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Bis-NHC Aluminium and Gallium Dihydride Cations $[(\mathrm{NHC})_2\mathrm{EH}_2]^+$ (E = Al, Ga)

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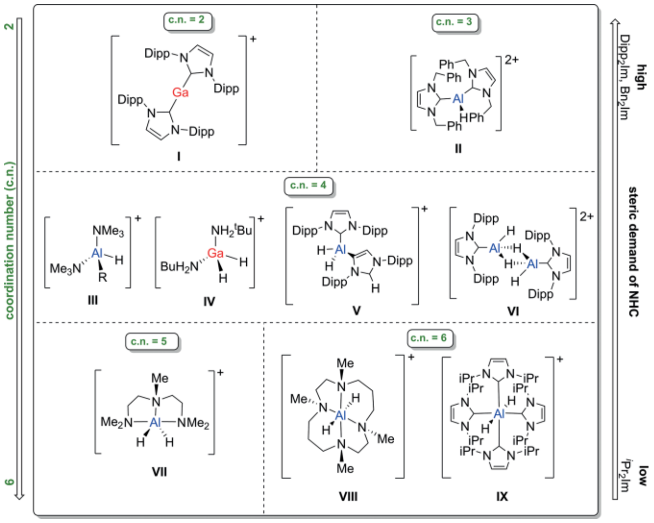
Abstract: The NHC alane and gallane adducts $(\mathrm{NHC})\cdot\mathrm{AlH}_2\mathrm{I}$ (NHC = $\mathrm{Me}_2\mathrm{Im}^{\mathrm{Me}}$ **7**, $i\mathrm{Pr}_2\mathrm{Im}$ **8**, $i\mathrm{Pr}_2\mathrm{Im}^{\mathrm{Me}}$ **9**) and $(\mathrm{NHC})\cdot\mathrm{GaH}_2\mathrm{I}$ (NHC = $\mathrm{Me}_2\mathrm{Im}^{\mathrm{Me}}$ **10**, $i\mathrm{Pr}_2\mathrm{Im}^{\mathrm{Me}}$ **11**, $\mathrm{Dipp}_2\mathrm{Im}$ **12**; $R_2\mathrm{Im}$ = 1,3-di-organyl-imidazolin-2-ylidene; Dipp = 2,6-diisopropylphenyl; *i*Pr = isopropyl; $\mathrm{Me}_2\mathrm{Im}^{\mathrm{Me}}$ = 1,3,4,5-tetra-methyl-imidazolin-2-ylidene) were prepared either by the simple yet efficient reaction of the NHC adduct $(\mathrm{NHC})\cdot\mathrm{AlH}_3$ with elemental iodine or by the treatment of $(\mathrm{NHC})\cdot\mathrm{GaH}_3$ with an excess of methyl iodide at room temperature. The reaction of one equivalent of the group 13 NHC complexes with an additional equivalent of the corresponding NHC afforded cationic aluminium and gallium hydrides $[(\mathrm{NHC})_2\cdot\mathrm{AlH}_2]^+\mathrm{I}^-$ (NHC = $\mathrm{Me}_2\mathrm{Im}^{\mathrm{Me}}$ **13**, $i\mathrm{Pr}_2\mathrm{Im}$ **14**, $i\mathrm{Pr}_2\mathrm{Im}^{\mathrm{Me}}$ **15**) and $[(\mathrm{NHC})_2\cdot\mathrm{GaH}_2]^+\mathrm{I}^-$ (NHC = $\mathrm{Me}_2\mathrm{Im}^{\mathrm{Me}}$ **16**, $i\mathrm{Pr}_2\mathrm{Im}^{\mathrm{Me}}$ **17**) and the *normal* and *abnormal* NHC coordinated compound $[(\mathrm{Dipp}_2\mathrm{Im})\cdot\mathrm{GaH}_2(a\mathrm{Dipp}_2\mathrm{Im})]^+\mathrm{I}^-$ **18**. Compounds **7**–**18** were isolated and characterized by means of elemental analysis, IR and multinuclear NMR spectroscopy and by X-ray diffraction of the compounds **7**, **9**, **10**, **15**, **16** and **18**.

Introduction

Aluminum and gallium hydrides are important reagents in organic and inorganic synthesis, e.g. for reductions and hydride transfer,[1,2] as well as important materials, in particular for hydride storage.[3] 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 co-worker synthesized and fully characterized the six- and five-coordinated aluminium hydride cations $[\{\mathrm{MeNCH}_2\mathrm{CH}_2\mathrm{N(Me)CH}_2\mathrm{CH}_2\mathrm{CH}_2\}_2\cdot\mathrm{AlH}_2]^+$ **VIII** and $[\{\mathrm{MeN(CH}_2\mathrm{CH}_2\mathrm{NMe}_2)\}\cdot\mathrm{AlH}_2]^+$ **VII** as their aluminium hydride $[\mathrm{AlH}_4]^-$ salts (see Scheme 1, **VII** & **VIII**).[4] The first four-coordinated aluminium hydride cation $[(\mathrm{NMe}_3)_2\cdot\mathrm{AlH}_2]^+$ **III** was reported by Roesky *et al.*, synthesized from a rather unforeseeable reaction. A mixture of $(\mathrm{NMe}_3)\cdot\mathrm{AlH}_2\mathrm{Cl}$, $(\mathrm{NMe}_3)\cdot\mathrm{AlH}_3$ and $t\mathrm{BuC{\equiv}CLi}$ leads to formation of $[(\mathrm{NMe}_3)_2\cdot\mathrm{AlH}_2]_2[(\mathrm{AlH})_8(\mathrm{CCH}_2t\mathrm{Bu})_6]$, in which the $[\mathrm{AlH}_2]^+$ cation is stabilized by two *Lewis*-bases NMe_3 (see Figure 1, **III**) and the carbaalanate cluster counterion $[(\mathrm{AlH})_8(\mathrm{CCH}_2t\mathrm{Bu})_6]^{2-}$, formed in course of the reaction, serves as a bulky, non-coordinating anion.[5] The first authenticated cationic gallium hydrides were presented by Parsons and co-workers.[6] Treatment of lithium gallium hydride with $[\mathrm{N}t\mathrm{BuH}_3]\mathrm{Cl}$ or $[\mathrm{N}s\mathrm{BuH}_3]\mathrm{Cl}$ leads to the formation of the salts $[(\mathrm{N}t\mathrm{BuH}_2)_2\mathrm{GaH}_2]^+$ and $[(\mathrm{N}s\mathrm{BuH}_2)_2\mathrm{GaH}_2]^+$ (see Figure 1, **IV**) as their chloride salts.[6]



Scheme 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 $[(i\mathrm{Pr}_2\mathrm{Im})_4\cdot\mathrm{AlH}_2]^+$ **IX** as a side product of the reaction of lithium aluminium hydride with an excess of $i\mathrm{Pr}_2\mathrm{Im}$ ($i\mathrm{Pr}_2\mathrm{Im}$ = 1,3-diisopropyl-imidazolin-2-ylidene, see Scheme 1, **IX**).[7] Stephan *et al.* presented recently a dinuclear dicationic aluminium hydride $[(\mathrm{Dipp}_2\mathrm{Im})\cdot\mathrm{AlH}(\mu\text{-H})]_2^{2+}$ **VI** in $[(\mathrm{Dipp}_2\mathrm{Im})\cdot\mathrm{AlH}(\mu\text{-H})]_2[\mathrm{B(C}_6\mathrm{F}_5)_4]_2$ {$\mathrm{Dipp}_2\mathrm{Im}$ = 1,3-bis(2,6-diisopropyl-phenyl)imidazolin-2-ylidene} and a three-coordinated mononuclear dication $[(\mathrm{Bn}_2\mathrm{Im})_2\cdot\mathrm{AlH}]^{2+}$ ($\mathrm{Bn}_2\mathrm{Im}$ = 1,3-dibenzylimidazolin-2-ylidene) in $[(\mathrm{Bn}_2\mathrm{Im})_2\cdot\mathrm{AlH}]_2\text{-}[\mathrm{B(C}_6\mathrm{F}_5)_4]$ **II** (see Scheme 1, **VI** & **II**).[8] Jones and Stasch *et al.*

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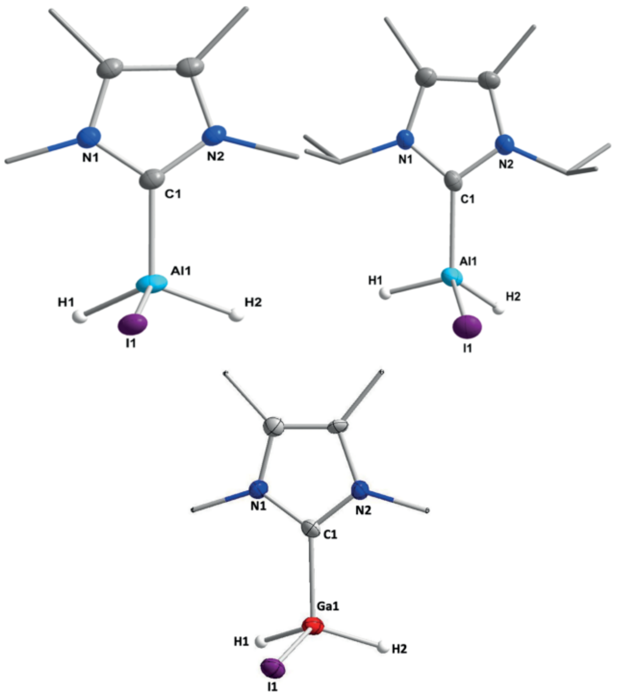


Figure 1. Molecular structure of (Me$_2$Im^{Me})•AlH$_2$I **7** (left), (*i*Pr$_2$Im^{Me})•AlH$_2$I **9** (right) and (Me$_2$Im^{Me})•GaH$_2$I **10** (down) in the solid state (ellipsoids set at the 50 % probability level). Selected bond lengths [Å] and angles [°]: **7**: C1–Al1 2.025(2), Al1–H1 1.61(4), 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); **9**: 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); **10**: Ga–C1 2.036(4), Ga–H1 1.52(6), Ga–H2 1.44(7), Ga–I 2.6415(6). C1–Ga–H1 109(2), C1–Ga–H2 108(2), C1–Ga–I 100.07(13), H1–Ga–H2 122(3), H1–Ga–I 110(2), H2–Ga–I 105(2).

reported the monocationic aluminium hydride [(Dipp$_2$Im)•AlH$_2$(*a*Dipp$_2$Im)]$^+$ **V** ("*a*" denotes "abnormal coordination") which is stabilized by one *normal* and one *abnormal* coordinated NHC (see Scheme 1, **V**).[9] Furthermore, Krossing and Jones *et al.* disclosed recently the synthesis of a "naked" Ga^I cation [(Dipp$_2$Im)$_2$Ga]$^+$ **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 1, **I**).[10] Thus, NHC stabilized cationic aluminium hydrides are rather scarce and NHC stabilized cationic gallium hydrides are currently unknown.

We[7,11] and others[12] investigate currently group 13 metal compounds (M = Al, Ga, In) which are stabilized with strong σ-donating NHC-ligands. The coordination of NHCs, for example, to alanes and gallanes leads to the synthesis of stable NHC metal hydride adducts.[7,11,12] 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,[13] for example the dialane [(Dipp$_2$Im)•AlH$_2$]$_2$ which was reported by Jones *et al.*[12,14] However, the formation of cationic aluminium and gallium dihydrides is rare and stabilization of [EH$_2$]$^+$ with two strong σ-donating NHC-ligands should lead to accessible hydroalane and hydrogallane cations. Herein we present the formation of such cationic bis-NHC aluminium and gallium hydrides from the reaction of (NHC)•AlH$_2$I and (NHC)•GaH$_2$I with additional NHC for the carbenes Me$_2$Im^{Me}, *i*Pr$_2$Im, *i*Pr$_2$Im^{Me}, and Dipp$_2$Im.

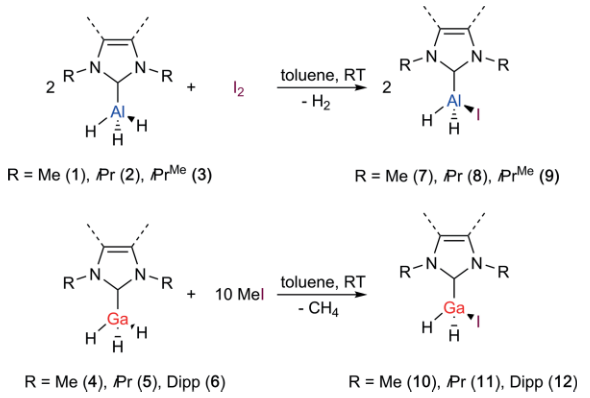
Results and Discussion

Cationic bis-NHC stabilized aluminium and gallium hydrides [(NHC)$_2$EH$_2$]$^+$ (E = Al, Ga) should be electronically and sterically saturated. Thus, our strategy was to synthesize adducts of the type (NHC)•EH$_2$I (E = Al, Ga) with a good leaving group iodide as precursor. Syntheses of NHC stabilized aluminium and gallium hydride chlorides are well known in the literature. NHC stabilized mono- and dichloroalanes and gallanes (NHC)•EH$_2$Cl and (NHC)•EHCl$_2$ (E = Al, Ga) are either accessible by the reaction of the NHCs with in situ generated "EH$_2$Cl" and "EHCl$_2$" or by dismutation between (NHC)•EH$_3$ and (NHC)•ECl$_3$ (E = Al, Ga).[9,12d,15] For the synthesis of NHC-stabilized iodoalanes only a few examples are available in the literature,[9,16] e.g. a report by Jones and Stasch *et al.* on the synthesis of (NHC)•AlH$_2$I adducts (NHC = Mes$_2$Im, Dipp$_2$Im) by dismutation between two equivalents of (NHC)•AlH$_3$ and one equivalent (NHC)•AlI$_3$. For the synthesis of diiodoalanes (NHC)•AlHI$_2$ (NHC = Mes$_2$Im, Dipp$_2$Im) the corresponding NHC stabilized aluminium hydrides were treated with an excess of methyl iodide. However, for the heavier gallium analogues only one example of a NHC stabilized iodogallane was presented in the literature so far, i.e. (Mes$_2$Im)•GaH$_2$I, which was prepared from the reaction of metastable "Ga^{I}I" with (Mes$_2$Im)•GaH$_3$.[16]

We were interested to develop a simple synthetic route to obtain the NHC adducts (NHC = Me$_2$Im^{Me}, *i*Pr$_2$Im, *i*Pr$_2$Im^{Me}) of iodoalane and iodogallane (NHC)•MH$_2$I (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$_2$Im^{Me} **1**, *i*Pr$_2$Im **2**, *i*Pr$_2$Im^{Me} **3**) with 0.5 equivalents of elemental iodine I$_2$ in toluene at room temperature. Straight after the addition of iodine, dissolved in minimum amounts of toluene, to a toluene solution of **1**–**3**, respectively, the solution discolored. After 15 min stirring at room temperature, all volatiles were removed *in vacuo* and the compounds (NHC)•AlH$_2$I (NHC = Me$_2$Im^{Me} **7**, *i*Pr$_2$Im **8**, *i*Pr$_2$Im^{Me} **9**) were isolated as colorless powders in excellent yields (**7**: 88 %, **8**: 97 %, **9**: 86 %) and purity (see Scheme 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} **10**, *i*Pr$_2$Im^{Me} **11**, Dipp$_2$Im **12**) 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 colourless compounds (NHC)•GaH$_2$I (NHC= Me$_2$Im^{Me} **10**, *i*Pr$_2$Im^{Me} **11**, Dipp$_2$Im **12**) within 30 min at room temperature in very good (**10**: 88 %, **11**: 76 %) to quantitative (**12**: 99 %) yield (see Scheme 2). The compounds **7**–**12** were characterized by NMR spectroscopy, IR spectroscopy, and elemental analysis. All new compounds show



Scheme 2. Synthesis of (NHC)•AlH$_2$I (NHC= Me$_2$Im^{Me} **7**, *i*Pr$_2$Im **8**, *i*Pr$_2$Im^{Me} **9**) and (NHC)•GaH$_2$I (NHC= Me$_2$Im^{Me} **10**, *i*Pr$_2$Im^{Me} **11**, Dipp$_2$Im **12**).

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 **7**–**12** are summarized in Table 1 and compared to their parent compounds **1**–**6**. The ^{27}Al{^{1}H} NMR resonances of the compounds **7**-**9** in solution were found at δ = 107.8 (**7**) ppm, 109.6 (**8**) ppm, and 109.0 (**9**) ppm. The signals are in good accordance with the literature-known resonances of NHC stabilized tetrahedral coordinated alanes, which lead to signals in the range of δ = 100 and 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 **7**–**12** were detected at δ = 4.54 (**7**) ppm, 4.63 ppm (**8**), 4.70 (**9**) ppm, 4.81 (**10**) ppm, 5.00 (**11**) ppm, and 4.13 (**12**) ppm, which are only slightly shifted compared to their corresponding metal hydride compounds (**1**: 4.48 ppm, **2**: 4.53 ppm, **3**: 4.60 ppm, **4**: 4.51 ppm, **5**: 4.66 ppm, **6**: 3.73 ppm).[7,12d] The characteristic E-H (E = Al, Ga) stretching vibrations of **7**–**12** were observed in the range between 1779–1889 cm^{-1} (see Table 1). The values compare well with Al–H respectively Ga–H stretches for related compounds such as (Dipp$_2$Im)•AlH$_2$I at 1830 cm^{-1} and (Mes$_2$Im)•GaH$_2$I at 1863 cm^{-1}.[9,16]

Single crystals of the compounds (Me$_2$Im^{Me})•AlH$_2$I **7**, (*i*Pr$_2$Im^{Me})•AlH$_2$I **9** and (Me$_2$Im^{Me})•GaH$_2$I **10** were grown by slow evaporation of saturated solutions in benzene at room temperature. The molecular structures of **7**, **9**, and **10** reveal the expected four coordinated NHC adducts (see Figure 1). (Me$_2$Im^{Me})•AlH$_2$I **7** crystallizes in the space group *C*2/*c*, (*i*Pr$_2$Im^{Me})•AlH$_2$I **9** in the orthorhombic space group P_{bca} and (Me$_2$Im^{Me})•GaH$_2$I **10** in the monoclinic space group P2$_1$/*n*. These molecules adopt a tetrahedral structure at the metal center, spanned by the NHC, two hydrogen atoms, and the iodine. The M–C$_{NHC}$ (M = Al, Ga) bond lengths of 2.025(2) Å (**7**), 2.039(3) Å (**9**) and 2.036(4) (**10**) differ only marginally from the bond lengths observed in the NHC aluminum(III) and gallium(III) hydride adducts.[17]

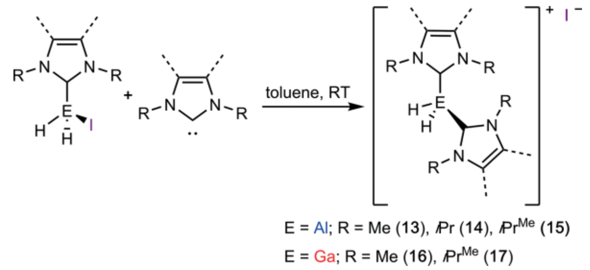
The alane adducts **7**–**9** are stable in solution at least up to the boiling point of toluene and show no decomposition or change in the ^{1}H NMR spectra. Heating the gallium compounds **10**–**12** in benzene to 80 °C leads to irreversible decomposition, which afforded elemental gallium as dark 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$_3$ **2** with an additional equivalent of the small NHC *i*Pr$_2$Im or the sterically demanding NHC Dipp$_2$Im.[7] Thus, we were interested in the reactivity of the NHC stabilized iodo alanes and gallanes with respect to their behavior upon addition of further NHC. The reaction of the alane compounds (Me$_2$Im^{Me})•AlH$_2$I **7**, (*i*Pr$_2$Im)•AlH$_2$I **8** and (*i*Pr$_2$Im^{Me})•AlH$_2$I **9** 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 was observed. These colorless precipitates were isolated and identified as the cationic bis-NHC adducts [(Me$_2$Im^{Me})$_2$•AlH$_2$]$^+$I– **13**, [(*i*Pr$_2$Im)$_2$•AlH$_2$]+I– **14** and [(*i*Pr$_2$Im^{Me})$_2$•AlH$_2$]+I– **15** (see Scheme 3). Similarly, the reaction of (Me$_2$Im^{Me})•GaH$_2$I **10** and (*i*Pr$_2$Im^{Me})•GaH$_2$I **11** with an additional equivalent of the NHC in toluene leads to the cationic bis-NHC adducts [(Me$_2$Im^{Me})$_2$•GaH$_2$]+I– **16** and [(*i*Pr$_2$Im^{Me})$_2$•GaH$_2$]+I– **17** as colorless solids in good yield and purity (Scheme 3). These compounds are the first examples of NHC stabilized cationic gallium dihydrides.

The compounds **13**–**17** are nearly insoluble in aromatic solvents such as benzene and toluene, only sparingly soluble and sufficiently stable in more polar solvents such as thf, aceto-

Table 1. Selected NMR [ppm] and IR [cm^{-1}] shifts of the compounds (Me$_2$Im^{Me})•AlH$_3$ **1**, (*i*Pr$_2$Im)•AlH$_3$ **2**, (*i*Pr$_2$Im^{Me})•AlH$_3$ **3**, (Me$_2$Im^{Me})•GaH$_3$ **4**, (*i*Pr$_2$Im^{Me})•GaH$_3$ **5**, (Dipp$_2$Im)•GaH$_3$ **6**, (Me$_2$Im^{Me})•AlH$_2$I **7**, (*i*Pr$_2$Im)•AlH$_2$I **8**, (*i*Pr$_2$Im^{Me})•AlH$_2$I **9**, (Me$_2$Im^{Me})•GaH$_2$I **10**, (*i*Pr$_2$Im^{Me})•GaH$_2$I **11** and (Dipp$_2$Im)•GaH$_2$I **12**.

	Al–H ^{1}H{^{27}Al}-NMR	Ga–H ^{1}H-NMR	NCN ^{13}C{^{1}H}-NMR	^{27}Al{^{1}H}-NMR	νAl/Ga–H
(Me$_2$Im^{Me})•AlH$_3$ (**1**)	4.48	–	168.7	106.4	1727[7]
(*i*Pr$_2$Im)•AlH$_3$ (**2**)	4.53	–	170.3	106.3	1719, 1776[7]
(*i*Pr$_2$Im^{Me})•AlH$_3$ (**3**)	4.60	–	170.0	107.8	1718, 1771[7]
(Me$_2$Im^{Me})•GaH$_3$ (**4**)	–	4.51	172.2	–	1767
(*i*Pr$_2$Im^{Me})•GaH$_3$ (**5**)	–	4.66	172.7	–	1773[12d]
(Dipp$_2$Im)•GaH$_3$ (**6**)	–	3.73	172.7	–	1799[12d]
(Me$_2$Im^{Me})•AlH$_2$I (**7**)	4.54	–	161.4	107.8	1796, 1827
(*i*Pr$_2$Im)•AlH$_2$I (**8**)	4.63	–	162.7	109.6	1792, 1809
(*i*Pr$_2$Im^{Me})•AlH$_2$I (**9**)	4.70	–	162.3	109.0	1779, 1825
(Me$_2$Im^{Me})•GaH$_2$I (**10**)	–	4.81	162.1	–	1895
(*i*Pr$_2$Im^{Me})•GaH$_2$I (**11**)	–	5.00	163.4	–	1839, 1889
(Dipp$_2$Im)•GaH$_2$I (**12**)	–	4.13	170.3	–	1886



Scheme 3. Synthesis of $[(Me_2Im^{Me})_2{\cdot}AlH_2]{+}I{-}$ **13**, $[(iPr_2Im)_2{\cdot}AlH_2]{+}I{-}$ **14**, $[(iPr_2Im^{Me})_2{\cdot}AlH_2]{+}I{-}$ **15**, $[(Me_2Im^{Me})_2{\cdot}GaH_2]{+}I{-}$ **16** and $[(iPr_2Im^{Me})_2{\cdot}GaH_2]{+}I{-}$ **17**.

nitrile, and acetone. Solutions of **13**–**15** in acetone show good solubility and to our surprise only slow decomposition to the corresponding imidazolium salts $[NHCH]^{+}I^{-}$ (NHC = Me_2Im^{Me}, iPr_2Im, iPr_2Im^{Me}) after hours. Samples dissolved in $[D_6]$acetone do not exchange the hydrogen atoms attached to the metal. These samples still reveal the characteristic Al–H bands in the IR spectrum after evaporation to dryness and thus some spectroscopic evidence is provided that the Al–H fragments of the cationic species are retained in $[D_6]$acetone, at least for the time of collecting the NMR spectra.

The compounds **16** and **17** have similar solubilities as the alane analogs, but they are less stable in acetonitrile and acetone and decompose readily to the imidazolium salts $[Me_2Im^{Me}H]{+}I{-}$ and $[iPr_2Im^{Me}H]{+}I{-}$ after a few hours at room temperature. Whereas the aluminium complexes **13**–**15** 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 **13**–**17** were characterized by NMR spectroscopy, IR spectroscopy, and elemental analysis. The most important NMR and IR data are summarized in Table 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 **13** and **14** in solution were not observed, whereas for **15** the resonance in thf solution was found at 108.7 (**15**) ppm. This signal is in good accordance with the literature known resonances of NHC stabilized tetrahedral coordinated alanes, which lie in the range between δ = 100 and 120 ppm.[7,11] The $^{1}H\{^{27}Al\}$ NMR resonances of the hydrides of **13** to **15** were not observed, but the hydrides of the gallium compounds were detected at δ = 4.17 (**16**) ppm and δ = 4.37 (**17**) ppm in the ^{1}H NMR spectra. The characteristic metal hydride stretching vibrations were located at 1772, 1791 cm^{-1} (**13**), 1820, 1825 cm^{-1} (**14**), 1799, 1819 cm^{-1} (**15**) as well as at 1826, 1839 cm^{-1} (**16**) and 1857, 1877 cm^{-1} (**17**) (see Table 2) and compare well with literature known cationic aluminium hydrides $[(Dipp_2Im){\cdot}AlH_2(aDipp_2Im)]^{+}I^{-}$ and $[(Bn_2Im)_2{\cdot}AlH]_2[B(C_6F_5)_4]_2$[8,9] or the amine stabilized gallium hydride $[(NH_2tBu)_2{\cdot}GaH_2]Cl$ at 1927 cm^{-1}.[6]

Single crystals of the compounds $[(iPr_2Im^{Me})_2{\cdot}AlH_2]{+}I{-}$ **15** and $[(Me_2Im^{Me})_2{\cdot}GaH_2]{+}I{-}$ **16** were grown by slow evaporation of a saturated solution in benzene respectively acetonitrile at room temperature (see Figure 2). $[(iPr_2Im^{Me})_2{\cdot}AlH_2]{+}I{-}$ **15** crystallizes in the triclinic space group $P\bar{1}$ and $[(Me_2Im^{Me})_2{\cdot}GaH_2]{+}I{-}$ **16** 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 (**15**) and 2.027(4) Å and 2.025(4) Å (**16**) differ only marginally from the bond lengths observed in the aluminum(III) and gallium(III) hydride adducts. Compared to the mixed hydride iodide complexes **7** and **9** the bond lengths M–H1 and M–H2 (M = Al, Ga) of the salts **15** and **16** are slightly shortened. Due to the lower steric demand of the NHCs compared to $Dipp_2Im$ 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)° (**15**) and 104.32(14)° (**16**) are much smaller than those found for $[(Dipp_2Im){\cdot}AlH_2(aDipp_2Im)]{+}I{-}$ [114.24(8)°].[9] Interestingly the angle between the two hydrides and the metal centre

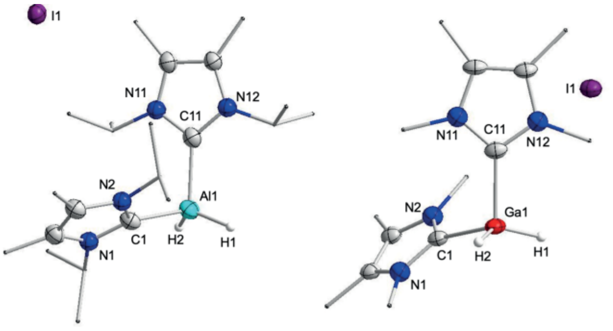


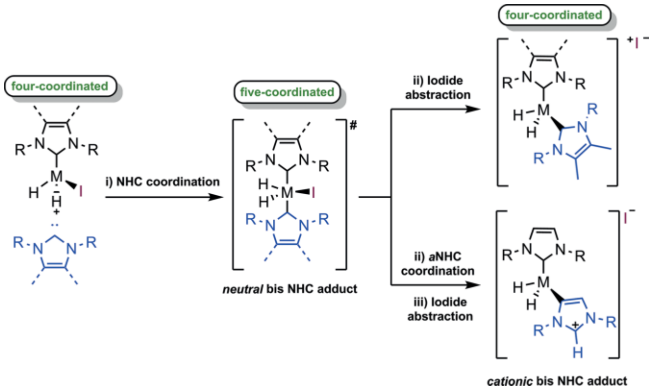
Figure 2. Molecular structure of $[(iPr_2Im^{Me})_2{\cdot}AlH_2]{+}I{-}$ **15** (left) and $[(Me_2Im^{Me})_2{\cdot}GaH_2]{+}I{-}$ **16** (right) in the solid state (ellipsoids set at the 50 % probability level). Selected bond lengths [Å] and angles [°]: **15**: C1–Al1 2.048(4), C11–Al1 2.050(3), Al1–H1 1.47(4), Al1–H2 1.49(5); H1–Al1–H2 122.0(3), C1–Al1–H1 107.0(17), C1–Al1–H2 108.0(2), C1–Al1–C11 102.20(12), C11–Al1–H1 107.5(16), C11–Al1–H2 108.7(19); **16**: C1–Ga1 2.027(4), C11–Ga1 2.025(4), Ga1–H1 1.38(7), Ga1–H2 1.29(4); H1–Ga1–H2 129.0(4), C1–Ga1–H1 109.0(3), C1–Ga1–H2 105.0(3), C1–Ga1–C11 104.32(14), C11–Ga1–H1 104(3), C11–Ga1–H2 102(3).

Table 2. Selected NMR [ppm] and IR [cm^{-1}] shifts of the compounds $[(Me_2Im^{Me})_2{\cdot}AlH_2]{+}I{-}$ **13**, $[(iPr_2Im)_2{\cdot}AlH_2]{+}I{-}$ **14** $[(iPr_2Im^{Me})_2{\cdot}AlH_2]{+}I{-}$ **15**, $[(Me_2Im^{Me})_2{\cdot}GaH_2]{+}I{-}$ **16**, $[(iPr_2Im^{Me})_2{\cdot}GaH_2]{+}I{-}$ **17** and $[(Dipp_2Im){\cdot}GaH_2(aDipp_2Im)]{+}I{-}$ **18**.

	Ga–H ^{1}H-NMR	NCN $^{13}C\{^{1}H\}$-NMR	$^{27}Al\{^{1}H\}$-NMR	νAl/Ga–H
$[(Me_2Im^{Me})_2{\cdot}AlH_2]I$ (**13**)	–	–	–	1772, 1791
$[(iPr_2Im)_2{\cdot}AlH_2]I$ (**14**)	–	–	–	1820, 1825
$[(iPr_2Im^{Me})_2{\cdot}AlH_2]I$ (**15**)	–	–	108.7	1799,1819
$[(Me_2Im^{Me})_2{\cdot}GaH_2]I$ (**16**)	4.17	–	–	1826, 1839
$[(iPr_2Im^{Me})_2{\cdot}GaH_2]I$ (**17**)	4.37	162.8	–	1857, 1877
$[(Dipp_2Im){\cdot}GaH_2(aDipp_2Im)]I$ (**18**)	3.23	171.6	–	1858,1876

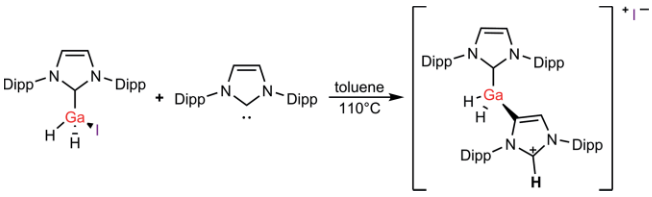
H1–Al–H2 of 122(3)° (**15**) and H1–Ga–H2 of 129(4)° (**16**) are quite large compared to C1–Al1–C11 of 102.20(12) (**15**) and C1–Ga1–C11 of 104.32(14) (**16**), which accounts for more metal p-character in the corresponding M–C (M = Al, Ga) bond according to Bent's rule.

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 4, i). We detected 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.[7] Calculations have shown that the five coordinated bis-NHC adducts of group 13 hydrides are higher in energy and less stable than the four coordinated tetrahedral mono NHC adducts and are often intermediates of further reactions.[18] Instead of NHC ring expansion we observe 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 4, ii). The strong σ-donating alkyl-substituted NHCs stabilize the cationic electron deficient metal centre in its 8VE count.



Scheme 4. Proposed mechanism of the formation of bis NHC aluminium- and gallium hydride cations.

To further evaluate the influence of the sterics of the NHC on the reaction and to compare the reactivity with aluminium and gallium hydrides, we additionally reacted the iodogallane adduct (Dipp$_2$Im)·GaH$_2$I **12** 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.[9] The reaction of (Dipp$_2$Im)·GaH$_2$I **10** 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 [(Dipp$_2$Im)·GaH$_2$(*a*Dipp$_2$Im)]+I– **18** (see Scheme 5), which is stabilized with a *normal* and *abnormal* coordinated NHC. The salt [(Dipp$_2$Im)·GaH$_2$(*a*Dipp$_2$Im)]+I– **18** was isolated from toluene as a colourless powder in good yield (**18**: 54 %) and excellent purity.



Scheme 5. Synthesis of [(Dipp$_2$Im)·GaH$_2$(*a*Dipp$_2$Im)]+I– **18**.

The compound **18** was characterized by NMR spectroscopy, IR spectroscopy, and elemental analysis. The most important NMR and IR data are summarized in Table 2. 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 δ = 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 and is in accordance with the resonance observed for (Dipp$_2$Im)·GaH$_2$I **12** at δ = 170.3 ppm. The characteristic metal hydride stretching vibrations were observed at 1858 and 1876 cm^{-1} (see Table 2) and compare well with literature-known cationic aluminium hydrides [(Dipp$_2$Im)·AlH$_2$(*a*Dipp$_2$Im)]$^+$I$^-$ at 1811 and 1827 cm^{-1}.[6]

Single crystals of the compound [(Dipp$_2$Im)·GaH$_2$(*a*Dipp$_2$Im)]+I– **18** were grown by slow evaporation of a saturated solution in acetonitrile at room temperature (see Figure 3). [(Dipp$_2$Im)·GaH$_2$(*a*Dipp$_2$Im)]+I– **18** 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$_{\text{NHC}}$ bond length is slightly shorter for the *abnormal* coordinated NHC [Ga–C$_{a\text{NHC}}$ = 2.0164(22) Å] compared with the *normal* coordinated NHC [Ga–C$_{\text{NHC}}$ = 2.0570(23) Å] as expected due to less steric demand and better σ-donating properties of the *abnormal* NHC. These results are in good accordance with the aluminium analog cation [(Dipp$_2$Im)·AlH$_2$(*a*Dipp$_2$Im)]+I– presented earlier by Jones and Stasch *et al.* [Al–C$_{a\text{NHC}}$ = 2.012(2) Å and Ga–C$_{\text{NHC}}$ = 2.051(2) Å].[9]

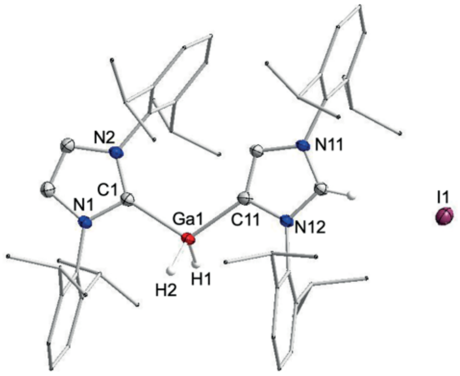


Figure 3. Molecular structure of [(Dipp$_2$Im)·GaH$_2$(*a*Dipp$_2$Im)]+I– **18** in the solid-state (ellipsoids set at the 50 % probability level). Selected bond lengths [Å] and angles [°]: C1–Ga1 2.057(2), C11–Ga1 2.016(2), Ga1–H1 1.46(4), Ga1–H2 1.58(4); H1–Ga1–H2 116.0(2), C1–Ga1–H1 101.4(14), C1–Ga1–H2 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 **18** follows a similar mechanism postulated by Jones and Stasch *et al.* for the aluminium analogue 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 (Dipp$_2$Im)$_2$•AlH$_2$I. 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 4 & 5).

Conclusion

The synthesis of the NHC-stabilized cationic aluminium- and gallium hydrides [(NHC)$_2$•AlH$_2$]+I– (NHC = Me$_2$Im^{Me} **13**, *i*Pr$_2$Im **14**, *i*Pr$_2$Im^{Me} **15**) and [(NHC)$_2$•GaH$_2$]+I– (NHC = Me$_2$Im^{Me} **16**, *i*Pr$_2$Im^{Me} **17**), 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} **7**, *i*Pr$_2$Im **8**, *i*Pr$_2$Im^{Me} **9**) and (NHC)•GaH$_2$I (NHC = Me$_2$Im^{Me} **10**, *i*Pr$_2$Im^{Me} **11**), respectively. The NHC iodo alanes and iodo gallanes **7**–**12** were prepared *via* a simple yet 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} **16**, *i*Pr$_2$Im^{Me} **17**) 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– **18**, in which *normal* and *abnormal* coordination of the NHC was observed.

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were carried out under an inert atmosphere of argon by using standard Schlenk-line and glovebox techniques as reported previously.[19] All reactions were performed in oven-dried glassware. Toluene and *n*-hexane were obtained from a solvent purification system (Innovative Technology). C$_6$D$_6$, [D$_8$]thf, CD$_3$CN, and [D$_6$]acetone were purchased from Sigma-Aldrich and stored over molecular sieve. The carbenes Me$_2$Im^{Me},[20] *i*Pr$_2$Im,[20] *i*Pr$_2$Im^{Me},[20] Dipp$_2$Im[21] and the compounds (Me$_2$Im^{Me})•AlH$_3$ **1**,[7] (*i*Pr$_2$Im)•AlH$_3$ **2**,[7] (*i*Pr$_2$Im^{Me})•AlH$_3$ **3**,[7] (Me$_2$Im^{Me})•GaH$_3$ **4**,[12] (*i*Pr$_2$Im^{Me})•GaH$_3$ **5**,[12] (Dipp$_2$Im)•GaH$_3$ **6**[12] were synthesized according to reported procedures. Elemental iodine and methyl iodide were purchased from Sigma-Aldrich and used as received. Elemental analyses were performed in the micro-analytical laboratory of the University of Würzburg with an Elementar vario micro cube. Infrared spectra were recorded on a Bruker alpha spectrometer as solids using an ATR unit. ^{1}H, ^{27}Al, and ^{13}C{^{1}H} NMR spectra were recorded at 298 K on a Bruker Avance 400 spectrometer [^{1}H, 400.4 MHz; ^{13}C{^{1}H}, 100.7 MHz; ^{27}Al, 104.3 MHz]. ^{1}H NMR chemical shifts are listed in parts per million (ppm), are reported relative to TMS, and were referenced *via* residual proton resonances of the deuterated solvent (C$_6$D$_5$H: 7.16 ppm, [D$_8$]thf: 1.73, 3.58 ppm, CD$_3$CN: 1.94 ppm, [D$_6$]acetone: 2.05). ^{13}C{^{1}H} NMR resonances are reported relative to TMS using the natural-abundance carbon resonances of C$_6$D$_6$ (128.06 ppm), [D$_8$]thf (25.37, 67.57 ppm), CD$_3$CN (1.39, 118.7 ppm) and [D$_6$]acetone (29.92, 206.68 ppm).[22]

(Me$_2$Im^{Me})•AlH$_2$I (7): Elemental solid iodine (370 mg, 1.46 mmol) was added at room temperature to a solution of (Me$_2$Im^{Me})•AlH$_3$ (450 mg, 2.92 mmol) **1** dissolved in 15 mL of toluene and the resulting solution was stirred for 45 minutes. The solvent was evaporated to dryness which gave **7** as colourless powder. Yield: 706 mg (86 %). Crystals of **7** suitable for X-ray diffraction were grown by slow evaporation of a saturated solution of **7** in benzene. 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). IR (ATR[cm^{-1}]): $\tilde{\nu}$ = 2949 (vw), 2922 (vw), 1827 (s, $\nu_{\text{Al–H, str.}}$), 1796 (s, $\nu_{\text{Al–H, str.}}$), 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). ^{1}H{^{27}Al}-NMR (400.1 MHz, C$_6$D$_6$, 298 K): δ [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): δ [ppm] = 7.6 (*C*H$_3$), 33.6 (NC*C*H$_3$C*C*H$_3$N), 125.8 (N*C*CN), 161.4 (N*C*N). ^{27}Al{^{1}H}-NMR (104.3 MHz, C$_6$D$_6$, 298 K): δ [ppm] = 107.8.

(*i*Pr$_2$Im)•AlH$_2$I (8): 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) **2** dissolved in 10 mL of toluene and the resulting solution was stirred for 2 hours. The solvent was evaporated to dryness which gave **8** as colourless powder. Yield: 1.31 g (97 %). 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). IR (ATR[cm^{-1}]): $\tilde{\nu}$ = 3151 (w), 3124 (w), 2976 (m), 2932 (w), 1860 (m), 1837 (m, $\nu_{\text{Al–H, str.}}$), 1809 (m), 1792 (m, $\nu_{\text{Al–H, str.}}$), 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). ^{1}H{^{27}Al}-NMR (400.1 MHz, C$_6$D$_6$, 298 K): δ [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): δ [ppm] = 22.9 (*i*Pr-*C*H$_3$), 51.8 (*i*Pr-*C*H), 117.5 (N*C*CN), 162.7 (N*C*N). ^{27}Al{^{1}H}-NMR (104.3 MHz, C$_6$D$_6$, 298 K): δ [ppm] = 109.6.

(*i*Pr$_2$Im^{Me})•AlH$_2$I (9): 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) **3** dissolved in 15 mL of toluene and the resulting solution was stirred for 45 minutes. The solvent was evaporated to dryness which gave **9** as colourless powder. Yield: 1.06 g (88 %). Crystals of **9** suitable for X-ray diffraction were grown by slow evaporation of a saturated solution of **9** in benzene. 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). IR (ATR[cm^{-1}]): $\tilde{\nu}$ = 2977 (w), 2933 (vw), 1825 (m, $\nu_{\text{Al–H, str.}}$), 1779 (s, $\nu_{\text{Al–H, str.}}$), 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). ^{1}H{^{27}Al}-NMR (400.1 MHz, C$_6$D$_6$, 298 K): δ [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): δ [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*C*CN), 162.3 (N*C*N). ^{27}Al{^{1}H}-NMR (104.3 MHz, C$_6$D$_6$, 298 K): δ [ppm] = 109.0.

(Me$_2$Im^{Me})•GaH$_2$I (10): Methyl iodide (1.20 mL) was added to a solution of (Me$_2$Im^{Me})•GaH$_3$ **4** (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 **10** as colourless powder. Yield: 590 mg (88 %). Crystals of **10** suitable for X-ray diffraction were grown by slow evaporation of a saturated solution of the compound in benzene. 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). IR (ATR[cm^{-1}]): $\tilde{\nu}$ = 2921 (m), 1895 (s, $\nu_{\text{Ga–H, str.}}$), 1650 (m), 1577 (m), 1435 (m), 1391 (w), 1371 (m), 848 (m), 755 (s), 743 (s), 677 (s), 633 (s), 456 (s). ^{1}H-NMR (400.1 MHz, C$_6$D$_6$, 298 K): δ [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): δ [ppm] = 7.8 (*C*H$_3$), 33.7 (NC*C*H$_3$C*C*H$_3$N), 125.7 (N*C*CN), 162.1 (N*C*N).

(iPr$_2$Im^{Me})·GaH$_2$I (11): Methyl iodide (245 µL) was added to a solution of (iPr$_2$Im^{Me})·GaH$_3$ **5** (100 mg, 395 µmol) in 10 mL of toluene at room temperature *via* a syringe and stirred for 30 minutes. The solvent was evaporated which gave compound **11** as colourless powder. Yield: 111 mg (75 %). $C_7H_{14}N_2GaI$ [322.83 g/mol] found (calculated) [%]: C, 34.75 (34.87); H, 5.65 (5.85); N, 7.37 (7.39). IR (ATR[cm^{-1}]): $\tilde{\nu}$ = 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). ^{1}H-NMR (400.1 MHz, C_6D_6, 298 K): δ [ppm] = 1.09 (d, 12 H, $^3J_{HH}$ = 7.1 Hz, iPr-CH_3), 1.42 (s, 6 H, NCCH_3CCH_3N), 5.00 (s$_{br}$, 2 H, Ga-H), 5.32 (sept$_{br}$, 2 H, iPr-CH). ^{13}C{^{1}H}-NMR (100.6 MHz, C_6D_6, 298 K): δ [ppm] = 9.7 (NCCH$_3$CCH$_3$N), 21.4 (iPr-CH$_3$), 52.6 (iPr-CH), 126.2 (NCCN), 163.4 (NCN).

(Dipp$_2$Im)·GaH$_2$I (12): Methyl iodide (500 µL) was added to a solution of (Dipp$_2$Im)·GaH$_3$ **6** (400 mg, 867 µmol) in 10 mL of toluene at room temperature *via* a syringe and stirred for 30 minutes. The solvent was evaporated which gave compound **9** as colourless powder. Yield: 509 mg (99 %). Elemental analysis $C_{27}H_{38}N_2GaI$ [587.24 g/mol] found (calculated) [%]: C, 55.35 (55.22); H, 6.82 (6.52); N, 4.75 (4.77). IR (ATR[cm^{-1}]): $\tilde{\nu}$ = 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). ^{1}H-NMR (400.1 MHz, C_6D_6, 298 K): δ [ppm] = 0.98 (d, 12 H, $^3J_{HH}$ = 7.1 Hz, iPr-CH_3), 1.42 (d, 12 H, $^3J_{HH}$ = 7.1 Hz, iPr-CH_3), 2.69 (sept, 4 H, $^3J_{HH}$ = 7.1 Hz, iPr-CH), 4.13 (s$_{br}$, 2 H, Ga-H), 6.45 (s, 2 H, NCHCHN), 7.09 (m, 4 H, aryl-C$_{meta}$$H$), 7.22 (m, 2 H, aryl-C$_{para}$$H$). ^{13}C{^{1}H}-NMR (100.6 MHz, C_6D_6, 298 K): δ [ppm] = 23.3 (iPr-CH$_3$), 25.6 (iPr-CH$_3$), 29.1 (iPr-CH), 124.5 (aryl-C$_{meta}$H), 131.2 (aryl-C$_{para}$H), 134.2 (aryl-C$_{ipso}$), 145.6 (aryl-C$_{ortho}$), 170.3 (NCN).

[(Me$_2$Im^{Me})$_2$·AlH$_2$]+I– (13): Toluene (15 mL) was added to a mixture of (Me$_2$Im^{Me})·AlH$_2$I **7** (200 mg, 714 µmol) and Me$_2$Im^{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 colourless precipitate was filtered off and washed with *n*-hexane. The colourless solid was dried *in vacuo* to afford compound **13**. Yield: 260 mg (90 %). $C_{14}H_{26}N_4AlI$ [404.28 g/mol] found (calculated) [%]: C, 41.12 (41.59); H, 6.47 (6.48); N, 13.36 (13.86). IR (ATR[cm^{-1}]): $\tilde{\nu}$ = 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). ^{1}H-NMR (400.1 MHz, [D$_6$]Acetone, 298 K): δ [ppm] = 2.35 (s, 12 H, NCCH_3CCH_3N), 3.93 (s, 12 H, CH_3). Al-H not observed. ^{13}C{^{1}H}-NMR (100.6 MHz, [D$_6$]Acetone, 298 K): δ [ppm] = 8.3 (CH$_3$), 34.1 (NCCH$_3$CCH$_3$N), 127.9 (NCCN). NCN not observed. ^{27}Al{^{1}H}-NMR (104.3 MHz, [D$_6$]Acetone, 298 K): No signal observed.

[(iPr$_2$Im)$_2$·AlH$_2$]+I– (14): Toluene (15 mL) was added to a mixture of (iPr$_2$Im)·AlH$_2$I **7** (100 mg, 325 µmol) and iPr$_2$Im (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 colourless precipitate was filtered off and washed with *n*-hexane. The colourless solid was dried *in vacuo* to afford compound **14**. Yield: 92 mg (62 %). $C_{18}H_{34}N_4AlI$ [460.38 g/mol] found (calculated) [%]: C, 46.49 (46.96); H, 7.35 (7.44); N, 11.74 (12.17). IR (ATR[cm^{-1}]): $\tilde{\nu}$ = 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). ^{1}H-NMR (400.1 MHz, [D$_6$]Acetone, 298 K): δ [ppm] = 1.64 (d, 24 H, $^3J_{HH}$ = 6.9 Hz, iPr-CH_3), 4.96 (sept, 4 H, iPr-CH), 7.93 (4 H, NCHCHN). Al-H not observed. ^{13}C{^{1}H}-NMR (100.6 MHz, [D$_6$]Acetone, 298 K): δ [ppm] = 23.1 (iPr-CH$_3$), 53.8 (iPr-CH), 121.3 (NCCN). NCN not observed. ^{27}Al{^{1}H}-NMR (104.3 MHz, [D$_6$]Acetone, 298 K): No signal observed.

[(iPr$_2$Im^{Me})$_2$·AlH$_2$]+I– (15): Toluene (15 mL) was added to a mixture of (iPr$_2$Im^{Me})·AlH$_2$I **8** (200 mg, 595 µmol) and iPr$_2$Im^{Me} (107.3 mg, 595 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 colourless precipitate was filtered off and washed with *n*-hexane. The colourless solid was dried *in vacuo* to afford compound **15**. Yield: 270 mg (88 %). Crystals of **15** suitable for X-ray diffraction were grown by slow evaporation of a saturated solution of **15** in benzene. $C_{22}H_{42}N_4AlI$ [516.49 g/mol] found (calculated) [%]: C, 41.12 (41.59); H, 6.47 (6.48); N, 13.36 (13.86). IR (ATR[cm^{-1}]): $\tilde{\nu}$ = 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). ^{1}H-NMR (400.1 MHz, [D$_8$]thf, 298 K): δ [ppm] = 1.53 (d, 24 H, $^3J_{HH}$ = 6.9 Hz, iPr-CH_3), 2.35 (s, 12 H, NCCH_3CCH_3N), 4.94 (sept, 4 H, iPr-CH). Al-H not observed. ^{13}C{^{1}H}-NMR (100.6 MHz, [D$_8$]thf, 298 K): δ [ppm] = 11.2 (NCCH$_3$CCH$_3$N), 22.7 (iPr-CH$_3$), 53.9 (iPr-CH), 129.1 (NCCN), NCN not observed. ^{27}Al{^{1}H}-NMR (104.3 MHz, [D$_8$]thf, 298 K): δ [ppm] = 108.7.

[(Me$_2$Im^{Me})$_2$·GaH$_2$]+I– (16): Toluene (15 mL) was added to a mixture of (Me$_2$Im^{Me})·GaH$_2$I **9** (50 mg, 155 µmol) and Me$_2$Im^{Me} (19.2 mg, 155 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 colourless precipitate was filtered off and washed with *n*-hexane. The colourless solid was dried *in vacuo* to afford compound **16**. Yield: 38 mg (55 %). Crystals of **16** suitable for X-ray diffraction were grown by slow evaporation of a saturated solution of **16** in benzene. $C_{14}H_{26}N_4GaI$ [447.02 g/mol] found (calculated) [%]: C, 37.45 (37.62); H, 5.78 (5.86); N, 11.87 (12.53). IR (ATR[cm^{-1}]): $\tilde{\nu}$ = 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). ^{1}H-NMR (400.1 MHz, CD_3CN, 298 K): δ [ppm] = 2.15 (s, 12 H, NCCH_3CCH_3N), 3.61 (s, 12 H, CH_3), 4.17 (s$_{br}$, 2 H, Ga-H), (s$_{br}$, 4 H, iPr-CH). ^{13}C{^{1}H}-NMR (100.6 MHz, CD_3CN, 298 K): δ [ppm] = 8.9 (CH$_3$), 35.0 (NCCH$_3$CCH$_3$N), 128.5 (NCCN). NCN not observed.

[(iPr$_2$Im^{Me})$_2$·GaH$_2$]+I– (17): Toluene (15 mL) was added to a mixture of (iPr$_2$Im^{Me})·GaH$_2$I **11** (75 mg, 198 µmol) and iPr$_2$Im^{Me} (39 mg, 198 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 colourless precipitate was filtered off and washed with *n*-hexane. The colourless solid was dried *in vacuo* to afford compound **17**. Yield: 56 mg (51 %). $C_{22}H_{42}N_4GaI$ [559.23 g/mol] found (calculated) [%]: C, 45.98 (47.25); H, 7.45 (7.57); N, 9.51 (10.02). IR (ATR[cm^{-1}]): $\tilde{\nu}$ = 2972 (m), 1877 (m, $\nu_{Ga–H,\ str.}$), 1857 (m, $\nu_{Ga–H,\ str.}$), 1626 (m), 1555 (s), 1446 (m), 1376 (m), 1365 (m), 1231 (s), 1190 (s), 1110 (s), 764 (m), 678 (m), 659 (m), 521 (m). ^{1}H-NMR (400.1 MHz, [D$_8$]thf, 298 K): δ [ppm] = 1.52 (d, 24 H, $^3J_{HH}$ = 6.9 Hz, iPr-CH_3), 2.40 (s, 12 H, NCCH_3CCH_3N), 4.37 (s$_{br}$, 2 H, Ga-H), 4.98 (sept, 4 H, iPr-CH). ^{13}C{^{1}H}-NMR (100.6 MHz, [D$_8$]thf, 298 K): δ [ppm] = 11.3 (NCCH$_3$CCH$_3$N), 22.1 (iPr-CH$_3$), 54.1 (iPr-CH), 129.3 (NCCN), 162.8 (NCN).

[(Dipp$_2$Im)·GaH$_2$(aDipp$_2$Im)]+I– (18): Toluene (10 mL) was added to a mixture of (Dipp$_2$Im)·GaH$_2$I **12** (200 mg, 341 µmol) and Dipp$_2$Im (133 mg, 341 µmol) 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 colourless precipitate was filtered off and washed with *n*-hexane. The colourless solid was dried *in vacuo* to afford compound **18**. Crystals of compound **18** suitable for X-ray diffraction were grown by slow evaporation of a saturated solution of **18** in acetonitrile. Yield: 180 mg (54 %). $C_{54}H_{74}N_4GaI$ [975.79 g/mol] found (calculated) [%]: C, 66.06 (66.40);

H, 7.78 (7.74); N, 5.64 (5.74). IR (ATR[cm^{-1}]): $\tilde{\nu}$ = 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). ^{1}H-NMR (400.1 MHz, CD$_3$CN, 298 K): δ [ppm] = 0.96 (d, 6 H, $^{3}J_{HH}$ = 7.1 Hz, *a*NHC-*i*Pr-C*H*$_3$), 1.03 (d, 6 H, $^{3}J_{HH}$ = 7.1 Hz, *a*NHC-*i*Pr-C*H*$_3$), 1.13 (d, 6 H, $^{3}J_{HH}$ = 7.1 Hz, *a*NHC-*i*Pr-C*H*$_3$), 1.14 (d, 12 H, $^{3}J_{HH}$ = 7.1 Hz, NHC-*i*Pr-C*H*$_3$), 1.17 (d, 12 H, $^{3}J_{HH}$ = 7.1 Hz, NHC-*i*Pr-C*H*$_3$), 1.33 (d, 6 H, $^{3}J_{HH}$ = 7.1 Hz, *a*NHC-*i*Pr-C*H*$_3$), 2.12 (d-sept, 4 H, $^{3}J_{HH}$ = 7.1 Hz, *a*NHC-*i*Pr-C*H*), 2.50 (sept, 4 H, $^{3}J_{HH}$ = 7.1 Hz, NHC-*i*Pr-C*H*), 3.22 (s$_{br}$, 2 H, Ga-*H*), 4.26 (d, 1 H, $^{4}J_{HH}$ = 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, $^{4}J_{HH}$ = 1.44 Hz, *a*NHC-NC*H*N). ^{13}C{^{1}H}-NMR (100.6 MHz, CD$_3$CN, 298 K): δ [ppm] = 22.6 (*a*NHC -*i*Pr-CH$_3$), 23.3 (NHC-*i*Pr-CH$_3$), 23.7 (*a*NHC-*i*Pr-CH$_3$), 24.8 (NHC-*i*Pr-CH$_3$), 25.6 (*a*NHC-*i*Pr-CH$_3$), 25.9 (*a*NHC-*i*Pr-CH$_3$), 29.4 (*a*NHC-*i*Pr-CH), 29.5 (*a*NHC-*i*Pr-CH), 29.8 (NHC-*i*Pr-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-NCHN) 146.1 (*a*NHC-NCCHN), 146.4 (*a*NHC-NCCHN), 147.3 (NHC-NCHCHN), 171.7 (NCN).

Crystallographic Details

Crystals were immersed in a film of perfluoropolyether oil on a glass fiber MicroMountTM (MiTeGen) and transferred to a Rigaku XtaLAB Synergy-DW diffractometer with Hy-Pix-6000HE detector and monochromated Cu-K_α equipped with an Oxford Cryo 800 cooling unit. Data were collected at 100 K. The images were processed with 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.[23] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were usually assigned to idealized positions and were included in structure factors calculations.

Deposition Numbers 1993675 (**7**), CCDC-1993679 (**9**), CCDC-1993676 (**10**), CCDC-1993677 (**15**), CCDC-1993678 (**16**) and CCDC-2013190 (**18**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Crystal Data of (Me$_2$Im^{Me})·AlH$_2$I (7): C$_{13}$H$_{20}$AlIN$_2$, M$_r$ = 358.19, colorless block, 0.20 × 0.17 × 0.14 mm, orthorhombic group P_{bca}, a = 24.6229(3) Å, b = 8.35440(10) Å, c = 15.6920(2) Å, α = 90°, β = 64.043(5)°, γ = 101. 37770(10)°, V = 3164.57(7) Å^3, T = 100(10) K, Z = 8, $\rho_{\text{calcd.}}$ = 1.504 g cm^{-3}, μ = 16.292, F(000) = 1424, 15990 reflections, in h(–30/31), k(–10/10), l(–19/19) measured in the range 3.6850° < θ < 76.9390°, completeness 98.0 %, 3012 independent reflections, 2946 observed reflections [$I > 2\sigma(I)$], 168 parameters, 0 restraints; all data: R_1 = 0.0297 and wR_2 = 0.0758, $I > 2\sigma(I)$: R_1 = 0.0301 and wR_2 = 0.00761, Goof 1.097, largest difference peak/hole 1.379/–0.697 e Å^{-3}.

Crystal Data of (*i*Pr$_2$Im^{Me})·AlH$_2$I (9): C$_{11}$H$_{22}$AlIN$_2$, M$_r$ = 336.18, colorless block, 0.22 × 0.22 × 0.12 mm, monoclinic group $C2/_c$, a = 15.7664(3) Å, b = 10.9910(2) Å, c = 17.1308(4) Å, α = 90°, β = 90°, γ = 90°, V = 3164.57(7) Å^3, T = 99.99(10) K, Z = 8, $\rho_{\text{calcd.}}$ = 1.504 g cm^{-3}, μ = 17.320, F(000) = 1344, 15340 reflections, in h(–13/19), k(–13/13), l(–21/21) measured in the range 5.5540° < θ < 76.4870°, completeness 98.0 %, 2714 independent reflections, 2434 observed reflections [$I > 2\sigma(I)$], 150 parameters, 0 restraints; all data: R_1 = 0.0355 and wR_2 = 0.0939, $I > 2\sigma(I)$: R_1 = 0.0392 and wR_2 = 0.0967, Goof 1.070, largest difference peak/hole 1.735/–0.892 e Å^{-3}.

Crystal Data of (Me$_2$Im^{Me})·GaH$_2$I (10): C$_7$H$_{14}$N$_2$GaI, M$_r$ = 322.83, colorless block, 0.17 × 0.13 × 0.06 mm, monoclinic group $P2_1/n$, a = 9.1674(3) Å, b = 9.9889(2) Å, c = 12.4319(3) Å, α = 90°, β = 108.739(3)°, γ = 90°, V = 1078.07(5) Å^3, T = 100.0(5) K, Z = 4, $\rho_{\text{calcd.}}$ = 1.989 g cm^{-3}, μ = 25.555, F(000) = 616, 5683 reflections, in h(–8/11), k(–12/11), l(–15/11) measured in the range 3.270° < θ < 70.075°, completeness 100.0 %, 2049 independent reflections, 1968 observed reflections [$I > 2\sigma(I)$], 112 parameters, 0 restraints; all data: R_1 = 0.0444 and wR_2 = 0.0456, $I > 2\sigma(I)$: R_1 = 0.1148 and wR_2 = 0.1161, Goof 1.030, largest difference peak/hole 2.28/–1.62 e Å^{-3}.

Crystal Data of [(*i*Pr$_2$Im^{Me})$_2$·AlH$_2$]+I– (15): C$_{14}$H$_{26}$N$_4$AlI, M$_r$ = 404.28, colorless block, 0.17 × 0.01 × 0.06 mm, triclinic group $P\bar{1}$, a = 10.1308(3) Å, b = 13.0257(4) Å, c = 13.5023(5) Å, α = 76.396(3)°, β = 82.890(3)°, γ = 79.406(3)°, V = 1696.21(1) Å^3, T = 100.01(1) K, Z = 2, $\rho_{\text{calcd.}}$ = 1.241 g cm^{-3}, μ = 7.833, F(000) = 662, 14143 reflections, in h(–12/12), k(–15/19), l(–16/16) measured in the range 3.380° < θ < 72.101°, completeness 99.7 %, 6674 independent reflections, 6226 observed reflections [$I > 2\sigma(I)$], 354 parameters, 0 restraints; all data: R_1 = 0.0377 and wR_2 = 0.0400, $I > 2\sigma(I)$: R_1 = 0.0994 and wR_2 = 0.1007, Goof 1.090, largest difference peak/hole 1.40/–1.08 e Å^{-3}.

Crystal Data of [(Me$_2$Im^{Me})$_2$·GaH$_2$]+I– (16): C$_{14}$H$_{26}$N$_4$GaI, M$_r$ = 447.02, colorless block, 0.15 × 0.09 × 0.06 mm, monoclinic group $P2_1/n$, a = 11.8570(4) Å, b = 11.7644(3) Å, c = 13.5361(5) Å, α = 90°, β = 90.219(3)°, γ = 90°, V = 1888.14(11) Å^3, T = 99.99(10) K, Z = 4, $\rho_{\text{calcd.}}$ = 1.572 g cm^{-3}, μ = 14.799, F(000) = 888, 4267 reflections, in h(–11/14), k(–16/6), l(–16/16) measured in the range 4.968° < θ < 68.230°, completeness 95.9 %, 3314 independent reflections, 2923 observed reflections [$I > 2\sigma(I)$], 197 parameters, 0 restraints; all data: R_1 = 0.0381 and wR_2 = 0.0428, $I > 2\sigma(I)$: R_1 = 0.0994 and wR_2 = 0.1031, Goof 1.029, largest difference peak/hole 1.60/–0.60 e Å^{-3}.

Crystal Data of [(Dipp$_2$Im)·GaH$_2$(*a*Dipp$_2$Im)]+I– (18): C$_{54}$H$_{74}$N$_4$GaI, M$_r$ = 975.79, colorless block, 0.24 × 0.15 × 0.13 mm, monoclinic group $P2_1/n$, a = 10.86080(10) Å, b = 22.4035(3) Å, c = 21.5667(2) Å, α = 90°, β = 92.6500(10)°, γ = 90°, V = 5242.00(10) Å^3, T = 100.00(10) K, Z = 4, $\rho_{\text{calcd.}}$ = 1.236 g cm^{-3}, μ = 5.607, F(000) = 2040, 27454 reflections, in h(–12/13), k(–28/27), l(–26/23) measured in the range 2.846° < θ < 77.506°, completeness 97.6 %, 10888 independent reflections, 10009 observed reflections [$I > 2\sigma(I)$], 565 parameters, 0 restraints; all data: R_1 = 0.0383 and wR_2 = 0.0417, $I > 2\sigma(I)$: R_1 = 0.1017 and wR_2 = 0.1036, Goof 1.059, largest difference peak/hole 1.19/–1.68 e Å^{-3}.

Supporting Information (see footnote on the first page of this article): Electronic Supplementary Information (ESI) available: NMR and IR spectroscopic data.

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