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Normal and abnormal NHC coordination in cationic hydride iodide complexes of aluminium

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The mixed *N*-heterocyclic carbene (NHC) complexes $\text{NHCAIH}_x\text{I}_{3-x}$, where NHC is IDip or IMes ($(\text{HCNAr})_2\text{C}$; Ar = 2,6-*i*Pr₂C₆H₃ = Dip (IDip); or 2,4,6-Me₃C₆H₂ = Mes (IMes)), $x = 1$ or 2, were either prepared from NHCAIH_3 and NHCAI_3 or by halogenation of NHCAIH_3 with MeI. Reaction of $[(\text{IDip})\text{AlH}_x\text{I}_{3-x}]$, with $x = 0-3$, with another equivalent of a IDip afforded either fluxional equilibria in benzene solution for $x = 0$, no reaction for $x = 3$, or the new mixed *normal-abnormal* NHC-coordinated ionic complexes $[(\text{IDip})\text{AlH}_2(a\text{IDip})\text{I}]$ (**9**) and $[(\text{IDip})\text{AlHI}(a\text{IDip})\text{I}]$ (**10**), where *a*IDip is the *abnormal* IDip carbene tautomer bonded through its 4-position. The molecular structures of **9** and **10** were determined and show slightly shorter Al–C(*a*IDip) than Al–C(IDip) distances. In addition, a complex containing $[(\text{IDip})\text{AlI}_2(a\text{IDip})\text{I}]$ (**11**) was structurally characterized though could not intentionally be synthesised. Possible formation mechanisms for **9-11** are discussed and the *normal* and *abnormal* IDip coordination to the aluminium(III) centre is believed to occur for steric reasons.

Introduction

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N-heterocyclic carbenes (NHCs) have found wide applications in chemistry for example as part of improved transition metal catalysts and for the stabilization of unusual main group molecules.^{1,2} As strong σ -donor ligands, these are ideally suited for the complexation of typically electron-deficient molecular aluminium(III) fragments,³ but have also recently been instrumental in the synthesis of donor-stabilized low oxidation state aluminium complexes.⁴⁻⁷ Coordination to NHCs has for example allowed the synthesis of thermally stable aluminium hydride^{8,9} complexes with sterically demanding NHC ligands, such as [(IMes)AlH₃] **1** (IMes = (HCNMe₃)₂C:, Me₃ = 2,4,6-Me₃C₆H₂),¹⁰ [(IDip)AlH₃] **2** (IDip, often named IPr, = (HCNDip)₂C:, Dip = 2,6-*i*Pr₂C₆H₃),¹¹ and related compounds,¹² showing a considerable improvement of their thermal stability over N- and P-donor adducts.¹³ Along with a range of other structurally characterised NHCAIH₃ complexes,¹⁴ a series of rare and reactive NHC-coordinated aluminium hydride cations has been obtained,^{15,16} see Figure 1, such as the dinuclear dicationic IDip example **A**, the monomeric example **B** with a three-coordinated AlH centre,¹⁵ and the ionic complex **C** containing both *normal* (e.g. imidazol-2-ylidene) and *abnormal*¹⁷ (e.g. imidazol-4-ylidene) NHC coordination in its anion.¹⁶

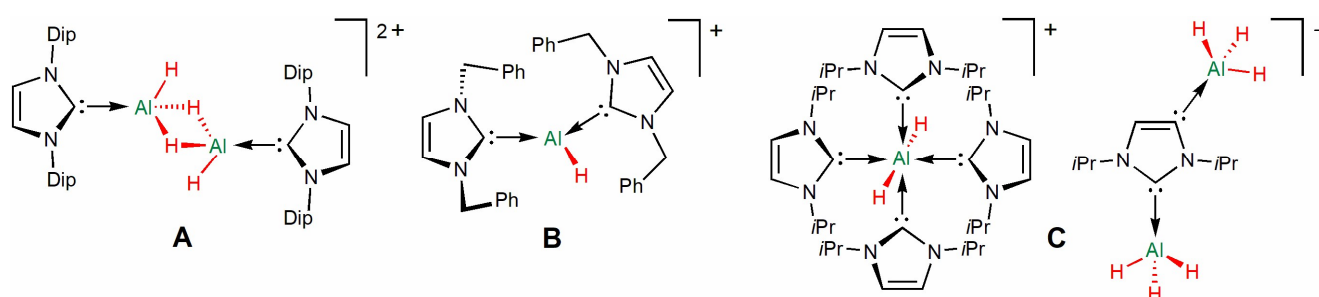


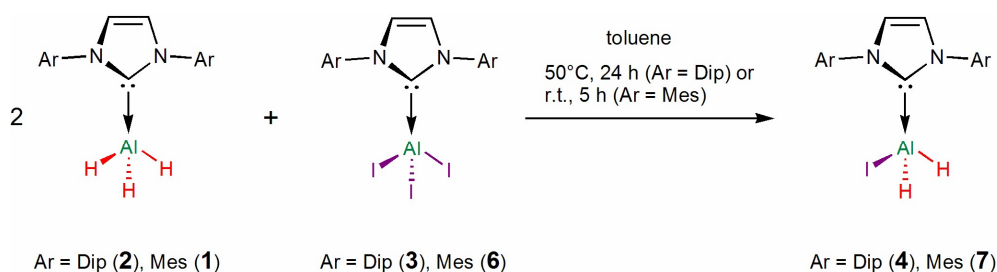
Figure 1. Cationic NHC-stabilised AlH complexes.

NHCAIH₃ complexes have further been used to break down the stable ring system of some NHCs via ring expansion and ring opening reactions.^{16,18,19} Given that many of the reactions that form reactive NHC-coordinated AlH cations or AlH-induced NHC breakdown products were achieved with relatively small NHC ligands, we started a study to attempt the coordination of two sterically demanding NHC ligands to one aluminium(III) centre bearing both hydride ligands and iodide substituents as potential leaving groups.

Results and discussion

Synthesis of $\text{NHCAIH}_{3-n}\text{I}_n$ ($n = 1, 2$) complexes

Several mixed aluminium hydride-halide complexes stabilized by NHC ligands have been reported previously.²⁰ These were for example obtained by treating NHCAIH_3 complexes with halogenating agents such as amine·HX ($X = \text{Cl}, \text{Br}$) or by using NHC ligands with 4,5-dihalogenated imidazol-2-ylidene ligands. We were interested in the simple molecules $\text{NHCAIH}_x\text{I}_{3-x}$ with NHC = IDip and IMes, and $x = 1$ and 2, containing iodide ligands as good leaving groups. Therefore we reacted two equivalents of $[(\text{IDip})\text{AlH}_3]$ **2**¹¹ with one equivalent of $[(\text{IDip})\text{AlI}_3]$ **3**²¹ in toluene or benzene at room temperature. The reaction was slow and only reached *ca.* 90% conversion after six days and selectively formed the new complex $[(\text{IDip})\text{AlH}_2\text{I}]$ **4**. Alternatively, heating the reaction mixture for 24 h to 50 °C achieved a good yield of $[(\text{IDip})\text{AlH}_2\text{I}]$ **4**, see scheme 1. The reaction of one equivalent of $[(\text{IDip})\text{AlH}_3]$ **2** with two equivalent of $[(\text{IDip})\text{AlI}_3]$ **3** was very slow, though heating this mixture to 50 °C for two days led to full consumption of **2** and the formation of a mixture of $[(\text{IDip})\text{AlH}_2\text{I}]$ **4**, $[(\text{IDip})\text{AlHI}_2]$ **5** and $[(\text{IDip})\text{AlI}_3]$ **3** in an approximate ratio of **4**:**5**:**3** \approx 40:16:44. Increasing the temperature to 80 °C shifted the composition of the mixture in favour of $[(\text{IDip})\text{AlHI}_2]$ **5** (ratio **4**:**5**:**3** \approx 12:60:28), which remained largely unchanged when the temperature was further risen to 100 °C. Similarly, using two equivalents of $[(\text{IMes})\text{AlH}_3]$ **1** and one equivalent of $[(\text{IMes})\text{AlI}_3]$ **6**²¹ in an aromatic solvent at room temperature selectively afforded $[(\text{IMes})\text{AlH}_2\text{I}]$ **7** after 5 h, scheme 1. The reaction of $[(\text{IMes})\text{AlH}_3]$ **1** with *ca.* two equivalents of $[(\text{IMes})\text{AlI}_3]$ **6** slowly formed a mixture of $[(\text{IMes})\text{AlH}_2\text{I}]$ **7**, $[(\text{IMes})\text{AlHI}_2]$ **8** and $[(\text{IMes})\text{AlI}_3]$ **6** at room temperature that largely converted to $[(\text{IMes})\text{AlHI}_2]$ **8** after heating for several hours to 50°C though did not show a completely pure product as judged by ¹H NMR spectroscopy. The syntheses of $[(\text{IDip})\text{AlH}_2\text{I}]$ **4** and $[(\text{IMes})\text{AlHI}_2]$ **7** could be translated to a facile preparation in excellent isolated yield on a preparative scale using this method.



Scheme 1. Synthesis of $[(\text{IDip})\text{AlH}_2\text{I}]$ **4** and $[(\text{IMes})\text{AlHI}_2]$ **7**.

Because this methodology has been convenient for the synthesis of $[(\text{IDip})\text{AlH}_2\text{I}]$ **4** and $[(\text{IMes})\text{AlH}_2\text{I}]$ **7**, though not for pure samples of $[(\text{IDip})\text{AlHI}_2]$ **5** and $[(\text{IMes})\text{AlHI}_2]$ **8**, we tested

reactions of a halogenating agent, MeI, with [(IDip)AlH₃] **2** and [(IMes)AlH₃] **1**, respectively. The addition of five equivalents of MeI to **2** in deuterated benzene at room temperature revealed full consumption of the starting material and formation of a mixture of [(IDip)AlH₂I] **4**, [(IDip)AlHI₂] **5** (ratio **4**:**5** ≈ 85:15) immediately after addition as judged by ¹H NMR spectroscopy, see Figure 2. After 30 h, mainly the formation of [(IDip)AlHI₂] **5** is evident (Figure 2), see scheme 2. After longer reaction times, more [(IDip)AlI₃] **3** was slowly formed. All products [(IDip)AlH₂I] **4**, [(IDip)AlHI₂] **5** and [(IDip)AlI₃] **3** can be observed at different stages of the reaction, see Figure 1. On a preparative scale, the reaction of [(IDip)AlH₃] **2** with five equivalents of methyl iodide in toluene for 37 h followed by removal of all volatiles afforded the desired [(IDip)AlHI₂] **5** in good purity. Analogously, [(IMes)AlHI₂] **8** was prepared from [(IMes)AlH₃] **1** with five equivalents of methyl iodide in toluene after 6 h, see scheme 2. As part of this wider study, the molecular structure of [(IDip)Al(Ph)I₂] was determined and is included in the ESI (Figure S4).

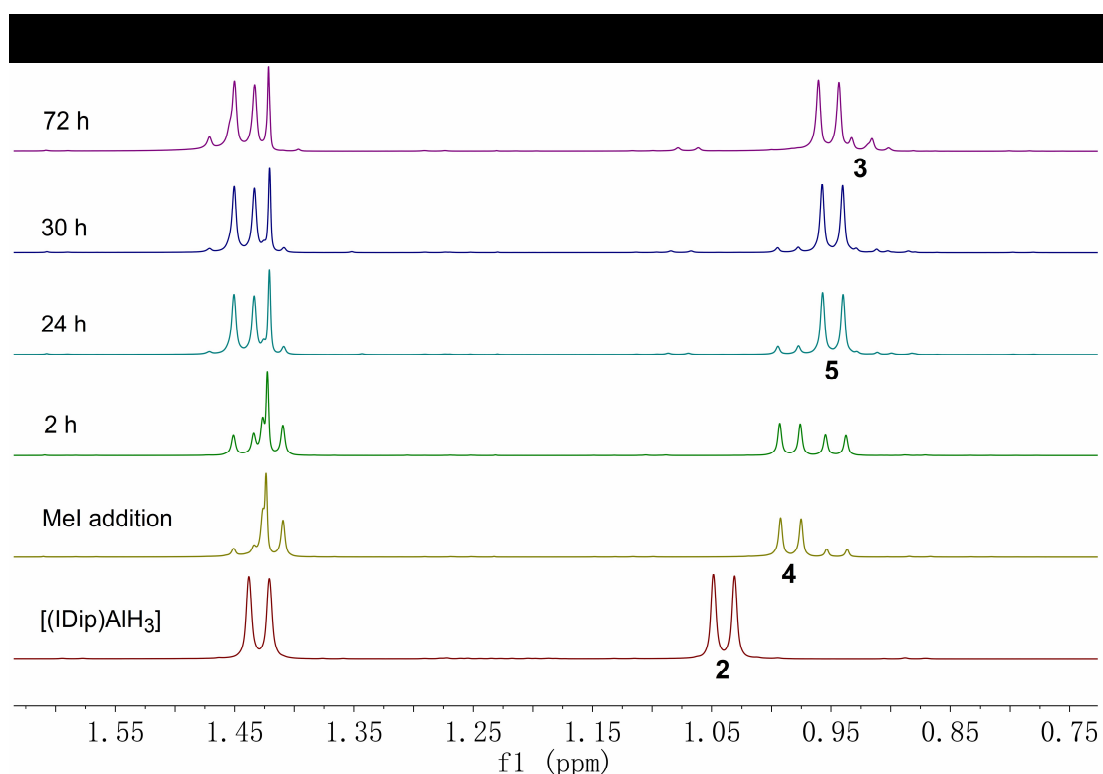
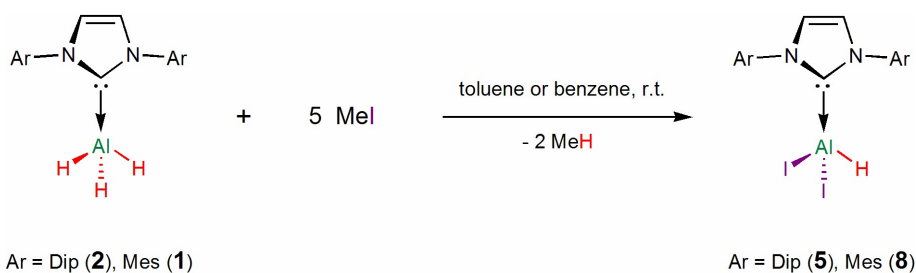


Figure 2. ¹H NMR spectra (400 MHz, in deuterated benzene, excerpt) of the reaction of [(IDip)AlH₃] **2** with five equivalents of MeI at room temperature showing the region of the Dip-isopropyl methyl groups. The singlet at *ca.* 1.43 ppm is due to methyl iodide.



Scheme 2. Synthesis of [(IDip)AlHI₂] **5** and [(IMes)AlHI₂] **8**.

All complexes [(IDip)AlH₂I] **4**, [(IDip)AlHI₂] **5**, [(IMes)AlH₂I] **7**, and [(IMes)AlHI₂] **8**, show resonances for a highly symmetric ligand environment in their ¹H NMR and ¹³C{¹H} NMR spectra comparable to those of their parent NHCAIH₃ and NHCAlI₃ compounds.^{10,11,21} ¹H NMR spectra of isolated IDip derivatives **4** and **5** show that the complexes are stable when heated to 80°C overnight whereas those of IMes, **7** and **8** are initially stable at 80°C though slowly form some decomposition products that are not simple dismutation complexes from H/I scrambling. IR spectra of these complexes show two bands (1807 cm⁻¹ with shoulder at *ca.* 1830 cm⁻¹ for **4**, and 1846 and 1802 cm⁻¹ for **7**) for those of type NHCAIH₂I and one band (one band with two sharp maxima of 1884, 1869 cm⁻¹ for **5**, which may be due to differently oriented hydride ligands in the solid state, and 1869 cm⁻¹ for **8**) for those of NHCAIHI₂; the former examples having lower wavenumbers. These values compare well with Al-H stretches from related examples, *e.g.* 1798 cm⁻¹ for [(IMes)AlH₂Cl], 1851 cm⁻¹ for [(IMes)AlHCl₂], and 1888 cm⁻¹ for [(IMes)AlHBr₂].²⁰

Reactivity of NHCAIX₃ (X = H, I) complexes with an additional NHC ligand

We were interested in the possibility of coordinating two sterically demanding NHC ligands such as IDip or IMes to one aluminium(III) centre. We have chosen a combination of small ligands (hydrides) and good leaving groups (iodides) for our study. Thus, we first treated [(IDip)AlH₃] **2** with a further equivalent of IDip in deuterated benzene, see Figure 3. The ¹H NMR spectrum of this mixture, and for other ratios of **2** and IDip, shows resonances for one single NHC environment in solution, with a general broadening and shifting of the ligand resonances. This can be attributed to a ligand exchange equilibrium in solution, likely between both starting materials via an associated intermediate, possibly the pentacoordinated species [(IDip)₂AlH₃], see scheme 3. Single crystals obtained from this mixture were recovered [(IDip)AlH₃] **2**. An equilibrium via significant quantities of free AlH₃ is unlikely in our view due to the high thermal stability of [(IDip)AlH₃] **2** in solution and the solid state (decomposition around 230°C), and the fact that "free" AlH₃ would likely rapidly decompose to aluminium metal and hydrogen.¹³ For further insight into this equilibrium, variable temperature ¹H NMR spectroscopic experiments were performed on a 1:1 mixture of **2** and IDip in deuterated toluene (Figure S1). A single set of resonances for the IDip moieties was detected when cooling from room temperature that is broadened at 263 K and splits at an approximate coalescence temperature (*T_c*) of 245-250 K corresponding to an estimated $\Delta G^\ddagger \approx 12$ kcal/mol for this process. At lower temperatures, two sets of resonances for **2** and IDip were observed. A similar solution equilibrium can be observed for [(IMes)AlH₃] **1** and IMes showing one set of ligand resonances only at room temperature (Figure S2). This shows that routine ¹H NMR spectra are not sufficient to ascertain the purity of [(IMes)AlH₃] **1** and [(IDip)AlH₃] **2** with respect to excess of the free NHC ligand, especially since the AlH resonances are extremely broad and may not reliably integrate with

sufficient accuracy. We studied systems with mixed NHC ligands and the reaction of $[(\text{IDip})\text{AlH}_3]$ **2** with one equivalent of IMes rapidly forms $[(\text{IMes})\text{AlH}_3]$ **1** and IDip at room temperature. Accordingly, no significant conversion is observed when $[(\text{IMes})\text{AlH}_3]$ **1** is treated with one equivalent of IDip demonstrating the driving force to the carbene adduct of the least sterically hindered ligand.

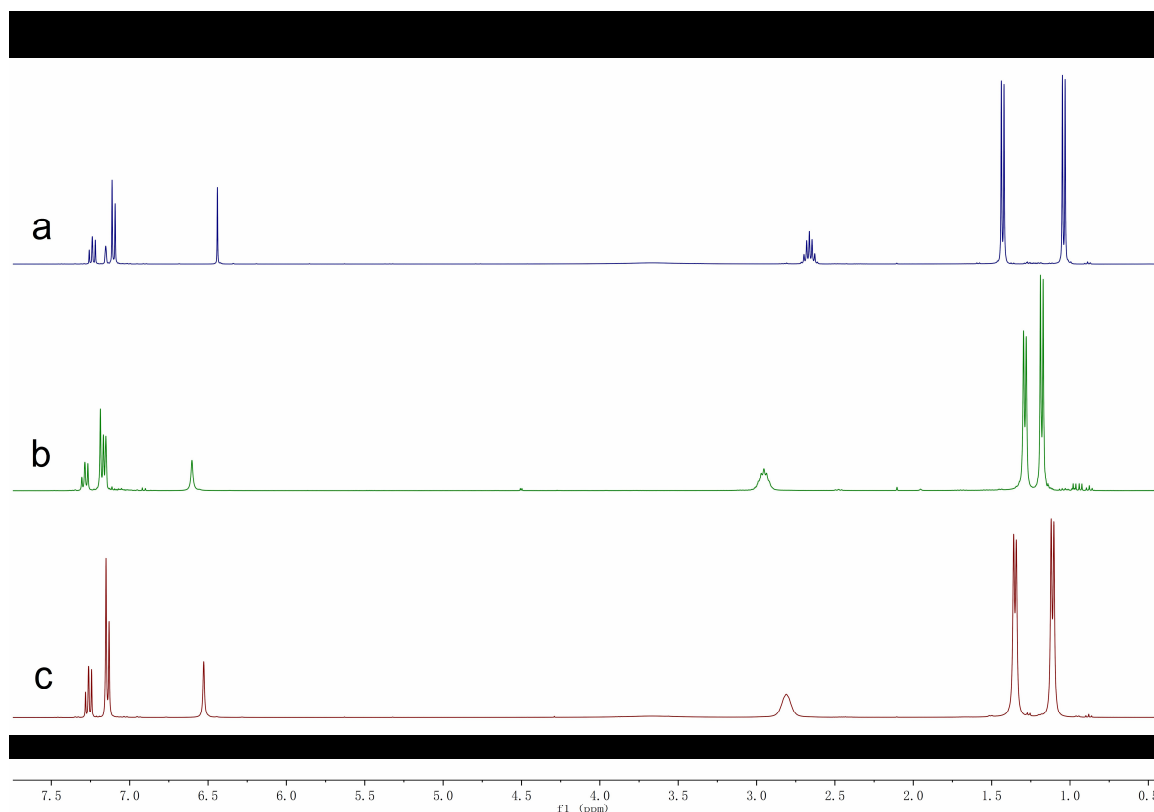
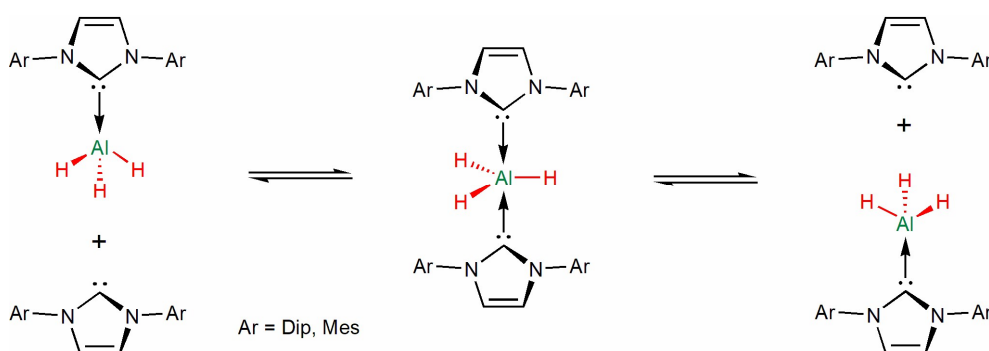


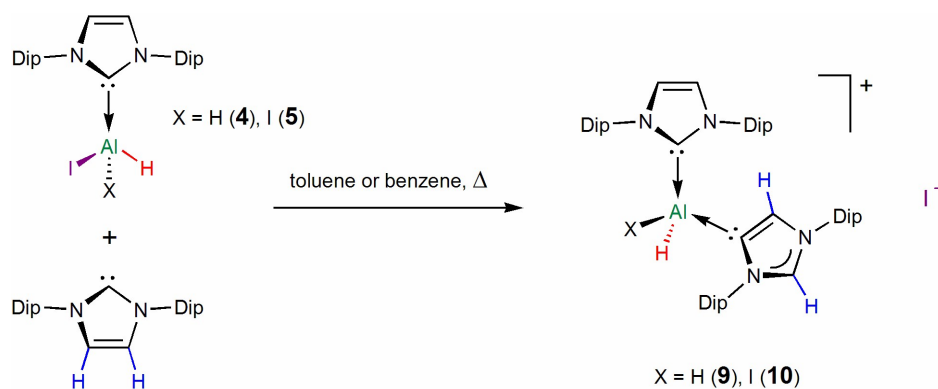
Figure 3. ^1H NMR spectra (400 MHz, in deuterated benzene) of a) (top) $[(\text{IDip})\text{AlH}_3]$ **2**; b) (middle) IDip; c), (bottom) $[(\text{IDip})\text{AlH}_3]$ **2** and IDip.



Scheme 3. Proposed equilibrium between $[(\text{IMes})\text{AlH}_3]$ **1** and IMes, and $[(\text{IDip})\text{AlH}_3]$ **2** and IDip.

When the iodide derivatives $[(\text{IDip})\text{AlH}_2\text{I}]$ **4** and $[(\text{IDip})\text{AlHI}_2]$ **5** were reacted with an additional equivalent of IDip, respectively, new species were formed and crystallised from the reaction mixtures. Complete consumption of the starting materials was detected when samples were heated

for 16 h at 85 °C. The new complexes formed as colourless crystals at elevated temperatures that hinted at their ionic and insoluble nature. Single crystal X-ray diffraction revealed the products to be $[(\text{IDip})\text{AlH}_2(\text{aIDip})]\text{I}$ **9** (from **4**) and $[(\text{IDip})\text{AlHI}(\text{aIDip})]\text{I}$ **10** (from **5**), respectively, where *aIDip* is the *abnormal* tautomer of IDip bound in 4-position, *i.e.* 1,3-bis(2,6-diisopropylphenyl)imidazol-4-ylidene, see Scheme 4 and Figure 4. In one instance, a crystal of $[(\text{IDip})\text{AlI}_2(\text{aIDip})]\text{I}$ **11**, that contained approximately 25% $[(\text{IDip})\text{AlHI}(\text{aIDip})]\text{I}$ **10** as judged by the disorder model of one iodide position in the complex was obtained from a reaction of $[(\text{IDip})\text{AlHI}_2]$ **5** and IDip that gave **10**, see Figure 4. We consequently performed the reaction of $[(\text{IDip})\text{AlI}_3]$ **3** and IDip but no reaction was observed with no evidence for the formation or precipitation of $[(\text{IDip})\text{AlI}_2(\text{aIDip})]\text{I}$ **11** or another product, even when heated at 100 °C for 16 h, see Figure S4. These experiments also showed that no fluxional equilibrium between $[(\text{IDip})\text{AlI}_3]$ **3** and IDip is observable at room temperature, unlike for the mixture of $[(\text{IDip})\text{AlH}_3]$ **2** and IDip (Scheme 3). Even at 105 °C (378 K) in deuterated toluene, a mixture of $[(\text{IDip})\text{AlI}_3]$ **3** and IDip shows separate sets of resonances that suggest that a similar equilibrium to that of $[(\text{IDip})\text{AlH}_3]$ **2** and IDip (Scheme 3) would require an activation barrier in excess of 18 kcal/mol. ^1H - ^1H NOESY NMR experiments carried out at 378 K in deuterated toluene did indicate a very slow IDip ligand exchange rate only. Consequently it is likely that the isolated small amount of $[(\text{IDip})\text{AlI}_2(\text{aIDip})]\text{I}$ **11** was not formed from an $[(\text{IDip})\text{AlI}_3]$ **3** impurity in $[(\text{IDip})\text{AlHI}_2]$ **5** during the synthesis of **10**, but likely from ligand exchange processes or an Al-H iodination reaction on solubilised $[(\text{IDip})\text{AlHI}(\text{aIDip})]\text{I}$ **10** to **11** before it precipitated. Longer reaction times of $[(\text{IDip})\text{AlI}_3]$ **3** and IDip at around 100 °C in deuterated benzene or toluene did afford small resonances in ^1H NMR spectra that suggest some conversion to an IDipH^+ or *aIDip*-species after about four days. Longer reaction times gave rise to resonances of further by-products in low concentrations and small quantities of insoluble products.



Scheme 4. Synthesis of $[(\text{IDip})\text{AlH}_2(\text{aIDip})]\text{I}$ **9** and $[(\text{IDip})\text{AlHI}(\text{aIDip})]\text{I}$ **10**.

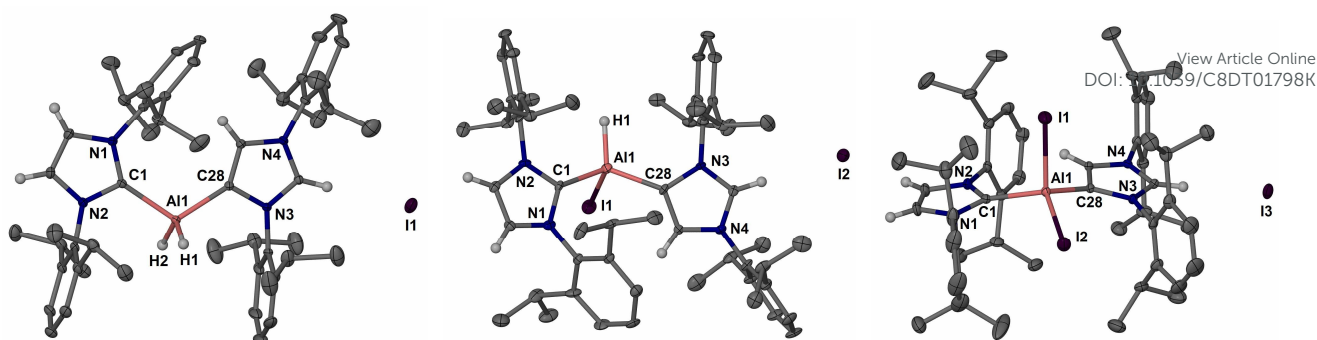


Figure 4. Molecular structures (25% thermal ellipsoid) of [(IDip)AlH₂(*a*IDip)]I **9**, (left) [(IDip)AlHI(*a*IDip)]I·C₆H₆ **10**·C₆H₆ (centre) and [(IDip)AlIX(*a*IDip)]I·2 C₆H₆ (X ≈ 75% I, 25% H), **11**_{0.75}·**10**_{0.25}·2 C₆H₆ (right). Only Al-H, except the minor proportion of **10** in **11**_{0.75}·**10**_{0.25}·2 C₆H₆, and NHC ring hydrogen atoms shown for clarity. Solvent molecules and minor disordered parts in **11**_{0.75}·**10**_{0.25}·2 C₆H₆ not shown.

Table 1. Selected bond distances (Å) and angles (°) for complexes **9-11**.

	9	10	11
C1-Al1	2.051(2)	2.031(13)	2.067(4)
C28-Al1	2.012(2)	1.998(13)	1.992(4)
Al1-X	1.54(2) (H1)	2.577(4) (I1)	2.5570(13) (I1)
	1.56(2) (H2)	1.55(2) (H1)	2.4964(13) (I2)
C1-Al1-C28	114.24(8)	119.2(5)	116.40(16)

The salts [(IDip)AlH₂(*a*IDip)]I **9**, [(IDip)AlHI(*a*IDip)]I·C₆H₆ **10**·C₆H₆ and [(IDip)AlIX(*a*IDip)]I·2 C₆H₆ (X ≈ 75% I, 25% H), **11**_{0.75}·**10**_{0.25}·2 C₆H₆, crystallized with a full formula unit in the asymmetric unit, are depicted in Figure 4 and selected metrical data is given in Table 1. In **9-11**, each salt contains a [(IDip)AlX₂(*a*IDip)]⁺ cation, with X being H and/or I, which have a central, distorted tetrahedral Al^{III} centre, balanced by an iodide counter anion. The IDip and *a*IDip heterocyclic planes in **9** having the least steric crowding around the Al centre are nearly coplanar and are slightly more twisted in **10** and **11**. The iodide counter anion shows an interaction to the N₂CH hydrogen of the *a*IDip ligand in the solid state of **9-11**. A short H···Dip_{centroid} contact with a distance of *ca.* 2.24 Å in **9** is found for the H in the 5-position of the *a*IDip ligand to a Dip group from the IDip ligand. The Al-C distances are as expected slightly shorter (by *ca.* 5 pm for the mean values) for the *abnormal* NHC Al-C(28) coordination compared with the *normal* NHC Al-C(1) coordination bond. This is not surprising given that *remote* and *abnormal* NHCs are even stronger donor ligands than popular imidazol-2-ylidenes and that *abnormal* NHC ligands show a smaller steric profile.^{1,15} The Al-C distances for the *normal* and *abnormal* NHC bonds reflect those of other

structurally determined complexes, for example Al-C(NHC) of 2.048(3) Å and Al-C (*a*NHC) of 2.006(3) Å in the anion of **C**.¹⁶ A series of aluminium complexes with abnormal NHC ligand coordination^{3,17,19,22} have been studied in recent years that show comparable features to compounds **9-11**.

Once crystallized, complexes [(IDip)AlH₂(*a*IDip)]I **9** and [(IDip)AlHI(*a*IDip)]I **10** do not show any significant solubility in aromatic solvents or THF. Due to their reactive Al-H moieties, the range of polar NMR solvents is very limited and hence no solution state NMR spectra could be recorded. *In-situ* reactions also showed no strong resonances that could be attributed to **9** or **10**. The complexes show Al-H stretching bands in their IR spectra (1827 and 1811 cm⁻¹ for **9**, and 1867 cm⁻¹ for **10**) that are comparable to those of the other hydride-iodide compounds with four-coordinate Al centres, *i.e.* **4**, **5**, **7** and **8**. NHC-stabilized AlH cation **B** shows an even higher wavenumber for the Al-H stretch (1963 cm⁻¹) due to its three-coordinate Al centre.¹⁵ The cation of **9**, [(IDip)AlH₂(*a*IDip)]⁺, was detected by mass spectrometry.

A related set of experiments was conducted between [(IMes)AlH₂I] **7** and [(IMes)AlHI₂] **8** with IMes, respectively. The solubilities of [(IMes)AlH₂I] **7** and [(IMes)AlHI₂] **8** are markedly lower than those of the related IDip complexes which impeded solution studies. These reactions produced an insoluble precipitate at room temperature when **7** was used. An IR spectrum of the residue shows weak bands at around 2000 cm⁻¹ though no comparable stretches to the Al-H bonds of IDip derivative **9**. A reaction between [(IMes)AlHI₂] **8** and IMes slowly proceeds at 80°C with some initial broadening and the formation of a product mixture including an IMesAl-complex with symmetric IMes resonances, possibly [(IMes)AlI₃] **6**, and some insoluble products.

Abnormal NHC-Al complexes have been found to be slightly lower in energy than directly comparable *normal* NHC-Al complexes for the sterically demanding NHC, *It*Bu = 1,3-di-*tert*-butylimidazol-2-ylidene.^{22c} A series of [(*aIt*Bu)MX₃] (M = Al, Ga, In; X = Me, *i*Bu, Cl) were formed from the free *normal* NHC *It*Bu and the Lewis-acidic formal three-coordinate MX₃ precursor and a related study formed [(*a*IDip)GaR₃] (R = CH₂SiMe₃, Cl) and related species.²³ Fast and reversible H-exchange processes were suggested to play a role in the isomerisation mechanism.^{22a}

Mechanistically, overall nucleophilic substitution of a neutral *a*IDip ligand for an iodide ligand, *e.g.* via a short-lived five-coordinated intermediate (*c.f.* the equilibria observed for [(IDip)AlH₃] **2** with IDip, scheme 3) or via short-lived [(IDip)AlX₂]⁺ (X = H, I) cations, is possible. The formation of *normal-abnormal* NHC complexes **9-11** is believed to occur due to steric reasons with the coordination of two *normal* IDip molecules to Al^{III} not resulting in strong metal-ligand interactions. Low concentrations of an *abnormal* carbene (*a*IDip) could be accessible in solution and form a stable product with an Al-C(*a*IDip) interaction. Alternatively, complexes [(IDip)AlX₃]

(X = H, I) could rearrange in solution in an equilibrium to a small and non-observed proportion of the *abnormal* NHC complexes [(*a*IDip)AlX₃] (X = H, I),²² which allows the approach of free IDip either after iodide elimination, *i.e.* on [(*a*IDip)AlX₂]⁺, or in a substitution reaction via an associative mechanism with a short-lived five-coordinate intermediate to **9** and **10**. The precipitation of products **9** and **10** formed in equilibria in solution provide a further driving force for their isolation.

The related cationic system [(IDip)₂ZnMe]⁺ rearranges to the more thermodynamically stable, and less sterically congested species [(IDip)ZnMe(*a*IDip)]⁺ in the presence of THF or IDip.²⁴ The mechanism for this reaction is suggested to involve deprotonation of a hydrogen in the 4-position of an IDip ligand in [(IDip)₂ZnMe]⁺ by free IDip. Cationic examples related to **9-11** from main group chemistry include the tin(II) complex [(IDip)SnX(*a*IDip)]OTf (X = Cl, OTf; ⁻OTf = triflate), formed from Sn(OTf)₂ and two equivalents of IDip,²⁵ and the group 15 complexes [(IDip)SbF₂(*a*IDip)][SbF₄],²⁶ [(*a*IDip)₂SbBr₂]Br and closely related species.²⁷ Similar mechanistic arguments to those for the Zn systems²⁴ were made for the formation of these *abnormal* NHC complexes including the deprotonation of the hydrogen in the 4-position of IDip-complexes by the free base IDip.²⁵⁻²⁷ ¹H NMR spectra on some tin and antimony complexes in THF-d₈ revealed the formation of IDipH⁺ from decomposition reactions.^{25,26}

Mechanistic considerations as discussed above highlight the most likely pathways to **9** and **10** though do not unequivocally explain why the reaction of [(IDip)AlI₃] **4** and IDip to give [(IDip)AlI₂(*a*IDip)]I **11** is significantly suppressed, especially when an outer Al-IDip deprotonation or Al-IDip isomerisation would be involved. Also, both H and I ligands appear to be required for a facile reaction which could be explained by a reductive elimination/oxidative addition²⁸ mechanism. The reductive elimination of HI from [(IDip)AlH₂I] **4** and [(IDip)AlHI₂] **5** by the relatively strong base IDip could potentially form the imidazolium salt IDipH⁺I⁻. The latter was not observed in solution state *in-situ* NMR spectra, however, small concentrations can't be ruled out. Its presence would also be explained by an IDip deprotonation mechanism. A reductive elimination could result in a short-lived low oxidation state intermediate such as (IDip)Al^IX (X = H or I), or an oligomer, that subsequently CH activates IDipH⁺I⁻ again and for steric reasons forms an *abnormal* IDip product. NHC-stabilised low oxidation state aluminium complexes are highly reactive species and examples have been predicted from quantum chemical calculations, proposed as reactive intermediates and few examples were isolated.⁴⁻⁷ Furthermore, reversible σ-bond metathesis between Al^{III}/Al^I species via reductive elimination and oxidative addition steps are known in a similar temperature range, for example between LAl^I (L = HC(MeCNDip)₂ or Cp* = C₅Me₅) and Cp*H to LAl^{III}(H)(Cp*).²⁹ The reaction of an anionic gallium(I) carbene analogue with IMesH⁺Cl⁻ afforded an oxidative addition product featuring an (IMes)Ga^{III}H fragment.³⁰ These studies show that the reaction steps are feasible. The insoluble nature of salts **9-10** precluded further solution state

studies with these compounds. The possibility that an AlH moiety acts as a base during the reaction to deprotonate an IDip ligand in the 4-position, *c.f.* the anion of **C**, and is thus required for the reaction has been considered. In this case H₂ would be a by-product and no traces for a H₂ resonance were observed in *in-situ* ¹H NMR spectra for reactions producing **9** and **10**. The fact that [(IDip)AlH₃] **2** and IDip exchange their ligands rapidly at temperatures below 0°C whereas the same exchange is suppressed for [(IDip)AlI₃] **4** and IDip at temperatures above 100°C may hint at an alternative mechanism that requires coordination of a second IDip ligand to aluminium which becomes increasingly difficult with more coordinated iodide ligands.

Conclusions

We have prepared the complexes [(IDip)AlH₂I] **4**, [(IDip)AlH₂I] **5**, [(IMes)AlH₂I] **7**, and [(IMes)AlH₂I] **8**, either via a ligand scrambling approach from appropriate quantities of NHCAIH₃ with NHCAI₃ which was preferable for the formation of the monoiodides **4** and **7**, or via iodination of NHCAIH₃ with an excess of methyl iodide to the diiodides **5** and **8**. Reactions of NHCAIX₃ (X = H, I) with one equivalent of NHC showed a reversible fluxional, dynamic behaviour for X = H, no reaction for X = I (NHC = IDip), or formed the new *normal-abnormal* NHC complexes [(IDip)AlH₂(*a*IDip)]I **9** and [(IDip)AlHI(*a*IDip)]I **10**, when **4** and **5** are used, respectively. The complexes **9**, **10** and [(IDip)AlIX(*a*IDip)]I (X ≈ 75% I, 25% H), **11**_{0.75}·**10**_{0.25}, were structurally characterized and show slightly shorter Al–C(*a*IDip) distances than Al–C(IDip) distances. The mixed *normal abnormal* IDip coordination to aluminium in **9-11** is believed to occur for steric reasons. Complex **11** could not be prepared from [(IDip)AlI₃] **3** and IDip under forcing conditions suggesting that mixed hydride and iodide on one Al centre are required for this reaction. Nucleophilic substitution and reductive elimination/oxidative addition mechanisms have been discussed for the formation of **9** and **10**.

Conflicts of interest

There are no conflicts to declare.

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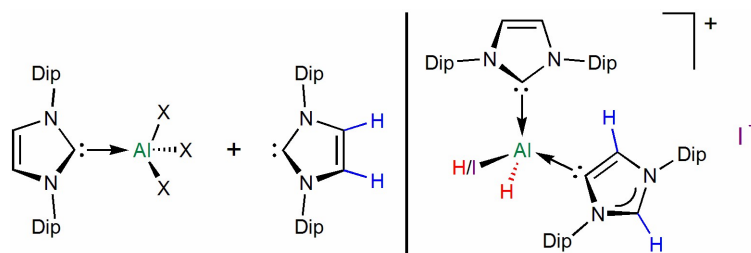
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Sterically demanding NHC aluminium hydride iodide complexes react with one equivalent of NHC to cationic mixed *normal-abnormal* NHC Al^{III} complexes.



X = H: *equilibrium*; X = I: *no reaction*; X = H, I: *products*