Aluminum−Ligand Cooperative N−H Bond Activation and an Example of Dehydrogenative Coupling

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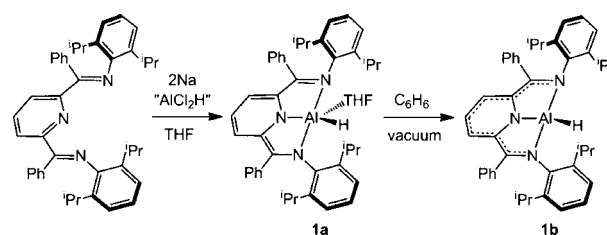
Ⓢ *Supporting Information*

ABSTRACT: Activation of N−H bonds by a molecular aluminum complex via metal−ligand cooperation is described. ($^{Ph}I_2P^{2-}$)AlH (**1b**), in which $^{Ph}I_2P^{2-}$ is a tridentate bis(imino)pyridine ligand, reacts with anilines to give the N−H-activated products ($^{Ph}HI_2P^-$)AlH-(NHAr) (**2**). When heated, **2** releases H_2 and affords ($^{Ph}I_2P^-$)Al(NHAr) (**3**). Complex **1b** catalyzes the dehydrogenative coupling of benzylamine to afford H_2, NH_3, and *N*-(phenylmethylene)benzenemethanamine.

To develop sustainable catalytic transformations using abundant metals such as aluminum, an understanding of bond activation reactions is a necessary first step. Introducing functionality into unactivated bonds continues to be of significant interest, and in particular, the activation of N−H bonds often relies on the oxidative addition of N−H bonds to a transition-metal center.[1] However, the activation of N−H bonds via oxidative addition to transition metals can be impeded by the tendency of the Lewis basic nitrogen atom to bind open coordination sites.[2] In contrast, heterolytic activation of N−H bonds is more likely to remain feasible even when amine coordination occurs as a first step.[2]

A heterolytic reaction pathway has led to limited but fruitful examples of N−H activation in both transition-metal and main-group chemistry. Milstein and co-workers reported the heterolytic activation of amines by Ru pincer complexes via a metal−ligand cooperative pathway.[3] Subsequently the complexes were shown to effect catalytic amine dehydrogenation.[4] Heterolytic activation of N−H bonds has also been accomplished via main-group frustrated Lewis pairs to achieve catalytic hydrogenation of unsaturated systems.[5] To date, main-group-mediated reactions have afforded stoichiometric N−H activation of aniline and ammonia[6] and both stoichiometric and catalytic dehydrogenation of amine boranes.[7] Heterolytic activation of alkynes has been observed at gallium.[8]

We previously explored the redox chemistry of iminopyridine complexes of aluminum.[9] Herein we report aluminum complexes of a tridentate bis(imino)pyridine ligand that is henceforth denoted by $^{Ph}I_2P$ (see Scheme 1 for its structure). We isolated the tetrahydrofuran (THF)-adduct and base-free aluminum hydride complexes ($^{Ph}I_2P^{2-}$)AlH(THF) (**1a**) and ($^{Ph}I_2P^{2-}$)AlH (**1b**) and found that **1b** effects activation of the N−H bonds in anilines via a metal−ligand cooperative pathway. These reactions afford ($^{Ph}HI_2P^-$)AlH(NHAr) [Ar = 2,6-diisopropylphenyl (Dipp) (**2a**), Ph (**2b**)]. When these complexes are heated, they release H_2, forming four-coordinate

Scheme 1

($^{Ph}I_2P^{2-}$)Al(NHAr) [Ar = Dipp (**3a**), Ph (**3b**)]. The syntheses of the aluminum hydride complexes followed a procedure adapted from our previous work on the related iminopyridine ligand system (Scheme 1).[9] The $^{Ph}I_2P$ ligand and 2 equiv of sodium metal were stirred together in THF for 24 h, during which time the initial green solution became dark purple. After addition of an "AlCl₂H" solution[10] and subsequent workup, **1a** was isolated as a burgundy powder in 71% yield. Complex **1a** was found to be diamagnetic, and the proton NMR spectrum was informative (Figure S1 in the Supporting Information). A broad feature at 4.60 ppm corresponded to the Al−H proton, and the resonances for the THF ligand were observed as broad singlets at 3.59 and 1.37 ppm. The IR spectrum displayed an Al−H stretching band at 1966 cm^{-1} (Figure S2 and Table S1), which is within the range for other known terminal aluminum hydride complexes.[11]

Single crystals of **1a** were grown via slow diffusion of pentane into a concentrated THF solution of **1a**, and the structure was determined by single-crystal X-ray diffraction (Figure 1). The geometry at the Al center is very close to square-pyramidal,
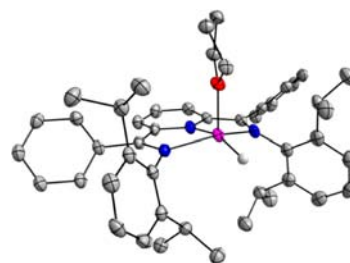

Figure 1. Solid-state structure of ($^{Ph}I_2P^{2-}$)AlH(THF) (**1a**). Pink, red, blue, gray, and white ellipsoids represent Al, O, N, C, and H atoms, respectively. The thermal ellipsoids have been set at 50% probability, and H atoms (except hydride) have been omitted.

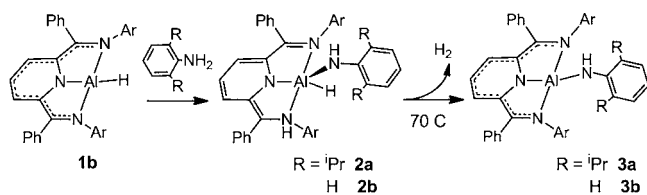with $\tau = 0.117$.[12] The bond lengths in **1a** are consistent with a twice-reduced oxidation state of the ligand, where the two-electron reduction event is formally localized at the pyridine nitrogen and one of the imine nitrogens (Tables S2 and S3).[9,13] Thus, the ligand is asymmetric with one formally imine N-donor [Al−N_{im} = 2.077(2) Å], an anionic pyridine [Al−N_{py} = 1.851(2) Å], and one anionic amido N-donor [Al−N_{am} = 1.954(2) Å]. The C−C bond distances in the pyridine ring alternate between long [1.405(3) Å] and short [1.380(3) Å], consistent with a loss of aromaticity. These results are also in agreement with the diamagnetism observed by NMR spectroscopy.

Extraction of **1a** into benzene followed by evaporation of the solvent in vacuo led to removal of THF from the Al coordination sphere and the formation of the tan-colored four-coordinate complex **1b**, as identified by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum indicated that the oxidation state of the ligand remained unchanged at 2−, that the Al−hydride resonance had shifted downfield to 4.74 ppm, and that the THF ligand resonances were no longer apparent (Figure S3). The IR absorption band for Al−H also shifted by 185 cm^{-1} to 1781 cm^{-1} (Figure S2). We could not obtain single crystals of **1b**, but all of the data we did acquire, including the results of combustion analysis, were consistent with the assignment of **1b** as four-coordinate ($^{Ph}I_2P^{2-}$)AlH. The electronic structure of the $^{Ph}I_2P^{2-}$ ligand, according to the ^{1}H NMR spectrum, is consistent with that of **3a** (vide infra). When **1b** was dissolved in THF, **1a** was observed in quantitative NMR yield.

Addition of H_2NDipp to a tan benzene solution of **1b** led to the immediate formation of a dark-blue solution (Scheme 2).

Scheme 2

X-ray diffraction analysis performed on a single crystal grown from the product revealed it to be ($^{Ph}HI_2P^-$)AlH(NHDipp) (**2a**), in which the N−H bond of H_2NDipp was added across the aluminum−amido bond in **1b** (Figure 2 left). To probe whether **2a** might have been the result of the large steric
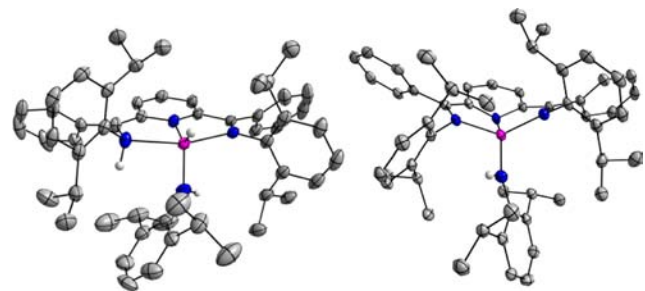
demand of the NHDipp$^-$ group, the reaction of **1b** with 1 equiv of aniline was investigated, and this led to formation of an analogous dark-blue product identified as ($^{Ph}HI_2P^-$)AlH-(NHPh) (**2b**) by ^{1}H NMR spectroscopy. In both **2a** and **2b**, the amido nitrogen atom of $^{Ph}I_2P^{2-}$ is protonated and the resulting anilido ligand is coordinated to the Al center.

Complexes **2a** and **2b** were found to be diamagnetic, and their ^{1}H NMR spectra clearly showed that protonation of the amido nitrogen in $^{Ph}I_2P^{2-}$ induced a higher degree of asymmetry to the ligand than was observed in **1a** or **1b** (Figures S4 and S5). For instance, all of the protons on the pyridine ring became inequivalent. The single-crystal X-ray structures for **2a** and **2b** confirmed the higher degree of asymmetry of the protonated $^{Ph}HI_2P^-$ ligand in comparison with $^{Ph}I_2P^{2-}$ in **1a**. For example, the alternating single and double bonds in the dearomatized pyridine ring of $^{Ph}HI_2P^-$ were even more distinct than they were in **1a** (Tables S2 and S3).

When either **2a** or **2b** was heated at 70 °C for several hours in toluene, 1 equiv of H_2 was released, as measured by GC-TCD analysis. The formation of the corresponding new red-brown four-coordinate complexes ($^{Ph}I_2P^{2-}$)Al(NHAr) [Ar = Dipp (**3a**), Ph (**3b**)] was concomitantly observed. Both **3a** and **3b** are diamagnetic, and their proton NMR spectra were similar to that of four-coordinate **1b** (Figures S6 and S7). To probe the mechanism of formation of **2b** and its conversion to **3b**, aniline-d_7 was employed. The ^{1}H NMR spectrum of **2b**-d_7 showed diminished intensity for the two N−H resonances and no change in the Al−H resonance (Figure S8). When **2b**-d_7 was heated, HD gas was observed (Figure S9), and the spectrum of **3b**-d_6 showed a decrease in the intensity of the N−H resonance (Figure S10). These results are in accord with Scheme 2.

Single crystals of **3a** were grown by chilling a concentrated hexane solution of **3a** at −25 °C for 3 days, and the X-ray crystal structure was determined (Figure 2 right). Complex **3a** is four-coordinate and best described as distorted tetrahedral, with a tetrahedrality of 51.6°.[14] Notably, N_{py} no longer lies in plane with the rest of $^{Ph}I_2P^{2-}$: the N_{im}−C_{im}−$C_{py(o)}$−N_{py} torsion angles are 5.2° and 8.1°, as compared to 1.5° and 1.87° in **1a**. This deviation presumably stems from the preference of the Al center for a tetrahedral geometry, which conflicts with the preference of PhI_2P^{2-} to be planar. The displacement of N_{py} from the plane removes it from the conjugated π system of the rest of the ligand, affording a symmetric conjugated system involving the N_{im}, C_{im}, and C_{py} atoms (Scheme 2 and Figure 2 right). The two C_{im}−N_{im} bond lengths are very similar at 1.374(3) and 1.370(3) Å, and this distance falls between that commonly observed for true C_{im}−N_{im} single and double bonds, as in the asymmetric closed-shell form of $^{Ph}I_2P^{2-}$. The two C_{im}−$C_{py(o)}$ bond lengths are also very similar at 1.424(3) and 1.426(3) Å, and the C−C bonds in the pyridine ring [1.394(3), 1.397(3), 1.399(3), and 1.383(3) Å] are equivalent and longer than the bonds in neutral pyridine. The symmetry of this geometric structure suggests an electronic structure similar to the biradical triplet state commonly observed with bis(imino)-pyridine ligands, in which a radical resides on each of the C_{im} atoms.[13] However, the bond lengths and angles in **3a** are more consistent with a structure in which these radicals are somewhat delocalized and, as indicated by NMR spectroscopy, anti-ferromagnetically coupled. Antiferromagnetic coupling in a two-electron-reduced bis(imino)pyridine ligand was observed previously in a nickel(II) complex.[15] Notably, in that case the

Figure 2. Solid-state structures of ($^{Ph}HI_2P^-$)AlH(NHDipp) (**2a**) and ($^{Ph}I_2P^{2-}$)Al(NHDipp) (**3a**). Pink, blue, gray, and white ellipsoids represent Al, N, C, and H atoms, respectively. The thermal ellipsoids have been set at 50% probability, and H atoms (except the hydride and N-bound protons) have been omitted.

I_2P ligand was also distorted from planarity with $N_{im}-C_{im}-C_{py(o)}-N_{py}$ torsion angles of 11.87° and 11.45°.

The ability of **1b** to activate N−H bonds via a metal−ligand cooperative mechanism prompted us to investigate its potential as an amine dehydrogenation catalyst. Benzylamine and 20 mol % **1b** was heated at reflux in toluene at 70 °C for 24 h, and the formation of *N*-(phenylmethylene)benzenemethanamine was observed with 75% conversion and 3.6 turnovers, as measured by GC−MS (Figure S11).[16] The formation of stoichiometric H_2 and NH_3 was observed by GC-TCD (Figure S12).

In conclusion, we have shown that a bis(imino)pyridine complex of aluminum activates N−H bonds via a metal−ligand cooperative mechanism and that this N−H bond activation event can initiate amine dehydrogenation catalysis and convert benzylamine into the homocoupled imine. Efforts to expand the scope of the bond activation and catalysis observed here are underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Preparation of complexes; X-ray data for **1a**, **2a**, and **3a**; CIF files; IR and NMR spectra; and GC-TCD and GC−MS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(16) This is comparable to turnover numbers achieved using main-group amine borane dehydrogenation catalysts.[7]