54b, 434
 80. L. M. M.-Prieto, C. Urbaneja, P. Palma, J. Cámpora, K. Philippot and B. Chaudret, *Chem. Commun.*, **2015**, 51, 4647
 81. A. V. Zhukhovitskiy, J. Geng and J. A. Johnson, *Chem. Eur. J.*, **2015**, 21, 5685
 82. a) D. Zhang and G. Zi, *Chem. Soc. Rev.*, **2015**, 44, 1898; b) S. Bellemin-Laponnaz and S. Dagorne, *Chem. Rev.*, **2014**, 114, 8747; c) S. J. Hock, L. Schaper, W. A. Hermann and F. E. Kühn, *Chem. Soc. Rev.*, **2013**, 42, 5073; d) V. P. Boyarskiy, K. V. Luzyanin and V. Y. Kukushkin, *Coord. Chem. Rev.*, **2012**, 256, 2029; e) H. D. Velazquez and F. Verpoort, *Chem. Soc. Rev.*, **2012**, 41, 7032.
 83. C. Fliedel, G. Schnee, T. Avilés and S. Dagorne, *Coord. Chem. Rev.*, **2014**, 275, 63
 84. M. Wu, A. M. Gill, Y. Lu, L. Falivene, Y. Li, R. Ganguly, L. Cavallo and F. García, *Dalton Trans.*, **2015**, 44, 15166
 85. Rohm and Hass Electronic Materials LLC, Synthesis of trimethylgallium, U.S. Patent 2006/47132 A1, **2006**
 86. I. Pérez, J. P. Sestelo and L. A. Sarandeses, *J. Am. Chem. Soc.*, **2001**, 123, 4155
 87. G. Davidson in *Characteristic Vibration of Compounds of Main Group Elements*, (Eds: G. Davidson), Royal Society of Chemistry, UK, **2001**, vol. 24, pp. 217
 88. S. Aldridge and A. J. Downs in *The Group 13 Metals, Aluminium, Gallium, Indium and Thallium: Chemical Patterns and Peculiarities*, (Eds: S. Aldridge, A. J. Downs), Wiley, UK, **2011**, vol 3.
 89. H. Jacobsen, A. Correa, A. Poater, C. Costabile and L. Cavallo, *Coord. Chem. Rev.*, **2009**, 253, 687
 90. L. Falivene, L. Caporaso, L. Cavallo and H. Jacobsen, *Dalton Trans.*, **2013**, 42, 7281

91. A. J. Arduengo, D. A. Dixon, K. Kumashiro, C. Lee, W. P. Power and K. W. Zilm, *J. Am. Chem. Soc.*, **1994**, *116*, 6361
92. P. S. Bagus, K. Hermann and C. W. Bauschlicher Jr., *J. Chem. Phys.*, **1984**, *80*, 4378; b) P. S. Bagus and F. Illas, *J. Chem. Phys.*, **1992**, *96*, 8962
93. M. E. Günay, N. Özdemir, M. Ulusoy, M. Uçak, M. Dinçer and B. Cetinkaya, *J. Organomet. Chem.*, **2009**, *694*, 2179
94. M. K. Denk, J. M. Rodezno, S. Gupta and A. J. Lough, *J. Organomet. Chem.*, **2001**, *617-618*, 242
95. N. R. Rightmire and T. P. Hanusa, *Dalton. Trans.*, **2016**, *45*, 2352
96. S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed and D. C. Waddell, *Chem. Soc. Rev.* **2012**, *41*, 413.
97. S. L. James, and T. Friščić, *Chem. Soc. Rev.* **2013**, *42*, 7484
98. M. A. P. Martins, C. P. Frizzo, D. N. Moreira, L. Buriol and P. Machado, *Chem. Rev.* **2009**, *109*, 4140.
99. A. L. Garay, A. Pichon and S. L. James, *Chem. Soc. Rev.* **2007**, *36*, 846.
100. B. Ranu and A. Stolle in *Ball Milling Towards Green Synthesis: Application, Projects, Challenges*, The Royal Society of Chemistry, UK, **2015**.
101. G. A. Bowmaker, N. Chaichit, C. Pakawatchai, B. W. Skelton and A. H. White, *Dalton. Trans.*, **2008**, 2926.
102. E. Boldyreva, *Chem. Soc. Rev.* **2013**, *42*, 7719.
103. D. W. Peters and R. G. Blair, *Faraday Discuss.*, **2014**, *170*, 83.
104. N. R. Rightmire, T. P. Hanusa and A. L. Rheingold, *Organometallics*, **2014**, *33*, 5952.
105. J. Wang, R. Ganguly, L. Yongxin, J. Díaz, H. S. Soo and F. García, *Dalton Trans.*, **2016**, *45*, 7941.
106. N. Kuhn, J. Fahl, R. Fawzi, C. M-Mößmer and M. Steimann, *Naturforsch. B.* **1998**, *53*, 720
107. M. L. Cole, C. Jones and P. C. Junk, *New. J. Chem.*, **2002**, *262*, 1296
108. P. L. Arnold, M. Rodden, K. M. Davis, A. C. Scarisbrick, A. J. Blake and C. Wilson, *Chem. Commun.*, **2004**, 1612
109. W. L. F. Armarego and C. L. L. Chai in *Purification of Laboratory Chemicals*, 5th Ed, , Elsevier (Singapore) Pte Ltd., **2007**.
110. SMART version 5.628, Bruker AXS Inc., Madison, WI, USA, **2001**.
111. Sheldrick, G. M.; SADABS V2014/4 (Bruker AXS Inc.), University of Göttingen, Göttingen, Germany, **2014**.
112. SHELXTL-2014/6 (Sheldrick, 2014); Bruker AXS Inc., Madison, WI, USA, **2014**.
113. L. Hintermann, *Belstein Journal Org. Chem.*, **2007**, *3*, 1.

Appendices

Appendix 1: % V_{Bur} and topographic steric maps

% V_{Bur} and topographic steric map for selected NHC Al alkyl complexes

Table A.1. % V_{Bur} and topographic steric map for selected Al complexes. The Al- $\text{C}_{\text{carbene}}$ bond lengths are the experimental values obtained by X-ray single crystal diffraction studies.

Entries	Complexes	Al- $\text{C}_{\text{carbene}}$ [Å]	% V_{Bur}^a	Topographic steric map
1	IMes•AlMe ₃ (122)	2.098(2)	31.7
2	SIMes•AlMe ₃ (123)	2.112(6)	32.0
3	Dipp•AlMe ₃ (124)	2.103(3)	33.1
4	SIPr•AlMe ₃ (125)	2.127(2)	36.1
5	liPr•AlMe ₃ (9)	2.124(6)	25.5

6 $\text{ItBu}\cdot\text{AlMe}_3$ (**18**) 2.162(2) 34.3

7 $\text{IMes}\cdot\text{AlMe}_3$ (**15**) 2.097(2) 31.8

8 $\text{IMes}\cdot\text{Al}(\text{C}_6\text{F}_5)_3$ (**29**) 2.061(3) 31.2

9 $\text{IMes}\cdot\text{Al}(\text{C}\equiv\text{CtBu})_3$
(**26**) 2.051(2) 25.3

10 $\text{IPr}\cdot\text{Al}((\text{CH}_2)_3\text{CH}_3)_3$
(**27**) 2.118(2) 32.6

% V_{Bur} calculations and topographic steric map parameters: All calculations were performed using crystallographic data (CIF). 3.50 Å was selected as the value for the sphere radius; Al- $\text{C}_{\text{carbene}}$ bond distances (X-ray crystal structure) were chosen for the metal-ligand bond; mesh spacing for numerical integration was scaled to 0.05; hydrogen atoms were omitted for the calculations; and bondi radii was scaled by 1.17.

Table A.2: % V_{bur} and topographic steric map for selected Al complexes. The Al- $\text{C}_{\text{carbene}}$ bond length is set at 2.0 Å.

Entries	Complexes	% V_{bur}^a	Topographic steric map
1	IMes•AlMe ₃ (122)	33.7
2	SIMes•AlMe ₃ (123)	34.1
3	Dipp•AlMe ₃ (124)	35.0
4	SIPr•AlMe ₃ (125)	38.5
5	liPr•AlMe ₃ (9)	27.2
6	ItBu•AlMe ₃ (18)	36.9

7 $\text{IMes}\cdot\text{AlMe}_3$ (**15**) 33.6

8 $\text{IMes}\cdot\text{Al}(\text{C}_6\text{F}_5)_3$ (**29**) 32.7

9 $\text{IMes}\cdot\text{Al}(\text{C}\equiv\text{CtBu})_3$ (**26**) 25.9

10 $\text{IPr}\cdot\text{Al}((\text{CH}_2)_3\text{CH}_3)_3$ (**27**) 34.9

% V_{Bur} calculations and topographic steric map parameters: All calculations were performed using crystallographic data (CIF). 3.50 Å was selected as the value for the sphere radius; distance of 2.00 Å was chosen for the metal-ligand bond; mesh spacing for numerical integration was scaled to 0.05; hydrogen atoms were omitted for the calculations; and bond radii was scaled by 1.17.

% V_{Bur} and topographic steric map for selected NHC Ga/In alkyl complexes

Table A.3 % V_{Bur} and topographic steric map for selected Ga/In complexes. The M- $\text{C}_{\text{carbene}}$ bond lengths is set at 2.0 Å.

Entries	Complexes	% V_{Bur}^a	Topographic steric map
1	IMes•GaMe ₃ (145)	32.2
2	SIMes•GaMe ₃ (146)	33.2
3	IPr•GaMe ₃ (147)	33.4
4	SIPr•GaMe ₃ (148)	34.7
5	IMes•InMe ₃ (149)	33.1

6 SiMes•InMe₃ (**150**) 34.3

7 IPr•InMe₃ (**151**) 34.6

8 SiIPr•InMe₃ (**152**) 35.6

9 IMes•AlMe₃ (**122**) 32.7

10 SiMes•AlMe₃ (**123**) 33.8

11 IPr•AlMe₃ (**124**) 34.6

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SIPr•AlMe₃ (125)

35.6

% V_{Bur} calculations and topographic steric map parameters: All calculations were performed using crystallographic data (CIF). 3.50 Å was selected as the value for the sphere radius; distance of 2.00 Å was chosen for the metal-ligand bond; mesh spacing for numerical integration was scaled to 0.05; hydrogen atoms were omitted for the calculations; and bond radii was scaled by 1.17.

Appendix 2: Solid State Structure for New Compounds

Appendix 2:

IMes $\rightarrow$ AlMe₃ (122)

SIMes $\rightarrow$ AlMe₃ (123)

IPr $\rightarrow$ AlMe₃ (124)

SIPr→AlMe₃ (125)

1,3-Bis(2,6-diisopropylphenyl)-2-methylimidazolium formate (126)

1,3-Bis(2,6-diisopropylphenyl)-imidazolinium carboxylates (132)

IMes imidazolium-2-amidinate (Dipp) (133)

SIMes imidazolium-2-amidinate (Dipp) (134)

IMes→GaMe₃ (145)

SIMes→**GaMe₃** (146)

IPr→**GaMe₃** (147)

SIPr→**GaMe₃** (148)

IMes→**InMe₃** (149)

SiMes $\rightarrow$ InMe $_3$ (150)

IPr $\rightarrow$ InMe $_3$ (151)

SIPr $\rightarrow$ InMe $_3$ (152)

Trimethylindium By-product (153)

IMes→GaCl₃ (161)

IMes→InCl₃ (162)

3-ethyl-1-(2-hydroxy-2-methylpropyl)-1H-imidazol-3-ium iodide (163)

3-ethyl-1-(2-hydroxy-2-phenylethyl)-1H-imidazol-3-ium iodide (164)

Appendix 3: Structures of Labelled Compounds (1-163)

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