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# Amplifying Reactivity of Metal Hydrides: A Heterotrimetallic NiAl<sub>2</sub>(μ<sup>2</sup>-H)<sub>2</sub> Catalyst for the Facile Dearomatization of *N*-Heterocycles

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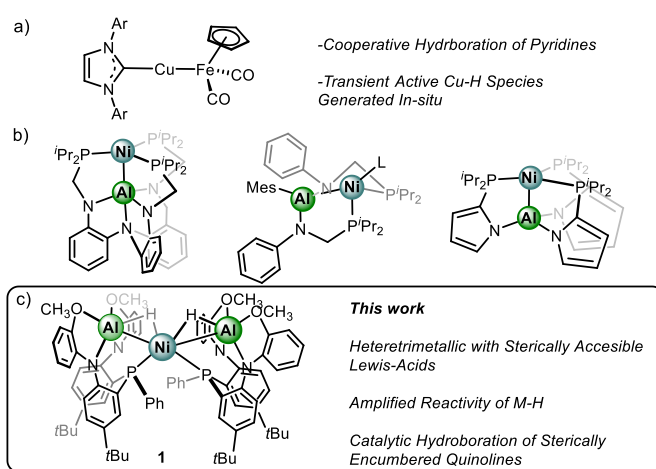
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**Abstract:** Identifying methods to modulate the reactivity of metal-hydrides are lacking yet highly desirable given the role they play in a plethora of catalytic applications. Herein we report novel methodology to amplify reactivity of metal hydrides through the design of well-defined heterometallic bridged hydride species. Catalytic hydroboration of quinolines was dramatically altered by the addition of a secondary metal to bridge the Al-hydride species **LAIH**. Specifically, the addition of Ni(COD)<sub>2</sub> led to the formation of novel heterotrimetallic species **1** which features Ni participating in 3-center-bonding with sterically accessible Al-H species and exhibits catalytic hydroboration of sterically encumbered quinolines and approximately a 400 times enhancement in catalytic reactivity in comparison to **LAIH**.

Metal-hydride complexes are fundamental organometallic species used in the catalytic conversion of organic substrates to a myriad of value-added products.<sup>1</sup> Metal-hydrides have often been implicated as intermediates in catalytic transformations including hydrogenation, hydroformylation, isomerization, as well as dearomatization of *N*-heterocycles through hydroboration and hydrosilylation.<sup>2-5</sup> Identifying methods to modulate the reactivity of metal-hydrides are often limited to the implementation of varying spectator ligands and metal centres in mononuclear systems. Multimetallic systems have been promising in generating reactive metal-hydride species and are an emerging field in homogenous catalysis.<sup>6-8</sup> However, the rational design of multimetallic species often relies on self-assembly of metals ions on ligand scaffolds and are thus, limited in predictive formation.<sup>9-11</sup> Well-defined heterometallic hydrides have recently been reported, including recent examples featuring Ni-Mg and Ni-Zn bridged hydrides, yet their utilization in catalysis is in their infancy.<sup>12-14</sup>

Various transition metal complexes are known to facilitate hydroboration of *N*-heterocycles, such as Rh,<sup>15</sup> Ru,<sup>16</sup> Fe,<sup>17</sup> and a recent example by the Findlater group featuring Ni.<sup>18</sup> In addition, complexes bearing redox-inactive metals such as La, Mg, and Zn as well as phospholenes are known to facilitate hydroboration of heterocycles.<sup>19-22</sup> While several catalysts are known for the transformation, the catalytically active metal-hydride species often remain elusive and are limited to few examples<sup>19-20, 23</sup> Mankad et al. reported the cooperative amplification of hydroboration with a bimetallic Cu-Fe system (Figure 1a).<sup>24</sup> This finding demonstrates a sharp enhancement in activity by using an isolated Cu-Fe complex and is hypothesized to proceed through *in situ* preactivation of a heterocycle followed by insertion by a transient Cu-H species. Though

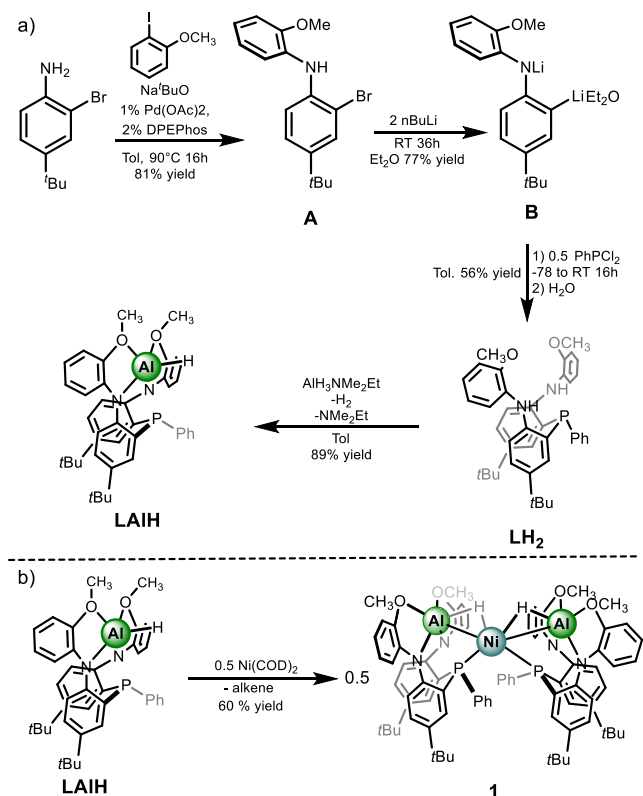
this is a pivotal finding, identifying the metal-hydride intermediates would bolster the degree of mechanistic insight available.



**Figure 1.** a) Multimetallic catalyst for hydroboration of *N*-heterocycles b) Examples of nickel-alane species c) Our novel heterotrimetallic hydride species with Ni and two Al centers

In the interest of further exploring cooperative transformations in multimetallic assemblies, well-defined heterometallic species incorporating Earth-abundant metals have been of interest with several relevant examples reported in the last decade.<sup>25-28</sup> Nickel-alane complexes have been of particular interest given the wide breadth of catalytic ability by nickel and the successful usage of aluminum additives as cocatalysts (Figure 1b).<sup>29-31</sup> However, Al is coordinatively saturated in most examples, rendering their primary role to modulating the electron density at the transition metal.

We sought to access well-defined heterometallic species bearing hydrides bridged between transition metals and sterically accessible Lewis-acidic metals to amplify the activity of hydride moieties in catalysis. We hypothesized using a phosphine ligand with two amine and methoxy donors would be ideal as the dianionic nature of the two amine moieties would lead to an accessible Al-hydride, upon metalation, to be bridged by transition metals; the methoxy substituent would aid in the stabilization of traditionally labile Al centers. The soft Ni center was postulated to coordinate to the soft phosphine centers and the Al-based hydrides. Herein, we report a novel heterotrimetallic NiAl<sub>2</sub>(μ<sup>2</sup>-H)<sub>2</sub> complex bearing bridging hydrides that demonstrates significantly amplified reactivity towards the hydroboration of quinolines compared to the main group precursor. (Figure 1c).



**Figure 2.** a) Synthesis of **LAIH** b) Synthesis of heterotrimetallic complex **1**

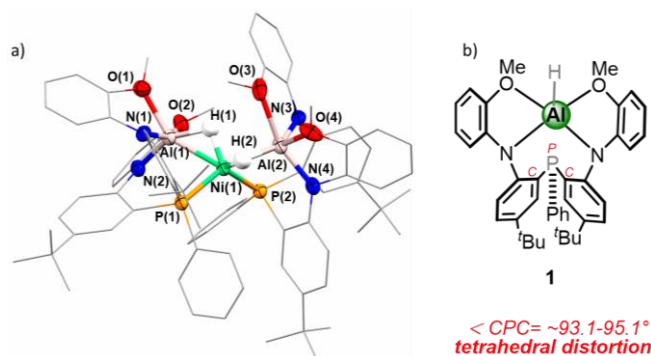
The ligand **LH<sub>2</sub>** can be prepared by a C-N cross coupling of 2-iodoanisole and 2-bromo 4-tertbutylaniline to generate **A**, followed by addition of two equivalents of *n*-butyllithium to deprotonate and undergo lithium halogen exchange, producing **B**. Species **B** is isolated and is then used to generate the phosphine **LH<sub>2</sub>** by addition to half of an equivalent of phenyldichlorophosphine. Ligand **LH<sub>2</sub>** is then metalated with Al by addition of alane-dimethylethylamine complex to form the aluminum monohydride **LAIH** (Figure 2a).

**LAIH** features a broad resonance at approximately 5.1 ppm,  $W_{1/2} = 134.4$  Hz, in the  $^1\text{H}$  NMR spectrum, consistent with previously characterized aluminum-hydrides. The lack of NH resonances suggests successful protonolysis of the amine donors. A shift in the chemical shift  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum is observed to -47.6 ppm, suggesting minimal interaction of the Al center to the phosphine center. Several aromatic resonances in both  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra experience a degree of broadening likely due to coupling with quadrupolar  $^{27}\text{Al}$  nucleus.

Metalation of **LAIH** with the secondary metal is then accomplished by addition of half of an equivalent of  $\text{Ni}(\text{COD})_2$ . The bright yellow solution is recrystallized to afford new heterotrimetallic complex **1** in moderate yield (Figure 2b). Heterotrimetallic complex (**LAIH**)<sub>2</sub>Ni was interrogated by NMR spectroscopy. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at room temperature features a broad singlet at 0.3 ppm with a  $W_{1/2}$  of approximately 160.1 Hz. The chemical shift indicates successful coordination of the phosphine center to a metal. The  $^1\text{H}$  NMR features two sets of resonances for tert-butyl, methoxy, and aromatic peaks. In addition, a broad apparent doublet is feature at -1.5 ppm; the chemical shift of the hydride resonance is consistent with a bridged Al-H-Ni moiety. These results indicate potential  $C_2$  symmetry. NMR studies at

lower temperatures result in the decoalescence of several resonances include the broad singlet in the room temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum which features two broad singlets at -2.10 and 2.12 ppm. Additionally, cooling the sample to -20 °C results in decoalescence of the hydride resonance in the  $^1\text{H}$  NMR spectrum. Heating the sample to 60 °C results in the sharpening of nearly all resonances supporting a pseudo  $C_2$  symmetry present in **1**.

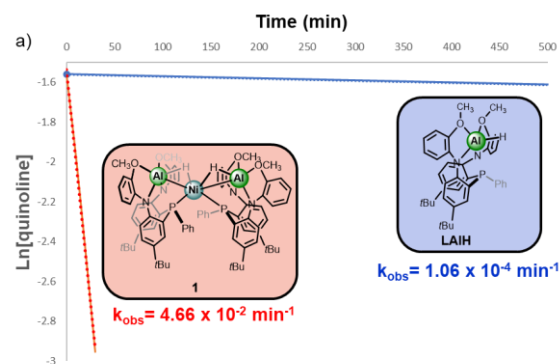
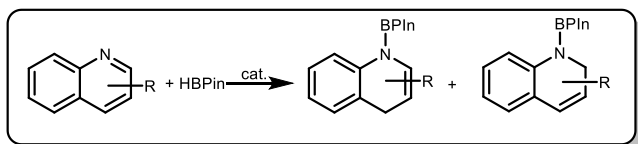
Single crystals of **1** were obtained by vapor diffusion of *n*-pentane into a saturated solution of **1** in benzene. Single-crystal X-ray diffraction studies confirm the site-specific binding of the Al centers to the N,O donor sites while the Ni center is bound to the softer phosphine donors of both **LAIH** moieties (Figure 3a). In addition, two hydride ligands were located on the electron difference map between Ni and Al that further support the 3-center bonding interactions between the Al-H-Ni. The Al center takes on a distorted square pyramidal geometry when considering the 4 N,O donors as well as the hydride. The Ni center takes on a distorted tetrahedral geometry consistent with known 18 electron Ni(0) species. Bond distances of the Ni-H are 1.57(3) and 1.60(3) Å. Intriguingly, the bond distances between Ni and Al are quite short, 2.3629(7) and 2.3658(7) Å, consistent with previously described Z-type donation in reported Ni-alane complexes, and is shorter than the sum of the covalent radii.<sup>29</sup>



**Figure 3.** a) Solid-state structure of **1** b) Distortion from tetrahedral geometry upon coordination of Al in **1**

A significant distortion is observed in both of the CPC bond angles of the *ipso* carbons on the substituted aryl groups (Figure 3b). The angles are measured at 93.10(9)° and 95.53(9)° which deviate from the expected angles for tetrahedral centers. The observed distortion is likely the result of coordination to the Al center which may force the aryl groups to compress closer together. The *ipso-ipso* CPC bond angles when including the unsubstituted phenyl group range from 102.35(9)° to 105.26(9)°.

We sought to explore the reactivity of complex **1** and evaluate the reactive nature of the hydride moieties in **1** in comparison to **LAIH**. Main group metal hydrides have been implicated as catalysts in hydroboration and hydrosilylation of ketones, and *N*-heterocycles. Examples featuring dearomatization of *N*-heterocycles by Al complexes are limited, and most demonstrate reactivity with Al(I) complexes rather than Al(III).<sup>32</sup> Correspondingly, when using catalytic quantities of **LAIH**, lackluster activity in the hydroboration of quinoline is observed.



b)

Entry	Substrate	Cat.	Temp (°C)	Time	Yield/Ratio
1		<b>1</b>	60	1 h	95 % (2:1)
2		<b>LAIH</b>	60	80 h	26 % (3:1)
3		<b>1</b>	60	14 h	94 % (1:5)
4		<b>LAIH</b>	60	14 h	7 %*
5		<b>1</b>	80	72 h	73 % (1:1)
6		<b>LAIH</b>	80	72 h	n.o
7**		<b>1</b>	80	4 d	10 % (4:1)
8		<b>LAIH</b>	80	4 d	n.o

**Figure 4.** a) The natural logarithm of concentration of quinoline vs time using 5 mol% catalyst **1** and 10% **LAIH** at 60°C. b) Substrate scope of hydroboration of quinolines by **1** and **LAIH**. Conditions include 5 mol% **1** or 10 mol% **LAIH** with one equivalent of quinoline and three equivalents of H-Bpin. NMR yield is calculated based on <sup>1</sup>H NMR integration and normalized to hexamethyldisioxane internal standard.\*conversion to 1,2 isomer too low to accurately describe ratio \*\* 20 mol % complex **1**

Gratifyingly, when using complex **1** as a catalyst for the hydroboration of quinoline, we observe substantially amplified activity with identical hydride concentrations (5% **1** vs 10% **LAIH**). After 1 hour at 60 °C we observe ~95% conversion of quinoline to the 1,4 and 1,2 isomers of the dearomatized heterocycle in a 2:1 ratio, respectively. Though complex **1** incorporates a redox-active metal, the mechanisms for hydroboration of heterocycles, including an example

bearing Ni,<sup>23</sup> do not involve a change of metal oxidation state, thus, the reactivity of the metal-hydride moieties are evaluated accordingly.

To gain more thorough comparative data, kinetics experiments were conducted to monitor the consumption of quinoline under with catalyst **1** and separately, with complex **LAIH**. Nearly complete consumption of quinoline over the course of 1 hour at 60 °C with 5 mol% of **1**, is observed. Under the same conditions, with double the mol % of catalyst loading of **LAIH** (to account for double the hydrides in **1**), only approximately 26% of quinoline is consumed over the course of 80 hours. The natural logarithm of concentration of quinoline vs time shows linear behavior and  $k_{\text{obs}}$  of  $4.66 \times 10^{-2} \text{ min}^{-1}$  for **1** and  $1.06 \times 10^{-4} \text{ min}^{-1}$  for **LAIH** were determined (Figure S7-2 and Figure S7-4, respectively). These results demonstrate a drastic enhancement in activity, approximately 400 times (Figure 4a).

Intrigued by the amplified catalytic ability of **1** and by the ability to individually interrogate each complex, substituted quinolines were examined including sterically encumbered alkyl and aryl substituted quinolines at the 2-, and 4- position. With exception to the 4-methyl quinoline, **LAIH** was completely inactive in the production of hydroborated heterocycles of the substituted quinolines. Complex **1** readily converted 4-methyl quinoline to the hydroborated 1,4 and 1,2 isomers over the course of 14 hours, in a ratio of 1:5, respectively. The favoring of the 1,2 isomer is likely related to the presence of the alkyl at the 4-position. Studies delineating the production of each individual isomer were hampered by the observation of an isomerization of the 1,2 isomer to the thermodynamically more favorable 1,4 isomer. Given the facile hydroboration of the examined quinolines by **1**, the sterically encumbering 2-methyl quinoline, which was synthesized only once in 13% yield over the course of 9 days in a previous report,<sup>19</sup> was probed. The hydroboration of 2-methyl quinoline displayed hydroboration in good yield (73%) over the course of 72 hours (Figure 4b entry 5). The 1,4 and 1,2 isomers were produced in a ratio of approximately 1:1. The previously undescribed hydroboration of 2-phenyl quinoline was examined and over 4 days at 80 °C, we observe only limited conversion to the 1,2 and 1,4 isomer (10%) (Figure 4b entry 7). The higher ratio in the formation of the 1,2 isomer from 2-methyl quinoline in comparison to quinoline (Figure 4b entry 1, 5, 7) can be ascribed to a potentially sluggish isomerization step to the 1,4 isomer; however, for 2-phenylquinoline, the 1,3 hydride transfer to access the 1,2 isomer may be less accessible.

The dramatically varied reactivity in **1** vs **LAIH** is intriguing. Indeed, multimetallic complexes bearing bridging hydrides ligands have proven capable in facilitating impressive molecular transformations in stoichiometric fashion,<sup>33-35</sup> yet bridging hydrides between transition metals and Lewis Acids are purported to exhibit less nucleophilicity rendering them less active in hydrogenation activity. However, studies have suggested that a 3-center-4 electron bond involving a transition metal, hydride, and anionic Lewis-acid result in markedly increased hydride nucleophilicity in comparison to terminal hydrides.<sup>36</sup> Complex **1** features Al centers that bear a  $\sigma$ -accepting role to Ni, generating a more electron-rich Al center compared to **LAIH** and a relatively electron-deficient Ni(0) center; however, further studies are needed to differentiate between a Ni(II) hydride with an alane/alumanyl assignment, versus alanes and Ni(0) designation. Bridging hydrides between transition metals and borane/boryl centers are established;<sup>37-40</sup> however, complex **1** is a rare experimental finding observing 3-center bonding of a hydride between Ni and Al.<sup>41-43</sup>

In summary, we have reported a novel, well-defined heterotrimetallic Ni-Al<sub>2</sub> complex bearing bridging hydride ligands. The crystal structure demonstrates close interactions between the Al and Ni centers. Complex **1** is a rare report of 3-center bonding between Al-H-Ni and is a result of a new strategy to produce sterically accessible Lewis-acidic centers to rationally amplify reactivity of metal-hydrides in catalysis. Previous studies where a secondary metal-additive directly affects reactivity are generally limited to the addition of redox-inactive metal cations to complexes featuring redox-active metals,<sup>44-45</sup> rather than the inverse reported here. The resultant bridged hydride moieties in **1** led to a sharp enhancement in the catalytic hydroboration of quinoline and notoriously challenging substituted quinolines. Mechanistic studies to elucidate the nature of the cooperative transformation and electronic structure studies on this novel heterotrimetallic species, are underway.

## ASSOCIATED CONTENT

### Supporting Information

The supporting information contains <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} spectra for all complexes, kinetics and scope experiments along with crystallographic information. CCDC 2231823 contains the supplementary crystallographic data for this paper.

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## CONFLICTS OF INTEREST

There are no conflicts to declare.

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