

## Imidazolyl Alanes

## Imidazolyl Alanes – Synthesis, Structures, and Reactivity Studies

Martin Simon,<sup>[a]</sup> Michael Radius,<sup>[a]</sup> Hanna E. Wagner,<sup>[a]</sup> and Frank Breher\*<sup>[a]</sup>

**Abstract:** Targeting the synthesis of Al/C based ambiphilic molecules, we investigated the dehydrohalogenation of a series of (benz)imidazole alane adducts. Depending on the steric bulk of the heterocycle, different dimeric products with various ring sizes were obtained. Dehydrohalogenation of the adduct of 1-mesityl imidazole (<sup>Mes</sup>Im) and 0.5 [tBu<sub>2</sub>AlBr]<sub>2</sub> furnished the dimer **2**, featuring a “classical” N-heterocyclic carbene (NHC) and a mesoionic or “abnormal” NHC (aNHC) subunit within a single molecule. The dimer is bound loosely enough to allow thermally induced isomerization of **2** into the isomers **2<sup>NHC</sup>** (all NHC) and **2<sup>aNHC</sup>** (all aNHC). Dehydrohalogenation of the adduct of 1-mesityl-2-methyl imidazole (<sup>Mes</sup>Im<sup>Me</sup>) and 0.5 [tBu<sub>2</sub>AlBr]<sub>2</sub> (**4**)

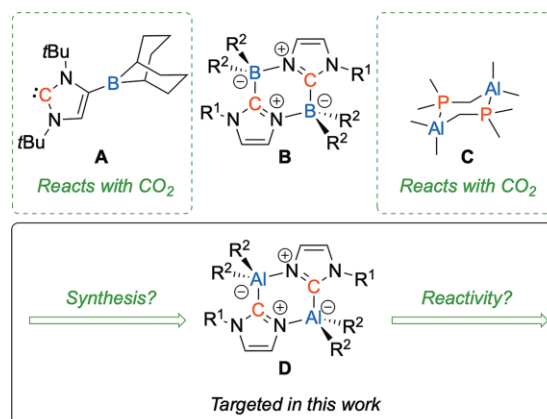
yielded the dimeric compound **5** consisting of two N-heterocyclic olefin (NHO) subunits. Although these six- and eight-membered heterocycles show no FLP-type reactivity towards small molecules like H<sub>2</sub>, CO or CO<sub>2</sub>, we observed an ambiphilic behavior of the imidazolyl alanes during our studies. Salt metathesis reactions using <sup>Mes</sup>Im resulted in the formation of **3**, which can be viewed as tBu<sub>2</sub>AlBr adduct of an Al/N ambiphile. Utilizing heterocycles such as benzimidazole or spiroindole provided the entry point to C–H (**7**, **9**) and N–H (**10**) activation products, most likely resulting from a reactivity of intermediate species as Al/C ambiphiles.

## Introduction

Since the concept of frustrated Lewis pairs (FLPs) was introduced some years ago, this research topic has emerged to one of the most intensively studied fields in modern p-block chemistry.<sup>[1]</sup> The adjustable properties of Lewis-acidity, -basicity and sterics allow for a tailored reaction control of both intra- and intermolecular systems, which enabled a remarkable development. FLPs were investigated in various chemical processes, broadening research subjects to multifarious application fields such as activation and fixation of small molecules, catalysis or as ambiphilic ligands.<sup>[1b,2]</sup>

Alongside of the “classical” combination of compounds based on group 13 and group 15 elements, which still is dominated by the archetypal B/P-pairing,<sup>[3]</sup> also B/N,<sup>[4]</sup> Al/P,<sup>[5]</sup> Ga/P,<sup>[5h,5n,6]</sup> and In/P-combinations<sup>[6a,6b]</sup> have recently been established, among others. Furthermore, considerable efforts have been made in developing Lewis-acidic group 14 and Lewis-basic group 15 combinations.<sup>[3,4,7–11]</sup> Few examples for FLPs comprising heavy group 14 Lewis bases<sup>[10c,12]</sup> or other nucleophilic C-bases are known,<sup>[13]</sup> and some of the so far re-

ported intermolecular FLPs comprise N-heterocyclic carbenes (NHC) and derivatives thereof<sup>[10a,14]</sup> as Lewis-basic component. Intramolecular systems still remain scars in literature. Tamm et al. were the first to report a backbone-functionalized NHC featuring a borane unit in the NHC backbone (**A**, Scheme 1).<sup>[15]</sup> As reported for most FLP systems, the reactive functional entities are spatially separated to provide “frustration”. Recently, Liu et al. showed that deprotonation of an *N*-boryl-substituted imidazolium salt resulted in the intermediate formation of an *N*-boryl-substituted NHC, which underwent an 1,2-migration yielding a C-imidazolyl-borane (**B**, Scheme 1).<sup>[16]</sup> Such compounds exhibit a strong tendency for dimerization as shown additionally by others with various substituents.<sup>[16,17]</sup> The structural motif **B** features an interesting starting point concerning a reactivity as hidden FLP/active Lewis Pair.<sup>[18]</sup>



Scheme 1. Structures of a B/C-based FLP **A**, dimeric imidazolylboranes **B** and an Al/P Lewis Pair **C** that reacts with CO<sub>2</sub>.

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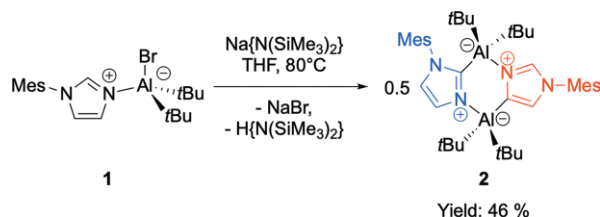
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Although several compounds with this architecture were described,<sup>[16,17]</sup> no reactivity studies for such with small molecules were reported until now. Inspired by our earlier findings on hidden aluminum phosphorus FLPs<sup>[19]</sup> and related B/C combinations<sup>[20]</sup> as well as the dimeric FLP **C** reported by Fontaine et al.,<sup>[21]</sup> we targeted imidazolyl-alanes (**D**) bearing a highly Lewis acidic aluminum atom in geminal position to the Lewis base. We anticipated that such dimers might show FLP-type reactivity, either as Al/C or Al/N FLP, depending on steric and electronic effects of the substituents. Herein we report our efforts in preparing imidazolyl alanes with various substituent patterns.

## Results and Discussion

### Alane-Substituted NHCs

The synthesis of an imidazolyl alane was attempted by dehydrohalogenation of <sup>Mes</sup>Im·tBu<sub>2</sub>AlBr **1** (see Experimental Section for the synthesis) by Na{N(SiMe<sub>3</sub>)<sub>2</sub>} in THF at 80 °C yielding compound **2** (Scheme 2, <sup>Mes</sup>Im = 1-mesityl imidazole). The product was isolated after recrystallization from hot toluene in 46 % yield. Interestingly, the deprotonation of the imidazoles selectively took place at two different positions of both heterocycles. Hence, **2** features a “classical” NHC and a mesoionic or “abnormal”<sup>[22]</sup> NHC subunit within a single molecule as evidenced by two carbene resonances in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum ( $\delta$  = 169.8 ppm for NHC and 150.8 ppm for aNHC, respectively). Additionally, four <sup>15</sup>N NMR chemical shifts and two well-separated sets of <sup>1</sup>H NMR resonances were detected.



Scheme 2. Dehydrohalogenation of **1** leading to formation of **2**. Blue indicates the NHC subunit, red the aNHC subunit.

The solid-state structure (Figure 1) revealed a non-planar topology for the central Al<sub>2</sub>C<sub>2</sub>N<sub>2</sub> ring system, which exhibits a torsion of 25.8° along Al1–C1–N2–Al2. Both aluminum atoms adopt distorted tetrahedral geometries. The Al–C<sup>NHC</sup> bond [ $d_{C1–Al1}$  = 207.3(2) pm] is elongated as compared to the Al–C<sup>aNHC</sup> bond [ $d_{C5–Al2}$  = 199.1(2) pm], which is most likely induced by steric repulsion of the Mes and tBu substituents. Nevertheless, these bond lengths are in line with reported aluminum NHC and aNHC compounds.<sup>[23]</sup> In contrast to the Al–C<sup>carbene</sup> bonds, the aluminum nitrogen distances of  $d_{Al1–N3}$  = 196.0(2) pm  $d_{Al2–N2}$  = 194.4(2) pm differ only slightly. It has to be noted that for dimeric imidazolyl boranes and triazolyl alanes, exclusively C<sub>2</sub> or C<sub>s</sub> symmetric species, deprotonated at the C2-position, were reported, highlighting the unique structure of **2**.<sup>[16,17,24]</sup>

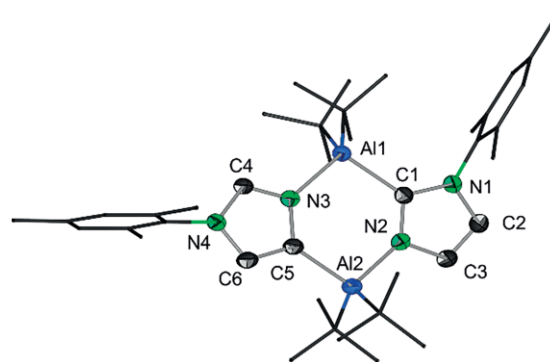
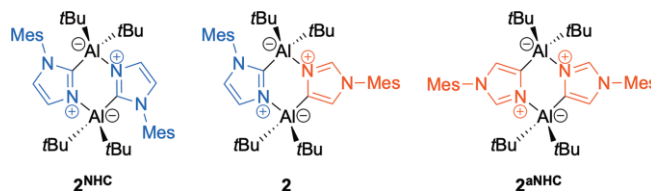


Figure 1. Molecular structure of **2** (30 % probability ellipsoids; hydrogen atoms are omitted and tBu and Mes groups are displayed as wire for clarity; space group  $P\bar{1}$ ). Selected bond lengths [pm] and angles [°]: Al1–C1 207.3(2), Al2–C5 199.1(2), Al1–N3 196.0(2), Al2–N2 194.4(2), C1–N2 135.5(3), C5–N3 140.3(3), N1–C1–N2 105.8(2), C6–C5–N3 105.7(2), C1–Al1–N3 101.8(8), C5–Al2–N2 101.9(8), Al2–N2–C1 132.3(1), Al1–N3–C5 130.3(1).

Since the <sup>1</sup>H NMR spectra of **2** showed the presence of further species in traces, which exhibit the same coupling pattern as **2**, a *pro rata* generation of the isomers **2**<sup>NHC</sup> and **2**<sup>aNHC</sup> was suggested (Scheme 3). Hence, thermal conversion of **2** into the symmetric species was investigated. Heating a sample of **2** to 80 °C in C<sub>6</sub>D<sub>6</sub> led to an intensity decrease of the <sup>1</sup>H NMR resonances of **2**, while the trace signals gained in intensity until an equilibrium of approximately 1 × **2**<sup>NHC</sup> + 2 × **2** + 1 × **2**<sup>aNHC</sup> was achieved, which corresponds to the statistic distribution of the subunits. Combined 2D NMR spectroscopic methods enabled the correlation of the imidazolium ring resonances to the **2**<sup>NHC</sup> and **2**<sup>aNHC</sup> isomers formed by thermal isomerization (see Supporting Information for details).



Scheme 3. Products **2**<sup>NHC</sup>, **2** and **2**<sup>aNHC</sup> by thermal isomerization of **2**. Blue indicates the NHC subunit, red the aNHC subunit.

Additionally, single crystals of **2**<sup>aNHC</sup> suitable for X-ray diffraction studies were obtained from the reaction mixture (Figure 2). The Al1–C3 bond [199.1(3) pm] is almost equal to **2** [cf.  $d_{Al2–C5}$  = 199.1(2) pm] and the same applies to the Al1–N2 bond of 195.7(3) pm [**2**: cf.  $d_{Al1–N3}$  = 196.0(2) pm].

The observed isomerization provided evidence that the central ring system of **2** is able to open up, which might result in the presence of a free Lewis-acid and -base in the solution, thus enabling FLP reactivity. Reactivity studies on **2** with small molecules such as H<sub>2</sub>, CO, CO<sub>2</sub>, COS, CS<sub>2</sub> and benzaldehyde in C<sub>6</sub>D<sub>6</sub>, however, revealed that no reactivity as hidden FLP is given, neither at ambient nor at elevated temperatures. Since in presence of the substrates also isomerization of **2** to **2**<sup>NHC</sup> and **2**<sup>aNHC</sup> was observed, it has to be concluded that also the latter two isomers show no FLP reactivity.

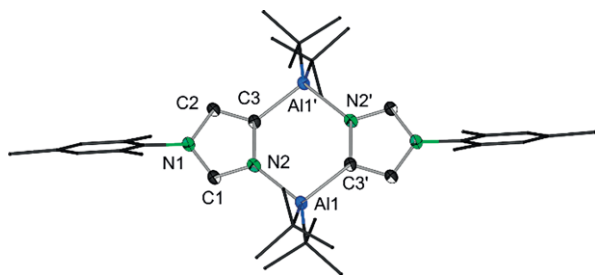
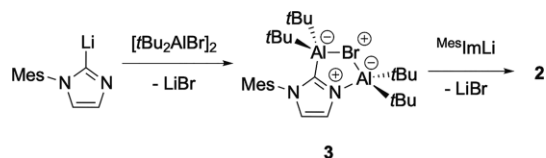


Figure 2. Molecular structure of **2**<sup>aNHC</sup> (30 % probability ellipsoids; hydrogen atoms and solvent molecules are omitted and *t*Bu and Mes groups are displayed as wire for clarity; space group *P* $\bar{1}$ ). Equivalent atoms are generated by 1 - *x*, 2 - *y*, 1 - *z*. Selected bond lengths [pm] and angles [°]: Al1'-C3 199.1(3), Al1-N2 195.7(3), N2-C3 140.6(3), N2-C1 132.9(4), N2-Al1-C3' 103.21(11), Al1-N2-C3 125.4(2), N2-C3-Al1' 125.4(2).

Although it seems to be clear that, once the six-membered heterocycles are formed, no FLP reactivity towards small molecules can be detected any more, we nonetheless observed ambiphilic behavior of the imidazolyl alanes during our studies. In an attempt to generate pure **2**<sup>NHC</sup>, in situ generated lithium salt <sup>Mes</sup>ImLi was applied in salt metathesis reactions with different amounts of [tBu<sub>2</sub>AlBr]<sub>2</sub> (Scheme 4). As proved by a previous hydrogen-deuterium-exchange experiment, <sup>Mes</sup>Im can be selectively deprotonated in C2-position by *n*BuLi (further experimental details are given in the Supporting Information). The subsequent reaction with [tBu<sub>2</sub>AlBr]<sub>2</sub> allowed for two interesting observations, namely 1) instead of isolating the six-membered ring compound **2**<sup>NHC</sup>, the asymmetric dimer **2** featuring both an NHC and an aNHC subunit has been isolated. Hence, a proton-coupled rearrangement has occurred, which has, however, already been reported by others.<sup>[14o,23e]</sup> 2) We were able to isolate and characterize compound **3** (Scheme 4), which can be viewed as adduct of monomeric imidazolyl alane with tBu<sub>2</sub>AlBr. Compound **3** is stable for several months at ambient temperature under Schlenk conditions, as isolated compound, as well as in solution (C<sub>6</sub>D<sub>6</sub>, hexane). The product **3** consists of a <sup>Mes</sup>Im unit, deprotonated at the C2-position ( $\delta^{13}\text{C} = 170.0$  ppm) and one tBu<sub>2</sub>Al group bound to C2 ( $\delta^{1\text{H}} = 1.09$  ppm) and one to the *N*-terminus ( $\delta^{1\text{H}} = 1.25$  ppm). The bromide adopts the bridging position between both aluminum entities.



Scheme 4. Stepwise synthesis of **2** via **3** in hexane at RT.

Since we only were able to obtain single crystals of poor quality, we performed some density functional theory studies (Figure 3). These show an Al1-C1 distance of 209.2 pm and an Al2-N2 bond length of 196.1 pm. Compared to the Al2-Br1 distance of 248.3 pm, Al1-Br1 was found to be much longer (256.6 pm). Analysis of the Wiberg bond indices additionally suggest a slightly stronger Al2-Br bond (0.58) as compared to the Al1-Br counterpart (0.43). Based on these findings it ap-

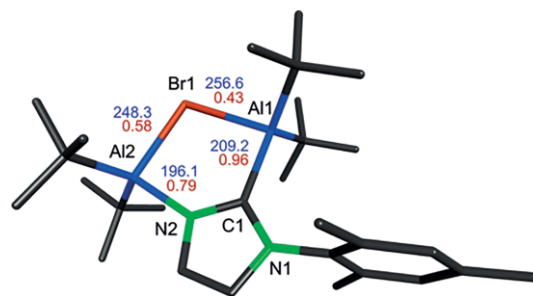
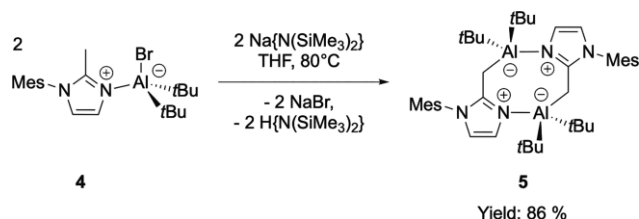


Figure 3. Calculated [(ri)-def2-TZVP/B3-LYP] molecular structure of **3**. Blue numbers indicate calculated bond lengths, red numbers the Wiberg bond indices. Hydrogen atoms are omitted for clarity.

pears that **3** can be described as tBu<sub>2</sub>AlBr adduct of an Al/N ambiphile.

### Alane-Substituted NHOs

In an attempt to selectively deprotonate the backbone of imidazole, a methyl group was introduced on C2 of <sup>Mes</sup>Im. The preparation of <sup>Mes</sup>Im<sup>Me</sup> was executed by a straightforward synthetic route, via deprotonation of <sup>Mes</sup>Im with *n*BuLi and subsequent reaction with MeI in toluene. The addition of stoichiometric amount of [tBu<sub>2</sub>AlBr]<sub>2</sub> to <sup>Mes</sup>Im<sup>Me</sup> furnished the respective adduct **4**. Dehydrohalogenation of **4** led to the formation of bis(alane) **5** (Scheme 5). Astonishingly, deprotonation of <sup>Mes</sup>Im<sup>Me</sup> apparently took place at the methyl group instead of the backbone leading to the N-heterocyclic olefin (NHO) structure.



Scheme 5. Dehydrohalogenation of **4** resulting in the bis(alane) **5**.

The solid-state structure of **5** displays a nearly C<sub>2</sub> symmetric species (Figure 4). Neither the Al-N nor the Al-C<sup>carbene</sup> distances of **5** differ significantly from **2** or **2**<sup>aNHC</sup>. As already observed for the latter two compounds, no reaction of **5** with H<sub>2</sub>, CO<sub>2</sub>, COS or CS<sub>2</sub> was observed in C<sub>6</sub>D<sub>6</sub>.

### Alane-Substituted Benzimidazoles

Targeting the sterically more crowded heterocycles, benzimidazole derivatives were used as precursors. Utilizing 1-methylbenzimidazole (<sup>Me</sup>BIm) as organic scaffold, the adduct <sup>Me</sup>BIm·tBu<sub>2</sub>AlBr (**6**) was prepared by addition of 0.5 [tBu<sub>2</sub>AlBr]<sub>2</sub> in toluene. Subsequent dehydrohalogenation using Na{N(SiMe<sub>3</sub>)<sub>2</sub>} in THF, however, again furnished an unexpected product (**7**, Scheme 6). As evidenced by NMR spectroscopic and X-ray crystallographic studies (Figure 5), a C-C bond formation between two heterocycles has been accomplished. The depro-

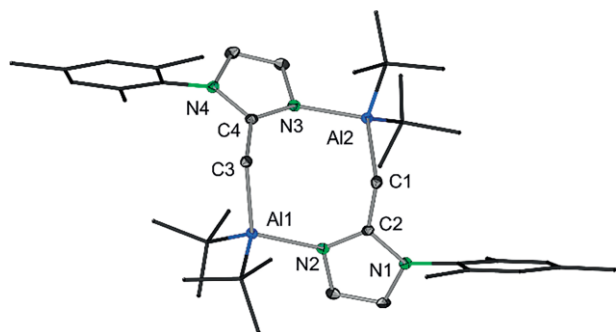
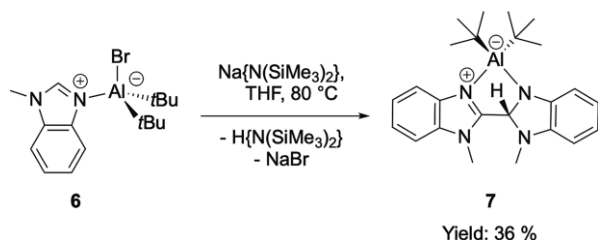


Figure 4. Molecular structure of **5** (30 % probability ellipsoids; hydrogen atoms are omitted and *t*Bu and Mes groups are displayed as wire for clarity; space group  $P2_1/n$ ). Selected bond lengths [pm] and angles [°]: C1–C2 145.3(3), C2–N1 136.5(3), C2–N2 133.8(3), N2–Al1 196.9(2), Al1–C3 203.8(2), C3–C4 146.3(3), C4–N4 136.3(3), C4–N3 133.7(3), N3–Al2 195.8(2), Al2–C1 203.2(2), N1–C2–N2 108.4(2), N4–C4–N3 108.4(2), C2–N2–Al1 131.4(2), N2–Al1–C3 110.8(9), C4–N3–Al2 132.8(2), N3–Al2–C1 110.5(9).

tonation of one <sup>Me</sup>BIm subunit suggested the intermediate formation of an alane-substituted NHC which underwent a C–H insertion at a second equiv. of <sup>Me</sup>BIm. Such reactivity was suggested for the formation of cyclene, leading to an analogue structural motif.<sup>[25]</sup> This at least strongly indicates the reactivity of the intermediate species as Al/C ambiphile. Another possibility would be the sequence: a) deprotonation of **6** and addition of the carbene to the electrophilic carbon atom of another molecule of **6**, with release of *t*Bu<sub>2</sub>AlBr.



Scheme 6. Synthesis of **7** from **6**.

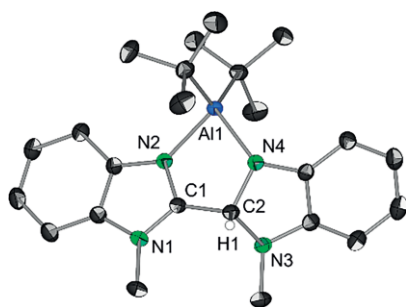
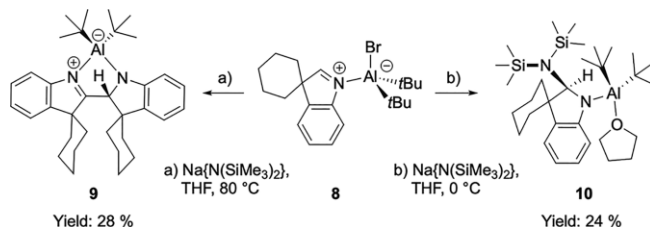


Figure 5. Molecular structure of **7** (30 % probability ellipsoids; hydrogen atoms except at C11 are omitted for clarity; space group  $P\bar{1}$ ). Selected bond lengths [pm] and angles [°]: Al1–N2 197.6(1), Al1–N4 188.8(1), C1–N2 134.6(2), C2–N4 147.8(2), C1–C2 146.3(2), N2–Al1–N4 85.2(5), Al1–N4–C2 115.8(9), N4–C2–C1 107.2(1), C2–C1–N2 119.6(1), C1–N2–Al1 110.7(9).

An analogous reaction was observed using precursor **8** featuring a spiroindole-scaffold (Scheme 7). Depending on the reaction conditions, either the C–H activation product **9**<sup>[22]</sup> or the N–H activation product **10** (Scheme 7, Figure 6) was isolated.

In each case, the products can be rationalized as insertion products of an *N*-alane-substituted CAAC<sup>[26]</sup> into a C–H (**9**) or an N–H (**10**). Such insertion of regular CAACs into various E–H bonds are known from the literature.<sup>[27]</sup> Again, and as discussed above, the reaction products may also result from nucleophilic addition reactions of a carbene (**9**) or and amide (**10**) to the electrophilic carbon atom of **8**, with release of *t*Bu<sub>2</sub>AlBr (**9**) or bromide from aluminum (**10**).



Scheme 7. Temperature-dependent preparation of **9** and **10** from **8**.

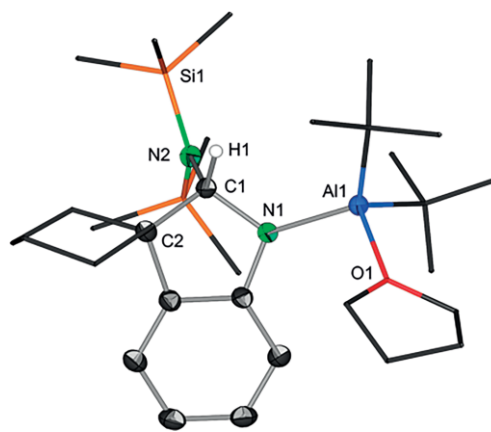


Figure 6. Molecular structure of **10** (30 % probability ellipsoids; hydrogen atoms except at C1 are omitted and bulky groups are displayed as wire for clarity; space group  $P\bar{1}$ ). Selected bond lengths [pm] and angles [°]: Al1–N1 187.6(2), N1–C1 148.8(2), C1–N2 149.5(2), N2–Si1 176.0(2), N2–Si2 176.3(2), Al1–N1–C1 124.4(1), N1–C1–N2 114.6(1).

## Conclusions

The dehydrohalogenation of a series of (benz-)imidazole alane adducts resulted in a variety of products depending on the steric bulk of the heterocycle. Utilizing <sup>Me</sup>SiIm yielded **2**, which comprises two different subunits. Thermally induced isomerization of **2** was observed to provide a statistically distributed mixture of the isomers **2**, **2**<sup>NHC</sup> or **2**<sup>aNHC</sup>. Dehydrohalogenation of methylated **4** afforded the sterically unencumbered NHO adduct **5**. Although these six- and eight-membered heterocycles show no FLP-type reactivity with small molecules like H<sub>2</sub>, CO or CO<sub>2</sub>, we observed an ambiphilic behavior of the imidazolyl alanes during our studies. Salt metathesis reactions using <sup>Me</sup>SiIm resulted in the formation of **3**, which can be viewed as *t*Bu<sub>2</sub>AlBr adduct of an Al/N ambiphile. Utilizing heterocycles such as benzimidazole or spiroindole provided the entry point to C–H (**7**, **9**) and N–H (**10**) activation products most likely resulting from a reactivity of intermediate species as Al/C ambiphiles. Further adjusting the sterics of both the heterocycles and the

substituents on aluminum might bear the potential for the generation of a monomeric imidazolyl-alane that could act as FLP. Indications for this have been provided by this study.

## Experimental Section

### General

All manipulations were performed under an argon atmosphere using standard Schlenk techniques.<sup>[28]</sup> All solvents were freshly distilled under argon from sodium and benzophenone (THF, toluene, hexane) or CaH<sub>2</sub> (dichloromethane) prior to use. C<sub>6</sub>D<sub>6</sub> and [D<sub>2</sub>]THF were distilled under argon from potassium/benzophenone prior to use. Air sensitive compounds were stored and weighed in glove boxes (Braun MB150 G-I and Unilab system). Solution NMR spectra were recorded using Bruker Avance instruments operating at <sup>1</sup>H Larmor frequencies of 300 or 400 MHz; chemical shifts are given relative to TMS for <sup>13</sup>C and <sup>1</sup>H. Coupling constants *J* are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as s, d, t, q, m, dd, dt, td, or ddd for singlets, doublets, triplets, quartets, multiplets, doublets of doublets, doublets of triplets, triplets of doublets or doublet of doublets of doublets, respectively. The abbreviation br is given for broadened signals. NMR samples were prepared in oven-dried 5 mm NMR tubes and sealed under argon. Standard Bruker software routines (TOPSPIN) were used for the 1D and 2D NMR measurements. IR spectra were recorded on a Bruker Alpha FT-IR spectrometer using the ATR technique (attenuated total reflection) on bulk material, and the data are quoted in wavenumbers (cm<sup>-1</sup>). The intensities of the absorption bands are indicated as vs. (very strong), s (strong), m (middle), w (weak), vw (very weak). Mass spectra and elemental analyses were recorded by the institutional technical laboratories of the Karlsruhe Institute of Technology (KIT).

All precursors were purchased from commercial sources and used as received. Mesityl imidazole,<sup>[29]</sup> spiro[cyclohexane-1,3'-indole],<sup>[30]</sup> [tBu<sub>2</sub>AlBr]<sub>2</sub>,<sup>[31]</sup> [tBu<sub>3</sub>Al],<sup>[32]</sup> and [tBu<sub>2</sub>AlH]<sub>3</sub><sup>[32]</sup> were prepared according to literature procedures. The compounds 1-mesityl-2-methylimidazole and spiro[cyclohexane-1,3'-indole] were described in the literature before. However, a modified synthesis is added in the Supporting Information for completeness. They also contain further information of the thermal isomerization of compound **2** and the selective deuteration of MesIm.

### Synthetic Procedures for Compounds 1–10

**Synthesis of Compound 1:** MesIm (1.118 g; 6.000 mmol; 1.0 equiv.) and [tBu<sub>2</sub>AlBr]<sub>2</sub> (1.327 g; 3.000 mmol; 0.5 equiv.) were placed in a Schlenk tube and dissolved in 20 mL of toluene. After 30 min the solvent was evaporated, and the crude product was crystallized from hot toluene by cooling to -20 °C. MesIm·tBu<sub>2</sub>AlBr **1** (2.368 g; 5.813 mmol; 97 %) was isolated as colorless crystals. M.p.: 133 °C; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 7.89 (t, <sup>4</sup>J<sub>HH</sub> = 1.3 Hz, H1, 1H), 7.14 (t, <sup>4</sup>J<sub>HH</sub> = 1.4 Hz, H3, 1H), 6.46 (d, <sup>4</sup>J<sub>HH</sub> = 0.6 Hz, *m*-Mes, 2H), 5.86 (t, H2, <sup>4</sup>J<sub>HH</sub> = 1.5 Hz), 2.00 (s, *p*-CH<sub>3</sub>(Mes), 3H), 1.44 (s, *o*-CH<sub>3</sub>(Mes), 6H), 1.36 (s, tBu, 18H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 140.2 (*p*-Mes), 139.7 (C1), 134.6 (*i*-Mes), 131.5 (*o*-Mes), 129.4 (*m*-Mes), 126.9 (C3), 121.7 (C2), 30.6 [C(CH<sub>3</sub>)<sub>3</sub>], 20.8 (*p*-CH<sub>3</sub>-Mes), 16.7 (*o*-CH<sub>3</sub>-Mes), 16.1 [C(CH<sub>3</sub>)<sub>3</sub>]; <sup>15</sup>N NMR (30 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 209.1 (s, N<sup>Al</sup>), 181.0 (s, N<sup>Mes</sup>); IR (ATR; cm<sup>-1</sup>): ν̄ = 3141 (vw), 2944 (w), 2921 (w), 2909 (w), 2888 (vw), 2865 (w), 2828 (m), 2157 (vw), 1612 (vw), 1521 (m), 1502 (w), 1461 (m), 1381 (vw), 1358 (vw), 1275 (w), 1230 (w), 1175 (vw), 1111 (s), 1097 (m), 1063 (vs), 1034 (vw), 1001 (w), 973 (w), 959 (m), 936 (vw), 856 (m), 812 (vs), 759 (s), 731 (vw), 670 (s), 653 (m), 592 (m), 576 (m), 541 (w),

498 (vw), 437 (m), 411 (vs), 391 (m); HRMS (EI): *m/z* calcd. for [C<sub>16</sub>H<sub>23</sub>AlN<sub>2</sub>Br]: 349.0860 + 351.0840 [M-C<sub>4</sub>H<sub>9</sub>], found 349.0194 + 351.0168; elemental analysis calcd. (%) for [C<sub>20</sub>H<sub>32</sub>AlN<sub>2</sub>Br]: C 58.97, H 7.92, N 6.88, Al 6.62, Br 19.61; found C 59.16, H 7.618, N 6.83.

**Synthesis of Compound 2:** MesIm·tBu<sub>2</sub>AlBr (**1**) (1.044 g; 2.563 mmol; 0.5 equiv.) and Na{N(SiMe<sub>3</sub>)<sub>2</sub>} (470 mg; 2.563 mmol; 0.5 equiv.) were suspended in 40 mL of THF and heated to 80 °C for a period of 24 h. After cooling to ambient temperature, the solvent was removed, the residue suspended in 20 mL of toluene and filtered. The filtrate was evaporated to dryness, the residue was suspended in pentane (2 × 5 mL) and the supernatant was removed. The crude product was crystallized from a saturated solution of hexane at 4 °C giving **2** (384 mg; 588.1 μmol; 46 %) as colorless crystals. M.p.: 291 °C; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 8.01 (d, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz, H1<sup>A</sup>, 1H), 7.53 (d, <sup>3</sup>J<sub>HH</sub> = 1.5 Hz, H3, 1H), 6.78 (d, <sup>4</sup>J<sub>HH</sub> = 1.1 Hz, H2<sup>A</sup>, 1H), 6.69 (d, <sup>4</sup>J<sub>HH</sub> = 0.6 Hz, *m*-Mes<sup>NHC</sup>, 2H), 6.56 (d, <sup>4</sup>J<sub>HH</sub> = 0.6 Hz, *m*-Mes<sup>aNHC</sup>, 2H), 6.36 (d, <sup>3</sup>J<sub>HH</sub> = 1.5 Hz, H2, 1H), 2.04 (s, *p*-CH<sub>3</sub>(Mes<sup>NHC</sup>), 3H), 2.02 (s, *p*-CH<sub>3</sub>(Mes<sup>aNHC</sup>), *o*-CH<sub>3</sub>(Mes<sup>NHC</sup>), 9H), 1.75 (s, *o*-CH<sub>3</sub>(Mes<sup>aNHC</sup>), 6H), 1.35 (s, tBu<sup>A</sup>, 18H), 1.02 (s, tBu<sup>B</sup>, 18H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 169.8 (C1), 150.8 (C3<sup>A</sup>), 139.9 (C1<sup>A</sup>), 139.4 (*i*-Mes<sup>NHC</sup>), 139.3 (*i*-Mes<sup>aNHC</sup>), 136.5 (*o*-Mes<sup>NHC</sup>), 136.4 (*p*-Mes<sup>NHC</sup>), 135.1 (*o*-Mes<sup>aNHC</sup>), 132.9 (*p*-Mes<sup>aNHC</sup>), 129.5 (*m*-Mes<sup>NHC</sup>), 129.3 (*m*-Mes<sup>aNHC</sup>), 129.1 (C2<sup>A</sup>), 128.0 (C3), 123.7 (C2), 31.9 (C(CH<sub>3</sub>)<sub>3</sub>-tBu<sup>B</sup>), 31.8 (C(CH<sub>3</sub>)<sub>3</sub>-tBu<sup>A</sup>), 20.9 (*p*-CH<sub>3</sub>(Mes<sup>aNHC</sup>)), 20.8 (*p*-CH<sub>3</sub>(Mes<sup>NHC</sup>)), 18.7 (*o*-CH<sub>3</sub>(Mes<sup>NHC</sup>)), 17.0 (*o*-CH<sub>3</sub>(Mes<sup>aNHC</sup>)), 15.5 (C(CH<sub>3</sub>)<sub>3</sub>-tBu<sup>B</sup>), 15.1 (C(CH<sub>3</sub>)<sub>3</sub>-tBu<sup>A</sup>); <sup>15</sup>N NMR (30 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 224.1 (s, N<sup>Al(NHC)</sup>), 218.5 (s, N<sup>Al(aNHC)</sup>), 196.3 (s, N<sup>Mes(NHC)</sup>), 182.0 (s, N<sup>Mes(aNHC)</sup>); IR (ATR; cm<sup>-1</sup>): ν̄ = 3134 (vw), 2936 (w), 2920 (w), 2864 (w), 2819 (s), 2753 (vw), 2691 (vw), 1734 (vw), 1609 (vw), 1542(vw), 1523 (w), 1486 (w), 1464 (m), 1383 (w), 1354 (vw), 1277 (vw), 1239 (w), 1217 (vw), 1180 (vw), 1114 (m), 1086 (w), 1034 (vw), 1003 (w), 981 (w), 955 (vw), 935 (vw), 853 (m), 835 (w), 810 (s), 769 (vw), 750 (w), 703 (vw), 669 (w), 615 (w), 578 (s), 540 (m), 490 (vs), 464 (m), 449 (m), 426 (s), 413 (m); HRMS (EI): *m/z* calcd. for [C<sub>36</sub>H<sub>53</sub>Al<sub>2</sub>N<sub>4</sub>]: 595.3901 [M-C<sub>4</sub>H<sub>9</sub>]; found 595.3104 [M-C<sub>4</sub>H<sub>9</sub>], 539.2395 [M-2C<sub>4</sub>H<sub>9</sub>]; elemental analysis calcd. (%) for [C<sub>40</sub>H<sub>62</sub>Al<sub>2</sub>N<sub>4</sub>]: C 73.58, H 9.57, N 8.58, Al 8.26; found C 73.76, H 9.275, N 8.55.

**Synthesis of Compound 3:** *n*BuLi (1.27 mL; 1.6 M in hexane; 2.032 mmol; 1.0 equiv.) was slowly added to a solution of MesIm (379 mg; 2.035 mmol; 1.0 equiv.) in 35 mL of hexane giving a yellow solution. [tBu<sub>2</sub>AlBr]<sub>2</sub> (900 mg; 2.035 mmol; 1.0 equiv.) in 35 mL of hexane was added and precipitation of a colorless solid in a colorless liquid was observed. After filtration and removal of the solvent, **3** (803 mg; 1.466 mmol; 72 %) was isolated as colorless powder. M.p.: 136 °C; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 6.89 (d, <sup>3</sup>J<sub>HH</sub> = 1.5 Hz, H3, 1H), 6.62 (q, <sup>4</sup>J<sub>HH</sub> = 0.7 Hz, *m*-Mes, 2H), 6.19 (d, <sup>3</sup>J<sub>HH</sub> = 1.5 Hz, H2, 1H), 1.97 (s, *p*-CH<sub>3</sub>(Mes), 3H), 1.83 (d, <sup>4</sup>J<sub>HH</sub> = 0.7 Hz, *o*-CH<sub>3</sub>(Mes), 6H), 1.25 (s, tBu<sup>A</sup>, 18H), 1.09 (s, tBu<sup>B</sup>, 18H); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 170.4 (C1), 140.1 (*i*-Mes), 135.9 (*o*-Mes), 134.7 (*p*-Mes), 129.6 (*m*-Mes), 126.0 (C3), 125.0 (C2), 30.9 (C(CH<sub>3</sub>)<sub>3</sub>-tBu<sup>B</sup>), 30.7 (C(CH<sub>3</sub>)<sub>3</sub>-tBu<sup>A</sup>), 20.9 (*p*-CH<sub>3</sub>(Mes)), 18.3 (*o*-CH<sub>3</sub>(Mes)), 17.0 (C(CH<sub>3</sub>)<sub>3</sub>-tBu<sup>A</sup>), 16.7 (C(CH<sub>3</sub>)<sub>3</sub>-tBu<sup>B</sup>); <sup>15</sup>N NMR (30 MHz, C<sub>6</sub>D<sub>6</sub>): δ [ppm] = 220.2 (s, N<sup>Al</sup>), 196.2 (s, N<sup>Mes</sup>); IR (ATR; cm<sup>-1</sup>): ν̄ = 2947 (w), 2914 (w), 2869 (w), 2832 (vs), 2701 (vw), 1610 (vw), 1592 (vw), 1486 (vw), 1465 (m), 1397 (w), 1385 (w), 1359 (vw), 1280 (vw), 1258 (w), 1174 (vw), 1123 (m), 1067 (vw), 1034 (vw), 1003 (w), 984 (vw), 960 (vw), 935 (vw), 853 (w), 811 (vs), 752 (s), 705 (vw), 671 (w), 614 (w), 590 (m), 540 (m), 473 (s), 451 (vw), 422 (vs), 399 (m); HRMS (EI): *m/z* calcd. for [C<sub>20</sub>H<sub>32</sub>AlN<sub>2</sub>]: 489.2006 + 491.1985 [M-C<sub>4</sub>H<sub>9</sub>]; found 489.1699 + 491.1683 [M-C<sub>4</sub>H<sub>9</sub>], 439.0170 + 351.0184 [M-2C<sub>4</sub>H<sub>9</sub>]; elemental analysis calcd. (%) for [C<sub>28</sub>H<sub>49</sub>Al<sub>2</sub>N<sub>2</sub>Br]: C 61.42, H 9.02, N 5.15, Al 9.85, Br 14.59; found C 59.84, H 8.501, N 4.94.

**Synthesis of Compound 4:**  $\text{Me}_3\text{Im}^{\text{Me}}$  (490 mg; 2.446 mmol; 1.0 equiv.) and  $[\text{tBu}_2\text{AlBr}]_2$  (541 mg; 2.447 mmol; 0.5 equiv.) were dissolved in 10 mL of toluene and stirred for 30 min. at ambient temperature. The solvent was evaporated, and the resulting oil was treated with pentane ( $3 \times 5$  mL) to yield a colorless solid. The crude product was dissolved in 20 mL of hot hexane and stored at  $-20^\circ\text{C}$  for crystallization. The supernatant was removed, and the crystals were dried under reduced pressure.  $\text{Me}_3\text{Im}^{\text{Me}}\cdot\text{tBu}_2\text{AlBr}$  (**4**) (590 mg; 1.400 mmol; 57 %) was isolated as colorless solid. M.p.:  $112^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 7.48 (d,  $^3J_{\text{HH}} = 1.8$  Hz, H4, 1H), 6.49 (dd,  $J_{\text{HH}} = 1.4$  Hz, 0.6 Hz, *m*-Mes, 2H), 5.85 (d,  $^3J_{\text{HH}} = 1.8$  Hz, H3, 1H), 2.20 (s, H1, 3H), 1.98 (s, *p*- $\text{CH}_3$ (Mes), 3H), 1.41 (s, *t*Bu, *o*- $\text{CH}_3$ (Mes), 24H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 148.0 (C2), 140.3 (*p*-Mes), 134.8 (*o*-Mes), 131.4 (*i*-Mes), 129.6 (*m*-Mes), 127.1 (C4), 119.9 (C3), 31.1 [ $\text{C}(\text{CH}_3)_3$ ], 20.9 (*p*- $\text{CH}_3$ (Mes)), 16.8 (*o*- $\text{CH}_3$ (Mes)), 14.4 [ $\text{C}(\text{CH}_3)_3$ ], 13.2 (C1);  $^{15}\text{N}$  NMR (30 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 203.3 (s,  $\text{N}^{\text{Al}}$ ), 180.6 (s,  $\text{N}^{\text{Mes}}$ ); IR (ATR;  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3164$  (vw), 3142 (vw), 2946 (w), 2920 (w), 2865 (w), 2825 (s), 2756 (vw), 2695 (vw), 2163 (vw), 1727 (vw), 1611 (vw), 1544 (vw), 1498 (w), 1462 (m), 1380 (vw), 1356 (vw), 1330 (vw), 1312 (vw), 1288 (w), 1231 (vw), 1182 (vw), 1166 (vw), 1143 (w), 1112 (w), 1105 (w), 1064 (w), 1014 (w), 973 (vw), 959 (vw), 936 (vw), 849 (w), 811 (s), 756 (s), 689 (m), 670 (w), 651 (w), 612 (vw), 586 (m), 576 (m), 540 (w), 496 (vw), 475 (m), 438 (vw), 409 (vs); HRMS (EI):  $m/z$  calcd. for  $[\text{C}_{17}\text{H}_{25}\text{AlBrN}_2]$  363.1016 + 365.0996 [ $M-\text{C}_4\text{H}_9$ ]; found 363.0257 + 635.0235 [ $M-(\text{C}_4\text{H}_9)$ ]; 320.9776 + 322.9764 [ $M-2(\text{C}_4\text{H}_9)$ ]; elemental analysis calcd. (%) for  $[\text{C}_{21}\text{H}_{34}\text{AlBrN}_2]$ : C 59.86, H 8.13, N 6.65, Al 6.40, Br 18.96; found C 59.79, H 8.065, N 6.78.

**Synthesis of Compound 5:** **4** (550 mg; 1.305 mmol; 0.5 equiv.) and  $\text{Na}\{\text{N}(\text{SiMe}_3)_2\}$  (240 mg; 1.309 mmol; 0.5 equiv.) were suspended in 20 mL of THF and stirred for 4 h at  $80^\circ\text{C}$ . The solvent was evaporated, the residue was taken up in 20 mL of toluene and the suspension was filtered. The filtrate was dried under vacuum and the remaining solid was washed with pentane ( $2 \times 5$  mL). **5** (382 mg; 561.0  $\mu\text{mol}$ ; 86 %) was isolated as colorless powder. Crystals were generated by cooling a saturated solution of **5**, in hot toluene, to ambient temperature. M.p.:  $265^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 7.12 (d,  $^3J_{\text{HH}} = 1.9$  Hz, H4, 2H), 6.69 (d,  $^4J_{\text{HH}} = 0.6$  Hz, *m*-Mes, 4H), 6.08 (d,  $^3J_{\text{HH}} = 1.9$  Hz, H3, 2H), 2.16 (s, H1, 4H), 2.05 (s, *o*- $\text{CH}_3$ (Mes), 12H), 1.97 (s, *p*- $\text{CH}_3$ (Mes), 6H), 1.10 (s, *t*Bu, 36H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 160.5 (C2), 139.1 (*p*-Mes), 135.3 (*i*-Mes), 132.9 (*o*-Mes), 130.1 (*m*-Mes), 124.3 (C4), 119.0 (C3), 31.8 [ $\text{C}(\text{CH}_3)_3$ ], 20.9 (*p*- $\text{CH}_3$ (Mes)), 19.1 (*o*- $\text{CH}_3$ (Mes)), 15.9 (C1), 11.2 [ $\text{C}(\text{CH}_3)_3$ ];  $^{15}\text{N}$  NMR (30 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 190.6 (s,  $\text{N}^{\text{Al}}$ ), 172.5 (s,  $\text{N}^{\text{Mes}}$ ); IR (ATR;  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3142$  (vw), 2940 (w), 2921 (w), 2863 (vw), 2813 (m), 2755 (vw), 2691 (vw), 2170 (vw), 2081 (vw), 1989 (vw), 1610 (vw), 1548 (vw), 1459 (m), 1440 (m), 1381 (m), 1356 (vw), 1301 (vw), 1286 (w), 1252 (vw), 1182 (vw), 1170 (vw), 1153 (vw), 1106 (w), 1070 (m), 1050 (s), 1002 (m), 933 (vw), 852 (w), 838 (vw), 811 (s), 756 (w), 744 (w), 728 (vw), 705 (vs), 663 (w), 637 (m), 604 (m), 577 (m), 570 (m), 545 (m), 520 (w), 501 (vw), 473 (s), 410 (s); HRMS (EI): decomposition; elemental analysis calcd. (%) for  $[\text{C}_{42}\text{H}_{66}\text{Al}_2\text{N}_4]$ : C 74.08, H 9.77, N 8.23, Al 7.92; found C 73.86, H 9.552, N 8.09.

**Synthesis of 6:**  $\text{Me}^{\text{B}}\text{Im}$  (1.000 g; 7.556 mmol; 1.0 equiv.) and  $[\text{tBu}_2\text{AlBr}]_2$  (1.600 g; 3.783 mmol; 0.5 equiv.) were dissolved in 20 mL of toluene and the solvent was evaporated after 30 min. The residue was suspended in 20 mL of hexane, filtered and washed with 10 mL of hexane. **6** (2.108 g; 5.967 mmol; 79 %) was isolated as colorless powder and can be crystallized from a saturated solution in hexane at  $4^\circ\text{C}$ . M.p.:  $162^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 8.62 (s, H1, 1H), 8.15–8.11 (m, H6, 1H), 7.02 (ddd,  $^3J_{\text{HH}} = 8.4$ , 7.3,  $^4J_{\text{HH}} = 1.2$  Hz, H5, 1H), 6.92 (ddd,  $^3J_{\text{HH}} = 8.2$ , 7.3,  $^4J_{\text{HH}} = 1.1$  Hz, H4, 1H), 6.48–6.44 (m, H3, 1H), 2.11 (s,  $\text{CH}_3$ , 3H), 1.45 (s, *t*Bu, 18H);  $^{13}\text{C}\{^1\text{H}\}$

NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 146.8 (C1), 137.8 (C7), 133.6 (C2), 125.06 (C4), 125.04 (C5), 119.1 (C6), 111.0 (C3), 31.1 [ $\text{C}(\text{CH}_3)_3$ ], 30.5 ( $\text{CH}_3$ ), 16.3 [ $\text{C}(\text{CH}_3)_3$ ];  $^{15}\text{N}$  NMR (30 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 189.9 (s,  $\text{N}^{\text{Al}}$ ), 149.7 (s,  $\text{N}^{\text{Me}}$ ). IR (ATR;  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 2953$  (vw), 2923 (vw), 2864 (vw), 2824 (w), 2161 (vw), 1529 (w), 1487 (vw), 1462 (w), 1417 (vw), 1373 (vw), 1337 (vw), 1293 (vw), 1252 (w), 1192 (w), 1074 (vw), 1012 (vw), 1000 (vw), 929 (w), 880 (vw), 813 (m), 775 (vw), 752 (vs), 736 (w), 621 (w), 586 (w), 536 (w), 513 (w), 427 (w), 403 (vs); HRMS (EI):  $m/z$  calcd. for  $[\text{C}_{12}\text{H}_{17}\text{AlN}_2\text{Br}]$ : 295.0390 + 297.0370 [ $M - \text{C}_4\text{H}_9$ ]; found 295.0332 + 297.0030, 252.9530 + 254.9500 [ $M - 2(\text{C}_4\text{H}_9)$ ]; elemental analysis calcd. (%) for  $[\text{C}_{16}\text{H}_{26}\text{AlN}_2\text{Br}]$ : C 54.40, H 7.42, N 7.93, Al 7.64, Br 22.62; found C 54.57, H 7.213, N 8.22.

**Synthesis of Compound 7:** **6** (516 mg; 1.460 mmol; 1.0 equiv.) and  $\text{Na}\{\text{N}(\text{SiMe}_3)_2\}$  (268 mg; 1.462 mmol; 1.0 equiv.) were dissolved in 40 mL of THF and stirred for 75 h at  $80^\circ\text{C}$ . The solvent was removed under reduced pressure from the resulting suspension. The residue was taken up in 20 mL of toluene and filtered. The red filtrate was dried under reduced pressure and washed with pentane ( $3 \times 5$  mL). The residue was crystallized from a saturated solution in toluene at  $4^\circ\text{C}$ . **7** (213 mg; 526.5  $\mu\text{mol}$ ; 36 %) was isolated as yellow crystals. M.p.:  $227^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 7.85–7.82 (m, Ar, 1H), 7.07–6.94 (m, Ar, 4H), 6.87–6.79 (m, Ar, 1H), 6.57–6.53 (m, Ar, 2H), 5.61 (s, NCHN, 1H), 2.55 (s,  $\text{CH}_3^{\text{A}}$ , 3H), 2.37 (s,  $\text{CH}_3^{\text{B}}$ , 3H), 1.36 (s, *t*Bu<sup>A</sup>, 9H), 1.35 (s, *t*Bu<sup>B</sup>, 9H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 159.0 (NCN), 147.5 (Ar-q), 146.1 (Ar-q), 143.7 (Ar-q), 136.3 (Ar-q), 125.3 (Ar), 124.7 (Ar), 122.3 (Ar), 118.5 (Ar), 117.5 (Ar), 111.0 (Ar), 110.1 (Ar), 109.0 (Ar), 85.7 (NCHN), 33.6 ( $\text{C}(\text{CH}_3)_3\text{-tBu}^{\text{A}}$ ), 31.3 ( $\text{C}(\text{CH}_3)_3\text{-tBu}^{\text{B}}$ ), 38.7 ( $\text{CH}_3^{\text{B}}$ ), 30.7 ( $\text{CH}_3^{\text{A}}$ ) 18.6 ( $\text{C}(\text{CH}_3)_3\text{-tBu}^{\text{A}}$  (only HMBC)), 18.0 ( $\text{C}(\text{CH}_3)_3\text{-tBu}^{\text{B}}$  (only HMBC));  $^{15}\text{N}$  NMR (30 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 143.0 ( $\text{N}^{\text{MeB}}$ ); IR (ATR;  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3060$  (vw), 2912 (vw), 2864 (vw), 2825 (m), 2192 (vw), 1588 (vw), 1512 (vw), 1488 (s), 1463 (m), 1415 (vw), 1377 (vw), 1353 (vw), 1337 (vw), 1316 (w), 1297 (w), 1283 (w), 1264 (m), 1248 (vw), 1216 (vw), 1187 (vw), 1112 (w), 1082 (vw), 1050 (w), 1013 (w), 992 (w), 939 (w), 901 (w), 813 (m), 794 (w), 763 (vw), 746 (vs), 730 (vs), 710 (w), 676 (vw), 629 (vw), 593 (w), 572 (w), 551 (m), 530 (vw), 460 (w), 443 (m), 432 (w), 412 (s); HRMS (EI):  $m/z$  calcd. for  $[\text{C}_{20}\text{H}_{24}\text{AlN}_4]$ : 347.1816 [ $M-\text{C}_4\text{H}_9$ ]; found 347.0821 [ $M-\text{C}_4\text{H}_9$ ]; elemental analysis calcd. (%) for  $[\text{C}_{24}\text{H}_{33}\text{AlN}_4]$ : C 71.26, H 8.22, N 13.85, Al 6.67; found C 69.25, H 8.027, N 12.89.

**Synthesis of Compound 8:** Spiro(cyclohexane-1,3'-indole) (1.696 g; 9.154 mmol; 1.0 equiv.) and  $[\text{tBu}_2\text{AlBr}]_2$  (2.045 g; 4.626 mmol; 0.5 equiv.) were dissolved in 20 mL of hexane, stirred for 30 min. at ambient temperature and stored at  $4^\circ\text{C}$  for crystallization. After removal of the supernatant the crystals were dried under reduced pressure. **8** (1.110 g; 2.731 mmol; 30 %) was isolated as red powder. M.p.:  $174.6^\circ\text{C}$  (decomposition);  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 9.30 (s, H1, 1H), 8.27–8.24 (m, H7, 1H), 7.02–6.87 (m, H4, H5, H6, 3H), 1.38 (s, *t*Bu, 18H), 1.25–0.99 (m, Cy, 10H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 188.2 (C1), 147.9 (C3), 143.9 (C8), 128.6 (C6), 128.4 (Ar), 123.4 (Ar), 121.7 (C7), 57.5 (C2), 30.94 [ $\text{C}(\text{CH}_3)_3$ ], 30.87 (Cy), 24.9 (Cy), 23.1 (Cy), 16.2 [ $\text{C}(\text{CH}_3)_3$ ];  $^{15}\text{N}$  NMR (30 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  [ppm] = 261.4 (NAL); IR (ATR;  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 3154$  (vw), 2920 (vw), 2908 (vw), 2865 (vw), 2827 (w), 2816 (w), 2696 (vw), 2497 (vw), 2322 (vw), 2289 (vw), 2258 (vw), 2243 (vw), 2223 (vw), 2194 (vw), 2175 (vw), 2164 (vw), 2136 (vw), 2111 (vw), 2100 (vw), 2081 (vw), 2063 (vw), 2038 (vw), 2019 (vw), 2010 (vw), 1999 (vw), 1973 (vw), 1953 (vw), 1925 (vw), 1912 (vw), 1883 (vw), 1747 (vw), 1550 (vw), 1512 (vw), 1461 (w), 1379 (vw), 1355 (vw), 1328 (vw), 1278 (vw), 1239 (vw), 1229 (vw), 1176 (vw), 1152 (vw), 1119 (vw), 1104 (vw), 1067 (vw), 1027 (vw), 1006 (vw), 975 (vw), 961 (vw), 937 (vw), 889 (vw), 857 (vw), 814 (m), 766 (w), 748 (s), 714 (vw), 674 (s), 654 (w), 630 (vw), 613 (w), 604 (m), 587 (w), 540 (w), 507 (w), 495 (w),

471 (vw), 459 (vw), 450 (vw), 422 (w), 409 (s), 397 (vs); HRMS (EI): decomposition; elemental analysis calcd. (%) for  $[C_{21}H_{33}AlBrN]$ : C 62.07, H 8.19, N 3.45, Al 6.64, Br 19.66; found C 62.53, H 8.067, N 3.66.

**Synthesis of 9: 8** (700 mg; 1.722 mmol; 1.0 equiv.) and  $Na\{N(SiMe_3)_2\}$  (352 mg; 1.920 mmol; 1.1 equiv.) were dissolved in 20 mL of THF and stirred for 16 h at ambient temperature. The solvent was removed under reduced pressure and the residue was suspended in 20 mL of pentane and filtered. The red filtrate was concentrated to 10 mL and stored at 4 °C for crystallization. After removal of the supernatant **9** (246 mg; 481.6  $\mu$ mol; mmol; 28 %) was isolated as colorless crystals. M.p.: 180 °C (decomposition);  $^1H$  NMR (300 MHz,  $C_6D_6$ ):  $\delta$  [ppm] = 7.85 (d,  $^3J_{HH} = 7.4$  Hz, H7', 1H), 7.47 (dd,  $^3J_{HH} = 7.5$  Hz,  $^4J_{HH} = 1.0$  Hz, H4, 1H), 7.32 (d,  $^3J_{HH} = 7.2$  Hz, H5', 1H), 7.23 (td,  $^3J_{HH} = 7.6$  Hz,  $^4J_{HH} = 1.3$  Hz, H5, 1H), 7.08 (dd,  $^3J_{HH} = 7.8$  Hz,  $^4J_{HH} = 0.7$  Hz, H4', 1H), 7.05 (td,  $^3J_{HH} = 7.7$  Hz,  $^4J_{HH} = 1.2$  Hz, H6, 1H), 6.93 (td,  $^3J_{HH} = 7.6$  Hz,  $^4J_{HH} = 1.1$  Hz, H6', 1H), 6.75 (td,  $^3J_{HH} = 7.4$  Hz,  $^4J_{HH} = 1.1$  Hz, H7, 1H), 4.94 (s, H1', 1H), 2.50–0.85 (m, Cy, 20H), 1.48 (s,  $tBu^A$ , 9H), 1.24 (s,  $tBu^B$ , 9H);  $^{13}C\{^1H\}$ -NMR (75 MHz,  $C_6D_6$ ):  $\delta$  [ppm] = 202.3 (C1), 154.2 (C3), 146.4 (C3'), 145.5 (C8'), 140.3 (C8), 128.7 (C5), 128.4 (C6), 127.0 (C6'), 125.7 (C5'), 124.7 (C4), 119.9 (C7'), 115.4 (C7), 111.17 (C4'), 81.7 (C1'), 58.9 (C2'), 51.8 (C2), 35.0 (Cy), 34.4 (Cy), 33.0 (Cy), 32.3 (C(CH<sub>3</sub>)<sub>3</sub>,  $tBu^A$ ), 30.9 (C(CH<sub>3</sub>)<sub>3</sub>,  $tBu^B$ ), 29.6 (Cy), 25.8 (Cy), 24.8 (Cy), 24.1 (Cy), 21.6 (Cy), 21.4 (Cy), 20.9 (Cy), 17.0 (C(CH<sub>3</sub>)<sub>3</sub>,  $tBu^B$  (only HMBC)), 16.7 (C(CH<sub>3</sub>)<sub>3</sub>,  $tBu^A$  (only HMBC));  $^{15}N$  NMR (30 MHz,  $C_6D_6$ ):  $\delta$  [ppm] = 264.8 ( $N^{coordinative}$ ); IR (ATR;  $cm^{-1}$ ):  $\tilde{\nu} = 2937$  (vw), 2862 (m), 2818 (w), 2753 (m), 2692 (vw), 2188 (vw), 2162 (vw), 2150 (vw), 2039 (vw), 2024 (vw), 1991 (vw), 1913 (vw), 1593 (vw), 1521 (w), 1469 (vw), 1455 (s), 1380 (s), 1355 (vw), 1330 (vw), 1317 (w), 1304 (vw), 1275 (m), 1251 (w), 1239 (w), 1205 (w), 1184 (vw), 1166 (vw), 1152 (vw), 1123 (vw), 1095 (vw), 1060 (vw), 1042 (w), 1026 (w), 1001 (w), 970 (vw), 926 (vw), 905 (w), 881 (w), 841 (vw), 810 (vw), 773 (s), 751 (w), 743 (s), 714 (vs), 692 (vw), 676 (w), 662 (vw), 608 (w), 586 (vw), 570 (m), 561 (m), 542 (w), 498 (m), 475 (vw), 455 (vw), 429 (s), 413 (vw), 400 (s); HRMS (EI):  $m/z$  calcd. for  $[C_{34}H_{47}AlN_2]$ : 510.3555 [M]; found 510.3063 [M], 453.3210 [M–C<sub>4</sub>H<sub>6</sub>], 396.1545 [M–2(C<sub>4</sub>H<sub>9</sub>)]; elemental analysis calcd. (%) for  $[C_{34}H_{47}AlN_2]$ : C 79.96, H 9.28, N 5.48, Al 5.28; found C 77.25, H 8.284, N 5.13.

**Synthesis of 10:**  $Na\{N(SiMe_3)_2\}$  (177 mg; 965.7  $\mu$ mol; 1.0 equiv.) was dissolved in 10 mL of THF and cooled to 0 °C. At this temperature a solution of **8** (392 mg; 964.6  $\mu$ mol; 1.0 equiv.) in 10 mL of THF, cooled to 0 °C, was added slowly. After 2 h stirring the solvent was removed at 0 °C under reduced pressure. The residue was suspended in 10 mL of pentane, filtered and the filtrate was stored at 4 °C for crystallization. After removal of the supernatant **10** (128 mg; 229.0  $\mu$ mol; 24 %) was isolated as yellow powder. M.p.: 38 °C (decomposition);  $^1H$  NMR (300 MHz,  $C_6D_6$ ):  $\delta$  [ppm] = 7.49 (dd,  $^3J_{HH} = 7.4$  Hz,  $^4J_{HH} = 1.5$  Hz, H4, 1H), 7.04 (ddd,  $^3J_{HH} = 7.9$  Hz,  $^3J_{HH} = 7.4$  Hz,  $^4J_{HH} = 1.4$  Hz, H6, 1H), 6.72 (td,  $^3J_{HH} = 7.3$  Hz,  $^4J_{HH} = 1.1$  Hz, H5, 1H), 6.44 (dd,  $^3J_{HH} = 7.9$  Hz,  $^4J_{HH} = 1.1$  Hz, H7, 1H), 5.11 (s, C1H, 1H), 3.59–3.51 (m, 1,4-THF, 4H), 2.45–1.55 (m, Cy, 10H), 1.40 (s,  $tBu^A$ , 9H), 1.25 (s,  $tBu^B$ , 9H), 0.90–0.85 (m, 2,3-THF, 4H), 0.51 (s, TMS<sup>A</sup>, 9H), 0.19 (s, TMS<sup>B</sup>, 9H);  $^{13}C\{^1H\}$  NMR (75 MHz,  $C_6D_6$ ):  $\delta$  [ppm] = 157.2 (C8), 137.4 (C3), 126.8 (C6), 126.1 (C4), 115.4 (C5), 111.2 (C7), 88.4 (C1), 73.1 (1,4-THF), 51.3 (C2), 39.3 (Cy), 32.8 (C(CH<sub>3</sub>)<sub>3</sub>,  $tBu^B$ ), 32.2 (C(CH<sub>3</sub>)<sub>3</sub>,  $tBu^A$ ), 31.2 (Cy), 26.6 (Cy), 24.8 (2,3-THF), 24.0 (Cy), 22.8 (Cy), 17.3 (C(CH<sub>3</sub>)<sub>3</sub>,  $tBu^B$ ), 15.7 (C(CH<sub>3</sub>)<sub>3</sub>,  $tBu^A$ ), 6.3 (TMS<sup>B</sup>), 5.6 (TMS<sup>A</sup>);  $^{15}N$  NMR (30 MHz,  $C_6D_6$ ):  $\delta$  [ppm] = 102.3 ( $N^{Al}$ ), 48.4 ( $N^{N(SiMe_3)_2}$ );  $^{29}Si$  NMR (60 MHz,  $C_6D_6$ ):  $\delta$  [ppm] = 6.70 (Si<sup>TMSA</sup>), –2.71 (Si<sup>TMSB</sup>); IR (ATR;  $cm^{-1}$ ):  $\tilde{\nu} = 2928$  (w), 2863 (vw), 1592 (vw), 1557 (vw), 1464 (w), 1450 (w), 1380 (vw), 1356 (vw), 1327 (vw), 1281 (vw), 1249 (m), 1213 (w), 1182 (vw), 1037 (w), 1023 (vw), 989 (m), 961 (w), 927 (w), 905 (m),

887 (s), 861 (w), 831 (vs), 810 (s), 768 (m), 750 (s), 739 (s), 672 (w), 638 (vw), 623 (vw), 608 (vw), 575 (m), 558 (w), 544 (vw), 505 (vw), 457 (w), 438 (w), 417 (s); HRMS (EI):  $m/z$  calcd. for  $[C_{31}H_{58}AlN_2OSi_2]$ : 557.3903 [M – H]; found 557.3625 [M – H]; elemental analysis calcd. (%) for  $[C_{31}H_{58}AlN_2OSi_2]$ : C 66.61, H 10.64, N 5.01, Al 4.83, O 2.86, Si 10.05; found C 65.84, H 10.110, N 4.80.

CCDC 1980987 (for **1**), 1980936 (for **2**), 1980933 (for **2<sup>aNH</sup>**), 1980934 (for **5**), 1980986 (for **6**), 1980935 (for **7**), 1980988 (for **8**), and 1980937 (for **10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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