# JULIUS-MAXIMILIANS-UNIVERSITÄT WÜRZBURG

# NHC-STABILIZED ALANES AND GALLANES

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# List of Publications

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| Publication | Position |
|---|---|
| A. Hock, H. Schneider, M. J. Krahfuß, U. Radius, *Hydride Amide and Hydride Phenolate Complexes of NHC Coordinated Aluminum*, *Zeitschrift für Allgemeine und Anorganische Chemie*, **2018**, *21*, 1243-1251. | Chapter 2 |
| A. Hock, L. Werner, C. Luz, U. Radius, *N-Heterocyclic Carbene and Cyclic (Alkyl)(Amino)Carbene Adducts of Gallium Hydrides, Gallium Chlorides and Gallium Hydrochlorides*, *Dalton Transaction*, **2020**, Accepted Manuscript, DOI: 10.1039/D0DT02070B. | Chapter 3 |
| A. Hock, L. Werner, M. Riethmann, U. Radius, *Bis-NHC Aluminium and Gallium dihydride cations [(NHC)$_2$EH$_2$]$^+$ (E = Al, Ga)*, *European Journal of Inorganic Chemistry*, **2020**, Accepted Manuscript, DOI: 10.1002/eijc.202000720. | Chapter 4 |

Further publications:

H. Schneider, A. Hock, R. Bertermann, U. Radius, *Reactivity of NHC Alane Adducts towards N-Heterocyclic Carbenes and Cyclic (Alkyl)(amino) carbenes: Ring Expansion, Ring Opening, and Al−H Bond Activation*, *Chemistry – A European Journal,* **2017**, *50*, 12387-12398.

H. Schneider, A. Hock, A. D. Jaeger, D. Lentz, U. Radius, *NHC· Alane Adducts as Hydride Sources in the Hydrodefluorination of Fluoroaromatics and Fluoroolefins*, *European Journal of Inorganic Chemistry*, **2018**, *36*, 4031-4043.

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*CHAPTER I*


*N-HETEROCYCLIC CARBENES AS LIGANDS IN ALUMINIUM
AND GALLIUM CHEMISTRY*

# 1 *N*-HETEROCYCLIC CARBENES AS LIGANDS IN ALUMINIUM AND GALLIUM CHEMISTRY

*Lewis* base stabilized alanes and gallanes show high potential in material science and inorganic as well as reductants in organic synthesis.[1-4] Aluminium hydrides are of interest due to their ability as hydrogen storage materials[5-8], use as recuctants in organic synthesis and as volatile precursors in chemical vapour deposition technologies.[9-11] Amine and phosphine stabilized gallium hydrides are suitable precursor molecules for group 13/15 semiconductors and emitting materials.[12-17] The chemistry of amine and phosphine stabilized alane- and a variety of homo and hetereoleptic dialane and gallane adducts are reported in literature in detail.[18-23] Since the discovery of the first stable carbene by Bertrand *et al.* (1988)[24] and the isolation of the first classical NHC by Arduengo *et al.* (1991)[25] their input as ligands in transition metal chemistry and catalysis raised furious.[26-28] Over the last years the use of NHCs in main group element chemistry was on the rise as well. NHCs proved to be effective ligands for the stabilization of reactive low valent main group element compounds and enabled a variety of structurally new group 13 species. The origin of this chemistry goes back a long time but in the last five years the chemistry of *N*-heterocyclic carbene (NHC) stabilized aluminium and gallium hydrides has been on the rise. Therefore, an overview of the most important advances in chemistry of NHC stabilized heavier group 13 elements (E = Al, Ga) over the last years is presented.

## 1.1 NHC stabilized aluminium complexes

### 1.1.1 NHC stabilized aluminium(III) hydrides

Since the synthesis of the first NHC stabilized alane adduct (Mes$_2$Im)·AlH$_3$ **I-1** by Arduengo *et al.* in a ligand exchange reaction of the trimethylamine alane adduct (NMe$_3$)·AlH$_3$ with the corresponding NHC a variety of further adducts has been reported.[29] NHC stabilized alanes were synthesized mainly by base substitution starting from (NMe$_3$)·AlH$_3$ or by salt elimination of lithium hydride in the reaction of either the free NHC or the corresponding imidazolium salt with lithium aluminium hydride (see Scheme I-1).[23, 30-36]
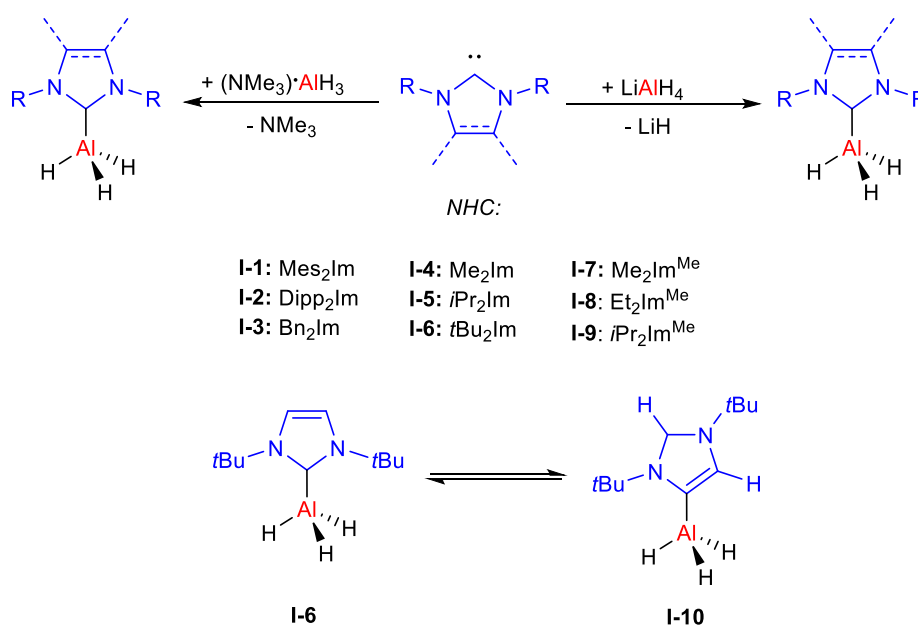


*Scheme I.1: Synthesis of NHC stabilized aluminium(III) hydrides.*

In the $^1$H and $^{13}$C{$^1$H} NMR spectra the resonances of the aluminium bound hydrides respectively carbene carbon atoms are generally broadened due the quadrupole moment of the $^{27}$Al nucleus. In the $^1$H NMR spectra the Al-H hydrides are detected in a range between 3.5 – 4.7 ppm. In the $^{13}$C{$^1$H} NMR spectra the resonances of the carbene carbon atoms arise at 168.7 – 178.2 ppm, high field shifted compared to the free NHCs. The $^{27}$Al NMR signals are also broadened due the quadrupole moment of

the [27]Al nucleus and can often not be observed. However, the resonance can be detected in many cases in the solid-state $^{27}Al\{^1H\}$ NMR of such adducts. We recently reported the synthesis of various NHC stabilized parent alanes and demonstrated that the NMR spectra in solution and in the solid state are consistent. The [27]Al signals can be detected in a range of 103 – 108 ppm in solution and in the solid state, which is a characteristic range for tetrahedrally coordinated aluminium. In the IR spectra of these adducts the characteristic Al-H stretching vibrations appear in the range between 1640 and 1800 cm$^{-1}$. X-ray crystal structures on these adducts reveal Al-$C_{NHC}$ bond lengths in a narrow range between 2.00 and 2.15 Å, dependent on the steric demand and σ-donation properties of the NHC used.[23, 30-36]

Scheer *et al.* observed for the adduct **I-6** stabilized by the sterically demanding *t*Bu$_2$Im ligand (= 1,3-di*tert*butylimidazolin-2-ylidene) the isomerisation between the *normal* and *abnormal* NHC coordination mode of the NHC in the alane adduct (see Scheme I.1), in dependence on the used solvent. Surprisingly, the isomerisation occurs slowly in the solid state as well.[35] The Al-$C_{aNHC}$ bond length of 2.026 Å is expected to be shorter compared to the Al-$C_{NHC}$ bond length of 2.0838 Å due to less steric hindrance and stronger donation properties of the *abnormal* NHC in (*a*$^t$Bu$_2$Im)·AlH$_3$ **I-10** ("*a*" denotes "abnormal" coordination mode) . In contrast to amine and phosphine stabilized aluminium hydrides the NHC adducts are thermally stable in solution up to the boiling point of even toluene and in the solid state up to 240 °C until decomposition occurs. However, they are still both air and moisture sensitive. Winter *et al.* reported recently that the adducts **I-8** and **I-9** can be sublimed at 120 °C and 50 mTorr in 40 – 58 % and they discussed this class of compounds for applications as ALD precursors.[36] Kickelbick and coworkers recently investigated the influence of reaction parameters on nanoparticle size *via* catalytic decomposition of amine, phosphine and carbene alane adducts.[37] Aluminium nanoparticles were prepared from catalytic decomposition of (Mes$_2$Im)·AlH$_3$ **I-1**. Compared to the amine and phosphine aluminium hydride adducts the carbene adduct showed the slowest decomposition and only yielded severely sintered and agglomerated particles. However, the best results of particle sizes and morphologies were observed for the decomposition of sterically less demanding amine stabilized alanes.[37]

Inoue *et al.* demonstrated the catalytic activity of NHC stabilized alanes in dehydrocoupling reactions of amine-boranes.[38] Furthermore our group recently reported the use of the alane adducts as hydride source in hydrodefluorination reactions of fluoroaromatics and fluoroolefins in some detail.[39] Very recently Stasch and coworkers observed the formation of Robinson's NHC stabilized diborane(4) by the reaction of (Dipp$_2$Im)·AlH$_3$ **I-2** with free Dipp$_2$Im and commercially available B$_2$pin$_2$ in a halide-free approach.[40]

Scheer *et al.* reported the synthesis of the first parent NHC stabilized phosphanylalane (Dipp$_2$Im)·AlH$_2$PH$_2$ **I-11** from the reaction of (Dipp$_2$Im)·AlH$_2$X (X = Cl, I) with LiPH$_2$·DME.[41] In addition, the phosphido-substituted adduct (Dipp$_2$Im)·AlH$_2$PCy$_2$ **I-12** was synthesized as well in a salt elimination reaction starting from (Dipp$_2$Im)·AlH$_2$X (X = Cl, I) and Li[PCy$_2$]. These compounds are under investigations for the use as novel precursor for CVD-processes to obtain group 13/15 materials.

## 1.1.2 NHC stabilized aluminium(III) halides

Roesky *et al.* reported the first synthesis of the NHC aluminium(III) chloride adduct (Me$_2$Im$^{Me}$)·AlCl$_3$ **I-13** by the simple reaction of the free NHC with aluminium(III) chloride AlCl$_3$ in toluene.[42] Further NHC stabilized aluminium(III) chloride adducts were isolated in the last years using a similar synthetic route (see Scheme I.2). The analogue aluminium(III) iodide adducts (NHC)·AlI$_3$ (NHC = Dipp$_2$Im **I-16**, Mes$_2$Im **I-17**) are also accessible *via* the direct reaction of the free NHCs with aluminium(III) iodide AlI$_3$ (see Scheme I.2).[43] The aluminium iodide adducts are limited to sterically demanding NHCs and surprisingly no adducts of aluminium(III) bromide AlBr$_3$ are reported in the literature so far. For the reaction of AlBr$_3$ and AlI$_3$ a lower stability of the adducts was suggested as the formation of the corresponding imidazolium salts or ionic adducts as side products due to the good leaving groups bromide and iodide are significant side product channel.[44, 45]
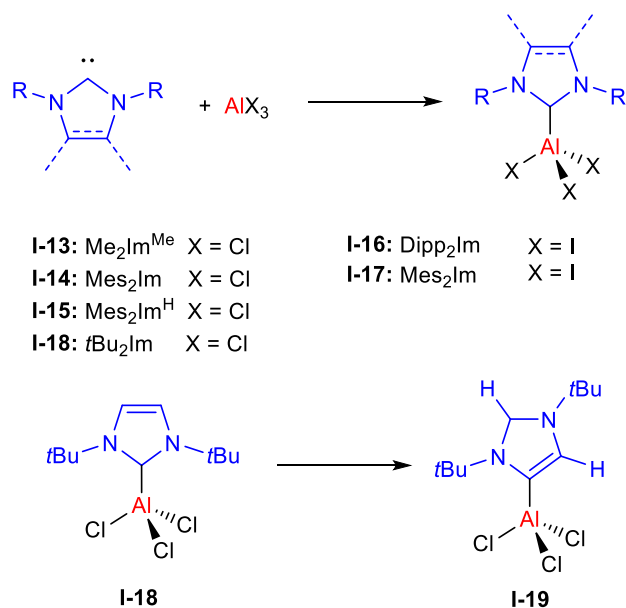
*Scheme I.2: Synthesis of NHC stabilized aluminium(III) halides.*

The adducts **I-13 – I-15** show high thermal stability and less air and moisture sensitivity compared to the parent alane adducts with exception of **I-18**, which undergoes a *normal*-to-*abnormal* NHC rearrangement to the corresponding (a$t$Bu$_2$Im)·AlCl$_3$ **I-19** complex.[46] The Al-C$_{NHC}$ bond lengths are in the characteristic range of 2.009 – 2.035 Å. The aluminium chloride adducts (Mes$_2$Im)·AlCl$_3$ **I-14** and (Mes$_2$Im$^H$)·AlCl$_3$ **I-15** were used as precatalysts in polyurethane synthesis.[47]

Furthermore, a number of carbene stabilized aluminium hydridohalides are reported in the literature.[30, 48, 49] These molecules are interesting precursor for substitution at the aluminium center and enable a diversity of functionalisation. The selective exchange of the hydrides by halides were reached by different synthetic routes so far. Cole and coworkers synthesized the mono- and dichloride alane adducts in a simple ligand exchange reaction of the trimethylamine or quinuclidine complexes with the free NHC (see Scheme I.3).[50, 51] On the similar route the NHC stabilized dibromide aluminium(III) hydride (Mes$_2$Im)·AlHBr$_2$ **I-22** were synthesized (see Scheme I.3). The synthesized compound (Mes$_2$Im)·AlHBr$_2$ **I-22** was achieved by the unusual reaction of the backbone dibromo-substituted NHC Mes$_2$Im$^{Br}$ with the quinuclidine alane adduct in a ligand exchange reaction.[50] Recently, Jones and Stasch *et al.* reported the synthesis of NHC supported mono- and diiodoalanes. The monoiodo adducts were synthesized by the stochiometric reaction of two equivalents of (NHC)·AlH$_3$ with one equivalent of

(NHC)·AlI$_3$ in a ligand scrambling reaction (see Scheme I.3).[45] The diiodoalanes are instead easily accessible by the reaction of the parent alane adducts with an excess of methyl iodide (see Scheme I.3).[45]



I-20: X= H   Y = Cl
I-21: X= Cl  Y = Cl
I-22: X= Br  Y = Br

I-23: Mes$_2$Im
I-24: Dipp$_2$Im

I-25: Mes$_2$Im
I-26: Dipp$_2$Im
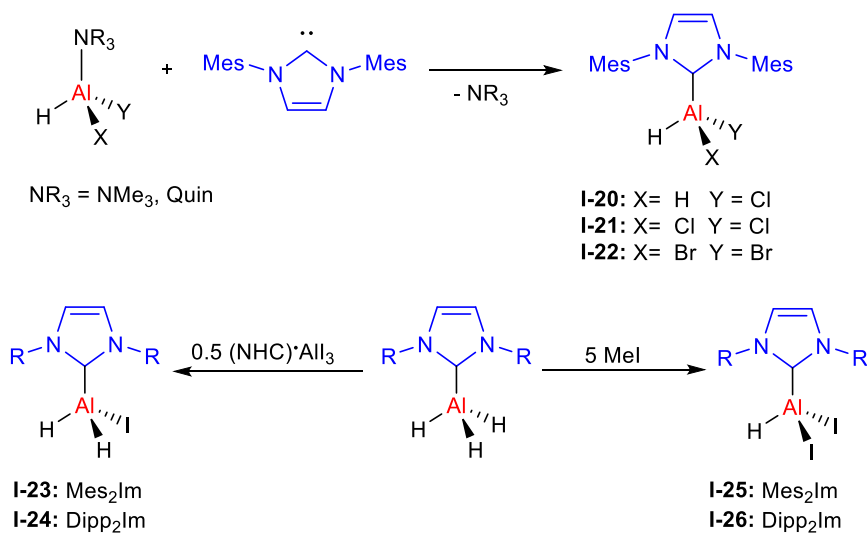
*Scheme I.3: Synthesis of NHC stabilized mixed hydrido halide alanes.*

The compounds **I-20 – I-22** were used as reagents for the hydroalumination of carbonyl and epoxide substrates, whereas the compounds **I-23 – I-26** are precursor for cationic alanes.[45, 50] Moreover, Tokitoh *et al.* reported the synthesis of NHC stabilized phosphanylalumane (Me$_2$Im$^{Me}$)·AlBr(Bbp)(PHMes) (Bbp = 2,6-di(bis(trimethylsilyl)methyl)phenyl) **I-27** bearing P-H and Al-Br moieties. The phosphanylalumane is inert towards reduction due to the decrease of the P-H bond acidity by the strong σ-donating NHC ligand. DFT calculations confirmed these results.[52, 53]

## 1.1.3 NHC stabilized aluminium(III) alkyls & aryls

Robinson *et al.* reported the first structurally characterized NHC stabilized trialkyl aluminium complex ($i$Pr$_2$Im$^{Me}$)·AlMe$_3$ **I-28** by the stochiometric reaction of AlMe$_3$ with the free NHC (see Scheme I.4).[54] In the last years a variety of other NHC stabilized trialkyl- and triaryl aluminium(III) adducts were reported (see Scheme I.4).[46, 55-58] The Al-C$_{NHC}$ bond length of the compounds **I-28 – I-37** are in the range of 2.00 to 2.20 Å and typically depend on the steric and electronic behaviour of the alkyl and aryl substituents at the aluminium center. The bond length increases with higher sterical demand and decreases with $\sigma$-donation capabilities of the substituent. The Al-C$_R$ bond lengths to the alkyl substituent are slightly shorter and lie in a range between 1.95 – 2.10 Å.

Kemnitz *et al.* presented recently the fluorination of (Mes$_2$Im$^H$)·AlMe$_3$ **I-30** with Me$_3$SnF in detail.[58] Chen *et al.* reported the activity of ($t$Bu$_2$Im)Al·(C$_6$F$_5$)$_3$ **I-35** (Mes$_2$Im)Al·(C$_6$F$_5$)$_3$ **I-36** in fast polymerisation of methyl methacrylate (MMA) and naturally renewable methylene butyrolactones (MBL) into high-molecular-weight polymers.[55] The combination of the sterically demanding NHCs $t$Bu$_2$Im and Mes$_2$Im with the *Lewis* acidic Al(C$_6$F$_5$)$_3$ shows frustrated *Lewis* pair (FLP) character and enables thus the catalytic activity in the polymerisation reaction. Furthermore (Dipp$_2$Im$^H$)·AlEt$_3$ **I-34** was used to catalyse ring-opening alkylation of *meso*-epoxides.[57] The combination of the sterical demand of the NHC and the substituent at the aluminium center determines the stability and reactivity of the adducts formed. Dagorne and coworkers observed for ($t$Bu$_2$Im)·AlR$_3$ (R= Me **I-30**, $i$Bu **I-32**) the isomerisation to the *abnormal* NHC complexes ($a^t$Bu$_2$Im)·AlR$_3$ (R= Me **I-38**, $i$Bu **I-39**) at ambient temperature (see Scheme I.4).[46, 56] The NHC stabilized aluminim(III) alkyls were further used in the activation of H$_2$ and in lactide ring-opening polymerisation catalysis.[33, 59, 60]
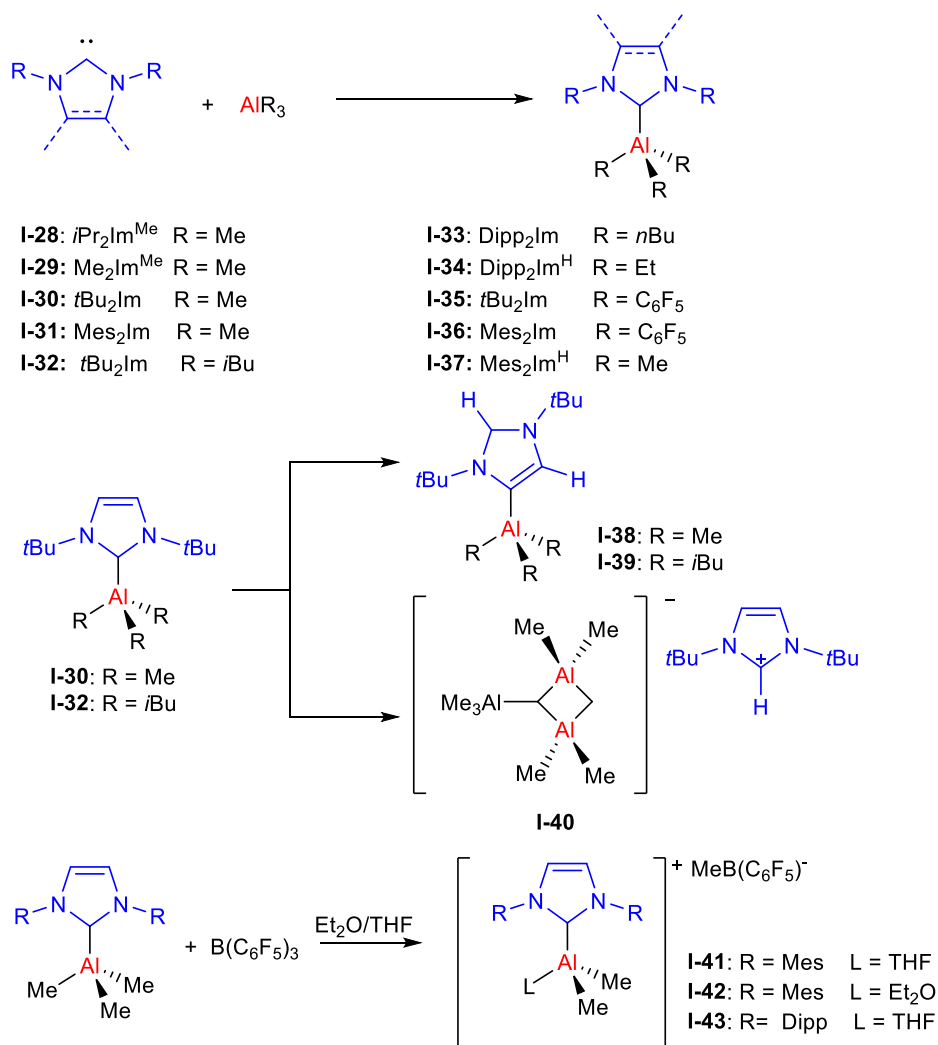
*Scheme I.4: Synthesis of NHC stabilized alky- and aryl aluminium(III) adducts.*

If an excess of $AlMe_3$ was added to $(tBu_2Im) \cdot AlMe_3$ **I-30** the anionic compound **I-40** $[Me_3Al(\mu^3\text{-}CH_2)(AlMe_2)_2(\mu^2\text{-}CH_3)]^-$, stabilized by the protonated imidazolium salt $[tBu_2Im\text{-}H]^+$, was formed (see Scheme I.4).[56] The same group reported the synthesis of the cationic NHC stabilized aluminim(III) alkyls $[(NHC) \cdot AlMe_2 \cdot L][MeB(C_6F_5)_3]$ (NHC = $Mes_2Im$, $Dipp_2Im$; L = $Et_2O$, THF).[61] The reaction of $(NHC) \cdot AlMe_3$ with $B(C_6F_5)_3$ in an ethereal solution ($Et_2O$, THF) led to the formation of the cationic complexes $[(Mes_2Im) \cdot AlMe_2 \cdot THF][MeB(C_6F_5)_3]$ **I-41**, $[(Mes_2Im) \cdot AlMe_2 \cdot OEt_2][MeB(C_6F_5)_3]$ **I-42** and $[(Dipp_2Im) \cdot AlMe_2 \cdot THF][MeB(C_6F_5)_3]$ **I-43** (see Scheme I.4). The cationic aluminium(III) alkyls were used in the ring-opening polymerization of lactide.[61] Roesky *et al.* reported the synthesis of a series of *Lewis*-base stabilized aluminium trialkynyl adducts.[62] The reaction of $AlCl_3$ with the free NHC $Me_2Im^{Me}$ and three equivalents of lithium acetylide

afforded the adduct (Me$_2$Im$^{Me}$)·Al(CC$t$Bu)$_3$ **I-44**. The Al-C$_{NHC}$ bond length of 2.051(2) Å observed in this complex is slightly shorter compared to those of the trialkyl and triaryl adducts.

Moreover, few examples of NHC stabilized alkyl aluminium hydrides are reported. Cowley *et al.* recently reported the synthesis of (NHC)·AlHCp*$_2$ (NHC = $i$Pr$_2$Im$^{Me}$ **I-45**, Me$_2$Im$^{Me}$ **I-46**) (see Scheme I.5).[63] The signals of the Cp* methyl groups in the $^1$H NMR spectra remain one singlet, indicating rapid sigmatropic rearrangement of the Cp* substituent. The η$^1$-Cp* coordination was confirmed by X-ray diffraction of single crystals of **I-45** and **I-46**. The Al-C$_{Cp*}$ bond length with 2.0901(15) Å and 2.0857(16) Å (**I-45**) and 2.082(2) Å and 2.072(2) Å (**I-46**) are slightly shorter compared to the gallium analogue (Me$_2$Im$^{Me}$)·GaHCp*$_2$ (2.102(5) Å and 2.119(5) Å).[64] The Al-C$_{NHC}$ distances of 2.0571(15) Å (**I-45**) and 2.069(2) Å (**I-46**) are similar to those of the previous mentioned parent alane adducts. The same group has shown that the stabilisation by the strong σ-donating NHC ligand prevents the reductive elimination of Cp*H with formation of Cp*Al$^I$ **I-57** reported earlier by Fischer *et al.*.[63, 65] The Radius group reported the synthesis of carbene stabilized dialkyl aluminium hydrides (NHC)·AlH$i$Bu$_2$ (NHC = $i$Pr$_2$Im **I-47**, Dipp$_2$Im **I-48**) (see Scheme I.5),[66] where the sterically demanding *iso*-butyl substituents inhibit Al-H bond activation induced by cAAC$^{Me}$.



R = Cp*, $i$Bu

**I-45**: $i$Pr$_2$Im$^{Me}$
**I-46**: Me$_2$Im$^{Me}$

**I-47**: $i$Pr$_2$Im
**I-48**: Dipp$_2$Im
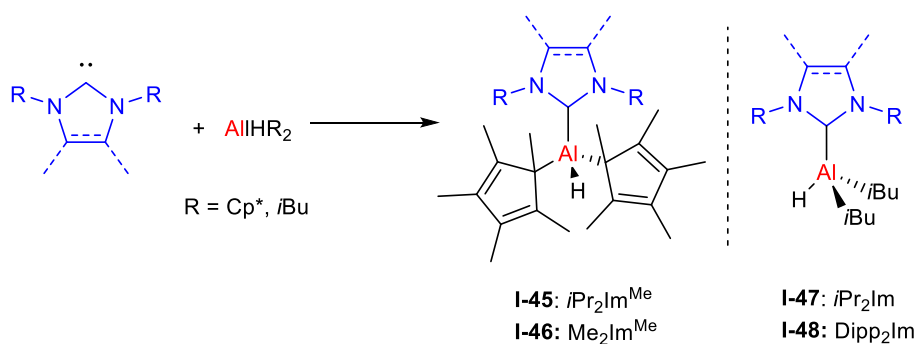
*Scheme I.5: Synthesis of NHC stabilized dialkyl- and aryl aluminium hydrides.*

Chiu *et al.* recently reported the synthesis of the NHC stabilized alkyl aluminium chlorides (Mes$_2$Im)·AlCl$_2$Cp* **I-49** and (Mes$_2$Im$^H$)·AlCl$_2$Cp* **I-50**.[67] The direct reaction of (AlCl$_2$Cp*)$_2$ with the corresponding NHC afforded the compounds **I-49** and **I-50** (see Scheme I.6). In the $^1$H NMR spectrum the methyl groups of Cp* were detected as a

sharp singlet at 1.53 ppm due to rapid sigmatropic rearrangement.[63] The triflate bridged dimer $(Cp^*AlOTf_2)_2$ **I-51** dissociated upon coordination of the NHCs $Mes_2Im$ and $Mes_2Im^H$ with formation of the Cp* aluminium triflate complexes $(NHC) \cdot AlCp^*OTf_2$ (NHC = $Mes_2Im$ **I-52**, $Mes_2Im^H$ **I-53**) (see Scheme I.6). The direct reaction of the compunds **I-49** and **I-50** with TMSOTf (TMSOTf = trimethylsilyl trifluoromethanesulfonate) did not lead to the formation of the Cp* aluminium triflate complexes $(NHC) \cdot AlCp^*OTf_2$. The Cp* ligand in these compounds adopts a $\eta^1$-Cp* coordination mode with $Al-C_{Cp^*}$ bond length of 1.9817(13) Å (**I-52**) and 1.976(3) Å (**I-53**) which are slightly shorter than the distance in **I-50** (2.012(4) Å). The $Al-C_{NHC}$ bond lengths of 2.0262(16) Å (**I-52**) and 2.062(3) Å (**I-53**) are also shorter compared to those observed for **I-50** (2.089(3) Å). The shorter bond lengths of **I-52** and **I-53** indicate a positive charge at the Al centers due to the weakly coordinating nature of the triflate anion. Additionally, the NHC stabilized Cp* aluminium triflate complexes were reacted with $MeNO_2$ and $CO_2$ leading insertion products into the Al-Cp*-bond with formation of $(Mes_2Im) \cdot Al(O_2NMeCp^*)(OTf)_2$ and $(Mes_2Im) \cdot Al(O_2CCp^*)(OTf)_2$.[67]
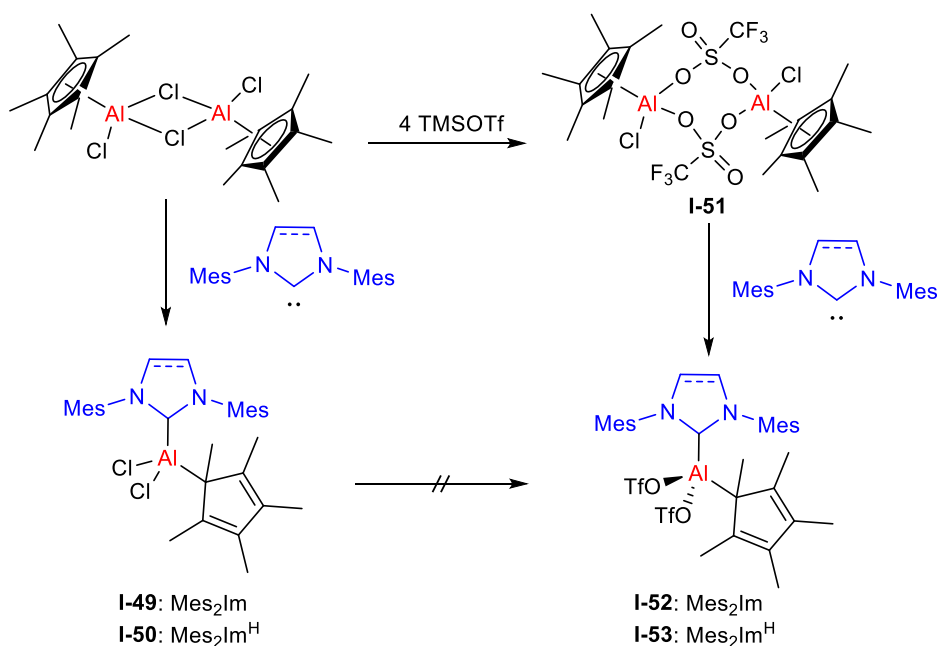


*Scheme I.6: Synthesis of NHC stabilized Cp* aluminium complexes.*

Braunschweig and coworkers reported the first *Lewis*-base mediated $Al^{II}$ to $Al^{I}$ and $Al^{III}$ disproportionation for the reaction of the dialane $(Cp^*AlBr)_2$ **I-54** with a series of *Lewis*-bases.[68] The reaction of the dialane **I-54** with $iPr_2Im$ or $cAAC^{Me}$, respectively lead to the formation of the NHC stabilized Cp* aluminium(III) bromides $(NHC)·AlCp^*Br_2$ (NHC = $iPr_2Im$ **I-55**, $cAAC^{Me}$ **I-56**) and $Cp^*Al(I)$ **I-57** in a disproportionation reaction (see Scheme I.7). In the $^1H$ NMR spectrum only one signal was observed for the Cp* moiety, indicating the mentioned hapticity change in solution rapid on the NMR timescale. The $Al-C_{Cp^*}$ distances of **I-55** (2.036(3) Å) and **I-56** (2.029(4) Å) compare well with those of the Cp* $Al^{III}$ chloride complex **I-50** (2.012(4) Å). The $Al-C_{NHC}$ bond lengths with 2.093(2) Å (**I-55**) and 2.047(4) Å (**I-56**) are similar as in **I-50** (2.089(3) Å).[67, 68]
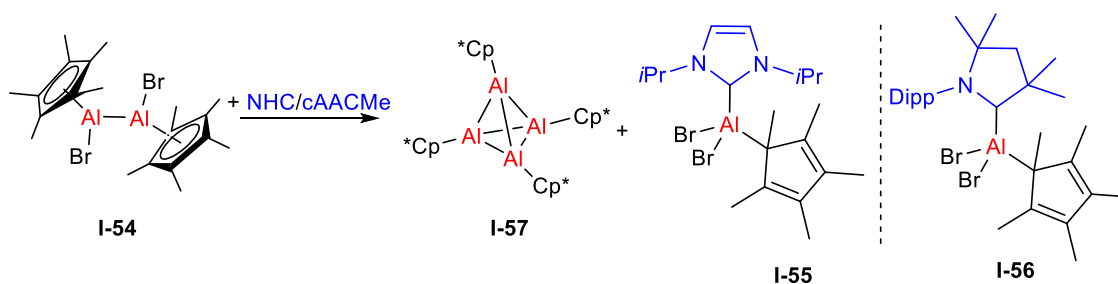


*Scheme I.7: Disproportionation of the dialane $(AlCp^*Br)_2$ I-54 induced by Lewis-bases.*

## 1.1.4 NHC stabilized cationic aluminium(III) hydrides

*Lewis* base stabilized cationic aluminium hydrides are rather scarce in the literature and cationic aluminium hydrides stabilized by NHCs are less common. Recently, Jones and Stasch *et al.* reported the synthesis of the monocationic aluminiumhydride $[(Dipp_2Im)·AlH_2(aDipp_2Im)]^+$ **I-58** stabilized by one *normal* and one *abnormal* coordinated NHC in $[(Dipp_2Im)·AlH_2(aDipp_2Im)]I$ **I-58**, which was obtained from the reaction of the iodoalane $(Dipp_2Im)·AlH_2I$ **I-24** with an additional equivalent of the corresponding NHC (see Scheme I.8).[45] An equilibrium in solution between the mono- and bis-NHC adduct, followed by *abnormal* coordination of one of the NHC ligand due to steric hindrance and subsequent iodine dissociation was suggested as the reaction path for the formation of these cationic aluminium hydrides. Precipitation of the insoluble cationic aluminium hydrides once formed in equilibrium in solution provided another driving force for the clean formation and isolation. The $Al-C_{aNHC}$ bond

length of 2.006(3) Å is shorter than the Al-C$_{NHC}$ bond length (2.048(3) Å), as expected. Interestingly for the reaction of (Mes$_2$Im)·AlH$_2$I **I-25** with an additional equivalent of the NHC no formation of a cationic species was observed.[45] The Radius group recently reported synthesis of a six-coordinated aluminium center [(*i*Pr$_2$Im)$_4$·AlH$_2$]$^+$ **I-59** as a side product of the reaction of lithium aluminium hydride with an excess of the small NHC *i*Pr$_2$Im (see Scheme I.8).
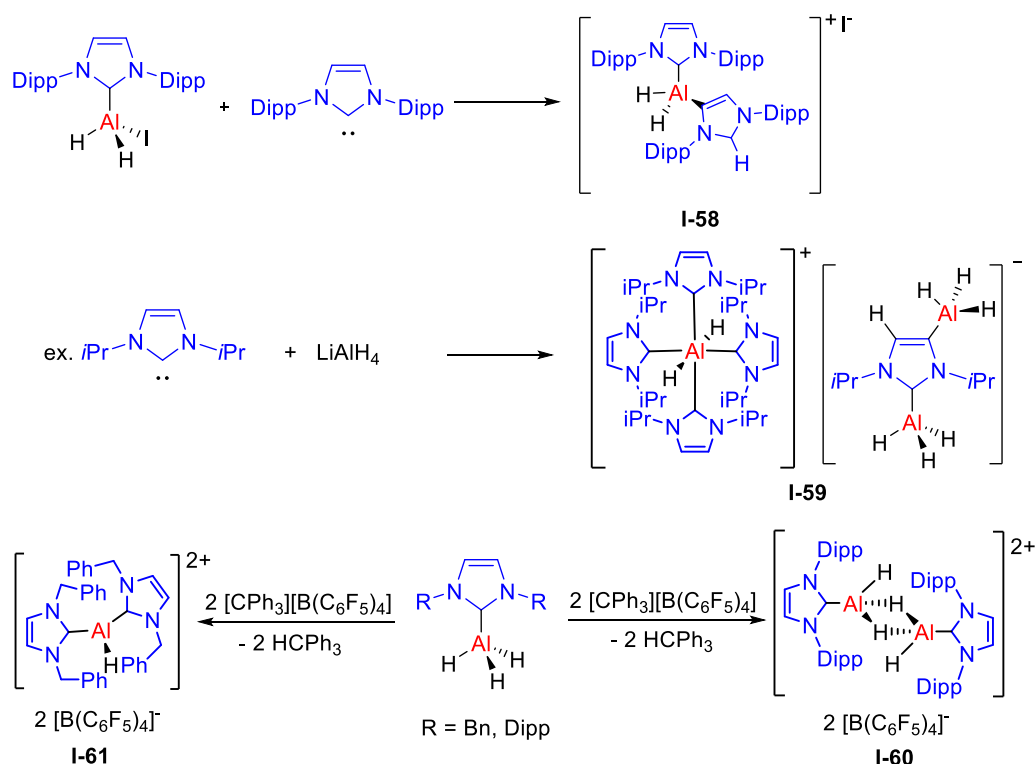


*Scheme I.8: Synthesis of NHC stabilized mono- and dicationic aluminium hydrides.*

Stephan *et al.* isolated both the monomeric and dimeric dicationic NHC stabilized aluminium hydrides [(Bn$_2$Im)$_2$·AlH][B(C$_6$F$_5$)$_4$]$_2$ **I-60** and [(Dipp$_2$Im)·AlH(μ-H)]$_2$[B(C$_6$F$_5$)$_4$]$_2$ **I-61**. In dependence on the steric demand of the NHC used the reaction of (NHC)·AlH$_3$ (NHC = Bn$_2$Im, Dipp$_2$Im) with [Ph$_3$C][B(C$_6$F$_5$)$_4$] as hydride acceptor leads to the formation of **I-60** and **I-61** (see Scheme I.8).[34] To get insight into the electronic structure of the unusual dicationic aluminium hydride **I-60**, DFT calculations and natural bond orbital (NBO) analysis were performed. The Al-base NBO has essentially pure 3p$_z$ character. The bonding NBO localized between the two carbon atoms of the

arene ring, which are closest to the Al-center, has $\pi$-symmetry as well and is oriented in a way that an overlap with the Al-base NBO occurs. This $\pi$-orbital interaction may promote the unexpected stability of the monomeric three-coordinate dicationic aluminium complex. The same group described a related Al-arene interaction for $(C_6H_{10})Al(C_6F_5)_3$ earlier.[69] The X-ray crystal structure confirms the calculations as one of the benzyl substituents of one of the $Bn_2Im$ ligands is oriented such that a C-C $\pi$-bond is located above the Al-center with Al-C distances of 3.124(5) Å and 2.572(4) Å, in a range enabling $\pi$-orbital interaction. The Al-Al distance in $[(Dipp_2Im)\cdot AlH(\mu-H)]_2[B(C_6F_5)_4]_2$ **I-61** (2.584(2) Å) is slightly shorter compared to an average Al-Al single bond (2.6375(8)- 2.675(1) Å) in Al(II) species.[73] The shorter Al-Al distance in **I-61** is consistent with the higher oxidation state and cationic charge at the aluminium atoms of **I-61** resulting in shorter Al-$H_{bridge}$ and thus Al-H bond lengths.[34]

## 1.1.5 NHC stabilized Dialuminium(II)hydrides

The stabilisation of main group element hydrides by *N*-heterocyclic carbenes paved the way for the synthesis of new low valent main group element complexes. Robinson and coworkers reported the synthesis of the first carbene stabilized neutral diborane $[(Dipp_2Im)\cdot BH_2]_2$ and diborene $[(Dipp_2Im)\cdot BH]_2$.[70] The reduction of $(Dipp_2Im)\cdot BBr_3$ lead to the formation of a mixture of the diborane and diborene. Braunschweig's group reported the synthesis of the carbene stabilized diborenes $[(Dep_2Im^H)BH]_2$ and $[(cAAC^{Me})BH]_2$ in a metal-free hydrogenation under mild conditions for the reaction of the corresponding highly reactive diborines with dihydrogen.[71, 72] However, subvalent NHC-stabilized aluminium compounds are rather scarce in the literature. Jones *et al.* first synthesized the NHC stabilized parent dialane $[(Dipp_2Im)AlH_2]_2$ **I-62** (see Scheme I.9).[73] The reaction of $(Dipp_2Im)\cdot AlH_3$ with the magnesium dimer $[Mg(Nacnac^{Mes})]_2$ afforded hydrogen atom transfer reduction with formation of the dialane **I-62** and the hydride bridged Mg(I) dimer $[(^{Mes}Nacnac)Mg(\mu-H)]_2$. The Al-Al bond length (2.6375 Å) is consistent with other known neutral compounds with Al-Al single bonds. The characteristic Al-H stretching bond vibrations were observed at 1682 cm$^{-1}$ and 1719 cm$^{-1}$ and compare well with literature known values.[73]
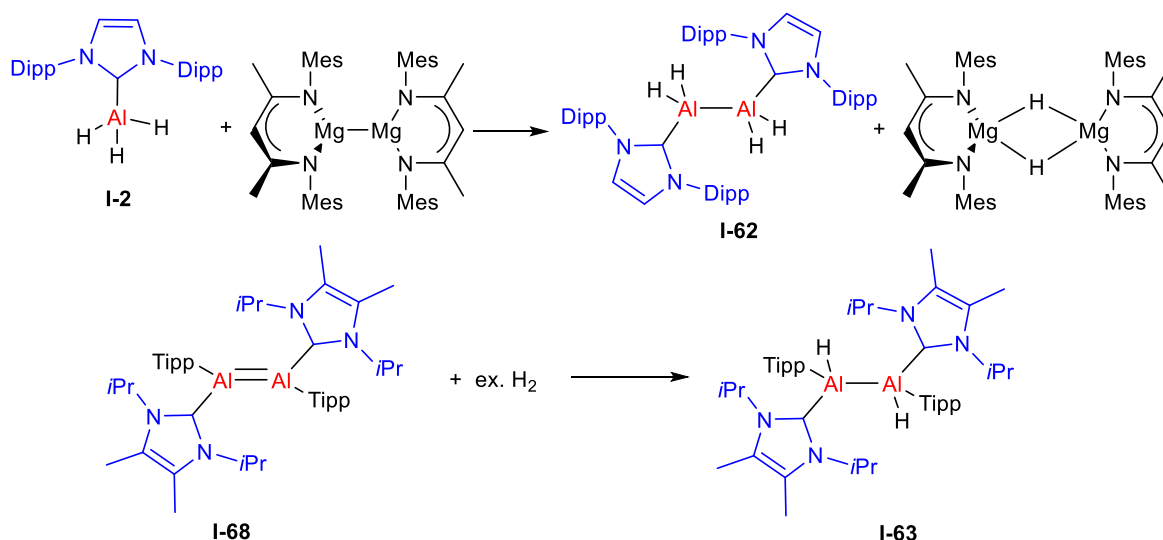
*Scheme I.9: Synthesis of NHC stabilized dialanes.*

Inoue *et al.* reported recently on synthesis and reactivity of neutral NHC stabilized dialumenes.[74] The reaction of the dialumene [(*i*Pr$_2$Im$^{Me}$)AlTipp]$_2$ **I-68** with elemental hydrogen led to the formation of the dialane [(*i*Pr$_2$Im$^{Me}$)AlHTipp]$_2$ **I-63** (see Scheme I.9). In the IR spectrum of **I-63** the characteristic Al-H stretching vibrations of the terminal hydrides were observed at 1593 cm$^{-1}$ and 1634 cm$^{-1}$ which compare well with other complexes containing Al-Al bonds.[73] Further DFT calculations on likely isomers of **I-63** including terminal hydrides, bridging hydrides and a combination of both confirm the formation of **I-63** as the thermodynamically most stable isomer of those considered. The calculated Al-H stretching frequencies for the terminal hydride substituents at 1634 cm$^{-1}$ and 1676 cm$^{-1}$ match well with the experimental data.[74]

## 1.1.6 NHC stabilized neutral Al=Al Multiple Bonds

Neutral multiple bonded aluminium compounds are highly reactive and undergo disproportionation to elemental aluminium and stable Al(III) species or side reactions with solvent molecules. First independent attempts of Power and Tokitoh *et al.* to isolate stable double bonded dialumene stabilized by bulky aryl substituents led to the formation of [2+4] cycloaddition products with benzene due to the reaction of the dialumene intermediates with the aromatic solvents (see Scheme I.10).[75, 76] The isolation of a stable dialumene failed until recently. Inoue *et al.* reported the synthesis

of the first neutral NHC stabilized dialumene [($i$Pr$_2$Im$^{Me}$)Al{Si(Me$^t$Bu$_2$)}]$_2$ **I-67**[77] from the reduction of the iodo- and bromoalane ($i$Pr$_2$Im$^{Me}$)·AlX$_2${Si(Me$^t$Bu$_2$)} (X = I **I-64**, Br **I-65**) adduct with three equivalents of KC$_8$ (see Scheme I.10). The same group expanded their work with the isolation of the aryl substituted dialumene [($i$Pr$_2$Im$^{Me}$)AlTipp]$_2$ **I-68**.[74] **I-68**, which is also accessible from the reduction of ($i$Pr$_2$Im$^{Me}$)·AlI$_2$Tipp **I-66** with KC$_8$ (see Scheme I.10).
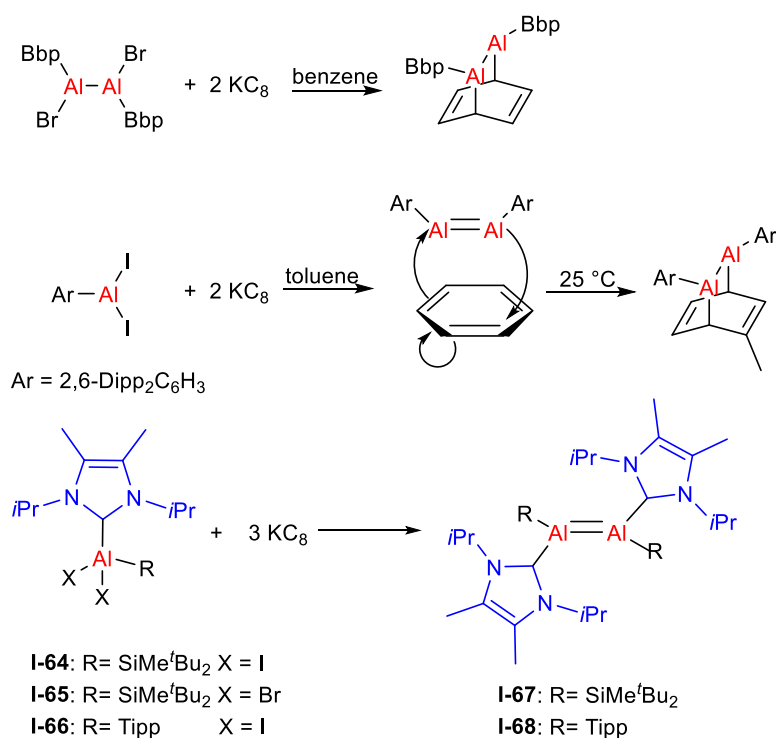


*Scheme I.10: Synthesis of dialumenes.*

The combination of a kinetic stabilization by the bulky silyl respectively aryl group and the strong *σ*-donating *Lewis* base $i$Pr$_2$Im$^{Me}$ enables the isolation of the first stable neutral dialumenes.[74, 77] The Al-Al bond length of 2.3943(16) Å observed for **I-67** is slightly shorter compared to that of the aryl substituted dialumene **I-68** (2.4039(8) Å).[74, 77] The aryl substituted dialumene adopts a *trans*-bent and twisted geometry, whereas the silyl substituted **I-67** crystallizes in a *trans*-planar geometry. The change of the geometry from planar to *trans*-bent/twisted due to switching from the bulky silyl to an aryl group has some precendence, as it was observed in disilene chemistry previousely.[78, 79] DFT calculation revealed that the structural difference of

**I-67** and **I-68** is mainly caused by the different steric demand of the ligands. Furthermore, the change from silyl to aryl ligand promotes a reduced HOMO-LUMO gap at the central Al=Al core and polarisation of the aluminium center differs due to the difference of electronegativity between C and Si. To confirm these differences between **I-67** and **I-68** Inoue *et al.* investigated the reactivity of the dialumenes with unsaturated organic compounds, small molecules ($CO_2$, $N_2O$, $O_2$, $H_2$) and some catalysis in detail.[74, 77] The reaction of **I-67** and **I-68** with $CO_2$, $N_2O$ and $O_2$ lead to the formation of the bridged oxo-complexes. The aryl substituted dialumene **I-68** is even activating dihydrogen (see Scheme I.9). The group assumed that the higher geometrical flexibility of **I-68** increases the catalytic activity. The silyl substituted dialumene **I-67** was proofed to catalyse the reduction of $CO_2$ to formic acid with pinacol borane selectively. Furthermore, the aryl stabilized dialumene **I-68** was proposed to act as a pre-catalyst in $CO_2$ hydroboration occurring through an initial hydroalumination of $CO_2$ and subsequent Al-O and B-H $\sigma$-bond methasis with formation of highly reduced species. The reported results are consistent to earlier described mechanisms of main group activation of $CO_2$.[80-82] In addition the dialumenes **I-67** and **I-68** act as pre-catalysts in the amine borane dehydrogenation of $(NMe_2H)\cdot BH_3$ with formation of the cyclic borane $(NMe_2)(BH_2)(NMe_2)(BH_2)$ as main product, the corresponding linear borane as side product, and the species $(NMe_2)BH$ and $(NMe_2)=BH_2$ in traces. The aryl stabilized dialumene **I-68** showed notably higher activity compared to **I-67**.

## 1.1.7 NHC stabilized Al=E (E = S, Te) Multiple Bonds

Examples for compounds with highly polarized Al=E bonds (E = O, S, Te) are also rather scarce in the literature as these bonds are extremely reactive and aluminium chalcogenides typically undergo spontaneous oligomerisation reactions. The first monoalumoxane was reported by Roesky and Stalke *et al.* The reaction of the β-diketiminato stabilized dimethyl aluminium with $H_2O\cdot B(C_6F_5)_3$ led to the formation of $LAl=O\cdot B(C_6F_5)_3$ (L = β-diketiminato ligand) (see Scheme I.11).[83] The Al=O bond is stabilized by the interaction of the oxygen atom with the bulky and strong Bronsted acidic $B(C_6F_5)_3$, which provides steric protection and prevents aggregation. The first neutral aluminium sulfide with a terminal Al=S double bond was reported by Nikonov

*et al.* in 2016.[84] The reaction of the β-diketiminato aluminium(I) **I-69** with cyclic thioureas afforded the first aluminium sulfides **I-70** and **I-71** in an oxidative C=S bond cleavage reaction at the aluminium(I) center (see Scheme I.11).[84] The Al-S bond length of 2.104(1) Å (**I-71**) is significantly shorter than the lowest value reported for Al-S single bonds (2.150-2.739 Å), e.g. for the Al-S bond of the deprotonated alumothiol {[$^{Dipp}$NacNacAl(SLi)$_2$(THF)$_3$]}$_2$ reported by Roesky *et al.* previousely.[85] DFT calculations were performed and supported the existence of the Al=S double bond. Furthermore, the double bond character of the Al=S bond was demonstrated by cycloaddition reaction of **I-70** and **I-71** with phenyl isothiocyanate. Independently, Inoue *et al.* synthesized the first electron precise aluminium telluride with an aluminium-tellurium double bond.[86] The reaction followed a three step synthetic route. Two equivalents of the tellurium transfer reagent *n*Bu$_3$PTe were added to the dimeric *N*-heterocyclic imine (NHI) stabilized aluminium dihydride (**I-72**) to obtain the aluminium ditelluride **I-73** *via* dehydrogenation and reduction of the chalcogen to the oxidation state -1. The bicyclic Al$_2$N$_2$Te$_2$ system of compound **I-73** was cleaved by nucleophilic attack and addition of an excess of the NHC Et$_2$Im$^{Me}$. One equivalent of the NHC acts as hydrogen acceptor with formation of Et$_2$Im$^{Me}$H$_2$ and reduction of the Te atom to the oxidation state -2 and two equivalents of the NHC used stabilize the *Lewis* acidic aluminium center with formation of the aluminium telluride **I-74** (see Scheme I.11). The abstraction of hydrogen from main group element hydrides with formation of NHC-H$_2$ and dehydrogenative coupling reactions was previously investigated for example for boranes, stannanes and phosphanes.[81, 87-89] The Al-Te bond length of 2.104(1) Å in **I-74** is the shortest reported so far. Theoretical studies confirmed the Al-Te multiple bond character and highly polar nature of the bond. Heating **I-74** in solution led to dimerization under formation of a tellurium-bridged four membered heterocyclic compound **I-75** (see Scheme 11).[86]
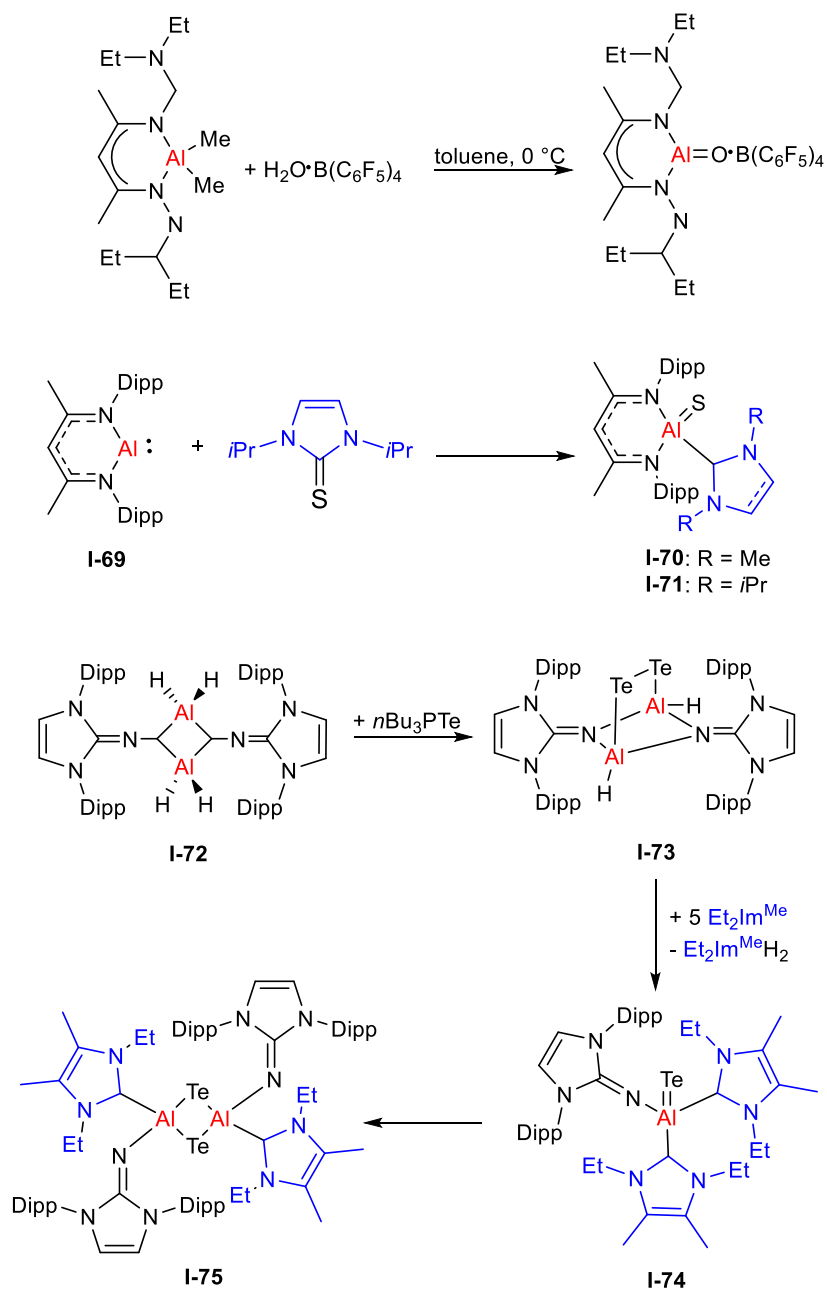
*Scheme I.11: Synthesis of NHC stabilized Al=E (E = S, Te) double bonds.*

## 1.1.8 NHC Ring expansion (RER) and Ring opening (ROR) reactions

NHCs proved to be robust ligands in transition metal and main group element chemistry. However, in the last decade a series of NHC ring expansion reactions (RERs) and ring opening reactions (RORs) were reported in which a main group element or even a transition metal inserts into the five-membered ring of the NHC.[90-101] Theoretical studies as well experimental evidences suggest that the initial step for the RER and ROR is the formation of a reactive adduct followed by E-H bond activation.[102-104] RER and ROR are well known for a series of element hydrides (e.g. Si-H[98], Be-H[105, 106], B-H[90, 92, 94, 107, 108]). But only three examples of aluminium hydride promoted NHC ring expansion have been reported so far.[36, 66, 109] Hill presented NHC ring expansion for the reaction of the β-diketiminato aluminium dihydride **I-76** with unsaturated aryl substituted NHCs with formation of the RER products **I-77** and **I-78** (see Scheme I.12).[110] NHC ring expansion is dictated by the steric demands of both the β-diketiminato ligand and NHC ligand used. DFT calculations revealed that the reaction proceeds *via* the formation of a highly reactive five-coordinated aluminium NHC adduct, which immediately undergoes Al-H bond activation with insertion of the Al-H moiety into the NHC ring and C-N bond cleavage. A second hydride transfer to the former carbene carbon atom provides the final product of the ring expansion reaction.[109] Winter *et al.* reported recently the NHC ring expansion of backbone saturated NHC $t$Bu$_2$Im$^H$ with two equivalents of the amine stabilized aluminium hydride (NMe$_3$)·AlH$_3$ with formation of the NHC ring expanded dialane **I-79** (see Scheme I.12).[36]
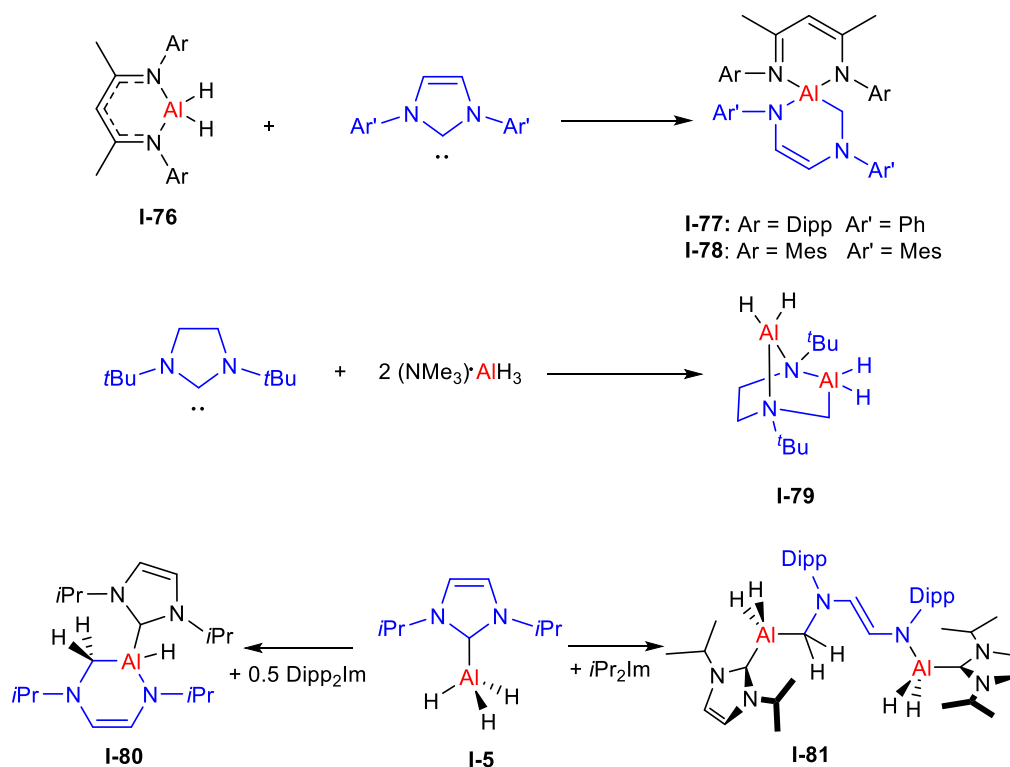
*Scheme I.12: NHC ring expansion and ring opening reaction with alanes.*

The Radius group reported NHC ring expansion as well as ring opening by treatment of the alane adduct (*i*Pr$_2$Im)·AlH$_3$ **I-5** with an additional equivalent NHC. For the reaction of **I-5** with the small NHC *i*Pr$_2$Im the formation of the RER product (*i*Pr$_2$Im)·AlH(RER-*i*Pr$_2$ImH$_2$) **I-80** was observed (see Scheme I.12).[66] In a first step a reactive bis-NHC adduct is formed followed by Al-H bond activation and insertion of one NHC moiety into one Al-H bond. Subsequent insertion of {(*i*Pr$_2$Im)·AlH$_2$} into the C-N bond leads to an intermediate which finally reacts with migration of a second hydride from aluminium to the former carbene carbon atom with formation of (*i*Pr$_2$Im)·AlH(RER-*i*Pr$_2$ImH$_2$) **I-80**. The reaction of **I-5** with the bulky NHC Dipp$_2$Im leads instead to NHC ring opening with formation of (*i*Pr$_2$Im)AlH$_2$(ROR-Dipp$_2$ImH$_2$)H$_2$Al·(*i*Pr$_2$Im) **I-81** (see Scheme I.12).[66] Compound **I-81** is still the only example of NHC ring opening with alanes.

## 1.1.9 cAAC stabilized aluminium hydrides

Another class of stable carbenes, cyclic(alkyl)(amino)carbenes (cAACs), have attracted intensively growing attention in the last few years.[111, 112] Due to formal replacement of one of the electronegative amino substituents of classical NHCs by stronger $\sigma$-donating alkyl groups, cAACs have a smaller HOMO-LUMO gap and are thus stronger electrophiles and nucleophiles compared to NHCs.[113, 114] These properties enable cAACs to activate small molecules (e.g. CO, $H_2$) and enthalpically strong single bonds such as B-H, B-C, C-H, and C-F.[66, 92, 97, 108, 111-119] Notable, no cAAC stabilized aluminium hydride (cAAC$^{Me}$)·AlH$_3$ is reported in the literature so far as E-H bond activation is preferred for the reaction of cAACs with main group element hydrides. Our group investigated the reaction of cAAC$^{Me}$ and the corresponding salt [cAAC$^{Me}$H][BF$_4$] with LiAlH$_4$, which led to the formation of cAAC$^{Me}$-H$_2$, starting material and unidentified decomposition products.[66] Ligand substitution starting from (NHC)·AlH$_3$ and cAAC$^{Me}$ was investigated as an alternative synthetic route for the synthesis of cAAC$^{Me}$ stabilized alanes. However this procedure leads to insertion of the cAAC$^{Me}$ into the Al-H bond, i.e. oxidative addition at the cAAC$^{Me}$ carbene carbon atom with formation of the compounds (NHC)·AlH$_2$(cAAC$^{Me}$H) (NHC = Me$_2$Im **I-82**, Me$_2$Im$^{Me}$ **I-83**, $i$Pr$_2$Im **I-84**, $i$Pr$_2$Im$^{Me}$ **I-85**, Dipp$_2$Im **I-86**) (see Scheme I.13) occurs.[66] The Al-C$_{NHC}$ bond lengths are in the range of 2.064(2) – 2.1011(19) Å and compare well with the parent NHC alane adducts. The Al-C$_{cAAC}$ bond lengths are slightly shorter, typically in the range between 2.00 and 2.05 Å in agreement with Al-C single bond lengths for NHC stabilized aluminium alkyls (1.94 – 2.10 Å).[54] To further investigate the influence of the steric demand at the aluminium center the NHC stabilized dialkyl aluminiumhydrides ($i$Pr$_2$Im)·AlH$i$Bu$_2$ **I-47** and (Dipp$_2$Im)·AlH$i$Bu$_2$ **I-47** were reacted with cAAC$^{Me}$. For the reaction of **I-48** insertion of the cAAC$^{Me}$ into the remaining Al-H bond under formation of the compound ($i$Pr$_2$Im)·Al$i$Bu$_2$(cAAC$^{Me}$) **I-87** was observed. For the sterically more demanding Dipp$_2$Im adduct no reaction was observed even at higher temperature.
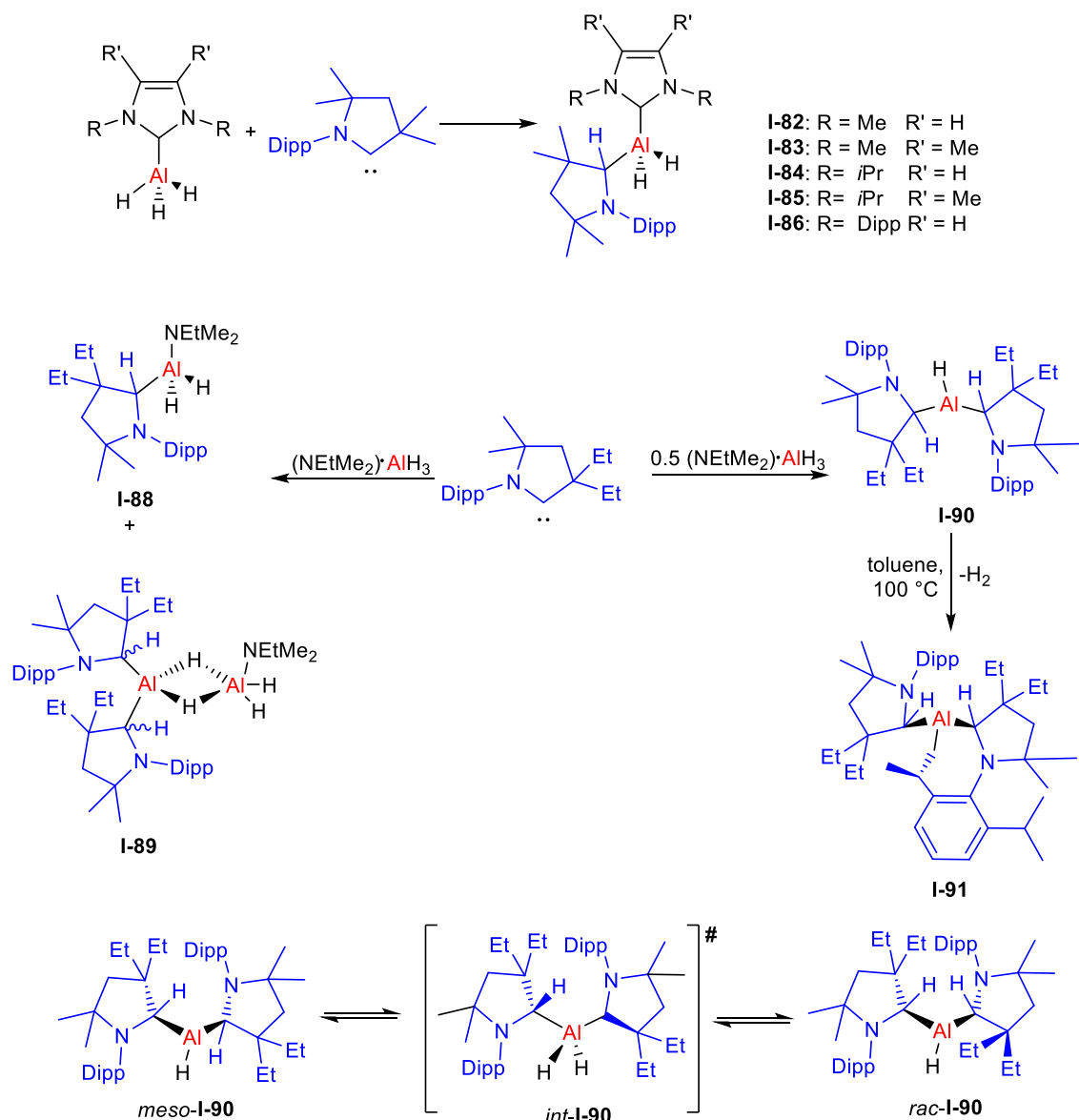
*Scheme I.13: Reactivity of cAACs with aluminium hydrides.*

Stephan *et al.* reported the reaction of cAAC$^{Et}$ with the amine stabilized aluminium hydride (NEtMe$_2$)·AlH$_3$. In dependence on the stochiometry used and the temperature applied three different cAAC$^{Et}$ insertion products were obtained. The stochiometric reaction of (NEtMe$_2$)·AlH$_3$ with one equivalent of cAAC$^{Et}$ at lower temperature afforded the alane (NEtMe$_2$)·AlH$_2$(cAAC$^{Et}$) **I-88** together with some dialane (cAAC$^{Et}$H)$_2$Al(μ-H)$_2$AlH$_2$·(NEtMe$_2$) **I-89**, which co-crystallized (see Scheme I.13). The Al-C$_{cAAC}$ bond length are in the range of 2.00 – 2.05 Å. Changing the stochiometric of cAAC$^{Et}$:(NEtMe$_2$)·AlH$_3$ to 2:1 led to the selective formation of (cAAC$^{Et}$H)$_2$AlH **I-90** (see Scheme I.13).[120] The Al-C$_{cAAC}$ bond lengths of 1.963(1) Å and 1.983(1) Å are shorter

compared to the NHC-alane insertion products presented above.[66] Compound **I-90** represents the first isolated neutral monomeric dialkyl aluminium hydride. VT and $^1$H-$^1$H EXSY NMR studies demonstrate that compound **I-90** exist in a dynamic equilibrium of diastereomers, which are connected *via* a reversible hydride migration between Al and the former cAAC$^{Et}$ carbon atom and formation of the intermediate (cAAC$^{Et}$)·AlH$_2$(cAAC$^{Et}$) **I-90-int** (see Scheme I.13). Heating **I-90** in solution afforded C-H bond activation of a cAAC$^{Et}$ *iso*-propyl group under release of dihydrogen and formation of (cAAC$^{Et}$H)Al(CHC(Et)$_2$CH$_2$C(Me)$_2$NC$_6$H$_3$-(*i*Pr)C(Me)CH$_2$ **I-91** (see Scheme I.13).[120]

## 1.1.10 cAAC stabilized aluminium chlorides

Roesky *et al.* synthesized the first cAAC stabilized aluminium(III) halides (cAAC$^{Me}$)·AlX$_3$ (X = Cl **I-92**, I **I-93**) by reaction of cAAC$^{Me}$ with aluminium(III) chloride or aluminium(III) iodide (see Scheme I.14).[43] The Al-C$_{cAAC}$ bond length of 2.037(1) Å lies in the range of Al-C$_{NHC}$ bond lengths presented previously. The same group reported the formation of (cAAC$^{Me}$)·AlCl$_2$(cAAC$^{Me}$H) **I-94** and (THF)·AlHCl(cAAC$^{Me}$H) **I-95** by treatment of the precursor "HAlCl$_2$" and "H$_2$AlCl" with cAAC$^{Me}$ (see Scheme I.14).[121]
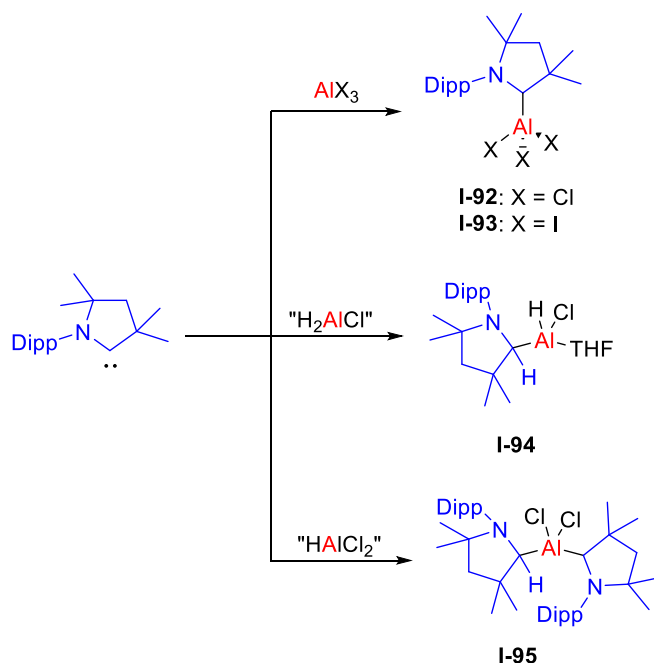


*Scheme I.14: cAAC stabilized aluminium chlorides.*

Treatment of the cAAC$^{Me}$ adduct **I-92** with KC$_8$ in the presence of an additional equivalent of cAAC$^{Me}$ afforded partial reduction and formation of the neutral carbene stabilized aluminium chloride radical (cAAC$^{Me•}$)$_2$·AlCl$_2$ **I-96** (see Scheme I.15).[122] In addition, the reaction of AlEt$_2$Cl and AlEtCl$_2$ with KC$_8$ in the presence of two equivalents cAAC$^{Me}$ led to the formation of the mono- and dialkyl aluminium radicals (cAAC$^{Me•}$)$_2$·AlEt$_2$ **I-97** and (cAAC$^{Me•}$)$_2$·AlEtCl **I-98**, respectively (see Scheme I.15).[123] Theoretical studies revealed that the unpaired electron in these radicals is mainly

located at one of the cAAC$^{Me}$ carbene carbon atoms due to the strong $\pi$-accepting character of cAACs. Therefore, the radicals **I-96** – **I-98** can be described as Al$^{III}$ species rather than Al$^{II}$ radicals even though the assignment of a formal oxidation state is unambiguous. The reaction of the cAAC$^{Me}$ stabilized aluminium halides **I-92** and **I-93** with the β-diketiminato aluminium(I) compound **I-99** resulted in the formation of asymmetric substituted Al(II)-Al(II) compounds **I-100** and **I-101** (see Scheme I.15), *i.e.* comproportionation occurred using these Al(I) and Al(III) precursors.[124] The Al-Al bond lengths of 2.6327(11) Å in **I-100** and of 2.5953(16) Å in **I-101** are slightly longer compared to literature known donor stabilized aluminium dihalogenides (2.527(6) – 2.546(3) Å).[125, 126] The Al-C$_{cAAC}$ bond lengths of 2.098(4) Å in **I-100** and 2.094(3) Å in **I-101** are only slightly longer than the values found in **I-92** presented above.
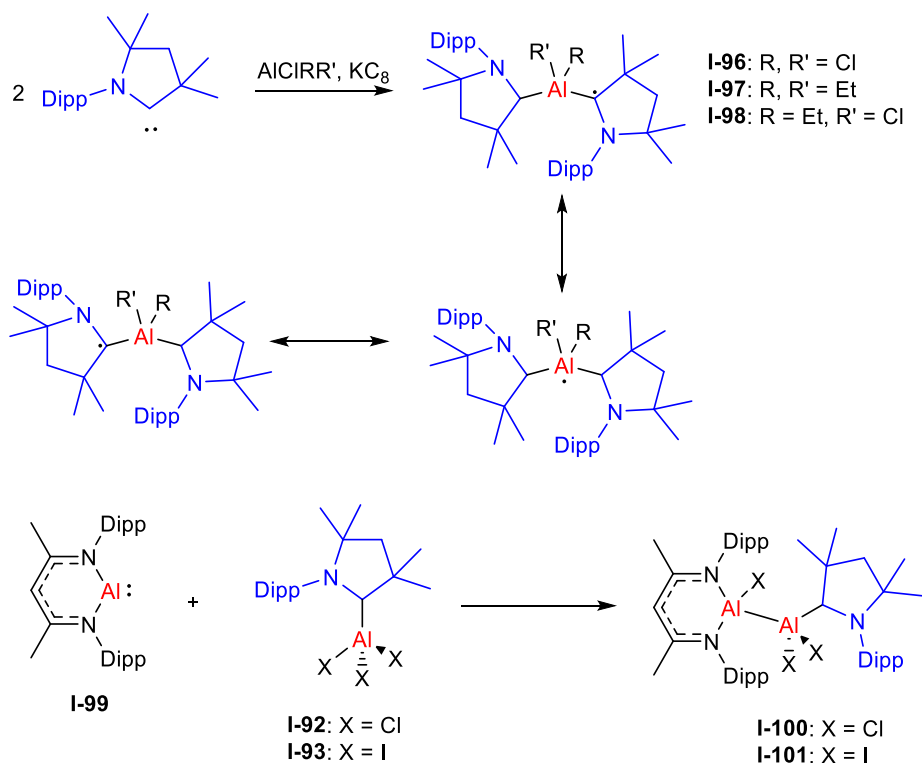


*Scheme I.15: cAAC stabilized neutral aluminium radicals and dialanes.*

Braunschweig *et al.* reported recently the synthesis of the first cAAC$^{Me}$ stabilized parent Al(I) hydride under ambient conditions.[127] Reduction of (cAAC$^{Me}$)·AlCl$_2$(cAAC$^{Me}$H) **I-95** with ca. 3 equivalents of potassium graphite in organic aromatic solvents led to the formation of the aluminene (cAAC$^{Me}$)$_2$Al(I)H **I-102** in good yield, which was isolated as

a dark green solid (see Scheme I.16). The Al-C$_{cAAC}$ bond lengths of 1.925(0) Å and 1.924(2) Å are roughly equal and differ only slightly from typical Al-C bonds (1.96 Å).[128] In the IR spectra of **I-102** the characteristic Al-H stretching frequency was observed at 1928 cm$^{-1}$, which compares well with the Al-H stretching vibration calculated with DFT methods at 1930 cm$^{-1}$. The nucleophilic character of the Al(I) center was experimentally established with the reaction of **I-102** with MeOTf (see Scheme I.16), which leads with methylation to a cationic Al(III) intermediate **I-103-int**, followed by insertion of one cAAC$^{Me}$ into the Al-H bond and simultaneous coordination of the triflate anion to give (cAAC$^{Me}$)·AlMeOTf(cAAC$^{Me}$H) **I-103**.[127] Theoretical calculations and experiments indicate that the electronic ground-state of **I-102** is best described as an Al(I) hydride with notable open-shell Al(III) singlet diradical character.
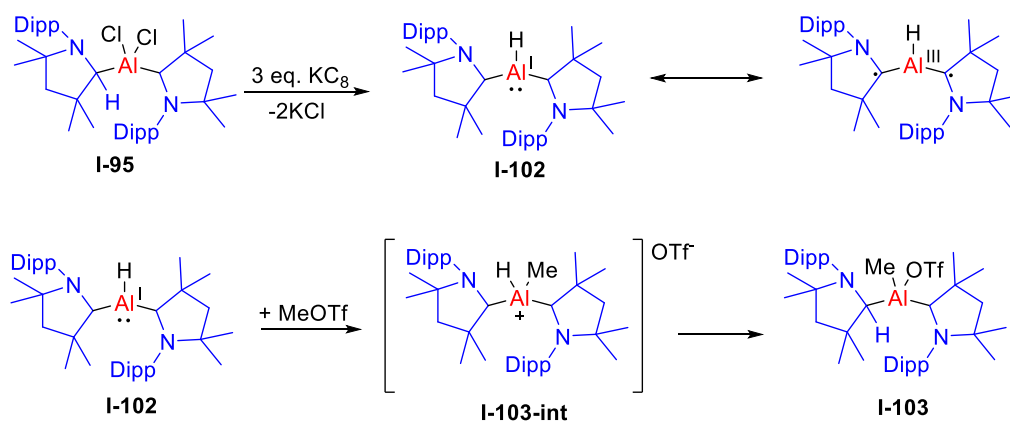


*Scheme I.16: Synthesis and reactivitiy of cAAC$^{Me}$ stabilized parent Al(I) hydride.*

## 1.1.11 NHC stabilized aluminium hydrides in transition metal chemistry

The reactivity of NHC stabilized alanes towards transition metal complexes is rather unexplored. Aldridge and coworkers investigated the coordination of the alane adduct (Dipp$_2$Im)·AlH$_3$ **I-2** and the six-membered ring NHC adducts (6-Mes$_2$Im)·AlH$_3$ **I-104** and (6-Dipp$_2$Im)·AlH$_3$ **I-105** towards some transition metal carbonyl complexes.[129, 130] The adducts **I-104** and **I-105** were synthesized from ligand exchange of the free NHCs with (NMe$_3$)·AlH$_3$ (see Scheme I.17). Treatment of the NHC alane adducts with [M(CO)$_4$(COD)] (M = Cr, Mo; COD = 1,5-cyclooctadien) led with replacement of the COD ligand to the formation of the neutral κ$^2$-H-σ-alane complexes [Mo(CO)$_4$(κ$^2$-

$H_3Al \cdot (NHC)$] (NHC = $Dipp_2Im$ **I-106**, $6\text{-}Mes_2Im$ **I-107**, $6\text{-}Dipp_2Im$ **I-108**) and [$Cr(CO)_4(\kappa^2\text{-}H_3Al \cdot (Dipp_2Im))$] **I-109** (see Scheme I.17).[129, 130] The Al-Mo distances of 2.581(1) Å (**I-106**), 2.621(1) Å (**I-107**) and 2.594(1) Å (**I-108**) are significantly shorter than the sum of the covalent radii (2.75 Å) and compare well with Al-Mo distances reported earlier *e.g.* for the hydride bridged complex [$Mo(Cp')(\mu\text{-}Al\mathit{i}BuH)$]$_2$ with 2.636(2) Å.[131, 132] The Al-$C_{NHC}$ distances (2.001(3) – 2.047(3) Å) are slightly shorter compared to the parent adducts (2.034(3) – 2.101(2) Å) due to electron withdrawal of the transition metal carbonyl and thus increased electrophilicity at the aluminium center. The reaction of **I-107** with [$Mo(CO)_3(CHT)$] (CHT = cycloheptatriene) instead led to crystallization of the dimeric compound [$Mo(CO)_3(H_3Al \cdot 6\text{-}Mes_2Im)$]$_2$ **I-110** (see Scheme I.17).[129] The Mo-Mo distance of 3.376(1) Å is consistent with a weak Mo-Mo interaction as reported in the fulvalene system [$Mo_2(\eta^5\text{-}C_{10}H_8)(CO)_6$] (3.371(1) Å).[133]
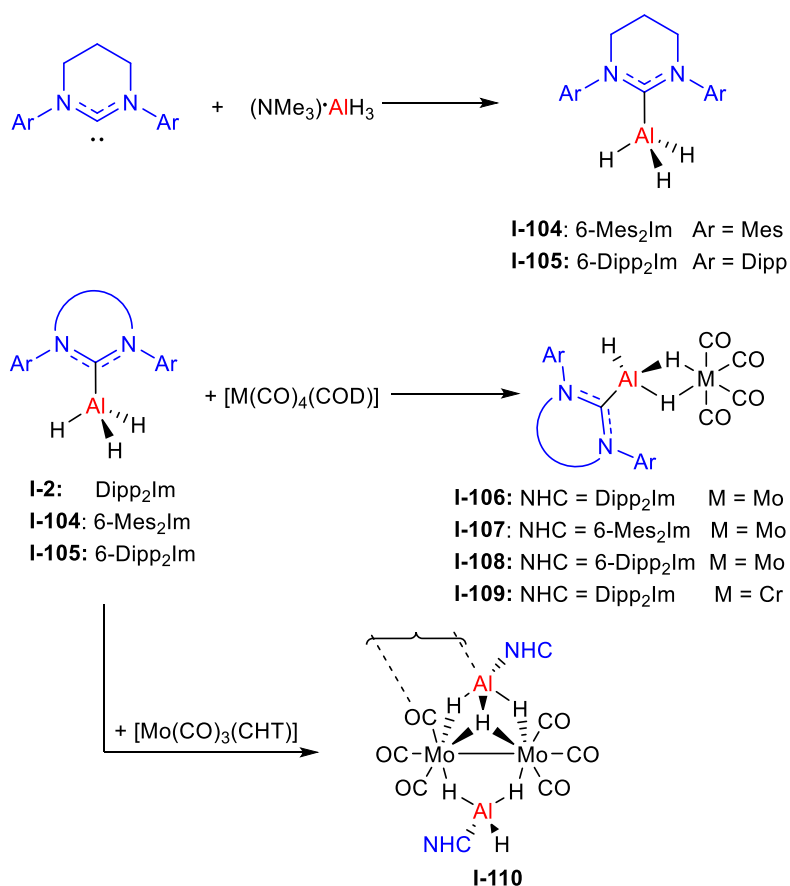


*Scheme I.17: Reactivity of NHC stabilized aluminium(III) hydrides with carbonyl transition metal complexes.*

Winter *et al.* presented the reaction of the NHC ring expanded dialane **I-79** (see Scheme I.12) with one equivalent of $Cp_2TiCl_2$, which gave the hydride bridged heterobimetallic Al-Ti complex **I-111** (see Scheme I.18). In course of the reaction the $Ti^{IV}$ center gets reduced to $Ti^{III}$ and two chloride ligands were transferred from titanium to aluminium.[134-136]
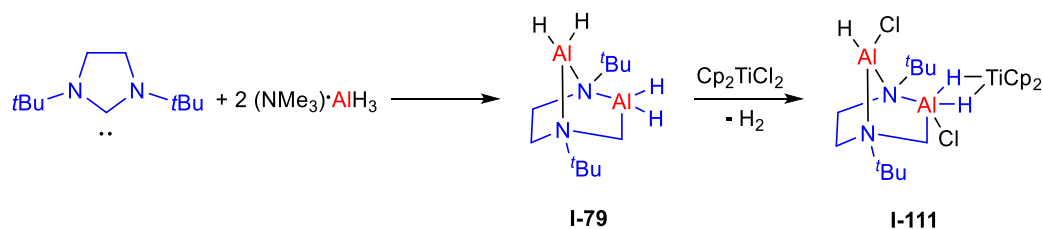


*Scheme I.18: Synthesis of the hydride bridged heterobimetallic Al-Ti complex **I-111**.*

Goicoechea and coworkers synthesized the first example of a transition metal complex containing anionic *N*-heterocyclic dicarbene ligands.[137, 138] Reduction of the NHC stabilized manganese or iron aryl complexes [M(Mes)$_2$(Dipp$_2$Im)] (M = Mn **I-112**, Fe **I-113**) with KC$_8$ afforded the highly air- and moisture- sensitive anionic bis(dicarbene) complexes K[(Mes)M(aDipp$_2$Im)$_2$] (M = Mn **I-114**, Fe **I-115**) (see Scheme I.19). The reaction of the manganese complex **I-114** with two equivalents of triethyl aluminium AlEt$_3$ in the presence of the cation sequestering agent 2,2,2-crypt led to formation of the complex [K(2,2,2- crypt)][(Mes)Mn{(aDipp$_2$Im)·AlEt$_3$}$_2$] **I-116** (see Scheme I.19).[138] For the reaction of the iron complex **I-113** with KC$_8$ in presence of 2,2,2-crypt the selective coordination of one and two equivalents of AlEt$_3$ was reached and the complexes [K(2,2,2-crypt)][(Mes)Fe(aDipp$_2$Im)(aDipp$_2$Im)·AlEt$_3$] **I-117** and [K(2,2,2-crypt)][(Mes)Fe{(aDipp$_2$Im)·AlEt$_3$}$_2$] **I-118** were formed (see Scheme I.19).[137] The Al-C$_{NHC}$ bond lengths lie in a range of 2.092(5) Å and 2.103(4) Å and are in good agreement with the values for NHC stabilized aluminium alkyls presented previously.
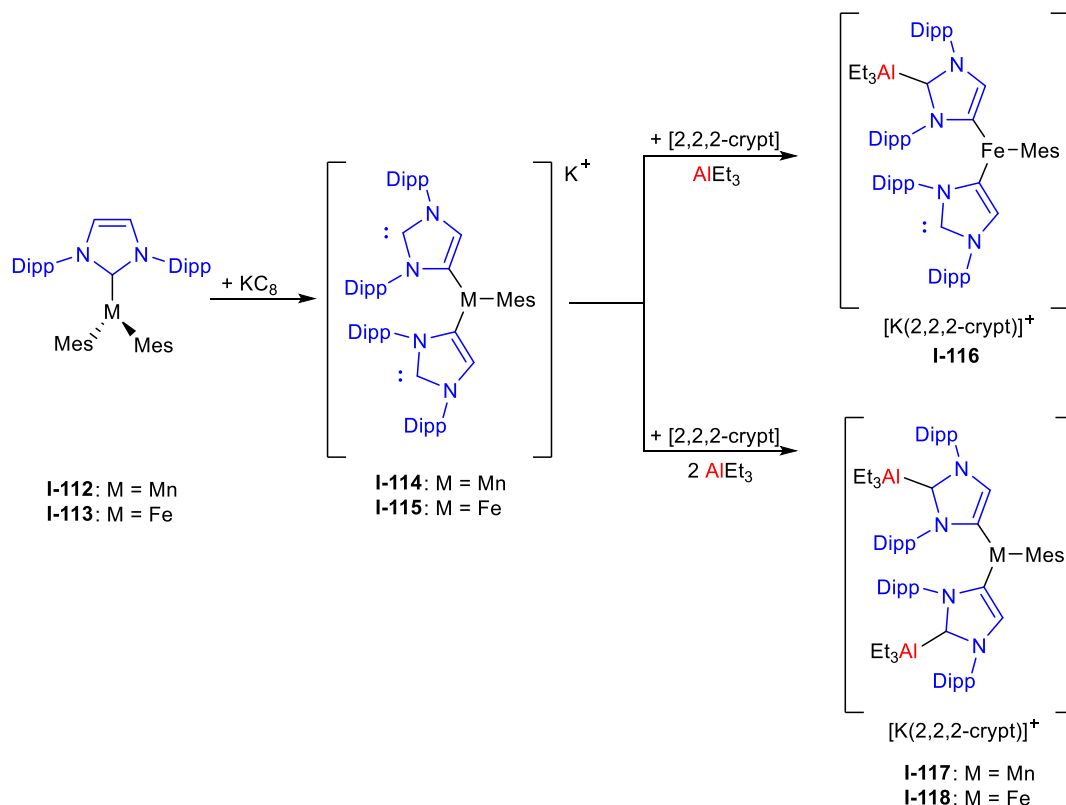
*Scheme I.19: Synthesis of dicarbene stabilized mixed manganese and iron triethyl aluminium complexes.*

Driess *et al.* reported the synthesis of the first hydridoaluminium(I) iron complex [bis(NHC)·Al(H)[Fe(CO)$_4$] **I-122** by employing the chelating bis-NHC ligand **I-119**.[44] The complex **I-122** is synthesized by stepwise redox transformation of the cationic bis-NHC aluminium(III)bromide [(bis-NHC)·AlBr$_2$]$^+$Br **I-120**. **I-120** is formed by treatment of the bis-NHC ligand with aluminium(III) bromide (AlBr$_3$) (see Scheme I.20). The Al-C$_{NHC}$ bond lengths of 2.018(5) Å and 2.027(5) Å are similar to the bond distance in (Dipp$_2$Im)·AlI$_3$ **I-16** (2.031 Å). The reaction of the cationic bis-NHC aluminium bromide **I-120** with the iron carbonyl metalate K$_2$Fe(CO)$_4$ leads to the formal reduction at the aluminium center and formation of the bromidoaluminium(I) iron complex [bis(NHC)·Al(Br)[Fe(CO)$_4$] **I-120** (see Scheme I.20). In the final step a subsequent halogen/hydride exchange reaction of **I-121** with potassium hydride (KH) or K[BHR$_3$] (R = Et, *s*Bu), repectively, leads to the highly reactive hydridoaluminium(I) iron complex [bis(NHC)·Al(H)[Fe(CO)$_4$] **I-122** (see Scheme 20). **I-122** reacts immediately in THF and THP (THP = tetrahydropyrane) solutions under C-H or C-O activation (see Scheme I.20). The formation of the cleavage product from THF or THP depends on the hydride

source used. If KH was used in THF and THP the compounds [(bisNHC)·Al(2-*cyclo*-OC$_4$H$_7$)Fe(CO)$_4$] **I-123** and [(bisNHC)·Al(2-*cyclo*-OC$_5$H$_9$)Fe(CO)$_4$] **I-124** were formed *via* α-C-H bond activation of the ether. Metathesis of **I-121** with K[BHR$_3$] (R = Et, *s*Bu) instead leads to formation of the THF ring-opening product [(bisNHC)·Al(O*n*Bu)Fe(CO)$_4$] **I-125** (see Scheme I.20).[44]
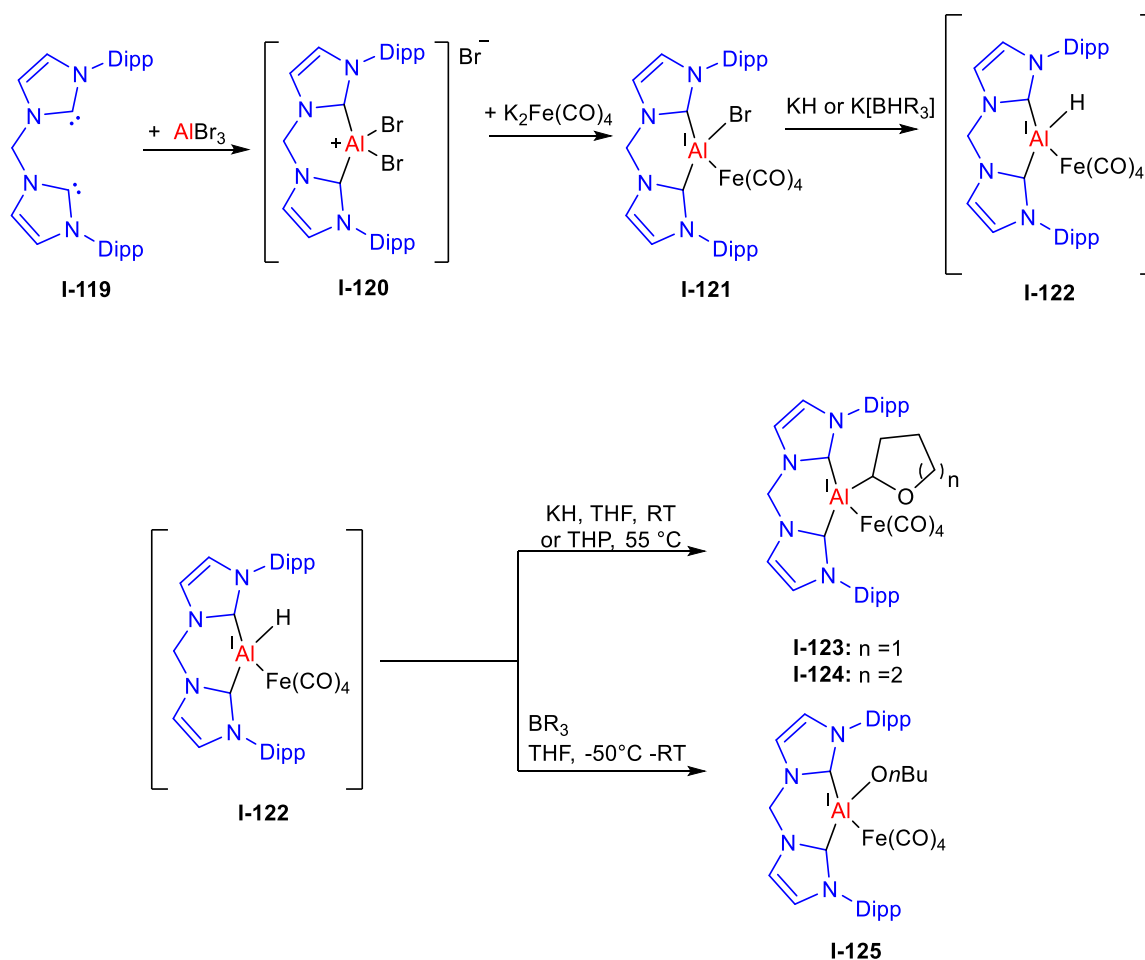


*Scheme I.20: Synthesis and reactivity of the first bis-NHC stabilized aluminium(I) iron complex.*

## 1.1.12 NHC stabilized β-diketiminato aluminium hydrides & amides

Since the isolation of the first stable monomeric β-diketiminato aluminium(I) complex **I-99**[139] by Roesky *et al.* in 2000 reactivity studies were performed to investigate the bahaviour of the singlet aluminium(I) atom with respect to transition metal complexes and small molecule activation. Compound **I-99** was reacted with small NHCs (NHC = $Me_2Im^{Me}$, $iPr_2Im^{Me}$)[140] which led to formation of the NHC stabilized aluminium hydrides (NHC = $Me_2Im^{Me}$ **I-126**, $iPr_2Im^{Me}$ **I-127**) (see Scheme I.21). The Al-N bond lengths of **I-127** (1.844(3) Å, 1.853(2) Å) are slightly shorter compared to other Al-N$_{β\text{-diketiminato}}$ distances (1.875(4)-1.957(2) Å)[141] and are closer to the bond lengths for diamido aluminium monohydride (1.820(1) Å, 1.828(1) Å).[142] In the $^1H$ NMR spectra the resonance of the Al-*H* hydride was for both compounds detected as a broadened singlet at 4.80 ppm in the characteristic range for aluminium hydrides. In the IR spectra the Al-H stretching vibrations appear at 1810 cm$^{-1}$ (**I-126**) and 1809 cm$^{-1}$(**I-127**). The aluminium bonded hydride comes from one of the terminal methyl groups of the backbone from the β-diketiminato ligand. The exact mechanism of the hydrogen transfer is not clear until know.[140]
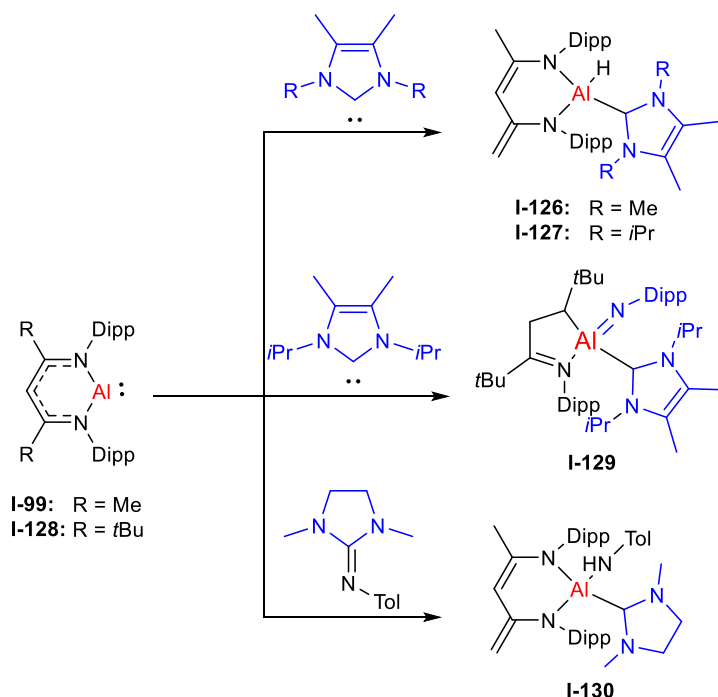


*Scheme I.21: NHC stabilized β-diketiminato aluminium hydrides & amides.*

Cui *et al.* presented the synthesis of the first structurally characterized monomeric imidoalane **I-129** formed in the reaction of the β-diketiminato aluminium(I) complex **I-128** with *i*Pr$_2$Im$^{Me}$ (see Scheme I.21).[143] The same group reported the C-N bond cleavage of an *iso*-cyanide previously.[144] It has suggested that the NHC coordinates to **I-128** with formation of a donor-acceptor or zwitterionic species, which subsequently undergoes reductive cleavage of the C-N bond similar to the mechanism reported earlier for the C-N bond cleavage of an *iso*-cyanide. The Al-N bond length of 1.705(2) Å represents the shortest Al-N distance reported so far, shorter (4.5 %) than the Al-N bond distance in the planar cyclic compound (MeAlNAr)$_3$ (1.1782(4) Å).[145, 146] DFT calculations confirm the existence of an Al-N multiple bond in this complex. Reactions of **I-129** with CO, phenyl acetylene and aniline indicate a highly reactive Al-N imide bond.

Nikonov and coworkers reported recently C=N bond cleavage of the cyclic guanidine TolN=Me$_2$Im$^H$ with formation of the NHC stabilized aluminium amido complex (Me$_2$Im$^H$)·Al($^{Dipp}$NacNac)(NHTol) **I-130** [147] (see Scheme I.21), which occurs with deprotonation of one of the methyl groups in the NacNac ligand backbone. A mechanism was proposed which suggest the oxidative addition of the guanidine to aluminium with formation of the imido intermediate (Me$_2$Im$^H$)·Al(=NTol)($^{Dipp}$NacNac) which subsequently rearranges to afford the much more stable NHC stabilized aluminium amido complex **I-130**. DFT calculations confirm the postulated mechanism.[148]

## 1.2 NHC stabilized gallium complexes

### 1.2.1 NHC stabilized gallium(III) hydrides

The synthesis of the heavier NHC stabilized gallium(III) hydrides is established in literature since the first reported complex ($i$Pr$_2$Im$^{Me}$)·GaH$_3$ **I-131** by Jones and Smithies *et al.* in 1998 [31] One important method for the formation of this class of compounds is the substitution of the amine ligand of the trimethylamine-gallane adduct (NMe$_3$)·GaH$_3$ with NHCs (see Scheme I.22).[31] A second method available is dechlorohydrogenation of stable NHC-stabilized gallium chlorides, for example the reaction of (NHC)·GaCl$_3$ with a hydride source, typically three equivalents of K[HB$^n$Bu$_3$].**[149]** The third method employs the reaction of the free NHC or its imidazolium salt with *in situ* generated unstable lithium gallium hydride LiGaH$_4$ (see Scheme I.22).**[150]**



**I-131**: R = $i$Pr    R' = Me
**I-132**: R = Mes  R' = H
**I-133**: R = Dipp  R' = H
**I-134**: R = Xy     R' = H
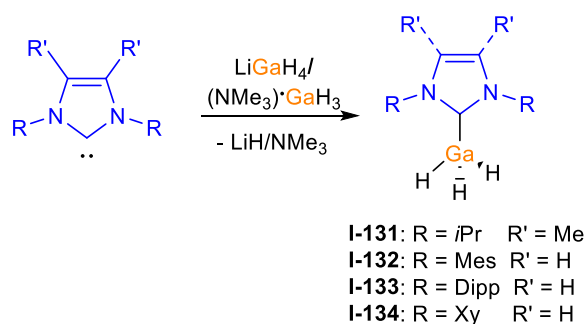
*Scheme I.22: Synthesis of NHC stabilized gallium(III) hydrides.*

Compared to the corresponding alane complexes, the gallium(III) hydrides are thermally less stable in the solid state as well as in solution. Thermal decomposition in solution typically occurs with formation of elemental gallium, the corresponding dihydroaminal NHC-H$_2$ and elemental dihydrogen. The solid-state structures of the adducts ($i$Pr$_2$Im$^{Me}$)·GaH$_3$ **I-131** and (Dipp$_2$Im)·GaH$_3$ **I-133** were reported.[31] The compounds adopt a tetrahedral structure with Ga-C$_{NHC}$ bond lengths of 2.071(5) Å (**I-131**) and 2.0545(14) Å (**I-133**). The resonances of the gallium bound hydrides and carbene carbon atoms in the $^1$H and $^{13}$C{$^1$H} NMR spectra appear as broad signals due to the binding to the gallium atom, a nucleus with a nuclear spin of I = 3/2 for both

major isotopes ($^{69}$Ga: 60.1%; $^{71}$Ga: 39.9%) and quadrupole moments of 17.1 fm$^2$ ($^{69}$Ga) and 10.7 fm$^2$ ($^{71}$Ga), respectively. In the $^1$H NMR spectra the Ga-H hydrides are typically detected in a range between 3.8 – 4.5 ppm. In the $^{13}$C{$^1$H} NMR spectra the resonances of the carbene carbon atom was reported only for **I-131** at 173.4 ppm, high-field shifted compared to the free NHC. In the IR spectra the characteristic Ga-H stretching vibrations appear in the range of 1775 – 1801 cm$^{-1}$.[31] The complex (Mes$_2$Im)·GaH$_3$ **I-132** was used as reductant for α-halogenated ketones to alcohols without dehalogenation and is active in the regioselective ring-opening of oxiranes.[31]

The Rivard group reported recently the synthesis of azido- and amido substituted gallium(III) hydrides, which are supported by NHC ligands.[149] The azido gallane (Mes$_2$Im)·GaH$_2$(N$_3$) **I-135** was synthesized by treatment of (Mes$_2$Im)·GaH$_2$I **I-157** with the lipophilic azide salt [$n$Bu$_4$N]N$_3$. In the $^1$H NMR spectra the Ga-H hydrides were detected at 4.52 ppm. In the IR spectra the characteristic azide band was observed at 2084 cm$^{-1}$, consistent with an asymmetric azide stretch at 2104 cm$^{-1}$ presented previously for (NMe$_3$)·GaCl$_2$(N$_3$).[151] The Ga-C$_{NHC}$ bond length (2.041(4) Å) is similar to values found in the parent gallane adducts. The same group demonstrated earlier the *Lewis*-acid induced N$_2$ elimination/hydride-shift for the reaction of (Dipp$_2$Im)·BH$_2$(N$_3$) with the strong electrophile MeOTf, which afforded the first stable adduct of the parent iminoborane [(Dipp$_2$Im)·HB=NHMe][OTf].[152] The synthesis of the analogue iminogallane [(Dipp$_2$Im)HGa=NHMe][OTf] was expected by the reaction of **I-135** with four equivalents MeOTf, but only the formation of the hydrido triflate complex (Mes$_2$Im)·GaH(OTf)$_2$ **I-136** was observed. The synthesis of **I-136** was also accomplished by reaction of (Mes$_2$Im)GaH$_3$ **I-132** with an excess of MeOTf. The synthesis of the amide-substituted gallium(III) dihydride (Mes$_2$Im)·GaH$_2$N(SiMe$_3$)$_2$ **I-137** was achieved by reaction of (Mes$_2$Im)·GaH$_2$Cl **I-149** with Li[N(SiMe$_3$)$_2$]. Very recently Scheer and coworkers reported the isolation of the parent NHC stabilized phosphanyl gallane (Dipp$_2$Im)·GaH$_2$PH$_2$ **I-138** and (Dipp$_2$Im)·GaH$_2$PCy$_2$ **I-139** following a similar synthetic route as presented above for the analogue phosphanyl alane.[41] Especially the parent phosphanyl gallane **I-138** may be a promising precursor in group 13/15 material chemistry.

## 1.2.2 NHC stabilized gallium(III) halides

The synthesis of the first NHC stabilized gallium(III) chloride $(Me_2Im^{Me}) \cdot GaCl_3$ **I-140** was reported by Roesky and coworkers in 2004.[42] The simple but efficient reaction of the free NHC with gallium(III) chloride afforded **I-140** (see Scheme I.23). Further carbene adducts of gallium(III) chloride were isolated following similar synthetic routes (see Scheme I.23).[153, 154] The analogue NHC gallium(III) bromides $(NHC) \cdot GaBr_3$ (NHC = $Mes_2Im$ **I-145**, $Dipp_2Im$ **I-146**) and one iodide adduct $(Dipp_2Im) \cdot GaI_3$ **I-147** are accessible by treatment of the corresponding gallium(III) halide with free NHCs (see Scheme I.23).[154, 155]
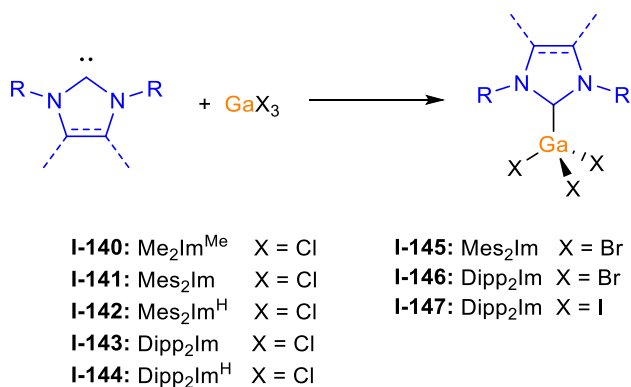


*Scheme I.23: Synthesis of NHC stabilized gallium(III) halides.*

The gallium(III) halide complexes show a high thermal stability and less air and moisture sensitivity compared to the parent gallium hydrides. The $Al\text{-}C_{NHC}$ distances are in the range of 1.954(4) and 2.016(2) Å and are slightly shorter compared to the parent gallium(III) complexes.[153] The NHC stabilized gallium(III) chlorides were used in the catalytic cyclization of enynes and arenynes.[154] Gandon and coworkers reported the synthesis of a NHC stabilized gallium(III) fluoride $(Dipp_2Im) \cdot GaF_3$ **I-148** by treatment of $(Dipp_2Im) \cdot GaCl_3$ **I-143** with three equivalents of $AgBF_4$.

In addition, several mono- and dichlorogallanes are reported in literature. NHC-stabilized monochlorogallanes $(NHC) \cdot GaH_2Cl$ (NHC = $Mes_2Im$ **I-149**, $Dipp_2Im$ **I-150**, $Xy_2Im$ **I-151**) were prepared either by the stoichiometric dismutation of the NHC-stabilized gallanes $(NHC) \cdot GaH_3$ and the corresponding NHC-stabilized gallium

chlorides (NHC)·GaCl$_3$ or the reaction of *in situ* generated "GaH$_2$Cl", which was obtained from the reaction of gallium(III) chloride with an excess of trimethylsilane SiMe$_3$H, with the free NHC (see Scheme I.24).**[150]** The synthesis of NHC stabilized dichlorogallanes (NHC)·GaHCl$_2$ (NHC = Mes$_2$Im **I-152**, Dipp$_2$Im **I-153**, Xy$_2$Im **I-154**) was achieved by similar approaches, either by the dismutation of one equivalent (NHC)·GaH$_3$ adduct and two equivalents (NHC)·GaCl$_3$ or by the reaction of *in situ* generated "GaHCl$_2$" with the corresponding NHC (see Scheme I.24).[150] These complexes are valuable precursors for further substitution reactions at gallium and formation of functionalized adducts, e.g. as starting materials for group 13/15 compounds.



**I-149:** Mes$_2$Im   X = H      **I-152:** Mes$_2$Im   X = Cl
**I-150:** Dipp$_2$Im   X = H      **I-153:** Dipp$_2$Im   X = Cl
**I-151:** Xy$_2$Im   X = H      **I-154:** Xy$_2$Im   X = Cl
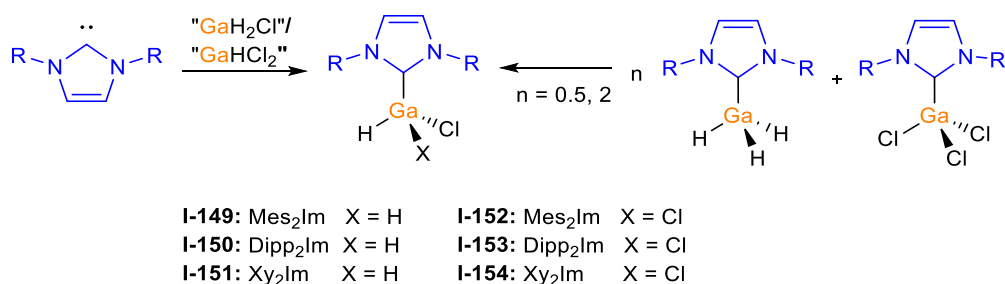
*Scheme I.24: Synthesis of NHC stabilized mono- dichlorogallium(III)hydrides.*

The synthesis of dibromogallium(III) hydrides is similar to the formation of the corresponding aluminium complex presented above.[48] The reaction of (Quin)·GaH$_3$ with the backbone brominated NHC Mes$_2$Im$^{Br}$ leads to formation of (Mes$_2$Im)·GaHBr$_2$ **I-155** in a hydride-halide exchange reaction (see Scheme I.25).[48] The reaction of (Mes$_2$Im)·GaH$_3$ **I-132** with two equivalents of (Mes$_2$Im)·GaBr$_3$ **I-145** afforded **I-155** as well. (Mes$_2$Im)·GaH$_2$Br **I-156** was obtained from the reaction of (Mes$_2$Im)·GaBr$_3$ **I-123** with either two equivalents of (Mes$_2$Im)·GaH$_3$ **I-142** an excess of triethylsilane SiEt$_3$H, or from the reaction of **I-123** with *n*BuLi (see Scheme I.25).[156]
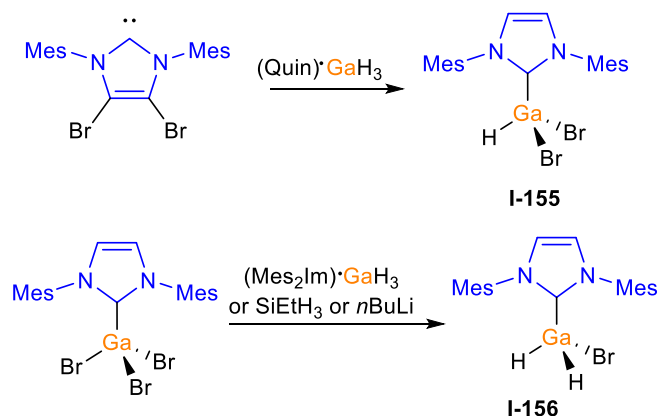
*Scheme I.25: Synthesis of (Mes₂Im)·GaHBr₂ **I-133** and (Mes₂Im)·GaH₂Br **I-134**.*

Treatment of gallium(I) iodide GaI with 0.5 equivalent of (Mes$_2$Im)·GaH$_3$ **I-142** afforded The monoiodogallium(III) hydride (Mes$_2$Im)·GaH$_2$I **I-157** with decomposition of elemental gallium as side product.[156] In the IR spectra of **I-157** the characteristic Ga-H stretching vibrations appear in the range of 1820 – 1917 cm$^{-1}$. The Ga-C$_{NHC}$ bond lengths of (Mes$_2$Im)·GaH$_2$Cl **I-148** (2.030(3) Å), (Mes$_2$Im)·GaHCl$_2$ **I-151** (2.005(6) Å) and (Mes$_2$Im)·GaH$_2$I **I-157** (2.022(4) Å) are similar to the parent gallane complexes.[150]

## 1.2.3 NHC stabilized digallium(II) halides

Amine and phosphine stabilized digallium(II) iodides are accessible *via* the reaction of "GaI" with the corresponding *Lewis*-base.[157] Jones and coworkers reported the reaction of *in situ* generated "GaI" with the sterically demanding NHC Dipp$_2$Im to yield the unusual anionic mono NHC stabilized tetraiododigallane [(Dipp$_2$Im)·GaI$_2$GaI$_3$]$^-$ [Dipp$_2$ImH]$^+$ **I-158** (see Scheme I.26).[157] Cole *et al.* reported later on the formation of the NHC stabilized digallane [(Mes$_2$Im)·GaI$_2$]$_2$ **I-159** in the similar reaction of "GaI" with free NHC at -78 °C (see Scheme I.26). The same group also prepared the digallane [(Mes$_2$Im)·GaCl$_2$]$_2$ **I-160** by treatment of Ga[GaCl$_4$] with the corresponding NHC (see Scheme I.26). Recently, Braunschweig and coworkers presented the synthesis of a series of NHC stabilized digallanes.[158] The dioxane tetrachlorodigallane adduct [(1,4-dioxane)·GaCl$_2$]$_2$ [159] was reacted with the NHCs Dipp$_2$Im and Dep$_2$Im$^H$ (Dep = 2,6-diethylphenyl) with formation of the digallanes [(NHC)·GaCl$_2$]$_2$ (NHC = Dipp$_2$Im **I-161**, Dep$_2$Im$^H$ **I-162**) (see Scheme I.26).[158]
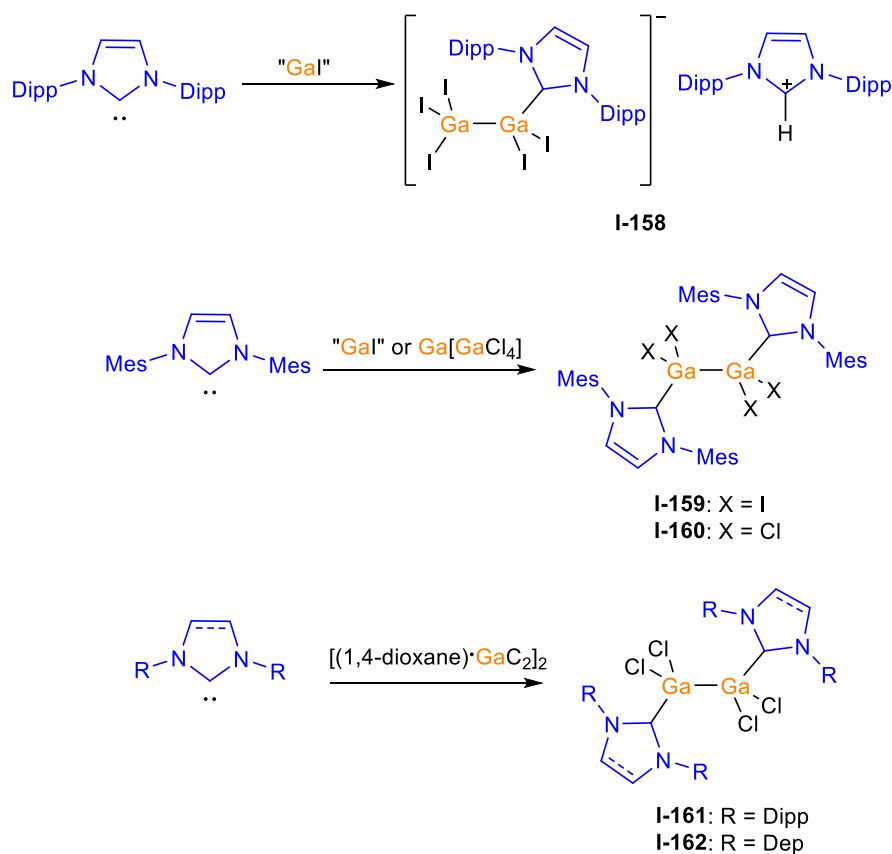
*Scheme I.26: Synthesis of NHC stabilized digallanes.*

The $^{13}C\{^{1}H\}$ NMR resonances of the NHC carbene carbon atoms of these compounds were detected in the range between 171.1 and 192.6 ppm, high-field shifted compared to the free NHCs.[158] The Ga-C$_{NHC}$ bond lengths are between 2.047(1) (**I-160**) Å and 2.078(1) Å (**I-162**) for the digallium(II) chlorides, which is in good agreement to the monogallium(III) chloride complexes. The Ga-Ga distances of 2.4243(17) Å (**I-160**) and 2.4243(17) Å (**I-162**) are similar to those reported for the amine and phosphine stabilized digallanes (2.243 – 2.448 Å).[157]

## 1.2.4 NHC stabilized gallium(III) alkyls & aryls

In the last years various NHC stabilized trialkylgallium(III) complexes were presented. Especially Wu and Dagorne and coworkers reported independently on the isolation and characterization of a series of these gallium complexes.[33, 46, 56, 60, 61, 160] The treatment of the free NHC with the corresponding trialkylgallium(III) afforded the formation of numerous compounds of the type (NHC)·GaR$_3$ (see Scheme I.27). According to X-ray analysis, these NHC gallanes adopt a tetrahedral structure with a four-coordinated gallium center. The Ga-C$_{NHC}$ distances are in the range of 2.105(4) – 2.137(2) Å. In the $^{13}$C{$^1$H} NMR spectra the carbene carbon atoms were detected in a range between 176.8 and 206.1 ppm which is consistent with the corresponding NHC stabilized parent gallanes. The adducts of the sterically demanding NHCs $t$Bu$_2$Im and Dipp$_2$Im (**I-167**, **I-168**) undergo *normal*-to-*abnormal* NHC rearrangement upon heating to yield the complexes (*a*NHC)·GaR$_3$ (see Scheme I.27).[46, 161, 162] The Ga-C$_{aNHC}$ bond length of 2.076(4) Å is shorter compared to the *normal* NHC coordinated adducts due to less steric hindrance and stronger *σ*-donation of the *a*NHC ligand.



**I-163**: Mes$_2$Im    R = Me
**I-164:** Mes$_2$Im$^H$   R = Me
**I-165:** Dipp$_2$Im    R = Me
**I-166:** Dipp$_2$Im$^H$   R = Me

**I-167:** $t$Bu$_2$Im    R = Me
**I-168:** $t$Bu$_2$Im$^H$   R = Me
**I-169**: Dipp$_2$Im    R = CH$_2$SiMe$_3$
**I-170:** Dipp$_2$Im    R = Et

**I-167**: Mes$_2$Im   R = Me
**I-168**: Dipp$_2$Im  R = CH$_2$SiMe$_3$

**I-171**: Mes$_2$Im   R = Me
**I-172**: Dipp$_2$Im  R = CH$_2$SiMe$_3$
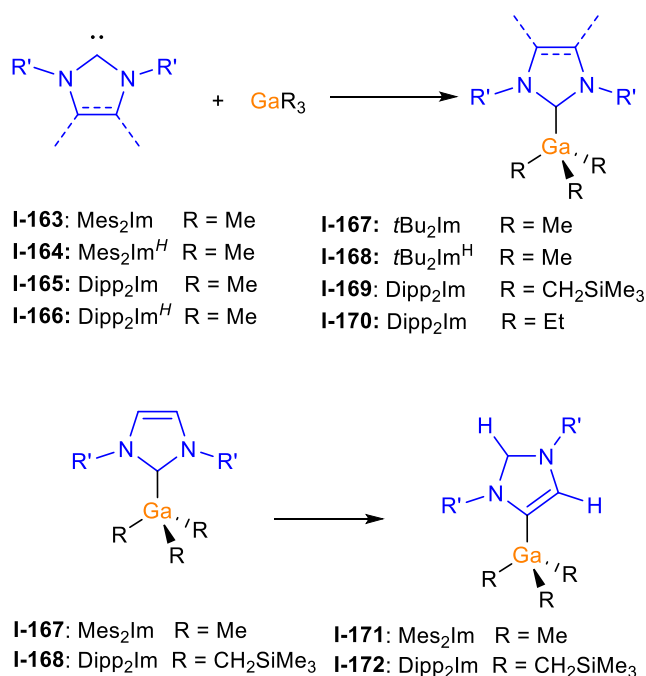
*Scheme I.27: Synthesis of NHC stabilized gallium(III) alkyls.*

The NHC stabilized trialkylgallium(III) complexes were used in the lactide ring-opening polymerisation and for $H_2$ activation.[60, 163] The reaction of the bulky adduct **I-168** with $H_2$ led to the formation of $tBu_2Im^H$-$H_2$ and $GaMe_3$. A similar $H_2$ activation was observed for the reaction of the $tBu_2Im/AliBu_3$ FLP system.[46] He*via* and coworkers reacted $Dipp_2Im$ with $Ga(CH_2SiMe_3)_3$ in the presence of $Li(TMP)$ (TMP = tetramethylpiperidine) with formation of the anionic *a*NHC gallium adduct $[(CH_2SiMe_3)_3Ga·(aDipp_2Im)][Li(THF)_2]$ **I-173**.[161] Treatment of **I-173** with MeOH afforded $(aDipp_2Im)·Ga(CH_2SiMe_3)_3$ **I-172**. The same group used the combination of the bulky $Ga(CH_2SiMe_3)_3$ as *Lewis*-acid with the strong base $tBu_2Im$ in FLP (= Frustrated *Lewis/Base* Pair) chemistry for the activation of several carbonyl compounds and small molecules.[162, 164] Furthermore, Zachara and coworkers synthesized a series of carbene stabilized dialkylgallium(III) alkoxides and investigated the opportunities and limitations for the controlled and stereoselective polymerisation of *rac*-lactide.[165]

Robinson *et al.* presented the synthesis of a mesityl digallium(II)chloride and the first neutral $Ga_6$-octahedron.[166] The reaction of $GaCl_2Mes$ with the free NHC $iPr_2Im^{Me}$ led to the formation of $(iPr_2Im^{Me})·GaCl_2Mes$ **I-174**. Treatment of **I-174** with three equivalents of $KC_8$ afforded the digallane $[(iPr_2Im^{Me})·GaClMes]_2$ **I-175** (see Scheme I.28). The Ga-Ga bond length of 2.447 Å and Ga-$C_{NHC}$ distance (1.978(2) Å) are consistent with other digallium(II) chlorides. The further reduction of **I-174** with elemental potassium led to formation of the first neutral octahedral $Ga_6$ cluster **I-176** (see Scheme I.28). Each gallium atom in this cluster is five-coordinated. The axial positions are occupied by two $(iPr_2Im^{Me})·Ga$-moieties and the four Mes-Ga groups are located at the equatorial sites. **I-176** is isoelectronic to the $[Ga_6[Si(CMe_3)_3]_4(CH_2C_6H_5)_2]^{-2}$ dianion.[167] Both are *closo*-clusters with 14 skeletal electrons, consistent with the Wade-rules.[168, 169]
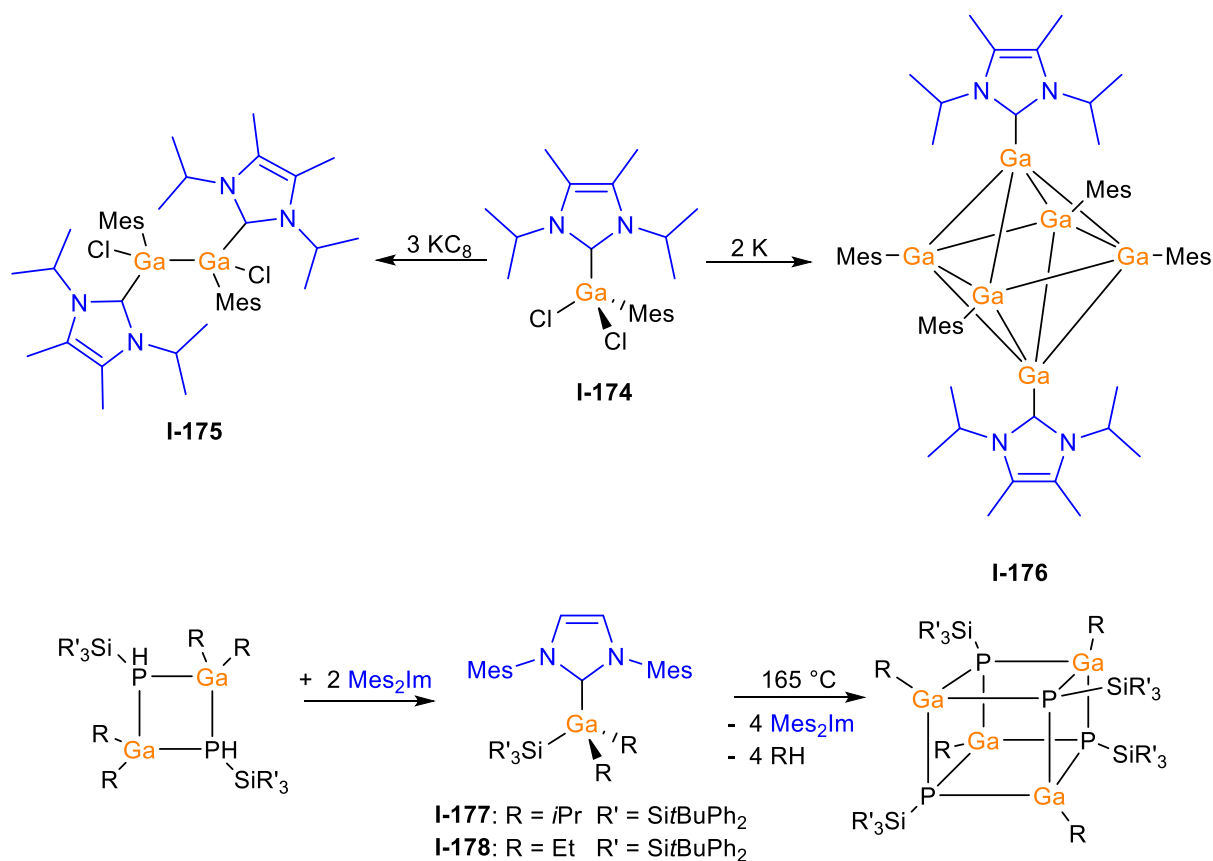
*Scheme I.28: Synthesis of NHC stabilized digallane and neutral Ga₆-octahedron and Ga-P-heterocubanes*

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Von Hänisch and coworkers reported the synthesis of a series of NHC stabilized dialkylgallium silylphosphanides.[170-172] The reaction of the cyclic gallium compounds [$i$Pr$_2$GaP(H)Si$t$BuPh$_2$]$_2$ and [Et$_2$GaP(H)Si$t$BuPh$_2$]$_2$ , respectively, with Mes$_2$Im led to cleavage of the four membered cycle and formation of (Mes$_2$Im)·GaR$_2$P(H)Si$t$BuPh$_2$ (R = $i$Pr **I-177**, R = Et **I-178**). The monomeric metal phosphides show a *trans* structure of the Si-P-Ga-NHC motif in the solid-state with an almost coplanar arrangement between P-H and the metal-bound substituent. Heating **I-177** and **I-178** to 165 °C in solution under partial vacuum afforded *cis* alkane elimination with formation of Ga-P-heterocubanes. For the sterically more demanding cyclic compound [$t$Bu$_2$GaP(H)Si$t$BuPh$_2$]$_2$ no reaction was observed with Mes$_2$Im or Dipp$_2$Im instead. The reaction with the small NHC $i$Pr$_2$Im, however, led to the formation of the ring-cleavage product ($i$Pr$_2$Im)·Ga$t$Bu$_2$P(H)Si$t$BuPh$_2$ **I-179**.[171] As an alternative route to monomeric species stabilized by the sterically more demanding NHCs the direct synthesis by salt elimination was investigated. The complexes (NHC)·Ga$t$Bu$_2$Cl (NHC = Mes$_2$Im **I-180**,

Dipp$_2$Im **I-181**) were reacted with K[P(H)Si$t$BuPh$_2$] to give with release of the NHC ligand the four-membered hetero cycles [$t$Bu$_2$GaP(H)Si$t$BuPh$_2$]$_2$. The synthesis of NHC stabilized cyclic gallium-phosphines was achieved by ligand exchange of [(NMe$_3$)·Ga(H)PSi$t$BuPh$_2$]$_2$ with the corresponding NHCs to yield [(NHC)·Ga(H)PSi$t$BuPh$_2$]$_2$ (NHC = $i$Pr$_2$Im **I-182**, B$i$Pr$_2$Im **I-183**).[170] The cyclic gallium phosphines both adopt a butterfly-type cyclic structure in the solid state.

## 1.2.5 NHC stabilized cationic gallium complexes

*Lewis*-base stabilized cationic gallium hydrides are rare in literature and no cationic NHC stabilized gallane has been reported yet. Nevertheless, some scarce cases of carbene supported cationic gallium complexes are known. Gandon and coworkers reported the synthesis of the cationic gallium(III) chloride complex [(Dipp$_2$Im)·GaCl$_2$][SbF$_6$] **I-184**, [154, 173] which was obtained from the reaction of (Dipp$_2$Im)·GaCl$_3$ **I-143** with AgSbF$_6$ (see Scheme I.29). The cationic complex **I-184** is extremely moisture sensitive and reacts with H$_2$O immediately to [(Dipp$_2$Im)·Ga(OH)$_2$][SbF$_6$] **I-185**. For the reaction of various saturated as well as unsaturated NHC stabilized gallium(III) chlorides (NHC)·GaCl$_3$ (NHC = Dipp$_2$Im, Dipp$_2$Im$^H$, Mes$_2$Im, Mes$_2$Im$^H$) with AgSbF$_6$ in the presence of electron-rich and -poor benzonitriles, a series of cationic gallium(III) chlorides was isolated (see Scheme I.29).[154] Cationic gallium(III) chlorides revealed high catalytic activity even at low temperature and low catalyst loading (as low as 1 %) for the cyclization of enynes and arenynes.[154, 173] Dagorne *et al.* reported the synthesis of the cationic NHC stabilized dialkylgallium(III) adducts [(NHC)·GaMe$_2$·THF][MeB(C$_6$F$_5$)$_3$] (NHC = Mes$_2$Im **I-190**, Dipp$_2$Im **I-191**) from (NHC)·GaMe$_3$ (NHC = Mes$_2$Im, Dipp$_2$Im) B(C$_6$F$_5$)$_3$ in THF. The stable cationic gallium(III) adducts were used in the ring-opening polymerisation of lactide.[61]
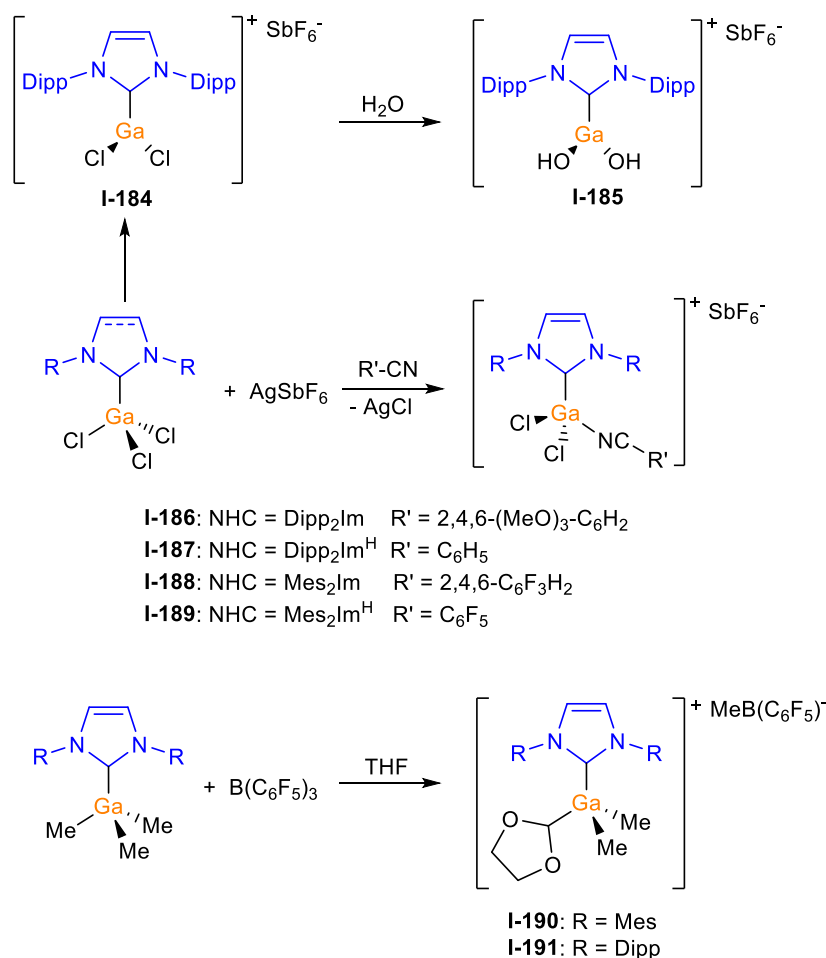
*Scheme I.29: Synthesis of NHC stabilized cationic gallium(III) complexes.*

Krossing and Jones *et al.* presented the isolation of the first cationic bis-NHC gallium(I) complexes [(NHC)$_2$·Ga][Al(OC(CF$_3$)$_3$)$_4$] (NHC = Mes$_2$Im **I-192**, Dipp$_2$Im **I-193**).[174] The reaction of the Ga$^+$[Al(OC(CF$_3$)$_3$)$_4$]$^-$ salt with two equivalents of the corresponding NHC in fluorobenzene afforded the formation of **I-192** and **I-193** (see Scheme I.30). The central gallium cation is two-coordinated in a bent fashion with a 118.2 ° C$_{NHC}$-Ga-C$_{NHC}$ angle. DFT calculations showed that the HOMO is essentially the s orbital at the gallium atom, whereas the LUMO has the form of a gallium p-orbital  which lies perpendicular to the coordination plane. Similar calculations and results are reported for catioinic Ga$^I$ bis-phosphane complexes.[175] Therefore, the tilted coordination of the carbene ligands allows *σ*-back-bonding interaction of the gallium lone-pair s-orbital with the empty p$_{NHC}$-orbitals. Moreover, the back-bonding interactions are needed to distribute the electron density all-over the molecule for stabilization.
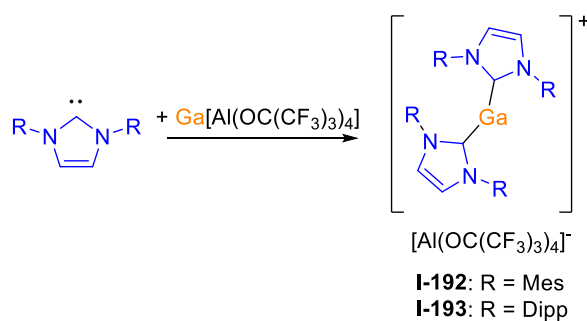
*Scheme I.30: Synthesis of bis-NHC stabilized gallium(I) cation.*

## 1.2.6 NHC stabilized neutral Ga=Ga multiple bonds

Wang and coworkers reported recently the synthesis of the neutral NHC stabilized digallene $[(iPr_2Im^{Me}) \cdot Ga(SiMetBu_2)]_2$ **I-195**.[176] The reduction of $(iPr_2Im) \cdot GaCl_2(SiMetBu_2)$ **I-194** with three equivalents of $KC_8$ afforded the digallene **I-195** as a dark purple solid (see Scheme I.31). **I-195** adopts a *trans*-planar geometry in the solid state, similar to *Lewis*-base stabilized diborenes and dialumenes.[70, 77] The Ga=Ga bond length of 2.341(3) Å is considerably shorter than the distance of 2.6268(7) Å observed in the neutral digallene $[Ga(2,6.Dipp_2C_6H_3)]_2$.[177] DFT calculations confirmed the Ga=Ga double bond character.
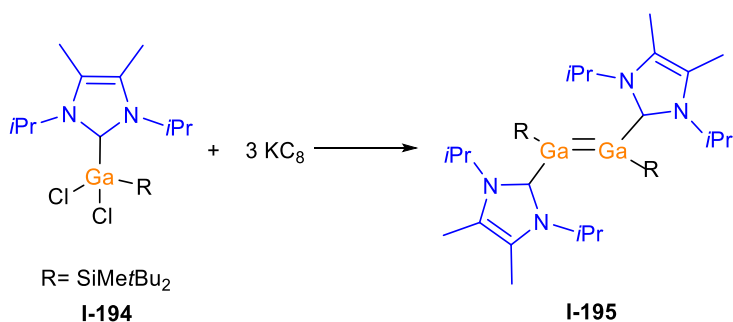


*Scheme I.31: Synthesis of the neutral NHC stabilized digallene **I-195**.*

Furthermore, Wang *et al.* investigated the mild chemical oxidation of the digallene **I-195**. Reaction of **I-195** with one or two equivalents of $[CPh_3][B(C_6(CF_3)_2H_3)_4]$, respectively, afforded the isolation of the first monocationic radical salt

$[(i\text{Pr}_2\text{Im}^{\text{Me}})\cdot\text{Ga}(\text{SiMetBu}_2)]_2^{\bullet+}[\text{B}(\text{C}_6(\text{CF}_3)_2\text{H}_3)_4]^-$ **I-196** and the dicationic salt $[(i\text{Pr}_2\text{Im}^{\text{Me}})\cdot\text{Ga}(\text{SiMetBu}_2)]_2^{2+}[\text{B}(\text{C}_6(\text{CF}_3)_2\text{H}_3)_4]_2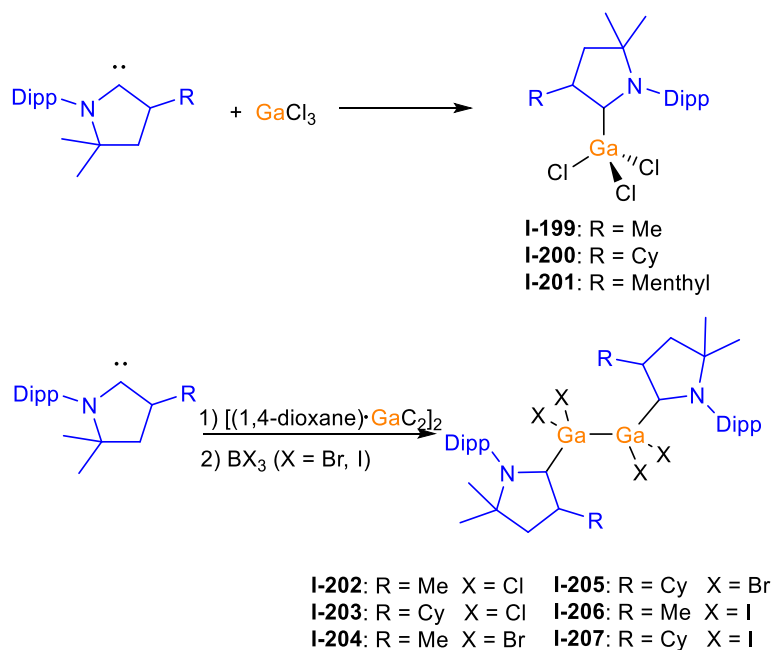$ **I-197** (see Scheme I.32) stabilized by NHCs.[176] Both salts are highly moisture- and oxygen sensitive. The Ga-Ga distance of **I-196** (2.4416(11) Å) is elongated compared to the value of **I-195** (2.341(2) Å), consistent with removal of one electron from the Ga-Ga $\pi$-bond and thus a formal bond order of 1.5. The dicationic compound **I-197** is markly different to **I-195** and **I-196**. The gallium atoms adopt a trigonal planar geometry and the planes at the gallium moieties are not coplanar anymore, consistent with a bond order of 1 and a $\pi$-bond order of 0.5. The Ga-Ga bond length of **I-197** (2.5508(10) Å) is close to reported Ga-Ga single bonds such as in $[\text{Ga}(\text{CH}(\text{SiMe}_3)_2]_2$ with 2.541(1) Å[178], which is in accordance with the removal of one more electron from the Ga-Ga $\pi$-bond. DFT calculations and EPR spectroscopy of **I-196** reproduced these results. Moreover, the reactivity of the radical cation **I-196** towards $n\text{Bu}_3\text{SnH}$ and cyclo-$\text{S}_8$ was investigated. Treatment of **I-196** with $n\text{Bu}_3\text{SnH}$ afforded the formation of the hydride abstraction product $[(i\text{Pr}_2\text{Im}^{\text{Me}})\cdot\text{Ga}(\text{SiMetBu}_2)(\text{H})\text{Ga}(\text{SiMetBu}_2)\cdot(i\text{Pr}_2\text{Im}^{\text{Me}})]^+[\text{B}(\text{C}_6(\text{CF}_3)_2\text{H}_3)_4]^-$ **I-198**, which is the first cationic gallium hydride complex with a Ga-Ga bond. The reaction of **I-196** with cyclo-$\text{S}_8$ instead leads to formation of a dicationic salt with a $\text{Ga}_4\text{S}_4$ core, which adopts a ladder-structure.
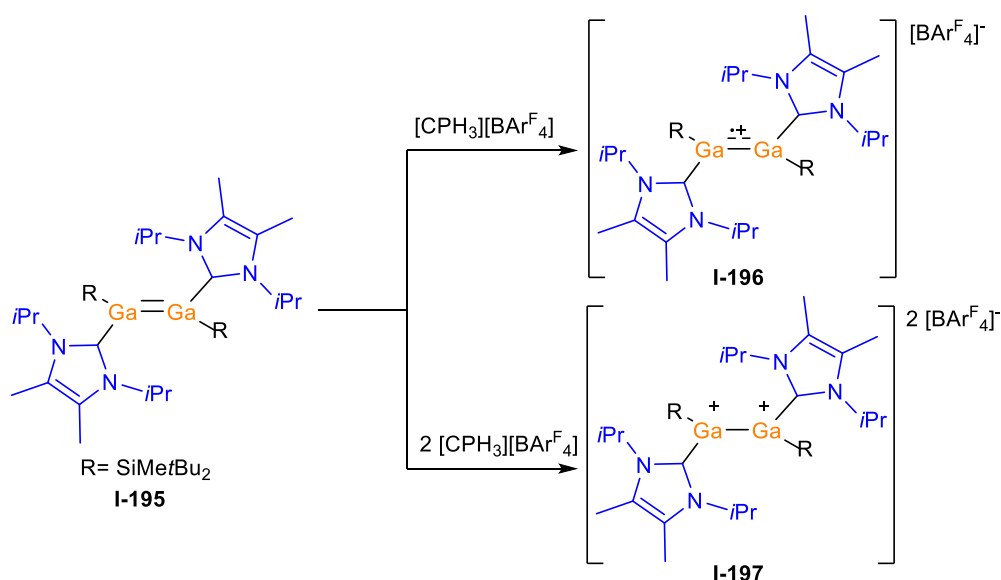


*Scheme I.32: Synthesis of the mono- and dicationic NHC stabilized digallenes.*

## 1.2.7 cAAC stabilized gallium chlorides

The stabilization of boranes and alanes with cAACs resulted in a series of reports in the last few years with new structurally and electronically behaviours in cAAC stabilized main group chemistry. Gallane adducts of cAACs are rather scarce in the literature. Gandon and coworkers reported the synthesis of cAAC$^R$ stabilized gallium(III) chlorides (cAAC$^R$)·GaCl$_3$ (cAAC$^R$ = cAAC$^{Me}$ **I-199**, cAAC$^{Cy}$ **I-200**, cAAC$^{Menthyl}$ **I-201**) (see Scheme I.33).[179] The Ga-C$_{cAAC}$ distances are in the range between 2.036(1) and 2.064(5) Å. Braunschweig *et al.* isolated the cAAC$^R$ stabilized digallium(II) chlorides [(cAAC$^R$)·GaCl$_2$]$_2$ (cAAC$^R$ = cAAC$^{Me}$ **I-202**, cAAC$^{Cy}$ **I-203**) which were obtained similarly to the synthetic route for NHC stabilized digallanes presented above (see Scheme I.33). In a halide exchange reaction of **I-202** and **I-203** with BBr$_3$ respectively BI$_3$ the corresponding cAAC$^R$ stabilized digallium(II) bromides and iodides were isolated (see Scheme I.33). The Ga-Ga bond lengths (2.441(1) – 2.481(1) Å) are consistent to the reported distances in the NHC stabilized digallanes. The Ga-C$_{cAAC}$ distances of 2.078(2) – 2.089(4) Å are slightly longer than those of the carbene stabilized gallium(III) chlorides.



**I-199**: R = Me
**I-200**: R = Cy
**I-201**: R = Menthyl

**I-202**: R = Me  X = Cl     **I-205**: R = Cy   X = Br
**I-203**: R = Cy   X = Cl    **I-206**: R = Me  X = I
**I-204**: R = Me  X = Br    **I-207**: R = Cy   X = I

*Scheme I.33: Sythesis of cAAC stabilized gallium(III) chlorides and digallium(II) chlorides.*

## 1.2.7 NHC stabilized galliumhydrides in transition metal chemistry

Besides the synthesis of the first hydridoaliuminium(I) iron complex **I-122**, Driess and coworkers isolated and fully characterized the first hydridogallium(I) iron complex [bis(NHC)·Ga(H)[Fe(CO)$_4$] **I-210** as well (see Scheme I.34).[44] Compared to the aluminium(I) complex, the gallium analogue is inert in ethereal solvents and was thus isolated and fully characterized. The suppression of the exergonic C-O bond activation of THF with **I-210** was rationalized by DFT calculations where a substantial kinetic barrier was calculated, as observed for the aluminium compound **I-122** (see Scheme I.20) which hinders the exergonic ring-cleavage.
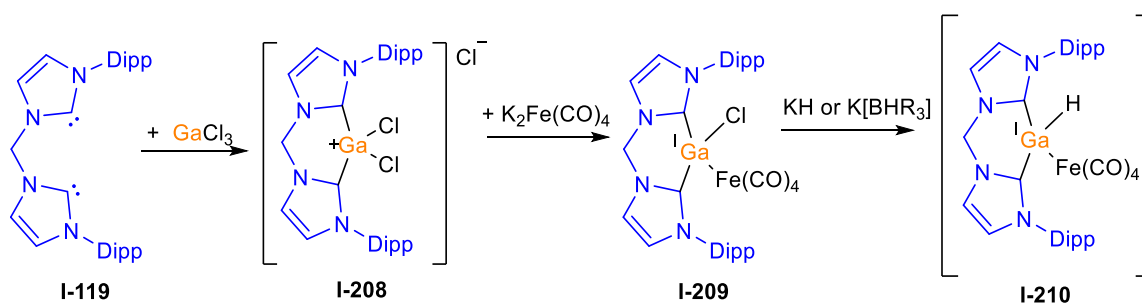


*Scheme I.34: Synthesis of the first bis-NHC stabilized hydridogallium(I) iron complex.*

*CHAPTER II*


*NHC-STABILIZED AMIDE AND PHENOLATE ALANES-*
*INTRODUCING ELECTRON-WITHDRAWING GROUPS INTO*
*NHC-ALANES*

# 2 NHC-STABILIZED AMIDE AND PHENOLATE ALANES-INTRODUCING ELECTRON-WITHDRAWING GROUPS INTO NHC-ALANES

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## 2.1 Introduction

Research in the last decades has shown that the use of N-Heterocyclic Carbenes (NHCs) and related molecules[97, 112, 114, 180-182] as (spectator) ligands in transition metal chemistry, catalysis, and main group element chemistry often offers a broad variety of novel structures, bonding situations and applications.[72, 183-197] Even the reaction of carbenes with the simplest main group element compounds, such as main group element hydrides, lead into a broad variety of reaction pathways.[198] Dependent on the electronic and steric parameters of the carbene and the nature of the main-group element hydride, different reactivities have been observed. The reaction with Brønsted acids like alcohols or hydrogen halides leads to simple deprotonation with formation of the corresponding imidazolium salt due to the basic character of NHCs (Scheme II.1, i).[175-181] The reaction of NHCs with more basic element hydrides affords completely different products as demonstrated for the reductive dehydrocoupling of phosphines into diphosphines or cyclooligophosphines using NHCs as E-H activator and H-acceptor (Scheme II.1, ii).[193] Furthermore, we and others reported that NHCs and cyclic (alkyl)(amino)carbenes (cAACs) are potent molecules for Si-H, B-H, P-H and even C-H, C-F, C-B, and B-B bond activation reactions resulting in the formation of E-E bond cleavage products (Scheme II.1, iii).[66, 87, 88, 90, 92, 94, 95, 98-100, 106-108, 193, 198-200] Especially Bertrand and coworkers investigated the activation of Si-H, B-H and P-H bonds with cAACs intensively and compared the different potential of E-H bond activation of NHCs and cAACs.[97, 116] In addition, we and others also demonstrated that some of these main group element NHC and cAAC compounds are prone to undergo ring expansion reactions (RER) or ring opening  reactions (ROR) of the carbenes employed (Scheme II.1, iv).[66, 87, 88, 90, 92, 94, 95, 98-100, 106-108, 193, 198-200] In

contrast, we also observed that the NHC $iPr_2Im$ and main group element halides react completely different and the reaction of NHCs with diphenyl dichloro silane $Ph_2SiCl_2$, for example, leads to deprotonation followed by rearrangement to the backbone tethered bis(imidazolium) salt [($^aHiPr_2Im)_2SiPh_2]_2^+2Cl^-$ ("$^a$" denotes "abnormal" coordination of the NHC) (Scheme II.1, v).[193]
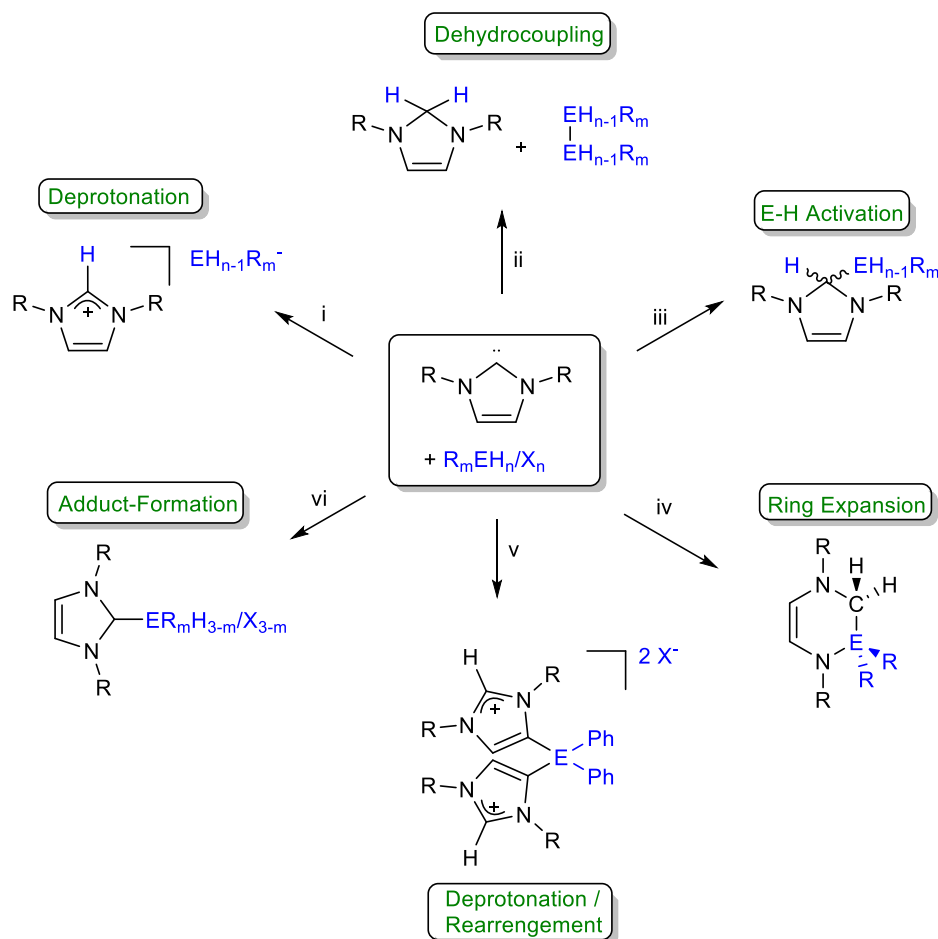


*Scheme II.1: NHC-mediated reactions of main-group element hydrogen compounds.*

NHC aluminum chemistry has been explored in more and more detail over the last few years.[34, 39, 46, 51, 63, 66, 73, 77, 109, 122, 123, 201] For NHC stabilized $AlH_3$ a variety of synthetic routes are established meanwhile in the literature.[31, 48, 51] Most common is the synthesis by salt elimination following the reaction of a NHC with lithium aluminum hydride or by base substitution of $(NMe_3)·AlH_3$. The application of NHCs and cAACs in aluminum chemistry enabled recently the synthesis of interesting substances with new

structural motifs such as the neutral aluminum dimer (Dipp$_2$Im)·H$_2$Al–AlH$_2$·(Dipp$_2$Im) reported by Jones *et al.* [73], a neutral compound {(*i*Pr$_2$Im$^{Me2}$)Al(*t*Bu$_2$MeSi)}$_2$ with an Al=Al double bond reported by Inoue *et al.*,[77] or cAAC stabilized neutral aluminum radicals as presented by Roesky *et al.*[122, 123]

But it is also known that Lewis acid-base adducts of aluminum hydrides are rather unstable. Aluminum alkyls and hydrides undergo a variety of reactions with NHCs beyond the formation of *Lewis* acid-base adducts (Scheme II.1, vi). It has thus been demonstrated that NHCs are not the most robust coligands for aluminum hydrides. NHC to *a*NHC rearrangement in the coordination sphere of aluminum[59] and ring expansion e.g. of a NHC in *β*-diketiminato aluminum dihydrides were observed.[12d] Recently, we isolated and (also structurally) characterized RER and ROR products for the reaction of *i*Pr$_2$Im (*i*Pr$_2$Im = 1,3-di*iso*propylimidazolin-2-ylidene) with (*i*Pr$_2$Im)·AlH$_3$ (Scheme II.2), and reported experimental studies concerning the mechanism of this reaction.[66] This transformation can be divided into four steps which include (i) bis-NHC adduct formation of NHC-AlH$_3$ with coordination of a second equivalent of NHC, (ii) hydride migration from aluminium to the carbene carbon atom of one of the NHCs, (iii) C-N bond cleavage and ring expansion of the hydride accepting NHC with insertion of {*i*Pr$_2$Im·AlH$_2$} into the NHC ring and (iv) stabilization of the ring expanded NHC *via* migration of a second hydride to the former carbene carbon atom (Scheme II.2, i). We have also demonstrated that the reaction of (*i*Pr$_2$Im)·AlH$_3$ with the sterically more demanding NHC Dipp$_2$Im (Dipp$_2$Im = Di(2,6-*iso*propylphenyl)imidazolin-2-ylidene) opens a different pathway and leads to the ROR product (*i*Pr$_2$Im)·AlH$_2$(ROR-Dipp$_2$ImH$_2$)H$_2$Al·(*i*Pr$_2$Im) with formation of one Al-C and one Al-N bond and migration of two hydrogen atoms (one hydrogen atom of each aluminum atom) to the former carbene carbon atom of Dipp$_2$Im (Scheme II.2, ii).[66] Beyond RER and ROR we also observed that the reaction of the NHC alane adducts with cAAC$^{Me}$ leads to Al-H bond cleavage and insertion of the cAAC into the Al-H bond. These Al-H oxidative addition products are - in contrast to the NHC stabilized aluminium hydrides - stable at higher temperatures and no cAAC ring expansion occurs (Scheme II.2, iii).[66] In addition we recently investigated the ability of the NHC alane adducts as hydride sources in the hydrodefluorination of fluoroaromatics and fluoroolefines.[39]
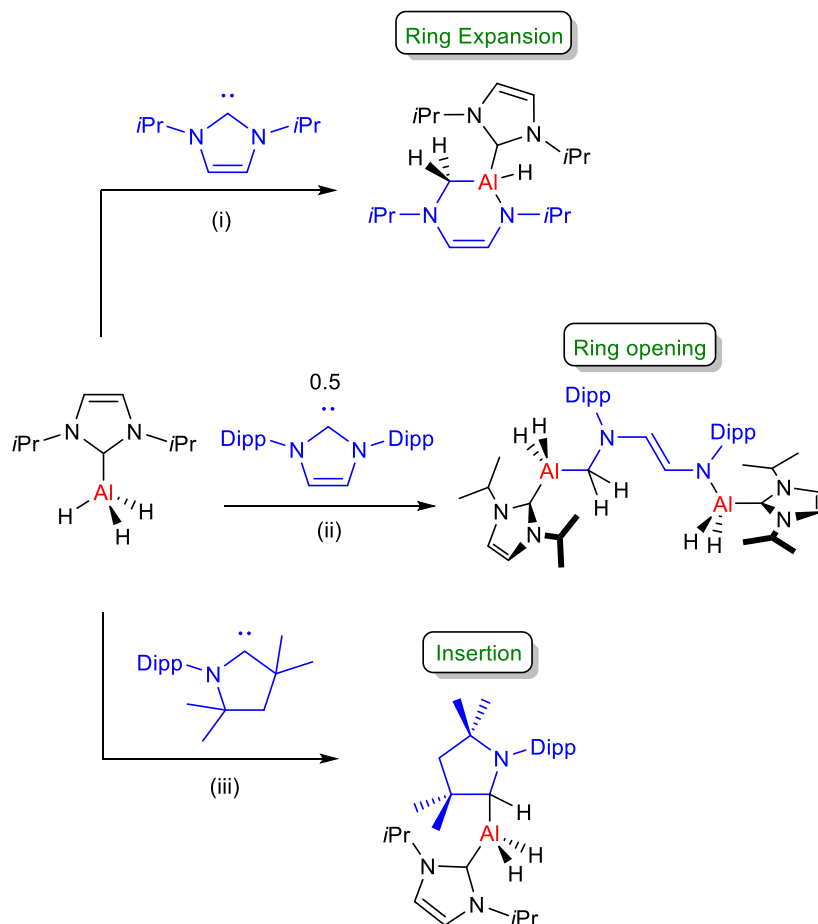
*Scheme II.2: Ring expansion (i), ring opening (ii) and insertion (iii) reaction of (iPr₂Im)·AlH₃ **II** with iPr₂Im (i), Dipp₂Im (ii) and cAAC^Me (iii).*

In total we have demonstrated that (i) NHC alane adducts are stable at ambient temperatures and that (ii) the addition of a second equivalent of NHC to (NHC)·AlH₃ (or the addition of more than one equivalent of NHC to an aluminium hydride AlH₃ precursor) leads to RER and ROR, respectively. Now we are interested in the reactivity of (NHC)·AlH₃ adducts and on the influence of substituents at aluminum on the stability of NHC alane adducts. Thus, we were interested to explore the reactivity of these carbene stabilized alanes with amines and alcohols, and to investigate the behavior of the resulting compounds at elevated temperatures as well as their reactivity with respect to the addition of carbenes. This chapter describes the influence of the introduction of electon-withdrawing substituents with π-donating properties as provided by amide or phenolate, on the stability of NHC-stabilized alanes.

## 2.2 Results and Discussion

We used two different approaches to synthesize amide ($NR_2$) substituted NHC alane adducts of the type $(NHC) \cdot AlH_2(NR_2)$. One method employs the reaction of $(NHC) \cdot AlH_3$ (usually synthesized *via* the reaction of $LiAlH_4$ with NHC, see[66]) with a secondary amine $NHR_2$ with hydrogen release, the other pathway starts with the reaction of another *Lewis* base alane adduct such as $(NMe_3) \cdot AlH_3$, for which one hydride substituent is replaced with the amide, followed by ligand exchange of the *Lewis* base ($NMe_3$) with the NHC (Scheme II.3).
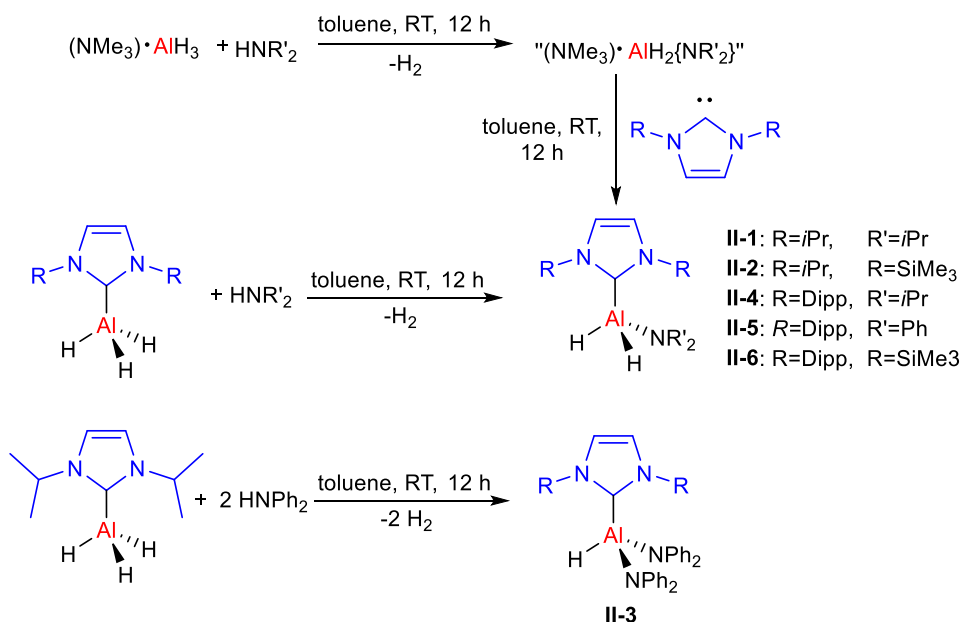


*Scheme II.3: Synthesis of the compounds (iPr₂Im)·AlH₂(NiPr₂)* **II-1**, *(iPr₂Im)·AlH(NPh₂)₂* **II-2**, *(iPr₂Im)·AlH₂(N{SiMe₃}₂)* **II-3**, *(Dipp₂Im)·AlH₂(NiPr₂)* **II-4**, *(Dipp₂Im)·AlH₂(NPh₂)* **II-5** *and (Dipp₂Im)·AlH₂(N{SiMe₃}₂)* **II-6**.

The compounds (*i*Pr₂Im)·AlH₂(N*i*Pr₂) **II-1**, (*i*Pr₂Im)·AlH(NPh₂)₂ **II-2** and (Dipp₂Im)·AlH₂(NPh₂) **II-5** are readily accessible from the reaction of the corresponding NHC alane adduct NHC·AlH₃ and the corresponding secondary amine HNR'₂ in a 1:1 stoichiometry at room temperature in toluene (Scheme II.3). After evaporation of all volatiles and further workup the compounds **II-1**, **II-2** and **II-5** can be isolated as colorless solids in excellent purity and in fair to very good overall yield (**II-1**: 33 %, **II-2**: 95 %, **II-5**: 64 %). The compounds (*i*Pr₂Im)·AlH₂(N{SiMe₃}₂) **II-3**, (Dipp₂Im)·AlH₂(N*i*Pr₂)

**II-4** and (Dipp$_2$Im)·AlH$_2$(N{SiMe$_3$}$_2$) **II-6** have been synthesized from the reaction of (NMe$_3$)·AlH$_3$ with the corresponding amine at room temperature in toluene, followed by the *in situ* addition of one equivalent of the corresponding NHC (Scheme II.3). The quantitative conversion of (NMe$_3$)·AlH$_3$ to the trimethylamine stabilized amide substituted alane adduct (NMe$_3$)·AlH$_2$(NR$_2$) was demonstrated for this reaction by NMR spectroscopy. However, the isolation of (NMe$_3$)·AlH$_2$(NR$_2$) was not necessary since the *in situ* reaction with NHC and subsequent workup saved synthetic steps and proceeded in good yields. The compounds **II-3**, **II-4** and **II-6** have been isolated as colorless solids in excellent purity and usually in good to very good overall yield (**II-3**: 80 %, **II-4**: 26 %, **II-6**: 82 %). For both pathways we isolated the monosubstituted products even if more than one equivalent of the amine HNR$_2$ was used for the reaction, with exception of the amine HNPh$_2$, which prefers for both stoichiometries the formation of compound **II-2**.

The compounds **II-1** - **II-6** were characterized using NMR spectroscopy, IR spectroscopy and elemental analysis. Signal patterns observed in the $^1$H and $^{13}$C{$^1$H} NMR spectra and the integration of the resonances of the proton NMR account for the still intact coordination of the NHC and the bonding of the amide substituent to aluminium atom. The most important NMR and IR data of **II-1** - **II-6** are summarized in Table II.1, where they are also compared to the compounds (*i*Pr$_2$Im)·AlH$_3$ **II** and (Dipp$_2$Im)·AlH$_3$ **IV**. In the $^{13}$C{$^1$H} NMR spectra the carbene carbon atom and in the $^1$H NMR spectra the aluminium hydride atoms are difficult to detect because the weak signals show broad resonances due to binding to the $^{27}$Al atom (I = 5/2) and the quadrupole moment (q = 14.7 fm$^2$) of this nucleus. However, the NHC carbene carbon atom of **II-1** - **II-6** are significantly high field shifted to 170.6 ppm for *i*Pr$_2$Im·AlH$_2$(N*i*Pr$_2$) **II-1**, 165.1 ppm for (*i*Pr$_2$Im)·AlH(NPh$_2$)$_2$ **II-2**, 169.7 ppm for (*i*Pr$_2$Im)·AlH$_2$(N{SiMe$_3$}$_2$) **II-3**, 178.2 ppm for (Dipp$_2$Im)·AlH$_2$(N*i*Pr$_2$) **II-4**, 175.2 ppm for (Dipp$_2$Im)·AlH$_2$(NPh$_2$) **II-5** and 177.3 ppm (Dipp$_2$Im)·for AlH$_2$(N{SiMe$_3$}$_2$) **II-6** compared to the free carbenes *i*Pr$_2$Im (211.6 ppm) and Dipp$_2$Im (220.5 ppm).[66] The resonances are in accordance with the signals observed for the unsubstituted adducts *i*Pr$_2$Im·AlH$_3$ (170.3 ppm) and Dipp$_2$Im·AlH$_3$ (178.2 ppm).[66] The $^1$H{$^{27}$Al} NMR spectra of **II-1**, **II-3**, **II-4, II-5** and **II-6** show a broad resonance for the aluminum hydrides at 4.86 ppm (**II-1**), 4.75 ppm (**II-3**), 4.01 ppm (**II-4**), 4.27 ppm  (**II-5**) and 4.27 ppm (**II-6**), which are shifted to lower field as compared to the resonance of *i*Pr$_2$Im·AlH$_3$ (4.53 ppm) and Dipp$_2$Im·AlH$_3$ (3.67 ppm).[66]

For the remaining hydride of compound **II-2** no signal was detected. The $^{27}$Al{$^1$H} NMR resonances for the compounds **II-1**, **II-2** and **II-3** in solution have been found at 112.1 ppm (**II-1**), 111.8 ppm (**II-2**) and 115.2 ppm (**II-3**). The signals are in good accordance to the literature known resonances in the range between 100 and 140 ppm for NHC aluminum hydride adducts. For the Dipp$_2$Im stabilized compounds **II-4** - **II-6** no $^{27}$Al{$^1$H} NMR signal in solution was observed, which is consistent with the findings for (Dipp$_2$Im)·AlH$_3$ **II** and (Dipp$_2$Im)·AlH$i$Bu$_2$.[66] The characteristic Al-H stretching vibrations of **II-1** - **II-6** were observed in the range between 1660 and 1800 cm$^{-1}$ (see Table II.1). For example, two IR bands were recorded for ($i$Pr$_2$Im)·AlH$_2${N$i$Pr$_2$} **II-1** at 1669 cm$^{-1}$ and 1729 cm$^{-1}$. For disubstituted ($i$Pr$_2$Im)·AlH(NPh$_2$)$_2$ **II-2** only one sharp IR absorption was recorded at 1780 cm$^{-1}$.

Compounds **II-1** - **II-6** are readily soluble in nonpolar solvents such as benzene or toluene and are stable even after heating up to the boiling point of these solvents. In contrast to NHC stabilized boron hydrides reported by Inoue *et al.*, which are substituted by nitrogen donor substituents,[95] no NHC RER was observed for the alane adducts **II-1** – **II-6** upon heating. Instead, continuous heating of solutions of the compounds **II-1** - **II-6** in benzene or toluene for several days to 90 °C did not result in any change of the NMR spectra or formation of any insoluble precipitate. The reaction of the compounds **II-1** - **II-3** with $i$Pr$_2$Im in a stoichiometric ratio of 1:1 for 72 h at 90 °C in benzene or toluene does not lead to any RER either, in sharp contrast to the NHC alane NHC-AlH$_3$. However, we do observe some decomposition for ($i$Pr$_2$Im)·AlH$_2$(N$i$Pr$_2$) **II-1**, and the reaction with $i$Pr$_2$Im leads in part to elimination of HN$i$Pr$_2$ and formation of $i$Pr$_2$ImH$_2$. The compound ($i$Pr$_2$Im)·AlH(NPh$_2$)$_2$ **II-2** shows no reaction with $i$Pr$_2$Im, whereas addition of $i$Pr$_2$Im to a solution of ($i$Pr$_2$Im)·AlH$_2$(N{SiMe$_3$}$_2$) **II-3** leads to rapid NHC exchange in solution, which might occur *via* a bis NHC addition product ($i$Pr$_2$Im)$_2$·AlH$_2${N(SiMe$_3$)$_2$} as observed for ($i$Pr$_2$Im)$_2$·AlH$_3$ before.[66] However, the proton NMR spectra of these mixtures reveal only one set of resonances for the NHC, and after workup only compound **II-3** was isolated. Moreover, no RER product was observed even in traces from these reactions.

*Table II.1: Selected NMR (ppm) and IR (cm$^{-1}$) shifts of the compounds (iPr$_2$Im)·AlH$_3$ **II**, (Dipp$_2$Im)·AlH$_3$ **IV**, (iPr$_2$Im)·AlH$_2$(NiPr$_2$) **II-1**, (iPr$_2$Im)·AlH$_2$(NPh$_2$) **II-2**, (iPr$_2$Im)·AlH$_2$(N{SiMe$_3$}$_2$) **II-3**, (Dipp$_2$Im)·AlH$_2$(NiPr$_2$) **II-4**, (Dipp$_2$Im)·AlH$_2$(NPh$_2$) **II-5** and (Dipp$_2$Im)·AlH$_2$(N{SiMe$_3$}$_2$) **II-6**.*

| | Al-*H* $^1$H{$^{27}$Al} NMR | $^{27}$Al{$^1$H} NMR | NCN $^{13}$C{$^1$H} NMR | $\nu$Al-*H* |
|---|---|---|---|---|
| (*i*Pr$_2$Im)·AlH$_3$ **II** | 4.53 | 106.3 | 170.3 | 1719,1776 |
| (Dipp$_2$Im)·AlH$_3$ **IV** | 3.67 | 107.9[a] | 178.2 | 1725, 1741, 1777 |
| (*i*Pr$_2$Im)·AlH$_2$(N*i*Pr$_2$) **II-1** | 4.86 | 112.1 | 170.6 | 1669, 1729 |
| (*i*Pr$_2$Im)·AlH(NPh$_2$)$_2$ **II-2** | - | 111.8 | 165.1 | 1780 |
| (*i*Pr$_2$Im)·AlH$_2$(N{SiMe$_3$}$_2$) **II-3** | 4.75 | 115.2 | 169.7 | 1755, 1785 |
| (Dipp$_2$Im)·AlH$_2$(N*i*Pr$_2$) **II-4** | 4.01 | - | 178.2 | 1735, 1779 |
| (Dipp$_2$Im)·AlH$_2$(NPh$_2$) **II-5** | 4.17 | - | 175.2 | 1790, 1798 |
| (Dipp$_2$Im)·AlH$_2$(N{SiMe$_3$}$_2$) **II-6** | 3.79 | - | 177.0 | 1777, 1786 |

[a] $^{27}$Al{$^1$H} NMR resonance in the solid state.

Similarly, the compounds **II-1** - **II-3** with Dipp$_2$Im in the stoichiometric ratio of 2:1 for 72 h at 90 °C in either benzene or toluene show also no reactivity to give RER or ROR products. If the Dipp$_2$Im stabilized NHC adducts **II-4** and **II-6** were reacted with *i*Pr$_2$Im, slow ligand exchange was observed, which was completed after approximately 12 h at 90 °C in benzene or toluene (see Scheme II.4).



R = *i*Pr (**II-4**) , SiMe$_3$ (**II-6**)          R = *i*Pr (**II-1**) , SiMe$_3$ (**II-2**)
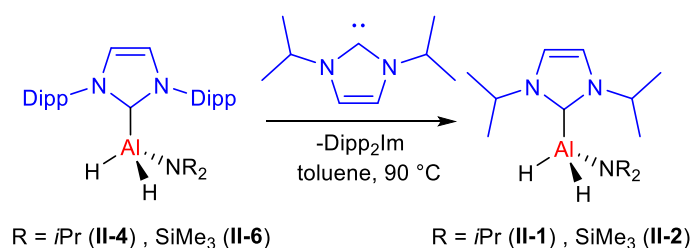
*Scheme II.4: Ligand exchange reaction of compounds **II-4** and **II-6** with iPr$_2$Im to yield compounds **II-1** and **II-2**.*

In addition, we investigated the reactivity of (*i*Pr$_2$Im)$_2$·AlH$_3$ and (Dipp$_2$Im)·AlH$_3$ **IV** with the phenol Mes-OH (Mes-OH = 2,4,6-Me$_3$C$_6$H$_2$-OH). The higher acidity of phenols compared to amines and the reduced steric demand of the phenoxide compared to the amide substituent should lead to alane adducts with more than one alkoxide

substituent. Jones and coworkers reported already the reaction of the alane adducts (Me$_4$Im)·AlH$_3$ and (Me$_2$$i$Pr$_2$Im)·AlH$_3$ of the backbone methylated NHCs Me$_4$Im and Me$_2$$i$Pr$_2$Im with three equivalents of phenol[49] and they isolated instead of the expected product NHC·Al(OPh)$_3$[49] the ionic imidazolium salts [NHC-H]$^+$[Al(OPh)$_4$]$^-$, which might be the reaction product of NHC·Al(OPh)$_3$ with an additional equivalent of phenol.
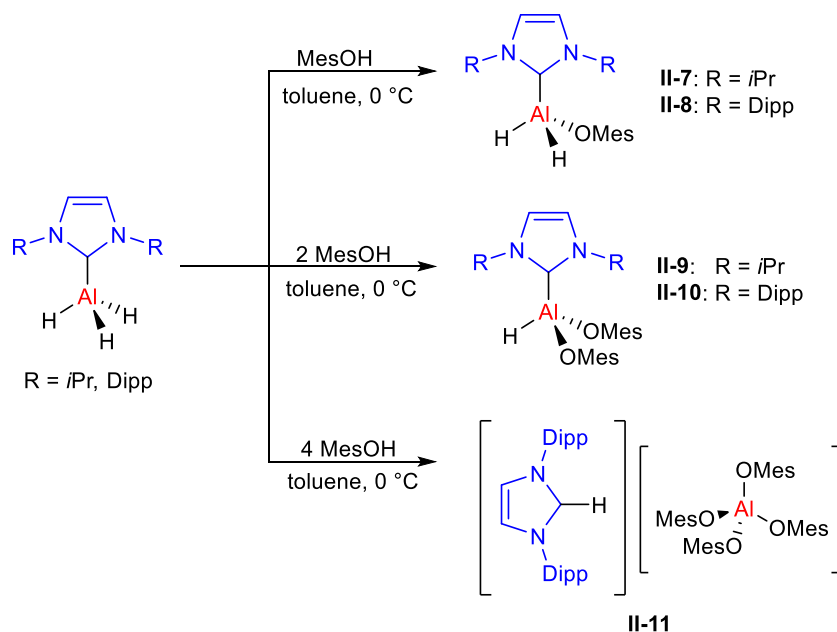


*Scheme II.5: Synthesis of the compounds ($i$Pr$_2$Im)·AlH$_2$(OMes) **II-7**,($i$Pr$_2$Im)·AlH(OMes)$_2$ **II-8**, (Dipp$_2$Im)·AlH$_2$(OMes) **II-9**, (Dipp$_2$Im)·AlH(OMes)$_2$ **II-10** and [Dipp$_2$ImH][Al(OMes)$_4$] **II-11**.*

We prepared the NHC adducts ($i$Pr$_2$Im)·AlH$_2$(OMes) **II-7**, ($i$Pr$_2$Im)·AlH(OMes)$_2$ **II-8**, (Dipp$_2$Im)·AlH$_2$(OMes) **II-9** and (Dipp$_2$Im)·AlH(OMes)$_2$ **II-10** from the reaction of ($i$Pr$_2$Im)·AlH$_3$ **II** and (Dipp$_2$Im)·AlH$_3$ **IV** with Mes-OH at 0 °C in toluene in different stoichiometric ratios (1:1 and 1:2) (Scheme II.5). These compounds have been isolated after workup as colorless solids in good yields (**II-7**: 44 %, **II-8**: 53 %, **II-9**: 50 %, **II-10**: 46 %). Compounds **II-7** - **II-10** were characterized using NMR spectroscopy, IR spectroscopy, elemental analysis and X-ray diffraction. The most important NMR shifts and IR signals are shown in Table II.3. The $^1$H NMR spectra display the expected isopropyl or diisopropylphenyl resonances, respectively, and the backbone proton signals for the coordinated NHC ligand. In addition, the resonances for the *ortho* and *para* methyl protons of the mesityl rest of the mesitylate ligand are detected at

2.08 ppm and 2.16 ppm **II-7**, 2.02 ppm and 2.13 ppm **II-8**, 2.05 ppm and 2.20 ppm **II-9** and 2.02 ppm and 2.14 ppm **II-10**, i.e. shifted to lower field compared to 2,4,6-trimethylphenol (1.97 ppm and 2.12 ppm). Because of the quadrupole moment of the aluminium nucleus, the Al-*H* hydrides were not observed. The $^{13}C\{^1H\}$ NMR spectra reveal all the expected resonances with exception of the NHC carbene carbon signal. However, Al-H bond stretching vibrations of the compounds **II-7** - **II-10** were recorded in the range between 1725 and 1825 cm$^{-1}$ as a broad resonance in the solid state (Table II.3). The $^{27}Al\{^1H\}$ resonances of the compounds **II-7** and **II-8** are significantly high field shifted in the range from 50 to 80 ppm compared to the unsubstituted compounds **II** and **IV** due to the $\pi$-donating O-bonded phenolate group, which increases the electronic density at the aluminum atom and leads to the high field shifts.

*Table II.2: Selected bond lengths of the compounds (iPr$_2$Im)·AlH(OMes)$_2$ **II-8**, (Dipp$_2$Im)·AlH$_2$(OMes) **II-9** and (Dipp$_2$Im)·AlH(OMes)$_2$ **II-10**.*

|  | **II-8** | **II-9** | **II-10** |
|---|---|---|---|
| Al-C$_{NHC}$ | 2.038(3) | 2.0451(19) | 2.0675(17) |
| Al-O1 | 1.714(2) | - | 1.7333(12) |
| Al-O2 | 1.719(2) | 1.7445(15) | 1.7174(12) |
| Al-H1 | 1.5(2) | 1.525(18) | 1.549(16) |

*Table II.3: Selected NMR (ppm) and IR (cm$^{-1}$) shifts of the compounds (iPr$_2$Im)·AlH$_3$ **II**, (Dipp$_2$Im)·AlH$_3$ **IV**, (iPr$_2$Im)·AlH$_2$(OMes) **II-7**, (iPr$_2$Im)·AlH(OMes)$_2$ **II-8**, (Dipp$_2$Im)·AlH$_2$(OMes) **II-9** and (Dipp$_2$Im)·AlH(OMes)$_2$ **II-10**.*

|  | $^{27}Al\{^1H\}$ NMR | $v_{Al-H}$ |
|---|---|---|
| (*i*Pr$_2$Im)·AlH$_3$ **II** | 106.3 | 1719, 1776 |
| (Dipp$_2$Im)·AlH$_3$ **IV** | 107.9[a] | 1725, 1741, 1777 |
| (*i*Pr$_2$Im)·AlH$_2$(OMes) **II-7** | 77.1 | 1736, 1784 |
| (*i*Pr$_2$Im)·AlH(OMes)$_2$ **II-8** | 50.8 | 1725 |
| (Dipp$_2$Im)·AlH$_2$(OMes) **II-9** | - | 1745, 1794 |
| (Dipp$_2$Im)·AlH(OMes)$_2$ **II-10** | - | 1825 |

Single crystals of the compounds (*i*Pr$_2$Im)·AlH(OMes)$_2$ **II-8**, (Dipp$_2$Im)·AlH$_2$(OMes) **II-9** and (Dipp$_2$Im)·AlH(OMes)$_2$ **II-10** were grown from saturated *n*-hexane solutions of these compounds at -30 °C. The molecular structures of **II-8**, **II-9** and **II-10** reveal the expected four coordinated NHC adducts (see Figure II.1 and Table II.2). (Dipp$_2$Im)·AlH$_2$(OMes) **II-9** crystallizes in the monoclinic space group *P*2$_1$/*c* and (*i*Pr$_2$Im)·AlH(OMes)$_2$ **II-8** and (Dipp$_2$Im)·AlH(OMes)$_2$ **II-10** in the triclinic space group *P*$\bar{1}$. These molecules adopt a tetrahedral structure at the aluminium center, spanned by the NHC (*i*Pr$_2$Im for **II-8** and Dipp$_2$Im for **II-9** and **II-10**), one or two phenolate and the remaining hydrogen atom(s). The Al-C$_{NHC}$ bond length of 2.038(3) Å (**II-8**), 2.0451(19) Å (**II-9**) and 2.0675(17) Å (**II-10**) differ only marginally from aluminum carbene carbon atom bond distance observed in (*i*Pr$_2$Im)·AlH$_3$ **II** [2.0405(17)] Å and (Dipp$_2$Im)·AlH$_3$ **IV** [2.0556(13)] Å[66] or found for compound **II-6** (see Figure II.1). The Al-O distances (see Table II.2) are in good accordance with the literature known compound [Me$_4$ImH][Al(OPh)$_4$] 1.730(3) Å as well.[49]

The reaction of (Dipp$_2$Im)·AlH$_3$ **IV** with 3 (or more) equivalents of Mes-OH at 0 °C in toluene led to the imidazolium salt [Dipp$_2$ImH][Al(OMes)$_4$] **II-11**, which has been isolated as a colorless solid in good yield (48 %) (Scheme II.5). Compound **II-11** was characterized using multinuclear NMR spectroscopy and elemental analysis. The $^1$H NMR resonances show the splitting of the backbone protons into two sharp signals at 2.03 and 2.07 ppm due to the interaction with the carbene carbon bonded proton. The carbene-*H* was detected at 8.16 ppm. In the $^{13}$C NMR spectra all expected resonances were observed. Instead of the formation of the compound (Dipp$_2$Im)·Al(OMes)$_3$, the reaction of **IV** with 3 equivalent Mes-OH led to the formation of compound **II-11**, which confirms the findings of Jones *et al.* on the reactivity of NHC stabilized alanes with acidic phenols. Jones suggested that the mononuclear neutral tris(aryloxide) aluminum unit requires steric hindrance at the 2,6-phenyl position of the aryloxide and that the generated imidazolium cations possess p$K_a$ values above that of phenols (9.98).[49]
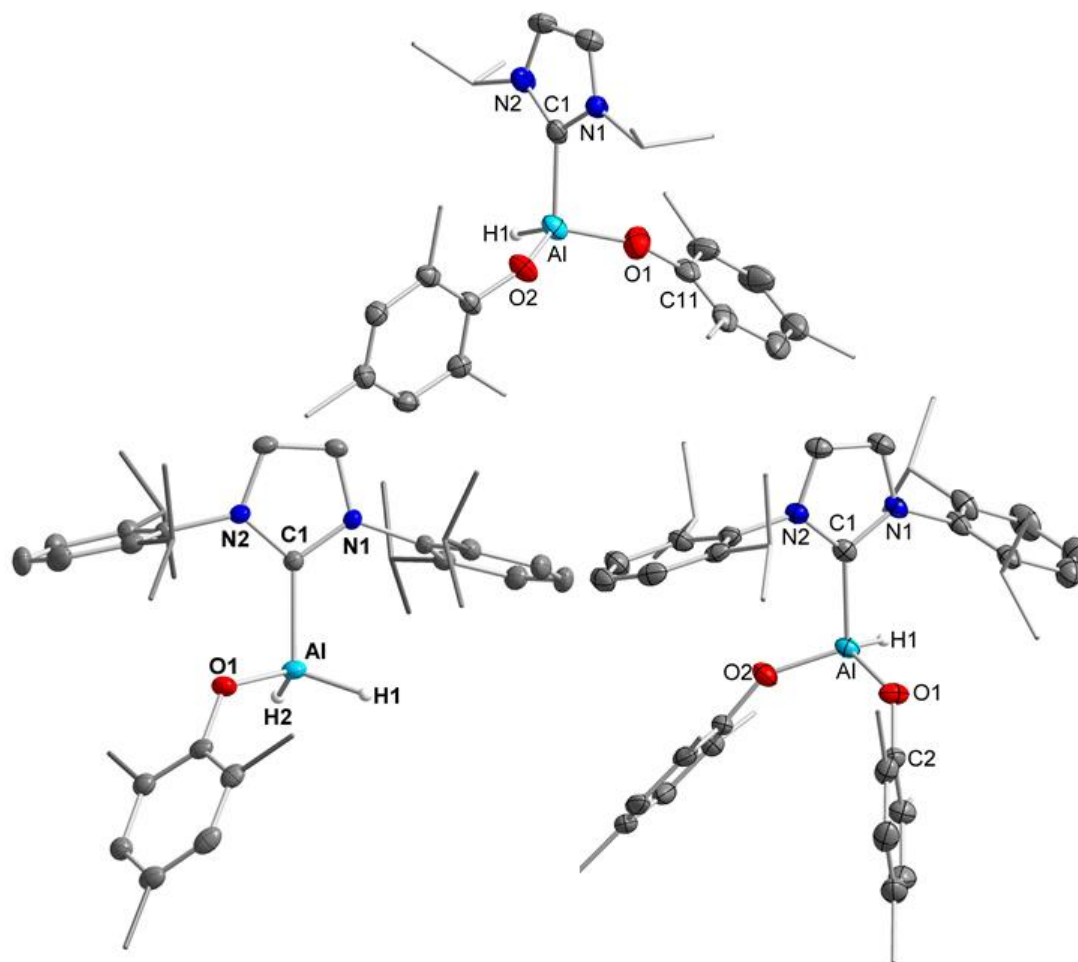
*Figure II.1: Molecular structure of (iPr₂Im)·AlH(OMes)₂ **II-8** (top), (Dipp₂Im)·AlH₂(OMes) **II-9** (bottom left) and (Dipp₂Im)·AlH(OMes)₂ **II-10** (bottom right) in the solid state (ellipsoids set at 50% probability level. Hydrogen atoms with exception of those attached to aluminium are omitted for clarity. Selected bond lengths [Å] and angles [°]: **II-8**: Al-C1 2.038(3), Al-H1 1.5(2), Al-O1 1.714(2), Al-O2 1.719(2), C1-N1 1.347(3), C1-N2 1.348(3); O1-Al-O2 108.56(11), C1-Al-O1 99.85(10), C1-Al-O2 104.14(11), C1-Al-H1 110.6(9), O1-Al-H1 116.0(9), O2-Al-H1 115.9(9); **II-9**: Al-C1 2.0451(19), Al-H1 1.525(18), Al-O1 1.7445(15), C1-N1 1.352(2), C1-N2 1.355(2); O1-Al-H1 112.0(7), O1-Al-H2 112.9(7), C1-Al-O1 100.05(7), C1-Al-H1 107.6(7), C1-Al-H2 109.0(7), H1-Al-H2 114.1(9); **II-10**: Al-C1 2.0675(17), Al-H1 1.549(16), Al-O1 1.7333(12), Al-O2 1.7174(12), C1-N1 1.354(2), C1-N2 1.362(2); O1-Al-O2 112.06(6), C1-Al-O1 104.99(6), C1-Al-O2 106.40(6), C1-Al-H1 104.2(6), O1-Al-H1 113.0(6), O2-Al-H1 115.1(6).*

Compounds **II-7** - **II-10** are moderate soluble in nonpolar solvents such as benzene or toluene, but they are readily soluble in more polar solvents such as CH₂Cl₂ and are stable even after heating solutions of the compound to the boiling point of these solvents. No NHC RER was observed for the alane adducts **II-7** - **II-10** upon heating or upon reaction with additional NHCs. Instead, continuous heating of solutions of the compounds **II-7** - **II-10** in benzene or toluene for several days to 90 °C did not result in any change of the NMR spectra or formation of any insoluble precipitate.

## 2.3 Conclusion

We have shown that NHC alane adducts are valuable starting materials for a further functionalization/substitution at the aluminum atom. The reaction of (NHC)·AlH$_3$ (NHC = $i$Pr$_2$Im, Dipp$_2$Im) with secondary amines with different steric demand leads to the formation of the NHC substituted aluminum amides (NHC)·AlH$_2$(NR$_2$) **II-1, II-3 - II-6**. These compounds reveal a higher stability in solution as compared to NHC alanes (NHC)·AlH$_3$, and ring expansion or ring opening of the NHC - as observed for the NHC alane adducts (NHC)·AlH$_3$ - does not occur in the presence of an excess of the carbene. As an exception, the reaction of ($i$Pr$_2$Im)·AlH$_2$(N$i$Pr$_2$) with $i$Pr$_2$Im led to the formation of $i$Pr$_2$ImH$_2$ and HN$i$Pr$_2$. The reaction of ($i$Pr$_2$Im)·AlH$_3$ **II** with HNPh$_2$ led to substitution of two hydrides, even if a ratio of 1:1 was used for this reaction, and the bisamide ($i$Pr$_2$Im)·AlH(NPh$_2$)$_2$ was isolated. For the reaction of the compounds ($i$Pr$_2$Im)·AlH$_3$ **I** and (Dipp$_2$Im)·AlH$_3$ **IV** with Mes-OH in different stoichiometric ratios we isolated the compounds ($i$Pr$_2$Im)·AlH$_2$(OMes) **II-7**, ($i$Pr$_2$Im)·AlH(OMes)$_2$ **II-8**, (Dipp$_2$Im)·AlH$_2$(OMes) **II-9** and (Dipp$_2$Im)·AlH(OMes)$_2$ **II-10**. In contrast to the reaction with secondary amines (with exception of the formation of compound **II-2**), multiple substitution was achieved rather easily. The reaction of **IV** with three equivalents of the phenol led to formation of the imidazolium salt [Dipp$_2$ImH]$^+$[Al(OMes)$_4$]$^-$ **II-11**. The compounds **II-7 - II-10** are stable in solution at elevated temperatures and do not show any ring expansion or ring opening in the presence of additional NHC. Thus, electron-withdrawing $\pi$-donor substituents such as amides and phenolates, but also halides (see Chapter 3) seem to modify the *Lewis*-acidity of the aluminum atom in a way that the attack of a second NHC ligand is not possible and ring expansion or ring opening does occur. In contrast the high electronegative N and O substituents increase the *Lewis*-acidity of the aluminum atom, which leads to stronger Al-H and Al-C bonds and less reactive hydrides.

*CHAPTER III*

*DEVELOPMENT OF NHC GALLANE CHEMISTRY - NHC AND CAAC ADDUCTS OF GALLIUM HYDRIDES, GALLIUM CHLORIDES AND GALLIUM HYDROCHLORIDES*

# 3 DEVELOPMENT OF NHC GALLANE CHEMISTRY - *NHC AND CAAC ADDUCTS OF GALLIUM HYDRIDES, GALLIUM CHLORIDES AND GALLIUM HYDROCHLORIDES*

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## 3.1 Introduction

The reaction of *N*-heterocyclic carbenes (NHCs) and cyclic (alkyl)(amino)carbenes (cAACs) with the simplest main group element compounds such as main group hydrides lead to a broad variety of reaction products.[111, 198] Because of their different stereo-electronic properties,[202] NHCs and related molecules realize different pathways in their reactions with group 13 hydrides. NHC-stabilized boranes are reported to be remarkably stable.[203] Since the first isolation of carbene-stabilized boranes by Kuhn *et al.* their importance in main group chemistry increased rapidly because of their simple synthesis and high stability even against air and moisture.[204] The *Lewis* acid-base adducts (see Scheme III.1, III.I) are easily accessible *via* the reaction of the *in situ* generated NHCs with common stable borane sources such as (THF)·$BH_3$ or ($SMe_2$)·$BH_3$.[205] B-H bond activation is preferred in the reaction with cAACs due to the stronger $\pi$-accepting character of these molecules compared to NHCs,[112, 119, 190] and only one ($cAAC^{cy}$)·$BH_3$ adduct of a bulky carbene was reported by Bertrand *et al.* (Scheme III.1, III.II).[97] Furthermore, carbene-stabilized diboranes and diborenes are accessible by reduction of the carbene-stabilized (NHC)·$BBr_3$ or the selective splitting of dihydrogen with carbene-stabilized diborynes (see Scheme III.1, III.III & III.IV).[70, 206-209]
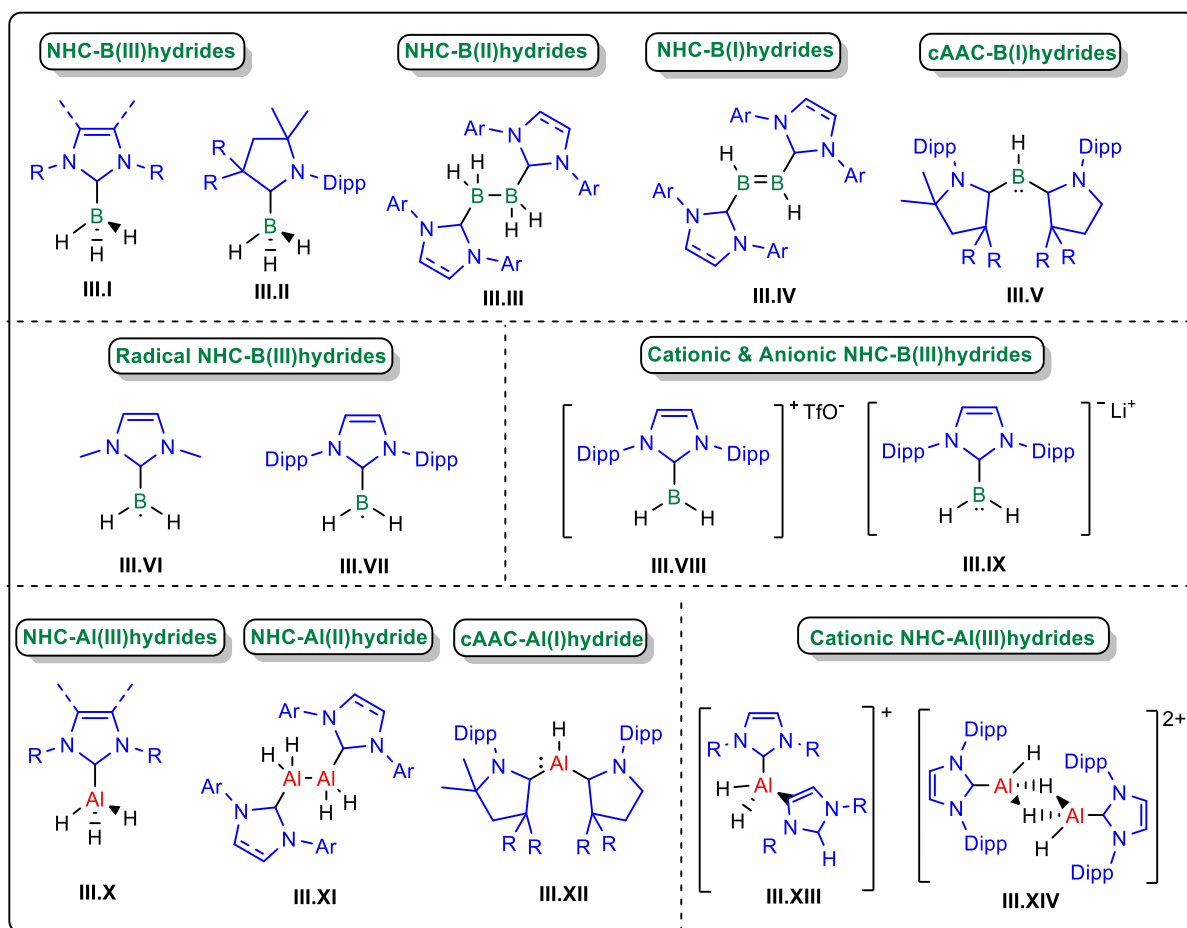
*Scheme III.1: NHC- and cAAC-stabilized group 13 hydrides.*

In 2011, Bertrand and coworkers reported the synthesis of the first parent borylene $(cAAC^{Cy})_2 \cdot BH$ by reduction of $(cAAC^{Cy}) \cdot BBr_3$ with $KC_8$ in presence of an additional equivalent $cAAC^{cy}$ (see Scheme III.1, III.V).[186, 210] Furthermore, a large number of neutral, NHC-stabilized borane radicals were reported (see Scheme III.1, III.VI & III.VII),[211-213] which are of interest due to their application in organic synthesis and in polymerization reactions.[214] These radicals were easily prepared *in situ* by hydrogen abstraction from the NHC borane adducts with hydrogen acceptors, e.g. AIBN or hydrogen peroxide. [213] Some rare and reactive cationic and anionic NHC-stabilized boranes are documented in the literature (see Scheme III.1, III.VIII & III.IX).[215-217]

The analogue NHC alane adducts were first reported by Arduengo *et al.* and can be synthesized from the reaction of the NHC with lithium aluminum hydride (see Scheme III.1, X).[29, 66] There are no examples of a stable adducts $(cAAC) \cdot AlH_3$ reported yet.

Jones *et al.* presented the first example of a neutral NHC-stabilized dialane *via* reaction of (Dipp$_2$Im)·AlH$_3$ with a magnesium(I) dimer (see Scheme III.1, XI).[73] Recently, Braunschweig *et al.* reported the synthesis of the first carbene-stabilized parent aluminum(I) hydride from reduction of (cAAC$^{Me}$)·AlCl$_2$(cAAC$^{Me}$H) with KC$_8$ (see Scheme III.1, XII). Aside from neutral carbene alane adducts there are some rare examples of cationic aluminum hydrides.[34, 45] Stephan *et al.* presented recently a dinuclear dicationic aluminum hydride [(Dipp$_2$Im)·AlH($\mu$-H)]$_2$$^{2+}$ in [(Dipp$_2$Im)·AlH($\mu$-H)]$_2$[B(C$_6$F$_5$)$_4$]$_2$) and a three-coordinated mononuclear dication [(Bn$_2$Im)$_2$·AlH]$_2$[B(C$_6$F$_5$)$_4$] (see Scheme III.1, III.XIV).[34] Jones and Stasch *et al.* reported the monocationic aluminum hydride [(Dipp$_2$Im)·AlH$_2$(*a*Dipp$_2$Im)]I ("*a*" denotes "abnormal" coordination) stabilized by one *normal* and one *abnormal* coordinated NHC (see Scheme III.1, III.XIII).[45]

Surprisingly, only a few reports exist currently on the reactivity of carbene-stabilized gallanes. Rivard and coworkers investigated the synthesis and reactivity of azido- and amido-substituted gallium hydrides to use these compounds as potential precursors to form HGaNH complexes and bulk gallium nitride (GaN).[149] Scheer *et al.* reported also just recently phosphido-substituted gallium hydrides as potential precursors for group 13/15 materials.[41] Braunschweig and coworkers synthesized a series of carbene-stabilized digallanes and investigated some substitution reactions of the halide substituent.[158]

We demonstrated earlier that reactions of NHCs or cAACs with selected boranes, diboron(4) esters or arylboronate esters lead to activation and (reversible) insertion of the carbene into the B-H, B-B or B-C bond and/or to ring expansion (RER) of the NHC or cAAC (see Scheme III.2).[90, 92, 107, 108] Recently we reported NHC ring expansion from the reaction of *i*Pr$_2$Im-stabilized (*i*Pr$_2$Im = 1,3-di*iso*propylimidazolin-2-ylidene) aluminum hydride, (*i*Pr$_2$Im)·AlH$_3$, with an additional equivalent of *i*Pr$_2$Im. The reaction of (*i*Pr$_2$Im)·AlH$_3$ with the sterically more demanding NHC Dipp$_2$Im (Dipp$_2$Im = bis(2,6-*iso*propylphenyl)imidazolin-2-ylidene) in a 2:1 ratio leads to the ring opening reaction (ROR) product (*i*Pr$_2$Im)·AlH$_2$(ROR-Dipp$_2$ImH$_2$)H$_2$Al·(*i*Pr$_2$Im) (see Scheme III.2). Furthermore, the reaction of NHC alane adducts such as (*i*Pr$_2$Im)·AlH$_3$ with cAAC$^{Me}$ leads to Al-H bond activation with insertion of the cAAC$^{Me}$ into the Al-H bond (see Scheme III.2).[66] Furthermore, we investigated the influence of the substitution of

hydride substituents with amide and phenolate groups on the reactivity of NHC-stabilized alane adducts and demonstrated that these compounds are not prone to undergo either RER or ROR upon reaction with additional NHC.[218] We also investigated the use of NHC alane adducts as hydride sources in the hydrodefluorination of fluoroaromatics and fluoroolefins.[39]
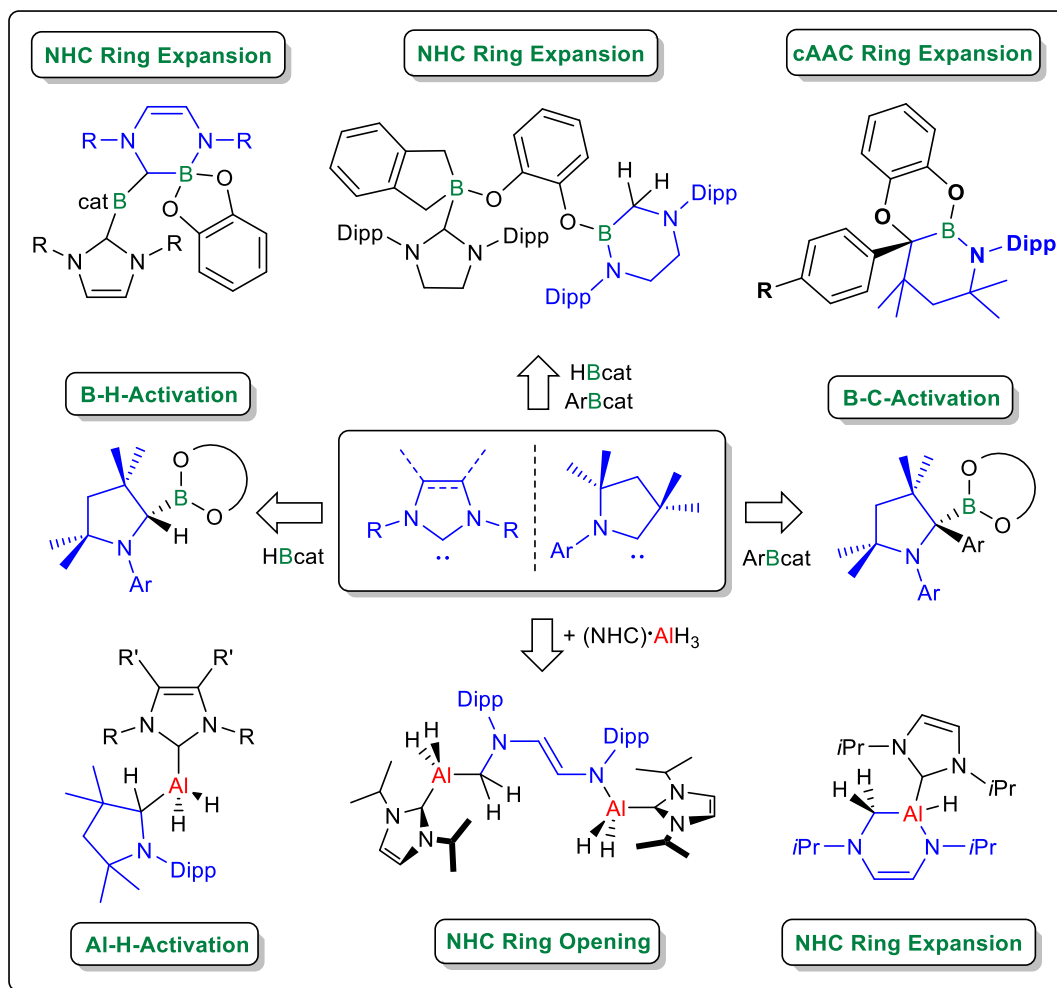


*Scheme III.2: Reactivity of NHCs and cAACs with boranes and alanes.*

Our investigations on synthesis and reactivity of NHC alane adducts drew our attention to the analogue gallane compounds. The synthesis of some NHC-stabilized gallanes, mono- and dichlorogallanes was reported before[48, 150] and it is known that *Lewis*-donor stabilized gallium hydrides are rather unstable and easily undergo reductive dehydrogenation. However, the substitution of hydrogen atoms by halide substituents

in these gallane adducts increases the Ga-H bond strength due to halide $\sigma$-electron withdrawal to stabilize the adduct with respect to dehydrogenation and decomposition (see also Chapter 2).[23, 150] Herein, investigations concerning the development of NHC gallane chemistry is reported, e.g. the synthesis and reactivity of novel carbene-stabilized gallanes and chlorogallanes with NHCs and cAAC[Me] with a focus on the influence of halide substitution on the reactivity and stability of these compounds.

## 3.2 Results and Discussion

Several synthetic routes are already reported in the literature to prepare NHC-stabilized *Lewis* acid-base adducts of gallanes and chlorogallanes.[31, 154, 156] One important method is the substitution of the trimethylamine ligand of the trimethylamine-gallane adduct $(NMe_3) \cdot GaH_3$ with NHCs.[31] A second important method is the dechlorohydrogenation of stable NHC-stabilized gallium chlorides, i.e. the reaction of $(NHC) \cdot GaCl_3$ with a hydride source, typically three equivalents of $K[HB^nBu_3]$.[149] A third method employs the reaction of the free NHC or its imidazolium salt with *in situ* generated unstable lithium gallium hydride $LiGaH_4$.[150] Following our studies on NHC-stabilized aluminum hydrides[66] we decided to use the latter method to synthesize the $(NHC) \cdot GaH_3$ adducts $(Me_2Im^{Me}) \cdot GaH_3$ **III-1**, $(iPr_2Im) \cdot GaH_3$ **III-2**, $(iPr_2Im^{Me}) \cdot GaH_3$ **III-3** and $(Dipp_2Im^H) \cdot GaH_3$ **III-4**. These adducts are accessible from the reaction of *in situ* generated $LiGaH_4$ with the corresponding NHC at -78 °C in diethyl ether (Scheme III.3). Further workup gave the adducts **III-1** – **III-4** as colorless crystalline solids in excellent purity and good isolated yield (**III-1**: 77 %, **III-2**: 52 %, **III-3**: 58 % **III-4**: 59 %).
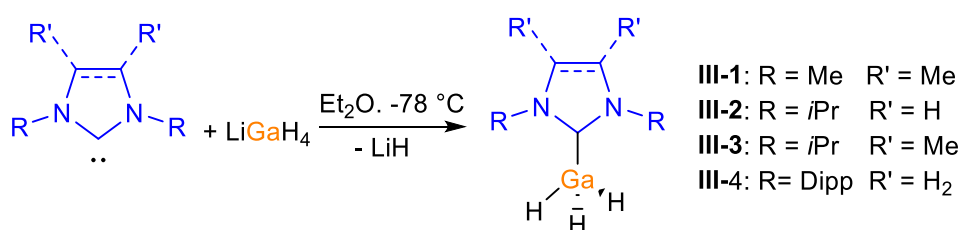


*Scheme III.3: Synthesis of the compounds $(Me_2Im^{Me}) \cdot GaH_3$ **III-1** and $(iPr_2Im) \cdot GaH_3$ **III-2**, $(iPr_2Im^{Me}) \cdot GaH_3$ **III-3** and $(Dipp_2Im^H) \cdot GaH_3$ **III-4**.*

The adducts **III-1** – **III-4** were characterized by multinuclear NMR, IR spectroscopy and elemental analysis. Selected NMR (ppm) and IR ($cm^{-1}$) data of **III-1** – **III-4** are summarized in Table III.1. The characteristic Ga-H bond stretching vibrations of **III-1** – **III-4** were observed at 1767 $cm^{-1}$ (**III-1**), 1797 $cm^{-1}$ (**III-2**), 1773 $cm^{-1}$ (**III-3**) and 1790 $cm^{-1}$ (**III-4**), which is in good accordance with the stretching frequency reported for $(iPr_2Im^{Me}) \cdot GaH_3$ at 1775 $cm^{-1}$.[31] In the ^{1}H NMR spectra the resonances of the Ga-H hydrides appear as very broad signals due to the bonding to the gallium atom, a

nucleus with a nuclear spin of I = 3/2 for both major isotopes ([69]Ga: 60.1%; [71]Ga: 39.9%) and quadrupole moments of 17.1 fm$^2$ ([69]Ga) and 10.7 fm$^2$ ([71]Ga), respectively. The gallium-bound hydrogen atoms of **III-1** – **III-4** were detected at 4.51 ppm (**III-1**), 4.56 ppm (**III-2**), 4.66 ppm (**III-3**) and 3.58 ppm (**III-4**). In the $^{13}$C{$^1$H} NMR spectrum the NHC carbene carbon atoms are also difficult to detect because of the direct neighborship to gallium, but were localized as weak and broadened resonances at 172.1 ppm (**III-1**), 173.3 ppm (**III-2**), 172.7 ppm (**III-3**) and 205.9 ppm (**III-4**), significantly high-field shifted compared to the resonances of the free carbenes at 212.7 ppm (Me$_2$Im$^{Me}$), 211.6 ppm (iPr$_2$Im) and 244.0 ppm (Dipp$_2$Im$^H$).[21] The molecular structures of (Me$_2$Im$^{Me}$)·GaH$_3$ **III-1** and (Dipp$_2$Im$^H$)·GaH$_3$ **III-4** (Figure III.1) were confirmed by X-Ray diffraction. The gallium center is in a tetrahedral environment, spanned by one NHC ligand and three hydrogen atoms. The angles between the NHC ligand and the hydrogen substituents are in a range between 108 and 118 °. The hydride and as well the carbene carbon atom bond length to the gallium center of Ga-C$_{NHC}$ 2.054 Å (**III-1**), 2.076 Å (**III-4**), Ga-H$_1$ 1.462 Å (**III-1**), 1.51(4) Å (**III-4**), Ga-H$_2$ 1.423 Å (**III-1**), 1.493 Å (**III-4**) and Ga-H$_3$ 1.544 Å (**III-1**), 1.483 Å (**III-4**) are in good agreement to the bond lengths detected in (iPr$_2$Im$^{Me}$)·GaH$_3$.[31]
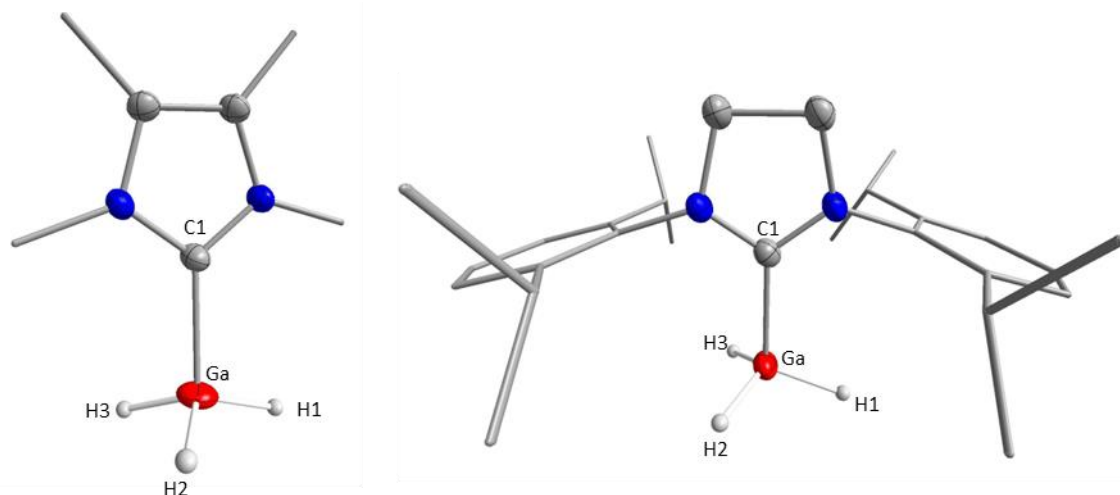


*Figure III.1: Molecular structure of (Me$_2$Im$^{Me}$)·GaH$_3$ **III-1** and (Dipp$_2$Im$^H$)·GaH$_3$ **III-4** in the solid state (ellipsoids set at 50% probability level). Hydrogen atoms with exception of those attached to gallium are omitted for clarity. Selected bond lengths [Å] and angles [°]: **III-1**: Ga-C1 2.0541(19), Ga-H1 1.46(3), Ga-H2 1.42(4), Ga-H3 1.54(4). C1-Ga-H1 109.0(13), C1-Ga-H2 100.4(15), C1-Ga-H3 108.6(15), H1-Ga-H2 108.(2), H1-Ga-H3 111.(2), H2-Ga-H3 119.(2); **III-4**: Ga-C1 2.0755(18), Ga-H1 1.51(4), Ga-H2 1.49(3), Ga-H3 1.48(3). C1-Ga-H1 101.7(17), C1-Ga-H2 106.1(12), C1-Ga-H3 99.3(11), H1-Ga-H2 111.6(19), H1-Ga-H3 112.5(16), H2-Ga-H3 114.(2).*

*Table III.1: Selected NMR (ppm) shifts and IR (cm$^{-1}$) stretching frequencies of the compounds (Me$_2$Im$^{Me}$)·GaH$_3$ **III-1**, (iPr$_2$Im)·GaH$_3$ **III-2**, (iPr$_2$Im$^{Me}$)·GaH$_3$ **III-3**, (Dipp$_2$Im$^H$) GaH$_3$ **III-4**, (iPr$_2$Im$^{Me}$)·GaH$_2$Cl **III-9**, (Dipp$_2$Im)·GaH$_2$Cl **III-10**, (Dipp$_2$Im$^H$)·GaH$_2$Cl **III-11**, (iPr$_2$Im$^{Me}$)·GaHCl$_2$ **III-12**, (Dipp$_2$Im)·GaHCl$_2$ **III-13**, (Dipp$_2$Im$^H$)·GaHCl$_2$ **III-14** and (cAAC$^{Me}$)·GaHCl$_2$ **III-15**.*

| | Ga-*H* | NCN | $\nu$Ga-H |
|---|---|---|---|
| | $^1$H NMR | $^{13}$C{$^1$H} NMR | |
| (Me$_2$Im$^{Me}$)·GaH$_3$ **III-1** | 4.51 | 172.1 | 1767 |
| (*i*Pr$_2$Im)·GaH$_3$ **III-2** | 4.56 | 173.3 | 1774 |
| (*i*Pr$_2$Im$^{Me}$)·GaH$_3$ **III-3** | 4.66 | 172.7 | 1773 |
| (Dipp$_2$Im$^H$) GaH$_3$ **III-4** | 3.57 | 205.9 | 1790 |
| (*i*Pr$_2$Im$^{Me}$)·GaH$_2$Cl **III-9** | 5.60 | 166.9 | 1836 |
| (Dipp$_2$Im)·GaH$_2$Cl **III-10** | 4.66 | 181.6 | 1878 |
| (Dipp$_2$Im$^H$)·GaH$_2$Cl **III-11** | 4.56 | 198.0 | 1877 |
| (*i*Pr$_2$Im$^{Me}$)·GaHCl$_2$ **III-12** | 6.18 | 160.8 | 1945 |
| (Dipp$_2$Im)·GaHCl$_2$ **III-13** | 5.19 | 167.9 | 1932 |
| (Dipp$_2$Im$^H$)·GaHCl$_2$ **III-14** | 5.08 | 191.1 | 1933 |
| (cAAC$^{Me}$)·GaHCl$_2$ **III-15** | 4.98 | - | 1946 |

Due to our work on the reactivity of NHC-stabilized alanes[66] (*vide supra*) we were interested in the behavior of the heavier gallium analogues. In contrast to NHC-stabilized aluminum hydrides, the *Lewis* acid-base adducts **III-1 – III-4** are unstable in solution when heated to the boiling point of benzene. This decomposition leads to the formation of the dihydroaminal NHC-H$_2$ (NHC = Me$_2$Im$^{Me}$, *i*Pr$_2$Im, *i*Pr$_2$Im$^{Me}$, Dipp$_2$Im$^H$) and elemental gallium, which was observed as metallic mirror. NHC-H$_2$ was identified by $^1$H NMR spectroscopy.

We also investigated the reaction of the adducts (NHC)·GaH$_3$ **III-1 – III-4** with additional equivalents of carbene (Me$_2$Im$^{Me}$, *i*Pr$_2$Im, *i*Pr$_2$Im$^{Me}$ and Dipp$_2$Im$^H$) at temperatures up to 90 °C in solution, as we have demonstrated earlier that for the corresponding

aluminum compounds the stability of the bis(NHC) adducts is much lower compared to the mono(NHC) adducts. We were not able to isolate any bis(NHC) adducts of the type $(NHC)_2 \cdot GaH_3$, but we identified either the formation of the bis(NHC) adducts $(NHC)_2 \cdot GaH_3$ (NHC = $Me_2Im^{Me}$, $Dipp_2Im^H$) in solution or fast NHC exchange in solution by $^1H$ NMR spectroscopy (Scheme III.4).



R = Me   R' = Me
R = *i*Pr   R' = H
R = *i*Pr   R' = Me
R= Dipp   R' = $H_2$
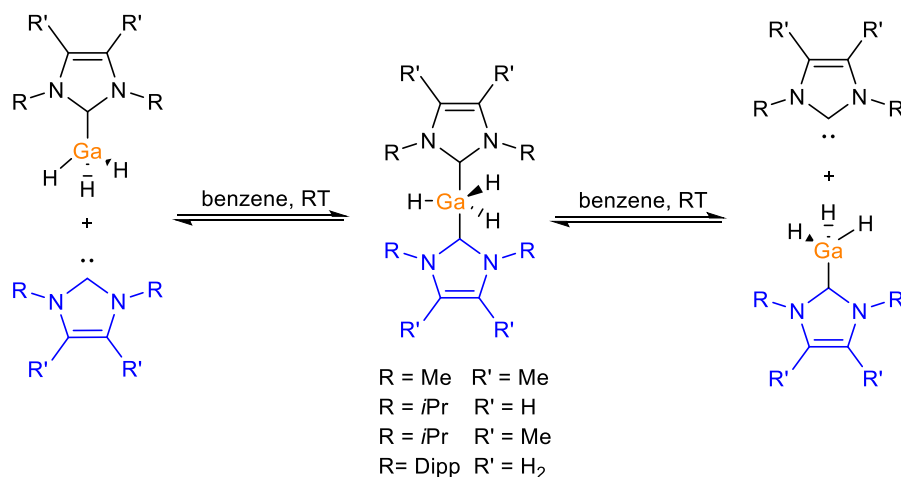
*Scheme III.4: Proposed fast NHC exchange in solution of the compounds **III-1 – III-4** after addition of another equivalent of the NHC.*

The reaction of $(Me_2Im^{Me}) \cdot GaH_3$ **III-1**, for example, with an additional equivalent of the NHC $Me_2Im^{Me}$ gives rise to only one set of signals for the NHC ligands in the $^1H$ and $^{13}C\{^1H\}$ spectra of the mixture, which lie in between the signals for compound **III-1** and the free NHC $Me_2Im^{Me}$. However, the signal of the NHC carbene carbon atom was detected at 164.0 ppm in the $^{13}C\{^1H\}$ spectrum, highfield shifted compared to the resonance observed for compound **III-1** (172.1 ppm) and the free NHC (212.7 ppm).[219] The fact that the NHC carbene carbon resonance of the bis(NHC) adduct $(Me_2Im^{Me})_2 \cdot GaH_3$ at 164.0 ppm is not located in-between the resonances of the NHC and $(Me_2Im^{Me}) \cdot GaH_3$ favors the formation of the bis(NHC) adduct $(NHC)_2 \cdot GaH_3$ in solution over a fast NHC exchange in solution. Similar five-coordinated species $(NHC)_2 \cdot AlH_3$ have been observed as intermediates for the ring expansion and ring opening of alane adducts. However, neither RER or ROR of the NHCs were observed for the gallane adducts upon heating these solutions to the boiling point of benzene for a couple of days. Instead, the formation of NHC-$H_2$ and decomposition to elemental

gallium was observed. If a combination of two different NHCs was used for this reaction, the preferential formation of NHC-H$_2$ of the added NHC was observed. We therefore assume that an uncoordinated NHC attacks the adduct and reacts as hydride acceptor.

Cyclic (alkyl)(amino)carbenes (cAACs) are stronger electrophiles and nucleophiles compared to NHCs and are thus more reactive with respect to E-H bond activation. To our surprise, neither cAAC$^{Me}$ nor [cAAC$^{Me}$H]$^+$BF$_4^-$ does react with *in situ* generated "LiGaH$_4$" in a salt methathesis reaction to yield an adduct (cAAC$^{Me}$)·GaH$_3$. Instead, both reaction pathways led to the formation of cAAC$^{Me}$H$_2$ and some unidentified decomposition products. We also tried to synthesize cAAC adducts of gallane by ligand exchange of (NHC)·GaH$_3$ adducts with cAAC$^{Me}$, which leads to insertion of the cAAC$^{Me}$ into the Ga-H bond. Similar to reactions as observed earlier for the alane adducts (NHC)·AlH$_3$,[66] different NHC gallane adducts (NHC)·GaH$_3$ were reacted with cAAC$^{Me}$ to afford the insertion products (NHC)·GaH$_2$(cAAC$^{Me}$H) (Scheme III.5). This reaction already proceeds at low temperatures and no intermediate bis(carbene) adducts of the type (NHC)·GaH$_3$·(cAAC$^{Me}$) were observed by NMR spectroscopy. The compounds (Me$_2$Im$^{Me}$)·GaH$_2$(cAAC$^{Me}$H) **III-5**, (*i*Pr$_2$Im$^{Me}$)·GaH$_2$(cAAC$^{Me}$H) **III-6** and (Dipp$_2$Im)·GaH$_2$(cAAC$^{Me}$H) **III- 7** were isolated from hexane solutions as colorless solids in moderate isolated yields (**III-5**: 31 %, **III-6**: 30 %. **III-7**: 49 %).



III-5: R = Me   R' = Me
III-6: R = *i*Pr   R' = Me
III-7: R= Dipp  R' = H
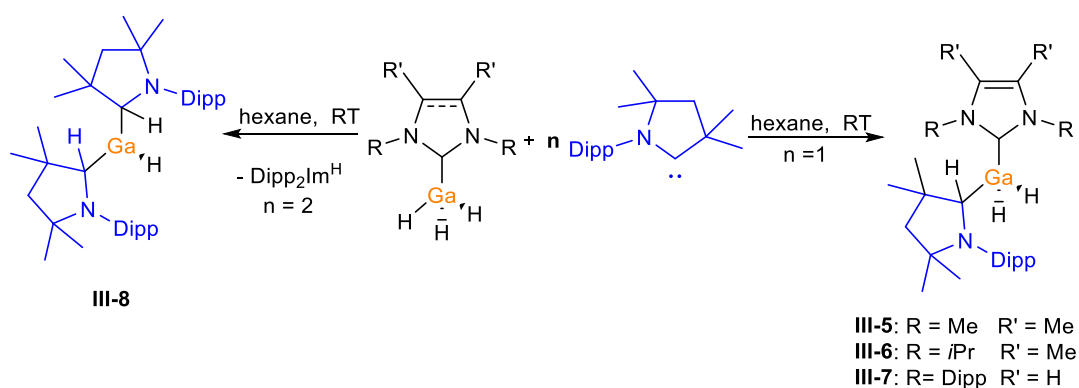
*Scheme III.5: Synthesis of the compounds (Me$_2$Im$^{Me}$)·GaH$_2$(cAAC$^{Me}$H)* **III-5**, *(iPr$_2$Im$^{Me}$)·GaH$_2$(cAAC$^{Me}$H)* **III-6** *and (Dipp$_2$Im)·GaH$_2$(cAAC$^{Me}$H)* **III-7** *and (cAAC$^{Me}$H)$_2$GaH* **III-8**.

No NHC-stabilized cAAC insertion product into the Ga-H bond was observed for the reaction of (Dipp$_2$Im$^H$)·GaH$_3$ **III-4**, i.e. the gallane adduct of the backbone-saturated NHC Dipp$_2$Im$^H$, with cAAC$^{Me}$. Instead, the reaction with two equivalents of cAAC$^{Me}$ led to the 1,1-hydrogallation of both cAAC molecules with elimination of Dipp$_2$Im$^H$ and formation of the dialkylgallane (cAAC$^{Me}$H)$_2$GaH **III-8** in moderate yield (35 %, Scheme III.5). Compound **III-8** represents the first isolated example of a neutral monomeric dialkyl gallium hydride. The molecular structure of **III-8** was determined by X-ray diffraction (Figure III.2). Compound **III-8** crystallizes in form of the *rac(S,S)*-isomer (in a 95:5 % disorder with the *rac(R,R)*-isomer) in the orthorhombic space group P*b*cn. The molecular structure as well as bond length and bond angles of the major isomer *rac(S,S)*-**III-8** are presented in Figure III.3, which reveals the presence of two chiral carbon centers at the former cAAC$^{Me}$ carbene carbon atoms.
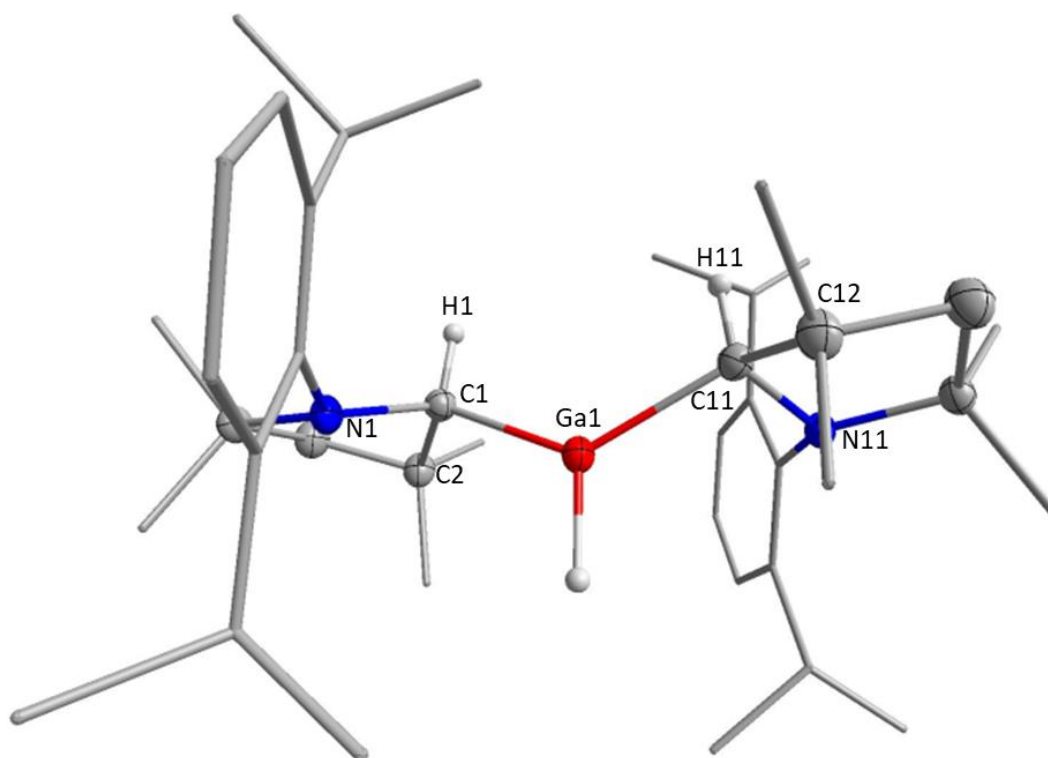


*Figure III.2: Molecular structure of rac(S,S)-* **III-8** *in the solid state (ellipsoids set at 50% probability level). Hydrogen atoms with exception of those attached to gallium and to C1 as well as the disordering are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ga1–C1 2.0094(14), Ga1–C1' 2.0094(14), Ga1–H1A 1.40(3), C1–N8 1.4711(16), C1–C23 1.5446(18), C1–H21 0.978(17); C1-Ga1-C1' 129.69(8), C1-Ga1-H1A 115.16(4), C1-Ga1-H1A 115.16(4), N8-C1-C23 101.92(10), N8-C1-Ga1 108.89(9), C23-C1-Ga1 116.68(9), N8-C1-H21 112.7(10), C23-C1-H21 108.0(10), Ga1-C1-H21 108.6(10).*

Compound **III-8** was characterized by multinuclear NMR spectroscopy, elemental analysis and IR spectroscopy. The ${}^1$H NMR spectrum of compound **III-8** in thf-d$_8$ at room temperature shows the resonances of a 1:1.3 mixture of the *rac(S,S)/rac(R,R)*-isomer (which cannot be distinguished by NMR spectroscopy) and the *meso*-form of compound **III-8**. For example, the resonances of the cAAC-Dipp substituent *i*Pr methine protons split into two sets of two inequivalent septets at 3.23 ppm, 3.37 ppm, 3.89 ppm and 4.06 ppm together with two cAAC${}^{Me}$-C*H* signals at 3.72 ppm and 3.77 ppm and the corresponding ${}^{13}$C NMR resonances of the former carbene carbon atom at 76.9 ppm and 77.0 ppm. The Ga-*H* hydride was not detected by NMR spectroscopy due to the quadrupole moment of the gallium nucleus, but a characteristic Ga-H bond stretch was observed at 1921 cm${}^{-1}$ in the solid-state IR spectrum of the compound. We assume a (reversible) equilibrium in solution between *meso*-**III-8** and *rac*-**III-8** (Scheme III.6), as ${}^1$H-${}^1$H NOESY/COSY NMR studies at room temperature show site exchange of the C$_{Dipp}$-H and C$_{cAAC}$-H protons.

A plausible pathway for the isomerization of **III-8** would be the hydride migration from a cAAC${}^{Me}$-C*H* substituent to the gallium atom to form the tetrahedral intermediate (cAAC${}^{Me}$)·GaH$_2$(cAAC${}^{Me}$H) *int*-**III-8**, which was not observed by NMR spectroscopy. Insertion of the cAAC${}^{Me}$ back into one of the Ga-H bonds (or hydride migration of a gallium hydride to the cAAC) results in an inversion of one of the stereocenters of one cAAC${}^{Me}$ ligand in *int*-**III-8** to produce either *meso*-**III-8** or *rac*-**III-8** (see Scheme III.6).
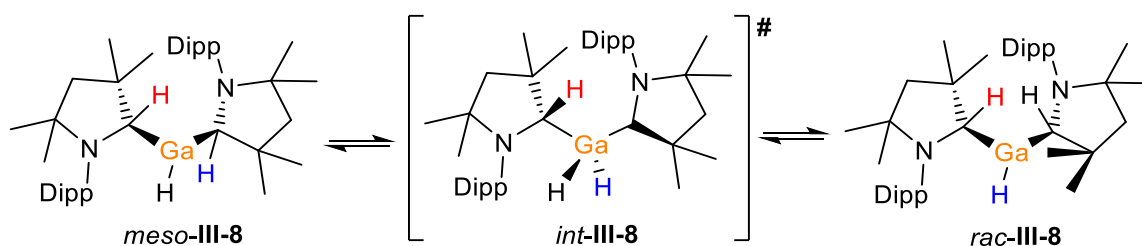


*Scheme III.6: Proposed mechanism of the isomerization of meso-**8** to rac-**8** in solution.*

*rac(R,R)*-**8**: + 2.9 kJ/mol

*rac(S,S)*- **8**: + 0.1 kJ/mol

*meso*-**8**: 0.0 kJ/mol
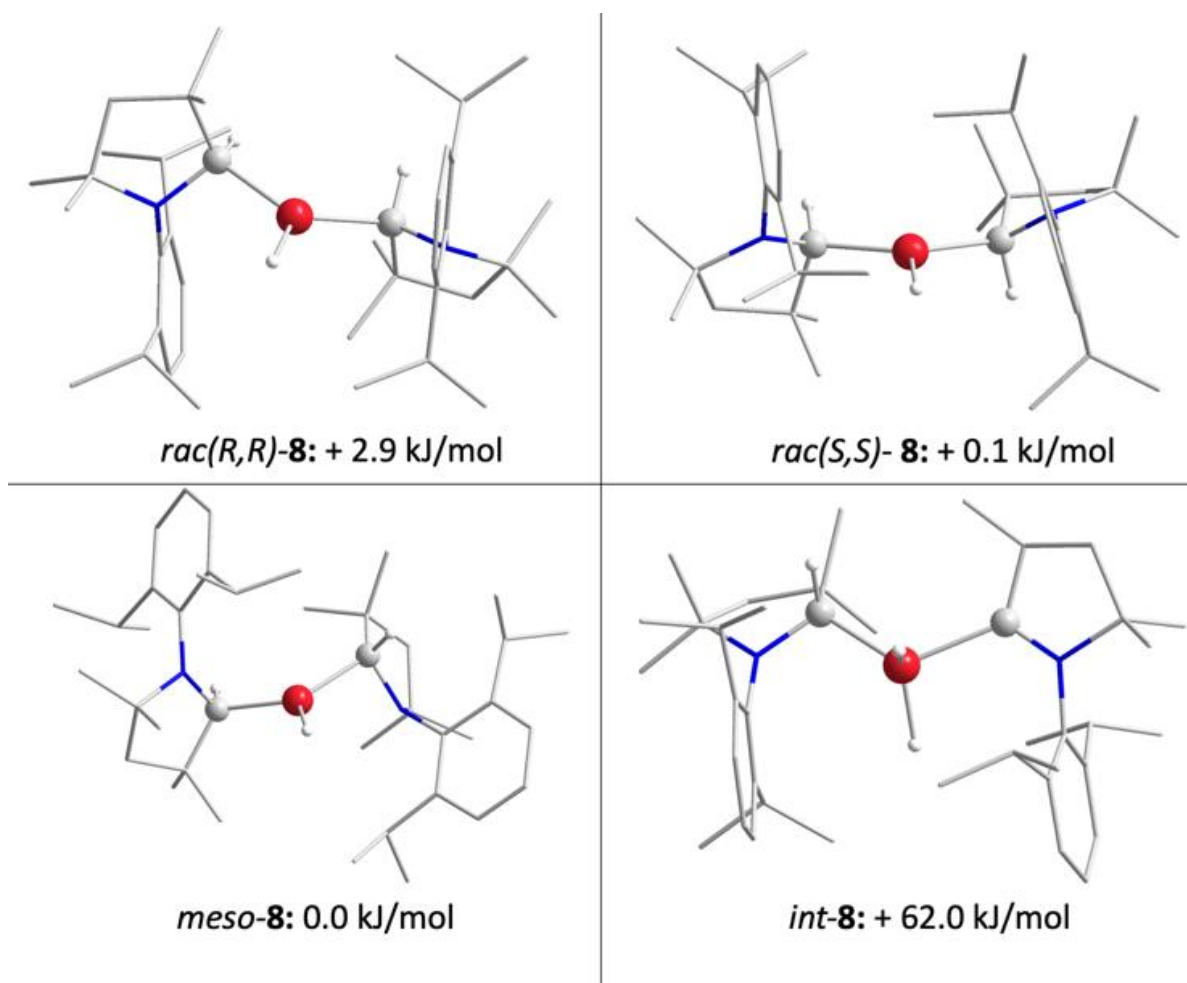
*int*-**8**: + 62.0 kJ/mol

*Figure III.3: DFT optimized (M06-2X/Ga: def2-TZVP, C, H, N: def2-SVP) structures and relative energies of different isomers of **III-8**.*

DFT calculations (M06-2X/Ga: def2-TZVP, C, H, N: def2-SVP, see Figure III.3) have been performed on the compounds (cAAC$^{Me}$H)$_2$GaH *meso*-**III-8**, *rac(R,R)*-**III-8**, *rac(S,S)*-**III-8** and (cAAC$^{Me}$)·GaH$_2$(cAAC$^{Me}$H) *int*-**III-8**. The energies calculated for *meso*-**III-8** and *rac(S,S)*-**III-8** are nearly the same and differ only by 0.1 kJ/mol, which lies within the accuracy of the method employed. The isomer *rac(R,R)*-**III-8** lies only 2.9 kJ/mol above *meso*-**III-8** and the small energy differences calculated for these diastereomer explain the mixture observed in the NMR spectrum of **III-8**. The compound *int*-**III-8** is also a minimum on the energy hypersurface of **III-8**, but 62.0 kJ/mol higher in energy compared to *meso*-**III-8**. If the isomerization process of **III-8** proceeds *via* hydride migration from a cAAC$^{Me}$-C*H* substituent to the gallium atom *via* (cAAC$^{Me}$)·GaH$_2$(cAAC$^{Me}$H) *int*-**III-8**, the barrier for this process should be at least 62.0 kJ/mol and the process should be feasible at room temperature.

Stephan *et al.* recently reported the interconversion of an analogous aluminum diastereomers (cAAC$^{Et}$H)$_2$AlH, which has been obtained from the reaction of (NEtMe$_2$) ·AlH$_3$ with two equivalents of cAAC$^{Et}$. DFT calculations at the M06-2X/def2-SVP level of theory revealed a computed ΔH of 14.2 kJ/mol for the conversion of the *meso-* to the *rac*-isomer of the aluminum compound, which was also in good agreement with the NMR experiments.[120] Stephan *et al.* did also not succeed in detecting the corresponding aluminum dihydride either. A similar 1,2-hydride shifting mechanism was also proposed for the formation of (cAAC$^{Me}$)·BH$_2$(cAAC$^{Me}$H) by Braunschweig *et al.*, who isolated the cAAC-stabilized dihydroborane (cAAC$^{Me}$)·BH$_2$(cAAC$^{Me}$H), i.e. the boron analogue of int-**III-8**.[220] NMR data and DFT calculations performed on (cAAC$^{Me}$)·BH$_2$(cAAC$^{Me}$H) revealed that the hydrogen on the former carbene carbon atom exchanges rapidly with the boron-bound hydrides. According to DFT calculations (SMD(thf), ONIOM [M06-2X/6-311+G(d),PM6]), the latter compound is 33.5 kJ/mol more stable than (cAAC$^{Me}$H)$_2$BH, which in turn defied isolation and characterization. Thus, the chemistry of boranes and alanes or gallanes seem to be complementary, which presumably reflects the different E-H bonding energies for B-H vs. Al-H and Ga-H. Whereas the minimum of the equilibrium between (cAAC$^{R}$)·EH$_2$(cAAC$^{R}$H) and (cAAC$^{R}$H)$_2$EH (E = B, Al, Ga) lies on the side of the dihydroborane (cAAC$^{Me}$)·BH$_2$(cAAC$^{Me}$H) for the boron compounds, the global energy minimum lies for the aluminum and gallium compounds on the side of the di(alkyl)monohydride (cAAC$^{R}$H)$_2$EH (E = Al, Ga).

The gallium bis(alkyl) compound **III-8** is stable in solution up to the boiling point of benzene and does not react with an additional equivalent of cAAC$^{Me}$ or NHC. This is in contrast to the behavior of (cAAC$^{Et}$H)$_2$AlH, which leads upon heating to the C-H bond activation of one of the methyl groups of a Dipp moiety. [120] The compounds **III-5** – **III-7** (Scheme III.5) are also stable up to 90 °C in solution for several days and no ring expansion or related decomposition occurs. Furthermore, the compounds **III-5** – **III-7** do not react with additional cAAC$^{Me}$ in a ligand exchange or insertion reaction. Compounds **III-5** – **III-7** were characterized by multinuclear NMR spectroscopy, elemental analysis and IR spectroscopy. Important spectroscopic data are summarized in Table III.2. Due to the chirality of the former carbene carbon atom of the cAAC$^{Me}$ the $^1$H and $^{13}$C{$^1$H} NMR spectra show resonances for each hydrogen and carbon atom separately. For example, the resonances of the cAAC$^{Me}$ methine protons

of $(i\text{Pr}_2\text{Im}^{Me})\cdot\text{GaH}_2(\text{cAAC}^{Me}\text{H})$ **III-6** emerge as two septets at 3.82 ppm and 4.51 ppm. The methine protons of the NHC ligand remain equivalent due to the free rotation around the Ga-$C_{NHC}$ axis. The remaining Ga-$H$ protons are detected as two strongly broadened doublets (see Table III.2). In the $^{13}C\{^1H\}$ NMR spectra the resonances of the former cAAC$^{Me}$ carbene carbon atom are significantly shifted from free cAAC$^{Me}$ at 313.5 ppm[221] or coordinated cAAC at ca. 240 ppm[113] to signals in a range between 67.2 and 69.8 ppm. The resonances of the NHC carbene carbon atoms at 174.4 ppm (**III-5**), 175.3 ppm (**III-6**) and 183.6 ppm (**III-7**) are in good agreement with the signals observed for the corresponding (NHC)·GaH$_3$ adducts (172.1 ppm **III-1** and 172.7 ppm **III-3**).

*Table III.2: Selected NMR (ppm) shifts and IR (cm$^{-1}$) stretching vibrations of the compounds $(Me_2Im^{Me})\cdot GaH_2(cAAC^{Me}H)$ **III-5**, $(iPr_2Im^{Me})\cdot GaH_2(cAAC^{Me}H)$ **III-6**, $(Dipp_2Im)\cdot GaH_2(cAAC^{Me}H)$ **III-7** and $(iPr_2Im^{Me})\cdot GaCl_2(cAAC^{Me}H)$ **III-17**.*

| | Ga-$H$ $^1$H NMR | NCN $^{13}C\{^1H\}$ NMR | cAACCH $^{13}C\{^1H\}$ NMR | $\nu$Ga-H |
|---|---|---|---|---|
| (Me$_2$Im$^{Me}$)·GaH$_2$(cAAC$^{Me}$H) **III-5** | 3.73 | 174.4 | 68.8 | 1781 |
| (iPr$_2$Im$^{Me}$)·GaH$_2$(cAAC$^{Me}$H) **III-6** | 4.01 | 175.3 | 69.3 | 1813 |
| (Dipp$_2$Im)·GaH$_2$(cAAC$^{Me}$H) **III-7** | 3.26, 3.73 | 183.6 | 67.2 | 1781 |
| (iPr$_2$Im$^{Me}$)·GaCl$_2$(cAAC$^{Me}$H) **III-17** | - | 165.4 | 76.0 | - |

The molecular structures of **III-5** – **III-7** were determined by X-ray diffraction (Figure III.4). The compounds (Me$_2$Im$^{Me}$)·GaH$_2$(cAAC$^{Me}$H) **III-5** and (Dipp$_2$Im)·GaH$_2$(cAAC$^{Me}$H) **III-7** crystallize in the triclinic space group $P\bar{1}$, (iPr$_2$Im$^{Me}$)·GaH$_2$(cAAC$^{Me}$H) **III-6** in the monoclinic space group $P2_1/c$. Each of these molecules adopt a tetrahedral coordination at the gallium atom, spanned by the NHC (Me$_2$Im$^{Me}$ **III-5**, iPr$_2$Im$^{Me}$ **III-6** and Dipp$_2$Im **III-7**), the cyclic(alkyl)(amino)carbene alkyl group and two hydride substituents. The Ga–$C_{NHC}$ bond length of **III-5** (2.0696 Å), **III-6** (2.1008 Å) and **III-7** (2.1094 Å) differ only marginally from the gallium NHC carbon atom bond distance observed in (Me$_2$Im$^{Me}$)·GaH$_3$ **III-1** (2.0540 Å). The Ga–$C_{cAACH}$ bond lengths of

2.0332(6) Å, 2.0340(7) Å and 2.0294(8) Å are close to values observed for other NHC stabilized gallium alkyl compounds (2.0 to 2.1 Å), e.g. for $(Me_2Im^{Me}) \cdot GaHCp*_2$ (2.057(5) Å) and $(Dipp_2Im) \cdot Ga(CH_2\{Si(CH_3)\})_3$ (2.0034(15) Å).[64, 198]
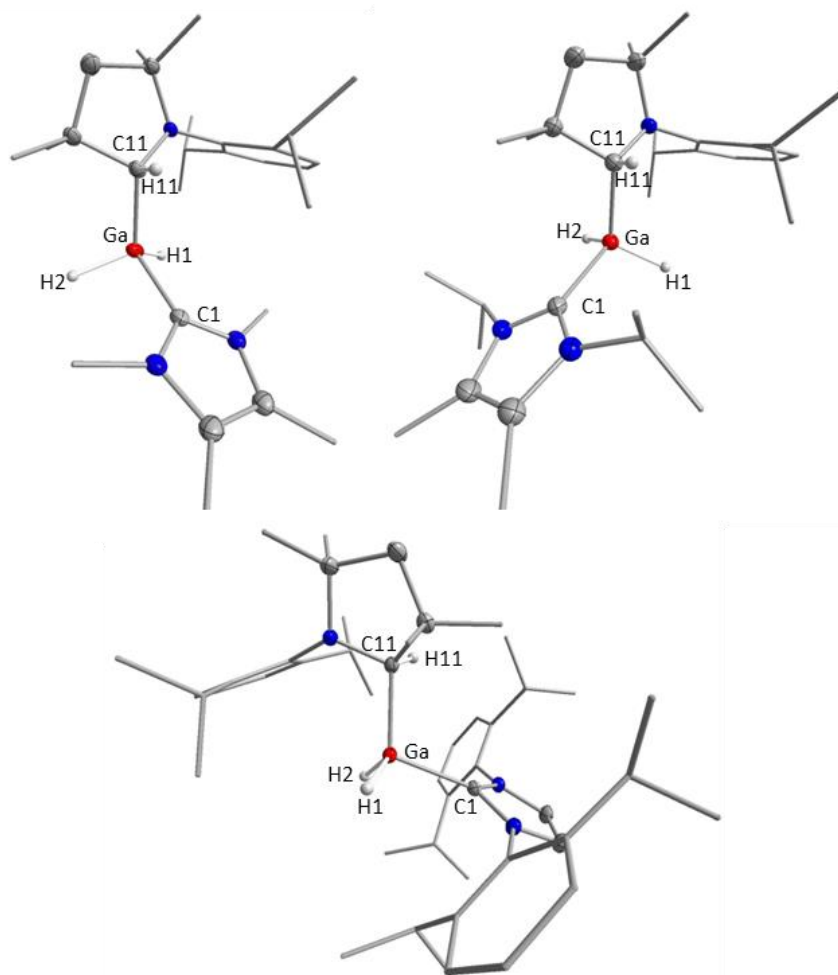


*Figure III.4: Molecular structures of $(Me_2Im^{Me}) \cdot GaH_2(cAAC^{Me}H)$ **III-5** (top left), $(iPr_2Im^{Me}) \cdot GaH_2(cAAC^{Me}H)$ **III- 6** (top right) and $(Dipp_2Im) \cdot GaH_2(cAAC^{Me}H)$ **III-7** (bottom) in the solid state (ellipsoids set at 50% probability level). Hydrogen atoms with exception of those attached to gallium and to the former carbene carbon atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: **III-5**: Ga–C1 2.0696(16), Ga–C11 2.0332(16), Ga–H1 1.58(3), Ga1–H2 1.43(3). C1-Ga-C11 108.70(6), C1-Ga-H1 102.1(10), C1-Ga-H2 106.3(11), H1-Ga-H2 111.4(15), H1-Ga-C11 110.2(10), H2-Ga-C11 117.0(11). **III-6**: Ga–C1 2.1008(15), Ga–C11 2.0340(15), Ga–H1 1.48(3), Ga–H2 1.43(3). C1-Ga-C11 108.70(6), C1-Ga-H1 104.3(10), C1-Ga-H2 105.7(9), H1-Ga-H2 113.3(13), H1-Ga-C11 110.8(10), H2-Ga-C11 113.5(9). **III-7**: Ga–C1 2.1094(13), Ga–C11 2.0294(13), Ga–H1 1.439(19), Ga–H2 1.48(2). C1-Ga-C11 110.70(5), C1-Ga-H1 101.3(8), C1-Ga-H2 100.7(9), H1-Ga-H2 112.5(11), H1-Ga-C11 114.5(8), H2-Ga-C11 115.2(9).*

NHC-stabilized monochlorogallanes (NHC)·GaH$_2$Cl were prepared by the stoichiometric dismutation of the NHC-stabilized gallanes (NHC)·GaH$_3$ and the corresponding NHC-stabilized gallium chlorides (NHC)·GaCl$_3$.[150] The adducts (*i*Pr$_2$Im$^{Me}$)·GaH$_2$Cl **III-9**, (Dipp$_2$Im)·GaH$_2$Cl **III-10** and (Dipp$_2$Im$^H$)·GaH$_2$Cl **III-11** were synthesized from the reaction of two equivalents of (NHC)·GaH$_3$ with one equivalent of (NHC)·GaCl$_3$ in toluene at 50 °C. The compounds **III-9** - **III-11** were obtained as pure colorless microcrystalline powders in good yield (**III-9**: 77 %, **III-10**: 72 % and **III-11**: 69 %, see Scheme III.7).
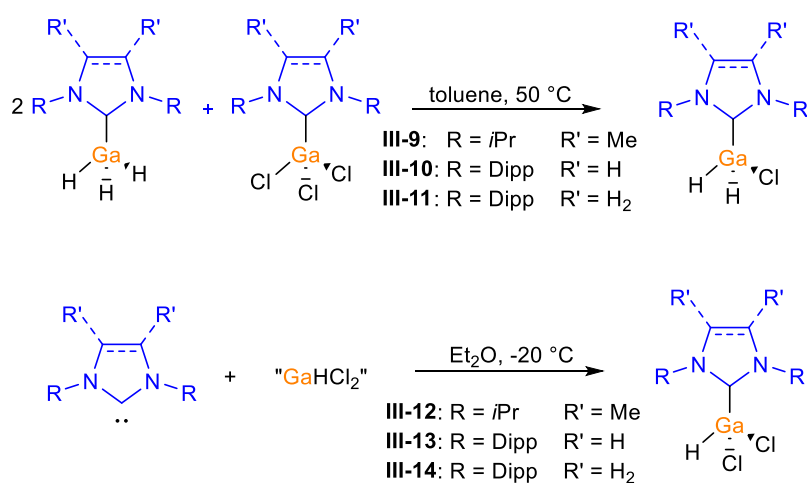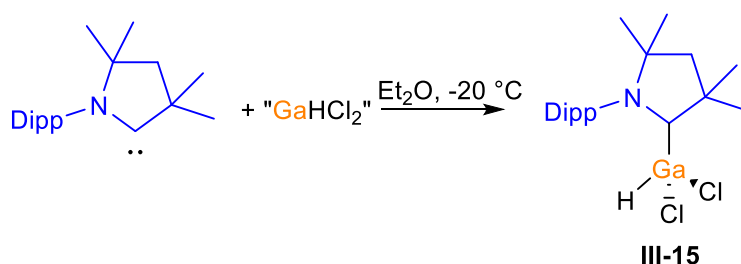


*Scheme III.7: Synthesis of the compounds (iPr$_2$Im$^{Me}$)·GaH$_2$Cl **III-9**, (Dipp$_2$Im)·GaH$_2$Cl **III-10**, (Dipp$_2$Im$^H$)·GaH$_2$Cl **III-11**, (iPr$_2$Im$^{Me}$)·GaHCl$_2$ **III-12**, (Dipp$_2$Im)·GaHCl$_2$ **III-13** and (Dipp$_2$Im$^H$)·GaHCl$_2$ **III-14**.*

For the synthesis of NHC-stabilized dichlorogallanes (NHC)·GaHCl$_2$ we have found it advantageous not to proceed *via* a similar procedure, i.e. dismutation of one equivalent (NHC)·GaH$_3$ adduct with two equivalents (NHC)·GaCl$_3$, but to react *in situ* generated "GaHCl$_2$" with the corresponding NHC. Thus, the dichlorogallane adducts (*i*Pr$_2$Im$^{Me}$)·GaHCl$_2$ **III-12** and (Dipp$_2$Im)·GaHCl$_2$ **III-13** were prepared from the reaction of gallium trichloride with an excess of triethylsilane, followed by stabilization of the *in situ* generated "GaHCl$_2$" with the corresponding NHC. (*i*Pr$_2$Im$^{Me}$)·GaHCl$_2$ **III-12** and (Dipp$_2$Im)·GaHCl$_2$ **III-13** were isolated as pure colorless solids in very good yield (**III-12**: 83 %, **III-13**: 73 %) and purity (see Scheme III.7). Only for the synthesis of (Dipp$_2$Im$^H$)·GaHCl$_2$ **III-14** the dismutation of one equivalent of the (Dipp$_2$Im$^H$)·GaH$_3$

adduct with two equivalents of $(Dipp_2Im^H)\cdot GaCl_3$ proved to be more efficient and compound **III- III-14** was isolated as colorless solid in good yield (**III-14**: 78 %, see Scheme III.7).

The compounds **III-9** – **III-14** were characterized by multinuclear NMR, IR spectroscopy and elemental analysis. Selected NMR (ppm) and IR ($cm^{-1}$) data of the compounds **III-9** – **III-14** are summarized in Table III.1. The characteristic Ga-H bond stretching vibrations of the compounds **III-9** – **III-14**, which were observed in the range between 1836 – 1878 $cm^{-1}$ and 1932-1945 $cm^{-1}$ (Table 4), are in good agreement with those reported for the adduct $(Mes_2Im)\cdot GaH_2Cl$ at 1870 $cm^{-1}$ earlier.[150] In the $^1H$ NMR spectra of **III-9** – **III-14** the Ga-*H* shifts appear as broad singlets at 5.60 ppm (**III-9**), 4.66 ppm (**III-10**), 4.56 ppm (**III-11**), 6.18 ppm (**III-12**), 5.19 ppm (**III-13**) and 5.08 ppm (**III-14**). In the $^{13}C\{^1H\}$ NMR spectrum the carbene carbon atom gives rise to a resonance at 166.9 ppm (**III-9**), 181.6 ppm (**III-10**), 198.0 ppm (**III-11**), 160.8 ppm (**III-12**), 167.9 ppm (**III-13**) and 191.1 ppm (**III-14**), significantly shifted compared to the resonance of the corresponding uncoordinated NHCs and in accordance for other NHC adducts e.g. $(Mes_2Im)\cdot GaH_2Cl$ at 172.3 ppm.[150]

As noted above, we were not able to synthesize $(cAAC^{Me})\cdot GaH_3$ from either the reaction of $cAAC^{Me}$ or $[cAAC^{Me}H]^+BF_4^-$ with *in situ* generated "LiGaH₄" and the use of NHC adducts $(NHC)\cdot GaH_3$ leads to insertion of the $cAAC^{Me}$ into the Ga-H bond. To our surprise, the reaction of *in situ* generated "GaHCl₂" with $cAAC^{Me}$ afforded cleanly the adduct $(cAAC^{Me})\cdot GaHCl_2$ **III-15** in very good yield (74 %, see Scheme III.8).



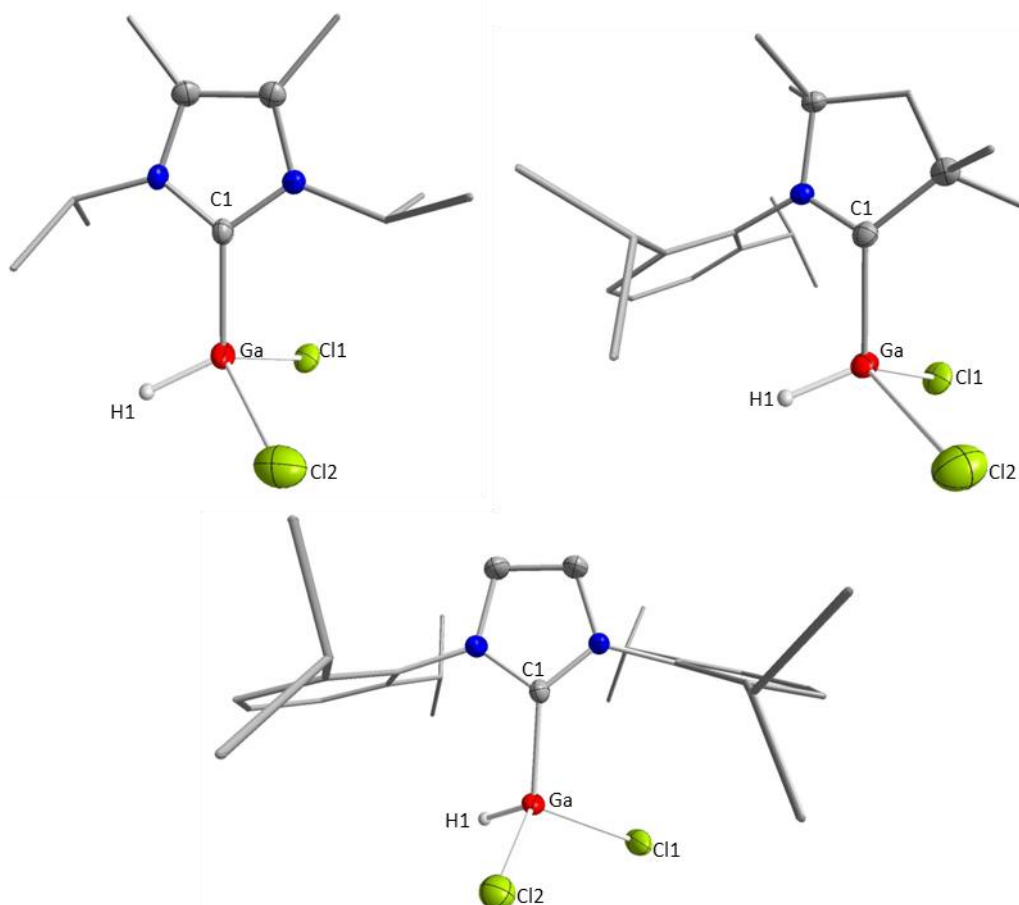*Scheme III.8: Synthesis of the compound $(cAAC^{Me})\cdot GaH_2Cl$ **III-15**.*

*Figure III.5: Molecular structures of (iPr$_2$Im$^{Me}$)·GaHCl$_2$ III-12 (top left), (Dipp$_2$Im)·GaHCl$_2$ III-13 (bottom) and (cAAC$^{Me}$)·GaHCl$_2$ III-15 (top right) in the solid state (ellipsoids set at 50% probability level). Hydrogen atoms with exception of those attached to gallium were omitted for clarity. Selected bond lengths [Å] and angles [°] III-12: Ga–C1 2.0194(4), Ga–H1 1.51(8), Ga–Cl1 2.2165(13), Ga–Cl2 2.2138(13). C1-Ga-H1 120.(3), C1-Ga-Cl1 106.11(14), C1-Ga-Cl2 104.46(11), H1-Ga-Cl1 112.(3), H1-Ga-Cl2 108.(3), Cl1-Ga-Cl2 105.95(5). III-13: Ga–C1 2.0337(18), Ga–H1 1.61(2), Ga1–Cl1 2.1956(5), Ga–Cl2 2.2165(5). C1-Ga-H1 116.8(8), C1-Ga-Cl1 110.16(5), C1-Ga-Cl2 103.70(5), H1-Ga-Cl1 106.6(8), H1-Ga-Cl2 114.0(8), Cl1-Ga-Cl2 104.98(2). III-15: Ga–C1 2.053(2), Ga–H1 1.42(3), Ga–Cl1 2.2149(6), Ga–Cl2 2.2168(6). C1-Ga-H1 116.2(13), C1-Ga-Cl1 106.38(6), C1-Ga-Cl2 105.85(6), H1-Ga-Cl1 109.7(12), H1-Ga-Cl2 113.4(13), Cl1-Ga-Cl2 104.46(3).*

In this case no insertion of the cAAC$^{Me}$ carbene carbon atom into the Ga-H bond occurred, and so far, no other *Lewis* acid-base adduct of cAACs with a gallium hydride has been reported. The reaction of cAACs with aluminum and gallium hydrides preferentially led to insertion of cAAC into the E-H bond (E = Al, Ga) which was demonstrated by us and others previously.[66,120,121] Compound **III-15** was characterized by NMR spectroscopy, elemental analysis and IR spectroscopy. The Ga-H proton was detected as a broad singlet at 4.98 ppm in the $^1$H NMR spectrum, the

resonance of the cAAC$^{Me}$ carbene carbon atom was not observed in the $^{13}$C{$^1$H} NMR spectrum due to the quadrupole moment of the bonding partner gallium.

The molecular structures of (*i*Pr$_2$Im$^{Me}$)·GaHCl$_2$ **III-12**, (Dipp$_2$Im)·GaHCl$_2$ **III-13** and (cAAC$^{Me}$)·GaHCl$_2$ **III-15** were determined by X-Ray diffraction and are shown in Figure III.5. (*i*Pr$_2$Im$^{Me}$) GaHCl$_2$ **III-12** crystallizes in the monoclinic space group *Cc*, (Dipp$_2$Im)·GaHCl$_2$ **III-13** in *P*2$_1$/*c* and (cAAC$^{Me}$)·GaHCl$_2$ **III-15** in the orthorhombic space group Pbca. These three molecules adopt a tetrahedral geometry at gallium, spanned by the carbene (*i*Pr$_2$Im$^{Me}$ **III-12**, Dipp$_2$Im **III-13** and cAAC$^{Me}$ **III-15**), the hydride and two chloride substituents. The Ga-C$_{Carbene}$ bond length of 2.0186 Å (**III-12**), 2.0337 Å (**III-13**) and 2.0532 Å (**III-15**) differ only marginally from the Ga-C$_{Carbene}$ bond distance reported earlier for (Mes$_2$Im)·GaHCl$_2$ (2.0056 Å).[150]

We and others reported earlier a much higher thermal stability of NHC alane adducts (NHC)·AlH$_3$ compared to the gallium analogues (NHC)·GaH$_3$ (*vide supra*), whereas NHC adducts of gallium trichloride (NHC)·GaCl$_3$ are stable in solution at least to the reflux temperature of toluene. Thus, we were interested whether this increase in stability is also reflected for the adducts of gallium hydrido chlorides. Cole and McKay *et al.* demonstrated earlier that thermal decomposition occurs for (Mes$_2$Im)·GaHCl$_2$ upon heating in solution to the boiling point of toluene and they characterized Mes$_2$ImH$_2$ and the imidazolium salt [Mes$_2$ImH]$^+$Cl$^-$ as products of the decomposition process *via* $^1$H NMR spectroscopy.[155] Heating solutions of the NHC- and cAAC$^{Me}$-stabilized dichlorogallanes **III-12** - **III-14** to the boiling point of benzene over several days does not lead to any changes in the $^1$H NMR spectra. However, when a solution of (cAAC$^{Me}$)·GaHCl$_2$ **III-15** was heated to the boiling point of toluene decomposition to (cAAC$^{Me}$)·GaCl$_3$ , cAAC$^{Me}$H$_2$ and other unidentified species occur, but no insertion of the cAAC into the Ga-H bond or formation of the digallane [(cAAC$^{Me}$)·GaCl$_2$]$_2$ with H$_2$ release was observed.

As presented above, insertion of the cAAC into the Ga-H bond was achieved when the NHC gallane adducts were employed as the gallium source. Similarly, we also tried to react the compounds (NHC)·GaH$_2$Cl and (NHC)·GaHCl$_2$ (NHC = *i*Pr$_2$Im$^{Me}$, Dipp$_2$Im, Dipp$_2$Im$^H$) and (cAAC$^{Me}$)·GaHCl$_2$ **III-15** with an additional equivalent cAAC$^{Me}$. No reaction occurred for **III-15**, presumably due to steric shielding (cAAC$^{Me}$ is larger as Dipp$_2$Im),[113] but the adducts of the smaller NHCs such as (*i*Pr$_2$Im$^{Me}$)·GaH$_2$Cl **III-9** and

($i$Pr$_2$Im$^{Me}$)·GaHCl$_2$ **III-12** react selectively with insertion of the cAAC carbene carbon atom into the Ga-H bond (Scheme III.9). The compounds ($i$Pr$_2$Im$^{Me}$)·GaHCl(cAAC$^{Me}$H) **III-16** and ($i$Pr$_2$Im$^{Me}$)·GaCl$_2$(cAAC$^{Me}$H) **III-17** are stable in solution, and further cAAC$^{Me}$ insertion molecule into the Ga-H bond of ($i$Pr$_2$Im$^{Me}$)·GaHCl(cAAC$^{Me}$H) **III-16** nor the exchange of the NHC with cAAC$^{Me}$ was observed for ($i$Pr$_2$Im$^{Me}$)·GaCl$_2$(cAAC$^{Me}$H) **III-17**.



**16**: X = H
**17**: X = Cl
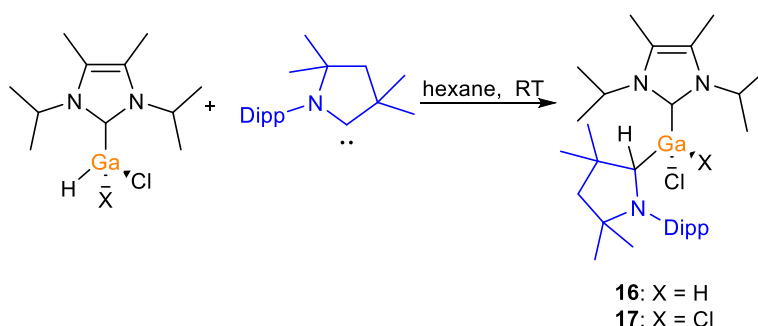
*Scheme III. 9: Synthesis of the compounds (iPr$_2$Im$^{Me}$)·GaHCl(cAAC$^{Me}$H)* **III-16** *and (iPr$_2$Im$^{Me}$)·GaCl$_2$(cAAC$^{Me}$H)* **III-17**.

The insertion of cAAC$^{Me}$ into the Ga-H bond of ($i$Pr$_2$Im$^{Me}$)·GaH$_2$Cl leads to the formation of diastereomers as both the Ga central atom and the (former) cAAC$^{Me}$ carbene carbon atom are stereocenters in the product. Thus, two sets of signals were observed in the $^1$H and $^{13}$C{$^1$H} NMR spectra of **III-16**. Integration of the $^1$H NMR spectrum shows that the product was formed as a 1:1 racemic mixture of the complexes, which is in accordance with the molecular structure of this compound (Figure III.6). Complex **III-16** crystallizes in the achiral space group $P\bar{1}$ with two stereoisomers in the asymmetric unit, i.e. the R(Ga)S(C)-isomer and the S(Ga)R(C)-isomer of **III-16**. It is noteworthy that in both cases the hydrogen atom attached to gallium and the hydrogen atom attached to the cAAC$^{Me}$ carbene carbon atom are in *trans* position.
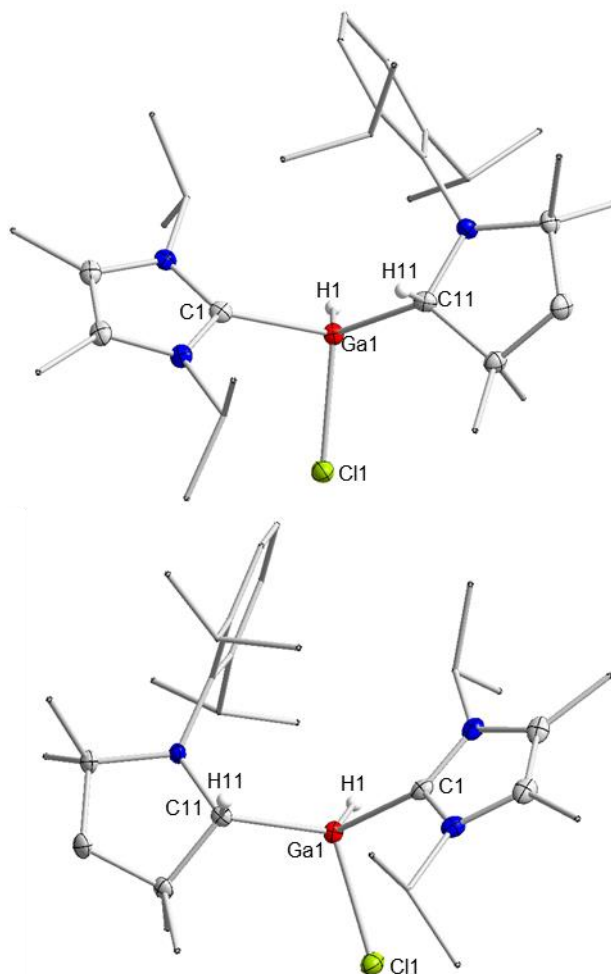
*Figure III.6: Molecular structure of R(Ga)S(C)-**III-16** (top) and S(Ga)R(C)-**II-16** (right) in the solid state (ellipsoids set at 50% probability level). Hydrogen atoms with exception of those attached to gallium and to the former carbene carbon atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: R(Ga)S(C)-**III-16**: Ga-C1 2.065(3), Ga-C11 2.019(2), Ga-H1 1.52(8), Ga1-Cl1 2.3063(7). C1-Ga-C11 114.01(10), C1- Ga-H1 108.0(12), C1-Ga-Cl 98.20(7), H1- Ga-Cl1 101.2(12), H1-Ga-C11 120.1(12), Cl1-Ga-C11 112.52(7); S(Ga)R(C)-**III-16**: Ga–C1 2.066(3), Ga–C11 2.013(2), Ga–H1 1.54(3), Ga1–Cl1 2.3035(7). C1-Ga-C11 114.83(10), C1-Ga-H1 106.6(13), C1-Ga-Cl1 97.88(7), H1- Ga-Cl1 103.0(13), H1-Ga-C11 118.6(13), Cl1-Ga-C11 113.37(7).*

Compound ($i$Pr$_2$Im$^{Me}$)·GaCl$_2$(cAAC$^{Me}$H) **III-17** was characterized using NMR spectroscopy, elemental analysis and IR spectroscopy. The NMR shifts and IR spectroscopic data are in accordance with other Ga-H insertion products and are summarized in Table 4. Single crystals of ($i$Pr$_2$Im$^{Me}$)·GaCl$_2$(cAAC$^{Me}$H) **III-17** were isolated by slow evaporation of a saturated solution of the compound in benzene. The molecular structure of **III-17** (Figure III.7) reveals a slightly distorted tetrahedron at gallium. The Ga-C$_{NHC}$ bond of 2.0695 Å and the Ga-C$_{cAAC}$ bond of 1.9996 Å are slightly

shorter than those observed for ($i$Pr$_2$Im$^{Me}$)·GaH$_2$(cAAC$^{Me}$H) **III-6**. The most important bond lengths of the compounds **III-5** – **III-7** and **III-17** are summarized in Table III.3.
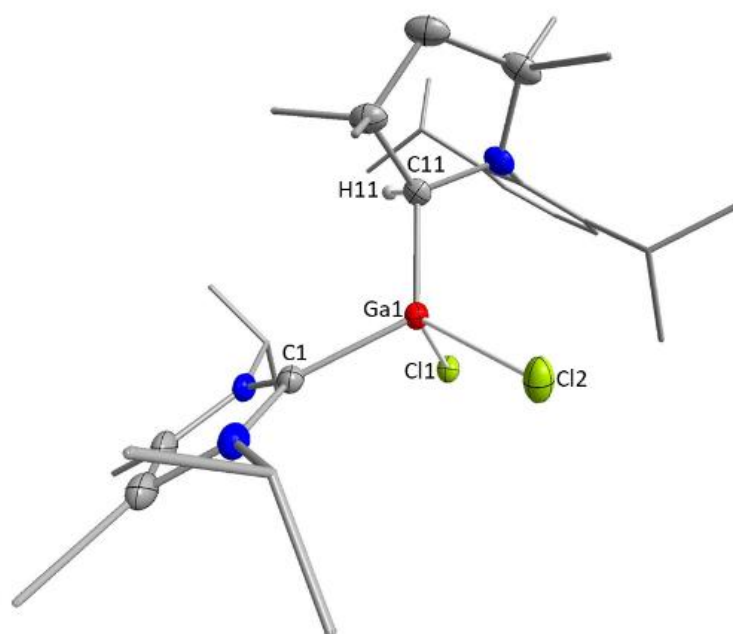


*Figure III.7: Molecular structure of (iPr$_2$Im$^{Me}$)·GaCl$_2$(cAAC$^{Me}$H) **III-17** in the solid state (ellipsoids set at the 50% probability level). Hydrogen atoms with exception of those attached to the former carbene carbon atom were omitted for clarity. Selected bond lengths [Å] and angles [°]: Ga-C1 2.065(15), Ga-C11 1.9996(16), Ga-Cl1 2.2266(4), Ga-Cl2 2.2415(4). C1-Ga-C11 117.73(6), C1-Ga-Cl1 115.24(5), C1-Ga-Cl2 109.09(4), Cl11-Ga-Cl2 101.916(16), Cl1-Ga-C11 109.45(5), Cl2-Ga-C11 115.24(5).*

*Table III.3 Selected bond lengths [Å] of the compounds (Me$_2$Im$^{Me}$)·GaH$_2$(cAAC$^{Me}$H) **III-5**, (iPr$_2$Im$^{Me}$)·GaH$_2$(cAAC$^{Me}$H)        **III-6**,        (Dipp$_2$Im)·GaH$_2$(cAAC$^{Me}$H)        **III-7**        and (iPr$_2$Im$^{Me}$)·GaCl$_2$(cAAC$^{Me}$H) **III-17**.*

|                        | III-5  | III-6  | III-7  | III-17 |
|------------------------|--------|--------|--------|--------|
| Ga-C$_{NHC}$           | 2.0696 | 2.1008 | 2.1094 | 2.0695 |
| Ga-C$_{cAAC}$          | 2.0332 | 2.0340 | 2.0294 | 1.9996 |
| Ga-H1                  | 1.5760 | 1.4841 | 1.4390 | -      |
| Ga-H2                  | 1.4344 | 1.4344 | 1.4789 | -      |
| Ga-Cl1                 | -      | -      | -      | 2.2266 |
| Ga-Cl2                 | -      | -      | -      | 2.2415 |

Different reaction pathways were observed for the reaction of the chlorogallane adducts of the sterically more demanding NHCs (Dipp₂Im)·GaH₂Cl **III-10**, (Dipp₂Imᴴ)·GaH₂Cl **III-11**, (Dipp₂Im)·GaHCl₂ **III-13** and (Dipp₂Imᴴ)·GaHCl₂ **III-14** with an additional equivalent of cAACᴹᵉ. The reaction of the compounds **III-10** and **III-11** leads with elimination of the NHC (Dipp₂Im, Dipp₂Imᴴ) selectively to insertion of two cAACᴹᵉ molecules into the Ga-H bond and thus to formation of the bisalkyl chlorogallane (cAACᴹᵉH)₂GaCl **III-18** (Scheme III.10). For the adduct of the backbone-saturated NHC Dipp₂Imᴴ, i.e. (Dipp₂Imᴴ)·GaH₂Cl **III-11**, quantitative conversion was already observed at room temperature, whereas for the reaction of cAACᴹᵉ with (Dipp₂Im)·GaH₂Cl **III-10** heating to the boiling point of toluene was required. However, in contrast to the insertion into the Ga-H bond for these dihydrides, the dichloro gallanes seem to be more stable as the reaction of (Dipp₂Imᴴ)·GaHCl₂ **III-14** with an additional equivalent of cAACᴹᵉ leads selectively to substitution of Dipp₂Imᴴ and formation of (cAACᴹᵉ)·GaHCl₂ **III-15** (Scheme III.10) at room temperature. Ligand exchange was also observed for the reaction of (Dipp₂Im)·GaHCl₂ **III-13** with cAACᴹᵉ, but completeness was not achieved for this reaction even after stirring the solution at 110 °C in toluene for 24 h. Compound **III-18** is stable in solution for several days at the boiling point of benzene and shows no reaction with an additional equivalent of cAACᴹᵉ.
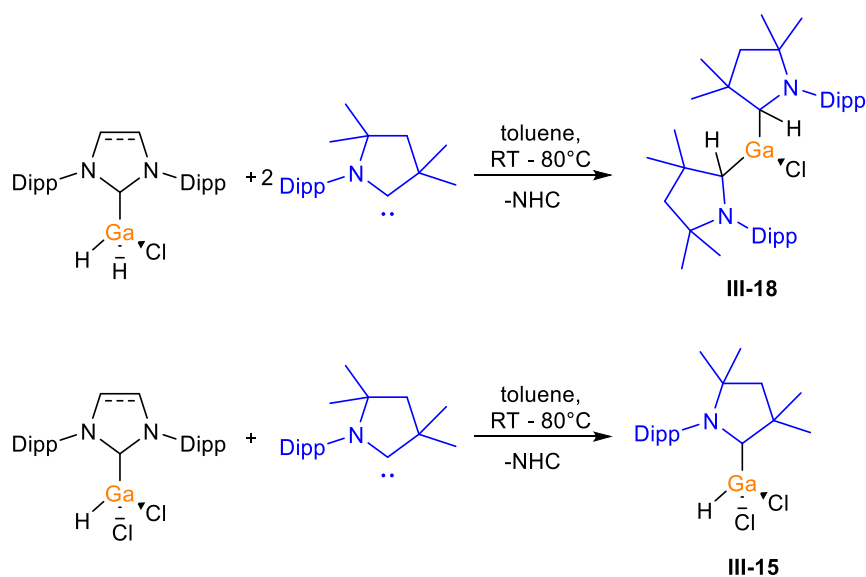


*Scheme III.10: Synthesis of the compounds (cAACᴹᵉ)·GaHCl₂ **III-5** and (cAACᴹᵉH)₂GaCl **III-18**.*

Compound **III-18** is the chloro analogue of (cAAC$^{Me}$H)$_2$GaH **III-8**. Due to the formation of two chirality centers at the former cAAC$^{Me}$ carbene carbon atoms we expected a similar splitting of the resonances in solution NMR as observed before for **III-8** and an equilibrium in solution between *meso*-**III-18** and *rac*-**III-18**. Accordingly, the resonances of the cAAC-Dipp substituent *i*Pr methine protons split into two sets of two inequivalent septets at 3.09 ppm, 3.19 ppm, 4.10 ppm and 4.37 ppm in the $^1$H NMR spectrum of **III-18** recorded in C$_6$D$_6$ at room temperature. Two resonances were observed at 3.84 ppm and 4.10 ppm for the cAAC$^{Me}$-C*H protons* and the former carbene carbon atom gives rise to two sets of signals at 82.9 ppm and 83.9 ppm in the $^{13}$C NMR spectrum. $^1$H-$^1$H coupling NMR studies were performed to get insight into a possible isomerization mechanism, similar as observed for the isomerization of **III-8** in solution. However, these experiments provided no evidence for a site exchange of the cAAC$^{Me}$-C*H* and the cAAC$^{Me}$$_{Dipp}$-C*H* protons (see Figure III.8), even at a temperature of 100 °C. According to DFT calculations (M06-2X/Ga: def2-TZVP, C, H: def2-SVP, see Figure III.9) performed on the compounds (cAAC$^{Me}$H)$_2$GaCl *meso*-**III-18**, *rac(R,R)*-**III-18**, *rac(S,S)*-**III-18** and (cAAC$^{Me}$)·GaHCl(cAAC$^{Me}$H) *int*-**III-18** the situation is similar as observed for **III-8**, but the energy differences for the different isomers of (cAAC$^{Me}$H)$_2$GaCl are more pronounced. The energy difference calculated for *meso*-**III-18** and *rac(S,S)*-**III-18** are 1.9 kJ/mol in favor of *rac(S,S)*-**III-18**, which is the isomer of lowest energy. The isomer *rac(R,R)*-**III-18** lies considerable higher in energy, 10.4 kJ/mol above *meso*-**III-18** and *int*-**III-8** lies 60.9 kJ/mol above *rac(S,S)*-**III-18**. As we have no evidence here for isomerization, we conclude that the barrier for such a process *via* hydride migration should be significantly higher compared to **III-8**, presumably due to p$_\pi$-p$_\pi$ interaction between the vacant gallium p orbital and occupied orbitals at the chloride substituent.
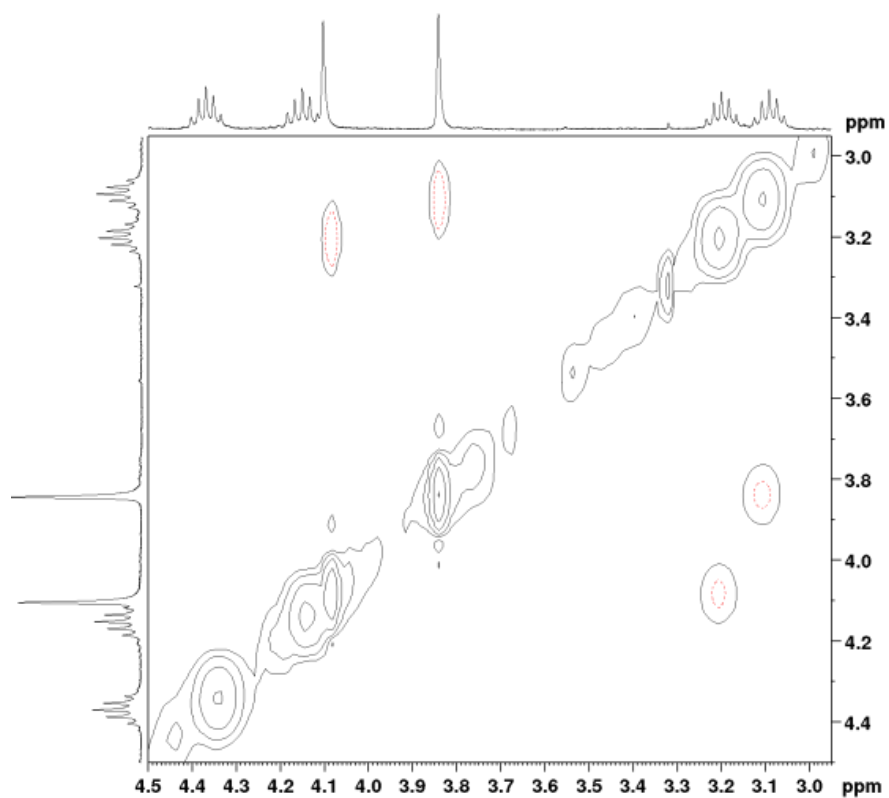
*Figure III.8: $^1H$-$^1H$-NOESY/COESY NMR of **III-18** in $C_6D_6$ at room temperature.*



*rac(R,R)*-**18**: + 10.4 kJ/mol

*rac(S,S)*-**18**: 0.0 kJ/mol

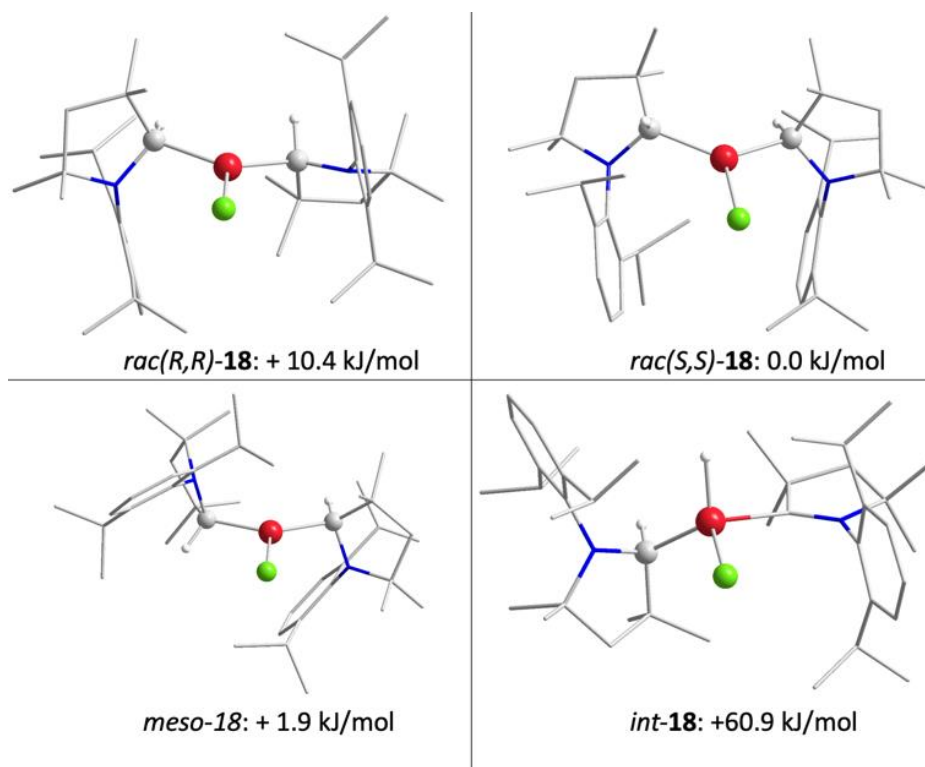*meso*-**18**: + 1.9 kJ/mol

*int*-**18**: +60.9 kJ/mol

*Figure III.9: DFT optimized (M06-2X/Ga: def2-TZVP, C, H: def2-SVP) structures and relative energies of different isomers of **III-18**.*

## 3.3 Conclusion

A detailed report on the synthesis of NHC gallane adducts (NHC)·GaH$_3$, (NHC)·GaH$_2$Cl, and (NHC)·GaHCl$_2$ as well as the reactivity of these adducts with cAAC$^{Me}$ is presented. The NHC gallane adducts (NHC)·GaH$_3$ (NHC = Me$_2$Im$^{Me}$ **III-1**, *i*Pr$_2$Im **III-2** and Dipp$_2$Im$^H$ **III-4**) were synthesized *via* the reaction of the NHC with *in situ* prepared lithium gallium hydride. The NHC-stabilized monochloro gallanes (NHC)·GaH$_2$Cl were obtained from substituent dismutation, i.e. the 2:1 stoichiometric reaction of (NHC)·GaH$_3$ and (NHC)·GaCl$_3$ (NHC = *i*Pr$_2$Im$^{Me}$, Dipp$_2$Im), and NHC dichlorogallane adducts (NHC)·GaHCl$_2$ were synthesized from the reaction of the NHC with *in situ* generated "GaHCl$_2$". The reaction of "GaHCl$_2$" with cAAC$^{Me}$ afforded the adduct (cAAC$^{Me}$)·GaHCl$_2$ **III-15** in good yield, which is the first example of a cAAC-stabilized H-gallane adduct. The compounds (NHC)·GaH$_3$ (NHC = Me$_2$Im$^{Me}$ **III-1**, *i*Pr$_2$Im **III-2** and Dipp$_2$Im$^H$ **III-4**) are unstable in solution upon heating and decompose to elemental gallium and the corresponding dihydroaminal NHC-H$_2$. An equilibrium with the bis-NHC adducts (NHC)$_2$·GaH$_3$ were observed in solution after addition of NHC to (NHC)·GaH$_3$, which also leads to decomposition but – in contrast to the alane adducts – no ring expansion or ring opening of the NHCs occurs. Replacement of the hydride substituents with chloride enhances the stability of the NHC adducts, i.e. with increasing chloride content the adducts become more and more stable: (NHC)·GaH$_3$ < (NHC)·GaH$_2$Cl < (NHC)·GaHCl$_2$ < (NHC)·GaCl$_3$.

The reaction of cAAC with NHC-stabilized H-gallanes (and alanes) typically leads to insertion of the cAAC into the E-H bond (E = Al, Ga).[66] We present here the reaction of different adducts (NHC)·GaH$_3$ with cAAC$^{Me}$, which leads to oxidative addition of Ga-H to the carbene carbon atom to yield compounds (NHC)·GaH$_2$(cAAC$^{Me}$H) (NHC = Me$_2$Im$^{Me}$ **III-5**, *i*Pr$_2$Im$^{Me}$ **III-6**, Dipp$_2$Im **III-7**). These insertion products are stable in solution up to the boiling point of benzene and are not prone to further insertion of cAAC$^{Me}$. However, the reaction of (Dipp$_2$Im$^H$)·GaH$_3$ afforded with insertion of two equivalents of cAAC$^{Me}$ into the Ga-H bonds the bisalkyl gallium hydride (cAAC$^{Me}$H)$_2$GaH **III-8** selectively. Reactions of (NHC)·GaH$_2$Cl and (NHC)·GaHCl$_2$ (NHC = *i*Pr$_2$Im$^{Me}$, Dipp$_2$Im) with cAAC$^{Me}$ led to the formation of different products, depending on the steric demand of the NHC used. For the sterically less demanding *i*Pr$_2$Im$^{Me}$ ligand the insertion of cAAC$^{Me}$ into the Ga-H bond was achieved with

formation of ($i$Pr$_2$Im$^{Me}$)·GaClH(cAAC$^{Me}$H) **III-16** and ($i$Pr$_2$Im$^{Me}$)·GaCl$_2$(cAAC$^{Me}$H) **III-17**. In contrast, the reaction of the monochloro gallane adducts (NHC)·GaH$_2$Cl, stabilized with the sterically more demanding Dipp$_2$Im and Dipp$_2$Im$^H$ ligands, led to the selective insertion of two equivalents cAAC$^{Me}$ into both Ga-H bonds and extrusion of the NHC ligand to yield the bisalkyl gallium chloride (cAAC$^{Me}$H)$_2$GaCl **III-18**. For the dichlorogallane adducts (NHC)·GaHCl$_2$ quantitative ligand exchange occurs with formation of (cAAC$^{Me}$)·GaHCl$_2$ **III-15.**
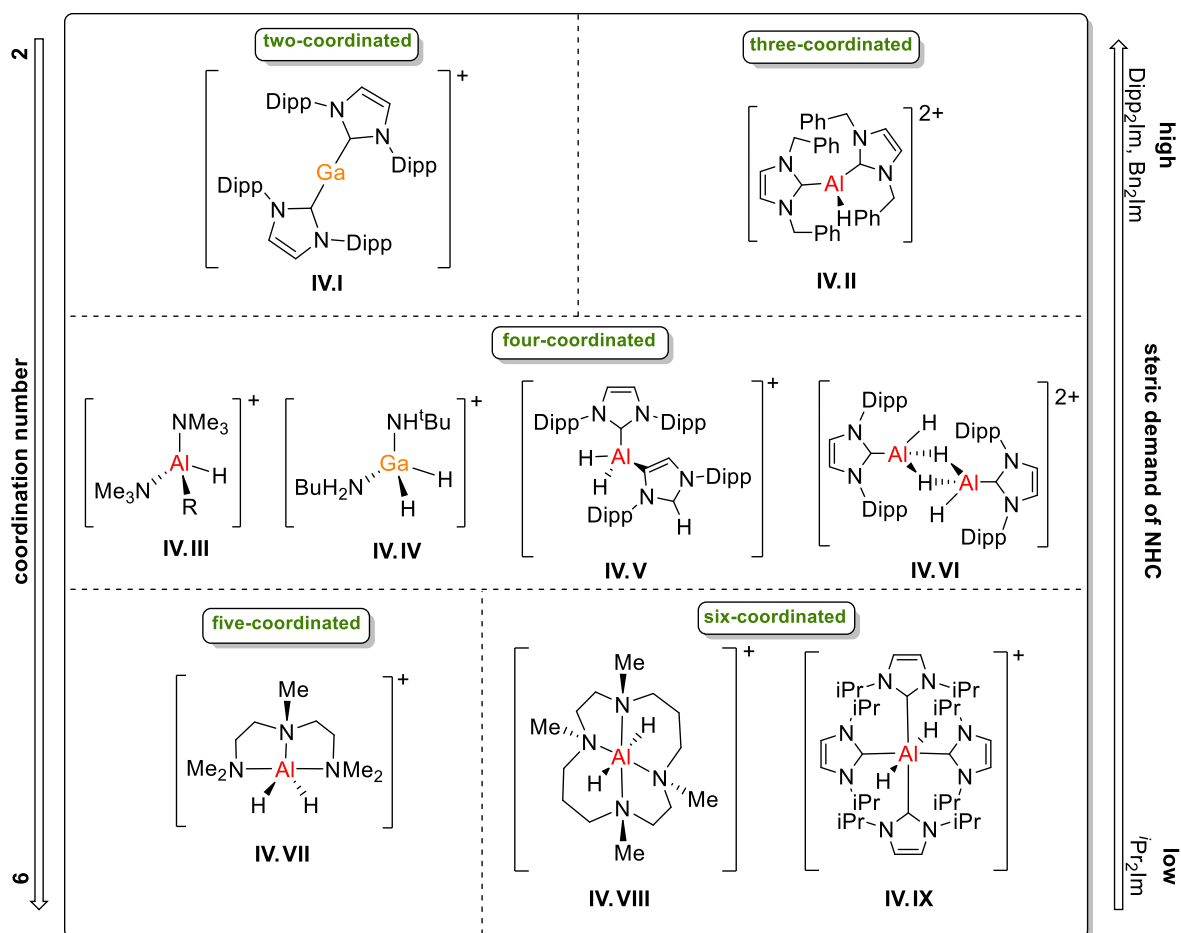
# CHAPTER IV


# BIS-NHC ALUMINIUM AND GALLIUM DIHYDRIDE CATIONS $[(NHC)_2 \cdot EH_2]^+$ $(E = Al, Ga)$

# 4 BIS-NHC ALUMINIUM AND GALLIUM DIHYDRIDE CATIONS [(NHC)$_2$·EH$_2$]$^+$ (E = Al, Ga)

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## 4.1 Introduction

Aluminum and gallium hydrides are important reagents in organic and inorganic synthesis, e.g. for reductions, hydride transfer and important materials, in particular for hydride storage.[222-229] The majority of aluminum and gallium hydride species are either neutral or anionic, whereas cationic *Lewis*-base stabilized aluminium and especially gallium hydrides are rather scarce in the literature. Atwood and coworkers synthesized and fully characterized the six- and five-coordinated aluminium hydride cations [(MeNCH$_2$CH$_2$N(Me)CH$_2$CH$_2$CH$_2$)$_2$)·AlH$_2$]$^+$ **IV.VIII** and [(MeN(CH$_2$CH$_2$NMe$_2$)·AlH$_2$]$^+$ **IV.VII** as their aluminium hydride [AlH$_4$]$^-$ salts (see Scheme IV.1, **IV.VII & IV.VIII**).[230] The first four-coordinated aluminium hydride cation [(NMe$_3$)$_2$·AlH$_2$]$^+$ **IV.III** was reported by Roesky *et al.*, synthesized from a rather unforeseeable reaction. A mixture of (NMe$_3$)·AlH$_2$Cl, (NMe$_3$)·AlH$_3$ and $t$BuC≡CLi leads to formation of [(NMe$_3$)$_2$·AlH$_2$]$_2$[(AlH)$_8$(CCH$_2$$^t$Bu)$_6$], in which the [AlH$_2$]$^+$ cation is stabilized by two *Lewis*-bases NMe$_3$ (see Scheme IV.1, **IV.III**) and the carbaalanate cluster counter-ion [(AlH)$_8$(CCH$_2$$^t$Bu)$_6$]$^{2-}$, formed in course of the reaction, serves as a bulky, non-coordinating anion.[231] The first authenticated cationic gallium hydrides were presented by Parsons and coworkers.[6] Treatment of lithium gallium hydride with [N$^t$BuH$_3$]Cl or [N$^{sec}$BuH$_3$]Cl leads to the formation of [(N$^t$BuH$_2$)$_2$GaH$_2$]$^+$ and [(N$^{sec}$BuH$_2$)$_2$GaH$_2$]$^+$ (see Scheme IV.1, **IV.IV**) as their chloride salts.[232]

*Scheme IV.1: Lewis-base stabilized aluminium and gallium cations.*

Aluminium or gallium hydride cations stabilized by *N*-heterocyclic carbenes (NHCs) are less common. Recently we reported the synthesis of a six-coordinated aluminium cation [(*i*Pr$_2$Im)$_4$·AlH$_2$]$^+$ **IV.IX** as a side product of the reaction of lithium aluminium hydride with an excess of *i*Pr$_2$Im (*i*Pr$_2$Im = 1,3-di-*iso*-propyl-imidazolin-2-ylidene, see Scheme IV.1, **IV.IX**).[66] Stephan *et al.* presented recently a dinuclear dicationic aluminium hydride [(Dipp$_2$Im)·AlH($\mu$-H)]$_2$$^{2+}$ **IV.VI** in [(Dipp$_2$Im)·AlH($\mu$-H)]$_2$[B(C$_6$F$_5$)$_4$]$_2$ (Dipp$_2$Im = 1,3-bis(2,6-di*iso*propyl-phenyl)imidazolin-2-ylidene) and a three-coordinated mononuclear dication [(Bn$_2$Im)$_2$·AlH]$^{2+}$ (Bn$_2$Im = 1,3-dibenzylimidazolin-2-ylidene) in [(Bn$_2$Im)$_2$·AlH]$_2$[B(C$_6$F$_5$)$_4$] **IV.II** (see Scheme IV.1, **IV.VI** & **IV.II**).[34] Jones and Stasch *et al.* reported the monocationic aluminium hydride [(Dipp$_2$Im)·AlH$_2$(*a*Dipp$_2$Im)]$^+$ **IV.VI** ("*a*" denotes "abnormal coordination") which is stabilized by one *normal* and one *abnormal* coordinated NHC (see Scheme IV.1, **IV.VI**).[45] Furthermore, Krossing and Jones *et al.* disclosed recently the synthesis of a "naked" Ga(I) cation

[(Dipp$_2$Im)$_2$Ga]$^+$ **IV.I** stabilized by a sterically demanding NHC and a non-coordinating anion as counterion in [(Dipp$_2$Im)$_2$Ga][Al(OC(CF$_3$)$_3$)$_4$] (see Scheme IV.1, **IV.I**).[174] Thus, NHC stabilized cationic aluminium hydrides are rather scarce and NHC stabilized cationic gallium hydrides are currently unknown.

We[39, 66, 218] and others[23, 29, 33, 48, 150, 233, 234] investigate currently group 13 metal compounds (M = Al, Ga, In) which are stabilized with strong $\sigma$-donating NHC-ligands. The coordination of NHCs, for example, to alanes and gallanes leads to the synthesis of stable NHC metal hydride adducts. Thermally stable examples such as (Dipp$_2$Im)·MH$_3$ (M = Al, Ga, In) have been prepared particularly for sterically demanding NHCs. Moreover, the syntheses of some low-valent, NHC-stabilized dinuclear hydrodialane and hydrodigallene compounds were presented,[77, 176, 235] for example the dialanes [(Dipp$_2$Im)·AlH$_2$]$_2$ which were reported by Jones *et al.*[73] However, the formation of cationic aluminium and gallium dihydrides is rare and stabilization of [EH$_2$]$^+$ with two strong $\sigma$-donating NHC-ligands should lead to accessible hydroalane and hydrogallane cations. In this chapter investigations concerning the synthesis of cationic bis-NHC aluminium and gallium hydrides is presented.
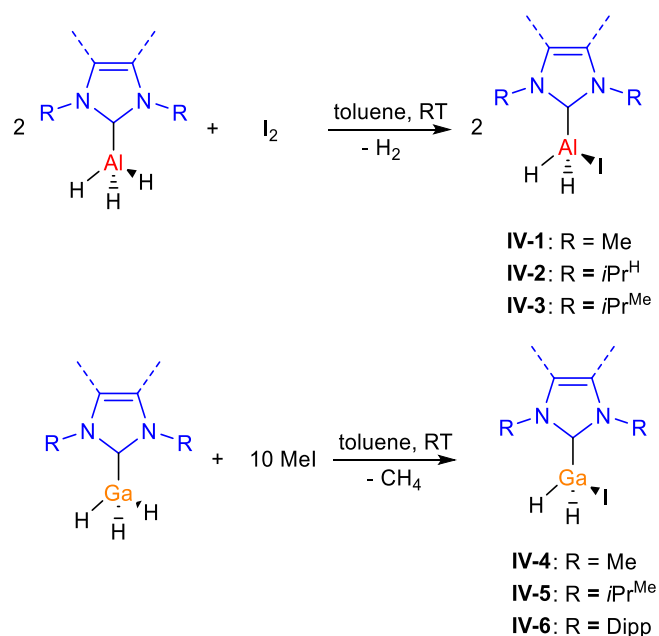
## 4.2 Results and Discussion

Cationic bis-NHC stabilized aluminium and gallium hydrides $[(NHC)_2EH_2]^+$ (E = Al, Ga) should be electronically and sterically saturated. Thus, our strategy was to synthesize adducts of the type $(NHC)·EH_2I$ (E = Al, Ga) with a good leaving group iodide as precursor. Synthesis of NHC stabilized aluminium and gallium hydride chlorides are well known in literature. NHC stabilized mono- and dichloroalanes and gallanes $(NHC)·EH_2Cl$ and $(NHC)·EHCl_2$ (E = Al, Ga) are either accessible by the reaction of the NHCs with *in situ* generated "$EH_2Cl$" and "$EHCl_2$" or by dismutation between $(NHC)·EH_3$ and $(NHC)·ECl_3$ (E = Al, Ga).[30, 45, 48, 149, 150, 155, 236, 237] For the synthesis of NHC-stabilized iodoalanes only a few examples are available in the literature,[45, 238] e.g. a report by Jones and Stasch *et al.* on synthesis of $(NHC)·AlH_2I$ adducts (NHC = $Mes_2Im$, $Dipp_2Im$) by dismutation between two equivalents of $(NHC)·AlH_3$ and one equivalent of $(NHC)·AlI_3$. For the synthesis of diiodoalanes $(NHC)·AlHI_2$ (NHC = $Mes_2Im$, $Dipp_2Im$) the corresponding NHC stabilized aluminium hydrides were treated with an excess of methyl iodide. However, for the heavier gallium analogues only one example of NHC stabilized iodogallane was presented in the literature so far, i.e. $(Mes_2Im)·GaH_2I$, which was prepared from the reaction of metastable "Ga(I)I" with $(Mes_2Im)·GaH_3$.[156]

We were interested in developing a simple synthetic route to obtain the NHC adducts (NHC = $Me_2Im^{Me}$, $iPr_2Im$, $iPr_2Im^{Me}$) of iodoalanes and iodogallanes $(NHC)·MH_2I$ (M = Al, Ga) of sterically less demanding NHCs in a way that may be transferred to large quantity synthesis. Therefore, we reacted the compounds $(NHC)·AlH_3$ (NHC = $Me_2Im^{Me}$ **I**, $iPr_2Im$ **II**, $iPr_2Im^{Me}$ **III**) with 0.5 equivalents of elemental iodine $I_2$ in toluene at room temperature. Immediately after addition of iodine, dissolved in minimum amounts of toluene, to a toluene solution of **I** - **III**, respectively, the solution discoloured. After 15 minutes of stirring at room temperature all volatiles were removed *in vacuo* and the compounds $(NHC)·AlH_2I$ (NHC = $Me_2Im^{Me}$ **IV-1**, $iPr_2Im$ **IV-2**, $iPr_2Im^{Me}$ **IV-3**) were isolated as colorless powders in excellent yields (**IV-1**: 88 %, **IV-2**: 97 %, **IV-3**: 86 %) and purity (see Scheme IV.2).

For the reaction of (NHC)·GaH$_3$ with elemental iodine, however, consistently the formation of small amounts of (NHC)·GaI$_3$ was observed, independent on the stoichiometry used and even after short reaction times. Therefore, the gallane compounds (NHC)·GaH$_2$I (NHC = Me$_2$Im$^{Me}$ **IV-4**, *i*Pr$_2$Im$^{Me}$ **IV-5**, Dipp$_2$Im **IV-6**) were synthesized by the reaction of the NHC gallane adduct (NHC)·GaH$_3$ with an excess of methyl iodide at room temperature. This reaction affords selectively the colorless compounds (NHC)·GaH$_2$I (NHC= Me$_2$Im$^{Me}$ **IV-4**, iPr$_2$Im$^{Me}$ **IV-5**, Dipp$_2$Im **IV-6**) within 30 minutes at room temperature in very good (**IV-4**: 88 %, **IV-5**: 76 %) to quantitative (**IV-6**: 99 %) yield (see Scheme IV.2).



IV-1: R = Me
IV-2: R = *i*Pr$^H$
IV-3: R = *i*Pr$^{Me}$

IV-4: R = Me
IV-5: R = *i*Pr$^{Me}$
IV-6: R = Dipp

*Scheme IV.2: Synthesis of (NHC)·AlH$_2$I (NHC= Me$_2$Im$^{Me}$ **IV-1**, iPr$_2$Im **IV-2**, iPr$_2$Im$^{Me}$ **IV-3**) and (NHC)·GaH$_2$I (NHC= Me$_2$Im$^{Me}$ **IV-4**, iPr$_2$Im$^{Me}$ **IV-5**, Dipp$_2$Im **IV-6**).*

*Table IV.1: Selected NMR (ppm) and IR (cm$^{-1}$) shifts of the compounds (Me$_2$Im$^{Me}$)·AlH$_3$ **I**, (iPr$_2$Im)·AlH$_3$ **II**, (iPr$_2$Im$^{Me}$)·AlH$_3$ **III**, (Me$_2$Im$^{Me}$)·GaH$_3$ **III-1**, (iPr$_2$Im$^{Me}$)·GaH$_3$ **III-3**, (Dipp$_2$Im)·GaH$_3$ **V**, (Me$_2$Im$^{Me}$)·AlH$_2$I **IV-1**, (iPr$_2$Im)·AlH$_2$I **IV-2**, (iPr$_2$Im$^{Me}$)·AlH$_2$I **IV-3**, (Me$_2$Im$^{Me}$)·GaH$_2$I **IV-4**, (iPr$_2$Im$^{Me}$)·GaH$_2$I **IV-5** and (Dipp$_2$Im)·GaH$_2$I **IV-6**.*

| | Al-*H* | Ga-*H* | NCN | | $^{27}$Al{$^1$H} NMR | $\nu$Al/Ga-H |
| | $^1$H{$^{27}$Al} NMR | $^1$H NMR | $^{13}$C{$^1$H} NMR | | | |
|---|---|---|---|---|---|---|
| (Me$_2$Im$^{Me}$)·AlH$_3$ **I** | 4.48 | - | 168.7 | | 106.4 | 1727[7] |
| (*i*Pr$_2$Im)·AlH$_3$ **II** | 4.53 | - | 170.3 | | 106.3 | 1719, 1776[7] |
| (*i*Pr$_2$Im$^{Me}$)·AlH$_3$ **III** | 4.60 | - | 170.0 | | 107.8 | 1718, 1771[7] |
| (Me$_2$Im$^{Me}$)·GaH$_3$ **III-1** | - | 4.51 | 172.2 | | - | 1767 |
| (*i*Pr$_2$Im$^{Me}$)·GaH$_3$ **III-3** | - | 4.66 | 172.7 | | - | 1773[12d] |
| (Dipp$_2$Im)·GaH$_3$ **V** | - | 3.73 | 172.7 | | - | 1799[12d] |
| (Me$_2$Im$^{Me}$)·AlH$_2$I **IV-1** | 4.54 | - | 161.4 | | 107.8 | 1796, 1827 |
| (*i*Pr$_2$Im)·AlH$_2$I **IV-2** | 4.63 | - | 162.7 | | 109.6 | 1792, 1809 |
| (*i*Pr$_2$Im$^{Me}$)·AlH$_2$I **IV-3** | 4.70 | - | 162.3 | | 109.0 | 1779, 1825 |
| (Me$_2$Im$^{Me}$)·GaH$_2$I **IV-4** | - | 4.81 | 162.1 | | - | 1895 |
| (*i*Pr2Im$^{Me}$)·GaH$_2$I **IV-5** | - | 5.00 | 163.4 | | - | 1839, 1889 |
| (Dipp$_2$Im)·GaH$_2$I **IV-6** | - | 4.13 | 170.3 | | - | 1886 |

The compounds **IV-1** - **IV-6** were characterized by NMR spectroscopy, IR spectroscopy, and elemental analysis. All new compounds show NHC resonances in their $^1$H and $^{13}$C{$^1$H} NMR-spectra similar as observed for the corresponding alane and gallane adducts. The most important NMR and IR data of **IV-1** – **IV-6** are summarized in Table IV.1 and compared to their parent compounds. The $^{27}$Al{$^1$H} NMR resonances of the compounds **IV-1** - **IV-3** in solution were found at $\delta$ = 107.8 (**IV-1**) ppm, 109.6 (**IV-2**) ppm and 109.0 (**IV-3**) ppm. The signals are in good accordance to the literature-known resonances of NHC stabilized tetrahedral coordinated alanes, which lead to signals in the range of $\delta$ = 100 - 120 ppm.[11] The $^1$H or $^1$H{$^{27}$Al} NMR resonances of

the hydride substituents bound to the central metal atom for the compounds **IV-1** - **IV-6** were detected at $\delta$ = 4.54 (**IV-1**) ppm, 4.63 ppm (**IV-2**), 4.70 (**IV-3**) ppm, 4.81 (**IV-4**) ppm, 5.00 (**IV-5**) ppm and 4.13 (**IV-6**) ppm, which are slightly highfield shifted compared to their corresponding metal hydride compounds (**I**: 4.48 ppm, **II**: 4.53 ppm, **III**: 4.60 ppm, **III-1**: 4.51 ppm, **III-3**: 4.66 ppm, **V**: 3.73 ppm).[30, 66] The characteristic E-H (E = Al, Ga) stretching vibrations of **IV-1** - **IV-6** were observed in the range between 1779 – 1889 $cm^{-1}$ (see Table IV.1). The values compare well with Al-H and Ga-H stretching vibrations for related compounds such as (Dipp$_2$Im)·AlH$_2$I (1830 $cm^{-1}$) and (Mes$_2$Im)·GaH$_2$I (1863 $cm^{-1}$).[9, 16]

Single crystals of the compounds (Me$_2$Im$^{Me}$)·AlH$_2$I **IV-1**, (iPr$_2$Im$^{Me}$)·AlH$_2$I **IV-3** and (Me$_2$Im$^{Me}$)·GaH$_2$I **IV-4** were grown by slow evaporation of saturated solutions in benzene at room temperature. The molecular structures of **IV-1**, **IV-3** and **IV-4** reveal the expected four coordinated NHC adducts (see Figure IV.1). (Me$_2$Im$^{Me}$)·AlH$_2$I **IV-1** crystallizes in the space group *C*2/*c*, (iPr$_2$Im$^{Me}$)·AlH$_2$I **IV-3** in the orthorhombic space group *Pbca* and (Me$_2$Im$^{Me}$)·GaH$_2$I **IV-4** in the monoclinic space group *P*2$_1$/*n*. These molecules adopt a tetrahedral structure at the metal centre, spanned by the NHC, two hydrogen atoms and the iodine. The M-C$_{NHC}$ (M = Al, Ga) bond length of 2.025(2) Å (**IV-1**), 2.039(3) Å (**IV-3**) and 2.036(4) Å (**IV-4**) differ only marginally from the bond lengths observed in the NHC aluminum(III)- and gallium(III)hydride adducts.[31]
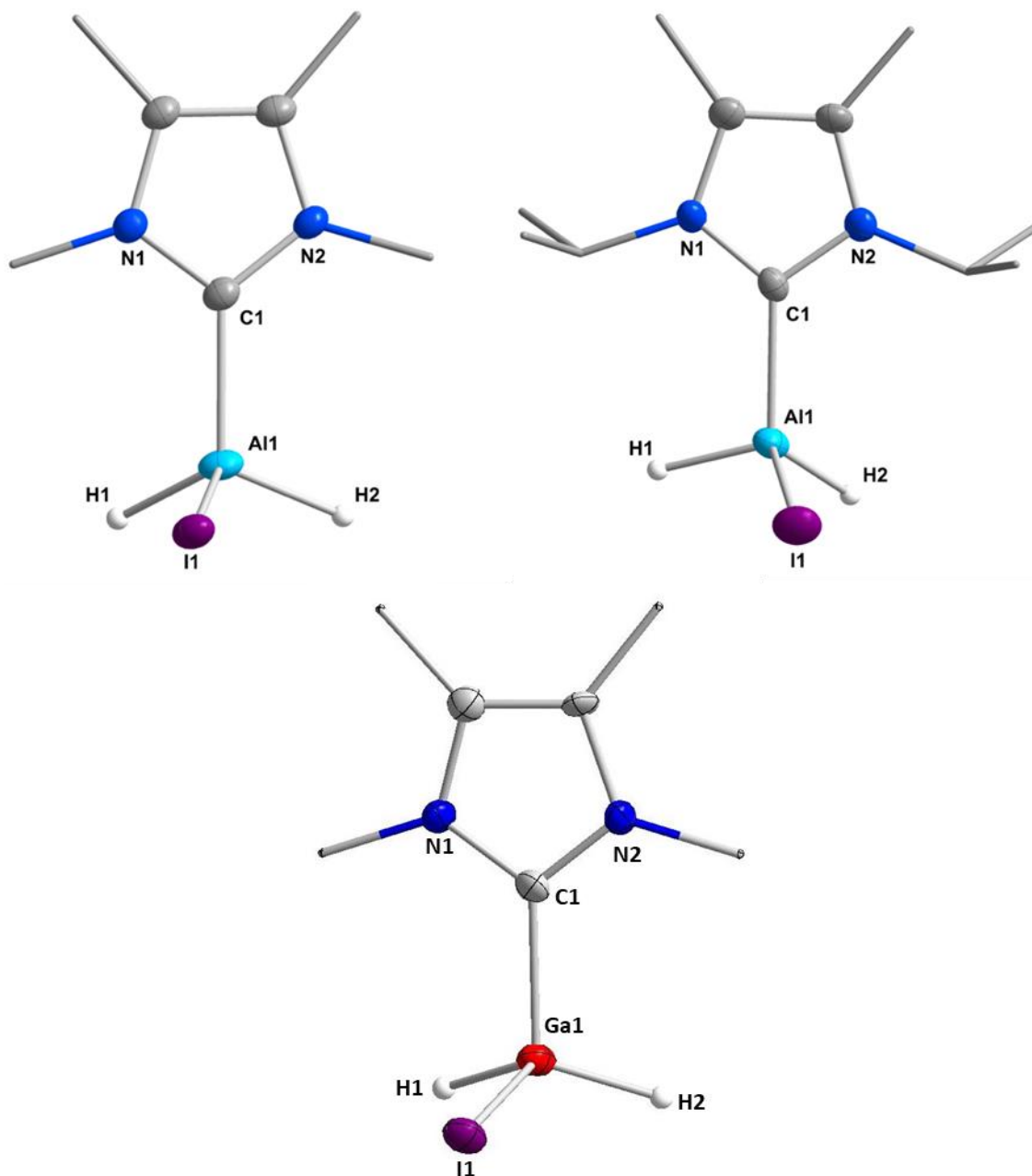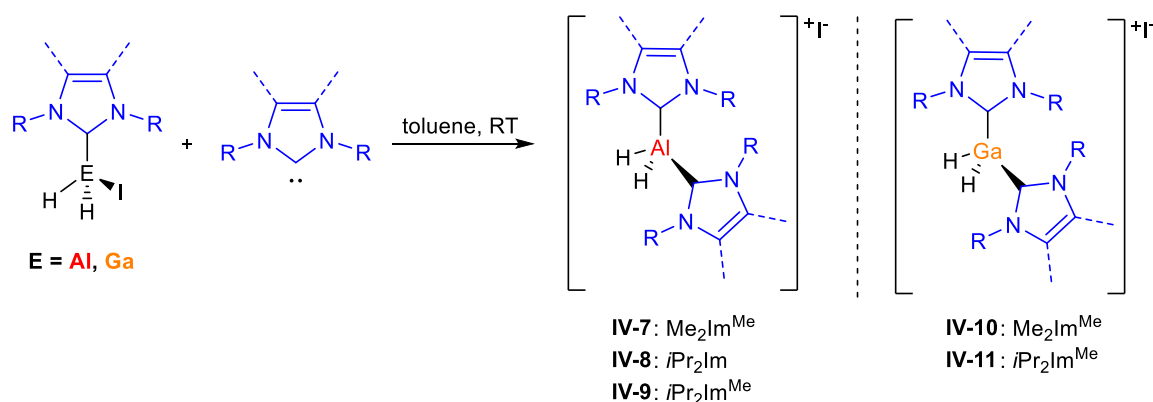
*Figure IV.1: Molecular structure of (Me₂Im^{Me})·AlH₂I **IV-1** (left), (iPr₂Im^{Me})·AlH₂I **IV-3** (right) and (Me₂Im^{Me})·GaH₂I **IV-4** (down) in the solid state (ellipsoids set at the 50% probability level). Hydrogen atoms with exception of those attached to aluminium and gallium were omitted for clarity. Selected bond lengths [Å] and angles [°]: **IV-1**: C1-Al1 2.025(2), Al1-H1 1.61(4), Al1-H2 1.66(4), Al1-I1 2.586(8); H1-Al1-H2 109.4(18), H1-Al1-I1 108.7(12), H2-Al1-I1 106.5(14), C1-Al1-H1 114.3(14), C1-Al1-H2 106.5(14), C1-Al1-I1 105.88(7); **IV-3**: C1-Al1 2.039(3), Al1-H1 1.58(5), Al1-H2 1.60(4), Al1-I1 2.5960(10); H1-Al1-H2 104 (2), H1-Al1-I1 110.5(17), H2-Al1-I1 111.1(14), C1-Al1-H1 106.7(18), C1-Al1-H2 120.2(14), C1-Al1-I1 103.77(9); **IV-4**: Ga-C1 2.036(4), Ga-H1 1.52 (6), Ga-H2 1.44(7), Ga-I1 2.6415(6). C1-Ga-H1 109(2), C1-Ga-H2 108(2), C1-Ga-I1 100.07(13), H1-Ga-H2 122(3), H1-Ga-I1 110(2), H2-Ga-I1 105(2).*

The alane adducts **IV-1** - **IV-3** are stable in solution at least up to the boiling point of toluene and show no decomposition or change in the $^1$H NMR spectra. Heating the gallium compounds **IV-4** - **IV-6** in benzene to 80 °C leads to irreversible decomposition, which afforded elemental gallium as dark grey precipitate and NHC-H$_2$ according to $^1$H NMR spectroscopy.

We reported earlier on NHC ring expansion and NHC ring opening by treating (*i*Pr$_2$Im)·AlH$_3$ **II** with an additional equivalent of the small NHC *i*Pr$_2$Im or the sterically demanding NHC Dipp$_2$Im.[7b] Thus, we were interested in the reactivity of the NHC stabilized iodo alanes and gallanes with respect to their behaviour upon addition of further NHC. The reaction of the alane compounds (Me$_2$Im$^{Me}$)·AlH$_2$I **IV-1**, (*i*Pr$_2$Im)·AlH$_2$I **IV-2** and (*i*Pr$_2$Im$^{Me}$)·AlH$_2$I **IV-3** with an additional equivalent of the corresponding NHC in benzene or toluene led immediately to the formation of a colorless precipitate. The $^1$H NMR spectrum of the mixture shows only one broadened set of signals for the NHC ligands in solution. Heating the solution to 80 °C does not lead to any change in the $^1$H NMR spectra of the compounds and no formation of either ring expansion or ring opening products were observed. These colorless precipitates were isolated and identified as the cationic bis-NHC adducts [(Me$_2$Im$^{Me}$)$_2$·AlH$_2$]I **IV-7**, [(*i*Pr$_2$Im)$_2$·AlH$_2$]I **IV-8** and [(*i*Pr$_2$Im$^{Me}$)$_2$·AlH$_2$]I **IV-9** (see Scheme IV.3). Similarly, the reaction of (Me$_2$Im$^{Me}$)·GaH$_2$I **IV-4** and (*i*Pr$_2$Im$^{Me}$)·GaH$_2$I **IV-5** with an additional equivalent of NHC in toluene leads to the cationic bis-NHC adducts [(Me$_2$Im$^{Me}$)$_2$·GaH$_2$]I **IV-10** and [(*i*Pr$_2$Im$^{Me}$)$_2$·GaH$_2$]I **IV-11** as colorless solids in good yield and purity (Scheme IV.3). These compounds are the first examples of NHC stabilized cationic gallium dihydrides.



E = Al, Ga

IV-7: Me$_2$Im$^{Me}$
IV-8: *i*Pr$_2$Im
IV-9: *i*Pr$_2$Im$^{Me}$

IV-10: Me$_2$Im$^{Me}$
IV-11: *i*Pr$_2$Im$^{Me}$

*Scheme IV.3: Synthesis of [(Me$_2$Im$^{Me}$)$_2$·AlH$_2$]I **IV-7**, [(iPr$_2$Im)$_2$·AlH$_2$]I **IV-8**, [(iPr$_2$Im$^{Me}$)$_2$·AlH$_2$]I **IV-9**, [(Me$_2$Im$^{Me}$)$_2$·GaH$_2$]I **IV-10** and [(iPr$_2$Im$^{Me}$)$_2$·GaH$_2$]I **IV-11**.*

The compounds **IV-7** - **IV-11** are nearly insoluble in aromatic solvents such as benzene and toluene, only sparingly soluble and sufficiently stable in more polar solvents such as thf, acetonitrile and acetone. Solutions of **IV-7** - **IV-9** in acetone show good solubility and to our surprise only slow decomposition to the corresponding imidazolium salts [NHCH]$^+$I$^-$ (NHC = Me$_2$Im$^{Me}$, $i$Pr$_2$Im, $i$Pr$_2$Im$^{Me}$) after several hours. The compounds **IV-10** and **IV-11** have similar solubilities as the alane analogues, but they are less stable in acetonitrile and acetone and decompose readily to the imidazolium salts [Me$_2$Im$^{Me}$H]I and [$i$Pr$_2$Im$^{Me}$H]I after a few hours at room temperature. Whereas the aluminium complexes **IV-7** - **IV-9** are stable up to the boiling point of benzene, the gallium complexes decompose to give considerable amounts of the corresponding imidazolium salts and other unidentified species at this temperature.

The compounds **IV-7** - **IV-11** were characterized by NMR spectroscopy, IR spectroscopy and elemental analysis. The most important NMR and IR data are summarized in Table IV.2. The $^1$H and $^{13}$C{$^1$H} NMR spectra show one set of resonances for the NHC ligands due to free rotation of the carbenes along the Al-C-bonds in solution. The $^{27}$Al{$^1$H} NMR resonances of the compounds **IV-7** and **IV-8** in solution were not observed, whereas for **IV-9** the resonance in thf solution was found at 108.7 (**IV-9**) ppm. This signal is in good accordance with literature known resonances of NHC stabilized tetrahedral coordinated alanes, which lie in the range between $\delta$ = 100 and 120 ppm.[7,11] The $^1$H{$^{27}$Al} NMR resonances of the hydrides of **IV-7** to **IV-9** were not observed, but the hydrides of the gallium compounds were detected at $\delta$ = 4.17 (**IV-10**) ppm and $\delta$ = 4.37 (**IV-11**) ppm in the $^1$H NMR spectra. The characteristic metal hydride stretching vibrations were located at 1772, 1791 cm$^{-1}$ (**IV-7**), 1820, 1825 cm$^{-1}$ (**IV-8**), 1799, 1819 cm$^{-1}$ (**IV-9**), 1826, 1839 cm$^{-1}$ (**IV-10**) and 1857, 1877 cm$^{-1}$ (**IV-11**) (see Table IV.8) and compare well with literature known cationic aluminium hydrides [(Dipp$_2$Im)·AlH$_2$($a$Dipp$_2$Im)]$^+$I$^-$ and [(Bn$_2$Im)$_2$·AlH]$_2$[B(C$_6$F$_5$)$_4$]$_2$[34] or the amine stabilized gallium hydride [(NH$_2${}$^t$Bu)$_2$·GaH$_2$]Cl at 1927 cm$^{-1}$.[232]

Single crystals of the compounds [($i$Pr$_2$Im$^{Me}$)$_2$·AlH$_2$]I **IV-9** and [(Me$_2$Im$^{Me}$)$_2$·GaH$_2$]I **IV-10** were grown by slow evaporation of a saturated solution in benzene and acetonitrile at room temperature (see Figure IV.2). [($i$Pr$_2$Im$^{Me}$)$_2$·AlH$_2$]I **IV-9** crystallizes in the triclinic space group $P\bar{1}$ and [(Me$_2$Im$^{Me}$)$_2$·GaH$_2$]I **IV-10** in the monoclinic space group P2$_1$/n. The molecules adopt a tetrahedral structure each, spanned by the two NHC ligands and two hydrogen atoms. The M-C$_{NHC}$ (M = Al, Ga) bond lengths of 2.048(3) Å and

2.050(3) Å (**IV-9**) and 2.027(4) Å and 2.025(4) Å (**IV-10**) only differ marginally from the bond lengths observed in the aluminum(III) and gallium(III) hydride adducts. Compared to the mixed hydride iodide complexes **IV-1** and **IV-4** the bond lengths M-H1 and M-H2 (M = Al, Ga) of the salts **IV-9** and **IV-10** are slightly shortened. Due to the lower steric demand of the NHCs compared to Dipp$_2$Im all NHCs are coordinated in a normal mode. The angles between the two NHCs and the metal centre (C1-Al-C11) and (C1-Ga-C11) of 102.20(12)° (**IV-9**) and 104.32(14)° (**IV-10**) are much smaller compared to those found for [(Dipp$_2$Im)·AlH$_2$(aDipp$_2$Im)]I (114.24(8)°).[45] Interestingly the angle between the two hydrides and the metal centre (H1-Al-H2) with 122.(3)° (**IV-9**) and (H1-Ga-H2) 129.(4)° (**IV-10**) are quite large. The increased s-character of the MOs used for the M-H (M = Al, Ga) bonds resulting from release of the electronegative iodine could be reasonable for the expanded angle. Therefore, the decreased C1-M-C11 (M = Al, Ga) angles are the consequence of more p-character of the MOs used for the corresponding M-C (M = Al, Ga) bonds.
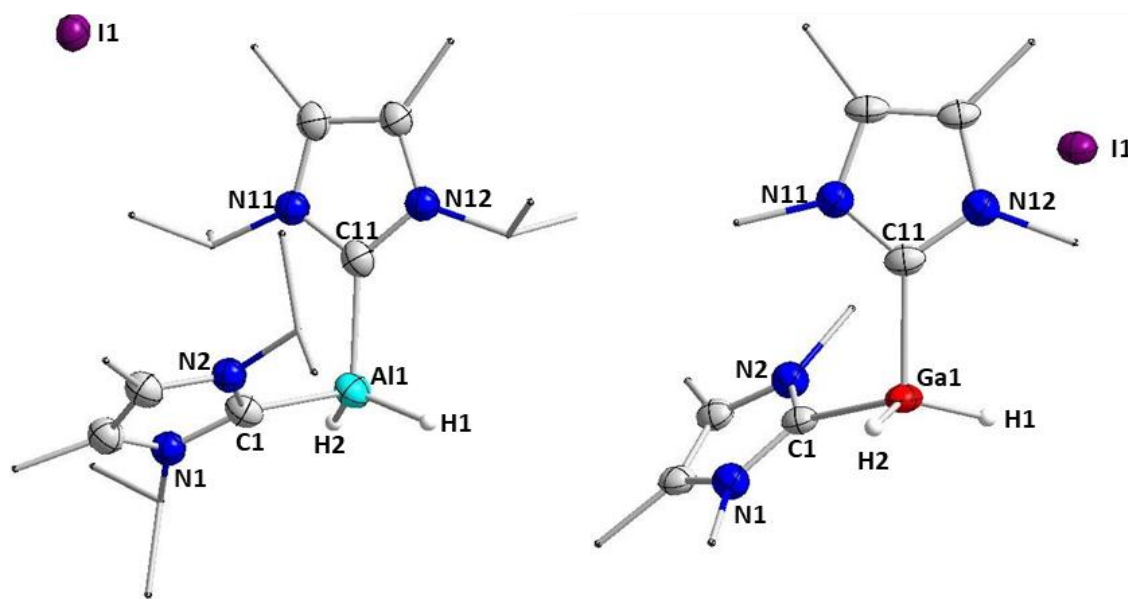


*Figure IV.2: Molecular structure of [(iPr$_2$Im$^{Me}$)$_2$·AlH$_2$]I **IV-9** (left) and [(Me$_2$Im$^{Me}$)$_2$·GaH$_2$]I **IV-10** (right) in the solid state (ellipsoids set at the 50% probability level). Hydrogen atoms with exception of those attached to aluminium and gallium were omitted for clarity. Selected bond lengths [Å] and angles [°]: **IV-9**: C1-Al1 2.048(4), C11-Al1 2.050(3), Al1-H1 1.47(4), Al1-H2 1.49(5); H1-Al1-H2 122.(3), C1-Al1-H1 107.0(17), C1-Al1-H2 108.(2), C1-Al1-C11 102.20(12), C11-Al1-H1 107.5(16), C11-Al1-H2 108.7(19); **IV-10**: C1-Ga1 2.027(4), C11-Ga1 2.025(4), Ga1-H1 1.38(7), Ga1-H2 1.29(4); H1-Ga1-H2 129.(4), C1-Ga1-H1 109.(3), C1-Ga1-H2 105.(3), C1-Ga1-C11 104.32(14), C11-Ga1-H1 104(3), C11-Ga1-H2 102(3).*

*Table IV.2 Selected NMR (ppm) and IR (cm$^{-1}$) shifts of the compounds [(Me$_2$Im$^{Me}$)$_2$·AlH$_2$]I **IV-7**, [(iPr$_2$Im)$_2$·AlH$_2$]I **IV-8**, [(iPr$_2$Im$^{Me}$)$_2$·AlH$_2$]I **IV-9**, [(Me$_2$Im$^{Me}$)$_2$·GaH$_2$]I **IV-10**, [(iPr$_2$Im$^{Me}$)$_2$·GaH$_2$]I **IV-11** and [(Dipp$_2$Im)·GaH$_2$(aDipp$_2$Im)]I **IV-12**.*

| | Ga-*H* <br> $^1$H NMR | N*C*N <br> $^{13}$C{$^1$H} NMR | $^{27}$Al{$^1$H} NMR | $v_{Al/Ga-H}$ |
|---|---|---|---|---|
| [(Me$_2$Im$^{Me}$)$_2$·AlH$_2$]I **IV-7** | - | - | - | 1772, 1791 |
| [(*i*Pr$_2$Im)$_2$·AlH$_2$]I **IV-8** | - | - | - | 1820, 1825 |
| [(*i*Pr$_2$Im$^{Me}$)$_2$·AlH$_2$]I **IV-9** | - | - | 108.7 | 1799, 1819 |
| [(Me$_2$Im$^{Me}$)$_2$·GaH$_2$]I **IV-10** | 4.17 | - | - | 1826, 1839 |
| [(*i*Pr$_2$Im$^{Me}$)$_2$·GaH$_2$]I **IV-11** | 4.37 | 162.8 | - | 1857, 1877 |
| [(Dipp$_2$Im)·GaH$_2$(*a*Dipp$_2$Im)]I **IV-11** | 3.23 | 171.6 | - | 1858, 1876 |

We propose that the reaction follows an associative substitution pathway in which the NHC coordinates to (NHC)·AlH$_2$I to form a neutral five coordinated intermediate bis-NHC adduct (NHC)$_2$·EH$_2$I (E = Al, Ga; Scheme IV.4, i). Our group observed earlier for the NHC ring expansion or ring opening of (NHC)·AlH$_3$ in the presence of NHC such a bis-NHC aluminium hydride adduct (*i*Pr$_2$Im)$_2$·AlH$_3$ which was the reactive intermediate for ring expansion.[66] Calculations have shown that the five coordinated bis-NHC adducts of group 13 hydrides are higher in energy and therefore less stable than the four coordinated tetrahedral mono NHC adducts and are often intermediates of further reactions.[102, 103] Instead of NHC ring expansion, we observed in the case of (NHC)$_2$·EH$_2$I stabilization by an elimination of the good leaving group iodide to give the four-coordinated tetrahedral aluminium or gallium cation, respectively (see Scheme IV.4, ii). The strong σ-donating alkyl substituted NHCs stabilize the cationic electron deficient metal centre in its 8 valence electron count.
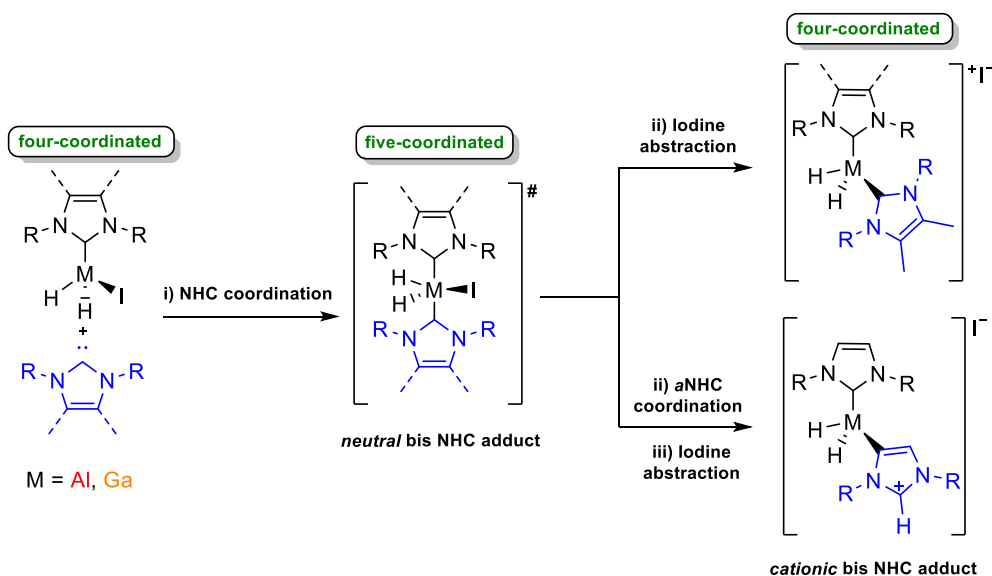
*Scheme IV. 4: Proposed mechanism of the formation of bis NHC aluminium- and gallium hydride cations.*

To further investigate the influence of the steric demand of the NHC on the reaction and to compare the reactivity with aluminium and gallium hydrides, we reacted the iodogalane adduct (Dipp$_2$Im)·GaH$_2$I **IV-6** with an additional equivalent of the NHC. For aluminium, Jones and Stasch *et al.* isolated earlier [(Dipp$_2$Im)·AlH$_2$(*a*Dipp$_2$Im)]I, in which the NHCs coordinate the cation in a *normal* and an *abnormal* NHC fashion.[45] The reaction of (Dipp$_2$Im)·GaH$_2$I **IV-6** with Dipp$_2$Im in benzene at room temperature afforded a soluble product which shows only one broadened set of signals for the NHC ligands in the $^1$H NMR spectrum. We assume that for this large NHC an equilibrium exists in solution between free Dipp$_2$Im and coordinated NHC in (Dipp$_2$Im)·GaH$_2$I. Heating the mixture up to the boiling point of toluene affords a colorless precipitate of the cation [(Dipp$_2$Im)·GaH$_2$(*a*Dipp$_2$Im)]I **IV-12** (see Scheme IV.5), which is stabilized with a *normal* and *abnormal* coordinated NHC. The compound [(Dipp$_2$Im)·GaH$_2$(*a*Dipp$_2$Im)]I **IV-12** was isolated from toluene as colorless powder in good yield (54 %) and excellent purity.
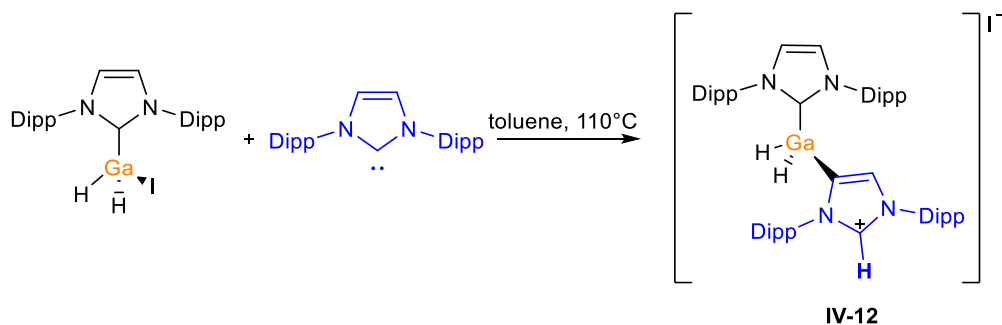
*Scheme IV.5: Synthesis of [(Dipp$_2$Im)·GaH$_2$(aDipp$_2$Im)]I **IV-12**.*

The compound **IV-12** was characterized by NMR spectroscopy, IR spectroscopy and elemental analysis. The most important NMR and IR data are summarized in Table IV.8. The $^1$H NMR spectrum shows one set of signals for the *normal* and one set for the *abnormal* coordinated NHC. The hydrides were detected at $\delta$ = 3.23 ppm in the $^1$H NMR spectrum. In the $^{13}$C{$^1$H} NMR spectrum the carbene carbon atom of the *normal* coordinating NHC was detected at 171.6 ppm, which is in good accordance to the compound (Dipp$_2$Im)·GaH$_2$I **IV-12** at $\delta$ = 170.3 ppm. The characteristic metal hydride stretching vibrations were observed at 1858 and 1876 cm$^{-1}$ (see Table IV.8) and compare well with the literature known cationic aluminium dihydride [(Dipp$_2$Im)·AlH$_2$(aDipp$_2$Im)]$^+$I$^-$ (1811, 1827 cm$^{-1}$).[45]

Single crystals of the compound [(Dipp$_2$Im)·GaH$_2$(aDipp$_2$Im)]I **IV-12** were grown by slow evaporation of a saturated solution in acetonitrile at room temperature (see Figure IV.3). [(Dipp$_2$Im)·GaH$_2$(aDipp$_2$Im)]I **IV-12** crystallizes in the monoclinic space group *P*2$_1$/*n*. The molecule adopts a tetrahedral structure spanned by one *normal* and one *abnormal* NHC ligand and the two hydrogen atoms. The Ga-C$_{NHC}$ bond length is slightly shorter for the *abnormal* coordinated NHC (Ga-C$_{aNHC}$ = 2.0164(22) Å) compared with the *normal* coordinated NHC (Ga-C$_{NHC}$ = 2.0570(23) Å) as expected due to less steric demand and better $\sigma$-donating properties of the ab*normal* NHC. These results are in good accordance with the aluminium analogue cation [(Dipp$_2$Im)·AlH$_2$(aDipp$_2$Im)]I presented earlier by Jones and Stasch *et al.* (Al-C$_{aNHC}$ = 2.012(2) Å and Ga-C$_{NHC}$ = 2.051(2) Å).[45]

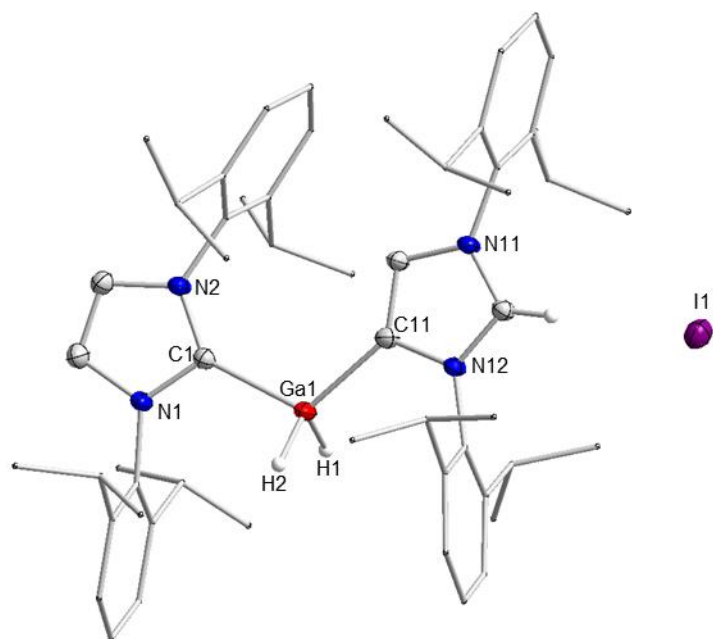*Figure IV.3: Molecular structure of [(Dipp₂Im)·GaH₂(aDipp₂Im)]I* **IV-12** *in the solid state (ellipsoids set at the 50% probability level). Hydrogen atoms with exception of those attached to the abnormal former carbene carbon atom and gallium were omitted for clarity. Selected bond lengths [Å] and angles [°]: C1-Ga1 2.057(2), C11-Ga1 2.016(2), Ga1-H1 1.46(4), Ga1-H2 1.58(4); H1-Ga1-H2 116.(2), C1-Ga1-H1 101.4(14), C1-Ga1-H2 102.6(15), C1-Ga1-C11 113.55(9), C11-Ga1-H1 111.6(14), C11-Ga1-H2 111.1(16).*

We propose that the formation of the compound **IV-12** follows a similar mechanism postulated by Jones and Stasch *et al.*[45] for the aluminium analogue compound and the earlier discussed cationic bis NHC alanes and gallanes. We also observe an equilibrium in solution *via* a reactive five-coordinated bis NHC stabilized intermediate (Dipp₂Im)₂·AlH₂I. Due to steric demand of both NHCs, stabilization of the compound was reached by steric relief, i.e. (ii) switching one of the NHCs into an *abnormal* coordination mode and (iii) abstraction of the good iodide leaving group, to yield the four-coordinated gallium cation (see Scheme IV.4 & IV.5).

## 4.3 Conclusion

The synthesis of the NHC-stabilized cationic aluminium- and gallium hydrides [(NHC)$_2$·AlH$_2$]I (NHC = Me$_2$Im$^{Me}$ **IV-7**, $i$Pr$_2$Im **IV-8**, $i$Pr$_2$Im$^{Me}$ **IV-9**) and [(NHC)$_2$·GaH$_2$]I (NHC = Me$_2$Im$^{Me}$ **IV-10**, $i$Pr$_2$Im$^{Me}$ **IV-11**), balanced by an iodide counter anion, is reported. These cations are accessible in good yields and high purity *via* the direct reaction of the free carbenes (Me$_2$Im$^{Me}$, $i$Pr$_2$Im, $i$Pr$_2$Im$^{Me}$) with the corresponding group 13 NHC hydride iodide complexes (NHC)·AlH$_2$I (NHC = Me$_2$Im$^{Me}$ **IV-1**, $i$Pr$_2$Im **IV-2**, $i$Pr$_2$Im$^{Me}$ **IV-3**) and (NHC)·GaH$_2$I (NHC = Me$_2$Im$^{Me}$ **IV-4**, $i$Pr$_2$Im$^{Me}$ **IV-5**), respectively. The NHC iodo alanes and iodo gallanes **IV-1 - IV-6** were prepared *via* a simple efficient synthesis starting from (NHC)·EH$_3$ (NHC = Me$_2$Im$^{Me}$, $i$Pr$_2$Im$^{Me}$; E = Al, Ga) and either elemental iodine or methyl iodide. The compounds [(NHC)$_2$·GaH$_2$]I (NHC = Me$_2$Im$^{Me}$ **IV-9**, $i$Pr$_2$Im$^{Me}$ **IV-10**) are the first examples of NHC stabilized gallium hydride cations reported. Additionally, we investigated the influence of the steric demand of the NHC used and synthesized [(Dipp$_2$Im)·GaH$_2$($a$Dipp$_2$Im)]I **IV-12**, in which *normal* and *abnormal* coordination of the NHC was observed.
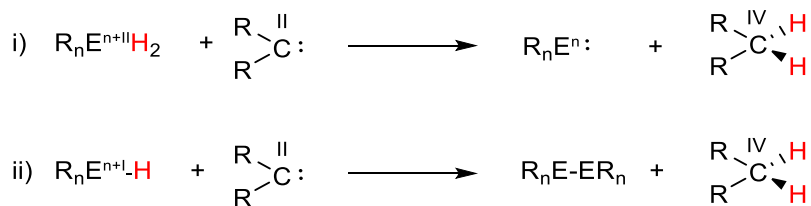
CHAPTER V


CARBENES AS REDUCTANT IN GROUP 13 CHEMISTRY

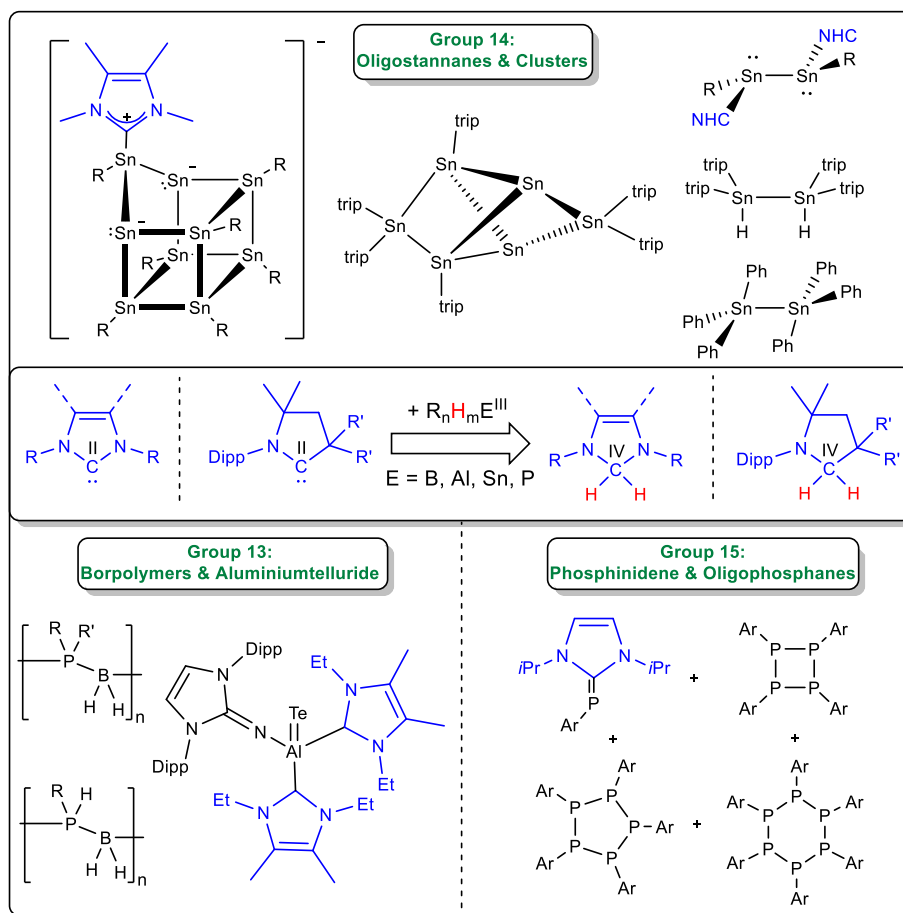# 5 CARBENES AS REDUCTANT IN GROUP 13 CHEMISTRY

## 5.1 Introduction

It has been shown over the last decade that enthalpically strong bonds such as H-H, H-N, C-C, B-C, N-C, O-C and Si-C bonds can be cleaved by singlet carbenes and related molecules such as *N*-heterocyclic carbenes (NHCs) and cyclic(alkyl)(amino)carbenes (cAACs).[90, 92, 94, 97-99, 107, 108, 111-114, 116-119, 198, 239] A central electronic property of these singlet carbenes is a occupied $\sigma$- and a vacant $p_\pi$-type orbital at the carbene carbon atom, which leads simultaneously to an electrophilic and nucleophilic center. This characteristic mimics the situation typically found in transition-metal complexes and enables the activation of small molecules and the insertion of carbenes into enthalpically strong single bonds.[114, 118, 198] The reaction products of the carbon(IV) compounds resulting from these insertions reveal different stabilities, mainly in dependence on the HOMO-LUMO gap of the carbene used and on the single bond added. Many of these oxidative addition products are thermodynamically stable and do not undergo further reactions.[66, 90, 92, 108, 120, 121, 127] However, we and others demonstrated that some of these insertion products are labile with respect to ring expansion (RER) or ring opening reactions (ROR) of NHCs and cAACs.[36, 66, 90, 94, 97-100, 106, 108, 109] For polyhydrides, the reductive elimination of a dihydroaminal $R_2Im-H_2$ was reported, which is then equivalent to the metal-free reduction of main group element hydrides using NHCs as hydrogen acceptor. For example the reaction of main group element dihydrides $R_nEH_2$ with NHC leading to a dihydroaminal formally provide subvalent species $R_nE$, which most probably further react in subsequent transformations (see Scheme V.1, i) Furthermore, it is conceivable that monohydrides $R_nE-H$ react with carbenes to yield a dihydroaminal with dehydrogenative bond formation to afford for example $R_n-E-E-R_n$ (see Scheme V.1, ii). For both reactions some examples are already available in the literature.

i) $R_nE^{n+II}H_2$ + $\underset{R}{\overset{R}{>}}C\colon^{II}$ ⟶ $R_nE^n\colon$ + $\underset{R}{\overset{R}{>}}C^{IV}\overset{H}{\underset{H}{<}}$

ii) $R_nE^{n+I}$-$H$ + $\underset{R}{\overset{R}{>}}C\colon^{II}$ ⟶ $R_nE$-$ER_n$ + $\underset{R}{\overset{R}{>}}C^{IV}\overset{H}{\underset{H}{<}}$

*Scheme V.1: Dehydrogenative coupling of main group element hydrides with NHCs.*

We reported the dehydrocoupling of triorganotin monohydrides induced by the small NHCs *i*Pr$_2$Im and *i*Pr$_2$Im$^{Me}$ with formation of distannanes (see Scheme V.2).[87] Furthermore, we also demonstrated that *i*Pr$_2$Im can be used in metal free dehydrogenative coupling of secondary and primary phosphines.[88] Depending on the stoichiometric between the phosphine and the NHC used, the formation of diphosphines, cyclic oligophosphines and NHC phosphinidene adducts was observed (see Scheme V.1).[88] Wesemann and coworkers reported the NHC-induced reductive elimination of dihydrogen from tin hydrides in some detail.[89, 240, 241] In dependence on the steric demand of the tin aryl substituent and the stochiometric employed different low valent monomeric, dimeric and oligomeric organotin species were observed (see Scheme V.1).[89, 240, 241] Inoue *et al.* reported recently the synthesis of an aluminium telluride using Et$_2$Im$^{Me}$ as hydrogen acceptor (see Scheme V.2).[86, 233, 242] Manners *et al.* introduced a metal free dehydropolymerisation of phosphine-boranes using cAACs as hydrogen acceptors with reductive elimination of cAAC-H$_2$.[243] In course of this reaction cAAC$^{Me}$ inserts into the P-H bond of the phosphine-boranes followed by thermolysis to give the hydrogenated carbene cAAC$^{Me}$H$_2$ and the polymers (see Scheme V.1). Remarkably, for the sterically more demanding cAAC$^{Cy}$ dehydropolymerisation was observed already after one hour at ambient temperatures.

*Scheme V.2: Carbenes as reductant in main group element hydride chemistry.*

In all these examples the carbene may be considered as reductant, in which the carbon atom gets oxidized from oxidation state +2 in the carbene to oxidation state +4 in the dihydroaminal $R_2$Im-$H_2$. As already early reports on the NHC chemistry of group 13 hydrides demonstrated NHC-$H_2$ formation with decomposition of the compounds[49, 149, 157, 244, 245] we wondered if NHCs and related molecules may be used for a targeted, controlled synthesis of subvalent group 13 compounds by hydride abstraction. We recently reported the reaction of cAAC$^{Me}$ with the NHC stabilized parent alanes and gallanes leading to exceptionally stable oxidative addition products (NHC)·$MH_2$(cAAC$^{Me}$H) (M = Al, Ga),[66, 237] which did not eliminate NHC-$H_2$ or cAAC$^{Me}$-$H_2$ even at higher temperatures of 110 °C. This work is expended on substituted aluminum and gallium hydrides using the pentamethylcyclopentadienyl substituent, since it provides additional stability to potentially subvalent reaction products. Herein the synthesis of NHC stabilized pentamethylcyclopentadienyl aluminium and gallium

dihydrides (NHC)·$MH_2Cp^*$ (M = Al, Ga) is described as well as their further reactivity of the resulting compounds with NHCs and cAAC$^{Me}$. We provide evidence that NHCs and cAAC$^{Me}$ may be used as reducing reagents to provide monovalent Cp*E (E = Al, Ga) from these hydride precursors.

## 5.2 Results and Discussion

Cyclopentadienyl substituted aluminium hydrides are excellent precursors for the synthesis of low valent aluminium(I) species. Fischer *et al.* reported the metal free reductive elimination of Cp*H from heating up Cp*$_2$AlH with formation of Cp*Al$^I$ in a clean reaction.[65] To our surprise, there are currently only a few examples of reports on NHC-stabilized heavier group 13 element (E= Al, Ga) cyclopentadienyl complexes. Cowley and coworkers reported the synthesis of the NHC stabilized compounds (NHC)·Cp*$_2$AlH (NHC= Me$_2$Im$^{Me}$, *i*Pr$_2$Im$^{Me}$) to investigate the influence of ligand coordination on the reductive elimination of Cp*H from these aluminium(III) complexes.[63] It was demonstrated that the strong $\sigma$-donating NHC ligands increase the stability of the aluminium(III) adducts, inhibit reductive elimination of Cp*H even at high temperatures (100 °C), and thus no formation of Cp*Al$^I$ was observed.[65] The same group described the unusual formation of (Me$_2$Im$^{Me}$)·Cp*$_2$GaH in the reaction of Cp*$_3$Ga with the small NHC Me$_2$Im$^{Me}$.[64]

NHC-stabilized complexes (NHC)·Cp*EH$_2$ (E = Al, Ga) with only one Cp* substituent were synthesized either from the reaction of (Cp*AlH$_2$)$_3$ with one equivalent of the corresponding NHC or from the reaction of (NHC)·GaH$_2$I (NHC = Me$_2$Im$^{Me}$ **IV-4**, *i*Pr$_2$Im$^{Me}$ **IV-5**, Dipp$_2$Im **IV-6**) (see Chapter IV)[246] with KCp* (Scheme V.3). The reaction of (Cp*AlH$_2$)$_3$ with one equivalent of the corresponding NHCs Me$_2$Im$^{Me}$, *i*Pr$_2$Im$^{Me}$, Dipp$_2$Im in *n*-hexane at room temperature afforded the compounds (NHC)·Cp*AlH$_2$ (NHC = Me$_2$Im$^{Me}$ **V-1**, *i*Pr$_2$Im$^{Me}$ **V-2**, Dipp$_2$Im **V-3**), which were isolated as colourless powders in good yields (**V-1**: 75 %, **V-2**: 47 %, **V-3**: 55 %; see Scheme V.3). The gallane adducts were synthesized starting from (NHC)·GaH$_2$I (NHC = Me$_2$Im$^{Me}$ **IV-4**, *i*Pr$_2$Im$^{Me}$ **IV-5**, Dipp$_2$Im **IV-6**) (see Chapter IV) and KCp* in toluene at room temperature, which led to formation of (NHC)·Cp*GaH$_2$ (NHC = Me$_2$Im$^{Me}$ **V-4**, *i*Pr$_2$Im$^{Me}$ **V-5**, Dipp$_2$Im **V-6**) in moderate to good yields (**V-4**: 66 %, **V-5**: 46 %, **V-6**: 40 %; see Scheme V.3).
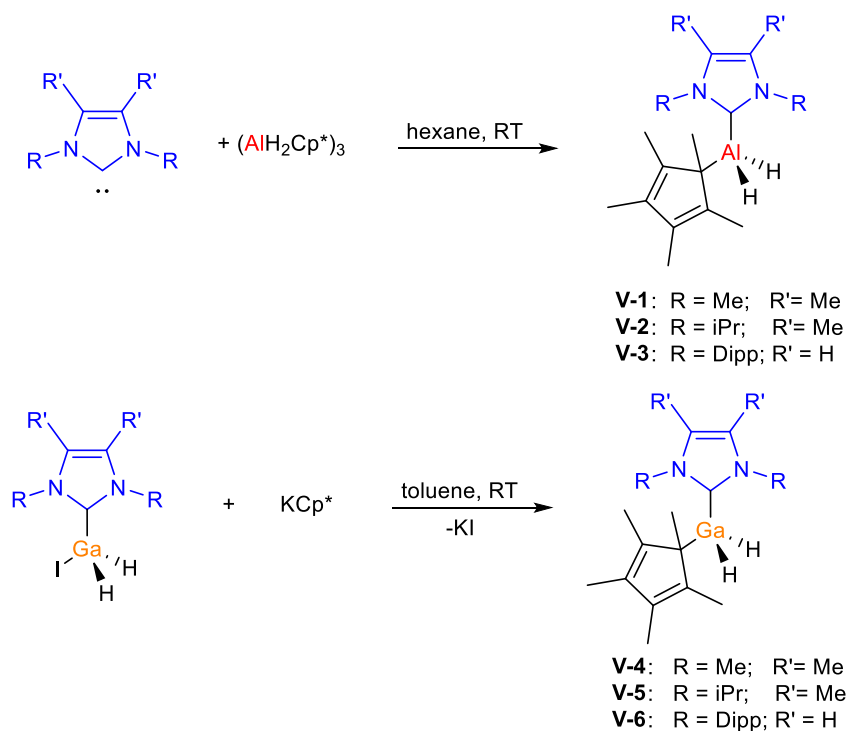
*Scheme V.3: Synthesis of (NHC)·Cp\*AlH$_2$ (NHC= Me$_2$Im$^{Me}$ **V-1**, iPr$_2$Im$^{Me}$ **V-2**, Dipp$_2$Im **V-3**) and (NHC)·Cp\*GaH$_2$ (NHC= Me$_2$Im$^{Me}$ **V-4**, iPr$_2$Im$^{Me}$ **V-5**, Dipp$_2$Im **V-6**).*

The central atoms of the compounds **V-1** – **V-6** are 8 valence electron metal centers, if the pentamethylcyclopentadienyl ligand coordinates in a $\eta^1$ fashion. Thus, $\eta^1$ hapticity of the Cp\* substituent was confirmed by X-ray diffraction analysis of single crystals of (Me$_2$Im$^{Me}$)·Cp\*AlH$_2$ **V-1**, (Dipp$_2$Im)·Cp\*AlH$_2$ **V-3** and (Me$_2$Im$^{Me}$)·Cp\*GaH$_2$ **V-4** (see Figure V.1). Single crystals of these compounds were grown by slow evaporation of a saturated solution in benzene at room temperature. The molecule structures of **V-1**, **V-3** and **V-4** reveal four coordinated NHC adducts (see Figure V.1), which adopt a tetrahedral coordination at the metal center, spanned by the NHC, two hydride atoms and the $\eta^1$-Cp\* ligand. The M-C$_{NHC}$ (M = Al, Ga) bond lengths of 2.02938(17) Å (**V-1**), 2.1020(14) Å (**V-3**) and 2.0333(14) Å (**V-4**) differ only marginally from the bond lengths observed in other NHC aluminium(III)- and gallium(III) hydride adducts.[31] The M-C$_{Cp*}$ (M = Al, Ga) bond lengths 2.0695 Å (**V-1**), 2.0891 Å (**V-3**) of the alanes are slightly shorter than the bond length 2.0875(14) Å observed for (Me$_2$Im$^{Me}$)·Cp\*GaH$_2$ (**V-4**) and are similar to the values reported for other carbene stabilized pentamethylcyclopentadienyl aluminium chlorides and bromides.[67, 68]
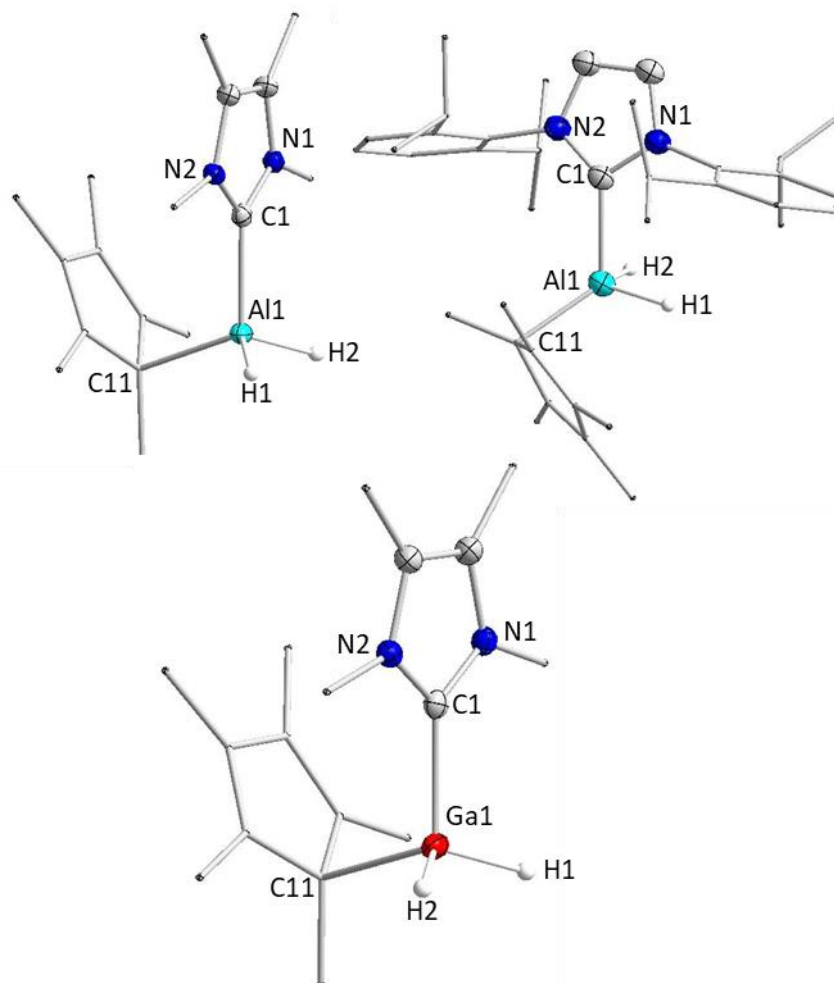
*Figure V.1: Molecular structures of (Me$_2$Im$^{Me}$)·Cp\*AlH$_2$ **V-1** (top left), (Dipp$_2$Im)· Cp\*AlH$_2$ **V-3** (top right) and (Me$_2$Im$^{Me}$)·Cp\*GaH$_2$ **V-4** (bottom) in the solid state (ellipsoids set at the 50% probability level). Hydrogen atoms with exception of the hydride substituents H1 and H2 are omitted for clarity. Selected bond lengths [Å] and angles [°]:**V-1**: Al1-C1 2.0296(17), Al1-C11 2.0699(18), Al1-H1 1.430(13), Al1-H2 1.576(17) ;C1-Al1-C11 110.19(7), C1-Al1-H1 108.2(7), C11-Al1-H1 111.7(6), C1-Al1-H2 105.7(6), C11-Al1-H2 112.1(6), H1-Al1-H2 108.6(9); **V-3**: Al1-C11 2.0900(14), Al1-C1 2.1010(13), Al1-H2 1.638(12), Al1-H1 1.455(18); C11-Al1-C1 120.01(6), C11-Al1-H2 116.1(5), C1-Al1-H2 93.3(5), C11-Al1-H1 113.4(7), C1-Al1-H1 100.8(7), H2-Al1-H1 110.7(9); **V-4**: Ga1-C1 2.033(14), Ga1-C11 2.0875(14), Ga1-H1 1.50(2), Ga1-H2 1.48(2); C1-Ga1-C11 106.49(5), C1-Ga1-H2 107.9(9), C11-Ga1-H2 110.7(8), C1-Ga1-H1 106.2(8), C11-Ga1-H1 111.2(8), H2-Ga1-H1 113.9(12).*

The compounds **V-1 - V-6** were characterized by NMR spectroscopy, IR spectroscopy, and elemental analysis. The most important NMR and IR data of **V-1 - V-6** are summarized in Table V.1. In solution, sigmatropic rearrangement of the (NHC)·MH$_2$ (M

= Al, Ga) moiety around the pentamethylcyclopentadienyl ligand is fast on the NMR timescale, as the ^{1}H NMR spectra of these compounds reveal instead of the three distinct resonances of the Cp* methyl groups expected for slow migration two singlets in a 4:1 ratio for the aluminium hydrides **V-1 - V-4** and only one sharp singlet for the gallium compounds **V-4 - V-6** (see Table V.1). The ^{1}H NMR resonances of the hydride substituents bound to the central gallium atom for the compounds **V-4 - V-6** were detected at $\delta$ = 4.90 ppm (**V-4**), 4.75 ppm (**V-5**) and 3.66 ppm (**V-6**). For **V-1 - V-3** the hydride resonances bound to the aluminium atom were not observed due to the quadrupole moment of the $^{27}Al$ nucleus, but broadened absorptions for hydride stretching frequencies were observed at 1713 (**V-1**), 1712 (**V-2**) and 1760 (**V-3**) cm$^{-1}$ in the IR spectrum. In the $^{13}C\{^1H\}$ NMR spectra resonances for the carbene carbon atom of the compounds **V-1 – V-6** were found at $\delta$ = 168.6 ppm (**V-1**), 179.0 ppm (**V-2**), 169.5 ppm (**V-3**), 171.4 ppm (**V-6**) and 182.6 ppm (**V-6**), which are only slightly shifted compared to the parent NHC stabilized alanes and gallanes.[31]

The alane adducts **V-1 - V-3** are stable in solution at least up to the boiling point of benzene (80 °C) and show no decomposition or change in the ^{1}H NMR spectra. These results are in good accordance with findings of Cowley and coworker on the increased stability of Cp*$_2$AlH upon coordination with strong $\sigma$-donating NHCs, which inhibit reductive elimination of Cp*H.[63] Heating of the gallium compounds ($i$Pr$_2$Im$^{Me}$)·Cp*GaH$_2$ **V-5** and (Dipp$_2$Im)·Cp*GaH$_2$ **V-6** in benzene up to a temperature of 60 °C leads to irreversible and quantitative (on the NMR scale) reductive elimination/dismutation at gallium, which affords (NHC)·GaH$_3$, Cp*H, free NHC and Cp*Ga$^I$, which were characterized by ^{1}H NMR spectroscopy. We assume that dissolved (NHC)·Cp*GaH$_2$ lies at higher temperatures in a reversible equilibrium with (NHC)·GaH$_3$ and (NHC)·Cp*$_2$GaH, and that the latter eliminates Cp*H with formation of the free NHC and Cp*Ga$^I$ (see Scheme V.4). The reductive elimination should be preferred thermodynamically as well entropically as in the case of gallium.

*Table V.1: Selected NMR (ppm) and IR (cm$^{-1}$) shifts of the compounds (NHC)·Cp\*AlH$_2$ (NHC= Me$_2$Im$^{Me}$ **V-1**, iPr$_2$Im$^{Me}$ **V-2**, Dipp$_2$Im **V-3**) and (NHC)·Cp\*GaH$_2$ (NHC= Me$_2$Im$^{Me}$ **V-4**, iPr$_2$Im$^{Me}$ **V-5**, Dipp$_2$Im **V-6**).*

| | Cp\*-C$H_3$ | Ga-$H$ | NCN | $\nu$Al/Ga-H |
|---|---|---|---|---|
| | $^1$H NMR | $^1$H NMR | $^{13}$C{$^1$H} NMR | |
| (Me$_2$Im$^{Me}$)·Cp\*AlH$_2$ **V-1** | 2.02, 2.05 | - | - | 1713 |
| (*i*Pr$_2$Im$^{Me}$)·Cp\*AlH$_2$ **V-2** | 2.18, 2.22 | - | 168.6 | 1712 |
| (Dipp$_2$Im)·Cp\*AlH$_2$ **V-3** | 1.87, 1.89 | - | 179.0 | 1760 |
| (Me$_2$Im$^{Me}$)·Cp\*GaH$_2$ **V-4** | 2.15 | 4.75 | 169.5 | - |
| (*i*Pr$_2$Im$^{Me}$)·Cp\*GaH$_2$ **V-5** | 1.99 | 4.89 | 171.4 | 1862 |
| (Dipp$_2$Im)·Cp\*GaH$_2$ **V-6** | 1.86 | 3.66 | 182.6 | 1785 |
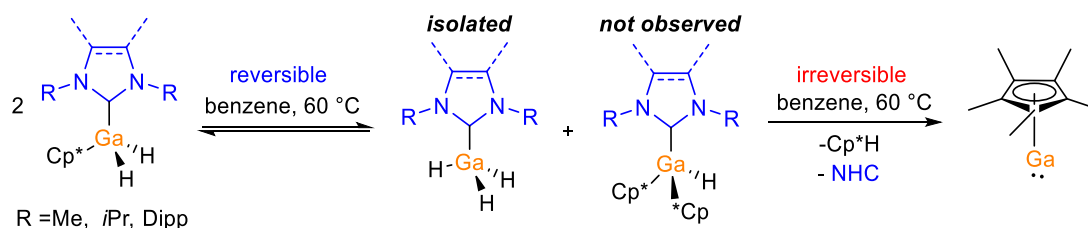


*Scheme V.4: Proposed mechanism of the reductive elimination reaction.*

However, heating of (Me$_2$Im$^{Me}$)·Cp\*GaH$_2$ **V-4**, the gallium compound of the small and very basic NHC Me$_2$Im$^{Me}$, to 80 °C in benzene leads to reductive elimination products only slowly and in traces, which is also in accordance with the isolation and characterization of (Me$_2$Im$^{Me}$)·Cp\*$_2$GaH by Cowley *et al.* as reported earlier. [64] Thus reductive elimination of Cp\*H depends on the size of the NHC employed, *i.e.* it is preferred for sterically more demanding NHCs.

To further evaluate the influence of the donor/acceptor strength of the NHC used on the decomposition and to compare the reactivity of aluminium and gallium hydrides, we additionally reacted (Cp\*AlH$_2$)$_3$ with the sterically demanding, backbone saturated NHC Dipp$_2$Im$^H$ and the iodogallane adduct (Dipp$_2$Im$^H$)·GaH$_2$I (see Chapter 4) with

KCp*. The reaction of (Dipp$_2$Im$^H$)·GaH$_2$I with KCp* leads at room temperature immediately and quantitatively to (Dipp$_2$Im$^H$)·GaH$_3$, Cp*H, free NHC and Cp*Ga$^I$ according to $^1$H NMR spectroscopy, and no formation of (Dipp$_2$Im$^H$)·Cp*GaH$_2$ was observed at all.

For the reaction of (Cp*AlH$_2$)$_3$ with Dipp$_2$Im$^H$ in C$_6$D$_6$ at room temperature a splitting of the NHC resonances was observed in the $^1$H NMR spectra after 30 min, similar to the signal sets reported earlier for NHC ring expansion products.[90, 92, 94] Thus, the reaction of (Cp*AlH$_2$)$_3$ with Dipp$_2$Im$^H$ in benzene leads already at room temperature to the ring expansion product (RER-Dipp$_2$ImH$_2$)AlCp* **V-7** (see Scheme V.5).
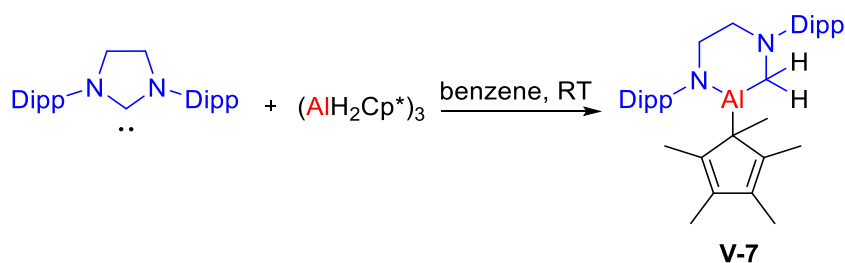


*Scheme V.5: Synthesis of the NHC ring expansion product (RER-Dipp$_2$ImH$_2$)AlCp\*.*

For the better π-accepting NHC Dipp$_2$Im$^H$ the Al-H bond activation with insertion of the carbene into the Al-H bond is preferred. Immediately after insertion the NHC ring expansion occurs and the stable six-membered heterocyclic ring was formed. We already observed the preference of backbone saturated NHCs to undergo NHC ring expansion even at ambient temperature with boranes earlier.[90, 92]

Compound **V-7** was characterized by NMR spectroscopy, IR spectroscopy and elemental analysis. In the $^1$H NMR spectra the resonances of the NHC backbone split into a multiplet between 3.17 and 3.26 ppm, those of the Dipp methine protons into two septets at 3.67 ppm and 3.76 ppm and a singlet at 2.21 ppm arises from the AlC*H$_2$*N protons located at the former carbene carbon atom. For the Cp* methyl protons one sharp singlet at 1.71 ppm was detected, indicating fast sigmatropic rearrangement of the Cp* substituent. The $^{13}$C{$^1$H} NMR spectrum of **V-7** shows a characteristic high-field shifted resonance of the former carbene carbon atom AlC*H$_2$N at 40.2 ppm, and the IR spectrum of isolated **V-7** reveals no remaining Al-H stretching vibration.

Despite some effort single crystals of **V-7** suitable for X-ray diffraction were never obtained from saturated solutions of the compound in different solvents. However, if compound **V-7** was reacted with $Me_2Im^{Me}$ in $C_6D_6$ and the solution was slowly evaporated, yellow single crystals suitable for X-ray diffraction of the adduct $(Me_2Im^{Me})\cdot AlCp^*(RER\text{-}Dipp_2Im^HH_2)$ **V-8** (see Figure V.2) are formed. Compound **V-8** crystallizes in the orthorhombic space group $P2_12_12$. The central aluminium atom is coordinated in a distorted tetrahedral environment by the former carbene carbon atom and the nitrogen atom of the ring-expanded $Dipp_2Im^H$, the $Cp^*$ substituent and the coordinating NHC $Me_2Im^{Me}$. The $Al\text{-}C_{NHC}$ bond length of 2.043(2) Å (**V-8**) is slightly longer compared to those of the NHC stabilized adduct $(Me_2Im^{Me})\cdot Cp^*AlH_2$ **V-1** (2.02938(17) Å). However, the $Al\text{-}C_{Cp^*}$ bond length (2.113(2) Å) compares well with other NHC adducts $(NHC)\cdot Cp^*AlH_2$.
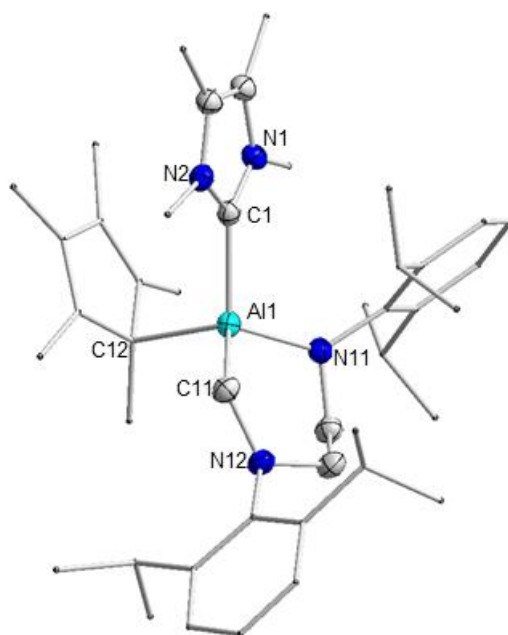


*Figure V.2: Molecular structure of $(Me_2Im^{Me})\cdot AlCp^*(RER\text{-}Dipp_2Im^HH_2)$ **V-8** in the solid state (ellipsoids set at the 50% probability level). Hydrogen atoms as well as the disordering are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al1-C1 2.043(2), Al1-C11 2.029(2), Al1-C12 2.113(2), Al1-N11 1.852(2); C1-Al1-C11 114.78(10), C1-Al1-C12 103.97(9), C1-Al1-N11 108.63(9), C11-Al1-C12 110.73(10), C11-Al1-N11 100.61(10).*

Cyclic alkyl(amino)carbenes (cAACs) are stronger electrophiles and nucleophiles compared to NHCs and are thus more reactive with respect to E-H bond activation.[111, 112] We recently reported the reaction of cAAC$^{Me}$ with the NHC stabilized parent alanes and gallanes.[66, 237] We demonstrated that the reaction of cAAC$^{Me}$ with the (NHC)·AlH$_3$ adducts leads to insertion of the cAAC$^{Me}$ carbene carbon atom into the Al-H bond to yield (NHC)·AlH$_2$(cAAC$^{Me}$H).[66] The reaction of cAAC$^{Me}$ with the heavier gallane analogue (NHC)·GaH$_3$ depends on the steric demand of the NHC in use. Smaller NHCs such as Me$_2$Im$^{Me}$ and $i$Pr$_2$Im$^{Me}$ led to insertion of one equivalent cAAC$^{Me}$ into one Ga-H bond whereas sterically more demanding NHCs such as Dipp$_2$Im and Dipp$_2$Im$^H$ led to insertion of two equivalents cAAC$^{Me}$ with elimination of the NHC and formation of the bisalkyl gallane (cAAC$^{Me}$H)$_2$GaH (see Chapter 3). These oxidative addition products are all stable in solution up to the boiling point of toluene and no ring expansion reaction or reductive elimination of the cAAC$^{Me}$ ligand was observed.[237]

The reaction of (Me$_2$Im$^{Me}$)·Cp*AlH$_2$ **V-1** with cAAC$^{Me}$ in toluene leads immediately to insertion of the cAAC$^{Me}$ carbene carbon atom into the Al-H bond of **V-1** with formation of the compound (Me$_2$Im$^{Me}$)·AlHCp*(cAAC$^{Me}$H) **V-9** (see Scheme V.6).
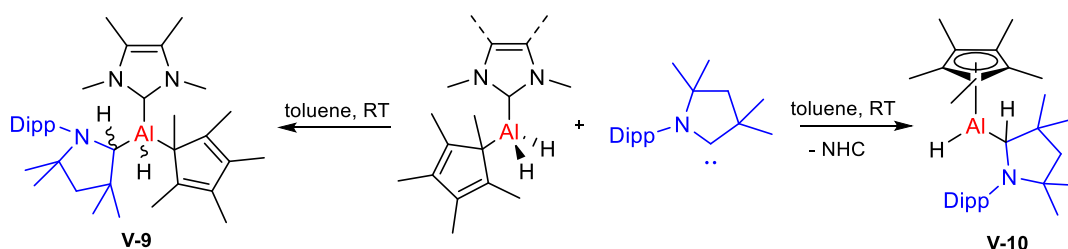


*Scheme V.6: Reaction of (NHC)·Cp*AlH$_2$ (NHC = Me$_2$Im$^{Me}$, iPr$_2$Im$^{Me}$, Dipp$_2$Im) with cAAC$^{Me}$.*

Single crystals of *rac*-(Me$_2$Im$^{Me}$)·(R/R)AlHCp*(cAAC$^{Me}$H) **V-9** suitable for X-ray diffraction were grown by slow evaporation of a saturated solution in benzene at room temperature (see Figure V.3). Compound **V-9** crystallizes in form of the *rac*(R,R)-isomer in the monoclinic space group *P*2$_1$/c. The moleculare structure of **V-9** reveals the presence of two chiral centers. One at the central aluminium atom and the second at the former cAAC$^{Me}$ carbene carbon atom.

Compound **V-9** was characterized by multinuclear NMR spectroscopy, IR spectroscopy and elemental analysis. The $^1$H NMR spectrum of compound **V-9** in $C_6D_6$ in solution at room temperature shows only the resonances of the *rac*(S,S)/*rac*(R,R)-isomer, which cannot be distinguished by NMR spectroscopy. For the diastereomeric *meso*(S/R)/*meso*(R/S) isomer one additional set of signals would be expected in the NMR spectra. The $^1$H and $^{13}$C{$^1$H} NMR spectra of *rac-* **V-9** reveal resonances for each set of hydrogen atoms and carbon atoms of the cAAC$^{Me}$ separately due to the chirality of the former cAAC$^{Me}$ carbene carbon atom. For example, the resonances of the cAAC Dipp isopropyl methine protons emerge as two septets at 3.19 ppm and 3.69 ppm. The diastereotopic $CH_2$ protons are observed as two doublets at 1.91 ppm and 2.30 ppm, the methyl groups of the cAAC backbone as four separate singlets at 1.25 ppm, 1.28 ppm, 1.32 ppm and 1.85 ppm and the hydrogen atom bound to the former cAAC$^{Me}$ carbene carbon atom as a singlet at 3.69 ppm. The methyl resonances of the NHC ligand split into four singlets due to hindered rotation of the NHC around the Al-$C_{NHC}$ axis. The Cp* methyl groups give rise to a singlet at 1.67 ppm. In the $^{13}$C{$^1$H} NMR spectrum, the resonance of the former cAAC$^{Me}$ carbene carbon atom is significantly high field shifted from 313.5 ppm (free cAAC$^{Me}$) to 69.9 ppm, broadened by the interaction with the $^{27}$Al nucleus. The resonance of the Me$_2$Im$^{Me}$ carbene carbon atom at 170.6 ppm is only slightly shifted compared to (Me$_2$Im$^{Me}$)·AlH$_2$(cAAC$^{Me}$) at 174.4 ppm reported earlier. The IR spectrum shows the characteristic Al-H stretching vibration of the aluminium hydride atom at 1770 cm$^{-1}$.
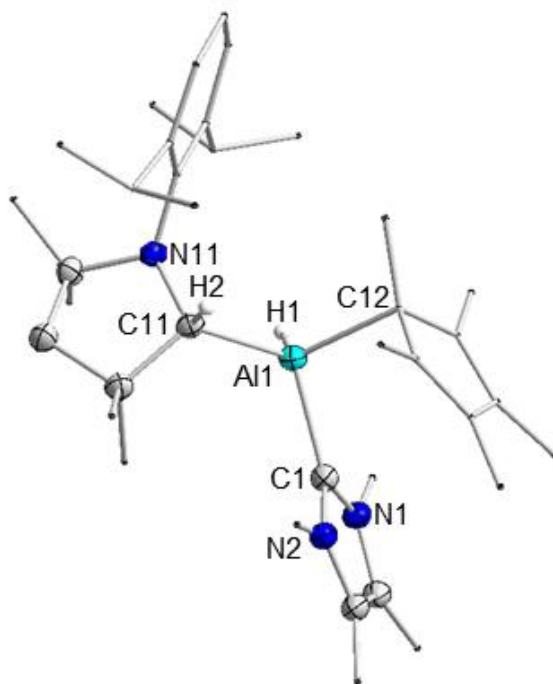
*Figure V.3: Molecular structure of (Me₂Im^{Me})·(R/R)AlHCp\*(cAAC^{Me}H) rac(R,R)-**V-9** in the solid state (ellipsoids set at the 50% probability level). Hydrogen atoms with exception of H1 and H2 are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al1-C1 2.0760(13), Al1-C11 2.0572(13), Al1-C12 2.1186(14), Al1-H1 1.561(18); H1-Al1-C11 111.8(12), C11-Al1-C1 100.90(7), C1-Al1-C11 119.43(5), C1-Al1-H1 103.8(6), C1-Al1-C12 113.95(5), C11-Al1-H1 107.2(6), C11-Al1-C12 101.03(5).*

Heating a solution of *rac*-**V-9** in $C_6D_6$ to 70 °C for 12 hours leads to a full conversion into another compound judged by ^{1}H NMR. At this temperature irreversible isomerisation of *rac*-**V-9** into a thermodynamically more stable isomer takes place, presumably to *meso*-**V-9**. A full conversion of *rac*-**V-9** in boiling toluene can already be accomplished after 4 hours. The compound *meso*-**V-9** was isolated from toluene as pale yellow powder in 70 % yield and *meso*-**V-9** was characterized by NMR and IR spectroscopy. The ^{1}H and ¹³C{^{1}H} NMR spectra of *meso*-**V-9** reveal the same NMR coupling patterns as *rac*-**V-9**. The resonances of the cAAC Dipp isopropyl methine protons emerge as two septets at 3.66 ppm and 3.80 ppm, one of them considerable shifted to lower field (*rac*-**V-9**: 3.19 ppm and 3.69 ppm), whereas some other resonances, including the resonance of the former cAAC^{Me} carbene carbon atom and the Me₂Im^{Me} carbene atom in the ¹³C{[1]H] NMR of *meso*-**V-9** are similar to *rac*-**V-9**. The IR spectra of *meso*-**V-9** reveals the Al-H stretching vibration at 1711 cm^{-1}.

DFT calculations (M06-2x/def2-TZVP(Ga);def2-SVP(H,C,N); see Figure V.4) have been performed on the model compounds *rac*(*R,R*)-(Me₂Im)·CpAlH(cAAC^MeH), *rac*(*S,S*)-(Me₂Im)·CpAlH(cAAC^MeH), *meso*(*R,S*)-(Me₂Im)·CpAlH(cAAC^MeH) and *meso*(*S,R*)-(Me₂Im)·CpAlH(cAAC^MeH). The *rac*(*R,R*)-isomer (+59.9 kJ/mol) as well as the *meso*(*R,S*)-isomer (+31.9 kJ/mol) and *meso*(*S,R*)-isomer (+19.7 kJ/mol) lie significantly higher in energy compared to the *rac*(*S,S*)-isomer and thus the *rac*(*S,S*)-isomer should be the isomer obtained after heating.
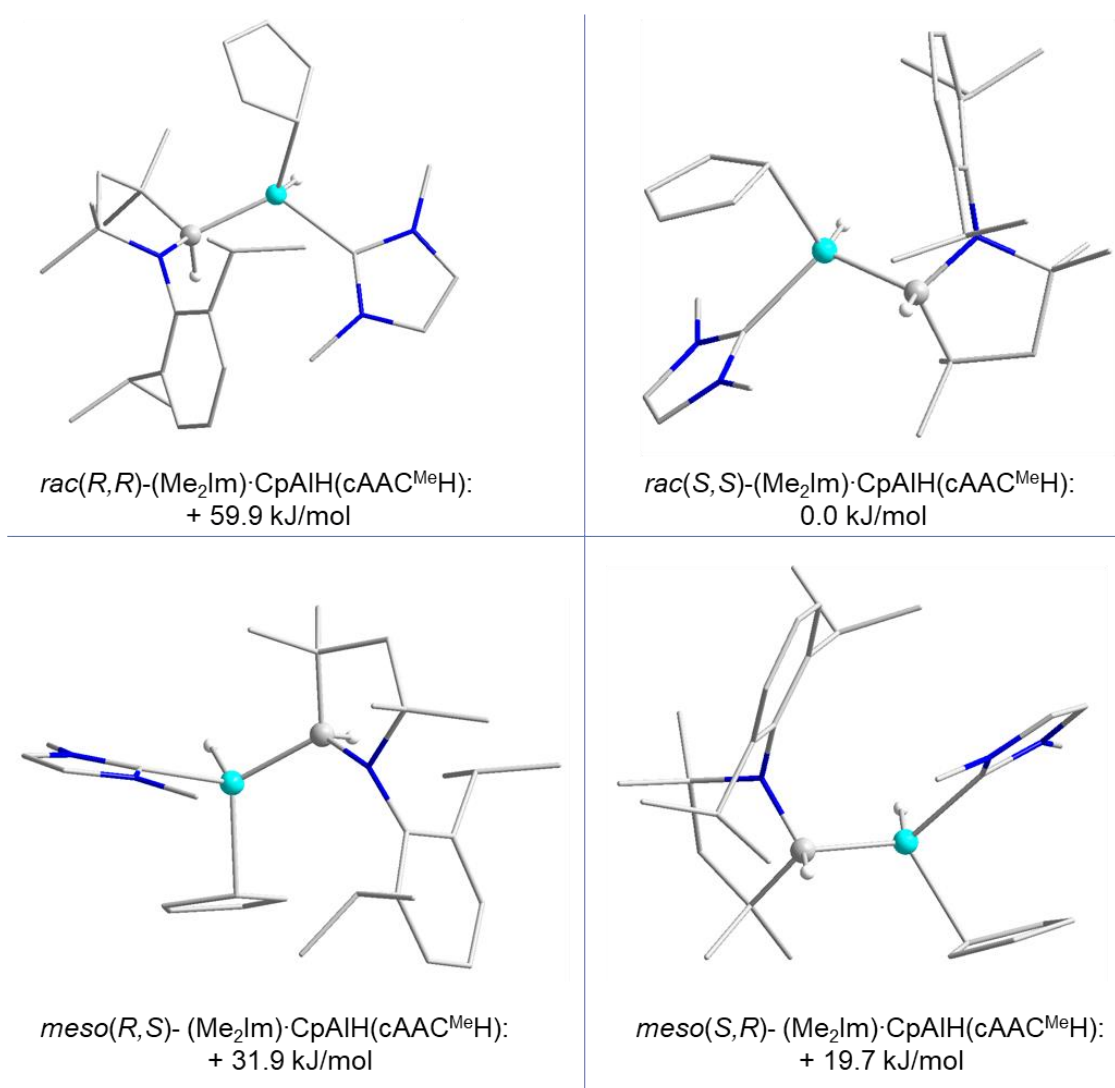


*rac*(*R,R*)-(Me₂Im)·CpAlH(cAAC^MeH): + 59.9 kJ/mol

*rac*(*S,S*)-(Me₂Im)·CpAlH(cAAC^MeH): 0.0 kJ/mol

*meso*(*R,S*)- (Me₂Im)·CpAlH(cAAC^MeH): + 31.9 kJ/mol

*meso*(*S,R*)- (Me₂Im)·CpAlH(cAAC^MeH): + 19.7 kJ/mol

*Figure V.4: DFT optimized (M06-2x/def2-TZVP(Ga);def2-SVP(H,C,N)) structures and relative energies of different isomers oft he model compound (Me₂Im)·Cp\*AlH(cAAC^MeH).*

The adducts **V-2** and **V-3** of the sterically more demanding NHCs *i*Pr₂Im^Me and Dipp₂Im react with cAAC^Me (see Scheme V.6) with insertion of the cAAC^Me into the Al-H bond

and liberation of the NHC ligand. Free NHC was observed in the $^1$H NMR spectra of the reaction mixtures. The resulting compound (cAAC$^{Me}$H)Cp*AlH **V-10** can also be synthesized from the reaction of (Cp*AlH$_2$)$_3$ and cAAC$^{Me}$ (see Scheme V.7). Compound **V-10** is stable in solution at least up to the boiling point of benzene (80 °C) and shows no decomposition or change in the $^1$H NMR spectra.
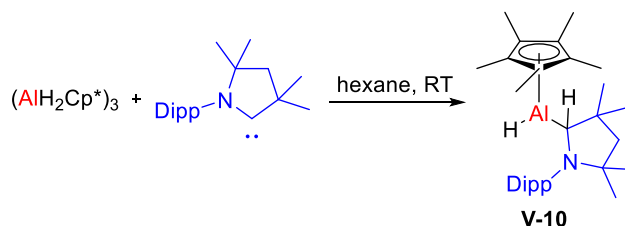


*Scheme V.7: Synthesis of the (cAAC$^{Me}$H)Cp*AlH **V-10**.*

The Cp* methyl protons of **V-10** give rise to a sharp singlet at 1.75 ppm in the $^1$H NMR. The $\eta^5$ hapticity of the Cp* substituent was confirmed in this case by X-ray diffraction analysis (Figure V.5) of single crystals of **V-10**, which were obtained from the slow evaporation of a saturated solution in benzene at room temperature. (cAAC$^{Me}$H)Cp*AlH **V-10** crystallizes in the monoclinic space group *Cc*. The Al-C$_{\eta5\text{-}Cp^*}$ bond lengths between 2.244 Å and 2.334 Å of **V-10** are expected longer than the bond lengths of the $\eta^1$ coordinated compounds (carbene)·AlBr$_2$Cp* (*i*Pr$_2$Im: 2.029(4) Å, cAAC$^{Me}$: 2.036(3) Å) but the values are in good accordance with the $\eta^5$ coordinated aluminium compounds (pyridine)·Cp*AlBr$_2$ (2.21 - 2.36 Å) and Cp*Al (2.29 - 2.37 Å).[68, 247] The Al-C$_{cAAC}$ bond length of 2.0048(18) Å compares well with the distance in (NHC)·AlH$_2$(cAAC$^{Me}$H) (2.0226(19) - 2.039(2) Å).[66]

Compound **V-10** does not react with an additional equivalent of cAAC$^{Me}$ or the NHCs *i*Pr$_2$Im$^{Me}$ and Dipp$_2$Im in C$_6$D$_6$. However, reaction of **V-10** with the small NHC Me$_2$Im$^{Me}$ in C$_6$D$_6$ at room temperature leads selectively and quantitively (as judged from NMR spectroscopy) to the formation of rac-**V-9** with a change of the hapticity of Cp* from $\eta^5$ to $\eta^1$.
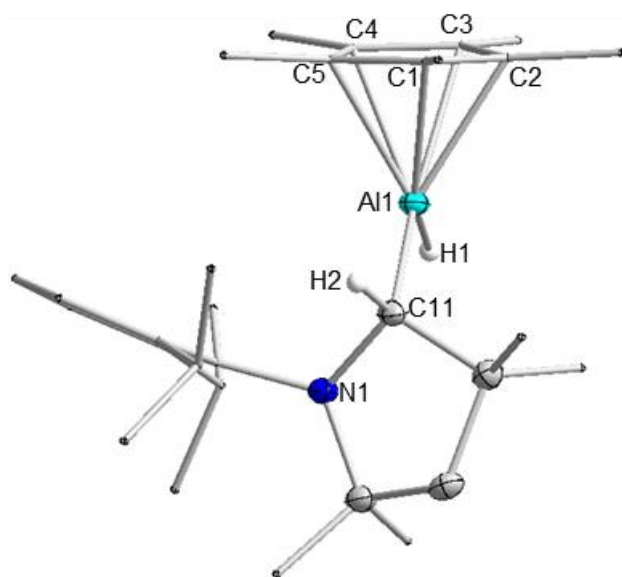
*Figure V.5: Molecular structure of (cAAC^{Me}H)Cp\*AlH **V-10** in the solid state (ellipsoids set at the 50% probability level). Hydrogen atoms with exception of H1 and H2 are omitted for clarity. Selected bond lengths [Å] and angles [°]: C11-Al1 2.0048(18), Al1-H1 1.57(3), Al-C1 2.2591(18), Al-C2 2.2603(18), Al-C3 2.3364(19), Al-C4 2.3093(19), Al-C5 2.2440(19); H1-Al1-C11 111.8(12), C11-Al1-C1 100.90(7), C11-Al1-C2 124.23(7), C11-Al1-C3 159.75(8), C11-Al1-C4 143.87(8), C11-Al1-C5 109.59(8), H-Al1-C1 146.6(12), H1-Al1-C2 113.3(12), H1-Al1-C3 86.5(12), H1-Al1-C4 94.2(12), H1-Al1-C5 129.2(12).*

The gallium hydride adducts (NHC)·Cp\*GaH$_2$ **V-4** - **V-6** were also reacted with cAAC$^{Me}$ to further compare the reactivity of the alane and gallane compounds. For the reaction of (Me$_2$Im$^{Me}$)·Cp\*GaH$_2$ **V-4** with cAAC$^{Me}$ in C$_6$D$_6$ at room temperature no change in the $^1$H NMR spectrum was observed after 24 hours. Heating the mixture up to 90 °C for 12 hours leads to reductive elimination of cAAC$^{Me}$-H$_2$ and formation of Cp\*Ga$^I$ **V-11** and the free NHC. The adducts **V-5** and **V-6**, stabilized by the sterically more demanding NHCs $i$Pr$_2$Im$^{Me}$ and Dipp$_2$Im react with cAAC$^{Me}$ even faster. Full conversion to cAAC$^{Me}$-H$_2$ and Cp\*Ga$^I$ was reached after 4 hours at 60 °C. In the case of the reaction of (Dipp$_2$Im)·GaH$_2$Cp\* **V-6** with cAAC$^{Me}$, which proceeds in toluene at room temperature, Cp\*GaI **V-11** was isolated as colorless oil in moderate yield of 42 % (see Scheme V.8). Compound **V-11** was characterized by $^1$H and $^{13}$C{$^1$H} NMR spectroscopy and the NMR spectra obtained are in good accordance to literature data.[248] Cp\*Ga$^I$ was prepared in different ways. Schnöckel et al. reported the synthesis from the reaction of metastable solutions of Ga$^I$Cl with Cp\*$_2$Mg or Cp\*Li,

respectively.[249] Jutzi *et al.* reported the reductive dehalogenation of Cp*GaI$_2$ with elemental potassium to yield Cp*Ga$^I$.[248] The same research group reported the synthesis of Cp*Ga$^I$ from the reaction of Green's Ga$^I$I with KCp*.[250] To the best of our knowledge the presented results of the metal free reduction from Ga$^{III}$ to Ga$^I$ under mild conditions with a carbene as reductant is first reported. For the reduction mechanism an oxidative addition intermediate (cAAC$^{Me}$H)Cp*GaH *int*-**V-11** analogue to compound **V-10** is suggested but was not observed in case of gallium. An immediately reductive elimination of cAAC$^{Me}$-H$_2$ with formation of Cp*Ga$^I$ **V-11** is suggested, which should be entropically as well as thermodynamically favoured in the case of gallium.
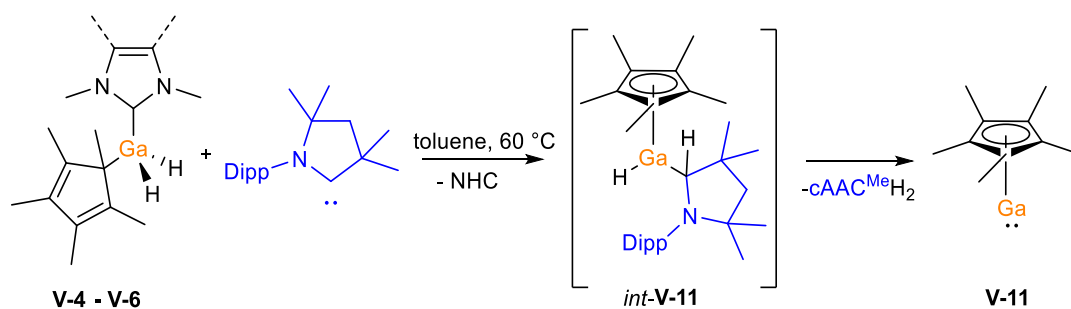


*Scheme V.8: Reaction of (NHC)·Cp*GaH$_2$ (NHC = Me$_2$Im$^{Me}$, iPr$_2$Im$^{Me}$, Dipp$_2$Im) with cAAC$^{Me}$.*

## 5.3 Conclusion

The metal free reduction of main group element hydrides with carbenes as reductant was described for boranes, stannanes and phosphanes in some detail in the literature earlier. The carbenes were used as dihydrogen acceptors with formation of the corresponding dihydroaminal NHC-H$_2$ during the reduction. In this chapter the first metal free reduction of gallanes with carbenes is presented. The synthesis of NHC-stabilized pentamethylcyclopentadienyl aluminium- and gallium dihydrides (NHC)·Cp*AlH$_2$ (NHC = Me$_2$Im$^{Me}$ **V-1**, $i$Pr$_2$Im$^{Me}$ **V-2**, Dipp$_2$Im **V-3**) and (NHC)·Cp*GaH$_2$ (NHC = Me$_2$Im$^{Me}$ **V-4**, $i$Pr$_2$Im$^{Me}$ **V-5**, Dipp$_2$Im **V-6**) can be achieved in good yields and high purity *via* the direct reaction of the free carbenes with (AlH$_2$Cp*)$_3$ or the reaction of the gallane adducts (NHC)·GaH$_2$I with KCp*. The alane compounds **V-1 – V-3** are exceptionally stable in solution up to the boiling point of even toluene, whereas the gallane compounds **V-4 – V-6** undergo reductive elimination of Cp*H with formation of Cp*Ga$^I$ **V-11** at higher temperature. Furthermore the NHC ring expansion reaction of the saturated Dipp$_2$Im$^H$ was observed for the reaction of the free NHC with (AlH$_2$Cp*)$_3$ and (RER-Dipp$_2$Im$^H$H$_2$)AlCp* **V-7** was isolated. The molecular structure of the NHC ring expansion product was determined by crystallization of the NHC stabilized RER product (Me$_2$Im$^{Me}$)·AlCp*(RER-Dipp$_2$Im$^H$H$_2$) **V-8**. Compound **V-7** is a rare example of NHC ring expansion products of alanes. Furthermore, the reactivity of the alane and gallane adducts towards cAAC$^{Me}$ was investigated. For the alane compound **V-1** the insertion of cAAC$^{Me}$ into the Al-H bond was observed with selective formation of the rac-isomer (Me$_2$Im$^{Me}$)·AlHCp*(cAAC$^{Me}$H) *rac*-**V-9** at room temperature. Heating up a solution of compound *rac*-**V-9** affords irreversible isomerisation with formation of *meso*-**V-9**. The reaction of the compounds **V-2** and **V-3** with cAAC$^{Me}$ instead leads to formation of the exceptionally stable oxidative addition product (cAAC$^{Me}$H)Cp*AlH **V-10** under release of the NHC. The reaction of the gallane adducts **V-3 – V-6** with cAAC$^{Me}$ instead lead immediately to reductive elimination of cAAC$^{Me}$-H$_2$ and formation of Cp*Ga$^I$ **V-11**, which could be isolated in moderate yield. These results represent the first example of metal-free Ga$^{III}$ to Ga$^I$ reduction with carbenes under ambient conditions.

# 6 EXPERIMENTAL SECTION

## 6.1 General Procedures

All reactions and subsequent manipulations were performed under an argon atmosphere using standard Schlenk techniques or in a glovebox (Innovative Technology Inc. and Braun Uni Lab). All reactions were carried out in oven-dried glassware. Solvents were purified by distillation from an appropriate drying agent (toluene, benzene, pentane, diethyl ether, thf from sodium/potassium alloy with benzophenone as indicator). Halocarbons, *n*-hexane and acetonitrile were dried and deoxygenated using an Innovative Technology Inc. Pure-Solv 400 Solvent Purification System, and further deoxygenated by using the freeze-pump-thaw method.

Deuterated solvents ($C_6D_6$, toluene-$d_8$, thf-$d_8$, $CD_2Cl_2$, $CD_3Cl$, acetone-$d_6$, $CD_3CN$) were purchased from Sigma-Aldrich and stored over molecular sieve.

## 6.1.1 Analytical Methods

**Elemental analysis**

Elemental analyses (C, H, N, S) were measured with a 'vario Micro cube' from Elementar for combustion analysis.

## 6.1.2 Spectroscopic Methods

**IR Spectroscopy**

All IR spectra were recorded on a NICOLET 380 FT-IR or a Bruker Alpha FT-IR spectrometer using ATR. Dependent on the intensity of the vibration bands, the intensity was assigned to the following abbre*via*tions: very strong (vs), strong (s), middle (m), weak (w) and very weak (vw).

## NMR Spectroscopy

All NMR spectra were recorded on Bruker Avance 200 ($^1$H, 199.9 MHz; $^{13}$C, 50.3 MHz), Avance 400 ($^1$H, 400.4 MHz; $^{13}$C, 100.7 MHz, $^{27}$Al, 104.3 MHz), or Avance 500 ($^1$H, 500.1 MHz; $^{13}$C, 125.8 MHz) spectrometers and were measured at 298 K. $^1$H NMR chemical shifts are expressed in parts per million (ppm) and are referenced *via* residual proton resonances of the corresponding deuterated solvent $C_6D_5H$ ($^1$H: $\delta$ = 7.16 ppm, $C_6D_6$), $C_7D_7H$ ($^1$H: $\delta$ = 2.08, 6.97, 7.01, 7.09 ppm, $d_8$-toluene), $CDHCl_2$ ($^1$H: $\delta$ = 5.32 ppm, $CD_2Cl_2$), $CHCl_3$ ($^1$H: $\delta$ = 7.26 ppm, $CDCl_3$), $CD_2HCN$ ($\delta$ = 1.94 ppm, $CD_3CN$), acetone-$d_6$ ($\delta$ = 2.05 ppm), thf-$d_8$ ($\delta$ = 1.73, 3.58 ppm). $^{13}$C NMR spectra are reported relative to TMS using the carbon resonances of the deuterated solvent $C_6D_6$ ($^{13}$C: $\delta$ = 128.06 ppm), $d_8$-toluene ($^{13}$C: $\delta$ = 20.43, 125.13, 127.96, 128.87, 137.48 ppm), $CD_2Cl_2$ ($^{13}$C: $\delta$ = 53.84 ppm), $CDCl_3$ ($^{13}$C: $\delta$ = 77.16 ppm), $CD_3CN$ ($\delta$ = 1.39, 118.7 ppm), acetone-$d_6$ ($\delta$ = 29.9, 206.7 ppm), thf-$d_8$ ($\delta$ = 25.3, 67.6 ppm). All $^{13}$C NMR and $^{27}$Al spectra are $^1$H broadband decoupled. The coupling constants ($J$) are given in Hertz (Hz) without consideration of the sign. For multiplicities, the following abbreviations are used: s = singlet, d = doublet, t = triplet, quart = quartet, sept = septet, m = multiplet, br = broad.

## 6.2 Starting Materials

Me$_2$Im$^{Me}$ (1,3,4,5-tetramethylimidazolin-2-ylidene)[26, 27, 219, 251-253], *i*Pr$_2$Im (1,3-di*iso*propylimidazolin-2-ylidene)[254, 255], *i*Pr$_2$Im$^{Me}$ (1,2-di*iso*propyl-4,5-dimethylimidazolin-2-ylidene)[26, 219, 256], Dipp$_2$Im (1,3-bis,2,6-di*iso*propylphenyl)imidazolin-2-ylidene)[26, 219, 256], Dipp$_2$Im$^H$ (1,3-(2,6-di-*iso*-propylphenyl)imidazolidin-2-ylidene)[26, 219, 256], cAAC$^{Me}$[111, 112, 118, 257] and (AlH$_2$Cp*)$_3$[65] were prepared according to reported procedures. All other reagents were purchased from ABCR or Sigma Aldrich and used as received.

**Synthesis of (Me$_2$Im$^{Me}$)·AlH$_3$ I**[66]

To a suspension of Me$_2$Im$^{Me}$ (500 mg, 3.96 mmol) in 20 mL Et$_2$O was added a suspension of lithium aluminium hydride (166 mg, 4.40 mmol) in 20 mL Et$_2$O at 0 °C and the reaction mixture was allowed to warm to room temperature overnight. All volatiles were removed *in vacuo* and the colorless residue was suspended in 15 mL toluene and the insoluble precipitate removed by filtration and washed with 10 mL of toluene. All volatiles were removed *in vacuo* and the residue suspended in 15 mL of *n*-hexane and filtered off and dried *in vacuo* to afford **I** as colorless powder.

**Yield**: 250 mg (1.61 mmol, 41 %), colorless powder.

**$^1$H-NMR** (400.1 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 1.19 (s, C$H_3$), 3.19 (s, NC(C$H_3$)C(C$H_3$)N).

**$^{13}$C{$^1$H}-NMR** (100.6 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 8.83 (C($C$H$_3$), 34.4 (N$C$H$_3$), 126.1 (N$C$(CH$_3$)$C$(CH$_3$N), 168.7 (NCN).

**$^{27}$Al{$^1$H}-NMR** (104.3 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 106.4.

**Synthesis of (*i*Pr$_2$Im)·AlH$_3$ II**[66]

To a suspension of *i*Pr$_2$Im (2.63 g, 17.4 mmol, d = 1.00 g/cm$^3$, 2.64 mL) was added a suspension of lithium aluminium hydride (729 mg, 19.2 mmol) in 40 mL Et$_2$O at 0 °C and the reaction mixture was allowed to warm to room temperature overnight. All

volatiles were removed *in vacuo* and the colorless residue was suspended in 25 mL toluene and the insoluble precipitate removed by filtration and washed with 15 mL of toluene. All volatiles were removed *in vacuo* and the residue suspended in 25 mL of *n*-hexane and filtered off and dried *in vacuo* to afford **II** as colorless powder.

**Yield**: 2.16 g (11.8 mmol, 68 %), colorless powder.

**$^{1}$H-NMR** (400.1 MHz, C$_6$D$_6$, 298 K): *δ* [ppm] = 0.94 (d, 6 H, $^{3}J_{HH}$ = 6.7 Hz, *i*Pr-C*H$_3$*), 5.24 (sept, 2 H, $^{3}J_{HH}$ = 6.7 Hz, *i*Pr-C*H*), 6.24 (s, 2 H, NC*H*C*H*N).

**$^{13}$C{$^{1}$H}-NMR** (100.6 MHz, C$_6$D$_6$, 298 K): *δ* [ppm] = 22.9 (*i*Pr-*C*H$_3$), 51.5 (*i*Pr-*C*H), 116.9 (N*C*H*C*HN), 170.3 (N*C*N).

**$^{27}$Al{$^{1}$H}-NMR** (104.3 MHz, C$_6$D$_6$, 298 K): *δ* [ppm] = 106.3.


## Synthesis of (*i*Pr$_2$Im$^{Me}$)·AlH$_3$ III[66]

To a suspension of *i*Pr$_2$Im$^{Me}$ (300 mg, 1.66 mmol) in 20 mL Et$_2$O was added a suspension of lithium aluminium hydride (70.0 mg, 1.84 mmol) in 20 mL Et$_2$O at 0 °C and the reaction mixture was allowed to warm to room temperature overnight. All volatiles were removed *in vacuo* and the colorless residue was suspended in 15 mL toluene and the insoluble precipitate removed by filtration and washed with 10 mL of toluene. All volatiles were removed *in vacuo* and the residue suspended in 15 mL of *n*-hexane and filtered off and dried *in vacuo* to afford **III** as colorless powder.

**Yield**: 150 mg (709 *μ*mol, 43 %), colorless powder.

**$^{1}$H-NMR** (400.1 MHz, C$_6$D$_6$, 298 K): *δ* [ppm] = (d, 6 H, $^{3}J_{HH}$ = 7.3 Hz, *i*Pr-C*H$_3$*), 1.51 (s, 6 H, NC(C*H$_3$*)C(C*H$_3$*)N), 5.44 (sept, 2 H, $^{3}J_{HH}$ = 7.3 Hz, *i*Pr-C*H*).

**$^{13}$C{$^{1}$H}-NMR** (100.6 MHz, C$_6$D$_6$, 298 K): *δ* [ppm] = 9.84 (NC(*C*H$_3$)C(*C*H$_3$)N), 21.6 (*i*Pr-*C*H$_3$), 52.4 (*i*Pr-*C*H), 125.9 (N*C*H*C*HN), 169.3 (N*C*N).

**$^{27}$Al{$^{1}$H}-NMR** (104.3 MHz, C$_6$D$_6$, 298 K): *δ* [ppm] = 107.8.

## Synthesis of (Dipp₂Im)·AlH₃ IV[66]

To a suspension of Dipp₂Im (2.50 mg, 6.34 mmol) in 40 mL Et₂O was added a suspension of lithium aluminium hydride (271 mg, 7.04 mmol) in 40 mL Et₂O at 0 °C and the reaction mixture was allowed to warm to room temperature overnight. All volatiles were removed *in vacuo* and the colorless residue was suspended in 25 mL toluene and the insoluble precipitate removed by filtration and washed with 15 mL of toluene. All volatiles were removed *in vacuo* and the residue suspended in 25 mL of *n*-hexane and filtered off and dried *in vacuo* to afford **IV** as colorless powder.

**Yield**: 1.95 g (4.66 mmol, 74 %), colorless powder.

**¹H-NMR** (400.1 MHz, C₆D₆, 298 K): δ [ppm] =  1.05 (d, 6 H, $^3J_{HH}$ = 7.3 Hz, *i*Pr-C*H₃*), 1.44 (d, 6 H, $^3J_{HH}$ = 7.3 Hz, *i*Pr-C*H₃*), 2.67 (sept, 4 H, $^3J_{HH}$ = 7.3 Hz, *i*Pr-C*H*), 6.45 (s, 2 H, NC*H*C*H*N), 7.10-7.12 (m, 4 H, Aryl_NHC-C*H*), 7.23-7.26 (m, 4 H, Aryl_NHC-C*H*).

**¹³C{¹H}-NMR** (100.6 MHz, C₆D₆, 298 K): δ [ppm] = 23.4 (*i*Pr-*C*H₃), 25.1 (*i*Pr-*C*H₃), 29.1 (*i*Pr-*C*H), 123.9 (Aryl_NHC-*C*H_p), 124.7 (Aryl_NHC-*C*H_m), 130.8 (Aryl_NHC-*C*H_o), 134.9 (Aryl_NHC-*C*H_i), 145.7 (N*C*HCHN), 178.2 (N*C*N).

## Synthesis of (Dipp₂Im)·GaH₃ V[150]

LiGaH₄ (5.68 mmol) was generated at -78 °C *in situ* from the reaction of GaCl₃ (1.00 g, 5,68 mmol) and LiH (114 mmol, 904 mg) in 40 mL Et₂O. Dipp₂Im (1.99 g, 5.11 mmol), dissolved in 15 mL Et₂O was added to this solution. After stirring over night at room temperature, the colorless, cloudy reaction mixture was filtered to remove LiH and all volatiles of the filtrate were removed *in vacuo*. The residue was suspended in 10 ml *n*-hexane, the product was filtered off and dried *in vacuo* to afford **V** as a colorless powder.

**Yield**: 1.70 g (3.68 mmol, 72 %), colorless powder.

**¹H-NMR (**400.4 MHz, C₆D₆, 298 K): δ [ppm] = 1.05 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr-C*H₃*), 1.43 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr-C*H₃*), 2.67 (sept, 4 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr-C*H*), 3.73 (s, 3 H, Ga*H₃*), 6.46 (s, 2 H, NC*H*C*H*N), 7.11 - 7.25 (m, 6 H, aryl-C*H*).

$^{13}$C{$^1$H}-NMR (100.7 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 23.4 (*i*Pr-*C*H$_3$), 25.0 (*i*Pr-*C*H$_3$), 29.1 (*i*Pr-*C*H), 123.7 (aryl-*C*$_{meta}$H), 124.2 (NC*H*C*H*N), 130.6 (aryl-*C*$_{para}$H), 135.2 (aryl-*C*$_{ipso}$), 145.7 (aryl-*C*$_{ortho}$), 181.6 (N*C*N).

## Synthesis of (*i*Pr$_2$Im$^{Me}$)·GaCl$_3$ VI[153]

To a suspension of *i*Pr$_2$Im$^{Me}$ (508 mg, 2.84 mmol) in 10 mL *n*-hexane was added a solution of gallium(III) chloride (500 mg, 2.84 mmol) in 10 mL *n*-hexane at 0 °C and the reaction mixture was allowed to warm to room temperature overnight. The product was filtered off and dried *in vacuo* to afford **VI** as a colorless powder.

**Yield**: 850 mg (2.37 mmol, 84 %), colorless powder.

$^1$H-NMR (400.4 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 1.03 (d, 12 H, $^3J_{HH}$ = 7.1 Hz, *i*Pr-C*H*$_3$), 1.44 (s, 6 H, N*C*(CH$_3$)C(*C*H$_3$)N), 5.71 (sept, 2 H, $^3J_{HH}$ = 7.1 Hz, *i*Pr-C*H*).

$^{13}$C{$^1$H}-NMR (100.7 MHz, C$_6$D$_6$, 298 K): $\delta$ = 9.54 (NC(*C*H)$_3$C(*C*H)$_3$N), 20.9 (*i*Pr-*C*H$_3$), 52.7 (*i*Pr-*C*H).

## Synthesis of (Dipp$_2$Im)·GaCl$_3$ VII[153]

To a suspension of Dipp$_2$Im (1.09 g, 2.84 mmol) in 10 mL *n*-hexane was added a solution of gallium(III) chloride (500 mg, 2.84 mmol) in 10 mL *n*-hexane at 0 °C and the reaction mixture was allowed to warm to room temperature overnight. The product was filtered off and dried *in vacuo* to afford **VII** as a colorless powder.

**Yield**: 1.49 g (2.63 mmol, 93 %), colorless powder.

$^1$H-NMR (400.4 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 0.95 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr-C*H*$_3$), 1.43 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr-C*H*$_3$), 2.66 (sept, 4 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr-C*H*), 6.42 (s, 2 H, NC*H*C*H*N), 7.07 - 7.25 (m, 6 H, aryl-C*H*).

$^{13}$C{$^1$H}-NMR (100.7 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 22.9 (*i*Pr-*C*H$_3$), 25.9 (*i*Pr-*C*H$_3$), 29.3 (*i*Pr-*C*H), 124.6 (NC*H*C*H*N), 125.7 (aryl-*C*$_{meta}$H), 131.8 (aryl-*C*$_{para}$H), 133.1 (aryl-*C*$_{ipso}$), 145.8 (aryl-*C*$_{ortho}$).

## Synthesis of (Dipp₂ImᴴH)·GaCl₃ VIII[153]

To a suspension of Dipp₂Imᴴ (300 mg, 770 $\mu$mol) in 10 mL *n*-hexane was added a solution of gallium(III) chloride (135 mg, 770 $\mu$mol) in 10 mL *n*-hexane at 0 °C and the reaction mixture was allowed to warm to room temperature overnight. The product was filtered off and dried *in vacuo* to afford **VIII** as a colorless powder.

**Yield**: 300 mg (0.53 mmol, 69 %), colorless powder.

**¹H-NMR** (400.4 MHz, C₆D₆, 298 K)**:** $\delta$ [ppm] = 1.06 (d, 12 H, *i*Pr-C*H*₃), 1.52 (d, 12 H, *i*Pr-C*H*₃), 3.19 (sept, 4 H, *i*Pr-C*H*), 3.45 (s, 4 H, NC*H*₂C*H*₂N), 7.05 - 7.19 (m, 6 H, aryl-C*H*).

**¹³C{¹H}-NMR:** (100.7 MHz, C₆D₆, 298 K): $\delta$ [ppm] = 24.3 (*i*Pr-*C*H₃), 25.4 (*i*Pr-*C*H₃), 29.2 (*i*Pr-*C*H), 53.5 (N*C*H₂*C*H₂N), 124.6 (aryl-*C*metaH), 126.9 (aryl-*C*paraH), 135.3 (aryl-*C*ipso), 146.7 (aryl-*C*ortho), 205.9 (N*C*N).

## Synthesis of (cAACᴹe)·GaCl₃ IX[179]

To a suspension of cAACᴹe (500 mg, 1.75 mmol) in 10 mL *n*-hexane was added a solution of gallium(III) chloride (308 mg, 1.75 mmol) in 10 mL *n*-hexane at 0 °C and the reaction mixture was allowed to warm to room temperature overnight. The product was filtered off and dried *in vacuo* to afford **IX** as a colorless powder.

**Yield**: 624 mg (1.35 mmol, 77 %), colorless powder.

**¹H-NMR** (400.4 MHz, C₆D₆, 298 K): $\delta$ [ppm] = 0.75 (s, 6 H, C(C*H*₃)₂), 1.01 (d, 6 H, $^3J_{HH}$ = 6.6 Hz, iPr-C*H*₃), 1.30 (s, 2 H, C*H*₂), 1.50 (d, 6 H, $^3J_{HH}$ = 6.6 Hz, *i*Pr-C*H*₃), 1.59 (s, 6 H, C(C*H*₃)₂), 2.51 (sept, 2 H, $^3J_{HH}$ = 6.6 Hz, *i*Pr-C*H*), 6.98 - 7.13 (m, 3 H, aryl-C*H*).

**¹³C{¹H}-NMR** (100.7 MHz, C₆D₆, 298 K): $\delta$ [ppm] = 24.6 (*i*Pr-*C*H₃), 26.6 (*i*Pr-*C*H₃), 28.4 (C(*C*H₃)₂), 29.0 (*i*Pr-*C*H), 29.3 (C(*C*H₃)₂), 49.9 (*C*(CH₃)₂), 56.7 (*C*H₂), 126.1 (aryl-*C*metaH), 131.2 (aryl-*C*paraH), 145.2 (aryl-*C*ipsoH).

## 6.3 Synthetic Procedures for Chapter 2

**Synthesis of (*i*Pr$_2$Im)·AlH$_2$(N*i*Pr$_2$) II-1**

HN*i*Pr$_2$ (231 µL, 1.65 mmol) was added at RT to a solution of (*i*Pr$_2$Im)·AlH$_3$ **II** (150 mg, 823 µmol) in 10 mL of toluene and stirred overnight. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. The colorless solid was filtered off and dried *in vacuo* to afford **II-1** as a colorless powder.

**Yield**: 76 mg (270 µmol, 33%), colorless powder

**Alternative procedure:** HN*i*Pr$_2$ (315 µL, 2.24 mmol) was added to a solution of (NMe$_3$)·AlH$_3$ (100 mg, 1.12 mmol) in 5 mL toluene and stirred over night at RT. *i*Pr$_2$Im (177 µL, 1.12 mmol) was added at RT to the solution and stirred for one more hour. All volatiles were removed *in vacuo* and the residue was suspended in 5 mL of *n*-hexane. The colorless solid was filtered off and dried *in vacuo* to afford **II-1** as colorless powder.

**Yield**: 86 mg (306 µmol, 27%), colorless powder

**Elemental Analysis** for C$_{15}$H$_{33}$AlN$_3$ [282.43 g/mol] found (calculated) [%]: C 62.71 (63.16), H 11.17 (11.83), N 14.98 (14.56).

**$^1$H-NMR** (400.1 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 1.03 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, NHC-*i*Pr-C*H$_3$*), 1.46 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, N-*i*Pr-C*H$_3$*), 3.48 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, N-*i*Pr-C*H*), 5.24 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, NHC-*i*Pr-C*H*), 6.23 (s, 2 H, NC*H*C*H*N).

**$^{13}$C{$^1$H}-NMR** (100.6 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 23.1 (NHC-*i*Pr-*C*H$_3$), 23.1 (N-*i*Pr-*C*H$_3$), 59.2 (N-*i*Pr-*C*H), 50.3 (NHC-*i*Pr-*C*H), 116.5 (N*C*H*C*HN), 170.6 (N*C*N).

**$^{27}$Al{$^1$H} NMR** (104.3 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 112.1.

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 522 (m), 756 (s, $_{vAl-H,}$), 954 (w), 1209 (w), 1370 (w), 1397 (w), 1669 (s, $_{vAl-H, str.}$), 1729 (s, $_{vAl-H, str.}$), 2947 (w $_{vC-H,str.}$).

## Synthesis of (*i*Pr₂Im)·AlH(NPh₂)₂ II-2

HNPh₂ (184 mg, 1.08 mmol) in 5 mL toluene was added to a solution of (*i*Pr₂Im)·AlH₃ **II** (100 mg, 0.54 mmol) in 5 mL toluene at RT and stirred for 3 days. The colorless suspension was dried *in vacuo* and the residue was suspended in 5 mL of *n*-hexane. The colorless precipitate was filtered off and dried *in vacuo* to afford **II-2** as a colorless powder.

**Yield**: 181 mg (0.51 mmol, 95%), colorless powder.

**Elemental Analysis** for $C_{21}H_{29}AlN_3$ [350.47 g/mol] found (calculated) [%]: C 76.00 (76.57), H 7.41 (7.40), N 10.76 (10.82).

**$^1$H-NMR** (400.1 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 0.809 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, NHC-*i*Pr-C$H_3$), 5.14 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, NHC-*i*Pr-C$H$), 6.05 (s, 2 H, NC$H$C$H$N), 6.76-6.80 (m, 2 H, aryl-NPh₂), 7.08-7.12 (m, 6H, aryl-NPh₂), 7.17-7.19 (m, 2 H, NPh₂).

**$^{13}$C{$^1$H}-NMR** (100.6 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 23.2 (NHC-*i*Pr-$C$H₃, 51.2 (NHC-*i*Pr-$C$H), 117.3 (N$C$H$C$HN), 120.1 (N-aryl-$C_{meta}$), 123.8 (N-aryl-$C_{para}$), 129.3 (N-aryl-$C_{ortho}$), 153.4 (N-aryl-$C_{ipso}$), 165.1 (N$C$N).

**$^{27}$Al{$^1$H} NMR** (104.3 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 111.8.

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 518 (m), 744 (s, $\nu_{Al-H}$), 926 (w), 1262 (w), 1394 (w), 1478 (w), 1780 (s, $\nu_{Al-H, str.}$), 3069 (w, $\nu_{C-H,str.}$).

## Synthesis of (*i*Pr₂Im)·AlH₂(N{SiMe₃}₂) II-3

HMDS (235 $\mu$L, 1.12 mmol) was added to a solution of (NMe₃)·AlH₃ (100 mg, 1.12 mmol) in 5 mL toluene at RT and stirred overnight. *i*Pr₂Im (171 $\mu$L, 1,12 mmol) was added to the colorless solution and stirred for one more hour. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. The colorless precipitate was filtered off and dried *in vacuo* to afford **II-3** as a colorless powder.

**Yield**: 307 mg (890 $\mu$mol, 80%), colorless powder.

**Elemental Analysis** for $C_{15}H_{37}AlN_3Si_2$ [342.63 g/mol] found (calculated) [%]: C 52.35 (52.58), H 10.62 (10.89), N 12.17 (12.26).

**$^1$H-NMR** (400.1 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 0.458 (s, 18 H, Si(C$H_3$)$_3$), 0.998 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, NHC-$i$Pr-C$H_3$), 4.75 (b, 2 H, Al-H), 5.49 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, NHC-$i$Pr-C$H$), 6.16 (s, 2 H, NC$H$C$H$N).

**$^{13}$C{$^1$H}-NMR** (100.6 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 5.33 (Si($C$H$_3$)$_3$), 23.2 (NHC-$i$Pr-$C$H$_3$), 50.4 (NHC-$i$Pr-$C$H), 116.7 (N$C$H$C$HN), 169.7 (N$C$N).

**$^{27}$Al{$^1$H} NMR** (104.3 MHz, C6D6, 298 K): $\delta$ [ppm] = 115.2.

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 495 (m), 755 (s, $\nu_{Al-H}$), 962 (w), 1242 (w), 1370 (w), 1392 (w), 1735 (s, $\nu_{Al-H, str.}$), 1779 (s, $\nu_{Al-H, str.}$), 2947 (w, $\nu_{C-H,str.}$).

### Synthesis of (Dipp$_2$Im)·AlH$_2$(N$i$Pr$_2$) II-4

HN$i$Pr$_2$ (156 $\mu$L, 1.12 mmol) was added to a solution of (NMe$_3$)·AlH$_3$ (100 mg, 1.12 mmol) in 5 mL toluene and stirred over night at RT. Dipp$_2$Im (435 mg, 1.12 mmol) in 5 mL toluene was added at RT to the solution and stirred for one more hour. All volatiles were removed *in vacuo* and the residue was suspended in 5 mL of *n*-hexane. Colorless crystals were obtained by storing the solution at -30 °C and isolated by filtration to afford **II-4** as colorless crystals.

**Yield**: 150 mg (289 $\mu$mol, 26%), colorless crystals.

**Elemental Analysis** for C$_{33}$H$_{53}$AlN$_3$ [518.79 g/mol] found (calculated) [%]: C 76.24 (76.40), H 10.05 (10.30), N 7.91 (8.10).

**$^1$H-NMR** (400.1 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 1.01 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, NHC-$i$Pr-C$H_3$), 1.12 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, NHC-$i$Pr-C$H_3$), 1.44 (d, 12 H, $^3J_{HH}$ = 6.6 Hz, N-$i$Pr-C$H_3$), 2.83 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, NHC-$i$Pr-C$H$), 3.00 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, N-$i$Pr-C$H$), 4.01 (b, 2 H, Al-H), 6.41 (s, 2 H, NC$H$C$H$N), 7.11-7.13 (m, 4 H, aryl-C$H$), 7.24-7.26 (m, 2 H, aryl-C$H$).

**$^{13}$C{$^1$H} NMR** (125.8 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 23.0 (N-$i$Pr-$C$H$_3$), 25.8 ($i$Pr-$C$H$_3$), 26.6 ($i$Pr-$C$H$_3$), 29.0 ($i$Pr-$C$H), 49.0 (N-$i$Pr-$C$H), 124.2 (aryl-$C_{meta}$H), 124.3 (N$C$H$C$HN), 130.8 (aryl-$C_{para}$H), 135.6 (aryl-$C_{ipso}$), 145.8 (aryl-$C_{ortho}$), 178.2 (N$C$N).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 697 (m), 754 (s, $\nu_{Al-H}$), 801 (w), 1384 (w), 1454 (w), 1466 (w), 1735 (s, $\nu_{Al-H, str.}$), 1779 (s, $\nu_{Al-H, str.}$), 2959 (w, $\nu_{C-H,str.}$).

## Synthesis of (Dipp$_2$Im)·AlH$_2$(NPh$_2$) II-5

HNPh$_2$ (184 mg, 816 $\mu$mol) in 5 mL toluene was added to a solution of (Dipp$_2$Im)·AlH$_3$ **IV** (341 mg, 816 $\mu$mol) in 10 mL toluene at RT and stirred for 3 days. The colorless suspension was dried *in vacuo* and the residue was suspended in 5 mL of *n*-hexane. The colorless precipitate was filtered off and dried *in vacuo* to afford **II-5** as colorless powder.

**Yield**: 306 mg (0.51 mmol, 64%), colorless powder.

**Elemental Analysis** for C$_{39}$H$_{49}$AlN$_3$ [586.82 g/mol] found (calculated) [%]: C 80.01 (79.82), H 8.29 (8.42), N 7.13 (7.16).

**$^1$H-NMR** (400.1 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 1.06 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, NHC-*i*Pr-C*H$_3$*), 1.30 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, NHC-*i*Pr-C*H$_3$*), 2.87 (sept, 2 H, $^3J_{HH}$ = 6.7 Hz, NHC-*i*Pr-C*H*), 4.27 (b, 2 H, Al-H), 6.51 (s, 2 H, NC*H*C*H*N), 6.79-6.81 (m, 4 H, NHC-aryl-C*H*), 6.87-6.90 (m, 2 H, N-aryl-C*H*), 7.13-7.15 (m, 6 H, N-aryl-C*H*), 7.26 (b, 2 H, N-aryl-C*H*), 7.29-7.34 (m, 2 H, NHC-aryl-C*H*).

**$^{13}$C{$^1$H} NMR** (125.8 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 22.6 (*i*Pr-*C*H$_3$), 26.0 (*i*Pr-*C*H$_3$), 29.1 (*i*Pr-*C*H), 118.8 (N-aryl-*C*$_{meta}$H), 123.1 (N-aryl-*C*$_{ortho}$H), 124.6 (NHC-aryl-*C*$_{meta}$H), 124.9 (N*C*H*C*HN), 128.6 (N-aryl-*C*$_{para}$H), 134.9 (aryl-*C*$_{para}$H), 134.9 (aryl-*C*$_{ipso}$), 145.8 (aryl-*C*$_{ortho}$), (N-aryl-*C*$_{ipso}$H), 175.2 (N*C*N).

**IR (ATR)**: $\tilde{v}$ [cm$^{-1}$] = 507 (m), 752 (s, $v_{Al-H}$), 925 (w), 1272 (w), 1462 (w), 1478 (w), 1790 (s, $v_{Al-H, str.}$), 1798 (s, $v_{Al-H, str.}$), 2947 (w, $v_{C-H,str.}$).

## Synthesis of (Dipp$_2$Im)·AlH$_2$(N{SiMe$_3$}$_2$) II-6

HMDS (235 $\mu$L, 1.12 mmol) was added to a solution of (NMe$_3$)·AlH$_3$ (100 mg, 1.12 mmol) in 5 mL toluene at RT and stirred overnight. Dipp$_2$Im (436 mg, 1,12 mmol) in 5 mL toluene was added to the colorless solution and stirred for one more hour. All volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane. The colorless precipitate was filtered off and dried *in vacuo* to afford **II-6** as a colorless powder.

**Yield**: 532 mg (920 $\mu$mol, 82%), colorless powder.

**Elemental Analysis** for $C_{33}H_{57}AlN_3Si_2$ [578.99 g/mol] found (calculated) [%]: C 66.42 (68.46), H 9.74 (9.92), N 7.06 (7.26).

**$^1$H-NMR** (400.1 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 0.204 (s, 18 H, Si(C$H_3$)$_3$), 0.96 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, NHC-$i$Pr-C$H_3$), 1.46 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, NHC-$i$Pr-C$H_3$), 2.81 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, NHC-$i$Pr-C$H$), 3.79 (b, 2 H, Al-H), 6.41 (s, 2 H, NC$H$C$H$N), 7.11-7.13 (m, 4 H, aryl-C$H$), 7.21-7.25 (m, 2 H, aryl-C$H$).

**$^{13}$C{$^1$H} NMR** (125.8 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 5.72 (Si($CH_3$)$_3$), 22.9 ($i$Pr-$CH_3$), 26.2 ($i$Pr-$CH_3$), 29.0 ($i$Pr-$CH$), 124.5 (aryl-$C_{meta}$H), 124.7 (N$C$H$C$HN), 130.9 (aryl-$C_{para}$H), 135.3 (aryl-$C_{ipso}$), 145.8 (aryl-$C_{ortho}$), 177.3 (N$C$N).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 501 (m), 721 (s, $\nu_{Al-H,}$), 954 (w), 1239 (w), 1464 (w), 1777 (s, $\nu_{Al-H, str.}$), 1786 (s, $\nu_{Al-H, str.}$), 2961 (w, $\nu_{C-H,str.}$).

## Synthesis of ($i$Pr$_2$Im)·AlH$_2$(OMes) II-7

Mes-OH (223 mg, 1.64 mmol) in 5 mL toluene was added to a solution of ($i$Pr$_2$Im)·AlH$_3$ **II** (300 mg, 1.64 mmol) in 5 mL toluene at RT and stirred for 12 h. The colorless suspension was dried *in vacuo* and the residue was suspended in 5 mL of *n*-hexane. The colorless precipitate was filtered off and dried *in vacuo* to afford **II-7** as colorless powder.

**Yield**: 227 mg (0.72 mmol, 44 %), colorless powder.

**Elemental Analysis** for $C_{18}H_{29}AlN_2O$ [317.43 g/mol] found (calculated) [%]: C 67.34 (68.11), H 8.81 (9.24), N 7.48 (8.85).

**$^1$H-NMR** (400.1 MHz, $CD_2Cl_2$, 298 K): $\delta$ [ppm] = 1.39 (d, 6 H, $^3J_{HH}$ = 7.1 Hz, $i$Pr-C$H_3$), 1.46 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, $i$Pr-C$H_3$), 2.08 (s, 12 H, Mes(C$H_3$)$_o$), 2.16 (s, 6 H, Mes(C$H_3$)$_p$), 5.13 (sept, 2 H, $^3J_{HH}$ = 6.9 Hz, $i$Pr-C$H$), 6.69 (s, 2 H, NC$H$C$H$N), 7.15 (s, 2 H, Mes(C$H_3$)$_m$).

**$^{13}$C{$^1$H}-NMR** (100.6 MHz, $CD_2Cl_2$, 298 K): $\delta$ [ppm] = 18.2 (Mes($CH_3$)$_o$), 20.7 (Mes($CH_3$)$_p$), 22.7 (NHC-$i$Pr-$CH_3$), 23.0 (NHC-$i$Pr-$CH_3$), 51.1 (NHC-$i$Pr-$CH$), 116.8 (N$C$H$C$HN), 126.2 (aryl$_{Mes}$-$C$H$_p$), 126.5 (aryl$_{Mes}$-$C$H$_m$), 129.2 (aryl$_{Mes}$-$C$H$_o$), 154.7 (aryl$_{Mes}$-$C$H$_i$).

$^{27}$**Al{$^1$H} NMR** (104.3 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 77.1.

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 431 (m), 752 (s, v$_{Al-H}$), 853 (w), 1207 (w), 1315 (w), 1480 (w), 1736 (s, v$_{Al-H, str.}$), 1964 (m), 2975 (w, v$_{C-H,str.}$).

### Synthesis of (*i*Pr$_2$Im)·AlH(OMes)$_2$ II-8

Mes-OH (372 mg, 2.73 mmol) in 5 mL toluene was added to a solution of (*i*Pr$_2$Im)·AlH$_3$ **II** (250 mg, 1.36 mmol) in 5 mL toluene at RT and stirred for 12 h. The colorless suspension was dried *in vacuo* and the residue was suspended in 5 mL of *n*-hexane. The colorless precipitate was filtered off and dried *in vacuo* to afford **II-8** as a colorless powder.

**Yield**: 325 mg (0.719 mmol, 53 %), colorless powder.

**Elemental Analysis** for C$_{27}$H$_{40}$AlN$_2$O$_2$ [451.61 g/mol] found (calculated) [%]: C 70.36 (71.27), H 8.81 (9.24), N 5.22 (6.22).

$^1$**H-NMR** (400.1 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 1.32 (d, 12 H, $^3$J$_{HH}$ = 7.2 Hz, *i*Pr-C$H_3$), 2.02 (s, 12 H, Mes(C$H_3$)$_o$, 2.13 (s, 6 H, Mes-(C$H_3$)$_p$), 5.48 (sept, 2 H, $^3$J$_{HH}$ = 6.8 Hz, *i*Pr-C$H$), 6.72 (s, 2 H, aryl$_{Mes}$-C$H_m$), 7.18 (s, 2 H, NC$H$C$H$N).

$^{13}$**C{$^1$H}-NMR** (100.6 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 17.8 (Mes(C$H_3$)$_o$), 20.6 (Mes(C$H_3$)$_p$), 23.9 (NHC-*i*Pr-C$H_3$), 51.7 (NHC-*i*Pr-C$H$), 118.1 (NC$H$C$H$N), 126.4 (Aryl$_{Mes}$-C$H_p$), 126.7 (Aryl$_{Mes}$-C$H_m$), 128.7 (Aryl$_{Mes}$-C$H_o$), 153.5 (Aryl$_{Mes}$-C$H_i$).

$^{27}$**Al{$^1$H} NMR** (104.3 MHz, C$_6$D$_6$, 298 K): $\delta$ = 50.8.

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 624 (m), 737 (w, v$_{Al-H}$), 959 (w), 1159 (w), 1207 (w), 1315 (w), 1480 (w), 1725 (w, v$_{Al-H, str.}$), 1724 (m), 2913 (w, v$_{C-H,str.}$), 2962 (w, v$_{C-H,str.}$).

### Synthesis of (Dipp$_2$Im)·AlH$_2$(OMes) II-9

Mes-OH (81 mg, 0.59 mmol) in 5 mL toluene was added to a solution of (Dipp$_2$Im)·AlH$_3$ **IV** (300 mg, 1.64 mmol) in 5 mL toluene at RT and stirred for 12 h. The colorless suspension was dried *in vacuo* and the residue was suspended in 5 mL of *n*-hexane.

The colorless precipitate was filtered off and dried *in vacuo* to afford **II-9** as a colorless powder.

**Yield**: 165 mg (0.29 mmol, 50 %), colorless powder.

**Elemental Analysis** for $C_{36}H_{49}AlN_2O$ [553.79 g/mol] found (calculated) [%]: C 77.85 (78.08), H 9.19 (9.10), N 5.01 (5.06).

**$^1$H-NMR** (400.1 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 1.02 (d, 6 H, $^3J_{HH}$ = 7.2 Hz, *i*Pr-C*H$_3$*), 1.37 (d, 6 H, $^3J_{HH}$ = 7.2 Hz, *i*Pr-C*H$_3$*), 2.05 (s, 12 H, Mes(C*H$_3$*)$_o$), 2.20 (s, 6 H, Mes(C*H$_3$*)$_p$), 2.77 (sept, 4 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr-C*H*), 6.40 (s, 2 H, NC*H*C*H*N), 6.78 (s, 2 H, Aryl$_{Mes}$-C*H*$_m$), 7.12-7.14 (m, 4 H, Aryl$_{NHC}$-C*H*), 7.24-7.28 (m, 2 H, Aryl$_{NHC}$-C*H*).

**$^{13}$C{$^1$H}-NMR** (100.6 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 17.8 (Mes(*C*H$_3$)$_o$), 20.8 (Mes(*C*H$_3$)$_p$), 23.1 (*i*Pr-*C*H$_3$), 25.3 (*i*Pr-*C*H$_3$), 29.2 (*i*Pr-*C*H), 124.2 (Aryl$_{NHC}$-*C*H$_m$), 124.4 (Aryl$_{NHC}$-*C*H$_p$), 125.6 (Aryl$_{Mes}$-*C*H$_p$), 127.3 (Aryl$_{Mes}$-*C*H$_m$), 128.9 (Aryl$_{Mes}$-*C*H$_o$), 130.8 (Aryl$_{NHC}$-*C*H$_o$), 134.6 (Aryl$_{NHC}$-*C*H$_i$), 145.8 (N*C*H*C*HN), 154.8 (Aryl$_{Mes}$-*C*H$_i$).

**IR (ATR)**: $\tilde{v}$ [cm$^{-1}$] = 503 (m), 7.15 (s, v$_{Al-H}$), 848 (w), 1258 (w), 1313 (w), 1480 (w), 1745 (s, v$_{Al-H, str.}$), 1794 (s, v$_{Al-H, str.}$), 2961 (w, v$_{C-H,str.}$).


**Synthesis of (Dipp$_2$Im)·AlH(OMes)$_2$ II-10**

Mes-OH (162 mg, 1.19 mmol) in 5 mL toluene was added to a solution of (Dipp$_2$Im)·AlH$_3$ **IV** (250 mg, 0.59 mmol) in 5 mL toluene at RT and stirred for 12 h. The colorless suspension was dried *in vacuo* and the residue was suspended in 5 mL of *n*-hexane. The colorless precipitate was filtered off and dried *in vacuo* to afford **II-10** as colorless powder.

**Yield**: 190 mg (0.28 mmol, 46 %), colorless powder.

**Elemental Analysis** for $C_{45}H_{59}AlN_2O_2$ [687.97 g/mol] found (calculated) [%]: C 77.62 (78.45), H 8.89 (8.92), N 3.78 (4.07).

**$^1$H-NMR** (400.1 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 0.99 (d, 6 H, $^3J_{HH}$ = 7.0 Hz, *i*Pr-C*H$_3$*), 1.29 (d, 6 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr-C*H$_3$*), 2.02 (s, 12 H, Mes(C*H$_3$*)$_o$), 2.14 (s, 6 H, Mes(C*H$_3$*)$_p$), 2.93 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*), 6.37 (s, 2 H, NC*H*C*H*N), 6.72 (s, 2 H, aryl$_{Mes}$-C*H*$_{metha}$), 7.02-7.04 (m, 4 H, aryl$_{NHC}$-C*H*), 7.18-7.20 (m, 2 H, aryl$_{NHC}$-C*H*).

**$^{13}$C{$^{1}$H}-NMR** (100.6 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 18.0 (Mes(C$H_3$)$_o$), 20.7 (Mes(C$H_3$)$_p$), 22.9 (*i*Pr-C$H_3$), 25.6 (*i*Pr-CH$_3$), 29.2 (*i*Pr-CH), 124.4 (Aryl$_{NHC}$-C$H_m$), 125.1 (Aryl$_{NHC}$-C$H_p$), 125.7 (Aryl$_{Mes}$-C$H_p$), 126.5 (Aryl$_{Mes}$-C$H_m$), 129.1 (Aryl$_{Mes}$-C$H_o$), 130.9 (Aryl$_{NHC}$-C$H_o$), 135.1 (Aryl$_{NHC}$-C$H_i$), 145.8 (N*C*H*C*HN), 154.6 (Aryl$_{Mes}$-C$H_i$).

**IR (ATR)**: $\tilde{v}$ [cm$^{-1}$] = 499 (w), 677 (m, $v_{C-H,str.}$), 758 (w, $v_{Al-H}$), 851 (m), 1114 (w), 1481 (w), 1825 (w, $v_{Al-H, str.}$), 2959 (w, $v_{C-H,str.}$).

## Synthesis of [Dipp$_2$ImH][Al(OMes)$_4$] II-11

Mes-OH (241 mg, 1.79 mmol) in 5 mL toluene was added to a solution of (Dipp$_2$Im)·AlH$_3$ **IV** (250 mg, 0.59 mmol) in 5 mL toluene at RT and stirred for 12 h. The colorless suspension was dried *in vacuo* and the residue was suspended in 5 mL of *n*-hexane. The colorless precipitate was filtered off and dried *in vacuo* to afford **II-11** as colorless powder.

**Yield**: 250 mg (0.28 mmol, 48 %), colorless powder.

**Elemental Analysis** for C$_{86}$H$_{81}$AlN$_2$O$_4$ [879.31 g/mol] found (calculated) [%]: C 78.82 (79.04), H 8.78 (8.53), N 2.88 (2.82).

**$^{1}$H-NMR** (400.1 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 1.18 (d, 6 H, $^{3}J_{HH}$ = 7.2 Hz, *i*Pr-C$H_3$), 1.27 (d, 6 H, $^{3}J_{HH}$ = 6.9 Hz, *i*Pr-C$H_3$), 2.03 (s, 12 H, Mes(C$H_3$)$_o$), 2.07 (s, 6 H, Mes(C$H_3$)$_p$), 2.29 (sept, 4 H, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr-C$H$), 6.55 (s, 2 H, Aryl$_{Mes}$-C$H_m$), 7.35 (d, 2 H, $^{4}J_{HH}$ = 3.6 Hz, NC$H$C$H$N), 7.40-7.42 (m, 4 H, Aryl$_{NHC}$-C$H$), 7.64-7.67 (m, 2 H, Aryl$_{NHC}$-C$H$), 8.16 (b, 1 H, NC$H$N).

**$^{13}$C{$^{1}$H}-NMR** (100.6 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 17.8 (Mes(C$H_3$)$_o$), 20.5 (Mes(C$H_3$)$_p$), 23.6 (*i*Pr-C$H_3$), 24.7 (*i*Pr-CH$_3$), 29.3 (*i*Pr-CH), 124.4 (Aryl$_{NHC}$-C$H_m$), 124.4 (Aryl$_{NHC}$-C$H_p$), 125.1 (Aryl$_{Mes}$-C$H_p$), 127.4 (Aryl$_{Mes}$-C$H_m$), 128.2 (Aryl$_{Mes}$-C$H_o$), 129.5 (Aryl$_{NHC}$-C$H_o$), 132.8 (Aryl$_{NHC}$-C$H_i$), 144.9 (N*C*H*C*HN), 155.5 (Aryl$_{Mes}$-C$H_i$).

**$^{27}$Al{$^{1}$H} NMR** (104.3 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 44.2.

**IR (ATR)**: $\tilde{v}$ [cm$^{-1}$] = 571 (w), 629 (m), 724 (m, $v_{C-H,str.}$), 897 (w), 1058 (m), 1261 (m), 1479 (m), 2960 (w, $v_{C-H,str.}$), 3142 (w, $v_{C-H,str.}$).

## 6.4 Synthetic Procedures for Chapter 3

### Synthesis of (Me₂Im^Me)·GaH₃ III-1

LiGaH$_4$ (5.68 mmol) was generated at -78 °C *in situ* from the reaction of GaCl$_3$ (1.00 g, 5.68 mmol) and LiH (904 mg, 114 mmol) in 40 mL Et$_2$O. Me$_2$Im$^{Me}$ (705 mg, 5.68 mmol), dissolved in 15 mL Et$_2$O was added to this solution. After stirring over night at room temperature, the colorless, cloudy reaction mixture was filtered to remove LiH and all volatiles of the filtrate were removed *in vacuo*. The residue was suspended in 10 ml *n*-hexane, the product was filtered off and dried *in vacuo* to afford **III-1**. Crystals suitable for X-ray diffraction of compound **III-1** were grown by slow evaporation of a saturated solution in benzene.

**Yield**: 660 mg (3,35 mmol, 60 %), colorless powder.

**Elemental Analysis** for C$_7$H$_{15}$N$_2$Ga (196.93 g/mol) found (calculated) [%]: C 42.52 (42.96), H 7.64 (7.68), N 14.07 (14.23).

**¹H-NMR** (400.4 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 1.16 (s, 6 H, C*H*$_3$), 3.14 (s, 6 H, NCC*H*$_3$CC*H*$_3$N), 4.51 (s, 3 H, Ga*H*$_3$).

**¹³C{¹H}-NMR** (100.7 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 7.9 (*C*H$_3$), 33.8 (NC*C*H$_3$C*C*H$_3$N), 124.9 (N*CC*N), 172.1 (N*C*N).

**IR (ATR):** $\tilde{v}$ [cm$^{-1}$] = 408 (s), 416 (m), 501 (s), 560 (s), 590 (s), 615 (m), 646 (s), 674 (s), 748 (s, v$_{Ga-H, b.}$), 782 (m), 848 (s), 877 (s), 985 (s), 1092 (m), 1127 (m), 1190 (m), 1284 (m), 1311 (m), 1343 (s), 1390 (s), 1403 (s), 1485 (s), 1767 (m, v$_{Ga-H, str.}$),1836 (w), 1897 (s), 1906 (s), 1929 (s), 1948 (m), 1986 (w), 2003 (w), 2165 (m), 2825 (s), 2880 (m), 2947 (w, v$_{C-H,str.}$), 2994 (w, v$_{C-H,str.}$), 3097 (w).

### Synthesis of (*i*Pr₂Im)·GaH₃ III-2

LiGaH$_4$ (5.68 mmol) was generated at -78 °C *in situ* from the reaction of GaCl$_3$ (1.00 g, 5,68 mmol) and LiH (904 mg, 114 mmol) in 40 mL Et$_2$O. *i*Pr$_2$Im (778 mg, 778 μL, 5.11 mmol), dissolved in 15 mL Et$_2$O was added to this solution. After stirring over night at room temperature, the colorless, cloudy reaction mixture was filtered to remove LiH and all volatiles of the filtrate were removed *in vacuo*. The residue was suspended in

10 ml *n*-hexane, the product was filtered off and dried *in vacuo* to afford **III-2** as a colorless powder.

Yield: 662 mg (2.94 mmol, 52 %), colorless powder.

**Elemental Analysis** for $C_9H_{19}N_2Ga$ (224.99 g/mol) found (calculated) [%]: C 42.73 (48.05), H 8.06 (8.51), N 10.79 (12.45).

**$^1$H-NMR** (400.4 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 0.93 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H$_3$*), 4.56 (s, 3 H, Ga-*H$_3$*), 5.20 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*), 6.22 (s, 2 H, NC*H*C*H*N).

**$^{13}$C{$^1$H}-NMR** (100.7 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 22.8 (*i*Pr-*C*H$_3$), 51.5 (*i*Pr-*C*H), 116.7 (NC*H*C*H*N), 173.3 (N*C*N).

**IR (ATR)**: $\tilde{v}$ [cm$^{-1}$] = 459 (m), 506 (s), 523 (s), 589 (s), 641 (m), 664 (s), 725 (s, v$_{Ga-H, b.}$), 751 (s), 801 (w), 1104 (w), 1115 (m), 1134 (w), 1206 (s), 1369 (m), 1460 (m), 1774 (s, v$_{Ga-H, str.}$), 1796 (m), 1846 (m), 2168 (w), 2960 (m, v$_{C-H,str.}$), 3156 (w).


**Synthesis of (*i*Pr$_2$Im$^{Me}$)·GaH$_3$ III-3**

LiGaH$_4$ (5.68 mmol) was generated at -78 °C *in situ* from the reaction of GaCl$_3$ (1.00 g, 5,68 mmol) and LiH (904 mg, 114 mmol) in 40 mL Et$_2$O. *i*Pr$_2$Im$^{Me}$ (921 mg,5.11 mmol), dissolved in 15 mL Et$_2$O was added to this solution. After stirring over night at room temperature, the colorless, cloudy reaction mixture was filtered to remove LiH and all volatiles of the filtrate were removed *in vacuo*. The residue was suspended in 10 ml *n*-hexane, the product was filtered off and dried *in vacuo* to afford **III-3** as a colorless powder.

**Yield**: 612 mg (2.96 mmol, 58 %), colorless powder.

**Elemental Analysis** for $C_{11}H_{23}N_2Ga$ (253.04 g/mol) found (calculated) [%]: C 49.48 (52.21), H 8.81 (9.16), N 10.39 (11.07).

**$^1$H-NMR** (400.4 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 1.12 (d, 12 H, $^3J_{HH}$ = 7.1 Hz, *i*Pr-C*H$_3$*), 1.52 (s, 6 H, NCC*H$_3$*CC*H$_3$*N), 4.66 (s, 3 H, Ga-*H$_3$*), 5.46 (sept, 2 H, $^3J_{HH}$ = 7.1 Hz, *i*Pr-C*H*).

**$^{13}$C{$^1$H}-NMR** (100.7 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 9.8 (NC*C*H$_3$C*C*H$_3$N), 21.5 (*i*Pr-*C*H$_3$), 52.4 (*i*Pr-*C*H), 125.6 (N*CC*N), 172.7 (N*C*N).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 518 (s), 558 (m), 733 (s, $\nu_{Ga\text{-}H,\,b.}$), 903 (w), 1105 (w), 1217 (w), 1217 (m), 1370 (w), 1773 (s, $\nu_{Ga\text{-}H,\,str.}$), 2962 (w, $\nu_{C\text{-}H,str.}$).

## Synthesis of (Dipp$_2$Im$^H$)·GaH$_3$ III-4

LiGaH$_4$ (1.13 mmol) was generated at -78 °C *in situ* from the reaction of GaCl$_3$ (220 mg, 1.13 mmol) and LiH (90.4 mg, 11.3 mmol) in 40 mL Et$_2$O. Dipp$_2$Im$^H$ (400 mg, 1.02 mmol), dissolved in 15 mL Et$_2$O was added to this solution. After stirring over night at room temperature, the colorless, cloudy reaction mixture was filtered to remove LiH and all volatiles of the filtrate were removed *in vacuo*. The residue was suspended in 10 ml *n*-hexane, the product was filtered off and dried *in vacuo* to afford **III-4** as a colorless powder. Crystals suitable for X-ray diffraction of compounds **III-4** were grown by slow evaporation of a saturated solution in benzene.

**Yield**: 273 mg (2.94 mmol, 59 %, colorless solid.

**Elemental Analysis** for C$_{27}$H$_{42}$N$_2$Ga (463.26 g/mol) found (calculated) [%]:  C 69.69 (69.84), H 9.00 (9.12), N 6.02 (6.03).

**$^1$H-NMR** (400.4 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 1.17 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr-C*H$_3$*), 1.53 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H$_3$*), 3.12 (sept, 4 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr-C*H*), 3.36 (s, 4 H, NC*H*C*H*N), 3.58 (s, 3 H, Ga-*H*), 7.08 - 7.24 (m, 6 H, aryl-C*H*).

**$^{13}$C{$^1$H}-NMR** (100.7 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 24.2 (*i*Pr-*C*H$_3$), 25.4 (*i*Pr-*C*H$_3$), 29.1 (*i*Pr-*C*H), 53.4 (N*C*H$_2$*C*H$_2$N), 124.6 (aryl-*C*$_{meta}$H), 129.9 (aryl-*C*$_{para}$H), 135.3 (aryl-*C*$_{ipso}$), 146.7 (aryl-*C*$_{ortho}$), 205.9 (N*C*N).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] : 458 (m), 522 (m), 619 (w), 716 (s, $\nu_{Ga\text{-}H,\,b.}$), 757 (m), 804 (m),1261 (w), 1322 (m), 1454 (m), 1484 (m), 1790 (s, $\nu_{Ga\text{-}H,\,str.}$), 2932(m).

## Synthesis of (Me$_2$Im$^{Me}$)·GaH$_2$(cAAC$^{Me}$H) III-5

A solution of cAAC$^{Me}$ (110 mg, 385 µmol) in 5 mL of thf was added at room temperature to a solution of (Me$_2$Im$^{Me}$)·GaH$_3$ **III-1** (75 mg, 385 µmol) in 5 mL of thf. After stirring overnight at room temperature, all volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-hexane and stored for crystallization over night at -30 °C. The precipitate was filtered off and dried *in vacuo* to afford **III-5** as a colorless powder.

Crystals suitable for X-ray diffraction of compound **III-5** were grown by slow evaporation of a saturated solution in benzene.

**Yield**: 58.0 mg (121 µmol, 31 %), colorless powder.

**Elemental Analysis** for $C_{27}H_{46}N_3Ga$ (482.41 g/mol) found (calculated) [%]: C 65.79 (67.22), H 9.61 (9.61), N 8.66 (8.71).

**¹H-NMR** (400.4 MHz, $C_6D_6$, 298K): $\delta$ [ppm] = 1.06 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, ₍cAAC₎*i*Pr-C*H₃*), 1.15 (s, 6 H, ₍NHC₎C*H₃*), 1.21 (s, 3 H, ₍cAAC₎C(C*H₃*)₂), 1.33 (s, 3 H, ₍cAAC₎C(C*H₃*)₂), 1.37 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, ₍cAAC₎*i*Pr-C*H₃*), 1.51 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, ₍cAAC₎*i*Pr-C*H₃*), 1.53 (s, 3 H, ₍cAAC₎C(C*H₃*)₂), 1.83 (s, 3 H, ₍cAAC₎C(C*H₃*)₂), 1.85 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, ₍cAAC₎*i*Pr-C*H₃*), 1.98 – 2.09 (m, 2 H, ₍cAAC₎C*H₂*), 3.02 (s, 6 H, ₍NHC₎NCC*H₃*CC*H₃*N), 3.69 – 3.76 (s, 1 H, ₍cAAC₎GaC*H* und sept, 1 H, $^3J_{HH}$ = 6.7 Hz, ₍cAAC₎*i*Pr-C*H*), 4.54 (sept, 1 H, $^3J_{HH}$ = 6.7 Hz, ₍cAAC₎*i*Pr-C*H*), 7.10 (m, 3 H, ₍cAAC₎aryl-C*H*).

**¹³C{¹H}-NMR** (100.7 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 7.8 (₍NHC₎*C*H₃), 24.7 (₍cAAC₎*i*Pr-*C*H₃), 25.8 (₍cAAC₎*i*Pr-*C*H₃), 26.4 (₍cAAC₎*i*Pr-*C*H₃), 27.0 (₍cAAC₎*i*Pr-*C*H₃), 27.4 (₍cAAC₎*i*Pr-*C*H), 29.1 (₍cAAC₎C(*C*H₃)₂), 29.4 (₍cAAC₎*i*Pr-*C*H), 29.5 (₍cAAC₎C(*C*H₃)₂), 29.5 (₍cAAC₎C(*C*H₃)₂), 31.9 (₍cAAC₎C(*C*H₃)₂), 33.7 (₍NHC₎NC*C*H₃C*C*H₃N), 41.4 (₍cAAC₎*C*(CH₃)₂), 61.1 (₍cAAC₎*C*H₂), 63.4 (₍cAAC₎*C*(CH₃)₂), 68.8 (₍cAAC₎Ga*C*H), 124.1 (₍cAAC₎aryl-*C*metaH), 124.7 (₍cAAC₎aryl-*C*metaH), 124.9 (₍NHC₎N*C*CH₃C*C*H₃N) 126.0 (₍cAAC₎aryl-*C*paraH), 143.2 (₍cAAC₎aryl-*C*ipso), 152.8 (₍cAAC₎aryl-*C*ortho), 153.2 (₍cAAC₎aryl-*C*ortho), 174.4 (₍NHC₎N*C*N).

**IR (ATR)**: $\tilde{v}$ [cm⁻¹] = 465 (s), 495 (m), 569 (m), 591 (m), 601 (m), 631 (s), 704 (s), 737 (w), 770 (s, ν₍Ga-H, b.₎), 796 (s), 849 (m), 1044 (m), 1098 (w), 1110 (m), 1150 (m), 1209 (m), 1248 (m), 1357 (m), 1371 (m), 1381 (m), 1433 (s), 1461 (m), 1746 (m), 1781 (m, ν₍Ga-H,str.₎), 1825 (m), 2858 (w), 2924 (m, ν₍C-H,str.₎).

## Synthesis of (*i*Pr₂Im^Me)·GaH₂(cAAC^MeH) III-6

A solution of cAAC^Me (113 mg, 395 µmol) in 5 mL of thf was added at room temperature to a solution of (*i*Pr₂Im^Me)·GaH₃ **III-3** (100 mg, 395 µl) in 5 mL of thf. After 5 min stirring at room temperature, all volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-pentane and stored for crystallization over night at -30 °C. The precipitate was filtered off and dried *in vacuo* to afford **III-6** as a colorless powder.

Crystals suitable for X-ray diffraction of compound **III-6** were grown by slow evaporation of a saturated solution in benzene.

**Yield**: 64mg (119 µmol, 30 %), colorless powder.

**Elemental Analysis** for $C_{31}H_{54}N_3Ga$ (538.52 g/mol) found (calculated) [%]: C 65.79 (69.14), H 9.61 (10.11), N 8.66 (7.80).

**¹H-NMR** (400.4 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 1.07 (d, 6 H, $^3J_{HH}$ = 7.1 Hz, NHC$i$Pr-C$H_3$), 1.10 (s, 3 H, cAACC(C$H_3$)$_2$), 1.12 (d, 6 H, $^3J_{HH}$ = 7.1 Hz, NHC$i$Pr-C$H_3$), 1.32 (s, 3 H, cAACC(C$H_3$)$_2$), 1.38 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, cAAC$i$Pr-C$H_3$), 1.44 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, cAAC$i$Pr-C$H_3$), 1.49 (s, 3 H, cAACC(C$H_3$)$_2$), 1.51 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, cAAC$i$Pr-C$H_3$), 1.51 (s, 6 H, NHCNCC$H_3$CC$H_3$N), 1.79 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, cAAC$i$Pr-C$H_3$), 1.85 (s, 3 H, cAACC(C$H_3$)$_2$), 1.95 - 2.09 (m, 2 H, cAACC$H_2$), 3.77 (d, 1 H, $^3J_{HH}$ = 3.5 Hz, cAACGaC$H$), 3.82 (sept, 1 H, $^3J_{HH}$ = 6.7 Hz, cAAC$i$PrC$H$), 4.51 (sept, 1 H, $^3J_{HH}$ = 6.7 Hz, cAAC$i$PrC$H$), 5.41 (sept, 2 H, $^3J_{HH}$ = 7.1 Hz, NHC$i$PrC$H$), 7.20-7.34 (m, 3 H, cAACaryl-C$H$).

**¹³C{¹H}-NMR** (100.7 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 9.9 (NHCNC*C*H$_3$C*C*H$_3$N), 21.4 (NHC$i$Pr-*C*H$_3$), 21.5 (NHC$i$Pr-*C*H$_3$), 25.4 (cAAC$i$Pr-*C*H$_3$), 26.0 (cAAC$i$Pr-*C*H$_3$), 26.1 (cAAC$i$Pr-*C*H$_3$), 27.4 (cAAC$i$Pr-*C*H), 27.7 (cAAC$i$Pr-*C*H$_3$), 29.1 (cAACC(*C*H$_3$)$_2$), 29.5 (cAAC$i$Pr-*C*H), 29.9 (cAACC(*C*H$_3$)$_2$), 30.1 (cAACC(*C*H$_3$)$_2$), 31.8 (cAACC(*C*H$_3$)$_2$), 41.4 (cAAC*C*(CH$_3$)$_2$), 52.3 (NHC$i$Pr-*C*H), 60.6 (cAAC*C*H$_2$), 63.4 (cAAC*C*(CH$_3$)$_2$), 69.3 (cAACGa*C*H), 124.1 (cAACaryl-*C*$_{meta}$H), 124.8 (cAACaryl-*C*$_{meta}$H), 125.6 (NHCNC*C*H$_3$C*C*H$_3$N), 126.2 (cAACaryl-*C*$_{para}$H), 142.3 (cAACaryl-*C*$_{ipso}$), 152.7 (cAACaryl-*C*$_{ortho}$), 153.1 (cAACaryl-*C*$_{ortho}$), 175.3 (NHCN*C*N).

**IR (ATR)**: $\tilde{v}$ [cm$^{-1}$] = 462 (s), 498 (s), 522 (s), 568 (s), 605 (m), 636 (s), 648 (m), 686 (s), 706 (s), 752 (s, $v_{Ga-H, b.}$), 769 (s), 791 (s), 906 (w), 1046 (m), 1109 (m), 1149 (w), 1208 (s), 1251 (m), 1303 (m), 1319 (m), 1370 (s), 1396 (m), 1433 (s), 1460 (s), 1760 (s, $v_{Ga-H,str.}$), 1813 (s, $v_{Ga-H,str.}$), 2860 (m), 2926 (m), 2970 (s, $v_{C-H,str.}$).

## Synthesis of (Dipp$_2$Im)·GaH$_2$(cAAC$^{Me}$H) III-7

A solution of cAAC$^{Me}$ (92.8 mg, 325 µmol) in 5 mL of thf was added at room temperature to a solution of (Dipp$_2$Im)·GaH$_3$ **V** (150 mg, 325 µmol) in 5 mL of thf. After 5 min stirring at room temperature, all volatiles were removed *in vacuo* and the residue was suspended in 10 mL of *n*-pentane and stored for crystallization over night at -

80 °C. The precipitate was filtered off and dried *in vacuo* to afford **III-7** as a colorless powder. Crystals suitable for X-ray diffraction of compound **III-7** were grown by slow evaporation of a saturated solution in benzene.

**Yield**: 120 mg (160 µmol, 49 %), colorless powder.

**Elemental Analysis** for $C_{47}H_{70}N_3Ga$ (746.83 g/mol) found (calculated) [%]: C 72.33 (75.59), H 9.10 (9.45), N 5.38 (5.63).

**$^1$H-NMR** (400.4 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 0.77 (d, 3 H, $^3J_{HH}$ = 6.8 Hz, $_{cAAC}i$Pr-C$H_3$), 0.92 (m, 12 H, $^3J_{HH}$ = 6.8 Hz, $_{NHC}i$Pr-C$H_3$), 1.06 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 1.18 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 1.29-1.32 (m, 12 H, $_{NHC}i$Pr-C$H_3$, $_{cAAC}i$Pr-C$H_3$ and $_{cAAC}$C(C$H_3$)$_2$), 1.35 (d, 3 H, $^3J_{HH}$ = 6.8 Hz, $_{cAAC}i$Pr-C$H_3$), 1.41 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, $_{NHC}i$Pr-C$H_3$),1.43 – 1.44 (m, 6 H, $_{cAAC}$C(C$H_3$)$_2$ and $_{cAAC}i$Pr-C$H_3$), 1.84 - 1.95 (m, 2 H, $_{cAAC}$C$H_2$), 2.65 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, $_{NHC}i$Pr-C$H$), 2.81 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, $_{NHC}i$Pr-C$H$), 3.42 (d, 1 H, $^3J_{HH}$ = 4.6 Hz, $_{cAAC}$GaC$H$), 3.48 (sept, 1 H, $^3J_{HH}$ = 6.8 Hz, $_{cAAC}i$Pr-C$H$), 4.15 (sept, 1 H, $^3J_{HH}$ = 6.8 Hz, $_{cAAC}i$Pr-C$H$), 6.41 (s, 2 H, NC$H$C$H$N), 7.05-7.23 (m, 9 H, $_{cAAC}$aryl-C$H$ und $_{NHC}$aryl-C$H$).

**$^{13}$C{$^1$H}-NMR** (100.7 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 22.7 ($_{NHC}i$Pr-$C$H$_3$), 22.8 ($_{NHC}i$Pr-$C$H$_3$), 25.0 ($_{cAAC}i$Pr-$C$H$_3$), 25.6 ($_{cAAC}i$Pr-$C$H$_3$), 25.9 ($_{cAAC}i$Pr-$C$H$_3$), 26.0 ($_{NHC}i$Pr-$C$H$_3$), 26.5 ($_{NHC}i$Pr-$C$H$_3$), 27.1 ($_{cAAC}i$Pr-$C$H$_3$), 27.1 ($_{cAAC}i$Pr-$C$H), 28.9 ($_{cAAC}$C($C$H$_3$)$_2$), 29.0 ($_{NHC}i$Pr-$C$H), 29.0 ($_{cAAC}i$Pr-$C$H), 29.3 ($_{NHC}i$Pr-$C$H), 29.5 ($_{cAAC}$C($C$H$_3$)$_2$) ,31.3 ($_{cAAC}$C($C$H$_3$)$_2$) ,31.6 ($_{cAAC}$C($C$H$_3$)$_2$), 40.8 ($_{cAAC}$$C$(CH$_3$)$_2$), 60.6 ($_{cAAC}$$C$H$_2$), 63.8 ($_{cAAC}$$C$(CH$_3$)$_2$), 67.2 ($_{cAAC}$Ga$C$H), 123.6 ($_{cAAC}$aryl-$C_{meta}$H), 124.3 ($_{cAAC}$aryl-$C_{meta}$H), 124.4 ($_{NHC}$aryl-$C_{meta}$H), 124.4 ($_{NHC}$aryl-$C_{meta}$H), 124.7 ($_{NHC}$N$C$H$C$HN), 125.9 ($_{cAAC}$aryl-$C_{para}$H), 130.7 ($_{NHC}$aryl-$C_{para}$H), 135.9 ($_{NHC}$aryl-$C_{ipso}$), 142.0 ($_{cAAC}$aryl-$C_{ipso}$), 145.5 ($_{NHC}$aryl-$C_{ortho}$), 145.9 ($_{NHC}$aryl-$C_{ortho}$), 152.6 ($_{cAAC}$aryl-$C_{ortho}$), 152.7 ($_{cAAC}$aryl-$C_{ortho}$), 183.6 ($_{NHC}$N$C$N).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 571 (w), 635 (s), 713 (s), 746 (s, $\nu_{Ga-H, b.}$), 770 (m), 1148 (m), 1210 (m), 1251 (m), 1274 (w), 1322 (m), 1351 (w), 1360 (m), 1383 (m), 1397 (m), 1458 (s), 1781 (m, $\nu_{Ga-H,str.}$), 1802 (m), 1823 (s), 1845 (s), 2863 (m), 2922 (m), 2961 (s, $\nu_{C-H,str.}$).

## Synthesis of (cAAC$^{Me}$H)$_2$GaH (*meso*-III-8) and (*rac*-III-8)

A solution of cAAC$^{Me}$ (100 mg, 346 μmol) in 5 mL of toluene was added at room temperature to a solution of (Dipp$_2$Im$^H$)·GaH$_3$ **III-4** (80.0 mg, 173 μmol) in 5 mL of toluene. After 12 h stirring at room temperature, the colorless crystalline residue was filtered off and dried *in vacuo* to afford **III-8** as a colorless crystalline powder. Crystals suitable for X-ray diffraction of the compound **III-8** were grown by slow evaporation of a saturated solution in benzene.

**Yield**: 38.0 mg (60.0 μmol, 35 %), colorless powder.

**Elemental Analysis** for C$_{42}$H$_{65}$GaN$_2$ (643.70 g/mol) found (calculated) [%]: C 74.46 (74.64), H 10.08 (10.18), N 4.29 (4.35).

Separation of the signals for the isomers *meso*-**III-8** and *rac*- **III-8** was not feasible in the $^1$H and $^{13}$C{$^1$H} spectra.

**$^1$H-NMR** (400.4 MHz, THF-d$_8$, 298 K, dr(*meso*-**III-8**:*rac*- **III-8**) = 1:1.3): δ [ppm] = 0,63 (s, 3H, C(C$H_3$)$_2$), 0.66 (d, 3H, $^3J_{HH}$ = 6.7 Hz, *i*Pr-C$H_3$), 0.80 (d, 3H, $^3J_{HH}$ = 6.7 Hz, *i*Pr-C$H_3$), 0.95 (s, 3H, C(C$H_3$)$_2$), 1.02 (s, 6H, C(C$H_3$)$_2$), 1.10 (s, 3H, C(C$H_3$)$_2$), 1.12 (d, 3H, $^3J_{HH}$ = 6.7 Hz, *i*Pr-C$H_3$), 1.16 (s, 2H, C$H_2$), 1.20 (s, 3H, C(C$H_3$)$_2$), 1.29 (s, 6H, C(C$H_3$)$_2$), 1.35 (d, 3H, $^3J_{HH}$ = 6.7 Hz, *i*Pr-C$H_3$), 1.43 (s, 3H, C(C$H_3$)$_2$), 1.81 (s, 2H, C$H_2$), 3.23 (sept, 1H, $^3J_{HH}$ = 6.7 Hz, *i*Pr-C$H$), 3.37 (sept, 1H, $^3J_{HH}$ = 6.7 Hz, *i*Pr-C$H$), 3.72 (d, 1H, $^3J_{HH}$ = 4.7 Hz, Ga–C$H$), 3.76 (d, 1H, $^3J_{HH}$ = 4.7 Hz, Ga–C$H$), 3.90 (sept, $^3J_{HH}$ = 6.7 Hz, 1H, *i*Pr-C$H$), 4.06 (sept, 1H, $^3J_{HH}$ = 6.7 Hz, *i*Pr-C$H$), 6.90-7.07 (m, 6H, aryl-C$H$).

**$^{13}$C{$^1$H}-NMR** (100.7 MHz, THF-d$_8$, 298 K): δ [ppm] = 24.4, 25.9, 26.4, 27.2, 27.3, 27.7, 27.8, 28.3, 28.9, 29.8, 30.1, 30.6, 30.9, 31.3, 31.89, 32.5, 42.1, 42. 9, 60.6, 60.8, 64.9, 65.3, 67.7, 67.9, 68.1, 76.9 ($_{cAAC}$GaC$H$), 77.0 ($_{cAAC}$GaC$H$), 125.3, 125.5, 125.6, 126.2, 127.4, 127.5, 141.2, 142.3, 152.1, 152.2, 152.5, 152.5.

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 2969 (s), 2948 (m), 1921 (w, $\nu_{Ga-H, str.}$), 1457 (m), 1430 (m), 1381 (m), 1362 (m), 1320 (m), 1305 (m), 1230 (m), 1102 (w), 769 (s, $\nu_{Ga-H, biege}$), 569 (m), 530 (m).

## Synthesis of (*i*Pr$_2$Im$^{Me}$)·GaH$_2$Cl III-9

To a solution of (*i*Pr$_2$Im$^{Me}$)·GaH$_3$ **III-3** (500 mg, 1,97 mmol) in 20 mL toluene was added a solution of (*i*Pr$_2$Im$^{Me}$)·GaCl$_3$ **VI** (342 mg, 985 $\mu$mol) in 10 mL toluene. After the solution was stirred for 24 h at 55 °C all volatiles were removed *in vacuo*. The residue was suspended in 10 mL *n*-hexane, the precipitate filtered off and dried *in vacuo* to afford **III-9** as a colorless powder.

**Yield**: 652 mg (2.26 mmol, 77 %), colorless powder.

**Elemental Analysis** for C$_{13}$H$_{23}$ClGaN$_2$(287.08 g/mol) found (calculated) [%]: C 46.21 (45.80), H 7.76 (8.04), N 9.60 (9.71).

**$^1$H-NMR** (400.4 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 1.11 (d, 12 H, $^3J_{HH}$ = 7.1 Hz, *i*Pr-C*H*$_3$), 1.49 (s, 6 H, NCC*H*$_3$CC*H*$_3$N), 5.36 (sept, 2 H, $^3J_{HH}$ = 7.1 Hz, *i*Pr-C*H*), 5.60 (s, 2 H, Ga-*H*$_2$).

**$^{13}$C{$^1$H}-NMR** (100.7 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 9.70 (NC*C*H$_3$C*C*H$_3$N), 21.6 (*i*Pr-*C*H$_3$), 52.5 (*i*Pr-*C*H), 126.0 (NC*C*N), 166.9 (N*C*N).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 2995 (w), 2936 (w), 2874 (w), 1890 (w) 1836 (s, v$_{Ga-H}$, str.), 1457 (w), 1438 (w), 1387 (w), 1370 (s), 1108 (m), 764 (m, vGa-H, b.), 748 (w), 704 (s), 674 (s), 492 (m).


## Synthesis of (Dipp$_2$Im)·GaH$_2$Cl III-10

To a solution of (Dipp$_2$Im)·GaH$_3$ **V** (300 mg, 650 $\mu$mol) in 10 mL toluene was added a solution of (Dipp$_2$Im)·GaCl$_3$ **VII** (184 mg, 325 $\mu$mol) in 10 mL toluene. After the solution was stirred for 24 h at 55 °C all volatiles were removed *in vacuo*. The residue was suspended in 10 mL *n*-hexan, the precipitate filtered off and dried *in vacuo* to afford **III-10** as a colorless powder.

**Yield**: 349 mg (702 $\mu$mol, 72 %), colorless powder.

**Elemental Analysis** for C$_{27}$H$_{39}$ClGaN$_2$ (496.80 g/mol) found (calculated) [%]: C 64.67 (65.28), H 7.66 (7.91), N 5.35 (5.64).

**$^1$H-NMR** (400.4 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 1.00 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr-C*H*$_3$), 1.40 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*$_3$), 2.68 (sept, 4 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr-C*H*), 4.66 (s, 3 H, Ga-*H*), 6.46 (s, 2 H, NC*H*C*H*N), 7.08 - 7.27 (m, 6 H, aryl-C*H*).

**$^{13}$C{$^1$H}-NMR** (100.7 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 23.1 (*i*Pr-CH$_3$), 25.4 (*i*Pr-CH$_3$), 29.1 (*i*Pr-*C*H), 124.3 (aryl-*C*$_{meta}$H), 124.7 (NC*H*C*H*N), 131.1 (aryl-*C*$_{para}$H), 134.1 (aryl-*C*$_{ipso}$), 145.7 (aryl-*C*$_{ortho}$), 181.6 (N*C*N).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 3153 (w), 3124 (w), 2963 (m), 2928 (w), 2870 (w), 1878 (m, $\nu_{Ga-H, str.}$), 1467 (m), 1112 (m), 803 (m), 757 (m), 732 (s, $\nu_{Ga-H}$), 673 (s).


## Synthesis of (Dipp$_2$Im$^H$)·GaH$_2$Cl III-11

To a solution of (Dipp$_2$Im$^H$)·GaH$_3$ **III-4** (150 mg, 320 $\mu$mol) in 10 mL toluene was added a solution of (Dipp$_2$Im$^H$)·GaCl$_3$ **VIII** (110 mg, 160 $\mu$mol) in 10 mL toluene. After the solution was stirred for 24 h at room temperature all volatiles were removed *in vacuo*. The residue was suspended in 10 mL *n*-hexan, the precipitate filtered off and dried *in vacuo* to afford **III-11** as a colorless powder.

**Yield**: 173 mg (350 $\mu$mol, 69 %), colorless powder.

**Elemental Analysis** for $C_{27}H_{39}ClGaN_2$ (496.80 g/mol) found (calculated) [%]: C 62.42 (65.01), H 7.89 (8.23), N 5.30 (5.62).

**$^1$H-NMR** (400.4 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 1.10 (d, 12 H, *i*Pr-C*H*$_3$), 1.50 (d, 12 H, *i*Pr-C*H*$_3$), 3.16 (sept, 4 H, *i*Pr-C*H*), 3.41 (s, 4 H, NC*H*$_2$C*H*$_2$N), 4.56 (s, 2 H, Ga-*H*), 7.05 - 7.21 (m, 6 H, arylC*H*).

**$^{13}$C{$^1$H}-NMR** (100.7 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 23.9 (*i*Pr-CH$_3$), 25.8 (*i*Pr-CH$_3$), 29.2 (*i*Pr-*C*H), 53.7 (N*C*H*C*HN), 124.8 (aryl*C*$_{meta}$H), 130.4 (aryl*C*$_{para}$H), 134.1 (aryl*C*$_{ipso}$), 146.7 (aryl*C*$_{ortho}$), 198.0 (N*C*N).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 2959 (m), 2904 (w), 1877 (m, $\nu_{Ga-H, str.}$), 1490 (m), 1455 (m), 1265 (m), 804 (m), 737 (s, $\nu_{Ga-H, b.}$), 631 (w), 447 (m).

## Synthesis of (*i*Pr₂Im^(Me))·GaHCl₂ III-12

SiEt₃H (820 $\mu$L, 5.11 mmol) was added to GaCl₃ (900 mg, 5.11 mmol) at -30 °C and the mixture was stirred for 1 h at 5 °C and all volatiles were removed *in vacuo*. A solution of *i*Pr₂Im^(Me) (921 mg, 5.11 mmol) in 25 mL Et₂O was added at -78 °C and stirred overnight. All volatiles were removed, and the residue was suspended in 15 mL *n*-hexane. The precipitate was filtered off and dried *in vacuo* to afford **III-12** as a colorless powder. Crystals suitable for X-ray diffraction of compound **III-12** were grown by slow evaporation of a saturated solution in benzene.

**Yield**: 1.36 g (4.22 mmol, 83 %), colorless powder.

**Elemental Analysis** for $C_{13}H_{22}Cl_2GaN_2$(321.04 g/mol) found (calculated) [%]: C 39.72 (40.91), H 6.49 (6.87), N 8.26 (8.67).

**¹H-NMR** (400.4 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 1.10 (d, 12 H, $^3J_{HH}$ = 7.1 Hz, *i*Pr-C$H_3$), 1.49 (s, 6 H, NCC$H_3$CC$H_3$N), 5.31 (sept, 2 H, $^3J_{HH}$ = 7.1 Hz, *i*Pr-C$H$), 6.18 (s, 1 H, Ga-$H$).

**¹³C{¹H}-NMR** (100.7 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 9.78 (NC$C$H₃C$C$H₃N), 21.6 (*i*Pr-$C$H₃), 52.5 (*i*Pr-$C$H), 126.8 (NC$C$N), 160.7 (N$C$N).

**IR (ATR)**: $\tilde{\nu}$ [cm⁻¹] = 2980 (w), 2937 (w), 1948 (s, $v_{Ga-H,\ str.}$), 1631 (w), 1464 (m), 1438 (w), 1392 (m), 1372 (m), 1351 (w), 1335 (w), 1290 (w), 1261 (w), 1223 (w), 1201 (w), 1165 (w), 1139 (w), 1108 (m), 1032 (w), 901 (w), 802 (w), 775 (w), 752 (m), 678 (s), 615 (s), 574 (w), 469 (w).

## Synthesis of (Dipp₂Im)·GaHCl₂ III-13

SiEt₃H (500 $\mu$L, 3.13 mmol) was added to GaCl₃ (551 mg, 3.13 mmol) at -30 °C and the mixture was stirred for 1 h at 5 °C and all volatiles were removed *in vacuo*. A solution of Dipp₂Im (1.21 g, 3.13 mmol) in 25 mL Et₂O was added at -78 °C and stirred overnight. All volatiles were removed, and the residue was suspended in 15 mL *n*-hexane. The precipitate was filtered off and dried *in vacuo* to afford **III-13** as a colorless powder. Crystals suitable for X-ray diffraction of compound **III-13** were grown by slow evaporation of a saturated solution in benzene.

**Yield**: 1.20 g (2.26 mmol, 73 %), colorless powder.

**Elemental Analysis** for $C_{27}H_{37}Cl_2GaN_2$ (528.16 g/mol) found (calculated) [%]: C 61.28 (61.16), H 7.18 (7.03), N 5.24 (5.28).

**$^1$H-NMR** (400.4 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 0.97 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, $i$Pr-C$H_3$), 1.41 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, $i$Pr-C$H_3$), 2.68 (sept, 4 H, $^3J_{HH}$ = 6.9 Hz, $i$Pr-C$H$), 5.19 (s, 1 H, Ga-$H$), 6.45 (s, 2 H, NC$H$C$H$N), 7.08 - 7.27 (m, 6 H, aryl-C$H$).

**$^{13}$C{$^1$H}-NMR** (100.7 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 22.9 ($i$Pr-$C$H$_3$), 25.7 ($i$Pr-$C$H$_3$), 29.2 ($i$Pr-$C$H), 124.3 (aryl-$C_{meta}$H), 124.4 (NC$H$C$H$N), 131.5 (aryl-$C_{para}$H), 133.3 (aryl-$C_{ipso}$), 145.7 (aryl-$C_{ortho}$), 167.9 (N$C$N).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 2963 (m), 1933 (m, $\nu_{Ga-H, str.}$), 1467 (w), 1454 (w), 1364 (w), 1209 (w), 1115 (m), 1061 (w), 800 (m), 755 (s), 614 (s).

## Synthesis of (Dipp$_2$Im$^H$)·GaHCl$_2$ III-14

To a solution of (Dipp$_2$Im$^H$)·GaH$_3$ **III-4** (100 mg, 216 $\mu$mol) in 10 mL toluene was added a solution of (Dipp$_2$Im$^H$)·GaCl$_3$ **VIII** (244 mg, 432 $\mu$mol) in 10 mL toluene. After the solution was stirred for 24 h at room temperature all volatiles were removed *in vacuo*. The residue was suspended in 10 mL *n*-hexane, the precipitate filtered off and dried *in vacuo* to afford **III-14** as a colorless powder.

**Yield**: 270 mg (508 $\mu$mol, 78 %), colorless powder.

**Elemental Analysis** for $C_{27}H_{39}Cl_2GaN_2$ (530.17 g/mol) found (calculated) [%]: C 61.79 (60.93), H 7.56 (7.39), N 5.11 (5.26).

**$^1$H-NMR** (400.4 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 1.08 (d, 12 H, $i$Pr-C$H_3$), 1.48 (d, 12 H, $i$Pr-C$H_3$), 3.19 (sept, 4 H, $i$Pr-C$H$), 3.46 (s, 4 H, NC$H_2$C$H_2$N), 5.06 (s, 1 H, Ga-$H$), 7.04 - 7.19 (m, 6 H, arylC$H$).

**$^{13}$C{$^1$H}-NMR** (100.7 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 23.9 ($i$Pr-$C$H$_3$), 26,1 ($i$Pr-$C$H$_3$), 29.2 ($i$Pr-$C$H), 54,1 (N$C$H$C$HN), 124.9 (aryl$C_{meta}$H), 130.7 (aryl$C_{para}$H), 133.2 (aryl$C_{ipso}$), 146.8 (aryl$C_{ortho}$), 191,1 (N$C$N).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 2962 (m), 1925 (m, $\nu_{Ga-H, str.}$), 1488 (s), 1457 (s), 1270 (s), 802 (m), 755 (m), 687 (m), 639 (m).

## Synthesis of (cAAC$^{Me}$)·GaHCl$_2$ III-15

SiEt$_3$H (300 $\mu$L, 1.87 mmol) was added to GaCl$_3$ (328 mg, 1.87 mmol) at -30 °C and the mixture was stirred for 1 h at 5 °C and all volatiles were removed *in vacuo*. A solution of cAAC$^{Me}$ (539 mg, 1.87 mmol) in 25 mL Et$_2$O was added at -78 °C and stirred overnight. All volatiles were removed, and the residue was suspended in 15 mL *n*-hexane. The precipitate was filtered off and dried *in vacuo* to afford **III-15** as a colorless powder. Crystals suitable for X-ray diffraction of compound **III-15** were grown by slow evaporation of a saturated solution in benzene.

**Yield**: 592 mg, (1.39 mmol, 74 %), colorless powder.

**Elemental Analysis** for C$_{20}$H$_{33}$Cl$_2$GaN (426.12 g/mol) found (calculated) [%]: C 56.41 (56.11), 7.68 (7.77), 3.19 (3.27).

**$^1$H-NMR** (400.4 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 0.74 (s, 6 H, C(C$H_3$)$_2$), 1.00 (d, 6 H, $^3J_{HH}$ = 7.0 Hz, *i*Pr-C$H_3$), 1.32 (s, 2 H, C$H_2$), 1.35 (d, 6 H, $^3J_{HH}$ = 7.0 Hz, *i*Pr-C$H_3$), 1.68 (s, 6 H, C(C$H_3$)$_2$), 2.55 (sept, 2 H, $^3J_{HH}$ = 6.6 Hz, *i*Pr-C$H$), 4.98 (s, 1 H, Ga-$H$), 6.89-7.07 (m, 3 H, aryl-C$H$).

**$^{13}$C{$^1$H}-NMR** (100.7 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 23.9 (*i*Pr-$C$H$_3$), 26.5 (*i*Pr-$C$H$_3$), 28.3 (C($C$H$_3$)$_2$), 29.0 (*i*Pr-$C$H), 29.2 (C($C$H$_3$)$_2$), 50.3 ($C$(CH$_3$)$_2$), 56.3 ($C$H$_2$), 125.5 (aryl-$C$H), 130.8 (aryl-$C_{para}$H), 145.3 (aryl-$C_{ipso}$H).

## Synthesis of (*i*Pr$_2$Im$^{Me}$)·GaHCl(cAAC$^{Me}$H) (*meso*-III-16) and (*rac*- III-16)

A solution of cAAC$^{Me}$ (50 mg, 156 $\mu$mol) in 5 mL of toluene was added at room temperature to a solution of (*i*Pr$_2$Im$^{Me}$)·GaH$_2$Cl **III-9** (50 mg, 156 $\mu$l) in 5 mL of toluene. After 5 min stirring at room temperature, all volatiles were removed *in vacuo* and the residue was suspended in 5 mL of *n*-pentane and the precipitate was filtered off and dried *in vacuo* to afford **III-16** as a colorless powder. Crystals suitable for X-ray diffraction of the compound **III-16** were grown by slow evaporation of a saturated solution in benzene.

**Yield**: 38 mg (17.4 mmol, 29 %), colorless powder.

**Elemental Analysis** for C$_{31}$H$_{53}$N$_3$GaCl (571.32 g/mol) found (calculated) [%]:  C 65.91 (64.99), H 9.82 (9.32), N 6.76 (7.33).

Separation of the signals for the isomers meso- **III-16** and rac- **III-16** was not feasible in the $^1$H and $^{13}$C{$^1$H} spectra.

**$^1$H-NMR** (400.4 MHz, C$_6$D$_6$, 298 K, dr(meso-**III-16**:rac-**III-16**) = 1:0.8): $\delta$ [ppm] = 0.57 (d, 6 H, $^3J_{HH}$ = 7.1 Hz, $_{NHC}i$Pr-C$H_3$), 0.94 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 1.03 (d, 6 H, $^3J_{HH}$ = 7.1 Hz, $_{NHC}i$Pr-C$H_3$), 1.07 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 1.09 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, $_{cAAC}i$Pr-C$H_3$), 1.10 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 1.18 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 1.19 (s, 6 H, $_{cAAC}$C(C$H_3$)$_2$), 1.21 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, $_{cAAC}i$Pr-C$H_3$), 1.27 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 1.39 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 1.40 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, $_{cAAC}i$Pr-C$H_3$), 1.45 (s, 6 H, $_{cAAC}$C(C$H_3$)$_2$), 1.47 (s, 6 H, $_{cAAC}$C(C$H_3$)$_2$), 1.48 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 1.49 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, $_{cAAC}i$Pr-C$H_3$), 1.53 (d, 3 H, $_{NHC}$NCC$H_3$CC$H_3$N), 1.58 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 1.62 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, $_{cAAC}i$Pr-C$H_3$), 1.69 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, $_{cAAC}i$Pr-C$H_3$), 1.70 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 1.86 (d, 6 H, $^3J_{HH}$ = 6.7 Hz, $_{cAAC}i$Pr-C$H_3$), 1.92 - 2.02 (m, 4 H, $_{cAAC}$C$H_2$), 2.17 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 3.49 (sept, 1 H, $^3J_{HH}$ = 6.7 Hz, $_{cAAC}i$PrC$H$), 3.69 (sept, 1 H, $^3J_{HH}$ = 6.7 Hz, $_{cAAC}i$PrC$H$), 3.77 (d, 1 H, $^3J_{HH}$ = 3.5 Hz, $_{cAAC}$GaC$H$), 3.84 (d, 1 H, $^3J_{HH}$ = 3.5 Hz, $_{cAAC}$GaC$H$), 4.38 (sept, 1 H, $^3J_{HH}$ = 6.7 Hz, $_{cAAC}i$PrC$H$), 4.52 (sept, 1 H, $^3J_{HH}$ = 6.7 Hz, $_{cAAC}i$PrC$H$), 4.92 (sept, 2 H, $^3J_{HH}$ = 7.1 Hz, $_{NHC}i$PrC$H$), 5.37 (b, 1 H, Ga-$H$), 5.46 (sept, 2 H, $^3J_{HH}$ = 7.1 Hz, $_{NHC}i$PrC$H$), 5.59 (b, 1 H, Ga-$H$), 6.91-7.41 (m, 3 H, $_{cAAC}$aryl-C$H$).

**$^{13}$C{$^1$H}-NMR** (100.7 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 7.97, 9.84, 9.89, 10.1, 14.4, 21.4, 21.5, 21.63, 21.65, 21.69, 21.7, 21.9, 22.6, 23.1, 25.05, 25.1, 25.2, 25.4, 25.7, 25.8, 25.9, 26.0, 26.1, 26.3, 26.5, 26.6, 26.8, 26.9, 27.3, 27.4, 28.7, 28.9, 29.1, 29.3, 29.5, 29.6, 29.8, 29.92, 29.98, 30.1, 30.8, 31,2, 31.6, 36.91, 31.97, 32.7, 32.8, 41.3, 42.1, 42.2, 42.6, 51.0, 52.4, 52.5, 60.0, 60.6, 61.2, 61.7, 63.3, 63.4, 63.7, 64.5, 69.7 ($_{cAAC}$GaC$H$), 70.8 ($_{cAAC}$GaC$H$), 124.2,.124.4, 124.7, 125.00, 125.03, 125.8, 126.1, 126.1, 126.3, 126.7, 126.8, 127.4, 127.9, 128.2, 128.4, 128.6, 128.7, 141.3 (aryl-C$H$), 142.7(aryl-C$H$), 151.6 (aryl-C$H$), 151.8 (aryl-C$H$), 152.3 (aryl-C$H$), 152.4 (aryl-C$H$), 153.3 (aryl-C$H$), 153.9 (aryl-C$H$), 169.6 (N$C$N), 170.0 (N$C$N).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 2962 (m), 2872 (w), 1926 (s, $_{VGa-H, str.}$), 1589 (m), 1490 (m), 1456 (w), 1323 (m), 1273 (m), 1185 (m), 1054 (w), 917 (w), 801 (m), 758 (w), 620 (m), 560 (w).

## Synthesis of (*i*Pr$_2$Im$^{Me}$)·GaCl$_2$(cAAC$^{Me}$H) III-17

A solution of cAAC$^{Me}$ (50 mg, 156 μmol) in 5 mL of toluene was added at room temperature to a solution of (*i*Pr$_2$Im$^{Me}$)·GaHCl$_2$ **III-12** (45 mg, 156 μl) in 5 mL of toluene. After 5 min stirring at room temperature, all volatiles were removed *in vacuo* and the residue was suspended in 5 mL of *n*-pentane and the precipitate was filtered off and dried *in vacuo* to afford **III-17** as a colorless powder. Crystals suitable for X-ray diffraction of the compound **III-17** were grown by slow evaporation of a saturated solution in benzene.

**Yield**: 38 mg (62 μmol, 40 %), colorless powder.

**Elemental Analysis** for C$_{31}$H$_{52}$N$_3$GaCl$_2$ (605.28 g/mol) found (calculated) [%]:  C 59.51 (61.20), H 8.62 (8.63), N 6.65 (6.92).

**$^1$H-NMR** (400.4 MHz, C$_6$D$_6$, 298 K): δ [ppm] = 1.03 (d, 6 H, $^3J_{HH}$ = 7.1 Hz, $_{NHC}$*i*Pr-C$H_3$), 1.09 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 1.15 (d, 6 H, $^3J_{HH}$ = 7.1 Hz, $_{NHC}$*i*Pr-C$H_3$), 1.31 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 1.37 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, $_{cAAC}$*i*Pr-C$H_3$), 1.39 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, $_{cAAC}$*i*Pr-C$H_3$), 1.41 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 1.46 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, $_{cAAC}$*i*Pr-C$H_3$), 1.66 (d, 3 H, $^3J_{HH}$ = 6.7 Hz, $_{cAAC}$*i*Pr-C$H_3$), 1.95 (d, 6 H, $_{NHC}$NCC$H_3$CC$H_3$N), 1.85 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 2.18 - 2.11 (m, 2 H, $_{cAAC}$C$H_2$), 3.44 (sept, 1 H, $^3J_{HH}$ = 6.7 Hz, $_{cAAC}$*i*PrC$H$), 3.85 (s, 1 H, $^3J_{HH}$ = 3.5 Hz, $_{cAAC}$GaC$H$),4.71 (sept, 1 H, $^3J_{HH}$ = 6.7 Hz, $_{cAAC}$*i*PrC$H$), 5.59 (sept, 2 H, $^3J_{HH}$ = 7.1 Hz, $_{NHC}$*i*PrC$H$), 7.13-7.28 (m, 3 H, $_{cAAC}$aryl-C$H$).

**$^{13}$C{$^1$H}-NMR** (100.7 MHz, C$_6$D$_6$, 298 K): δ [ppm] = 10.1 ($_{NHC}$NC$C$H$_3$C$C$H$_3$N), 22.2 ($_{NHC}$*i*Pr-$C$H$_3$), 22.8 ($_{NHC}$*i*Pr-$C$H$_3$), 25.0 ($_{cAAC}$*i*Pr-$C$H$_3$), 25.9 ($_{cAAC}$*i*Pr-$C$H$_3$), 26.3 ($_{cAAC}$*i*Pr-$C$H$_3$), 27.3 ($_{cAAC}$*i*Pr-$C$H), 27.6 ($_{cAAC}$*i*Pr-$C$H$_3$), 28.7 ($_{cAAC}$C($C$H$_3$)$_2$), 28.9 ($_{cAAC}$*i*Pr-$C$H), 32.1 ($_{cAAC}$C($C$H$_3$)$_2$), 32.8 ($_{cAAC}$C($C$H$_3$)$_2$), 33.8 ($_{cAAC}$C($C$H$_3$)$_2$), 42.2 ($_{cAAC}$$C$(CH$_3$)$_2$), 52.4 ($_{NHC}$*i*Pr-$C$H), 60.0 ($_{cAAC}$$C$H$_2$), 64.5 ($_{cAAC}$$C$(CH$_3$)$_2$), 76.0 ($_{cAAC}$Ga$C$H), 124.9 ($_{cAAC}$aryl-$C_{meta}$H), 125.0 ($_{cAAC}$aryl-$C_{meta}$H), 126.5 ($_{NHC}$N$C$CH$_3$C$C$CH$_3$N), 126.8 ($_{cAAC}$aryl-$C_{para}$H), 143.9 ($_{cAAC}$aryl-$C_{ipso}$), 159.1 ($_{cAAC}$aryl-$C_{ortho}$), 153.3 ($_{cAAC}$aryl-$C_{ortho}$), 164.5 ($_{NHC}$N$C$N).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 2974 (m), 2932 (m), 2869 (w), 1948 (s), 1551 (w), 1468 (m), 1374 (m), 1200 (w), 1133 (w), 1052 (w), 807 (m), 777 (s), 643 (s), 625 (s), 562 (m).

**Synthesis of (cAAC$^{Me}$H)$_2$GaCl (*meso*-III-18) and (*rac*- III-18)**

A solution of cAAC$^{Me}$ (116 mg, 402 µmol) in 5 mL of toluene was added at room temperature to a solution of (Dipp$_2$Im$^H$)·GaH$_2$Cl **III-11** (100 mg, 201 µmol) in 5 mL of toluene. After 12 h stirring at room temperature, the solution was evaporated to ca. 2 mL and the dark yellow residue was filtered off and dried *in vacuo* to afford **III-18** of a dark yellow solid.

**Yield**: 51.0 mg (74.4 µmol, 37 %), yellow powder.

**Elemental Analysis** for C$_{40}$H$_{64}$ClGaN$_2$ (678.14 g/mol) found (calculated) [%]: C 70.64 (70.85), H 9.67 (9.51), N 4.01 (4.13).

Separation of the signals for the isomers *meso*-**18** and *rac*-**18** was not feasible in the $^1$H and $^{13}$C{$^1$H} spectra.

**$^1$H-NMR** (400.4 MHz, C$_6$D$_6$, 298 K, dr(meso-**III-18**:rac- **III-18**) = 1:0.8): $\delta$ [ppm] = 0,93 (s, 3H, C(C$H_3$)$_2$), 0.98 (d, 6H, $^3J_{HH}$ = 5.7 Hz, $i$Pr-C$H_3$), 1.12 (s, 3H, C(C$H_3$)$_2$), 1.18 (d, 6H, $^3J_{HH}$ = 5.7 Hz $i$Pr-C$H_3$), 1.21-1.24 (m, 9H, C(C$H_3$)$_2$), 1.34-1.38 (m, 9H, C(C$H_3$)$_2$), 1.47-1.49 (m, 6H, $i$Pr-C$H_3$), 1.61 (s, 6H, C(C$H_3$)$_2$), 1.73-1.86 (m, 4H, CH$_2$), ), 3.09 (sept, 1H, $^3J_{HH}$ = 6.4 Hz, $i$Pr-C$H$), 3.19 (sept, 1H, $^3J_{HH}$ = 6.4 Hz, $i$Pr-C$H$), 3.84 (s, 1H, Ga–C$H$), 4.10 (s, 1H, Ga–C$H$), 4.15 (sept, 1H, $^3J_{HH}$ = 6.4 Hz, $i$Pr-C$H$), 4.37 (sept, 1H, $^3J_{HH}$ = 6.4 Hz, $i$Pr-C$H$), 7.02-7.14 (m, 6H, aryl-C$H$).

**$^{13}$C{$^1$H}-NMR** (100.7 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 24.4, 25.9, 26.4, 27.2, 27.3, 27.7, 27.8, 28.3, 28.9, 29.8, 30.1, 30.6, 30.9, 31.3, 31.89, 32.5, 42.1, 42. 9, 60.6, 60.8, 64.9, 65.3, 67.7, 67.9, 68.1, , 76.9 ($_{cAAC}$Ga$C$H), 77.0 ($_{cAAC}$Ga$C$H), 125.3, 125.5, 125.6, 126.2, 127.4, 127.5, 141.2, 142.3, 152.1, 152.2,152.5, 152.5.

## 6.5 Synthetic Procedures for Chapter 4

### Synthesis of (Me$_2$Im$^{Me}$)·AlH$_2$I IV-1

Elemental solid iodine (370 mg, 1.46 mmol) was added at room temperature to a solution of (Me$_2$Im$^{Me}$)·AlH$_3$ **I** (450 mg, 2.92 mmol) dissolved in 15 mL of toluene and the resulting solution was stirred for 45 minutes. The solvent was evaporated to dryness which gave **IV-1** as colorless powder. Crystals suitable for X-ray diffraction of the compound **IV-1** were grown by slow evaporation of a saturated solution in benzene.

Yield: 706 mg (2.51 mmol, 86 %), colorless powder.

**Elemental Analysis** for C$_7$H$_{14}$N$_2$AlI [280.09 g/mol] found (calculated) [%]: C 30.21 (30.02), H 5.05 (5.04), N 10.08 (10.00).

**$^1$H{$^{27}$Al}-NMR** (400.1 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 1.14 (s, 6 H, NCC*H$_3$*CC*H$_3$*N), 3.15 (s, 6 H, C*H$_3$*), 4.54 (s$_{br}$, 2 H, Al-*H*).

**$^{13}$C{$^1$H}-NMR** (100.6 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 7.6 (*C*H$_3$), 33.6 (NC*C*H$_3$C*C*H$_3$N), 125.8 (N*CC*N), 161.4 (N*C*N).

**$^{27}$Al{$^1$H}-NMR** (104.3 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 107.8.

**IR (ATR)**: $\tilde{v}$ [cm$^{-1}$] = 2949 (vw), 2922 (vw), 1827 (s, $v_{Al–H, str.}$), 1796 (s, $v_{Al–H, str.}$), 1646 (w), 1435 (m), 1403 (w), 1385 (w), 1370 (m), 1231 (vw), 1175 (vw), 846 (m), 768 (vs), 685 (vs), 633 (vs), 601 (s), 471 (s).

### Synthesis of (*i*Pr$_2$Im)·AlH$_2$I IV-2

Elemental solid iodine (557 mg, 2.19 mmol) was added at room temperature to a solution of (*i*Pr$_2$Im)·AlH$_3$ (800 mg, 4.39 mmol) **II** dissolved in 10 mL of toluene and the resulting solution was stirred for 2 hours. The solvent was evaporated to dryness which gave **IV-2** as colorless powder.

**Yield**: 1.31 g (4.25 mmol, 97 %), colorless powder.

**Elemental Analysis** for C$_9$H$_{18}$N$_2$AlI [308.14 g/mol] found (calculated) [%]: C 34.67 (35.08), H 5.96 (5.89), N 8.99 (9.09).

**$^1$H{$^{27}$Al}-NMR** (400.1 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 0.93 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, *i*Pr-C*H$_3$*), 4.63 (s$_{br}$, 2 H, Al-*H*), 5.17 (sept, 2 H, $^3J_{HH}$ = 6.7 Hz, *i*Pr-C*H*), 6.15 (s, 2 H, NC*H*C*H*N).

**$^{13}$C{$^1$H}-NMR** (100.6 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 22.9 (*i*Pr-*C*H$_3$), 51.8 (*i*Pr-*C*H), 117.5 (N*CC*N), 162.7 (N*C*N).

**$^{27}$Al{$^1$H}-NMR** (104.3 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 109.6.

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 3151 (w), 3124 (w), 2976 (m), 2932 (w), 1860 (m), 1837 (m, $\nu_{Al–H, str.}$), 1809 (m), 1792 (m, $\nu_{Al–H, str.}$), 1460 (m), 1430 (m), 1398 (m), 1371 (w), 1207 (s), 1174 (w), 1126 (m), 766 (s), 747 (s), 703 (m), 661 (s), 627 (s), 578 (s), 525 (m), 455 (m).

## Synthesis of (*i*Pr$_2$Im$^{Me}$)·AlH$_2$I IV-3

Elemental solid iodine (453 mg, 1.78 mmol) was added at room temperature to a solution of (*i*Pr$_2$Im$^{Me}$)·AlH$_3$ (750 mg, 3.57 mmol) **III** dissolved in 15 mL of toluene and the resulting solution was stirred for 45 minutes. The solvent was evaporated to dryness which gave **IV-3** as colorless powder. Crystals suitable for X-ray diffraction of the compounds **IV-3** were grown by slow evaporation of a saturated solution in benzene.

**Yield**: 1.06 g (3.14 mmol, 88 %), colorless powder.

**Elemental Analysis** for C$_{11}$H$_{22}$N$_2$AlI [336.20 g/mol] found (calculated) [%]: C 39.05 (39.30), H 6.50 (6.60), N, 8.11 (8.33).

**$^1$H{$^{27}$Al}-NMR** (400.1 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 1.11 (d, 12 H, $^3J_{HH}$ = 7.1 Hz, *i*Pr-C*H$_3$*), 1.44 (s, 6 H, NCC*H$_3$*CC*H$_3$*N), 4.70 (s$_{br}$, 2 H, Al-*H*), 5.39 (sept, 2 H, $^3J_{HH}$ = 7.1 Hz, *i*Pr-C*H*).

**$^{13}$C{$^1$H}-NMR** (100.6 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 9.7 (NC*C*H$_3$C*C*H$_3$N), 21.4 (*i*Pr-*C*H$_3$), 52.6 (*i*Pr-*C*H), 126.5 (N*CC*N), 162.3 (N*C*N).

**$^{27}$Al{$^1$H}-NMR** (104.3 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 109.0.

**IR (ATR)**: $\tilde{v}$ [cm$^{-1}$] = 2977 (w), 2933 (vw), 1825 (m, $v_{Al–H, str.}$), 1779 (s, $v_{Al–H, str.}$), 1624 (vw), 1455 (w), 1372 (m), 1337 (w), 1223 (m), 1168 (w), 1135 (w), 1115 (w), 1082 (w), 888 (w), 783 (s), 7058 (s), 666 (vs), 565 (m), 471 (m)

## Synthesis for (Me$_2$Im$^{Me}$)·GaH$_2$I IV-4

Methyliodide (1.20 mL) was added to a solution of (Me$_2$Im$^{Me}$)·GaH$_3$ **III-1** (400 mg, 2.03 mmol) in 10 mL of toluene at room temperature *via* a syringe and stirred for 30 minutes. The solvent was evaporated which gave compound **IV-4** as colorless powder. Crystals of compound **IV-4** suitable for X-ray diffraction were grown by slow evaporation of a saturated solution of the compound in benzene.

**Yield**: 590 mg (1.78 mmol, 88 %), colorless powder.

**Elemental Analysis** for C$_7$H$_{14}$N$_2$GaI [322.83 g/mol] found (calculated) [%]: C 25.66 (26.04), H 4.21 (4.37), N, 8.03 (8.68).

**$^1$H-NMR** (400.1 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 1.07 (s, 6 H, NCC*H$_3$*CC*H$_3$*N), 3.06 (s, 6 H, C*H$_3$*), 4.81 (s$_{br}$, 2 H, Ga-*H*).

**$^{13}$C{$^1$H}-NMR** (100.6 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 7.8 (*C*H$_3$), 33.7 (NC*C*H$_3$C*C*H$_3$N), 125.7 (N*CC*N), 162.1 (N*C*N).

**IR (ATR)**: $\tilde{v}$ [cm$^{-1}$] = 2921 (m), 1895 (s, $v_{Ga–H, str.}$), 1650 (m), 1577 (m), 1435 (m), 1391 (w), 1371 (m), 848 (m), 755 (s), 743 (s), 677 (s), 633 (s), 456 (s).

## Synthesis of (*i*Pr$_2$Im$^{Me}$)·GaH$_2$I IV-5

Methyliodide (245 $\mu$L) was added to a solution of (*i*Pr$_2$Im$^{Me}$)·GaH$_3$ **II-3** (100 mg, 395 $\mu$mol) in 10 mL of toluene at room temperature *via* a syringe and stirred for 30 minutes. The solvent was evaporated which gave compound **IV-5** as colorless powder.

**Yield**: 111 mg (296 $\mu$mol, 75 %), colorless powder.

**Elemental Analysis** for C$_7$H$_{14}$N$_2$GaI [322.83 g/mol] found (calculated) [%]: C 34.75 (34.87), H 5.65 (5.85), N 7.37 (7.39).

**¹H-NMR** (400.1 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 1.09 (d, 12 H, $^3J_{HH}$ = 7.1 Hz, *i*Pr-C*H*$_3$), 1.42 (s, 6 H, NCC*H*$_3$CC*H*$_3$N), 5.00 (s$_{br}$, 2 H, Ga-*H*), 5.32 (sept$_{br}$, 2 H, *i*Pr-C*H*).

**¹³C{¹H}-NMR** (100.6 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 9.7 (NC*C*H$_3$C*C*H$_3$N), 21.4 (*i*Pr-*C*H$_3$), 52.6 (*i*Pr-*C*H), 126.2 (N*CC*N), 163.4 (N*C*N).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 2962 (m), 1889 (s $\nu_{Ga–H, str.}$), 1839 (s, $\nu_{Ga–H, str.}$), 1488 (m), 1457 (m), 1385 (m), 1368 (m), 1272 (m), 1262 (m), 805 (s), 761 (s), 648 (s).

### Synthesis of (Dipp$_2$Im)·GaH$_2$I IV-6

Methyliodide (500 $\mu$L) was added to a solution of (Dipp$_2$Im)·GaH$_3$ **V** (400 mg, 867 $\mu$mol) in 10 mL of toluene at room temperature *via* a syringe and stirred for 30 minutes. The solvent was evaporated which gave compound **IV-6** as colorless powder.

**Yield**: 509 mg (866 $\mu$mol, 99 %), colorless powder.

**Elemental analysis** C$_{27}$H$_{38}$N$_2$GaI [587.24 g/mol] found (calculated) [%]: C 55.35 (55.22), H 6.82 (6.52), N, 4.75 (4.77).

**¹H-NMR** (400.1 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 0.98 (d, 12 H, $^3J_{HH}$ = 7.1 Hz, *i*Pr-C*H*$_3$), 1.42 (d, 12 H, $^3J_{HH}$ = 7.1 Hz, *i*Pr-C*H*$_3$), 2.69 (sept, 4 H, $^3J_{HH}$ = 7.1 Hz, *i*Pr-C*H*), 4.13 (s$_{br}$, 2 H, Ga-*H*), 6.45 (s, 2 H, NC*H*C*H*N), 7.09 (m, 4 H, aryl-C$_{meta}$*H*), 7.22 (m, 2 H, aryl-C$_{para}$*H*).

**¹³C{¹H}-NMR** (100.6 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 23.3 (iPr-CH3), 25.6 (iPr-CH3), 29.1 (iPr-CH), 124.5 (aryl-C$_{meta}$H), 131.2 (aryl-C$_{para}$H), 134.2 (aryl-C$_{ipso}$), 145.6 (aryl-C$_{ortho}$), 170.3 (NCN).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 2962 (s), 1886 (s $\nu_{Ga–H, str.}$), 1456 (s), 1299 (m), 1270 (m), 1257 (m), 1108 (m), 801 (s), 757 (s), 725 (s), 707 (m), 661 (s).

## Synthesis of [(Me₂Im^Me)₂·AlH₂]I IV-7

Toluene (15 mL) was added to a mixture of (Me₂Im^Me)·AlH₂I **IV-1** (200 mg, 714 µmol) and Me₂Im^Me (88.7 mg, 714 µmol) in a Schlenk flask. The reaction mixture was stirred for 16 hours at room temperature, then the solvent was evaporated. *n*-hexane (10 mL) was added to the residue and the colorless precipitate was filtered off and washed with *n*-hexane. The colorless solid was dried *in vacuo* to afford compound **IV-7**.

**Yield**: 260 mg (643 µmol, 90 %), colorless powder.

**Elemental Analysis** for $C_{14}H_{26}N_4AlI$ [404.28 g/mol] found (calculated) [%]: C 41.12 (41.59), H 6.47 (6.48), N 13.36 (13.86).

**¹H-NMR** (400.1 MHz, Acetone-d₆, 298 K): δ [ppm] = 2.35 (s, 12 H, NCC*H₃*CC*H₃*N), 3.93 (s, 12 H, C*H₃*). Al-*H* not observed.

**¹³C{¹H}-NMR** (100.6 MHz, Acetone-d₆, 298 K): δ [ppm] = 8.3 (*C*H₃), 34.1 (NC*C*H₃C*C*H₃N), 127.9 (N*C*CN). N*C*N not observed.

**²⁷Al{¹H}-NMR** (104.3 MHz, Acetone-d₆, 298 K): No signal observed.

**IR (ATR)**: $\tilde{\nu}$ [cm⁻¹] = 2976 (w), 1791 (s, $\nu_{Al–H, str.}$), 1772 (s, $\nu_{Al–H, str.}$), 1644 (m), 1575 (m), 1440 (w), 1388 (w), 851 (m), 767 (s), 753 (m), 708 (s), 650 (s), 576 (m), 474 (m).

## Synthesis of [(*i*Pr₂Im)₂·AlH₂]I IV-8

Toluene (15 mL) was added to a mixture of (*i*Pr₂Im)·AlH₂I **VI-2** (100 mg, 325 µmol) and *i*Pr₂Im (49.4 mg, 325 µmol) in a Schlenk flask. The reaction mixture was stirred for 16 hours at room temperature, then the solvent was evaporated. *n*-hexane (10 mL) was added to the residue and the colorless precipitate was filtered off and washed with *n*-hexane. The colorless solid was dried *in vacuo* to afford compound **IV-8**.

**Yield**: 92 mg (202 µmol, 62 %), colorless powder.

**Elemental Analysis** for $C_{18}H_{34}N_4AlI$ [460.38 g/mol] found (calculated) [%]: C 46.49 (46.96), H 7.35 (7.44), N 11.74 (12.17).

**¹H-NMR** (400.1 MHz, Acetone-d6, 298 K): δ [ppm] = 1.64 (d, 24 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr-C*H₃*), 4.96 (sept, 4 H, *i*Pr-C*H*), 7.93 (4 H, NC*H*C*H*N). Al-*H* not observed.

**$^{13}$C{$^1$H}-NMR** (100.6 MHz, Acetone-d$_6$, 298 K): $\delta$ [ppm] = 23.1 (*i*Pr-*C*H$_3$), 53.8 (*i*Pr-*C*H), 121.3 (N*CC*N). N*C*N not observed.

**$^{27}$Al{$^1$H}-NMR** (104.3 MHz, Acetone-d$_6$, 298 K): No signal observed.

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 3068 (m), 2976 (m), 1825 (m $\nu_{Al–H, str.}$), 1820 (m, $\nu_{Al–H, str.}$), 1403 (m), 1215 (s), 1134 (m), 792 (m), 769 (s), 717 (s), 678 (s), 664 (s), 576 (m), 480 (m).

## Synthesis of [(*i*Pr$_2$Im$^{Me}$)$_2$·AlH$_2$]I IV-9

Toluene (15 mL) was added to a mixture of (*i*Pr$_2$Im$^{Me}$)·AlH$_2$I **IV-3** (200 mg, 595 $\mu$mol) and *i*Pr$_2$Im$^{Me}$ (107.3 mg, 595 $\mu$mol) in a Schlenk flask. The reaction mixture was stirred for 16 hours at room temperature, then the solvent was evaporated. *n*-hexane (10 mL) was added to the residue and the colorless precipitate was filtered off and washed with *n*-hexane. The colorless solid was dried *in vacuo* to afford compound **IV-9**. Suitable crystals of compound **IV-9** for X-ray diffraction were grown by slow evaporation of a saturated solution in benzene.

**Yield**: 270 mg (524 $\mu$mol, 88 %), colorless powder.

**Elemental Analysis** for C$_{22}$H$_{42}$N$_4$AlI [516.49 g/mol] found (calculated) [%]: C 41.12 (41.59), H 6.47 (6.48), N 13.36 (13.86).

**$^1$H-NMR** (400.1 MHz, thf-d$_8$, 298 K): $\delta$ [ppm] = 1.53 (d, 24 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr-C*H*$_3$), 2.35 (s, 12 H, NCC*H*$_3$CC*H*$_3$N), 4.94 (sept, 4 H, *i*Pr-C*H*). Al-*H* not observed.

**$^{13}$C{$^1$H}-NMR** (100.6 MHz, thf-d$_8$, 298 K): $\delta$ [ppm] = 11.2 (NC*C*H$_3$C*C*H$_3$N), 22.7 (*i*Pr-*C*H$_3$), 53.9 (*i*Pr-*C*H), 129.1 (N*CC*N), N*C*N not observed.

**$^{27}$Al{$^1$H}-NMR** (104.3 MHz, thf-d$_8$, 298 K): $\delta$ [ppm] = 108.7.

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 2971 (m), 2932 (m), 1819 (m, $\nu_{Al–H, str.}$), 1799 (m, $\nu_{Al–H, str.}$), 1657 (m), 1627 (m), 1555 (m), 1446 (m), 1313 (m), 1190 (m), 1110 (m), 770 (s), 720 (s), 661 (s), 540 (m).

## Synthesis of [(Me₂Im^Me)₂·GaH₂]I IV-10

Toluene (15 mL) was added to a mixture of (Me$_2$Im$^{Me}$)·GaH$_2$I **IV-4** (50 mg, 155 $\mu$mol) and Me$_2$Im$^{Me}$ (19.2 mg, 155 $\mu$mol) in a Schlenk flask. The reaction mixture was stirred for 16 hours at room temperature, then the solvent was evaporated. *N*-hexane (10 mL) was added to the residue and the colorless precipitate was filtered off and washed with *n*-hexane. The colorless solid was dried *in vacuo* to afford compound **IV-10**. Suitable crystals of compound **IV-10** for X-ray diffraction were grown by slow evaporation of a saturated solution in benzene.

**Yield**: 38 mg (85.3 $\mu$mol, 55 %), colorless powder.

**Elemental Analysis** for C$_{14}$H$_{26}$N$_4$GaI [447.02 g/mol] found (calculated) [%]: C 37.45 (37.62), H 5.78 (5.86), N 11.87 (12.53).

**¹H-NMR** (400.1 MHz, CD$_3$CN, 298 K): $\delta$ [ppm] = 2.15 (s, 12 H, NCC*H₃*CC*H₃*N), 3.61 (s, 12 H, C*H₃*), 4.17 (s$_{br}$, 2 H, Ga-*H*), (s$_{br}$, 4 H, *i*Pr-C*H*).

**¹³C{¹H}-NMR** (100.6 MHz, CD$_3$CN, 298 K): $\delta$ [ppm] = 8.9 (*C*H$_3$), 35.0 (NC*C*H$_3$C*C*H$_3$N), 128.5 (N*C*C*N). N*C*N not observed.

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 3019 (w), 1839 (m, $\nu_{Ga–H, str.}$), 1826 (m, $\nu_{Ga–H, str.}$), 1646 (m), 1577 (m), 1440 (m), 1391 (m), 1209 (w), 851 (s), 764 (s), 744 (m), 695 (s), 642 (s), 572 (m), 452 (m).


## Synthesis of [(*i*Pr₂Im^Me)₂·GaH₂]I IV-11

Toluene (15 mL) was added to a mixture of (*i*Pr$_2$Im$^{Me}$)·GaH$_2$I **IV-5** (75 mg, 198 $\mu$mol) and *i*Pr$_2$Im$^{Me}$ (39 mg, 198 $\mu$mol) in a Schlenk flask. The reaction mixture was stirred for 16 hours at room temperature, then the solvent was evaporated. *n*-hexane (10 mL) was added to the residue and the colorless precipitate was filtered off and washed with *n*-hexane. The colorless solid was dried *in vacuo* to afford compound **IV-11**.

**Yield**: 56 mg (101 $\mu$mol, 51 %), colorless powder.

**Elemental Analysis** for C$_{22}$H$_{42}$N$_4$GaI [559.23 g/mol] found (calculated) [%]: C 45.98 (47.25), H 7.45 (7.57), N 9.51 (10.02).

**¹H-NMR** (400.1 MHz, thf-d$_8$, 298 K): $\delta$ [ppm] = 1.52 (d, 24 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr-C*H*$_3$), 2.40 (s, 12 H, NCC*H*$_3$CC*H*$_3$N), 4.37 (s$_{br}$, 2 H, Ga-*H*), 4.98 (sept, 4 H, *i*Pr-C*H*).

**¹³C{¹H}-NMR** (100.6 MHz, thf-d$_8$, 298 K): $\delta$ [ppm] = 11.3 (NC*C*H$_3$C*C*H$_3$N), 22.1 (*i*Pr-*C*H$_3$), 54.1 (*i*Pr-*C*H), 129.3 (N*CC*N), 162.8 (N*C*N).

**IR (ATR)**: $\tilde{v}$ [cm$^{-1}$] = 2972 (m), 1877 (m, $v_{Ga–H,\ str.}$), 1857 (m, $v_{Ga–H,\ str.}$), 1626 (m), 1555 (s), 1446 (m), 1376 (m), 1365 (m), 1231 (s), 1190 (s), 1110 (s), 764 (m), 678 (m), 659 (m), 521 (m).

**Synthesis of [(Dipp₂Im)·GaH₂(*a*Dipp₂Im)]I IV-12**

Toluene (10 mL) was added to a mixture of (Dipp₂Im)·GaH₂I **IV-6** (200 mg, 341 $\mu$mol) and Dipp₂Im (133 mg, 341 $\mu$mol) in a Schlenk flask. The reaction mixture was stirred for 16 hours at 110 °C, then the solvent was evaporated. *n*-hexane (10 mL) was added to the residue and the colorless precipitate was filtered off and washed with *n*-hexane. The colorless solid was dried *in vacuo* to afford compound **IV-12**. Suitable crystals of compound **IV-12** for X-ray diffraction were grown by slow evaporation of a saturated solution in acetonitrile.

**Yield**: 180 mg (184 $\mu$mol, 54 %), colorless powder.

**Elemental Analysis** for C$_{54}$H$_{74}$N$_4$GaI [975.79 g/mol] found (calculated) [%]: C 66.06 (66.40), H 7.78 (7.74), N 5.64 (5.74).

**¹H-NMR** (400.1 MHz, CD$_3$CN, 298 K): $\delta$ [ppm] = 0.96 (d, 6 H, $^3J_{HH}$ = 7.1 Hz, *a*NHC-*i*Pr-C*H*$_3$), 1.03 (d, 6 H, $^3J_{HH}$ = 7.1 Hz, *a*NHC-*i*Pr-C*H*$_3$), 1.13 (d, 6 H, $^3J_{HH}$ = 7.1 Hz, *a*NHC-*i*Pr-C*H*$_3$), 1.14 (d, 12 H, $^3J_{HH}$ = 7.1 Hz, NHC-*i*Pr-C*H*$_3$), 1.17 (d, 12 H, $^3J_{HH}$ = 7.1 Hz, NHC-*i*Pr-C*H*$_3$), 1.33 (d, 6 H, $^3J_{HH}$ = 7.1 Hz, *a*NHC-*i*Pr-C*H*$_3$), 2.12 (d-sept, 4 H, $^3J_{HH}$ = 7.1 Hz, *a*NHC-*i*Pr-C*H*), 2.50 (sept, 4 H, $^3J_{HH}$ = 7.1 Hz, NHC-*i*Pr-C*H*), 3.22 (s$_{br}$, 2 H, Ga-*H*), 4.26 (d, 1 H, $^4J_{HH}$ = 1.44 Hz, *a*NHC-NCC*H*N), 7.29 (s, 2 H, NHC- NC*H*C*H*N) 7.26-7.65 (m, 12 H, aryl-C*H*), 7.22 (m, 2 H, aryl-C$_{para}$*H*), 8.71 (d, 1 H, $^4J_{HH}$ = 1.44 Hz, *a*NHC-NC*H*N).

**$^{13}$C{$^1$H}-NMR** (100.6 MHz, CD$_3$CN, 298 K): $\delta$ [ppm] = 22.6 (*a*NHC -iPr-CH3), 23.3 (NHC-iPr-CH3), 23.7 (*a*NHC-iPr-CH3), 24.8 (NHC-iPr-CH3), 25.6 (*a*NHC-iPr-CH3), 25.9 (*a*NHC-iPr-CH3), 29.4 (*a*NHC-iPr-CH), 29.5 (*a*NHC-iPr-CH), 29.8 (NHC-iPr-CH), 125.2 (arylCH), 125.4 (arylCH), 125.5 (arylCH), 125.8 (arylCH), 127.1 (arylCH), 130.4 (arylCH), 131.8 (arylCH), 132.3 (arylCH), 132.6 (arylCH), 134.9 (arylCH), 139.5 (*a*NHC-N*C*HN) 146.1 (*a*NHC-NC*C*HN), 146.4 (*a*NHC-NC*C*HN), 147.3 (NHC-N*C*H*C*HN), 171.7 (NCN).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 2961 (s), 1876 (m, $\nu_{\text{Ga–H, str.}}$), 1858 (m, $\nu_{\text{Ga–H, str.}}$), 1540 (m), 1466 (m), 1329 (m), 1212 (w), 1188 (w), 805 (s), 755 (s), 742 (s), 690 (s), 464 (m).

## 6.6 Synthetic Procedures for Chapter 5

### Synthesis of (Me$_2$Im$^{Me}$)·Cp*AlH$_2$ V-1

(AlH$_2$Cp*)$_3$ (100 mg, 591 $\mu$mol) and Me$_2$Im$^{Me}$ (74.0 mg, 591 $\mu$mol) were dissolved in 7 mL $n$-hexane at room temperature and stirred for 12 hours. The colorless precipitate was filtered off and dried *in vacuo* to afford **V-1** as colorless powder. Crystals suitable for X-ray diffraction of compound **V-1** were grown by slow evaporation of a saturated solution in benzene.

**Yield**: 130 mg (443 $\mu$mol, 75 %), colorless powder.

**Elemental Analysis** for C$_{17}$H$_{29}$N$_2$Al (288.41 g/mol): found (calculated) [%]: C 64.21 (70.80), H 9.34 (10.41), N 9.74 (9.71).

**$^1$H-NMR** (400.4 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 1.12-1.18 (m, 6 H, C$H_3$), 2.00 (s, 3 H, Cp*C$_1$C$H_3$), 2.04 (s, 12 H, Cp*C$_{(2-5)}$C$H_3$), 3.13 (s, 6 H, NCC$H_3$CC$H_3$N).

**$^{13}$C{$^1$H}-NMR** (100.7 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 7.5 ($_{NHC}$C$H_3$), 11.7 (Cp*-$C$H$_3$), 33.5 ($_{NHC}$NC$C$H$_3$C$C$H$_3$N), 115.1 (Cp*$C$), 124.0 (N$C$CN).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 751 (s, $\nu_{Al-H, b.}$), 1713 (s, $\nu_{Al-H,str}$).

### Synthesis of (*i*Pr$_2$Im$^{Me}$)·Cp*AlH$_2$ V-2

(AlH$_2$Cp*)$_3$ **V-2** (50 mg, 295 $\mu$mol) and *i*Pr$_2$Im$^{Me}$ (54.9 mg, 295 $\mu$mol) were dissolved in 7 mL $n$-hexane at room temperature and stirred for 12 hours. The colorless precipitate was filtered off and dried *in vacuo* to afford **V-2** as colorless powder.

**Yield**: 48 mg (139 $\mu$mol, 47 %), colorless powder.

**Elemental Analysis** for C$_{21}$H$_{37}$N$_2$Al (344.52 g/mol): found (calculated) [%]: C 69.10 (73.21), H 10.22 (10.83), 7.85 N (8.13).

**$^1$H-NMR** (400.4 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = (d, 12 H, $^3J_{HH}$ = 7.1 Hz, *i*Pr-C$H_3$), 1.46 (s, 6 H, NCC$H_3$CC$H_3$N), 2.18 (s, 3 H, Cp*C$_1$C$H_3$), 2.22 (s, 12 H, Cp*C$_{(2-5)}$C$H_3$), 5.35 (sept, 2 H, $^3J_{HH}$ = 7.1 Hz, *i*Pr-C$H$).

**$^{13}$C{$^1$H}-NMR** (100.7 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 9.9 ($_{NHC}$NC*C*H$_3$C*C*H$_3$N), 12.5 (Cp\*-*C*H$_3$), 21.8 ($_{NHC}$*i*Pr-*C*H$_3$), 52.5 ($_{NHC}$*i*Pr-*C*H), 116.3 (Cp\**C*), 125.5 (N*CC*N), 168.6 (N*C*N).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 713 (s, $\nu_{Al-H, b.}$), 1712 (m, $\nu_{Al-H,str.}$).

## Synthesis of (Dipp$_2$Im)·Cp\*AlH$_2$ V-3

(AlH$_2$Cp\*)$_3$ (50 mg, 295 $\mu$mol) and Dipp$_2$Im (115 mg, 295 $\mu$mol) were dissolved in 7 mL *n*-hexane at room temperature and stirred for 12 hours. The colorless precipitate was filtered off and dried *in vacuo* to afford **V-3** as colorless powder. Crystals suitable for X-ray diffraction of compound **V-3** were grown by slow evaporation of a saturated solution in benzene.

**Yield**: 90 mg (162 $\mu$mmol, 55 %), colorless powder.

**Elemental Analysis** for C$_{37}$H$_{53}$N$_2$Al (553.83 g/mol): found (caclulated) [%]: C 74.58 (80.39), H 9.04 (9.66), N 4.68 (5.07).

**$^1$H-NMR** (400.4 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 0.97 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*$_3$), 1.42 (d, 12 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*$_3$), 1.88 (s, 3 H, Cp\*C$_1$C*H*$_3$), 1.89 (s, 12 H, Cp\*C$_{(2-5)}$C*H*$_3$), 2.83 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*), 6.45 (s, 2 H, NC*H*C*H*N), 7.06 – 7.18 (m, 6 H, aryl-C*H*).

**$^{13}$C{$^1$H}-NMR** (100.7 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 12.2 (Cp\*-*C*H$_3$), 22.9 ($_{NHC}$*i*Pr-*C*H$_3$), 26.0 ($_{NHC}$*i*Pr-*C*H$_3$), 28.9 ($_{NHC}$*i*Pr-*C*H), 117.0 (Cp\**C*), 124.3 ($_{NHC}$aryl-*C*$_{meta}$H), 124.7 ($_{NHC}$N*C*H*C*HN), 130.8 ($_{NHC}$aryl-*C*$_{para}$H), 135.6 ($_{NHC}$aryl-*C*$_{ipso}$), 145.7 ($_{NHC}$aryl-*C*$_{ortho}$), 179.0 ($_{NHC}$N*C*N).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 728 (s, $\nu_{Al-H, b.}$), 1760 (s, $\nu_{Al-H,str.}$).

## Synthesis of (Me$_2$Im$^{Me}$)·Cp\*GaH$_2$ V-4

(Me$_2$Im$^{Me}$)·GaH$_2$I **IV-4** (200 mg, 621 $\mu$mol) and KCp\* (130 mg, 747 $\mu$mol) were dissolved in 10 mL *n*-hexane. After stirring over night at room temperature, the colorless, cloudy reaction mixture was filtered to remove KI and all volatiles of the filtrate were removed *in vacuo*. The residue was suspended in 5 mL *n*-hexane, the product was filtered off and dried *in vacuo* to afford compound **V-4** as colorless powder.

Crystals suitable for X-ray diffraction of compound **V-4** were grown by slow evaporation of a saturated solution in benzene.

**Yield**: 135 mg (410 $\mu$mmol, 66 %), colorless powder.

**Elemental Analysis** for $C_{17}H_{29}N_2Ga$ [330.16 g/mol]: found (calculated) [%]: C, 59.51 (61.66); H, 8.91 (8.83); N, 8.71 (8.46).

**$^1$H-NMR** (400.1 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 1.21 (s, 6 H, NCC$H_3$CC$H_3$N), 1.99 (s, 15 H, Cp\*-C$H_3$), 3.06 (s, 6 H, C$H_3$), 4.90 (s$_{br}$, 2 H, Ga-$H$).

**$^{13}$C{$^1$H}-NMR** (100.6 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 7.7 (CH$_3$), 12.4 (Cp\*-$C$H$_3$), 33.9 (NC$C$H$_3$C$C$H$_3$N), 116.3 (Cp\*-$C$), 123.9 (N$CC$N), 169.5 (N$C$N).


**Synthesis of (*i*Pr$_2$Im$^{Me}$)·Cp\*GaH$_2$ V-5**

(*i*Pr$_2$Im$^{Me}$)·GaH$_2$I **IV-5** (100 mg, 265 $\mu$mol) and KCp\* (50.9 mg, 287 $\mu$mol) were dissolved in 10 mL *n*-hexane. After stirring over night at room temperature, the colorless, cloudy reaction mixture was filtered to remove KI and all volatiles of the filtrate were removed *in vacuo*. The residue was suspended in 5 mL *n*-hexane, the product was filtered off and dried *in vacuo* to afford compound **V-5** as colorless powder.

**Yield**: 47 mg (132 $\mu$mol, 46 %), colorless powder.

**Elemental Analysis** for $C_{21}H_{37}N_2Ga$ [386.22 g/mol]: found (calculated) [%]: C 66.12 (65.13); H 9.55 (9.63); N 8.49 (7.23).

**$^1$H-NMR** (400.1 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 1.10 (d, 12 H, $^3J_{HH}$ = 7.1 Hz, *i*Pr-C$H_3$), 1.45 (s, 6 H, NCC$H_3$CC$H_3$N), 2.15 (s, 15 H, Cp\*-C$H_3$), 4.75 (s$_{br}$, 2 H, Ga-$H$), 5.20 (sept$_{br}$, 2 H, $^3J_{HH}$ = 7.1 Hz, *i*Pr-C$H$).

**$^{13}$C{$^1$H}-NMR** (100.6 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 9.9 (NC$C$H$_3$C$C$H$_3$N), 13.0 (Cp\*-$C$H$_3$), 21.6 (*i*Pr-$C$H$_3$), 52.6 (*i*Pr-$C$H), 117.8 (Cp\*-$C$), 125.4 (N$CC$N), 171.4 (N$C$N).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 756 (s, $\nu_{Al-H, b.}$), 1862 (s, $\nu_{Al-H,str.}$).

## Synthesis of (Dipp$_2$Im)·Cp*GaH$_2$ V-6

(Dipp$_2$Im)·GaH$_2$I **IV-6** (100 mg, 265 $\mu$mol) and KCp* (50.9 mg, 287 $\mu$mol) were dissolved in 10 mL $n$-hexane. After stirring over night at room temperature, the colorless, cloudy reaction mixture was filtered to remove KI and all volatiles of the filtrate were removed *in vacuo*. The residue was suspended in 5 mL $n$-hexane, the product was filtered off and dried *in vacuo* to afford compound **V-6** as colorless powder.

**Yield**: 41 mg (122 $\mu$mol, 46 %), colorless powder.

**Elemental Analysis** for C$_{37}$H$_{53}$N$_2$Ga [594.35 g/mol]: found (cacluclated) [%]: C 72.14 (74.62); H 9.44 (8.97); N 4.58 (4.70).

**$^1$H-NMR** (400.1 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 0.97 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, $i$Pr-C$H_3$), 1.40 (d, 12 H, $^3J_{HH}$ = 6.7 Hz, $i$Pr-C$H_3$), 1,86 (s, 15 H, Cp*-C$H_3$), 2.81 (sept, 4 H, 3J$_{HH}$ = 6.8 Hz, $i$Pr-C$H$), 3.66 (s$_{br}$, 2 H, Ga-$H$), 6.50 (s, 2 H, NC$H$C$H$N), 7.07 (d, 4 H, 3J$_{HH}$ = 7.8 Hz, aryl-C$_{meta}H$), 7.11 - 7.20 (m, 2 H, aryl-C$_{para}H$).

**$^{13}$C{$^1$H}-NMR** (100.6 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 12.7 (Cp*-$C$H$_3$), 22.9 ($i$Pr-$C$H$_3$), 26.0 ($i$Pr-$C$H$_3$), 29.0  ($i$Pr-$C$H), 118.1 (CP*-$C$), 124.4 (aryl-$C_{meta}$H), 124.6 (N$C$H$C$HN), 130.7 (aryl-$C_{para}$H), 135.7 (aryl-$C_{ipso}$), 145.7 (aryl-$C_{ortho}$), 182.6 (N$C$N).

**IR (ATR)**: $\tilde{\nu}$ [cm$^{-1}$] = 798 (s, $\nu_{Al-H, b.}$), 1785 (s, $\nu_{Al-H,str.}$).

## Synthesis of (RER-Dipp$_2$Im$^H$H$_2$)AlCp* V-7

[AlH$_2$Cp*]$_3$ (25 mg, 148 $\mu$mol) and Dipp$_2$Im$^H$ (58.0 mg, 148 $\mu$mol) were dissolved in 5 mL benzene at room temperature and stirred for 12 hours. The solvent was reduced to ca. 2 mL. The residual solvent was slowly evaporated from -196 °C to room temperature *in vacuo* to afford **V-7** as colorless powder.

**Yield**: 58 mg (104 µmol, 70 %), colorless powder.

**Elemental Analysis** for C$_{37}$H$_{53}$N$_2$Al (553.83 g/mol): found (calculated) [%]: C 79.08 (80.10), H 9.52 (9.99), N 4.94 (5.05).

**$^1$H-NMR** (400.4 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 1.24 (d, 6 H, $^3J_{HH}$ = 7.4 Hz, $i$Pr-C$H_3$), 1.29 (d, 6 H, $^3J_{HH}$ = 7.4 Hz, $i$Pr-C$H_3$), 1.38 (d, 6 H, $^3J_{HH}$ = 7.4 Hz, $i$Pr-C$H_3$), 1.43 (d, 6 H, $^3J_{HH}$ = 7.4 Hz, $i$Pr-C$H_3$), 1.71 (s, 15 H, Cp*C$_1$C$H_3$), 2.21 (s, 2 H, RERCH$_2$), 3.17-3.26 (m,

4 H, NC*H*C*H*N), 3.67 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*), 3.76 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr-C*H*), 7.10 – 7.15 (m, 6 H, aryl-C*H*).

$^{13}$C{$^1$H}-NMR (100.7 MHz, C$_6$D$_6$, 298 K): δ [ppm] = 10.6 (Cp*-*C*H$_3$), 24.5 (NHC*i*Pr-*C*H$_3$), 24.9 (NHC*i*Pr-*C*H$_3$), 25.2(NHC*i*Pr-*C*H$_3$), 25.5 (NHC*i*Pr-*C*H$_3$), 27.7 (NHC*i*Pr-*C*H), 28.5 (NHC*i*Pr-*C*H), 28.7 (NHC*i*Pr-*C*H), 28.9 (NHC*i*Pr-*C*H), 40.2 (NHC-RER*C*H$_2$), 60.1 (NHC*N*CH$_2$CH$_2$N), 60.7 (NHC*N*CH$_2$CH$_2$N), 115.5 (Cp*-*C*), 124.0 (NHCaryl-*C*H), 124.5 (NHCaryl-*C*H), 126.3 (NHCaryl-*C*H), 127.9 (NHCaryl-*C*H), 128.2 (NHCaryl-*C*H), 147.1 (NHCaryl-*C*H), 147.4 (NHCaryl-*C*H), 148.2 (NHCaryl-*C*H), 148.8 (NHCaryl-*C*H), 151.4 (NHCaryl-*C*H).

**IR (ATR)**: no characteristic Al-H vibrations detected.

## Synthesis of *rac*-(Me$_2$Im$^{Me}$)·AlHCp*(cAAC$^{Me}$H) *rac*-V-9

(cAAC$^{Me}$H)AlHCp* **V-10** (50 mg, 113 µmol) and Me$_2$Im$^{Me}$ (14 mg, 113 µmol) were dissolved in 7 mL *n*-hexane at room temperature and stirred for 12 hours. The colorless precipitate was filtered off and dried *in vacuo* to afford **rac-9** as colorless powder. Crystals suitable for X-ray diffraction of compound **rac-V-9** were grown by slow evaporation of a saturated solution in benzene.

**Yield**: 22 mg (39 µmol, 35 %), colorless powder.

**Elemental Analysis** for C$_{25}$H$_4$N$_3$Al (574.47 g/mol): found (calculated) [%]: C 71.97 (77.44), H 10.02 (10.54), N 6.74 (7.32).

$^1$H-NMR (400.4 MHz, C$_6$D$_6$, 298 K): δ [ppm] = 1.18 (s, 3 H, cAAC*C*(C*H$_3$*)$_2$), 1.25 (s, 3 H, cAAC*i*Pr-C*H$_3$), 1.28 (s, 3 H, cAAC*i*Pr-C*H$_3$), 1.25 (s, 3 H, cAAC*i*Pr-C*H$_3$), 1.30 (s, 3 H, cAAC*C*(C*H$_3$*)$_2$), 1.32 (s, 3 H, NHC*C*H$_3$), 1.37 (d, 3 H, $^3J_{HH}$ = 7.4 Hz, cAAC*i*Pr-C*H$_3$), 1.45 (d, 3 H, $^3J_{HH}$ = 7.4 Hz, cAAC*i*Pr-C*H$_3$), 1.67 (s, 15 H, Cp*C*H$_3$), 1.79 (d, 3 H, $^3J_{HH}$ = 7.4 Hz, cAAC*i*Pr-C*H$_3$), 1.84 (s, 3 H, NHC*C*H$_3$), 1.38 (s, 3 H, cAAC*C*(C*H$_3$*)$_2$), 1.92 (d, 2 H, $^3J_{HH}$ = 7.4 Hz, cAAC*C*H$_2$), 1.93 (d, 3 H, $^3J_{HH}$ = 7.4 Hz, cAAC*i*Pr-C*H$_3$), 2.29 (d, 2 H, $^3J_{HH}$ = 7.4 Hz, cAAC*C*H$_2$), 3.06 (s, 3 H, NHC*C*H$_3$), 3.33 (s, 3 H, NHC*C*H$_3$), 3.69 (s, 1 H, Al-C-*H*), 3.19 (sept, 1 H, $^3J_{HH}$ = 6.8 Hz, cAAC*i*Pr-C*H*), 3.69 (s, 1 H, $^3J_{HH}$ = 6.8 Hz, cAAC*i*Pr-C*H*), 4.83 (s, 1 H, $^3J_{HH}$ = 6.8 Hz, cAAC*i*Pr-C*H*), 7.26-7.39 (m, 3 H, cAACaryl-C*H*).

$^{13}$C{$^1$H}-NMR (100.7 MHz, C$_6$D$_6$, 298 K): δ [ppm] = 7.7 (NHC*C*H$_3$), 7.8 (NHC*C*H$_3$), 12.8 (Cp*-*C*H$_3$) 25.6 (cAAC*i*Pr-*C*H$_3$), 26.0 (cAAC*i*Pr-*C*H$_3$), 26.4 (cAAC*i*Pr-*C*H$_3$), 27.6 (cAAC*i*Pr-

*C*H₃), 28.0 (cAAC*i*Pr-*C*H), 29.2 (cAACC(*C*H₃)₂), 29.5 (cAAC*i*Pr-*C*H), 32.5 (cAACC(*C*H₃)₂), 32.7 (cAACC(*C*H₃)₂), 33.5 (cAACC(*C*H₃)₂), 37.2 (NHCNC*C*H₃C*C*H₃N), 41.7 (cAAC*C*(CH₃)₂), 63.2 (cAAC*C*H₂), 63.8 (cAAC*C*(CH₃)₂), 69.9 (cAACGa*C*H), 118.5 (Cp*-*C*), 124.9 (cAACaryl-*C*metaH), 125.1 (cAACaryl-*C*metaH), 125.5 (NHCNC*C*H₃C*C*H₃N), 125.9 (cAACaryl-*C*paraH), 143.3 (cAACaryl-*C*ipso), 150.7 (cAACaryl-*C*ortho), 152.4 (cAACaryl-*C*ortho), 170.6 (NHCN*C*N).

**IR (ATR)**: $\tilde{\nu}$ [cm⁻¹] = 763 (s, ν$_{Al-H, b.}$), 1770 (s, ν$_{Al-H,str.}$).

## Synthesis of *meso*-(Me₂Im^Me)·AlHCp*(cAAC^MeH) *meso*-V-9

rac-(Me₂Im^Me)·AlHCp*(cAAC^MeH) **rac-V-9** (50 mg, 87 *μ*mol) was dissolved in 4 mL of toluene and stirred for 12 h at 110 °C. Removing all volatiles *in vacuo* affordmeso-**V-9** as pale yellow powder.

**Yield**: 35 mg (60.9 *μ*mol, 70 %), yellow powder.

**¹H-NMR** (400.4 MHz, C₆D₆, 298 K): *δ* [ppm] = 0.05 (d, 3 H, ³*J*HH = 7.4 Hz, cAAC*i*Pr-C*H₃*), 1.03 (s, 3 H, NHCC*H₃*), 1.03 (s, 3 H, cAACC(C*H₃*)₂), 1.16 (d, 3 H, ³*J*HH = 7.4 Hz, cAAC*i*Pr-C*H₃*), 1.21 (s, 3 H, cAAC*i*Pr-C*H₃*), 1.31 (s, 3 H, NHCC*H₃*), 1.45 (d, 3 H, ³*J*HH = 7.4 Hz, cAAC*i*Pr-C*H₃*), 1.77 (s, 3 H, cAAC*i*Pr-C*H₃*), 1.84 (s, 3 H, cAAC*i*Pr-C*H₃*), 1.86 (s, 15 H, Cp*C*H₃*), 1.98 (d, 2 H, ³*J*HH = 7.4 Hz, cAACC*H₂*), 2.13 (s, 3 H, cAACC(C*H₃*)₂), 2.15 (s, 3 H, NHCC*H₃*), 1.93 (d, 3 H, ³*J*HH = 7.4 Hz, cAAC*i*Pr-C*H₃*), 2.29 (d, 2 H, ³*J*HH = 7.4 Hz, cAACC*H₂*), 3.35 (s, 3 H, NHCC*H₃*), 3.69 (d, 1 H ⁴*J*HH = 3.6 Hz, Al-C-*H*), 3.66 (sept, 1 H, ³*J*HH = 6.8 Hz, cAAC*i*Pr-C*H*), 3.80 (sept, 1 H, ³*J*HH = 6.8 Hz, cAAC*i*Pr-C*H*), 6.68-7.04 (m, 3 H, cAACaryl-C*H*).

**¹³C{¹H}-NMR** (100.7 MHz, C₆D₆, 298 K): *δ* [ppm] = 7.6 (NHC*C*H₃), 7.8 (NHC*C*H₃), 13.7 (Cp*-*C*H₃), 22.10 (cAAC*i*Pr-*C*H₃), 24.9 (cAAC*i*Pr-*C*H₃), 25.6 (cAAC*i*Pr-*C*H₃), 26.9 (cAAC*i*Pr-*C*H₃), 28.1 (cAAC*i*Pr-*C*H), 28.3 (cAACC(*C*H₃)₂), 28.5 (cAAC*i*Pr-*C*H), 32.8 (cAACC(*C*H₃)₂), 33.1 (cAACC(*C*H₃)₂), 33.2 (cAACC(*C*H₃)₂), 33.8 (NHCNC*C*H₃C*C*H₃N), 33.9 (NHCNC*C*H₃C*C*H₃N), 42.6 (cAAC*C*(CH₃)₂), 62.5 (cAAC*C*H₂), 64.7 (cAAC*C*(CH₃)₂), 69.3 (cAACGa*C*H), 118.8 (Cp*-*C*), 123.1 (cAACaryl-*C*metaH), 123.2 (cAACaryl-*C*metaH), 124.8 (NHCNC*C*H₃C*C*H₃N), 125.9 (cAACaryl-*C*paraH), 146.4 (cAACaryl-*C*ipso), 150.7 (cAACaryl-*C*ortho), 152.2 (cAACaryl-*C*ortho), 168.0 (NHCN*C*N).

**IR (ATR)**: $\tilde{\nu}$ [cm⁻¹] = 762 (s, ν$_{Al-H, b.}$), 1711 (s, ν$_{Al-H,str.}$).

## Synthesis of (cAAC^MeH)Cp*AlH V-10

[AlH$_2$Cp*]$_3$ (50 mg, 295 $\mu$mol) and cAAC$^{Me}$ (85 mg, 295 $\mu$mol) were dissolved in 5 mL *n*-hexane at room temperature and stirred for 12 hours. The colorless precipitate was filtered off and dried *in vacuo* to afford**V-10** as colorless powder. Crystals suitable for X-ray diffraction of compound **V-10** were grown by slow evaporation of a saturated solution in benzene.

**Yield**: 92 mg (207 $\mu$mol, 70 %), colorless powder.

**Elemental Analysis** for C$_{30}$H$_{48}$NAl (449.70 g/mol): found (calculated) [%]: C 79.13 (80.13), H 10.96 (10.76), N 2.98 (3.11).

**$^1$H-NMR** (400.4 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 1.06 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 1.20 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, $_{cAAC}$*i*Pr-C$H_3$), 1.23 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 1.38 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 1.44 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, $_{cAAC}$*i*Pr-C$H_3$), 1.57 (s, 3 H, $_{cAAC}$C(C$H_3$)$_2$), 1.72 (s, 3 H, Cp*C$_1$C$H_3$), 1.74 (s, 12 H, Cp*C$_{(2-5)}$C$H_3$), 1.97-2.00 (m, 2 H, $_{cAAC}$C$H_2$), 2.58 (s, 1 H, Al-C-$H$), 3.19 (s, 1 H, $^3J_{HH}$ = 6.8 Hz, $_{cAAC}$*i*Pr-C$H$), 4.43 (s, 1 H, $^3J_{HH}$ = 6.8 Hz, $_{cAAC}$*i*Pr-C$H$), 7.09-7.21 (m, 3 H, $_{cAAC}$aryl-C$H$). **[1]**

**$^3$C{$^1$H}-NMR** (100.7 MHz, C$_6$D$_6$, 298 K): $\delta$ [ppm] = 10.6 (Cp*$C$H$_3$), 25.3 ($_{cAAC}$*i*Pr-$C$H$_3$), 25.3 ($_{cAAC}$*i*Pr-$C$H$_3$), 26.0 ($_{cAAC}$*i*Pr-$C$H$_3$), 27.0 ($_{cAAC}$*i*Pr-$C$H$_3$), 27.1 ($_{cAAC}$*i*Pr-$C$H), 28.7 ($_{cAAC}$*i*Pr-$C$H), 28.8 ($_{cAAC}$C($C$H$_3$)$_2$), 32.3 ($_{cAAC}$C($C$H$_3$)$_2$), 32.5 ($_{cAAC}$C($C$H$_3$)$_2$), 33.5 ($_{cAAC}$C($C$H$_3$)$_2$), 41.8 ($_{cAAC}$$C$(CH$_3$)$_2$), 59.8 ($_{cAAC}$$C$H$_2$), 64.7 ($_{cAAC}$$C$(CH$_3$)$_2$), 65.9 ($_{cAAC}$Al$C$H), 114.2 (Cp*$C_{(1-5)}$), 124.3 ($_{cAAC}$aryl-$C_{meta}$H), 125.7 ($_{cAAC}$aryl-$C_{meta}$H), 126.3 ($_{cAAC}$aryl-$C_{para}$H), 144.0 ($_{cAAC}$aryl-$C_{ipso}$), 150.9 ($_{cAAC}$aryl-$C_{ortho}$), 151.5 ($_{cAAC}$aryl-$C_{ortho}$).

## Synthesis of Cp*Ga^I V-11

A mixture of (Dipp$_2$Im)·GaH$_2$I **IV-6** (500 mg, 853 µmol) and KCp* (192 mg, 1.10 mmol) were dissolved in 7 mL of toluene. After stirring 4 hours at room temperature, the colorless, cloudy reaction mixture was filtered to remove KI and cAAC$^{Me}$ (242 mg, 848 mmol) was added to the solution. The mixture was stirred overnight and destilled at room temperature. Removing all volatiles *in vacuo* at 0 °C afforded **V-11** as colorless oil.

**Yield**: 70 mg (341 mmol, 40 %), colorless oil.

**$^1$H-NMR** (400.1 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 1.93 (s, 15 H, Cp*-C$H_3$).

**$^{13}$C{$^1$H}-NMR** (100.6 MHz, $C_6D_6$, 298 K): $\delta$ [ppm] = 9.9 (Cp*-$C$H$_3$), 113.6 (Cp*-$C$).

# 7 CRYSTALLOGRAPHIC DATA

## 7.1 Crystallographic Data Collection Parameters

Crystals were immersed in a film of perfluoropolyether oil on a glass fiber MicroMountTM (MiTeGen) and transferred to a Bruker D8 Apex-1 diffractometer with CCD area detector and graphitemonochromated Mo-Kα radiation or a Bruker D8 Apex-2 diffractometer with CCD area detector and graphite-monochromated Mo-Kα radiation equipped with an Oxford Cryosystems low-temperature device or a Rigaku XtaLAB Synergy-DW diffractometer with HyPix-6000HE detector and monochromated Cu-Kα equipped with an Oxford Cryo 800 cooling unit. Data were collected at 100 K. The images were processed with the Bruker or Crysalis software packages and equivalent reflections were merged. Corrections for Lorentz-polarization effects and absorption were performed if necessary and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. The structures were solved by using the ShelXTL software package.[258] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were usually assigned to idealized positions and were included in structure factors calculations. Refinement, analysis of the structures and the preparation of graphics were performed using SHELXTL,[259] ORTEP 3,[260] DIAMOND,[261] WinGX,[262] PLATON.[263]

## 7.2 CCDC-Numbers of published Compounds

The crystallographic data (cif-files) of the published compounds were uploaded to the CAMBRIDGE CRYSTALLOGRAPHIC DATA CENTRE (CCDC) and can be downloaded *via http://www.ccdc.cam.ac.uk*.

# Chapter 2

Crystallographic data (excluding structure factors) for the structures reported in Chapter 2 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no.s CCDC 1849169 (**II-8**), 1849170 (**II-9**) and CCDC 1849171 (**II-10**).

# Chapter 3

Crystallographic data (excluding structure factors) for the structures reported in Chapter 3 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no.s CCDC 2008675 (**III-1**), 2008679 (**III-4**), CCDC 2008682 (**III-5**), CCDC 2008681 (**III-6**), CCDC 2008676 (**III-7**), CCDC 1975620 (**III-8**), CCDC 1975614 (**III-12**), CCDC 2008677 (**III-13**), CCDC 2008678 (**III-15**), CCDC 2008683 (**III-16**) and CCDC 2008680 (**III-17**).

# Chapter 4

Crystallographic data (excluding structure factors) for the structures reported in Chapter 4 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no.s CCDC 1993675 (**IV-1**), 1993679 (**IV-3**), CCDC 1993676 (**IV-4**), CCDC 1993677 (**IV-9**), CCDC 1993678 (**IV-10**) and CCDC 2013190 (**IV-12**).

## 7.3 Crystallographic Data of the synthesized Compounds

# Chapter 5

($Me_2Im^{Me}$)·Cp*AlH$_2$ **V-1**: $C_{17}H_{29}AlN_2$, $M_r$ = 288.40, colorless, block, 0.37 x 0.36 x 0.28 mm, orthorhombic group Pbca, a = 11.1648(10) Å, b = 15.7523(16) Å, c = 20.0390(16) Å, $\alpha$ = 90°, $\beta$ = 90°, $\gamma$ = 90°, V = 3524.3(6) Å$^3$, T = 100(10) K, Z = 8, $\rho_{calcd.}$ = 1.087 g·cm$^{-3}$, μ = 0.109, F(000) = 1264, 31236 reflections, in h(−13/13), k(-19/19), l(-24/24) measured in the range 2.033 ° < θ < 26.019°, completeness 100 %, 3474 independent reflections, 2783 observed reflections (I > 2$\sigma$(I)), 199 parameters, 1 restraints; all data: $R_1$ = 0.1071 and $wR_2$ = 0.1162, I > 2$\sigma$(I): $R_1$ = 0.0419 and $R_2$ = 0.0569, Goof 1.031, largest difference peak/hole 0.90 /-0.25 e·Å$^{-3}$.

($Dipp_2Im$)·Cp*AlH$_2$ **V-3**: $C_{37}H_{53}AlN_2$, $M_r$ = 552.79, colorless, block, 0.25 x 0.23 x 0.15 mm, monoclinic group P2$_1$/n, a = 12.15590(10) Å, b = 17.0754(2) Å, c = 17.5505(2) Å, $\alpha$ = 90°, $\beta$ = 104.0520(10) °, $\gamma$ = 90°, V = 3533.89(7) Å$^3$, T = 100.00(10) K, Z = 4, $\rho_{calcd.}$ = 1.039 g·cm$^{-3}$, μ = 0.671, F(000) = 1208, 12235 reflections, in h(−15/15), k(-21/18), l(-21/22) measured in the range 3.666 ° < θ < 67.684°, completeness 99.9 %, 7321 independent reflections, 6551 observed reflections (I > 2$\sigma$(I)), 382 parameters, 1 restraints; all data: $R_1$ = 0.1308 and $wR_2$ = 0.1270, I > 2$\sigma$(I): $R_1$ = 0.0466 and $R_2$ = 0.0512, Goof 1.087, largest difference peak/hole 0.88 /-0.28 e·Å$^{-3}$.

($Me_2Im^{Me}$)·Cp*GaH$_2$ **V-4**: $C_{17}H_{29}GaN_2$, $M_r$ = 331.14, colorless, block, 0.20 x 0.18 x 0.12 mm, orthorhombic group Pbca, a = 11.04870(10) Å, b = 15.7247(2) Å, c = 20.1868(2) Å, $\alpha$ = 90°, $\beta$ = 90°, $\gamma$ = 90°, V = 3507.20(6) Å$^3$, T = 100(5) K, Z = 8, $\rho_{calcd.}$ = 1.254 g·cm$^{-3}$, μ = 2.072, F(000) = 1408, 12235 reflections, in h(−13/13), k(-11/19), l(-24/21) measured in the range 4.380 ° < θ < 70.076°, completeness 100 %, 3331 independent reflections, 3049 observed reflections (I > 2$\sigma$(I)), 198 parameters, 0 restraints; all data: $R_1$ = 0.0646 and $wR_2$ = 0.0661, I > 2$\sigma$(I): $R_1$ = 0.0240 and $R_2$ = 0.0266, Goof 1.044, largest difference peak/hole 0.30 /-0.32 e·Å$^{-3}$.

($Me_2Im^{Me}$)·AlCp*(RER-$Dipp_2Im^H$H$_2$) **V-8**: $C_{44}H_{67}AlN_4$, $M_r$ = 680.39, colorless, block, 0.14 x 0.09 x 0.06 mm, orthorhombic group P2$_1$2$_1$2, a = 24.6581(3) Å, b = 16.0674(3) Å, c = 10.49950(10) Å, $\alpha$ = 90°, $\beta$ = 90°, $\gamma$ = 90°, V = 4159.81(10) Å$^3$, T = 100:01(10) K, Z = 4, $\rho_{calcd.}$ = 1.086 g·cm$^{-3}$, μ = 0.665, F(000) = 1491, 11462 reflections, in h(−

25/30), k(-19/19), l(-12/12) measured in the range 3.283 ° < θ < 72.1:29°, completeness 99.9 %, 7887 independent reflections, 7189 observed reflections (I > $2\sigma(I)$), 483 parameters, 42 restraints; all data: $R_1$ = 0.0854 and $wR_2$ = 0.0889, I > $2\sigma(I)$: $R_1$ = 0.0365 and $R_2$ = 0.00427, Goof 1.041, largest difference peak/hole 0.24 /-0.23 e·Å$^{-3}$.

($Me_2Im^{Me}$)·(R/R)AlHCp*($cAAC^{Me}H$) *rac*(R,R)-**V-9**: $C_{37}H_{60}AlN_3$, $M_r$ = 573.86, colorless, block, 0.18 x 0.11 x 0.11 mm, monoclinic group P2$_1$/c, a = 11.06950(10) Å, b = 14.4129(2) Å, c = 22.1211(2) Å, $\alpha$ = 90°, $\beta$ = 97.8790(10)°, $\gamma$ = 90°, V = 3495.96(7) Å$^3$, T = 100.01(10) K, Z = 4, $\rho_{calcd.}$ = 1.090 g·cm$^{-3}$, μ = 0.698, F(000) = 1264, 16326 reflections, in h(–14/14), k(-17/18), l(-27/23) measured in the range 3.671 ° < θ < 77.469°, completeness 99 %, 7295 independent reflections, 6426 observed reflections (I > $2\sigma(I)$), 391 parameters, 0 restraints; all data: $R_1$ = 0.01185 and $wR_2$ = 0.01231, I > $2\sigma(I)$: $R_1$ = 0.0453 and $R_2$ = 0.00514, Goof 1.027, largest difference peak/hole 0.37 /- 0.25 e·Å$^{-3}$.

($cAAC^{Me}H$)Cp*AlH **V-10**: $C_{30}H_{48}AlN$, $M_r$ = 449.67, colorless, block, 0.34 x 0.19 x 0.11 mm, monoclinic group Cc, a = 11.1032(2) Å, b = 16.9744(3) Å, c = 14.8699(2) Å, $\alpha$ = 90°, $\beta$ = 100.2150(10)°, $\gamma$ = 90°, V = 2758.11(8) Å$^3$, T = 100.00(10) K, Z = 4, $\rho_{calcd.}$ = 1.083 g·cm$^{-3}$, μ = 0.743, F(000) = 992, 11153 reflections, in h(–13/13), k(-20/20), l(-18/13) measured in the range 4.813 ° < θ < 70.075°, completeness 100 %, 3909 independent reflections, 3989 observed reflections (I > $2\sigma(I)$), 306 parameters, 4 restraints; all data: $R_1$ = 0.0762 and $wR_2$ = 0.0767, I > $2\sigma(I)$: $R_1$ = 0.0284 and $R_2$ = 0.00290, Goof 1.044, largest difference peak/hole 0.30 /-0.20 e·Å$^{-3}$.

# 8 SUMMARY

This thesis describes the synthesis and reactivity of NHC-stabilized *Lewis*-acid/*Lewis*-base adducts of alanes and gallanes (NHC = Me$_2$Im$^{Me}$, *i*Pr$_2$Im, *i*Pr$_2$Im$^{Me}$, Dipp$_2$Im, Dipp$_2$Im$^H$). As this field of research has developed tremendously, especially in the last five years, the first chapter provides an overview of the current state of knowledge.
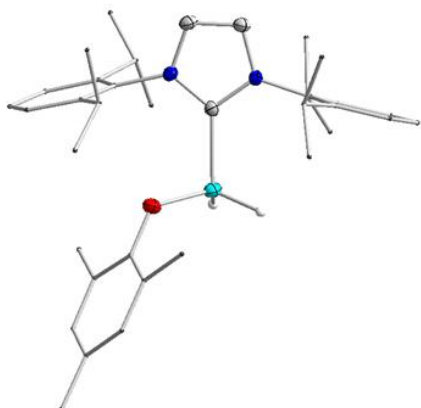


*Figure VIII.1: Molecular structure of (Dipp$_2$Im)·AlH$_2$(OMes)* **II-9**.

Previous work in the group has demonstrated that NHC-substituted alanes (NHC)·AlH$_3$ have a limited stability with respect to elimination of dihydroaminal NHC-H$_2$ or the ring expansion and ring opening of the NHC-ligand. The influence of electronegative π-donor-substituents on the stability of the NHC alane adducts is examined in chapter 2. For this purpose, the carbene stabilized alanes (NHC)·AlH$_3$ (NHC = *i*Pr$_2$Im, Dipp$_2$Im) were reacted with secondary amines of different steric demand. The reaction led to the formation of the substituted aluminium amides (NHC)·AlH$_2$(NR$_2$) **II-1** and **II-3** – **II-6**. An alternative synthetic route is the one pot reaction of (NMe$_3$)·AlH$_3$ with secondary amines and further reaction with the corresponding NHC. The reaction of (NHC)·AlH$_3$ with the stronger *Lewis* acidic alcohol mesitol leads, depending on the stoichiometry used, to the formation of the mono- and di-substituted aluminium phenolates (*i*Pr$_2$Im)·AlH$_2$(OMes) **II-7**, (*i*Pr$_2$Im)·AlH(OMes)$_2$ **II-8**, (Dipp$_2$Im)·AlH$_2$(OMes) **II-9** and (Dipp$_2$Im)·AlH(OMes)$_2$ **II-10**. The reaction of (Dipp$_2$Im)·AlH$_3$ **IV** with three equivalents of the alcohol afforded the imidazolium salt [Dipp$_2$ImH]$^+$[Al(OMes)$_4$]$^-$ **II-11**. Compared to the reaction with secondary amines, multiple substitution at the aluminium center was thus achieved even under mild conditions.

All of the NHC stabilized aluminium amides and phenolates revealed a significantly increased stability in solution compared to the parent aluminium(III) hydrides and no NHC ring expansion or ring opening reaction was observed in the presence of an excess of
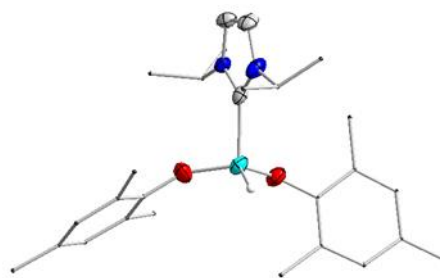


*Figure VIII.2: Molecular structure of (iPr$_2$Im)·AlH(OMes)$_2$* **II-8**.

carbene. The $\pi$-donor substituents saturate the *Lewis* acidic aluminium center and coordination of a second NHC-ligand was not observed. The strongly electronegative N and O substituents increase the *Lewis* acidity of the aluminium atom, which leads to stronger Al-C$_{NHC}$ as well as Al-H bonds, which inhibits the insertion of the carbene into the Al-H bond.

In Chapter 3 the development of the synthesis and reactivity of carbene-stabilized gallanes is presented. *Lewis*-base stabilized gallium hydrides usually have a lower thermal stability compared to their analogous aluminium compounds. The synthesis of NHC gallane adducts (NHC)·GaH$_3$, (NHC)·GaH$_2$Cl and (NHC)·GaHCl$_2$ and their reactivity towards NHCs and cAAC$^{Me}$ were investigated in detail. By treatment of *in situ* generated unstable lithium gallium hydride with the corresponding NHCs, new NHC-stabilized gallium(III) hydrides (NHC)·GaH$_3$ (NHC = Me$_2$Im$^{Me}$ **III-1**, *i*Pr$_2$Im **III-2** and
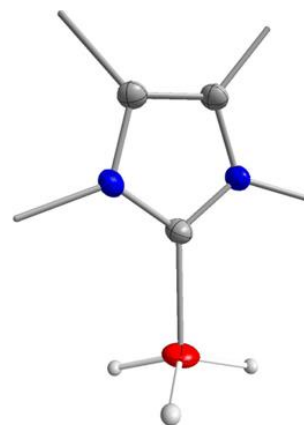


*Figure VIII.3: Molecular structure of **III-1**.*

Dipp$_2$Im$^H$ **III-4**) were prepared. The corresponding carbene stabilized monochlorogallanes were synthesized by the dismutation of (NHC)·GaH$_3$ and (NHC)·GaCl$_3$ (ratio 2:1; NHC = *i*Pr$_2$Im$^{Me}$, Dipp$_2$Im and Dipp$_2$Im$^H$; see Scheme VIII.1), whereas the NHC stabilized dichlorogallanes (NHC)·GaHCl$_2$ were formed in the reaction of *in situ* generated "GaHCl$_2$" with NHC. Furthermore, the first cAAC$^{Me}$ stabilized gallium hydride (cAAC$^{Me}$)·GaHCl$_2$ **III-15** was succesfully synthesized *via* this route (see Scheme VIII.1).



*Figure VIII.4: Molecular structure of **III-15**.*
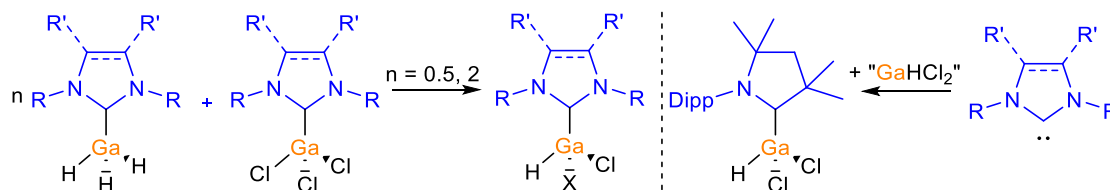


*Scheme VIII.1: Synthesis of carbene stabilized mono- and dichloro gallium hydrides.*

The NHC-stabilized gallium(III) hydrides decompose in solution upon heating to give elemental gallium, dihydrogen and the corresponding dihydroaminal NHC-$H_2$. In the presence of another equivalent of NHC, an equilibrium with the bis-NHC adducts $(NHC)_2 \cdot GaH_3$ was detected. However, in contrast to the aluminium hydrides, no NHC ring expansion or ring opening reaction was
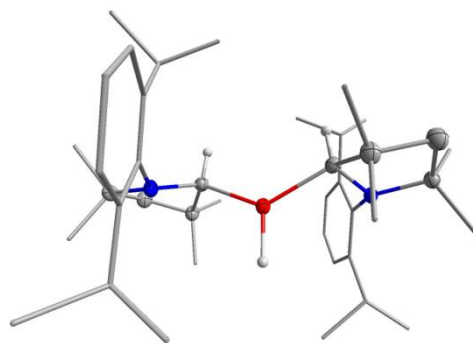


*Figure VIII.5: Molecular structure of **III-8**.*

observed. The substitution of the hydrides with chlorides led to an increased stability of the adducts with increasing chloride content. The reaction of cAAC$^{Me}$ with the gallanes leads to the insertion of the cAAC$^{Me}$ into the Ga-H bond, forming the compounds (NHC)·GaH$_2$(cAAC$^{Me}$H) (NHC = Me$_2$Im$^{Me}$ **III-5**, *i*Pr$_2$Im$^{Me}$ **III-6**, Dipp$_2$Im **III-7**) (see Scheme VIII.2). The compounds **III-5** - **III-7** are stable in solution up to 110 °C and no ring expansion, ring opening or reductive elimination of cAAC$^{Me}$H$_2$ was observed. The reaction of (Dipp$_2$Im$^H$)·GaH$_3$ **III-4** with two equivalents of cAAC$^{Me}$ selectively afforded the first monomeric bisalkyl gallium hydride (cAAC$^{Me}$H)$_2$GaH **III-8** (see Scheme VIII.2).
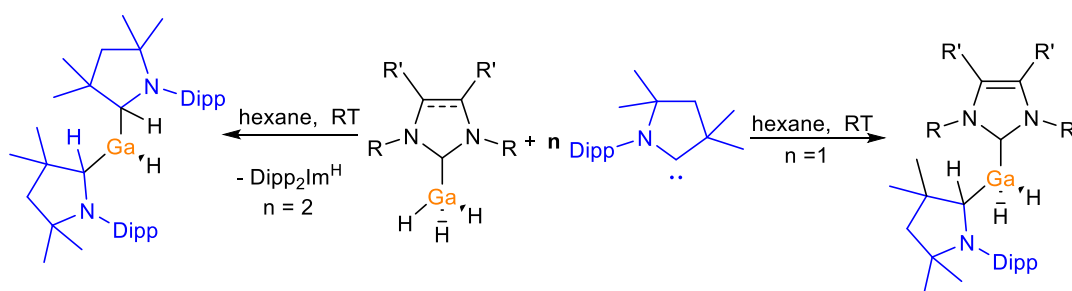


*Scheme VIII.2: Insertion of cAAC$^{Me}$ into Ga-H bonds.*

The reaction of the mono- and dichlorogallanes (NHC)·GaH$_2$Cl and (NHC)·GaHCl$_2$ (NHC = *i*Pr$_2$Im$^{Me}$, Dipp$_2$Im) with cAAC$^{Me}$ led to different products depending on the steric demand of the NHC ligand used. For *i*Pr$_2$Im$^{Me}$ the insertion of cAAC$^{Me}$ into the Ga-H bond and formation of (*i*Pr$_2$Im$^{Me}$)·GaHCl(cAAC$^{Me}$H) **III-16** and

($i$Pr$_2$Im$^{Me}$)·GaCl$_2$(cAAC$^{Me}$H) **III-17** was observed. The reaction of the chloro gallanes stabilized with the sterically more demanding carbenes Dipp$_2$Im and Dipp$_2$Im$^H$ with two equivalents of cAAC$^{Me}$ selectively afforded (cAAC$^{Me}$H)$_2$GaCl **III-18** (see Scheme VIII.3). Interestingly, the reaction of the corresponding dichlorogallanes with cAAC$^{Me}$ led to a quantitative ligand exchange to give the adduct (cAAC$^{Me}$)·GaHCl$_2$



Figure VIII.6: Molecular structure of **III-17**.

**III-15**. For (cAAC$^{Me}$H)$_2$GaH **III-8** a reversible isomerisation process in solution between (cAAC$^{Me}$H)$_2$GaH *meso*-**III-8** and (cAAC$^{Me}$H)$_2$GaH *rac*-**III-8** *via* a tetrahedrally coordinated intermediate (cAAC$^{Me}$)·GaH$_2$(cAAC$^{Me}$H) *int*-**III-8** is assumed (see Scheme VIII.3).
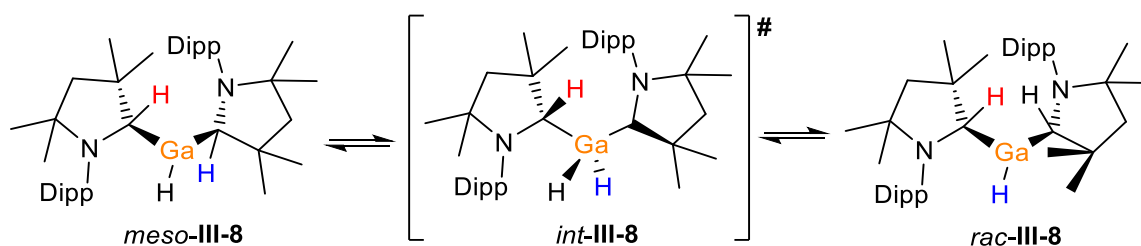


*Scheme VIII.3: Proposed mechanism of the isomerization of meso-**8** to rac-**8** in solution.*

Chapter 4 describes investigations concerning the synthesis and reactivity of NHC-stabilized iodoalanes and iodogallanes, which are suitable for the formation of cationic aluminium and gallium dihydrides. The NHC trieleiodides **IV-1** - **IV-6** were synthesized *via* an efficient synthetic route starting from the parent alanes and gallanes (NHC)·EH$_3$ (E = Al, Ga; NHC = Me$_2$Im$^{Me}$, $i$Pr$_2$Im, $i$Pr$_2$Im$^{Me}$, Dipp$_2$Im) and elemental iodine and methyl iodide, respectively (see Scheme VIII.4).
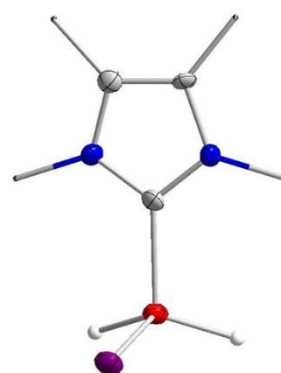


*Figure VIII.7: Molecular structure of **IV-4**.*
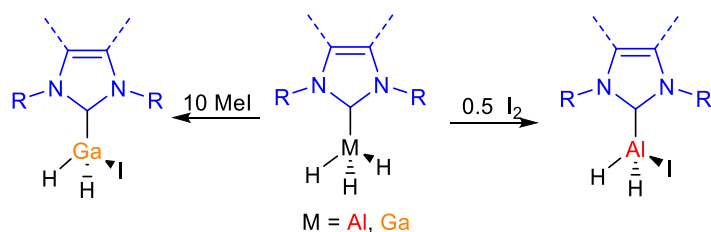
*Scheme VIII.4: Synthesis of NHC stabilized iodo aluminium- and gallium dihydrides.*

The reaction of (NHC)·EH$_2$I (E = Al, Ga) stabilized by the sterically less demanding NHCs (NHC = Me$_2$Im$^{Me}$, $i$Pr$_2$Im, $i$Pr$_2$Im$^{Me}$) with an additional equivalent of the NHC led to the formation of the cationic bis-NHC aluminium and gallium dihydrides [(NHC)$_2$·AlH$_2$]$^+$I$^-$ (NHC = Me$_2$Im$^{Me}$ **IV-7**, $i$Pr$_2$Im **IV-8**, $i$Pr$_2$Im$^{Me}$ **IV-9**) and [(NHC)$_2$·GaH$_2$]$^+$I$^-$ (NHC = Me$_2$Im$^{Me}$ **IV-10**, $i$Pr$_2$Im$^{Me}$ **IV-11**) (see Scheme VIII. 5). To investigate the influence of the steric demand of the NHC, the adduct (Dipp$_2$Im)·GaH$_2$I
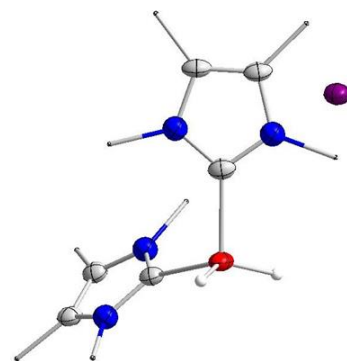


*Figure VIII.8: Molecular structure of **IV-10**.*

**IV-6** was reacted with an additional equivalent of Dipp$_2$Im. Due to the bulk of the NHC used, rearrangement of one of the NHC ligands from *normal* to *abnormal* coordination occurred and the cationic gallium dihydride [(Dipp$_2$Im)·GaH$_2$($a$Dipp$_2$Im)]I **IV-12** was formed (see Scheme VIII.5).
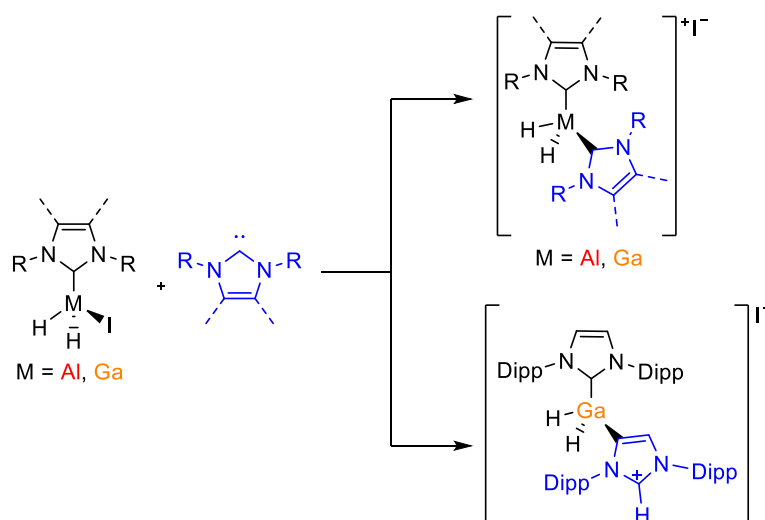


*Scheme VIII.5: Synthesis of cationic NHC stabilized aluminium- and gallium dihydrides.*
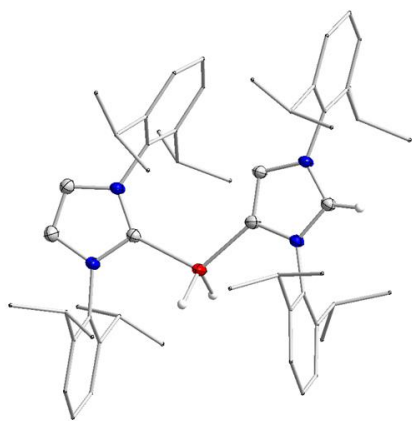
*Figure VIII.9: Molecular structure of **IV-12**.*

An associative substitution path is assumed for the reaction mechanism, in which the NHC reacts with (NHC)·EH$_2$I (E = Al, Ga) to give a neutral, five-coordinated intermediate (NHC)$_2$·EH$_2$I (E = Al, Ga). The stabilization of this reactive intermediate led to elimination of the good leaving group iodide to form the stable salts [(NHC)$_2$·EH$_2$]$^-$I$^+$ (see Scheme VIII.6). For the bulky NHC Dipp$_2$Im, additional stabilization was achieved by rearrangement of one of the NHC ligands from its *normal* to the *abnormal* coordination mode.
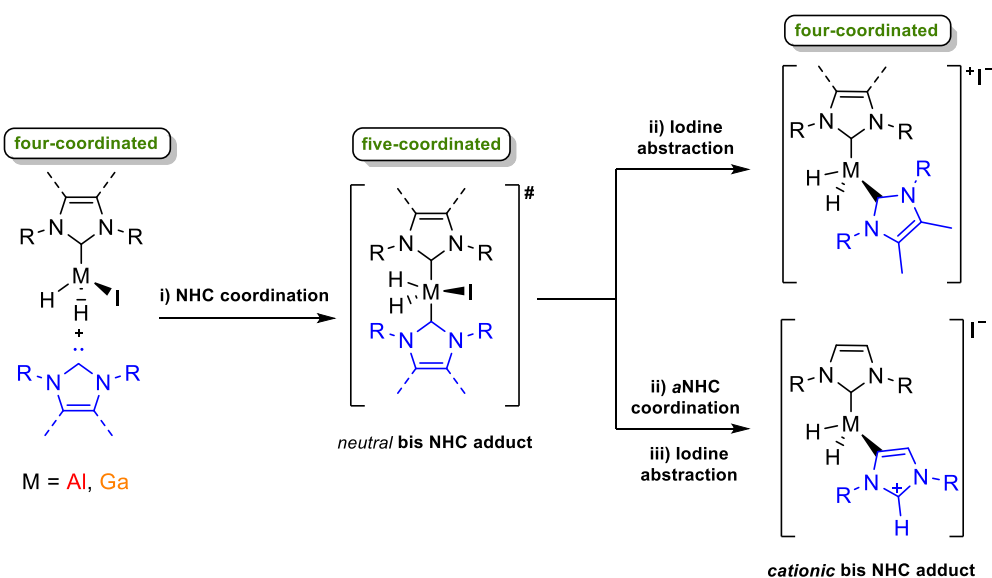


*Scheme VIII.6: Proposed mechanism of the formation of bis NHC aluminium- and gallium hydride cations.*

Chapter 5 of this thesis reports investigations concerning the reduction of cyclopentadienyl-substituted alanes and gallanes with singlet carbenes. NHC stabilized pentamethylcyclopentadienyl aluminium and gallium dihydrides (NHC)·Cp*MH$_2$ (E = Al, Ga) were prepared by the reaction of (AlH$_2$Cp*)$_3$ with the corresponding NHCs or by the salt elimination of (NHC)·GaH$_2$I with KCp* (see Scheme VIII.7).
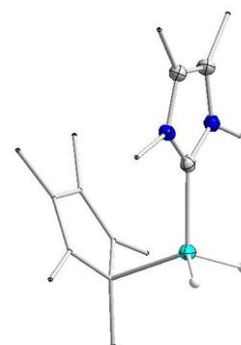
Figure VIII.10: Molecular structure of **V-1**.
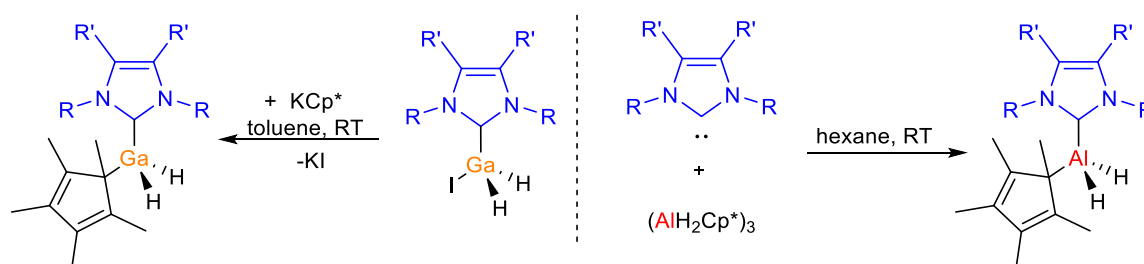


Scheme VIII.7: Synthesis of NHC stabilized pentamethylcyclopentadienyl aluminium- and gallium dihydrides.
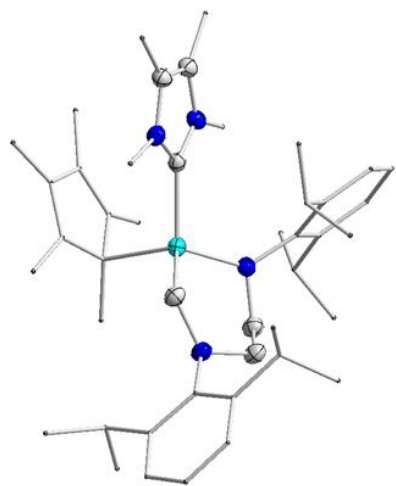


Figure VIII.11: Molecular structure of **V-8**.

The alanes **V-1** - **V-3** are stable in solution up to the boiling point of benzene (80 °C), whereas the gallanes **V-4** - **V-6** decompose at higher temperatures with reductive elimination of Cp*H and formation of Cp*Ga$^I$ **V-11**. A reversible equilibrium between (NHC)·GaH$_3$ and (NHC)·Cp*$_2$GaH is assumed. (NHC)·Cp*$_2$GaH undergoes reductive elimination of Cp*H with formation of Cp*Ga$^I$ and the free NHC. The reductive elimination is preferred for sterically demanding NHCs (Dipp$_2$Im > $i$Pr$_2$Im$^{Me}$ > Me$_2$Im$^{Me}$). In addition, NHC ring expansion of the backbone saturated carbene Dipp$_2$Im$^H$ was

observed for the reaction of the NHC with $(AlH_2Cp^*)_3$, which led to $(RER\text{-}Dipp_2Im^HH_2)AlCp^*$ **V-7** and $(Me_2Im^{Me})\cdot AlCp^*(RER\text{-}Dipp_2Im^HH_2)$ **V-8**, for the reaction of **V-7** with an additional equivalent of $Me_2Im^{Me}$. Furthermore, the reactivity of the adducts $(NHC)\cdot Cp^*EH_2$ (E = Al, Ga) towards $cAAC^{Me}$ was investigated. For the alane complex **V-1**, which is stabilized by the small NHC $Me_2Im^{Me}$, the insertion of $cAAC^{Me}$ into the Al-H bond led to the selective formation of the *rac*-isomers
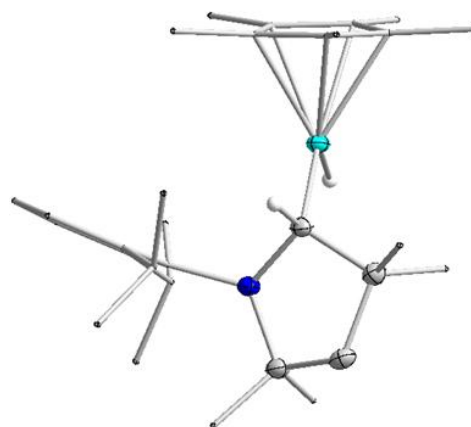


*Figure VIII.12: Molecular structure of rac-V-10.*

$(Me_2Im^{Me})\cdot AlHCp^*(cAAC^{Me}H)$ *rac*-**V-9** (see Scheme VIII. 8). Heating of *rac*-**V-9** in solution triggered the irreversible isomerization and formation of *meso*-**V-9**. The reaction of the adducts **V-2** and **V-3** stabilized by the sterically more demanding NHCs $iPr_2Im^{Me}$ and $Dipp_2Im$ afforded the exceptionally stable insertion product $(cAAC^{Me}H)Cp^*AlH$ **V-10** with liberation of the NHC (see Scheme VIII.8).
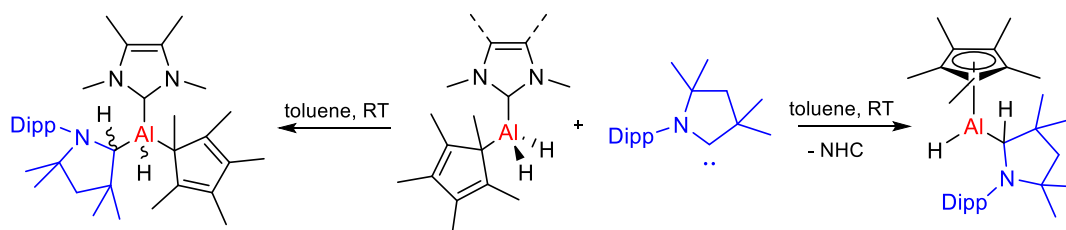


*Scheme VIII.8: Oxidative addition of Al-H at the carbene carbon atom.*

The reaction of the gallium hydrides $(NHC)\cdot Cp^*GaH_2$ **V-4** - **V-6** with $cAAC^{Me}$ led to the reductive elimination of $cAAC^{Me}H_2$ and formation of $Cp^*Ga^I$ **V-11**, instead (see Scheme VIII.9). The formation of a highly reactive intermediate insertion product $(cAAC^{Me}H)GaHCp^*$ int-**V-11** is suggested, which immediately undergoes reductive elimination of $cAAC^{Me}H_2$ and formation of stable $Cp^*Ga^I$ **V-11**. In the case of gallium, the reductive elimination should be both entropically and thermodynamically favored. This represents the first selective metal-free reduction of $Ga^{III}$ to $Ga^I$ with a carbene as hydrogen acceptor under mild conditions.
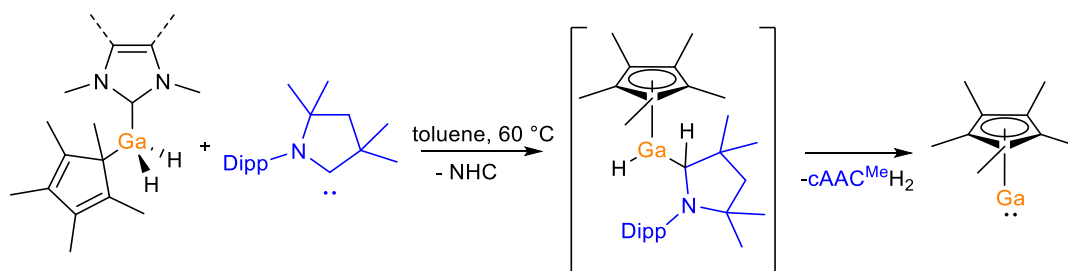
*Scheme VIII.9: Metall-free reductive elimination of gallium with cAAC$^{Me}$ as reductant.*

A variety of neutral and cationic carbene-stabilized alanes and gallanes are presented in this work. The introduction of electronegative $\pi$-donor substituents (Cl⁻, I⁻, OR⁻, NR$_2$⁻) and the investigations on the thermal stability of these compounds led to the conclusion that the stability of alanes and gallanes increased significantly by such a substitution. Investigations on the reactivity of the NHC adducts towards cAAC$^{Me}$ resulted in various insertion products of the carbene into the Al-H or Ga-H bonds and the first cAAC$^{Me}$ stabilized dichlorogallane was isolated. Furthermore, a first proof was provided that carbenes can be used specifically for the (formal) reduction of group 13 hydrides of the higher homologues. Thus, the synthesis of Cp*Ga$^{I}$ from the reaction of (NHC)·Cp*GaH$_2$ with cAAC$^{Me}$ was developed. In the future, this reaction pathway could be of interest for the preparation of other low-valent compounds of aluminium and gallium.

# 9 ZUSAMMENFASSUNG

Die vorliegende Arbeit befasst sich mit der Synthese und Reaktivität NHC stabilisierter *Lewis*-Säuren/*Lewis*-Basen Addukte (NHC = Me$_2$Im$^{Me}$, *i*Pr$_2$Im, *i*Pr$_2$Im$^{Me}$, Dipp$_2$Im, Dipp$_2$Im$^H$) von Alanen und Galanen. Da sich dieses Forschungsgebiet insbesondere in den letzten fünf Jahren rasant entwickelt hat, wird im ersten Kapitel dieser Arbeit eine Übersicht über den gegenwärtigen Kenntnisstand gegeben.

Nachdem in vorangegangenen Arbeiten in der Gruppe gezeigt werden konnte, dass NHC-substituierte Alane (NHC)·AlH$_3$ eine begrenzte Stabilität bezüglich einer möglichen Eliminierung von Dihydroaminal NHC-H$_2$ bzw. der Ringerweiterung oder Ringöffnung des NHC-Liganden aufweisen, wird in Kapitel 2 der Arbeit der Einfluss elektronegativer $\pi$-Donor-Substituenten am Aluminium auf die Stabilität der dargestellten NHC-Alan-Addukte untersucht. Dazu wurden die Carben stabilisierten Alane (NHC)·AlH$_3$ (NHC = *i*Pr$_2$Im, Dipp$_2$Im) mit sekundären Aminen unterschiedlichen sterischen Anspruchs umgesetzt. Dies führte zur Bildung der Aluminiumamide (NHC)·AlH$_2$(NR$_2$) **II-1** und **II-3** – **II-6**. Eine alternative Syntheseroute stellt die Eintopfreaktion ausgehend von (NMe$_3$)·AlH$_3$ mit sekundären Aminen und anschließender Umsetzung mit dem entsprechenden NHC dar.
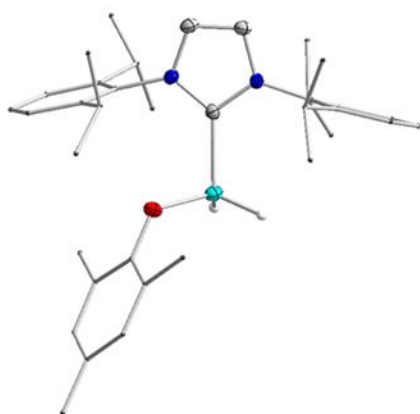


*Abbildung IX.1: Molekülstruktur von (Dipp$_2$Im)·AlH$_2$(OMes) **II-9**.*

Die Reaktion von (NHC)·AlH$_3$ mit dem stärker *Lewis*-sauren Alkohol Mesitol führt in Abhängigkeit von der gewählten Stöchiometrie zur Bildung der einfach und zweifach substituierten Aluminiumphenolate (*i*Pr$_2$Im)·AlH$_2$(OMes) **II-7**, (*i*Pr$_2$Im)·AlH(OMes)$_2$ **II-8**, (Dipp$_2$Im)·AlH$_2$(OMes) **II-9** und (Dipp$_2$Im)·AlH(OMes)$_2$ **II-10**, wohingegen die Umsetzung von (Dipp$_2$Im)·AlH$_3$ **IV** mit drei Äquivalenten des Alkohols zur Bildung des Imidazoliumsalzes [Dipp$_2$ImH]$^+$[Al(OMes)$_4$]$^-$ **II-11** führt. Im Vergleich zur Reaktion mit sekundären Aminen konnte hierbei selbst unter milden Bedingungen eine mehrfache Substitution am Aluminiumzentrum erreicht werden.

Alle dargestellten NHC-Aluminiumamide und Phenolate weisen im Vergleich zu den unsubstituierten Aluminiun(III)hydriden eine deutlich erhöhte Stabilität in Lösung auf und es konnte keine NHC Ringerweiterungs- oder Ringöffnungsreaktion in Gegenwart eines Überschusses an Carben beobachtet werden. Die $\pi$-Donor Substituenten sättigen das *Lewis*-
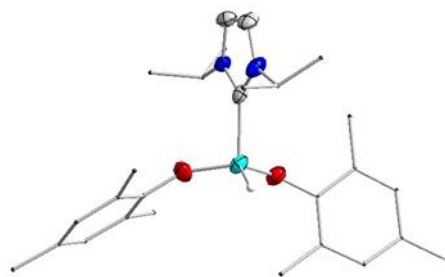


*Abbildung IX.2: Molekülstruktur von (iPr$_2$Im)·AlH(OMes)$_2$ **II-8**.*

saure Aluminiumzentrum ab, sodass eine Koordination eines zweiten NHC-Liganden nicht möglich ist. Ferner erhöhen die stark elektronegativen N- und O-Substituenten die *Lewis*-Acidität des Aluminiumatoms, das zu stärkeren Al-C$_{NHC}$, aber auch Al-H-Bindungen führt und vermutlich deshalb die Insertion des Carbens in diese Bindung erschwert ist.

Kapitel 3 beschreibt die Entwicklung der Synthese von Carben-stabilisierten Gallanen und Untersuchungen zu deren Reaktivität. *Lewis*-Basen stabilisierte Galliumhydride weisen üblicherweise im Vergleich zu ihren analogen Aluminium-Addukten eine geringere thermische Stabilität auf. Es wurde die Darstellung der NHC-Gallan-Addukte (NHC)·GaH$_3$, (NHC)·GaH$_2$Cl und (NHC)·GaHCl$_2$ und ihre Reaktivität gegenüber NHCs und cAAC$^{Me}$ im Detail untersucht. Durch die Umsetzung von *in situ* generiertem, instabilem Lithiumgalliumhydrid mit dem entsprechenden NHC gelang die Darstellung neuer NHC
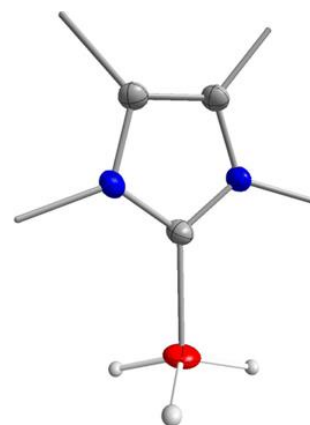


*Abbilung IX.3: Molekülstruktur von **III-1**.*
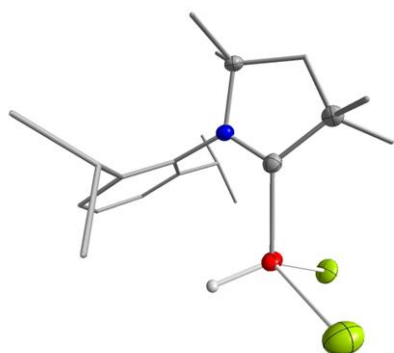


*Abbildung IX.4: Molekülstruktur von **III-15**.*

stabilisierter Gallium(III)hydride (NHC)·GaH$_3$ (NHC = Me$_2$Im$^{Me}$ **III-1**, *i*Pr$_2$Im **III-2** und Dipp$_2$Im$^H$ **III-4**). Die entsprechenden Carben stabilisierten Monochlorogallane wurden durch Dismutierung von (NHC)·GaH$_3$ und (NHC)·GaCl$_3$ (2:1) (NHC = *i*Pr$_2$Im$^{Me}$, Dipp$_2$Im und Dipp$_2$Im$^H$) dargestellt (siehe Schema IX.1), wohingegen die NHC stabilisierten Dichlorogallane (NHC)·GaHCl$_2$ durch die Umsetzung von *in situ* generiertem "GaHCl$_2$" mit den entsprechenden NHCs

synthetisiert wurden. Darüber hinaus gelang auf dieser Syntheseroute die Darstellung des ersten bekannten cAAC$^{Me}$ stabilisierten Galliumhydrides (cAAC$^{Me}$)·GaHCl$_2$ **III-15** (siehe Scheme IX.1).
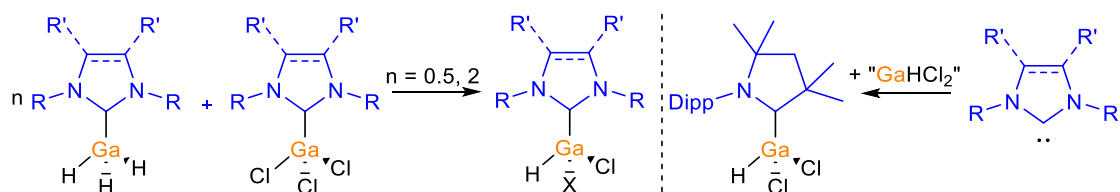


*Schema IX.1: Darstellung Carben stabilisierter Mono- und Dichlorogallane.*

Die NHC stabilisierten Gallium(III)hydride zersetzen sich in Lösung unter thermischer Belastung zu elementarem Gallium, Diwasserstoff und dem entsprechenden Dihydridoaminal NHC-H$_2$. In Gegenwart eines weiteren Äquivalents NHC wurde in Lösung ein Gleichgewicht mit den bis-NHC-Addukten (NHC)$_2$·GaH$_3$ beobachtet. Im Gegensatz zu den entsprechenden Aluminiumhydriden
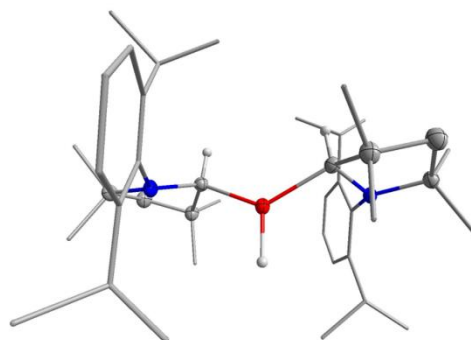


*Abbilung IX.5: Molekülstruktur von **III-8**.*

wurde jedoch keine NHC Ringerweiterungs- oder Ringöffnungsreaktion beobachtet. Durch die Substitution der Hydrid-Substituenten durch Chloride konnte mit zunehmendem Chlorierungsgrad eine erhöhte Stabilität der Addukte festgestellt werden. Die Reaktion von cAAC$^{Me}$ mit den NHC-stabilisierten Gallanen führt zur Insertion des cAAC$^{Me}$ in die Ga-H-Bindung unter Ausbildung von (NHC)·GaH$_2$(cAAC$^{Me}$H) (NHC = Me$_2$Im$^{Me}$ **III-5**, $i$Pr$_2$Im$^{Me}$ **III-6**, Dipp$_2$Im **III-7**) (siehe Scheme IX.2). Die Verbindungen **III-5** – **III-7** sind in Lösung bis 110 °C stabil und es wurde keine weitere Ringerweiterungs- und Ringöffnungsreaktion bzw. die reduktive Eliminierung von cAAC$^{Me}$H$_2$ beobachtet. Die Reaktion von (Dipp$_2$Im$^H$)·GaH$_3$ **III-4** mit zwei Äquivalenten cAAC$^{Me}$ führte selektiv zur Bildung des ersten monomeren Bisalkylgalliumhydrides (cAAC$^{Me}$H)$_2$GaH **III-8** (siehe Schema IX.2).
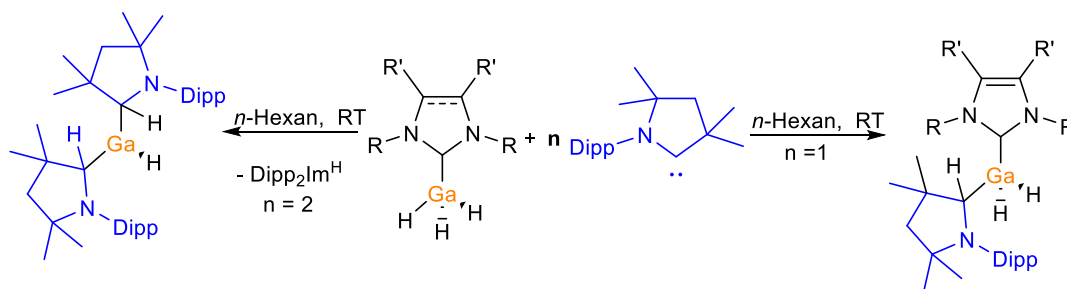
*Schema IX.2: Insertion von cAAC^{Me} in Ga-H-Bindungen.*

Die Reaktion der Mono- und Dichlorogallane (NHC)·GaH_2Cl und (NHC)·GaHCl_2 (NHC = *i*Pr_2Im^{Me}, Dipp_2Im) mit cAAC^{Me} führte in Abhängigkeit des sterischen Anspruches des NHC-Liganden zu unterschiedlichen Produkten. Für *i*Pr_2Im^{Me} wurde die Insertion von cAAC^{Me} in die Ga-H Bindung unter Bildung von (*i*Pr_2Im^{Me})·GaClH(cAAC^{Me}H) **III-16** und (*i*Pr_2Im^{Me})·GaCl_2(cAAC^{Me}H) **III-17** nachgewiesen. Im Gegensatz dazu führte die Reaktion der durch die



*Abbilung IX.6: Molekülstruktur von III-17.*

sterisch anspruchsvolleren Carbene Dipp_2Im und Dipp_2Im^H stabilisierten Chlorogallane mit zwei Äquivalenten cAAC^{Me} selektiv zur Bildung von (cAAC^{Me}H)_2GaCl **III-18**. Die Reaktion der entsprechenden Dichlorogallane mit cAAC^{Me} führte interessanterweise zu einem quantitativen Ligandenaustausch unter Bildung des Addukts (cAAC^{Me})·GaHCl_2 **III-15**.

Für (cAAC^{Me}H)_2GaH **III-8** wurde ein reversibler Isomerisierungsprozess in Lösung zwischen (cAAC^{Me}H)_2GaH *meso*-**III-8** und (cAAC^{Me}H)_2GaH *rac*-**III-8** über ein tetraedrisch koordiniertes Intermediat (cAAC^{Me})·GaH_2(cAAC^{Me}H) *int*-**III-8** beobachtet (siehe Schema IX.3).
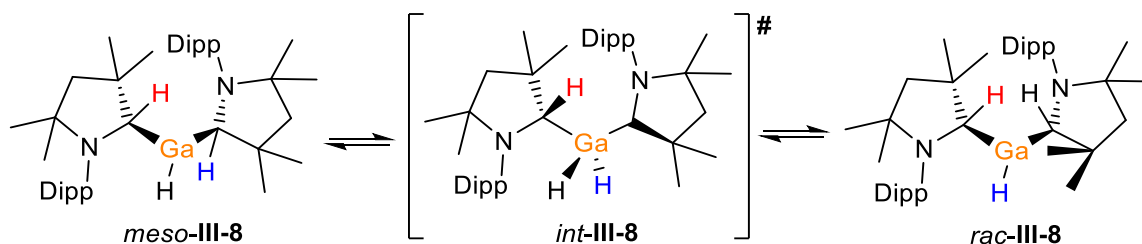
*Schema IX.3: Erwarteter Isomerisierungsprozess von (cAAC$^{Me}$H)$_2$GaH **III-8** in Lösung.*

Kapitel 4 beschreibt weitere Untersuchungen zur Synthese und Reaktivität Carben-stabilisierter Iodoalane und Iodogallane, welche zur Darstellung kationischer Aluminium- und Galliumdihydride geeignet sind. Die NHC-Iodotriele **IV-1** - **IV-6** wurden durch eine sehr effiziente Synthese ausgehend von NHC-stabilisierten Aluminium(III)- und Gallium(III)hydriden (NHC)·EH$_3$ (E = Al, Ga; NHC = Me$_2$Im$^{Me}$, $i$Pr$_2$Im, $i$Pr$_2$Im$^{Me}$, Dipp$_2$Im) und elementarem Iod bzw. Methyliodid dargestellt (siehe Scheme IX.4).
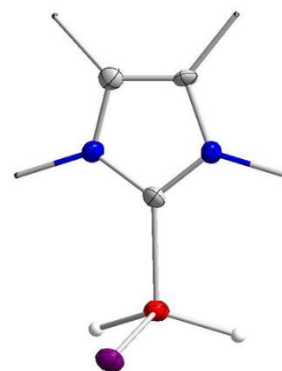


*Abbildung IX.7: Molekülstruktur von **IV-4**.*
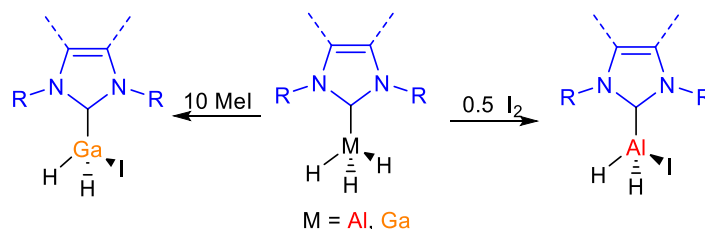


*Schema IX.4: Darstellung NHC stabilisierter Iodoalane- und Gallane.*

Die Reaktion der NHC-Iodotriele (NHC)·$EH_2I$ (E = Al, Ga), welche durch die weniger sterisch anspruchsvollen NHCs (NHC = $Me_2Im^{Me}$, $iPr_2Im$, $iPr_2Im^{Me}$) stabilisiert werden, mit einem zusätzlichen Äquivalent des entsprechenden NHCs führt zur Bildung der kationischen bis-NHC-Aluminium- und Galliumdihydride [(NHC)·$AlH_2$]$^+$I$^-$ (NHC = $Me_2Im^{Me}$ **IV-7**, $iPr_2Im$ **IV-8**, $iPr_2Im^{Me}$ **IV-9**) und [(NHC)$_2$·$GaH_2$]$^+$I$^-$ (NHC = $Me_2Im^{Me}$ **IV-10**, $iPr_2Im^{Me}$ **IV-11**) (siehe Schema IX.5). Um den Einfluss des sterischen
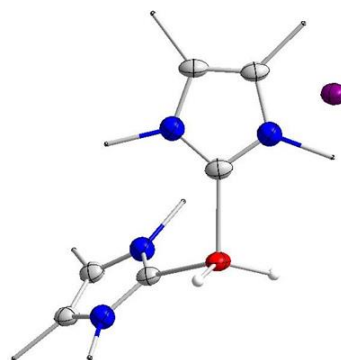


*Abbildung IX.8: Molekülstruktur von **IV-10**.*

Anspruchs des NHCs zu untersuchen, wurde das Addukt (Dipp$_2$Im)·$GaH_2I$ **IV-6** mit einem zusätzlichen Äquivalent Dipp$_2$Im umgesetzt. Aufgrund der Sterik der verwendeten Carbene führte die Umsetzung zur Umlagerung eines NHCs von *normaler* zu *abnormaler* Koordination unter Bildung des kationischen Galliumdihydrids [(Dipp$_2$Im)·$GaH_2$(*a*Dipp$_2$Im)]I **IV-12** (siehe Schema IX.5).
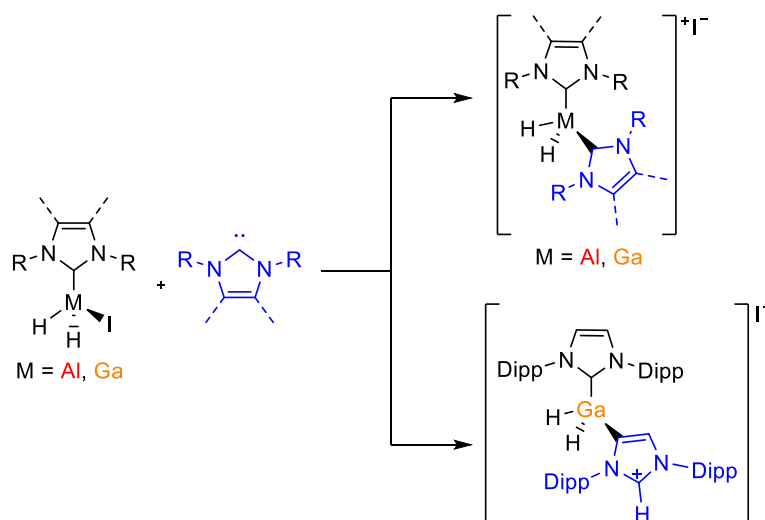


*Schema IX.5: Darstellung kationischer bis-NHC-stabilisierter Aluminium- und Galliumdihydride.*
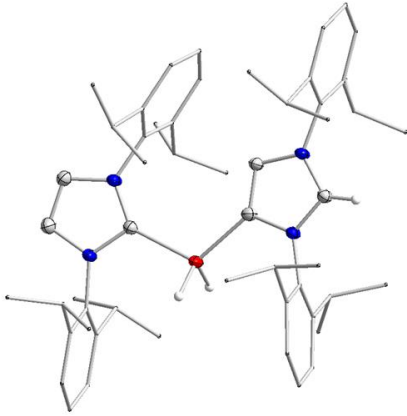
*Abbildung IX.9: Molekülstruktur von* **IV-12***.*

Für die Bildung der Kationen wird ein assoziativer Substitutionspfad vermutet, bei dem das zusätzliche NHC mit den vorliegenden NHC-Iodotrielen (NHC)·$EH_2I$ (E = Al, Ga) unter Bildung eines neutralen, fünffach koordinierten intermediären bis-NHC-Addukts (NHC)$_2$·$EH_2I$ (E = Al, Ga) reagiert. Die Stabilisierung des reaktiven Intermediates erfolgt durch die Eliminierung der guten Abgangsgruppe Iodid unter Freisetzung der stabilen tetraedrisch vierfach koordinierten Aluminium- und Galliumkationen (siehe Schema IX.6). Für das sterisch anspruchsvolle NHC Dipp$_2$Im wird eine zusätzliche Stabilisierung durch die Umlagerung eines koordinierenden NHCs von *normaler* zu *abnormaler* Koordination erreicht (siehe Schema IX.6).
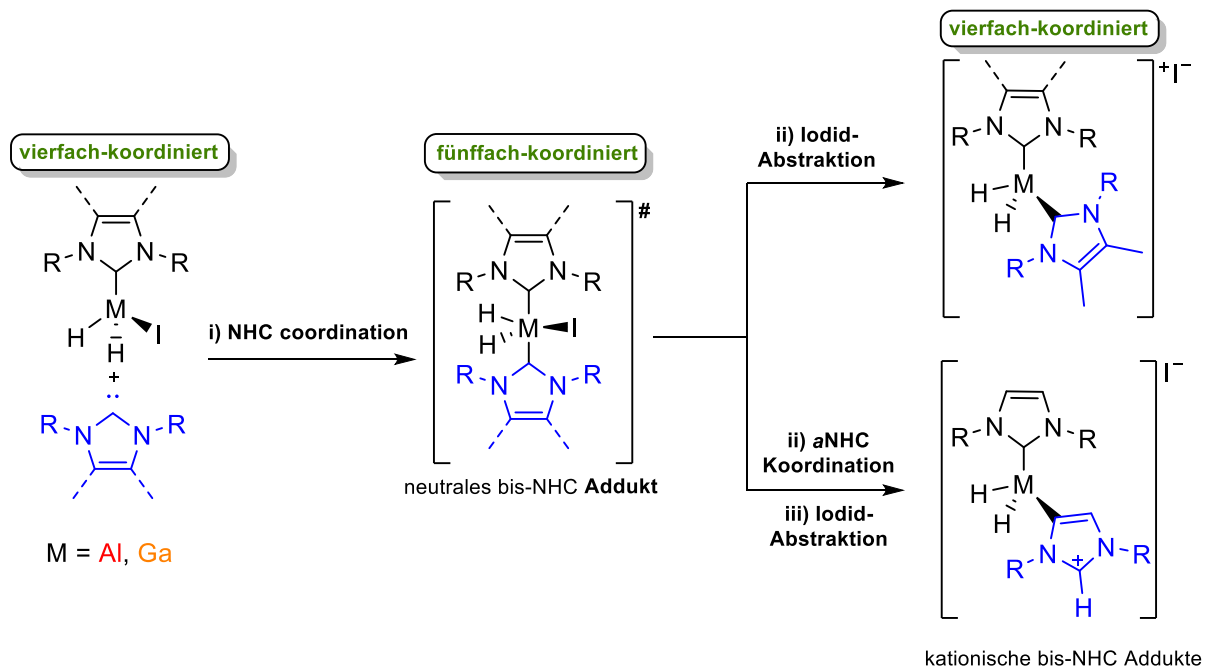


*Schema IX.6: Erwarteter Mechanismus der Darstellung kationischer bis-NHC-stabilisierter Aluminium- und Galliumdihydride.*

Im fünften Kapitel der Arbeit werden Untersuchungen zur Reduktion Cyclopentadienyl-substituierter Alane und Gallane mit Carbenen beschrieben. Die Darstellung NHC-stabilisierter Pentamethylcyclopentadienyl-Aluminium- und Galliumdihydride (NHC)·Cp*MH$_2$ (M = Al, Ga) erfolgte durch die direkte Umsetzung von (AlH$_2$Cp*)$_3$ mit den entsprechenden NHCs, bzw. durch Salzeliminierung ausgehend von (NHC)·GaH$_2$I mit KCp* (siehe Schema IX.7).
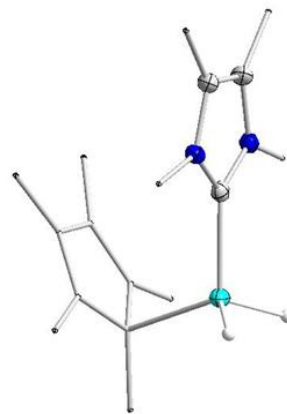


*Abbildung IX.10: Molekülstruktur von V-1.*
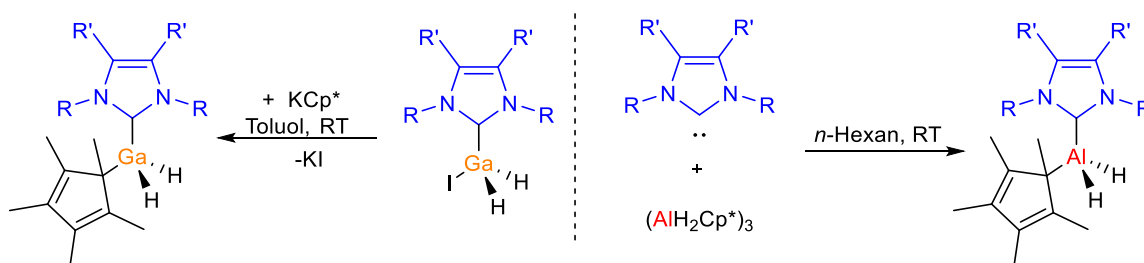


*Schema IX.7: Darstellung NHC stabilisierter Pentamethylcyclopentadienylaluminium- und galliumdihydride.*
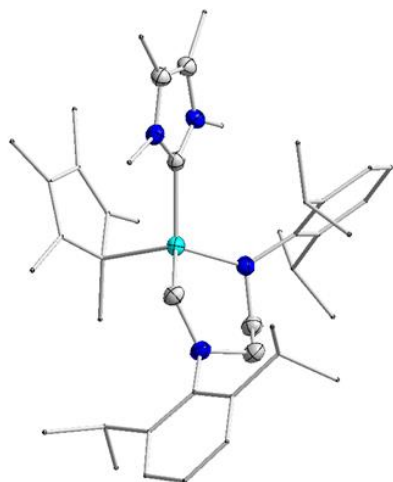


*Abbildung IX.11: Molekülstruktur von V-8.*

Die Alane **V-1** – **V-3** sind in Lösung bis zum Siedepunkt von Benzol (80 °C) stabil, wohingegen die Gallane **V-3** – **V-6** sich bei höheren Temperaturen unter reduktiver Eliminierung von Cp*H und Bildung von Cp*Ga$^I$ **V-11** zersetzen. Hierbei wird ein reversibles Gleichgewicht zwischen (NHC)·GaH$_3$ und (NHC)·Cp*$_2$GaH vermutet, wobei (NHC)·Cp*$_2$GaH der reduktiven Eliminierung von Cp*H unter Bildung von Cp*Ga$^I$ und freien NHC unterliegt. Die reduktive Eliminierung findet bevorzugt für sterisch anspruchsvolle NHCs (Dipp$_2$Im > $i$Pr$_2$Im$^{Me}$ > Me$_2$Im$^{Me}$) statt. Darüber hinaus wurde eine NHC Ringerweiterungsreaktion des im Rückgrat gesättigten Carbens Dipp$_2$Im$^H$ bei der Reaktion mit (AlH$_2$Cp*)$_3$ unter Ausbildung von

(RER-Dipp$_2$Im$^H$H$_2$)AlCp\* **V-7** bzw. (Me$_2$Im$^{Me}$)·AlCp\*(RER-Dipp$_2$Im$^H$H$_2$) **V-8** (aus der Reaktion mit einem weiteren Äquivalent Me$_2$Im$^{Me}$) beobachtet. Darüber hinaus wurde die Reaktivität der Addukte (NHC)·Cp\*EH$_2$ (E = Al. Ga) gegenüber cAAC$^{Me}$ untersucht. Für den Alan-Komplex **V-1**, der durch das kleine NHC Me$_2$Im$^{Me}$ stabilisiert wird, wurde die Insertion von cAAC$^{Me}$ in die Al-H-Bindung unter selektiver Bildung der rac-Isomere
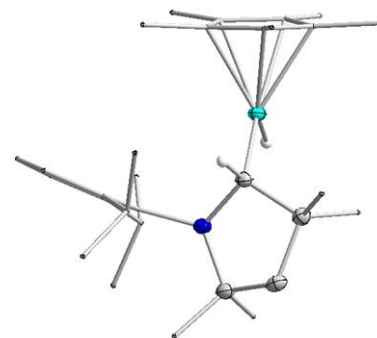


*Abbildung IX.12: Molekülstruktur von **V-10**.*

(Me$_2$Im$^{Me}$)·AlHCp\*(cAAC$^{Me}$H) *rac*-**V-9** beobachtet (siehe Schema IX.8). Das Erwärmen von *rac*-**V-9** in Lösung führte zur irreversiblen Isomerisierung unter Bildung von *meso*-**V-9**. Die Reaktion der durch die sterisch anspruchsvolleren NHCs *i*Pr$_2$Im$^{Me}$ und Dipp$_2$Im stabilisierten Addukte **V-2** und **V-3** mit cAAC$^{Me}$ führte hingegen zur Bildung des außergewöhnlich stabilen Insertionsproduktes (cAAC$^{Me}$H)Cp\*AlH **V-10** unter Abspaltung des NHC-Liganden (siehe Scheme IX.8).
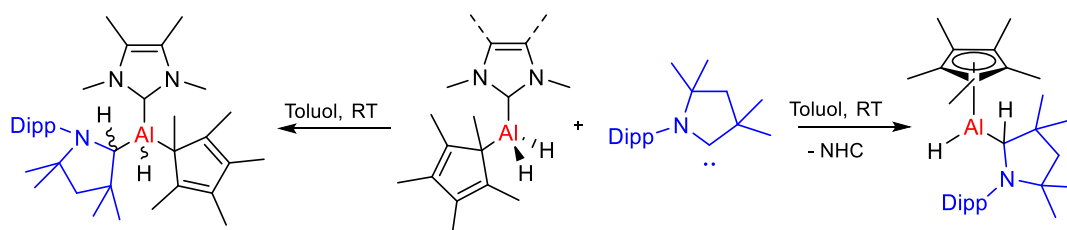


*Schema IX.8: Oxidative Addition von Al-H and das cAAC$^{Me}$ Carben-Kohlenstoffatom.*

Die Reaktion der Galliumhydride (NHC)·Cp\*GaH$_2$ **V-3** - **V-6** mit cAAC$^{Me}$ führte stattdessen direkt zur reduktiven Eliminierung von cAAC$^{Me}$H$_2$ unter Ausbildung von Cp\*Ga$^I$ **V-11** (siehe Schema IX.9). Es wird ein Reaktionsweg über ein sehr reaktives, intermediäres Insertionsprodukt (cAAC$^{Me}$H)GaHCp\* int-**V-11** vermutet, welches sofort einer reduktiven Eliminierung von cAAC$^{Me}$H$_2$ unter Bildung des stabilen Cp\*Ga$^I$ unterliegt. Die reduktive Eliminierung sollte sowohl entropisch, als auch thermodynamisch begünstigt sein. Dies stellt die erste bekannte metallfreie Reduktion von Ga$^{III}$ zu Ga$^I$ mit einem Carben als Wasserstoffakzeptor unter milden Bedingungen dar.
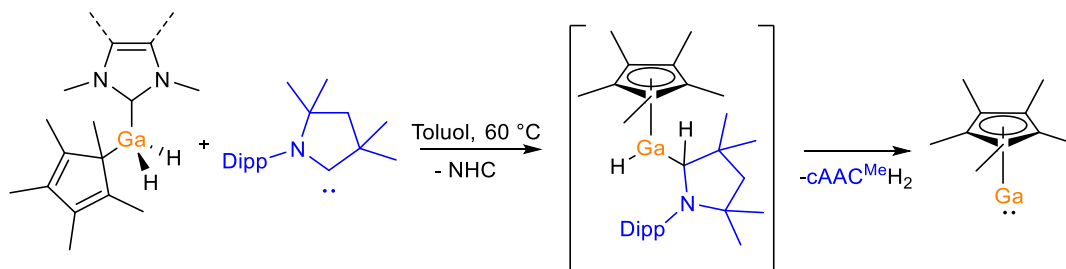
*Schema IX.9: Metallfreie Reduktion von Ga$^{III}$ zu Ga$^{I}$ mit cAAC$^{Me}$ als Reduktionsmittel.*

Im Rahmen dieser Arbeit wurden neutrale und kationische Carben-stabilisierte Alane und Gallane eingehend untersucht. Durch das Einführen elektronegativer $\pi$-Donor-Substituenten (Cl$^-$, I$^-$, OR$^-$, NR$_2^-$) und Untersuchungen zur thermischen Belastbarkeit dieser Verbindungen wurde nachgewiesen, dass sich die Stabilität der Alane bzw. Gallane durch eine derartige Substitution deutlich erhöht. Untersuchungen zur Reaktivität der NHC-Addukte gegenüber cAAC$^{Me}$ brachte diverse Insertionsprodukte des Carbens in Al-H bzw. Ga-H-Bindungen hervor. Ferner konnte das erste cAAC$^{Me}$-stabilisierte Dichlorogalliumhydrid dargestellt werden. Darüber hinaus wurde ein erster Nachweis erbracht, dass Carbene gezielt zur (formalen) Reduktion von Hydriden der höheren Homologen der Gruppe 13 verwendet werden können. So wurde die Synthese von Cp*Ga$^{I}$ aus der Reaktion von (NHC)·Cp*GaH$_2$ mit cAAC$^{Me}$ entwickelt. In Zukunft könnte dieser Reaktionspfad zur Darstellung niedervalenter Verbindungen der Triele Aluminium und Gallium von Interesse sein.

# 10 APPENDIX

## ABBRIVIATIONS

**_N_-Heterocyclic Carbenes**

| | |
|---|---|
| Me$_2$Im | 1,3-dimethylimidazolin-2-ylidene |
| _i_Pr$_2$Im | 1,3-di-_iso_-propylimidazolin-2-ylidene |
| _t_Bu$_2$Im | 1,3-ditertbutylimidazolin-2-ylidene |
| _t_Bu$_2$Im$^H$ | 1,3-ditertbutylimidazolidine-2-ylidene |
| Mes$_2$Im | 1,3-dimesitylimidazolin-2-ylidene |
| Mes$_2$Im$^H$ | 1,3-dimesitylimidazolidine-2-ylidene |
| Dipp$_2$Im | 1,3-(2,6-di-_iso_-propylphenyl)imidazolin-2-ylidene |
| Dipp$_2$Im$^H$ | 1,3-(2,6-di-_iso_-propylphenyl)imidazolidine-2-ylidene |
| _i_Pr$_2$Im$^{Me}$ | 1,3-di-_iso_-propyl-4,5-dimethylimidazolin-2-ylidene |
| Me$_2$Im$^{Me}$ | 1,3,4,5-tetramethylimidazolin-2-ylidene |
| cAAC$^{Me}$ | 1-(2,6-di-_iso_-propylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene |

**General**

| | |
|---|---|
| Ar | aryl |
| Bn | benzylic |
| cat | catecholato |
| cAAC | cyclic alkyl amino carbene |
| C$_6$D$_6$ | deuterated benzene |
| COD | 1,5-cyclooctadiene |

| | |
|---|---|
| COSY | correlation spectroscopy |
| CSD | Cambridge Structural Databse |
| Cy | cyclohexyl |
| Cp | cyclopentadien |
| Cp* | pentamethylcyclopentadien |
| DFT | Density Functional Theory |
| DIBAL | di-*iso*-butylaluminium hydride |
| Dipp | 2,6-di-*iso*-propylphenyl |
| DMAP | 4-dimethylaminopyridine |
| DME | dimethoxyethane |
| dppe | 1,2-bis(diphenylphosphino)ethane |
| dtbpy | 4,4'-di-*tert*-butyl-2,2'-bipyridine |
| EPR | electron paramagnetic resonance |
| Et | ethyl |
| $Et_2O$ | diethylether |
| eq. | Equivalents |
| EWG | electron withdrawing group |
| h | hour |
| HMBC | heteronuclear multiple bond correlation |
| HOMO | highest occupied molecule orbital |
| HRMS | High-resolution mass spectrometry |
| HSQC | heteronuclear single quantum coherence |
| *i*Pr | *iso*-propyl |
| *J* | coupling constant in NMR soectroscopy, Hz |

| | |
|---|---|
| LUMO | lowest unoccupied molecule orbital |
| M | molar concentration, 1 M = 1 mol/l |
| Me | methyl |
| MeCN | acetonitrile |
| Mes | mesityl |
| MesOH | mesitol |
| MHz | megahertz |
| min | minute |
| mol% | percentage by amount |
| MTBE | methyl *tert*-butyl ether |
| m/z | mass to charge ratio in MS |
| NBO | natural bond orbital |
| *n*Bu | *n*-butyl |
| neop | neopentylglycolato |
| NHC | *N*-hetreocyclic carbene |
| NMR | Nuclear magnetic resonance |
| OTf | triflate |
| Ph | phenyl |
| pin | pinacolato |
| ppm | parts per million |
| quin | qinolidine |
| RER | ring expansion reaction |
| ROR | ring opening reaction |
| r.t. | room temperature |

THF        tetrahydrofuran

Tipp       2,4,6-tri*iso*propylphenyl

TMS       trimethylsilyl

Tol         toluene

*t*Bu        *tert*-butyl

wt%       percent by weight

xy         xylyl

# LIST OF COMPOUNDS

**CHAPTER 2**

($i$Pr$_2$Im)·AlH$_2$(NiPr$_2$) **II-1**

($i$Pr$_2$Im)·AlH$_2$(NPh$_2$) **II-2**

($i$Pr$_2$Im)·AlH$_2$(N{SiMe$_3$}$_2$) **II-3**

(Dipp$_2$Im)·AlH$_2$(NiPr$_2$) **II-4**

(Dipp$_2$Im)·AlH$_2$(NPh$_2$) **II-5**

(Dipp$_2$Im)·AlH$_2$(N{SiMe$_3$}$_2$) **II-6**

($i$Pr$_2$Im)·AlH$_2$(OMes) **II-7**

($i$Pr$_2$Im)·AlH(OMes)$_2$ **II-8**

(Dipp$_2$Im)·AlH$_2$(OMes) **II-9**

(Dipp$_2$Im)·AlH(OMes)$_2$ **II-10**

[Dipp$_2$ImH][Al(OMes)$_4$] **II-11**

**CHAPTER 3**

($Me_2Im^{Me}$)·$GaH_3$ **III-1**

($iPr_2Im$)·$GaH_3$ **III-2**

($iPr_2Im^{Me}$)·$GaH_3$ **III-3**

($Dipp_2Im^H$) $GaH_3$ **III-4**

($Me_2Im^{Me}$)·$GaH_2$($cAAC^{Me}H$) **III-5**

($iPr_2Im^{Me}$)·$GaH_2$($cAAC^{Me}H$) **III-6**

($Dipp_2Im$)·$GaH_2$($cAAC^{Me}H$) **III-7**

($cAAC^{Me}$)$_2$GaH **III-8**

($iPr_2Im^{Me}$)·$GaH_2Cl$ **III-9**

($Dipp_2Im$)·$GaH_2Cl$ **III-10**

($Dipp_2Im^H$)·$GaH_2Cl$ **III-11**

($iPr_2Im^{Me}$)·$GaHCl_2$ **III-12**

($Dipp_2Im$)·$GaHCl_2$ **III-13**

($Dipp_2Im^H$)·$GaHCl_2$ **III-14**

($cAAC^{Me}$)·$GaHCl_2$ **III-15**

($iPr_2Im^{Me}$)GaHCl($cAAC^{Me}H$) **III-16**

($iPr_2Im^{Me}$)GaCl_2($cAAC^{Me}H$) **III-17**

($cAAC^{Me}H$)$_2$GaCl **III-18**


**CHAPTER 4**

($Me_2Im^{Me}$)·$AlH_2I$ **IV-1**

($iPr_2Im$)·$AlH_2I$ **IV-2**

($iPr_2Im^{Me}$)·$AlH_2I$ **IV-3**

(Me$_2$Im$^{Me}$)·GaH$_2$I **IV-4**

(*i*Pr$_2$Im$^{Me}$)·GaH$_2$I **IV-5**

(Dipp$_2$Im)·GaH$_2$I **IV-6**

[(Me$_2$Im$^{Me}$)$_2$·AlH$_2$]I **IV-7**

[(*i*Pr$_2$Im)$_2$·AlH$_2$]I **IV-8**

[(*i*Pr$_2$Im$^{Me}$)$_2$·AlH$_2$]I **IV-9**

[(Me$_2$Im$^{Me}$)$_2$·GaH$_2$]I **IV-10**

[(*i*Pr$_2$Im$^{Me}$)$_2$·GaH$_2$]I **IV-11**

[(Dipp$_2$Im)·GaH$_2$(aDipp$_2$Im)]I **IV-12**


## CHAPTER 5

(Me$_2$Im$^{Me}$)·Cp*AlH$_2$ **V-1**

(*i*Pr$_2$Im$^{Me}$)·Cp*AlH$_2$ **V-2**

(Dipp$_2$Im)·Cp*AlH$_2$ **V-3**

(Me$_2$Im$^{Me}$)·Cp*GaH$_2$ **V-4**

(*i*Pr$_2$Im$^{Me}$)·Cp*GaH$_2$ **V-5**

(Dipp$_2$Im)·Cp*GaH$_2$ **V-6**

(RER-Dipp$_2$Im$^H$H$_2$)AlCp* **V-7**

(Me$_2$Im$^{Me}$)·AlCp*(RER-Dipp$_2$Im$^H$H$_2$) **V-8**

(Me$_2$Im$^{Me}$)·GaHCp*(cAAC$^{Me}$H) rac-**V-9**

(Me$_2$Im$^{Me}$)·GaHCp*(cAAC$^{Me}$H) meso-**V-9**

(cAAC$^{Me}$H)Cp*AlH **V-10**

Cp*Ga$^I$ **V-11**

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**N-Heterocyclic Carbene and Cyclic (Alkyl)(Amino)Carbene Adducts of Gallium Hydrides, Gallium Chlorides and Gallium Hydrochlorides**

A. Hock, L. Werner, C. Luz and U. Radius, *Dalton Trans.*, 2020.

**DOI:** 10.1039/D0DT02070B

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**Hydride Amide and Hydride Phenolate Complexes of NHC Coordinated Aluminum**

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# -APPENDIX-

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