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# The Reactivity of NHC Alane Adducts towards *N*-Heterocyclic Carbenes and Cyclic (Alkyl)(Amino) Carbenes: Ring Expansion, Ring Opening, and Al-H Bond Activation

Heidi Schneider, Andreas Hock, Rüdiger Bertermann, and Udo Radius \*[a]

Dedicated to Professor Dieter Fenske on the occasion of his 75th birthday

Abstract: The synthesis of the mono NHC alane adducts of the type (NHC)·AIH<sub>3</sub> (NHC = Me<sub>2</sub>Im 1, Me<sub>2</sub>Im<sup>Me</sup> 2,  $iPr_2$ Im 3 and 3-d<sub>3</sub>,  $iPr_2$ Im<sup>Me</sup> 4, Dipp<sub>2</sub>Im 10) and (NHC)·Al*i*Bu<sub>2</sub>H (NHC = *i*Pr<sub>2</sub>Im 11, Dipp<sub>2</sub>Im 12) as well as their reactivity towards different types of carbenes is presented. While the mono NHC adducts remain stable at elevated temperatures, ring expansion reaction occurs when (*i*Pr<sub>2</sub>Im)·AIH<sub>3</sub> 3 is reacted with a second equivalent of the carbene iPr2Im to give (*i*Pr<sub>2</sub>Im)·AIH(RER-*i*Pr<sub>2</sub>ImH<sub>2</sub>) 6. In 6, {(*i*Pr<sub>2</sub>Im}AIH} is inserted into the NHC ring. In contrast, ring opening is observed with sterically more demanding Dipp<sub>2</sub>Im with formation of (*i*Pr<sub>2</sub>Im)·AIH<sub>2</sub>(ROR- $Dipp_2ImH_2)H_2AI \cdot (iPr_2Im)$  9. In 9, two {( $iPr_2Im$ )·AIH\_2} moieties stabilize the ring opened Dipp<sub>2</sub>Im. If two hydridic sites are blocked, the adducts are stable with respect to further ring expansion or ring opening, as exemplified by the adducts (*i*Pr<sub>2</sub>Im)·Al*i*Bu<sub>2</sub>H 11 and (Dipp<sub>2</sub>Im)·Al*i*Bu<sub>2</sub>H 12. The reaction of  $(NHC) \cdot AIH_3$  and  $(iPr_2Im) \cdot AIiBu_2H$  with  $cAAC^{Me}$ yields instead of ligand substitution, ring expansion or ring opening the products of an insertion of the carbone carbon atom into the AI-H bond (NHC)  $\cdot$  AIH<sub>2</sub>/*i*Bu<sub>2</sub>(cAAC<sup>Me</sup>H) **13–18**.



#### Introduction

Research on *N*-Heterocyclic Carbenes (NHCs) and related molecules <sup>[1]</sup> demonstrated in the last decade clearly that their application is not limited to the use as (spectator) ligands in transition metal chemistry and catalysis or to their application as stabilizers for subvalent main group element compounds <sup>[2-4]</sup>. Carbenes themselves show a rich diversity in their reaction pattern towards main group element hydrides and organyls.<sup>[5]</sup> We and others demonstrated earlier, that in dependence on the electronic and steric properties of the carbene and on the main group element compound used, various reaction channels are observed. With simple Brønsted acids like alcohols and hydrogen halides usually the basic character of the carbene dominates and deprotonation to the corresponding imidazolium salts occurs.<sup>[6]</sup> However, the carbene carbon atom combines a *Lewis* acidic (empty vacant  $p_z$  orbital) and a *Lewis* basic '

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Scheme 1. Carbene-mediated reactions of main-group element hydrides

(occupied  $sp_2$  orbital) site which enables singlet carbenes to undergo element element bond activation reactions beyond simple deprotonations (Scheme 1).

It was demonstrated earlier, for example, that cyclic (alkyl)(amino) carbenes (cAACs) provide a robust environment for Si–H, B–H, and P–H bond activation, and most recently we and others reported that even C–H and C– $F^{[7]}$  bond activation occurs with formation of the E–H respectively E–E bond cleavage products. In addition, we also showed recently that insertion of cAACs into the B-C bond of selected arylboronate esters is reversible and this reversibility may lead to the development of novel carbon centered organocatalysts.<sup>[8]</sup>

We currently assume that E–H (E = H, B, C, N, Si, P) or E–E bond activation is also the key step for any further reactivity of NHCs and cAACs. In the last few years reactions of NHCs with *Lewis* acidic hydrides such as silanes<sup>[9]</sup>, boranes<sup>[10]</sup> and beryllium hydrides<sup>[11]</sup> have been reported, which lead to ring expansion of the NHC, while the E–H or E–E bond activation is considered to be the crucial step of the reaction sequence.<sup>[12]</sup> We also provided lately the first example of a ring expansion reaction of a cAAC, using aryl catechol boronate esters. The *Lewis* acid/base adduct (cAAC)-BcatAr was observed, which subsequently reacts with

ring expansion of the cAAC. Furthermore, we have also shown for group 15 element hydrides that secondary and primary phosphines may be converted with NHCs into diphosphines or cyclooligophosphines by reductive dehydrocoupling,<sup>[9b]</sup> and closely related dehydrocoupling was also observed for organo tin hydrides. <sup>[13]</sup> E-H bond cleavage is likewise considered to be the initial step for this reaction channel, leading to an instable E-H activation product, which in turn leads to further reactions. Bertrand and coworkers demonstrated earlier, that alkyl(amino)carbene mediated P-H bond activation of phosphines provides the stable E-H oxidative addition products without any further reaction. [14] This example demonstrates nicely, that the progress after E-H bond activation at a carbene center depends strongly on the stability of the E-H oxidative addition product and thus on the main group element hydride employed. However, the result of the reaction between a carbene and a main group element hydride also depends on the nature of the carbene. We investigated recently, for example, in some detail the reactivity of different carbenes with catechol borane HBcat. This borane forms with backbone unsaturated NHCs (nPr<sub>2</sub>Im, *i*Pr<sub>2</sub>Im, *i*Pr<sub>2</sub>Im<sup>Me</sup> and Dipp<sub>2</sub>Im) *Lewis* acid-base adducts, which are stable at higher temperatures and no E-H bond cleavage or ring expansion reaction (RER) was observed for these molecules. In contrast, E-H bond activation occurs for the reaction of HBcat with the cyclic alkyl(amino)carbene cAAC<sup>Me</sup>, but no RER of the cAAC occurs. If the backbone saturated NHC Dipp<sub>2</sub>H<sub>2</sub>Im is used, adduct formation is followed by B-H activation and subsequent ring expansion reaction (vide infra) takes place. <sup>[10f]</sup>

Donor stabilized aluminum compounds have been of interest for several years, mainly due to the manifold application of alanes in organic and inorganic synthesis and lately also because of the potential of aluminum compounds as hydrogen storage systems. Besides the well-established chemistry of amine or phosphine stabilized mono alane adducts and adducts with oxygen based ligands, homoleptic (amine donors) as well as heteroleptic (amin/phosphor donors) bis alane adducts are established.<sup>[15]</sup> NHC aluminum chemistry is developed to some extend<sup>[15q, 16]</sup> and it is known that Lewis acid-base adducts of aluminum hydrides are rather unstable. Besides simple decomposition of the compounds to unidentified molecules, NHC to aNHC rearrangement in the coordination sphere of aluminum<sup>[17]</sup> and ring expansion reaction of a NHC in  $\beta$ -diketiminato aluminum dihydrides was observed.<sup>[16i]</sup> However, the utilization of carbenes in aluminum chemistry also facilitate the isolation of interesting with new molecular structures substances such as (Dipp<sub>2</sub>Im)·H<sub>2</sub>Al-AlH<sub>2</sub>·(Dipp<sub>2</sub>Im), obtained by magnesium(I) mediated dehydrogenative coupling of (Dipp<sub>2</sub>Im)·AIH<sub>3</sub><sup>[16f, 18]</sup> or a cAAC stabilized neutral aluminum radical<sup>[19]</sup> and the NHC



stabilized aluminum cation [(Dipp<sub>2</sub>Im)·AlH<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sup>[20]</sup>. Due to our experience on the reactivity of carbenes with phosphines, silanes, tin hydrides and especially boranes and the existing reports on the instability of some NHC aluminum compounds, we decided to take a closer look on the behavior of carbenes with different aluminum hydrides and we wish to report first results here.

#### **Results and Discussion**

Lewis acid-base adducts<sup>[15]</sup> with AIH<sub>3</sub> are known for guite a while now. There are several approaches to synthesize such Lewis acid-base adducts: One method involves the reaction of AlH<sub>3</sub> (usually obtained from the reaction of LiAlH<sub>4</sub> with H<sub>2</sub>SO<sub>4</sub>) with a two electron donor (e.g. amines and phosphines). These adducts are in some cases also accessible using the reaction of LiAlH<sub>4</sub> directly and the ligand (or the ligand salt) with salt elimination. A third important method is the substitution of the trimethylamine ligand of the adduct NMe3·AIH3.[15b-g, 15i-w, 21] In dependence on the basicity and the steric demand of the ligand used, formation of the alane adducts stabilized by one or two bases (two electron donor ligands) may occur.[15w] Known examples <sup>[15q, 16a-f, 16h, 16i, 18, 22]</sup> show that NHC stabilized alanes have been synthesized so far mainly via salt elimination from the reaction of NHCs with lithium aluminum hydride or from base substitution of NMe3·AIH3.[15q, 16a-e, 16i, 18, 21-22] For the presented study we opt to synthesize the (NHC)·AIH<sub>3</sub> adducts via the LiAIH<sub>4</sub> route.

The adducts (Me<sub>2</sub>Im)·AlH<sub>3</sub> **1**, (Me<sub>2</sub>Im<sup>Me</sup>)·AlH<sub>3</sub> **2**, (*i*Pr<sub>2</sub>Im)·AlH<sub>3</sub> **3** and (*i*Pr<sub>2</sub>Im<sup>Me</sup>)·AlH<sub>3</sub> **4** are readily accessible from the reaction of lithium aluminum hydride with the corresponding *N*-heterocyclic carbene at 0 °C in diethyl ether (Scheme 2). In course of the reaction, lithium hydride precipitates and can be separated by filtration. Further workup gave the adducts **1** to **4** as colorless crystalline solids in excellent purity and in fair to good overall yield (**1**: 56 %, **2**: 62 %, **3**: 73 %, **4**: 63 %). This method is also perfectly suitable to synthesize the corresponding deuterated adducts, as exemplified by the synthesis of (*i*Pr<sub>2</sub>Im)·AlD<sub>3</sub> **3**-*d*<sub>3</sub> is obtained starting from commercially available LiAlD<sub>4</sub> as a colorless solid in 57 % yield.

The adducts **1** to **4** were characterized using multinuclear NMR and IR spectroscopy and elemental analyses. The characteristic Al–H bond stretching vibrations of the compounds **1** – **4** were observed in the range between 1644 to 1784 cm<sup>-1</sup> (see SI).<sup>[15g, 15i, 15k, 15q, 15r, 15w, 21, 23]</sup> For example, two IR bands were recorded for (*i*Pr<sub>2</sub>Im)·AlH<sub>3</sub> **3** as a broad signal at 1719 cm<sup>-1</sup> and a shoulder at 1776 cm<sup>-1</sup> in the solid state. Three sharp IR bands were calculated for gas phase (*i*Pr<sub>2</sub>Im)·AlH<sub>3</sub> **3** at 1762, 1767 and 1787cm<sup>-1</sup> (scaling factor 0.9914 <sup>[24]</sup>) using DFT at the BP86/def2-SVP level. This assignment was further proven by a comparison of the Al-H/D IR bands of (*i*Pr<sub>2</sub>Im)·AlH<sub>3</sub> **3** and its deuterated isotope (*i*Pr<sub>2</sub>Im)·AlD<sub>3</sub> **3**-*d*<sub>3</sub>, which are significantly shifted to lower wavenumbers at 1250 cm<sup>-1</sup>. This is in agreement with the observation made for the amine adducts NMe<sub>3</sub>·AlH<sub>3</sub> (the Al-H stretch was detected as a broad band at 1792 cm<sup>-1</sup>) and

	AI- <i>H</i> <sup>1</sup> H{ <sup>27</sup> AI} NMR	N <i>C</i> N <sup>13</sup> C{ <sup>1</sup> H} NMR	<sup>27</sup> Al{ <sup>1</sup> H} NMR
(Me₂Im)·AlH₃ 1	4.39	172.2	105.8 <sup>[a]</sup>
Me <sub>2</sub> Im <sup>Me</sup> )·AIH <sub>3</sub> <b>2</b>	4.48	168.7	106.4 <sup>[a]</sup> 104.4 [ <sup>b]</sup>
( <i>i</i> Pr₂lm)∙AlH₃ <b>3</b>	4.53	170.3	106.3 <sup>[a]</sup> 105.3/105.8 <sup>[b]</sup>
( <i>i</i> Pr₂Im <sup>Me</sup> )⋅AlH₃ <b>4</b>	4.60	170.0	107.8 <sup>[a]</sup> 103.6/103.8 <sup>[b]</sup>
(Dipp <sub>2</sub> Im)·AIH <sub>3</sub> 10	3.67	178.2	107.9 <sup>[b]</sup>
( <i>i</i> Pr₂lm)⋅Al <i>i</i> Bu₂H <b>11</b>	4.71	173.1	139.4 <sup>[a]</sup> 138.9 <sup>[b]</sup>
(Dipp₂lm)·Al <i>i</i> Bu₂H <b>12</b>	3.97	180.5	137.0 <sup>[b]</sup>

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

 $NMe_3{\cdot}AID_3$  (the AI-D stretch was detected as a broad band at 1304  $cm^{-1}).^{[25]}$ 

The most important NMR shifts of the compounds 1 - 4 are summarized in Table 1. The proton NMR spectra of the NHC·AIH<sub>3</sub> adducts 1-4 in solution reveal sharp, significantly shifted resonances for the NHC ligand, whereas the aluminum bound hydrogen atoms appear as very broad peaks (range > 2.5 ppm) due to the direct binding to the  ${}^{27}$ Al atom (I = 5/2) and the resulting splitting in combination with the quadrupole moment (q = 14.7 fm<sup>2</sup>) of the aluminum nucleus. However, the aluminum bound hydrogen atoms of the adducts 1 to 4 can be detected in the <sup>1</sup>H{<sup>27</sup>Al} NMR spectrum in the range from 4.39 to 4.60 ppm. The proton NMR of the adduct 3 shows, for example, a doublet at 0.94 ppm for the methyl groups and a septet at 5.25 ppm for the methine protons of the iso-propyl substituent. The singlet of the backbone protons arises at 6.23 ppm, whereas the aluminum bound hydrides were detected as a broad singlet in the <sup>1</sup>H<sup>27</sup>Al} NMR spectrum at 4.53 ppm.

In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, the signals of (*i*Pr<sub>2</sub>Im)·AlH<sub>3</sub> 3 were detected at 22.9 (iPr-CH<sub>3</sub>), 51.6 (iPr-CH) and 117.0 (NCHCHN) ppm. The carbone carbon resonances of the (NHC)·AlH<sub>3</sub> adducts are usually also difficult to detect due to the quadrupole moment of the <sup>27</sup>Al core and appear as strongly broadened signals. The carbone carbon atom of  $(iPr_2Im) \cdot AIH_3$  3, for example, gives rise to a signal at 170.3 ppm, significantly shifted compared to the resonance of uncoordinated /Pr2lm at 211.6 ppm. In general, the NHC-AIH<sub>3</sub> adducts 1 - 4 with alkyl substituted NHCs reveal carbone carbon resonances in the range between 168.7 and 173.1 ppm. <sup>27</sup>Al{<sup>1</sup>H} NMR resonances of the alane adducts are typically observed in a region between 100 and 140 ppm. (tBu<sub>3</sub>P)·AlH<sub>3</sub>, for example, reveals a signal at 121.8 ppm<sup>[15i]</sup>, whereas the resonance of (Me<sub>3</sub>N)·AIH<sub>3</sub> is detected at 139.8 ppm.<sup>[15s]</sup> Compounds (Me<sub>2</sub>Im)·AIH<sub>3</sub> 1, (Me<sub>2</sub>Im<sup>Me</sup>)·AIH<sub>3</sub> 2, (*i*Pr<sub>2</sub>Im)·AIH<sub>3</sub> 3, and (*i*Pr<sub>2</sub>Im<sup>Me</sup>)·AIH<sub>3</sub> 4 show broad singlets in solution between 105.8 and 107.8 ppm and are thus in good agreement to the know NHC·AlH<sub>3</sub> adducts reported so far,  $(iPr_2Im^{Me})$ ·AlH<sub>3</sub> ( $\delta = 106 \text{ ppm})^{[16b]}$  and  $(Mes_2Im)$ ·AlH<sub>3</sub> ( $\delta = 107 \text{ ppm})^{[16a]}$ .

In addition to the NMR spectra in solution, we recorded the solid state NMR spectra of selected complexes (see SI). The resonances of the adducts 2 - 4 observed in the <sup>13</sup>C{<sup>1</sup>H} and <sup>27</sup>Al{<sup>1</sup>H} solid state NMR spectra are in good agreement to those detected in solution. These results provide some evidence that the Lewis acid-base adducts 1 to 4 adopt the same structures in both solution and solid state (for the X-ray crystal structures see below). The <sup>27</sup>Al{<sup>1</sup>H} HPDec/MAS NMR spectrum of (*i*Pr<sub>2</sub>Im)·AlH<sub>3</sub> 3 shows, for example, a signal with an isotropic shift at 105.8 ppm with the typical line shape (MAS second-order quadrupole powder pattern) for a tetrahedral sp<sup>3</sup>-Al atom with a quadrupolar coupling constant of 9967 kHz and a quadrupolar asymmetry parameter of 0.07. A second isotropic shift for a conformer is detected at 105.3 ppm with a guadrupolar coupling constant of 9710 kHz and a quadrupolar asymmetry parameter of 0.07 (see Figure 1). The signals of both conformers are in perfect agreement with the resonance at 106.3 ppm found in solution for (*IPr*<sub>2</sub>Im)·AIH<sub>3</sub> 3. The <sup>15</sup>N VACP/MAS NMR spectrum shows one resonance at -167.3 ppm for the nitrogen atoms of the NHC.

<sup>27</sup>Al{<sup>1</sup>H} NMR spectra in the solid state of the compounds (Me<sub>2</sub>Im<sup>Me</sup>)·AlH<sub>3</sub> **2** and (*i*Pr<sub>2</sub>Im<sup>Me</sup>)·AlH<sub>3</sub> **4** are likewise in perfect accordance with the resonances observed in the solution NMR spectra, which are compared to each other in Table 1, and show a similar line shape as presented for compound **3**.

The molecular structure of  $(Pr_2|m)$ ·AlH<sub>3</sub> **3** was confirmed by X-Ray diffraction and is shown in Figure 2. The hydrogen atoms bound to the aluminum atom of compound **3** have been located on the electron density map and were refined isotropically. The aluminum center is in a tetrahedral environment and coordinated by one NHC ligand and three hydrogen atoms. The angles spanned by the ligands are in a range between 104.1(8) and 113.5(10) °. The NHC aluminum as well as the aluminum hydride bond lengths of 2.0375(17) and 2.0405(17) Å for Al–C<sub>NHC</sub> and 1.492(19) to 1.56(2) Å for Al–H are in good agreement to the bond lengths of (Dipp<sub>2</sub>Im)·AlH<sub>3</sub> (Al–NHC: 2.0556(13) Å; Al–H: 1.510(17) to 1.546(17) Å) [<sup>16d</sup>] reported earlier.



Figure 1.<sup>27</sup>Al{<sup>1</sup>H} HPDec/MAS NMR spectrum of (*i*Pr<sub>2</sub>Im)·AlH<sub>3</sub> 3.



Figure 2. Molecular structure of ( $iPr_2Im$ )·AIH<sub>3</sub> 3 in the solid state (ellipsoids set at 50% probability level). Selected bond lengths [Å] and angles [°]: Al1–C1 2.0405(17), Al1–H1 1.54(2), Al1–H2 1.56(2), Al1–H3 1.492(19), Al2–C11 2.0375(17), Al2–H4 1.53(2), Al2–H5 1.52(2), Al2–H6 1.53(2). C1-Al1-H1 108.5(7), C1-Al1-H2 1.04.1(8), C1-Al1-H3 105.4(8), H1-Al1-H2 112.1(11), H1-Al1-H3 113.5(10), H2-Al1-H3 112.5(11), C11-Al2-H4 104.5(8), C11-Al2-H5 109.2(7), C11-Al2-H6 106.5(8), H4-Al2-H5 112.2(10), H4-Al2-H6 111.4(11), H5-Al2-H6 112.5(11).

The NHC adducts 1 to 4 are thermally stable in solution at least to the boiling point of toluene. Thus, a flame sealed NMR tube of 3 in toluene-d<sub>8</sub> was kept at 110 °C for several days without a change of its <sup>1</sup>H NMR spectrum. However, in course of our work we became aware of instabilities that already occur at room temperature. If an excess (more than one equivalent) of the NHC *i*Pr<sub>2</sub>Im was added to a suspension of lithium aluminum hydride, a side product was observed in significant amounts with a rather complicated NMR spectrum. The proton NMR spectra of these solutions reveal aside from the symmetric resonance pattern of the *i*Pr<sub>2</sub>Im moiety of **3** additional resonances, indicating an unsymmetrical *i*Pr<sub>2</sub>Im species. In a following stoichiometric reaction of isolated (iPr2Im)·AIH3 3 with one equivalent iPr2Im at 70 °C for 16 h, a change of the color of the solution from colorless (color of 3) to bright orange was observed. After workup, a bright yellow solid was isolated, highly soluble in commonly used organic solvents like n-hexane, toluene, diethyl ether and thf and reactive towards chlorinated solvents such as CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>. The yellow product, which was obtained in yields up to 63 %, is highly sensitive towards air and moisture. This compound was then identified as the ring expansion product (iPr<sub>2</sub>Im)-AIH(RER*i*Pr<sub>2</sub>ImH<sub>2</sub>) 6 (RER = ring expansion reaction) using multinuclear NMR spectroscopy, high resolution mass spectrometry and elemental analysis. Heating of a *d*<sub>6</sub>-benzene solution containing equimolar amounts of (*I*Pr<sub>2</sub>Im)·AIH<sub>3</sub> 3 and *I*Pr<sub>2</sub>Im to 70 °C for 9 h (see Figure 3) demonstrated that the reaction proceeds quantitative to the reaction product (*i*Pr<sub>2</sub>Im)·AIH(RER-*i*Pr<sub>2</sub>ImH<sub>2</sub>) 6. Immediately after addition of the NHC iPr2lm to the adduct (*i*Pr<sub>2</sub>Im)·AIH<sub>3</sub> 3 only one set of protons of *i*Pr<sub>2</sub>Im and (*i*Pr<sub>2</sub>Im)·AIH<sub>3</sub> 3 is detected at room temperature, which either indicates the initial formation of the bis NHC aluminum hydride adduct trans-(*i*Pr<sub>2</sub>Im)<sub>2</sub>·AIH<sub>3</sub> 5 with intact NHC moieties at the aluminum center or a rapid exchange of the NHCs on the NMR time scale. The major difference between the NMR spectrum of 3 and that of this



**Scheme 3.** Ring expansion and ring opening reaction of  $(iPr_2Im) \cdot AIH_3$  **3** with  $iPr_2Im$  and  $Dipp_2Im$ .

mixture lies in the resonance of the isopropyl methine protons, which shifts from 5.25 ppm in **3** to 4.86 ppm and appears as a broad resonance at higher temperatures (e.g. at 70°C). Similarly, the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of the solution reveals only one set of signals and, most significantly, a distinct down field shift of the NHC carbene carbon atom from 170.3 ppm for (*I*Pr<sub>2</sub>Im)·AIH<sub>3</sub> **3** to 188.9 ppm, while the aluminum resonance is detected at 107.2 ppm.

Once we realized that trans-(iPr2Im)2·AIH3 5 might be an important intermediate for this reaction, we synthesized and isolated this compound. Starting from  $iPr_2Im$  and  $(iPr_2Im) \cdot AIH_3$  3, trans-(iPr<sub>2</sub>Im)<sub>2</sub>·AIH<sub>3</sub> 5 was isolated in 40 % yield as a colorless solid. The resonances observed in the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were identical to those observed in solutions investigated for the ring opening process (vide supra). The aluminum resonance was found at 107.2 ppm, only marginally shifted from the resonance of **3** at 106.3 ppm. Trans-(*i*Pr<sub>2</sub>Im)<sub>2</sub>·AIH<sub>3</sub> **5** rearranges even in the solid state slowly to 6, which is recognizable by the change of the color of the solid from colorless to yellow. (*i*Pr<sub>2</sub>Im)·AIH(RER-*i*Pr<sub>2</sub>ImH<sub>2</sub>) **6** was also synthesized in solution from isolated 5. The formation of 6 can be easily spotted in the <sup>1</sup>H NMR spectrum (Figure 3 and Figure S43 in the SI), since the resonance of the NHC backbone at 6.45 ppm splits into one resonance at 6.38 ppm for the intact NHC attached to aluminum and into two doublets at 4.85 and 5.33 ppm for the asymmetrical NHC backbone of the ring expanded NHC. The resonances of the methine protons at 4.86 ppm also split into one set at 5.61 ppm (intact NHC) and into two septets at 3.12 ppm and 3.30 ppm (methine protons of the ring expanded /Pr2Im moiety). The diastereotopic AICH2N protons are detected as two broad doublets at 70°C (Figure 3) at 1.86 ppm and 2.37 ppm, but lead to sharp roofed doublets at room temperature with a geminal coupling constant of 12.3 Hz (see Figure S37, SI). The <sup>27</sup>Al{<sup>1</sup>H} NMR resonance of 6 is detected as a broad singlet at 119.9 ppm, significantly shifted from the resonance of (*i*Pr<sub>2</sub>Im)·AIH<sub>3</sub> 3 in solution at 106.3 ppm. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum shows a characteristic high field resonance for the former carbene carbon atom AICH<sub>2</sub>N at 29.7 ppm and two signals for the endocyclic methine carbon atoms at 53.1 and 57.6 ppm as well as for the methyl groups of the iso-propyl arms of the ring expanded NHC moiety at 18.9 ppm. The intact iPr2Im moiety gives rise to a broad





resonance of the carbone carbon atom at 169.8 ppm, marginally shifted from 170.3 ppm observed for ( $iPr_2Im$ )·AIH<sub>3</sub> **3**. As can be seen in Figure 3, no further intermediate was detected in solution. The infrared spectrum of isolated **6** reveals only *one* characteristic band for the AI–H stretching vibration at 1747 cm<sup>-1</sup>.

A conversion vs. time diagram of the ring expansion reaction (Figure S100) was created from the time dependent NMR study by integration of the resonances of the starting material (integral of the backbone of **3** minus integral of the splitted methine protons at 3.12 and 3.30 ppm of the ring opened NHC in 6) and of the product (integral of the splitted methine protons at 3.12 and 3.30 ppm of 6). The analysis of the kinetics (Figure S100-S103) reveals that the monomolecular decrease of the concentration of (*i*Pr<sub>2</sub>Im)<sub>2</sub>·AIH<sub>3</sub> **5** and the formation of **6** follows a first order rate law (Figure S101). In accordance with our NMR studies (formation of a bis NHC aluminum adduct 5 after addition of iPr<sub>2</sub>Im to a solution of (*I*Pr<sub>2</sub>Im)·AIH<sub>3</sub> 3 in C<sub>6</sub>D<sub>6</sub>) and the kinetics presented here we propose a monomolecular reaction mechanism (Scheme 4) starting from the bis NHC adduct 5 and leading to (*i*Pr<sub>2</sub>Im)·AIH(RER-*i*Pr<sub>2</sub>ImH<sub>2</sub>) 6 via an intramolecular insertion of the {( $iPr_2Im$ )·AIH} moiety into the ring of the second  $iPr_2Im$  unit. The rate constant is calculated to  $k = 7.32 \cdot 10^{-5} \text{ s}^{-1}$  with a half-life of 158 min at 70 °C. In addition to the kinetics we performed experiments with the deuterated adduct (*i*Pr<sub>2</sub>Im)·AID<sub>3</sub> 3-d<sub>3</sub>. The reaction of this compound with *i*Pr<sub>2</sub>Im afforded (*i*Pr<sub>2</sub>Im)·AID(RERiPr<sub>2</sub>ImD<sub>2</sub>) 6-d<sub>3</sub>, exclusively deuterated at the former NHC carbene carbon atom. This demonstrates that the hydrogen atoms transferred originate exclusively from (*i*Pr<sub>2</sub>Im)·AID<sub>3</sub> 3-d<sub>3</sub> and that the solvent is not involved in the reaction process. The reaction of iPr2Im performed with a 1:1 ratio of (iPr2Im)·AIH3 3 and (*i*Pr<sub>2</sub>Im)·AID<sub>3</sub> 3-d<sub>3</sub> led to the formation of (*i*Pr<sub>2</sub>Im)·AIH(RERiPr2ImH2) 6, (iPr2Im)·AID(RER-iPr2ImD2) 6-d3 and the H/D cross product (*i*Pr<sub>2</sub>Im)·AIH/D(RER-*i*Pr<sub>2</sub>ImHD) 6-[H/D]. The appearance of the H/D cross product (iPr2Im)H/D(RER-iPr2ImHD) 6-[H/D]

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might be explained by a bimolecular reaction mechanism, which would contrast our conclusions drawn from time dependent NMR experiment. However, 6-[H/D] may also originate from H/D exchange between the adducts (*i*Pr<sub>2</sub>Im)·AIH<sub>3</sub> 3 and (*i*Pr<sub>2</sub>Im)·AID<sub>3</sub> 3-d<sub>3</sub> before the bis NHC adduct trans-(iPr2Im)2·AIH3 5 is even formed. This is indeed the case, and was verified by the independent reaction of  $(i Pr_2 Im) \cdot AIH_3$  3 and  $(i Pr_2 Im) \cdot AIH_3$  **3**-*d*<sub>3</sub> in a 2:1 ratio in C<sub>6</sub>D<sub>6</sub>. Immediately after addition of the solvent a new set of signals was detected, which is shifted from the resonances of 3 and 3-d<sub>3</sub>. The resonances of the aluminum bound protons arise marginally shifted 4.52 ppm at compared those of (*i*Pr<sub>2</sub>Im)·AlH<sub>3</sub> 3 at 4.53 ppm, while the other resonances are detected at 0.98 (iPr-CH<sub>3</sub>, 3: 0.94 ppm, 3-d3: 0.95 ppm), 5.22 (iPr-

CH, 3: 5.25 ppm, 3-d<sub>3</sub>: 5.23 ppm), and 6.39 (NCHCHN, 3: 6.23 ppm, 3-d<sub>3</sub>: 6.30 ppm). The same behavior is observed for the resonance of the deuterated compound 3-d<sub>3</sub> in the deuterium NMR spectra. The signal of (*i*Pr<sub>2</sub>Im)·AIH<sub>2</sub>D 3-d<sub>1</sub> is observed at 4.55 ppm, while the deuterium resonance of (*i*Pr<sub>2</sub>Im)·AID<sub>3</sub> 3-d<sub>3</sub> arises at 4.57 ppm. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum the signal of the carbene carbon atom appears slightly shifted at 169.7 ppm (3: 170.3 ppm, 3-d<sub>3</sub>: 170.3 ppm). The most significant evidence is found in the infrared spectra of the compound, where the broad, intensive bands of (*i*Pr<sub>2</sub>Im)·AIH<sub>3</sub> 3 at 1719 cm<sup>-1</sup> and (*i*Pr<sub>2</sub>Im)·AID<sub>3</sub> 3-d<sub>3</sub> at 1250 cm<sup>-1</sup> are missing. Thus, we strongly believe that the emergence of the cross product originates from H/D exchange already between the starting material (*i*Pr<sub>2</sub>Im)·AIH<sub>3</sub> 3 and  $(iPr_2Im)\cdot AIH_3$  **3-***d*<sub>3</sub>. Furthermore, we assume a reaction mechanism as provided in Scheme 4: [9a, 12a] In the first step the bis NHC adduct is formed, followed from NHC insertion into one of the AI-H bonds of (NHC)-AIH<sub>3</sub> to give intermediate A. Subsequent amido transfer from the NHC carbon atom to the aluminum atom leads to intermediate B, which finally reacts with a hydride shift from the aluminum atom to the (former) carbene carbon atom with formation of the product 6.

We tried several times to obtain single crystals suitable for Xray diffraction of ( $iPr_2Im$ )-AlH(RER- $iPr_2ImH_2$ ) **6** from saturated solutions of the compound in different solvents, but failed. Usually, the crystal quality of the material obtained was even too poor to establish the connectivity properly. However, in one case we isolated the hydrolyzed form of **6** as good quality crystals. The result of the X-ray analysis of these crystals of the compound [{( $iPr_2Im$ )-Al(RER- $iPr_2ImH_2$ )}<sub>2</sub>( $\mu^2$ -O)] **7** is shown in Figure 4 (left). The central aluminum atom is coordinated in a distorted tetrahedral environment by the carbene carbon atom and the nitrogen atom of the ring expanded  $iPr_2Im$  moiety, the intact NHC molecule and the bridging oxygen atom. The NHC aluminum bond



**Scheme 4.** Proposed mechanism for the ring expansion reaction of  $(iPr_2lm) \cdot AlH_3$  **3** with  $iPr_2lm$  to give  $(iPr_2lm) \cdot AlH(RER - iPr_2lmH_2)$  **6** via the bis-NHC adduct *trans*- $(iPr_2lm) \cdot AlH_3$  **5**.

distance corresponds with 2.0709(18) Å to the one observed( $iPr_2Im$ )·AIH<sub>3</sub> **3** in with 2.0405(17) Å. The AI–C<sub>RER-NHC</sub> bond length of 1.999(2) Å and the AI–N<sub>RER-NHC</sub> of 1.8514(17) Å do not deviate from the literature known data of aluminum carbon (1.99 Å <sup>[26]</sup>) and aluminum nitrogen (1.88 Å <sup>[16i]</sup>) single bonds.

We also tried several times to obtain single crystals suitable for X-ray diffraction of *trans*-( $iPr_2Im$ )\_2·AIH\_3 **5** from saturated solutions of the compound in different solvents, but weren't successful likewise. Instead we characterized the compound  $[(iPr_2Im)_4 \cdot AIH_2][(H_3AI^{a}iPr_2Im) \cdot AIH_3]$  **8** (Figure 4, right) crystallographically, which was obtained from the reaction of  $(iPr_2Im) \cdot AIH_3$  **3** with  $iPr_2Im$  in Et<sub>2</sub>O repeatedly. Similarly, we repeatedly crystallized  $[(iPr_2Im)_4 \cdot AIH_2] [(iPr_2Im)_2Li(AIH_4)_2]$  with one molecule  $(iPr_2Im) \cdot AIH_3$  **3** in the unit cell starting from lithium

aluminum hydride and 2 equivalents of *i*Pr<sub>2</sub>Im in Et<sub>2</sub>O (Figure S104 in the SI). In the cationic part [(IPr2Im)4·AIH2]+ of these ionic compounds, the aluminum cation is surrounded by four NHC ligands and two transconfigured hydride ligands, which span an almost ideal octahedral coordination polyhedron around the metal ion. In the anionic part of 8, one {AlH<sub>3</sub>} unit is coordinated in a Lewis acid-base interaction by the NHC in 2-position, while another {AIH<sub>3</sub>} moiety is bound to the 4-position at the backbone of the same NHC, i.e. one *i*Pr<sub>2</sub>Im ligand coordinates in its "normal" and "abnormal" mode and thus bridges two {AIH<sub>3</sub>} units. The bond distances between the aluminum

atom and the NHCs in the cation of approximately 2.179 Å are larger compared to (*i*Pr<sub>2</sub>Im)·AlH<sub>3</sub> **3** (Al–C<sub>NHC</sub>: 2.039 Å), as expected for higher coordination numbers, whereas the Al-C distances of the anionic part of **8** (2.048(3) Å and 2.006(3) Å) are in perfect agreement to those observed for **3**. Aluminum hydride cations are relatively scarce and Stephan *et al.* presented only recently the closely related compounds [(Dipp<sub>2</sub>Im)·AlH<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and [(Cy<sub>2</sub>Im)<sub>2</sub>AlH][B(C<sub>6</sub>F<sub>6</sub>)<sub>4</sub>], which are the first examples of NHC stabilized aluminum cations.<sup>[16h]</sup> To our knowledge **8** is the first example of a NHC stabilized cationic aluminum center in the coordination number six. However, if crystals of **8** were dissolved in solvents like benzene, toluene, diethyl ether or THF, we isolated the adduct (*i*Pr<sub>2</sub>Im)<sub>2</sub>·AlH<sub>3</sub> **5** as the main component, usually contaminated with traces of **6**. NMR investigations in C<sub>6</sub>D<sub>6</sub>



**Figure 4.** Molecular structure of the hydrolyses product of [{(*i*Pr<sub>2</sub>Im)·Al(RER-*i*Pr<sub>2</sub>ImH<sub>2</sub>)}<sub>2</sub>(*μ*<sup>2</sup>-O)] **7** (left) and of [(*i*Pr<sub>2</sub>Im)<sub>4</sub>·AlH<sub>2</sub>][(H<sub>3</sub>Al<sup>a</sup>/Pr<sub>2</sub>Im)·AlH<sub>3</sub>] **8** (right) in the solid state (ellipsoids set at 50% probability level). Selected bond lengths [Å] and angles [°]: **7**: Al–C1 2.0709(18), Al–C11 1.999(2), Al–N4 1.8514(17), Al–O1 1.6996(6). C1-Al1-C11 108.01(8), C1-Al1-O1 108.38(6), C11-Al1-O1 114.48(6), N4-Al1-O1 118.69(6), C1-Al1-N4 104.10(7), C11-Al1-N4 102.29(8). **8**: Al1–C1 2.181(3), Al1–C11 2.189(3), Al1–C21 2.170(3), Al1-C31 2.176(3), Al1–H101 1.62(2), Al1–H100 1.60(3); C1-Al1-C11 91.43(11), C1-Al1-C21 179.23(12), C1-Al1-C31 89.94(11), C11-Al1-C21 88.88(11), C11-Al1-C31 177.97(12), C21-Al1-C31 89.77(11), C1-Al1-H100 88.7(9), C1-Al1-H101 90.4(9), C11-Al1-H100 91.8(9), C11-Al1-H101 89.4(8), C21-Al1-H101 90.6(9), C21-Al1-H101 90.3(9), C31-Al1-H100 89.7(9), C31-Al1-H101 89.1(8), H100-Al1-H101 178.5(13). Anion: Al2–C41 2.048(3), Al2–H104 1.52(3), Al2–H103 1.55(3), Al2–H102 1.55(3), Al3–H103 11.1(16) H102-Al2-H104 115.1(17), H103-Al2-H104 110.0(15).

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revealed the formation of **3**, **5**, **6**, and some hydrogenated NHC  $iPr_2ImH_2$  from these crystals in solution. Thus, complex **5** seems to be in a rather complicated equilibrium with other species in solution, from which ionic **8** seems to crystallize preferentially.

The reaction of  $(iPr_2Im) \cdot AIH_3$  3 with the sterically more demanding NHC Dipp<sub>2</sub>Im follows a different pathway (Scheme 3). Instead of a ring expansion reaction the ring opening of the Dipp2Im carbene was observed at 70 °C. The isolated product (*i*Pr<sub>2</sub>Im)·AIH<sub>2</sub>(ROR-Dipp<sub>2</sub>ImH<sub>2</sub>)H<sub>2</sub>AI·(*i*Pr<sub>2</sub>Im) 9 was identified via solution and solid state NMR spectroscopy, high resolution mass spectrometry and X-ray diffraction. Compound 9 is, similar to 6, highly sensitive towards air and moisture. The molecular structure of 9 confirms the ring opening of the sterically more demanding NHC Dipp<sub>2</sub>Im with two molecules (*i*Pr<sub>2</sub>Im)·AIH<sub>3</sub> in combination with formation of one AI-C and one AI-N bond and migration of two hydrogen atoms (one hydrogen atom of each aluminum atom) to the former carbone carbon atom of Dipp<sub>2</sub>Im (Figure 5). Both aluminum atoms adopt a tetrahedral structure, in which Al1 is coordinated by one *i*Pr<sub>2</sub>Im, two hydrogen atoms and the former carbene carbon atom C1, whereas the second aluminum atom Al2 is bound to the nitrogen atom of the ring opened Dipp<sub>2</sub>Im, to an *i*Pr<sub>2</sub>Im ligand and two hydrogen atoms. The AI-NHC bond lengths of 2.0518(4) and 2.066(4) Å are similar to those found in (*i*Pr<sub>2</sub>Im)·AIH<sub>3</sub> **3** (AI–NHC 2.0375(17) & 2.0405(17) Å). The unsaturated backbone of Dipp<sub>2</sub>Im remains in the ring opening product intact, as can be seen from the C2-C3 bond length of 1.337(5) Å, which is characteristic for a C–C double bond.

In the proton NMR spectrum of **9**, the characteristic resonance for the AlC $H_2$ N protons is detected as a singlet at 2.85 ppm, whereas the signals of the backbone of the ring opened Dipp<sub>2</sub>Im are detected as two roofed doublets at 5.70 and 6.05 ppm. The resonances of each *i*Pr<sub>2</sub>Im moiety are well separated from each other, those of the {(*i*Pr<sub>2</sub>Im)·AI<sup>1</sup>H<sub>2</sub>-CH<sub>2</sub>} unit are slightly high field



Different reactivity of group 13 element hydrides towards bulky NHCs have been reported so far. While the catechol borane adduct (Dipp<sub>2</sub>Im).BcatH is stable even at higher temperatures, the adduct (Dipp<sub>2</sub>H<sub>2</sub>Im)·BcatH undergoes at room temperature ring expansion reaction to afford (RER-Dipp<sub>2</sub>H<sub>2</sub>Im(H<sub>2</sub>))B-cat-Bcat (Dipp2H2Im). Bertrand et al. observed for the reaction of pinacol borane with the backbone saturated NHC Dipp<sub>2</sub>H<sub>2</sub>Im the formation of the dimeric ring opened compound pinB(ROR-Dipp<sub>2</sub>H<sub>2</sub>Im)<sub>2</sub>Bpin,<sup>[14]</sup> similarly as we reported the formation of a ring opening product for the reaction with Dipp<sub>2</sub>H<sub>2</sub>Im. The saturated NHC Dipp<sub>2</sub>H<sub>2</sub>Im reacts in a 2:2 ratio to yield a NHC ring expansion product at room temperature via C-N bond cleavage and further migration of the hydrides from two HBcat molecules to the former carbene-carbon atom. When equimolar amounts of (*i*Pr<sub>2</sub>Im)·AIH<sub>3</sub> 3 and Dipp<sub>2</sub>Im were used for the reaction, (*i*Pr<sub>2</sub>Im)·AIH<sub>2</sub>(ROR-Dipp<sub>2</sub>ImH<sub>2</sub>)H<sub>2</sub>AI·(*i*Pr<sub>2</sub> Im) 9 and free Dipp<sub>2</sub>Im



Figure 5. Molecular structure of (*P*r<sub>2</sub>Im)-AlH<sub>2</sub>(ROR-Dipp<sub>2</sub>ImH<sub>2</sub>)H<sub>2</sub>Al-(*P*r<sub>2</sub>Im) **9** in the solid state (ellipsoids set at 50% probability level). Selected bond lengths [Å] and angles [°]: Al1–C1 1.983(4), Al1–C11 2.051(4), Al1–H1 1.41(4), Al1–H2 1.59(4), C1–N1 1.449(4), N1–C2 1.394(4), C2–C3 1.337(5), N2–C3 1.415(4), N2–Al2 1.839(3), Al2–C21 2.066(4), Al2–H3 1.48(4), Al2 H4 1.60(4). C1-Al1-C11 112.39(17), C1-Al1-H1 120.9(15), C1-Al1-H2 101.5(13), C11-Al1-H1 104.0(15), C11-Al1-H2 101.4(14), C11-Al1-H2 101.4(14), H1-Al1-H2 105(2), C21-Al2-N2 114.97(14), C21-Al2-H3 105.7(14), C21-Al2-H4 100.4(14), N2-Al2-H3 114.2(14), N2-Al2-H4 109.7(14), H3-Al2-H4 114.6(19).

were isolated in a ratio of 1:1, and no further ring expansion or ring opening or exchange of the Lewis base NHC at aluminum occurs. We assume that the ring opening of Dipp<sub>2</sub>Im is due to the steric demand of the NHC. In contrast to this, the reaction of (*i*Pr<sub>2</sub>Im)·AIH<sub>3</sub> 3 with Mes<sub>2</sub>Im gives even at higher temperatures no ring expansion or ring opening reaction. When other Lewisbases like amines (NEt<sub>3</sub>) or phosphines (PPh<sub>3</sub>) were reacted with (*i*Pr<sub>2</sub>Im)·AIH<sub>3</sub> 3 at 70 °C for 2 days, no reaction was observed, ligand neither exchange or ring expansion/opening of the NHC.

Since we observed ring expansion or ring opening, respectively, for the reactions of ( $iPr_2Im$ )·AIH<sub>3</sub> **3** with the small, alkyl substituted NHC  $iPr_2Im$  and the sterically more demanding aryl substituted Dipp<sub>2</sub>Im, we became interested in (i) the stability of AIH<sub>3</sub> base adducts of sterically more demanding NHCs and (ii) the stability of NHC aluminum hydride base adducts, if we

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Scheme 5. Synthesis of the compounds (Dipp<sub>2</sub>Im)·AlH<sub>3</sub> 10, (*i*Pr<sub>2</sub>Im)·Al*i*Bu<sub>2</sub>H 11 and (Dipp<sub>2</sub>Im)·Al*i*Bu<sub>2</sub>H 12.

block two of the hydridic positions. Therefore, the adducts (Dipp<sub>2</sub>Im)·AIH<sub>3</sub> 10, (*i*Pr<sub>2</sub>Im)·AI*i*Bu<sub>2</sub>H 11 and (Dipp<sub>2</sub>Im)·AI*i*Bu<sub>2</sub>H 12 were synthesized (Scheme 5). (Dipp<sub>2</sub>Im)·AIH<sub>3</sub> 10 was prepared from the reaction of the NHC with lithium aluminum hydride, as described earlier by Jones et al.[16d] (Dipp2Im)·AIH3 was isolated in yields of 65 % as a colorless solid and was identified using multinuclear NMR spectroscopy, elemental analysis and IR spectroscopy. The AI-H signals of (Dipp2Im)·AIH3 10 were recorded at 3.67 ppm, slightly shifted compared to those of (*i*Pr<sub>2</sub>Im)·AIH<sub>3</sub> 3 at 4.53 ppm. The <sup>13</sup>C{<sup>1</sup>H} NCN resonance of Dipp2Im in 10 was observed at 178.2 ppm, at lower field compared to 1 - 4, which is in accordance with the comparatively deep field shifted NCN resonance of uncoordinated Dipp2Im (220.5 ppm). (Dipp<sub>2</sub>Im)·AIH<sub>3</sub> 10 reveals with our settings no detectable resonance in the <sup>27</sup>Al{<sup>1</sup>H} solution NMR spectrum, while in the solid-state <sup>27</sup>Al{<sup>1</sup>H} HPDec/MAS NMR spectrum of the compound a signal with an isotropic shift at 107.9 ppm was detected. This resonance reveals the typical line shape (MAS second-order quadrupolar powder pattern) for a tetrahedral sp<sup>3</sup>-Al atom with a quadrupolar coupling constant of 11943 kHz and a quadrupolar asymmetry parameter of 0.1. The <sup>15</sup>N VACP/MAS NMR spectrum shows one resonance at -180.0 ppm for the two nitrogen atoms of the symmetrical (Dipp<sub>2</sub>Im)·AIH<sub>3</sub> conformer. In the IR spectrum of adduct 10 the characteristic AI-H stretching vibrations were detected at 1725, 1741 and 1777 cm<sup>-1</sup>.

In contrast to the observations made for the alkyl substituted NHC adduct (*i*Pr<sub>2</sub>Im)·AlH<sub>3</sub> **3**, the bulkier (Dipp<sub>2</sub>Im)·AlH<sub>3</sub> **10** shows no reaction towards Dipp<sub>2</sub>Im. However, immediately after addition of Dipp<sub>2</sub>Im to solutions of (Dipp<sub>2</sub>Im)·AlH<sub>3</sub> **10** only one set of protons for the two NHCs were detected and the methine protons of the Dipp substituents broadened significantly in the <sup>1</sup>H-NMR spectrum, which accounts either for an rapid coordination equilibrium or the formation of a compound (Dipp<sub>2</sub>Im)<sub>2</sub>·AlH<sub>3</sub>. However, despite many efforts, the resonance of the carbene carbon atom was not detected in the <sup>13</sup>C{<sup>1</sup>H} NMR spectra. Heating of these solutions up to 110°C for several days in toluene*d*<sub>8</sub> did not lead to any further reaction.

For a closer investigation of the reactivity if two hydridic sites of the alane are blocked, the NHC adducts ( $iPr_2Im$ )·Al $iBu_2H$  **11** and (Dipp<sub>2</sub>Im)·Al $iBu_2H$  **12** were synthesized from the reaction of di-*iso*-butyl aluminum hydride with the corresponding *N*heterocyclic carbene in diethyl ether at 0 °C (Scheme 5). After all

volatiles were removed in vacuo, both adducts were isolated by crystallization from n-hexane at -60 °C as colorless solids in yields of 56 % (11) and 57 % (12). Important NMR data of both compounds are summarized in Table 1. These data fit well into the general picture as described previously. However, the aluminum resonance of (*i*Pr<sub>2</sub>Im)·Al*i*Bu<sub>2</sub>H **11** in the solution <sup>27</sup>Al{<sup>1</sup>H} NMR spectrum at 139.4 ppm is significantly shifted compared to the AIH<sub>3</sub> adducts (cf. 3: 106.3), and are in perfect agreement with the resonance detected in the solid state <sup>27</sup>Al{<sup>1</sup>H} HPDec/MAS NMR spectrum at 138.9 ppm. Compound 12, however, shows similar to 10 no detectable resonance in the <sup>27</sup>Al{<sup>1</sup>H} NMR spectrum, while in the solid state <sup>27</sup>Al{<sup>1</sup>H} HPDec/MAS NMR spectrum of the compound a signal with an isotropic shift at 137.0 ppm was observed. The quadrupolar coupling constant was determined to 15860 kHz with a quadrupolar asymmetry parameter of 0.29. A. The AI-H stretching vibrations of 11 and 12 were detected at 1681 cm<sup>-1</sup> (11) and at 1702 cm<sup>-1</sup> (12) in the IR spectrum of the complexes.

The addition of *i*Pr<sub>2</sub>Im to a solution of (*i*Pr<sub>2</sub>Im)·Al*i*Bu<sub>2</sub>H **9** leads to either the formation of a compound (*i*Pr<sub>2</sub>Im)<sub>2</sub>·Al*i*Bu<sub>2</sub>H or to a rapid exchange of the NHC ligands on an NMR time scale, similar as observed for the formation of (*i*Pr<sub>2</sub>Im)<sub>2</sub>·AlH<sub>3</sub> **5**. Only one set of protons is detected for the NHC in these solutions, However, in contrast to the ring expansion reaction observed for (*i*Pr<sub>2</sub>Im)·AlH<sub>3</sub> **3** / *i*Pr<sub>2</sub>Im to give (*i*Pr<sub>2</sub>Im)·AlH(RER-*i*Pr<sub>2</sub>ImH<sub>2</sub>) **6**, no further ring expansion was detected for (*i*Pr<sub>2</sub>Im)·Al*i*Bu<sub>2</sub>H / *i*Pr<sub>2</sub>Im up to a temperature of 110 °C (for several days). Similar observations were made for the reaction of (Dipp<sub>2</sub>Im)·Al*i*Bu<sub>2</sub>H **12** with one equivalent of *i*Pr<sub>2</sub>Im. Thus, blocking of two hydridic sites leads to adducts that seem to remain stable with respect to ring expansion.

Another class of stable carbenes, cyclic (alkyl)(amino) carbenes (cAACs) have attracted an enormously growing attention lately. These cAACs arise from the formal replacement of one of the electronegative amino substituents of NHCs by a stronger  $\sigma$ -donor alkyl group <sup>[27]</sup> Compared to NHCs, cAACs have a smaller HOMO-LUMO gap and are thus stronger electrophiles and nucleophiles. <sup>[28]</sup> These features enable cAACs to activate



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small molecules such as CO,  $H_2$ ,  $P_4$  and other enthalpically strong single bonds, such as B-H, B-C, C-H, and C-F. <sup>[7-8, 29]</sup>

Surprisingly, the reaction of lithium aluminum hydride with cAAC<sup>Me</sup> affords in our hands just the starting material and the adduct (cAAC<sup>Me</sup>)·AIH<sub>3</sub> was not formed. An alternative procedure for the synthesis of cAAC alane adducts would be ligand substitution starting from (NHC)-AIH<sub>3</sub> with cAAC<sup>Me</sup>. However, in this case insertion of the cAAC into the AI-H bond is observed, i. e. the reaction of (NHC)-AIH<sub>3</sub> with cAAC<sup>Me</sup> leads to AI-H bond activation to afford compounds of the type (NHC)·AIH<sub>2</sub>(cAAC<sup>Me</sup>H) (Scheme 6). These compounds represent the products of an oxidative addition of (NHC)·AIH<sub>3</sub> to cAAC<sup>Me</sup>, which seems to be independent on the steric demand of the NHC bound to the aluminum atom. The reaction of cAAC<sup>Me</sup> with (NHC)·AIH<sub>3</sub> (NHC = Me<sub>2</sub>Im 1, Me<sub>2</sub>Im<sup>Me</sup> 2, *i*Pr<sub>2</sub>Im 3, *i*Pr<sub>2</sub>Im<sup>Me</sup> 4), coordinated with small alkyl substituted NHCs, leads already at room temperature to  $(NHC) \cdot AIH_2(cAAC^{Me}H)$  (NHC = Me<sub>2</sub>Im **13**, Me<sub>2</sub>Im<sup>Me</sup> **14**, *i*Pr<sub>2</sub>Im **15**, *i*Pr<sub>2</sub>Im<sup>Me</sup> **16**) in form of colorless solids in good yield after workup (13: 58 %, 14: 66 %, 15: 78 %, 16: 66 %), NMR spectroscopic studies on the reaction of  $(IPr_2Im) \cdot AIH_3$  3 with an equimolar amount of cAAC<sup>Me</sup> revealed that product formation proceeds already at temperatures as low as -78 °C quantitatively to give (*i*Pr<sub>2</sub>Im)·AIH<sub>2</sub>(cAAC<sup>Me</sup>H) **15**. The formation of a likely bis carbene adduct (IPr2Im)(cAAC)·AIH3 was not observed at these temperatures. For the reaction of cAAC<sup>Me</sup> with the adduct of the sterically more demanding NHC Dipp<sub>2</sub>Im, (Dipp<sub>2</sub>Im)·AIH<sub>3</sub> 10, AI-H bond activation also occurs at room temperature and the product (Dipp<sub>2</sub>Im)·AIH<sub>2</sub>(cAAC<sup>Me</sup>H) 17 was isolated as a colorless solid in 49 % yield. The compound (*i*Pr<sub>2</sub>Im)·AIH<sub>2</sub>(cAAC<sup>Me</sup>H) 15 is stable up to 105 °C for several days. Similarly to the E-H bond activation product (cAAC<sup>Me</sup>H)Bcat <sup>[10f]</sup> no ring expansion reaction or ring opening reaction was observed up to this temperature. Furthermore, (*i*Pr<sub>2</sub>Im)·AIH<sub>2</sub>(cAAC<sup>Me</sup>H) **15** does not react with an additional equivalent of cAACMe, i.e. the two remaining AI-H bonds are stable with respect to further attack.

Compounds 13 - 17 were characterized by multinuclear NMR spectroscopy, elemental analyses, infrared spectroscopy and high resolution mass spectrometry. Important data are summarized in Table 2. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of 13 -17 reveal resonances for each set of hydrogen atoms and carbon atom of the cAAC separately due to the chirality of the former carbene carbon atom. For example, the methyl groups of the cAAC backbone of (*i*Pr<sub>2</sub>Im)·AIH<sub>2</sub>(cAAC<sup>Me</sup>H) **15** were detected as four separate singlets at 1.14, 1.31, 1.47 and 1.48 ppm and the diastereotopic CH<sub>2</sub> protons as roofed doublets of an AB spin system at 1.95 and 2.04 ppm. The resonances of the cAAC Dipp iso-propyl methyl protons emerge as doublets at 1.18 and 1.38 ppm, and the methine protons as two septets at 3.73 and 4.50 ppm. The resonances of the NHC ligand methine and backbone protons remain magnetic equivalent, which accounts for free rotation around the AI-C<sub>NHC</sub> axis. The aluminum bound protons, which are diastereotopic in 13 - 17, were detected as two broad singlets (e.g. at 3.90 and 4.33 ppm for 15) in the  $^1\text{H}\{^{27}\text{AI}\}$  NMR spectra of the compounds. In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra the resonance of the former cAAC<sup>Me</sup> carbene carbon atom is shifted significantly from 313.5 ppm in the cAAC itself to a signal in the range between 65.8 ppm and 72.2 ppm, which is

broadened by the interaction with the <sup>27</sup>Al nucleus. The resonance of the NHC carbene carbon atom lies in the range observed for the (NHC)·AlH<sub>3</sub> adducts, e. g. at 171.8 ppm for **15** compared to 170.3 ppm in 3. In general, the aluminum resonances of the compounds (NHC)·AIH<sub>2</sub>(cAAC<sup>Me</sup>H) are difficult to detect in the spectrum  $^{27}AI\{^{1}H\}$ NMR to our experience. For (Me<sub>2</sub>Im)·AIH<sub>2</sub>(cAAC<sup>Me</sup>H) 13, (Me<sub>2</sub>Im<sup>Me</sup>)·AIH<sub>2</sub>(cAAC<sup>Me</sup>H) 14 and (*i*Pr<sub>2</sub>Im)·AIH<sub>2</sub>(cAAC<sup>Me</sup>H) **15** the resonances appear as very broad signals at 116.5 ppm (13), 117.3 ppm (14) and 115.0 ppm (15). For the compounds (*i*Pr<sub>2</sub>Im<sup>Me</sup>)·AIH<sub>2</sub>(cAAC<sup>Me</sup>H) **16** and (Dipp<sub>2</sub>Im)·AIH<sub>2</sub>(cAAC<sup>Me</sup>H) 17 we could not detect signals in the solution <sup>27</sup>Al{<sup>1</sup>H} NMR spectra. The chemical shifts of the resonances of 13 in the solid-state <sup>13</sup>C{<sup>1</sup>H} and <sup>27</sup>Al{<sup>1</sup>H} HPDec/MAS NMR spectra match very good with those recorded in solution, which shows that solid-state and solution structure agree. For example, the resonance of **13** arises with an isotopic shift at 117.5 ppm in the <sup>27</sup>Al{<sup>1</sup>H} HPDec/MAS NMR spectrum, a quadrupolar coupling constant of 11380 kHz and a quadrupolar asymmetry parameter of 0.48. In the <sup>15</sup>N VACP/MAS the resonance of the NHC ligand is observed at -192.8 ppm, whereas the nitrogen atom of the former cAAC substituent emerges at -316.5 ppm. All the compounds (NHC)·AIH<sub>2</sub>(cAAC<sup>Me</sup>H) 13 - 17 show AI-H stretching vibrations in the infrared spectrum in the characteristic region between 1688 and 1804 cm<sup>-1</sup> (see Table 2 and SI).

The molecular structure of 14, 16 and 17 were determined by Xdiffraction (see Figure and Table 3). rav 6 (Me<sub>2</sub>Im<sup>Me</sup>)·AIH<sub>2</sub>(cAAC<sup>Me</sup>H) 14 crystallizes in the triclinic space group  $P\overline{1}$ , (*i*Pr<sub>2</sub>Im<sup>Me</sup>)·AIH<sub>2</sub>(cAAC<sup>Me</sup>H) **16** in the monoclinic space group  $P2_1/n$  and (Dipp\_2Im)·AIH<sub>2</sub>(cAAC<sup>Me</sup>H) **17** in the orthorhombic space group P212121. These molecules adopt a tetrahedral structure at the aluminum atom, spanned by the NHC (Me<sub>2</sub>Im<sup>Me</sup> for 14, *i*Pr<sub>2</sub>Im<sup>Me</sup> for 16 and Dipp<sub>2</sub>Im for 17), the cyclic (alkyl)(amino)carbene rest and the two remaining hydrogen

	AIC <i>H</i> <sup>1</sup> H{ <sup>27</sup> AI} NMR	AI <i>H</i> 2 <sup>1</sup> H{ <sup>27</sup> AI} NMR	<sub>CAAC</sub> AICH <sup>13</sup> C{ <sup>1</sup> H} NMR	NHCN <i>C</i> N <sup>13</sup> C{ <sup>1</sup> H} NMR	Al- <i>H</i> stretching vibration
13	3.35	4.00, 4.25	66.6	173.6	1688, 1796
14	3.39	4.07, 4.36	66.7	170.9	1749, 1797, 1687
15	3.39	3.90, 4.33	67.3	171.8	1739, 1773
16	3.44	3.89, 4.37	67.3	171.9	1721, 1772
17	3.02	3.02, 3.47	65.8	179.8	1779, 1804
18	3.12	_	72.2	174.4	_

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Figure 6. Molecular structure of (Me<sub>2</sub>Im<sup>Me</sup>)·AlH<sub>2</sub>(cAAC<sup>Me</sup>H) 14, (*i*Pr<sub>2</sub>Im<sup>Me</sup>)·AlH<sub>2</sub>(cAAC<sup>Me</sup>H) 16 and (Dipp<sub>2</sub>Im)·AlH<sub>2</sub>(cAAC<sup>Me</sup>H) 17 in the solid state (ellipsoids set at 50% probability level). Selected bond lengths [Å] and angles [°]: 14 (left): Al–C1 2.064(2), Al–C11 2.039(2), Al–C31 2.020(8) Al–H1 1.52(2), Al–H2 1.52(2). C1-Al-C11 104.89(9), C1-Al-C31 114.5(2), C1-Al-H1 104.3(8), C1-Al-H2 104.0(8), C11-Al-H1 120.7(8), C11-Al-H2 107.0(8), C31-Al-H1 93.0(9), C31-Al-H2 125.1(9), H1-Al-H2 114.2(12). 16 (middle): Al–C1 2.0868(19), Al–C21 2.0309(19), Al–H1 1.58(2), Al–H2 1.53(2). C1-Al-C21 107.74(8), C1-Al-H1 102.0(7), C1-Al-H2 103.8(8), C21-Al-H1 112.6(7), C21-Al-H2 114.7(8), H1-Al-H2 114.5(11). 17 (right): Al–C1 2.1011(19), Al–C31 2.0226(19), Al–H1 1.50(2), Al–H2 1.52(3). C1-Al-C31 111.44(7), C1-Al-H1 100.1(9), C1-Al-H2 102.2(9), C31-Al-H1 115.1(9), C31-Al-H2 114.1(9), H1-Al-H2 112.2(13).

atoms. The Al–C<sub>NHC</sub> bond length of **14** (2.064(2) Å) and **16** (2.0868(19) Å) differ only marginally from aluminum carbene carbon atom bond distance observed in (*i*Pr<sub>2</sub>Im)-AlH<sub>3</sub> **3** (2.0405(17) Å). The Al–C<sub>cAAC</sub> bond lengths of 2.039(2) Å (**14**), 2.0309(19) Å (**16**) and 2.0226(19) Å (**17**) fall in the same range, but are slightly longer compared to other typical NHC stabilized aluminum alkyl compounds (1.9 to 2.0 Å)<sup>[17, 26, 30]</sup>

We also tried to react the compounds ( $iPr_2Im$ )·Al $iBu_2H$  **11** and (Dipp<sub>2</sub>Im)·Al $iBu_2H$  **12** with cAAC<sup>Me</sup> (Scheme 7). The compound with the sterically more demanding carbene (Dipp<sub>2</sub>Im)·Al $iBu_2H$  **12** proved to be unreactive, while the reaction of ( $iPr_2Im$ )·Al $iBu_2H$  **11** with cAAC led to ( $iPr_2Im$ )·AlH<sub>2</sub>(cAAC<sup>Me</sup>H) **18**, which was isolated as a colorless solid in 41 %.

Compound **18** was characterized using multinuclear NMR spectroscopy, elemental analysis, and infrared spectroscopy. NMR and IR spectroscopy of this compound is in accordance with the other AI-H oxidative addition adducts (see Table 2 and SI). <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra reflect as described above the asymmetry of the compound, which is also reflected in the proton resonances of the *iso*-butyl substituent. The *I*Bu-CH<sub>3</sub> groups give





Table 3. Selected bond lengths of the compounds ( $Me_2Im^{Me}$ )·AIH2(cAAC^{Me}H) 14, ( $iPr_2Im^{Me}$ )·AIH2(cAAC^{Me}H) 16, and (Dipp2Im)·AIH2(cAAC^{Me}H)17.

	14	16	17
AI-C <sub>NHC</sub>	2.064(2)	2.0868(19)	2.1011(19)
AI-CCAAC	2.039(2)	2.0309(19)	2.0226(19)
AI–H1	1.52(2)	1.58(2)	1.50(2)
AI-H2	1.52(2)	1.53(2)	1.52(3)



Figure 7. Molecular structure of (*i*/Pr<sub>2</sub>Im)·Al*i*Bu<sub>2</sub>(cAAC<sup>Me</sup>H) **18** in the solid state (ellipsoids set at 50% probability level). Selected bond lengths [Å] and angles [°]: Al–C1 2.1419(18), Al–C10 2.0423(17), Al–C30 2.0056(18), Al–C34 2.0131(18). C1-Al-C10 106.48(7), C1-Al-C30 105.27(7), C1-Al-C34 113.74(7), C10-Al-C30 107.59(7), C10-Al-C34 109.09(7), C30-Al-C34 114.22(8).

rise to 4 doublets at 0.80, 1.06, 1.28 and 1.43 ppm, whereas the methine protons give rise to two multiplets at 2.02 and 2.36 ppm. The *i*Bu-CH<sub>2</sub> protons were detected as multiplets at - 0.45, -0.17, 0.53 and 1.08 ppm. Similar splitting of the *i*Bu-CH<sub>3</sub> carbon resonances occurs in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum. The molecular structure of (*i*Pr<sub>2</sub>Im)·AIH<sub>2</sub>(cAAC<sup>Me</sup>H) **18** (Figure 7) confirms the connectivity of the compound, which adopts a slightly distorted tetrahedron at aluminum. The AI–C<sub>NHC</sub> bond of 2.1419(18) Å is slightly longer then the bond lengths found in **14**, **16** and **17**, whereas the AI–C<sub>CAAC</sub> and AI–*i*Bu distances (2.0423(17), 2.0056(18) and 2.0131(18) Å) are similar to those observed before.

#### Conclusions

NHC alane adducts (NHC)·AIH<sub>3</sub> (NHC = Me<sub>2</sub>Im 1, Me<sub>2</sub>Im<sup>Me</sup> 2, iPr2Im 3 and 3-d<sub>3</sub>, iPr2Im<sup>Me</sup> 4, Dipp2Im 10) are readily accessible from the reaction of the NHC with lithium aluminum hydride/deuteride with lithium hydride/deuteride elimination. The secondary alane adducts (*i*Pr<sub>2</sub>Im)·Al*i*Bu<sub>2</sub>H 11 and (Dipp<sub>2</sub>Im)·Al/Bu<sub>2</sub>H 12 have been synthesized from the reaction of the NHC carbenes with di-iso-butylaluminum hydride. These adducts are stable at 110 °C for several days in solvents like toluene. However, if an excess of the NHC is present, NHC ring expansion or NHC ring cleavage occurs, depending on the NHC used. The reaction of (*i*Pr<sub>2</sub>Im)·AlH<sub>3</sub> **3** with *i*Pr<sub>2</sub>Im was investigated in some detail. Upon addition of the NHC, a bis(carbene) alane adduct (*i*Pr<sub>2</sub>Im)<sub>2</sub>·AIH<sub>3</sub> **5** forms, which decomposes to (*i*Pr<sub>2</sub>Im)·AIH(RER-*i*Pr<sub>2</sub>ImH<sub>2</sub>) 6. NMR studies reveal that this is a process of first order kinetics, presumably a reaction along the sequence (i) insertion of an NHC into one of the AI-H bonds of (NHC)·AIH<sub>3</sub>, (ii) subsequent intramolecular amido transfer from the NHC carbon atom to the Lewis acidic aluminum, and (iii) a hydride shift from the aluminum atom to the (former) carbene carbon atom with formation of the final product 6. The reaction of the deuterated adduct (*i*Pr<sub>2</sub>Im)·AID<sub>3</sub> **3-d<sub>3</sub>** with *i*Pr<sub>2</sub>Im led exclusively to  $(iPr_2Im) \cdot AID(RER - iPr_2ImD_2)$  6-d<sub>3</sub>, which supports the idea of an intramolecular concerted reaction pathway. However, the cross experiment using a 1:1 mixture of 3 and 3-d<sub>3</sub> and *i*Pr<sub>2</sub>Im as starting material led to some deuterium scrambling in the ring expanded product 6, but we could also demonstrate that the deuterium scrambling already takes place in the starting materials (i.e. in a mixture of 3 and 3-d<sub>3</sub>). The reaction of (*i*Pr<sub>2</sub>Im)·AIH<sub>3</sub> 3 with the sterically more demanding *N*-heterocyclic carbene Dipp<sub>2</sub>Im follows a different pathway and the ring opening of Dipp2Im was observed at 70 °C to give (iPr2Im)·AIH2(ROR- $Dipp_2ImH_2)H_2AI \cdot (iPr_2Im)$  9. The NHC adducts of the (*i*Pr<sub>2</sub>Im)·Al*i*Bu<sub>2</sub>H **11** and (Dipp<sub>2</sub>Im)·Al*i*Bu<sub>2</sub>H **12** were stable with respect to NHC ring expansion or NHC ring opening.

Compared to NHCs, cAACs possess a smaller HOMO-LUMO gap and are thus stronger electrophiles and nucleophiles. The reaction of (NHC)·AIH<sub>3</sub> with cAAC<sup>Me</sup> leads to Al–H bond cleavage and insertion of the cAAC into the Al–H bond to afford compounds of the type (NHC)·AIH<sub>2</sub>(cAAC<sup>Me</sup>H) (NHC = Me<sub>2</sub>Im **13**, Me<sub>2</sub>Im<sup>Me</sup> **14**, *i*Pr<sub>2</sub>Im **15**, *i*Pr<sub>2</sub>Im<sup>Me</sup> **16**, Dipp<sub>2</sub>Im **17**). These Al–H oxidative addition

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products remain stable at higher temperatures and no cAAC ring expansion occurs. The reaction of (iPr2lm)·AliBu2H 11 with cAAC<sup>Me</sup> leads also to AI-H bond activation, whereas the compound of the sterically more demanding Dipp<sub>2</sub>Im ligand, (Dipp<sub>2</sub>Im)·AliBu<sub>2</sub>H 12, proofed to be unreactive with respect to Al-H bond activation. In total, three major decomposition pathways of carbene alane adducts have been identified here, i.e. carbene ring expansion and ring opening as well as carbene insertion into the AI-H bond. These reactions require an excess of the carbene (i.e. NHC:Al > 1:1), 1:1 Lewis acid-base adducts NHC·AlH<sub>3</sub> are stable. Furthermore, our results also show that ring expansion and ring opening may be easily suppressed just by blocking two of the AI-H sites, as demonstrated here for (NHC)·AI/Bu<sub>2</sub>H, which is unreactive with respect of NHC ring destruction. However, Al-H bond activation with cAAC<sup>Me</sup> still happens for (*i*Pr<sub>2</sub>Im)·Al*i*Bu<sub>2</sub>H 11. In this case it is helpful to additionally increase the steric demand of the NHC employed, i.e. using the more bulky (Dipp2Im)·Al/Bu2H 12, which also suppresses the insertion of cAAC<sup>Me</sup> into the AI-H bond. Further investigations to substantiate these concepts are currently underway.

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**Keywords:** Aluminum • *N*-heterocyclic Carbene • cAAC • E–H Bond Activation • Ring Expansion Reaction

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