

# Aluminum Hydrides Stabilized by N-Heterocyclic Imines as Catalysts for Hydroborations with Pinacolborane

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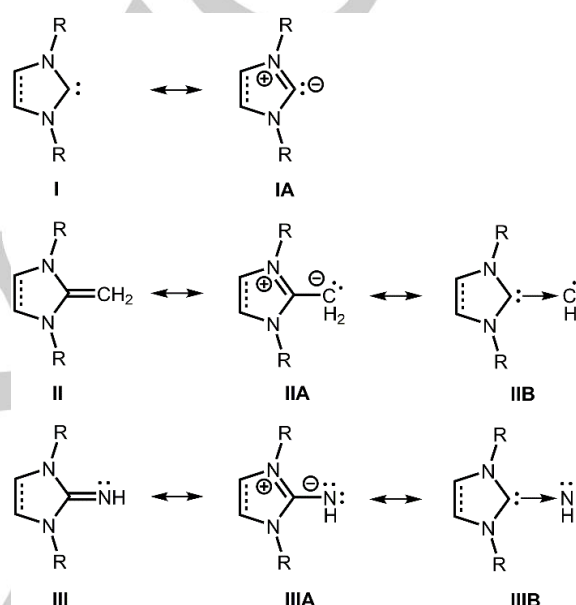
**Abstract:** The catalytic activity of the NHI-substituted aluminum hydrides  $\{L^{\text{Mes}}\text{AlH}_2\}_2$  (**1a**),  $\{L^{\text{Dip}}\text{AlH}_2\}_2$  (**1b**),  $\{L^{\text{Mes}}\text{Al}(\text{H})\text{OTf}\}_2$  (**2a**), and  $\{L^{\text{Dip}}\text{Al}(\text{H})\text{OTf}\}_2$  (**2b**) in the hydroboration of terminal alkynes (for **1**), as well as carbonyl compounds (for **2**) with pinacolborane (4,4,5,5-tetramethyl-1,3,2-dioxaborolane) is investigated ( $L^{\text{Mes}}\text{N}$  = 1,3-dimesityl-imidazolin-2-imino, Mes = 2,4,6-trimethylphenyl,  $L^{\text{Dip}}\text{N}$  = 1,3-bis(2,6-diisopropylphenyl)-imidazolin-2-imino, Tf = triflyl). With the implementation of **1** as a catalyst, the hydroboration of selected terminal arylalkynes requires elevated temperature (80 °C) to proceed. The less sterically congested **1a** produces faster conversions than the bulkier **1b**. With the use of **2** as a catalyst, the hydroboration of carbonyl compounds occurs at room temperature. An increased steric hindrance of the catalyst (**2a** vs. **2b**) does not mitigate the rate of conversion to a relevant degree.

## Introduction

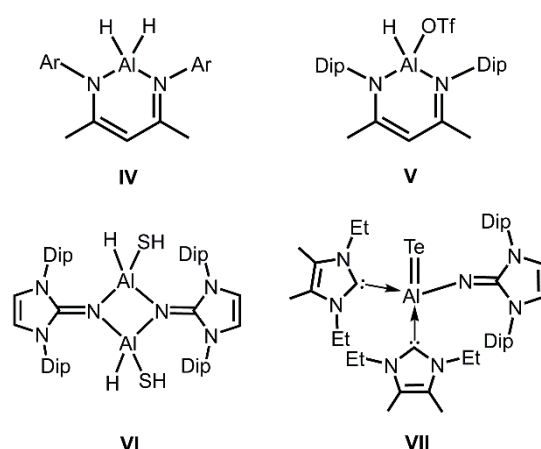
The ligand class of N-heterocyclic carbenes (NHCs) was introduced in pioneering work of Wanzlick and Öfele who described an NHC transition metal complex of mercury or chromium, respectively.<sup>[1]</sup> Since the seminal report<sup>[2]</sup> by Arduengo and coworkers on “free” NHCs (**I**, Figure 1), this compound class has found widespread application not only in transition-metal chemistry, but also in the field of main-group elements.<sup>[3,4]</sup> In general, NHCs may act as potent  $\sigma$ -electron pair donor and weak  $\pi$ -electron acceptor ligands. Moreover, the bulkiness of NHCs can be conveniently modified to meet individual requirements for kinetic stabilization of a target system. Consequently, the implementation of NHCs has resulted in the isolation of a variety of otherwise elusive main group metal species (e.g. complexes of boron(0), silicon(0), germanium(0), etc.).<sup>[4,5-7]</sup>

The ligand classes of N-heterocyclic olefins (NHOs, **II**)<sup>[8]</sup> and N-heterocyclic imines (NHIs, **III**)<sup>[9]</sup> are structurally related to NHCs and possess an exocyclic olefinic carbon atom and an imino nitrogen atom, respectively, that may bond to a Lewis acid (Figure 1). Based on the resonance structures **IIA**, as well as **III** and **IIIA**,

both of these ligands systems possess strongly  $\sigma$ -electron-donating character and, thus, NHCs, NHOs and NHIs resemble in their nature as  $2\sigma$ -electron donors. The canonical structure **II B** illustrates the relation between NHCs and NHOs (Figure 1). In contrast to NHCs and NHOs, the NHI system stands out as a



**Figure 1.** Archetypal ligand systems that comprise the five-membered N-heterocycle structure motif (saturated or unsaturated at the ligand backbone): carbene (**I**, NHC), olefin (**II**, NHO), and imine (**III**, NHI), as well as the selected resonance structures **IA–IIIB** (R = alkyl or aryl).



**Figure 2.** The 1,3-diketimino-based aluminum hydrides **IV** and **V**, as well as the N-heterocyclic imino complexes **VI** **VII** (Ar = 2,6-diethylphenyl, Dip = 2,6-diisopropylphenyl).

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potential  $\pi$ -electron donor which results from the supplementary lone pair at the imino nitrogen atom as shown by the resonance structures **IIIA** and **IIIB** (Figure 1).<sup>[9]</sup>

The use of imino group-based ligands (e.g. NHI, 1,3-diketimines, iminopyridines) has given access to a plethora of aluminum hydrides with salient applications as the activation of elemental sulfur, dehydrogenative coupling and the conversion into a rare aluminum chalcogen double-bonded species.<sup>[10,11,12]</sup> Very recently, Roesky and coworkers have demonstrated the catalytic activity of 1,3-diketimino-bonded aluminum hydrides (**IV**,

**V**, Figure 2) in the hydroboration of terminal alkynes, as well as of carbonyl groups with pinacolborane (4,4,5,5-tetramethyl-1,3,2-dioxaborolane, HBpin).<sup>[11c,13]</sup> Until the upcoming of these most remarkable results the field of catalytic hydroboration with dioxaborolanes (e.g. HBpin, catecholborane) had mostly been limited to transition-metal complexes.<sup>[14,15]</sup> Only a few examples for the use of main group metal complexes as catalysts in the hydroboration of unsaturated organic substrates had been reported (e.g. bulky amido-stabilized germanium(II) hydride, as well as tin(II) hydride, tris(oxazolinyl)phenylborato- or 1,3-diketiminato-substituted magnesium compounds).<sup>[16]</sup>

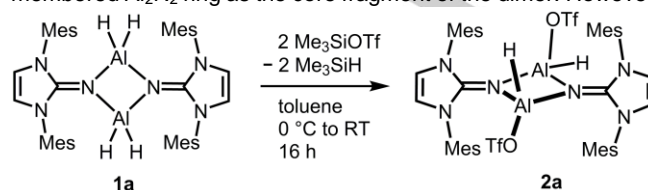
In the past years we have focused on the use of NHI-stabilized group 13 metal hydrides to gain access to elusive main group element species (e.g. **VI**, **VII**, Figure 2).<sup>[10d,12b,17]</sup> Notably, NHI-based ligand systems have attracted increasing attention in recent times due to their high efficiency in the stabilization of electron-deficient functional groups.<sup>[9,18]</sup> Inspired by the outstanding findings of Roesky and coworkers, we set out to test our NHI-substituted aluminum hydrides for activity in catalytic hydroborations using HBpin.<sup>[11c,13]</sup> Herein, we report the synthesis of the novel dimeric aluminum hydride  $\{L^{\text{Mes}}\text{Al}(\text{H})\text{OTf}\}_2$  (**2a**) and its application in catalytic hydroboration of selected aldehydes and ketones ( $L^{\text{Mes}}\text{N} = 1,3$ -dimesityl-imidazolin-2-imino; Mes = 2,4,6-trimethylphenyl, Tf = triflyl). Moreover, the earlier reported aluminum hydrides  $\{L^{\text{Mes}}\text{AlH}_2\}_2$  (**1a**),  $\{L^{\text{Dip}}\text{AlH}_2\}_2$  (**1b**), and  $\{L^{\text{Dip}}\text{Al}(\text{H})\text{OTf}\}_2$  (**2b**) were also examined with regard to their use as a catalyst in the hydroboration of carbonyl compounds and alkynes, respectively ( $L^{\text{Dip}}\text{N} = 1,3$ -bis(2,6-diisopropylphenyl)-imidazolin-2-imino).

## Results and Discussion

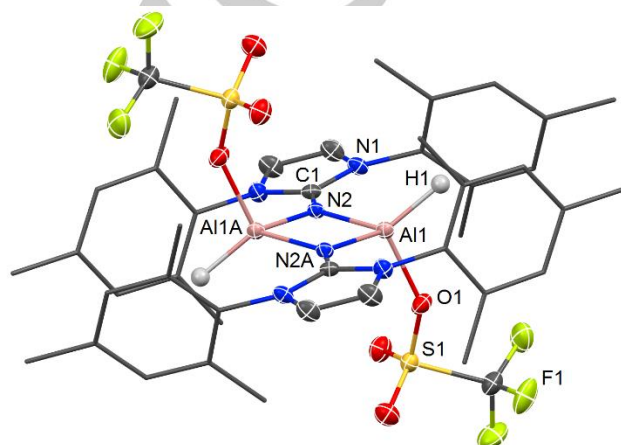
### Synthesis of New Aluminum Hydride

In order to complement our substance library for the intended catalytic study, we newly synthesized  $\{L^{\text{Mes}}\text{Al}(\text{H})\text{OTf}\}_2$  (**2a**) as a less sterically hindered congener of the NHI-stabilized aluminum hydride triflate  $\{L^{\text{Dip}}\text{Al}(\text{H})\text{OTf}\}_2$  (**2b**) that had been reported before.<sup>[17a]</sup> The conversion of the dimeric NHI-bonded aluminum dihydride  $\{L^{\text{Mes}}\text{AlH}_2\}_2$  (**1a**)<sup>[10d]</sup> with two equiv of  $\text{Me}_3\text{SiOTf}$  resulted in replacement of one hydride functionality per aluminum center versus a triflate group to afford the target compound (**2a**; Scheme 1). Notably, this type of reactivity had been described earlier.<sup>[17a,19]</sup> Interestingly, the remaining hydrides in **1a** show no tendency to react with excess  $\text{Me}_3\text{SiOTf}$  to furnish a hypothetical aluminum bistriflate derivative ( $\{L^{\text{Mes}}\text{Al}(\text{OTf})_2\}_2$ ).

Compound **1a** crystallized from toluene as a centrosymmetric dimer in the monoclinic space group  $C2/c$  (Figure 3). In reminiscence of **2b**, compound **2a** exhibits a nearly planar four-membered  $\text{Al}_2\text{N}_2$  ring as the core fragment of the dimer. However,



**Scheme 1.** Conversion of the imidazolin-2-imino aluminum dihydride **1a** to the aluminum hydride triflate **2a**.



**Figure 3.** Ellipsoid plot (50% level) of the molecular structure of **2a** in the solid state. Hydrogen atoms except on Al have been omitted. Mesityl groups are depicted as stick model. Selected bond lengths [Å] and bond angles [°]: Al1–H1 1.53(3), Al1–N2 1.875(2), Al1–N2A 1.878(2), Al1–O1 1.838(2), N1–C1 1.371(3), N2–C1 1.319(3), O1–Al1–N2 107.49(8), O1–Al1–N2A 109.52(8), N2–Al1–N2A 87.06(9), Al1–N2–Al1A 92.94(9).

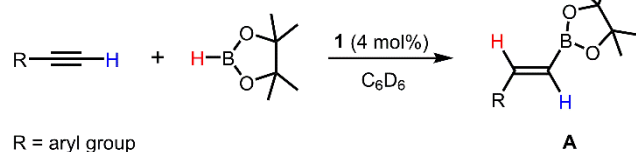
**2a** is marked by a *trans* configuration of the triflate groups at the central four-membered cycle in contrast to the *cis* arrangement of the triflate substituents in **2b**. A similar discrepancy had been observed for the stereo configuration of sulfido-functionalized aluminum compounds bearing an  $L^{\text{Mes}}\text{N}$  and an  $L^{\text{Dip}}\text{N}$  group for which the less bulky derivative prefers *trans*-orientation of the chalcogen atoms at the  $\text{Al}_2\text{N}_2$  ring, as well.<sup>[10d]</sup> The Al–N bond lengths in **2a** (1.875(2) Å, 1.878(2) Å) are very similar to the respective bond lengths in **2b** (1.849(3) Å, 1.872(3) Å) which suggests no significant impact of the steric hindrance of the iminato ligand, as well as the stereo configuration at the four-membered aluminacycle on the electronic situation at the Al centers in the solid state.

### Catalytic Study – Hydroboration of Alkynes

In resemblance to the approach of Roesky and coworkers,<sup>[11c]</sup> we carried out the reaction of 1 equiv HBpin with 1 equiv of terminal alkyne in the presence of a catalytic amount of **1** (4 mol%; Table 1). We used  $\text{C}_6\text{D}_6$  as solvent and a temperature of 80 °C was required to produce conversions on a reasonable

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timescale. In the case of aluminum dihydride **IV**,  $\text{CDCl}_3$  was used and the conversions were observed at 30 °C.<sup>[11c]</sup> When we tested  $\text{CDCl}_3$  as a medium, we found no significant impact of the solvent on the reaction outcome. The borylated *E*-alkenes of type **A** were



Entry	Substrate	Catalyst	Reaction Temp./Time	Yield <sup>a</sup> <b>A</b>
1.1		<b>1a</b>	80 °C 40 h	40%
1.2		<b>1a</b>	80 °C 40 h	80% <sup>b</sup>
1.3		<b>1a</b> <b>1b</b>	80 °C 12 h	71% <sup>c</sup> 19%
1.4		None	110 °C 24 h	15% <sup>d</sup>

**Table 1.** Catalytic hydroborations of terminal arylalkynes (1 equiv) with pinacolborane (1 equiv). Conversions were carried out in a flame-sealed NMR sample tube. *a*: The yield corresponds to the intensity ratio of **A** in the sum of the intensities of characteristic signals of **A** and the alkyne precursor as observed by <sup>1</sup>H NMR spectroscopy. No relevant amounts of regio- or stereoisomers of **A** were detected. *b*: 54% yield was observed after 28 h at 80 °C in  $\text{CDCl}_3$ . *c*: 84% yield was found after 24 h. *d*: this reaction was carried out in toluene-*d*<sub>6</sub>; only traces of the alkene (**A**) were observed after 12 h at 80 °C.

furnished and no relevant formation of stereo- or regioisomers was observed. The results of the catalytic hydroborations are summarized in Table 1: The conversion of the electron-poor substrate 1-HCC-3,5-( $\text{CF}_3$ )<sub>2</sub>- $\text{C}_6\text{H}_3$  catalyzed by **1a** proceeded slower (Entry 1.1, 40% yield in 40 h) than that of ( $\text{HCC}$ ) $\text{C}_6\text{H}_5$  (phenylacetylene, Entry 1.2, 80%, 40 h; note: 54% were observed after 28 h in  $\text{CDCl}_3$ ) as determined by <sup>1</sup>H NMR-spectroscopic analysis. In comparison, the electron-rich alkyne 1-HCC-4-NMe<sub>2</sub>- $\text{C}_6\text{H}_4$  reacted significantly faster to give 71% conversion after 12 h (Entry 1.3; 84% of alkene after 24 h). Obviously, this conversion benefits from the increased affinity of the electron-poor hydridoborane to electron-rich substrates.

The bulkier imino aluminum dihydride **1b** showed decreased activity as a catalyst (Entry 1.3, 19%, 12 h). For comparison, temperatures of 110 °C were needed to force the hydroboration of phenylacetylene by pinacolborane without the addition of catalyst. It is of note that **IV** promotes the respective conversion in 73% yield within 12 h at 30 °C.<sup>[11c]</sup>

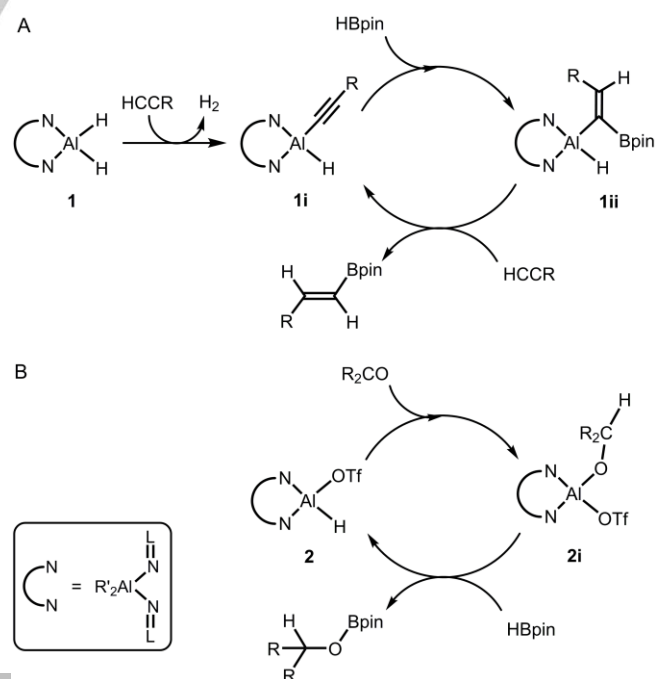
Following the catalytic cycle which was calculated by Roesky and coworkers for the use of **IV**, we suggest that the catalytically active aluminum alkynyl species **1i** is generated via dehydrocoupling of **1** with terminal alkyne (Scheme 2A).<sup>[11c]</sup> In

consequence, this type of reaction functions with terminal alkynes only as was verified by respective experiments with bisorganyl acetylenes.<sup>[11c]</sup> Hydroboration of the carbon-carbon triple bond in **1i** affords the intermediate aluminum complex **1ii** with the

borylated alkenyl group attached to the metal center. Via metathesis between **1ii** and substrate the protonated alkene is released and the aluminum alkynyl **1i** is regenerated. The conversion of **1** to **1i** is the overall rate-determining step of the process.

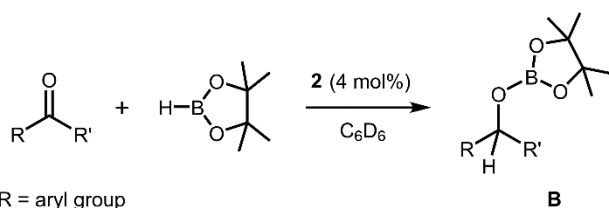
### Catalytic Study – Hydroboration of Carbonyl Groups

As Roesky and coworkers verified the applicability of the 1,3-diketimino-based aluminum triflate **V** as a catalyst in the hydroboration of aldehydes, as well as ketones, we treated 1 equiv of HBpin with 1 equiv of carbonyl-functionalized substrate with the addition of 4 mol% of **2** in  $\text{C}_6\text{D}_6$  (Table 2).<sup>[13]</sup> For aldehydes, the O-borylated products of type **B** formed in high yield within one day at room temperature as concluded from <sup>1</sup>H NMR spectroscopic analysis. Interestingly, benzaldehyde converted faster than electron-poor arylaldehyde (*i.e.* ( $\text{CHO}$ ) $\text{C}_6\text{F}_5$ ; Table 2, Entries 2.1 and 2.2) but not to the extensive degree implied by our alkyne hydroboration experiments (Table 1, Entries 1.1 and 1.2). Also, it converted at a comparable rate as did substrates with an electron-rich  $\pi$ -system (*e.g.* 1-CHO-4-OMe- $\text{C}_6\text{H}_4$  and 1-CHO-4-NMe<sub>2</sub>- $\text{C}_6\text{H}_4$ ; Entries 2.2-2.4). The catalytic hydroboration of the sterically hindered mesitylaldehyde proceeded similar to the less bulky substrates (Entry 2.5). Moreover, the use of the more sterically congested catalyst **2b** had only negligible impact on the formation of **B** (Entries 2.2, 2.3 and 2.5). We conclude that the rate of catalytic hydroboration of arylaldehydes at room temperature is only susceptible to a minor degree to the electronic, as well as the steric properties of the aryl group of the substrate. In addition, the bulkiness of the catalyst has no significant impact. With regard to the electronic effects, we presume that the increased electrophilicity of the carbonyl C-atom in ( $\text{CHO}$ ) $\text{C}_6\text{F}_5$



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**Scheme 2.** Suggested catalytic cycle of the hydroboration of terminal alkynes with **1** (A) or carbonyl compounds with **2** (B; R = aryl, R' = alkenyl, alkynyl, hydride).



Entry	Substrate	Catalyst	Reaction Temp./Time	Yield <sup>a</sup> <b>B</b>
2.1		<b>2a</b>	RT 24 h	60%
2.2		<b>2a</b> <b>2b</b>	RT 24 h	91% <sup>b</sup> 85%
2.3		<b>2a</b> <b>2b</b>	RT 24 h	91% 95%
2.4		<b>2a</b>	RT 8 h	35% <sup>c</sup>
2.5		<b>2a</b> <b>2b</b>	RT 24 h	85% 93%
2.6		<b>2a</b>	60 °C 6 h	53%
2.7		<b>2a</b>	60 °C 9 h	7%
2.8		None	50 °C 18 h	53%

**Table 2.** Catalytic hydroborations of carbonyl compounds (1 equiv) with pinacolborane (1 equiv). *a.* The yield reflects the intensity ratio of **B** in the sum of **B** and the carbonyl precursor as observed by <sup>1</sup>H NMR spectroscopy. *b.* The order of reagent addition was altered, otherwise the formation of an additional aryl species was observed. *c.* After 8 h of conversion time had elapsed the formation of various side products commenced. RT = room temperature.

which renders this substrate highly reactive toward hydride transfer is compensated by the reduced electron-donating character of the adjacent O-atom toward the Lewis acid (e.g. the boron- and the aluminum center). *Vice versa*, the electron-rich substrates would show increased affinity to the metal atom but reduced reactivity toward hydride sources. It should be noted that without the addition of catalyst the hydroboration of benzaldehyde with pinacolborane was found to occur at 50 °C and produced 53% conversion to **B** within 18 h (Entry 2.8).

When we converted 1-C(CH<sub>3</sub>)O-C<sub>6</sub>H<sub>5</sub> (acetophenone) with pinacolborane in the presence of a catalytic amount of **2a**, elevated temperatures (60 °C) were required to produce **B** on a reasonable timescale (Entry 2.6, 53%, 6 h). The diarylketone CO(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> (benzophenone) proved less inclined to undergo catalytic hydroboration at 60 °C (Entry 2.7, 7%, 9 h). In comparison, **V** catalyzes the hydroboration of acetophenone at significantly higher rates (51%, RT, 6 h).<sup>[13]</sup>

In accordance with the catalytic cycle suggested by Roesky and coworkers on the basis of theoretical methods for the use of **V**, we assume that in the initial step **2** transfers a hydride to the carbonyl group of the substrate to form the intermediate aluminum alkoxide **2i** which was identified as the rate-determining step (Scheme 2B) in the process.<sup>[13]</sup> In a metathesis reaction between **2i** and pinacolborane the O-borylated alkoxide is released and the aluminum hydride **2** is reformed.

Under consideration of the conversion rates for the catalytic reactions of pinacolborane with alkynes, as well as carbonyl compounds a generally lower activity of the dimeric NHI-substituted systems (**1**, **2**) with respect to the 1,3-diketimino aluminum hydrides of comparable steric hindrance (**IV**, **V**) must be concluded. Hydride transfer was identified as the rate-determining step in the hydroboration of alkynes, as well as of carbonyl compounds by theoretical methods.<sup>[11c,13]</sup> The comparison of theoretical indicators (e.g. Wiberg Bond Index for Al-H and NBO charge at Al/H) for the hydride donor strength of imidazolin-2-imino aluminum dihydride and 1,3-diketimino aluminum dihydride had suggested that the NHI derivative is the slightly more potent hydride transfer reagent.<sup>[17a]</sup> Thus, we presume that the lower activity of the NHI systems mainly derives from the decreased conformational flexibility of the planar four-membered Al<sub>2</sub>N<sub>2</sub> cycle in comparison to the less rigid six-membered ring in Roesky's 1,3-diketiminato aluminum complexes rather than from steric congestion of the metal center. For the 1,3-diketiminato complexes the perpetual increase and decrease of the metal center's coordination number which is typical for the substrate association and dissociation processes involved in catalytic conversions may require less costs of energy for conformational adaption of the ligand scaffold. Furthermore, we cannot rule out a negative cooperativity between the two catalytically active sites in **1** and **2**, respectively, that is substrate binding to one metal center of the dimer may hamper substrate conversion at the adjacent aluminum site.

## Conclusion

The implementation of main group metal complexes in catalysis is in its infancy. In this contribution, we studied the

catalytic hydroboration of terminal arylalkynes and carbonyl compounds (e.g. aldehydes, ketones) with pinacolborane using dimeric NHI-stabilized aluminum dihydrides (**1**) or aluminum hydride triflates (**2**). The hydroboration of alkynes proceeds faster if the  $\pi$ -system is rich in electron density and steric hindrance of the catalyst reduces conversion rates. In contrast, the hydroboration of carbonyl compounds is less prone to the electronic and steric properties of the substrates and the catalyst.

Future investigation will focus on the use of cationic aluminum hydrides in catalysis and expansion of the catalytic scope of hydrometallations toward other unsaturated functional groups (e.g. imines, nitriles, thioketones).

## Experimental Section

In a typical catalytic experiment an NMR sample tube was charged with the catalyst (**1** or **2**, 4 mol%), the substrate (alkyne or carbonyl compound, 1 equiv), pinacolborane (1 equiv) and  $C_6D_6$  (0.5 ml) in a *Glove Box Workstation*. The sample tube was flame-sealed at the Schlenk line and stored at 80 °C (alkyne reactions) or closed with a rubber cap supported by PTFE-coated tape and stored at RT in a *Glove Box Workstation* (carbonyl reactions). The progress of the reaction was monitored by  $^1H$  NMR spectroscopy. See the Supporting Information for further details.

## Acknowledgements

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**Keywords:** Aluminum • Homogenous catalysis • Hydrides • Hydrogen transfer • Reduction

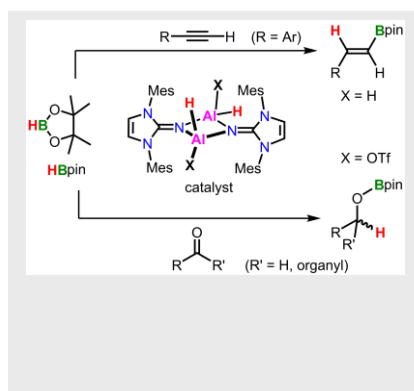
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## COMMUNICATION

N-heterocyclic imino-substituted aluminum dihydrides and aluminum hydride triflates with different degrees of steric hindrance were applied in the catalytic hydroboration of alkynes and carbonyl compounds with pinacolborane.



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