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Dehydrogenation of iron amido-borane and resaturation of the imino-borane complex⁺

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We report on the first isolation and structural characterization of an iron phosphinoimino-borane complex $Cp*Fe(\eta^2-H_2B=NC_6H_4PPh_2)$ by dehydrogenation of iron amido-borane precursor $Cp*Fe(\eta^1-H_3B-NHC_6H_4PPh_2)$. Significantly, regeneration of the amido-borane complex has been realized by protonation of the iron(II) imino-borane to the amino-borane intermediate $[Cp*Fe(\eta^2-H_2B-NHC_6H_4PPh_2)]^+$ followed by hydride transfer. These new iron species are efficient catalysts for 1,2-selective transfer hydrogenation of quinolines with ammonia borane.

Because of relevance to H₂ storage¹⁻¹⁰ and hydrogenation catalysis,11-15 metal amine-borane complexes16-18 and their dehydrogenated forms, such as amino-boranes²⁰⁻²² and iminoboranes⁴ are arising as a significant family in organometallic chemistry. In transition metal-catalyzed dehydrocoupling of amine-boranes and related transfer hydrogenations, the interactions between the metal and the borane fragment are essendehydrogenation tial to and the consequent transformations.16-20 Specifically, amino-borane complexes containing a M-H₂B=NR₂ moiety are the primary dehydrogenated species and are often identified as a resting point in the catalysis (Scheme 1a).20-22 Management of reversible dehydrogenation-regeneration reactions on a M-BH₂=NR₂ platform could provide a strategy with which to design efficient catalysts capable of operating sustainable syntheses.

Wider exploration of metal amino-borane chemistry is challenging since $M-H_2B$ = NH_2 species are very reactive toward H_2 release. In 2010, Aldridge *et al.* reported the isolation of [(IMes)₂Rh(H)₂(η^2 -H₂B= NR_2)] and [(IMes)₂Ir(H)₂(η^2 -H₂B= NR_2)] from the metal-catalyzed dehydrogenation of R_2 - $HN \cdot BH_3$.^{21*a*} At the same time, Alcaraz and Sabo-Etienne reported the preparation of (PCy₃)₂Ru(H)₂(η^2 -H₂B= NH_nMe_{2-n}) (n = 0-2) complexes^{22*a*} by the dehydrogenation of amine-boranes with the corresponding ruthenium precursors. Subsequently, a straightforward synthesis of Ru, Rh, and Ir amino-borane complexes by reaction of H_2B = NR_2 (R = iPr or Cy) with the bis(hydrogen) complexes of $M(H)_2(\eta^2-H_2)_2(PCy_3)_2$ or $[CpRu(PR_3)_2]^+$ fragments was developed.^{21b,22b} Turculet *et al.* have shown that the ruthenium-alkoxide complex is able to activate H₃B·NHR₂ producing hydrido ruthenium complex.²³ Notably, Weller and Macgregor found that dehydrocoupling of ammonia-borane by $[Ph_2P(CH_2)_3PPh_2Rh(\eta^6-C_6H_5F)]$ affords a μ -amino-borane bimetallic Rh complex, in which the simplest H₂B=NH₂ moiety is trapped on a rhodium dimer.^{20a}

Although iron-catalyzed dehydrocoupling of amine-boranes has attracted great interest,^{24–29} iron amine-borane complexes, their dehydrogenated derivatives, and especially the catalysis relevant to organic synthesis are largely unexplored. Recently, Kirchner *et al.* reported a pincer-type iron complex generated by protonation of the borohydride iron complex (PNP)Fe(H)(η^2 -BH₄) with ammonium salts.³⁰ Inspired by earlier research on M– H₂B=NR₂ chemistry, we intended to establish the reversible conversions of amino-borane complexes and their dehydrogenated forms in a synthetic piano-stool iron system. Herein, we report dehydrogenation of iron amido-borane complex Cp*Fe(η^1 -H₃B–NHC₆H₄PPh₂) (2) (Cp* = Me₅C₅⁻) to the iminoborane complex Cp*Fe(η^2 -H₂B=NC₆H₄PPh₂) (3), and

a) Fundamental step involved in catalytic amine-borane dehydrogenation

$$L_nM + H_3B\cdot NHR_2 \xrightarrow{-H_2} L_nM \overset{H}{\underset{H}{\overset{B==}}} B \overset{R}{\underset{R}{\overset{R}{\overset{H}}}}$$

b) Hypothetical dehydrogenation-regeneration of iron amido-borane



Scheme 1 Schematic representation of metal-based amine-borane dehydrogenation.

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resaturation of the imino-borane by stepwise protonation and hydride transfer (Scheme 1b). This new class of iron species is capable of catalyzing 1,2-selective transfer hydrogenation of quinolines with $H_3N \cdot BH_3$.

To synthesize the iron amido-borane complex, a new monomer, the iron tetrahydridoborate precursor Cp*Fe(η^2 -BH₄)(NCMe) (1), was prepared *in situ* by the reaction of [Cp*Fe(NCMe)₃]PF₆ with Bu₄NBH₄ in acetonitrile at room temperature for 5 min. Such ferrous borohydrides have been documented only rarely,³¹ since they are prone to form polynuclear iron borate clusters.^{32,33} The ¹¹B NMR spectrum of the reaction solution shows a quintet at δ 15.4 ($J_{BH} = 88$ Hz) for the BH₄⁻ ligand of 1, and this stands in contrast to the signal at δ -32.0 observed for Bu₄NBH₄. Upon storing the reaction mixture at -30 °C overnight, single crystals suitable for X-ray diffraction were obtained. Crystallographic analysis confirmed the structure of 1 as a piano-stool iron tetrahydridoborate compound (ESI, Fig. S1⁺).

Addition of phosphinoamine ligand 1,2-Ph₂PC₆H₄NH₂ to a solution of 1 in acetonitrile caused an instantaneous color change from deep blue to dark brown (Scheme 2). ESI-MS studies indicated the production of the iron amido-borane compound (2) with m/z = 481.1793 (calcd m/z = 481.1770), which was isolated in 87% yield. NMR spectra showed a boron resonance at δ -17.5, and a phosphorus resonance at δ 85.9. The ¹H NMR spectrum exhibits a characteristic hydride signal at δ –13.98, which is assigned to the bridging hydride Fe–*H*–B. Owing to exchange between the hydrogen atoms at the boron,³⁴ the terminal B-H resonances in the ¹H NMR spectrum are very broad and are obscured by the distinct Cp* signals. To assign the B-H hydride signals, the deuterated compound Cp*Fe(D₃B-NHC₆H₄PPh₂) (d-2) was synthesized from Cp*Fe(BD₄)(NCMe). In addition to the Fe–D–B signal at δ –13.98, the ²H NMR spectrum of *d*-2 displayed discrete peaks at δ 2.23 and 0.19 for the terminal B-D hydrides (Fig. 1).

When a C₆H₆ solution of 2 was held at 50 °C for 6 h the dehydrogenated imino-borane compound (3) was produced in 92% yield. The ESI-MS spectrum of 3 has a strong peak at m/z 479.1626 (calcd m/z = 479.1637) which can be compared to the peak at m/z = 481.1793 for 2. The isotopic distributions match well with the calculated values (see Fig. S3†). GC analysis shows that the reaction produced H₂ nearly quantitatively (see Fig. S4†). In solution, the ³¹P NMR spectrum of 3 displays a sharp signal at δ 71.9, in contrast to the peak at δ 85.9 for 2. The ¹¹B resonance shifts significantly, from δ –17.5 for 2 to δ 42.7 for 3 (Fig. S16†), and is particularly diagnostic of a three-coordinate boron atom.^{21,35} This result indicates the B=N



Scheme 2 Synthetic route to imino-borane complex.



double bond character in the dehydrogenated form of the amido-borane complex. In the ¹H NMR spectrum, the Fe–*H*–B signal was observed at δ –17.91 with the integral of 2H, and no characteristic signal for a terminal B–*H* hydride was found. To confirm the formation of an imino-borane compound, the hydrogen decoupling was also carried out with compound *d*-2 and monitored by ²H NMR spectra. Only a deuterium signal was observed at δ –17.91 for Fe–*D*–B, indicating the formation of *d*-3 (Fig. 1). When the dehydrogenation was conducted in a J-Young tube in C₆D₆, a characteristic triplet corresponding to HD appeared at δ 4.43 ($J_{\rm HD}$ = 45 Hz) in the ¹H NMR spectrum (Fig. S18†).³⁶

The structures of **2** and **3** were verified by X-ray crystallographic analysis (Fig. 2). Consistent with NMR spectroscopic analysis, the BH₃ moiety in **2** is stabilized by one of the B-H bonds binding at the Fe–NH unit to form an Fe–H–B–N fourmembered metallacycle. This metal–ligand cooperative binding mode increased the B–H bond length in the bridging B– H(1) bond to 1.362 Å *vs.* 1.129 Å and 1.121 Å for the two terminal B–H bonds. The B–N bond length of 1.545(3) Å in **2** is slightly shorter than that in H₃B·NH₃ ($d_{B-N} = 1.58(2)$ Å).³⁷ Crystallographic analysis of **3** confirmed an imino-borane complex with a Cp*Fe(η^2 -H₂B=NC₆H₄PPh₂) framework. After dehydrogenation of **2**, striking structural changes were observed. The N atom



Fig. 2 Solid-sate structure (50% probability thermal ellipsoids) of (a) complex 2 and (b) 3. For clarity, hydrogen atoms of Cp* and phenyl rings are omitted.

has been become detached from Fe, while the BH_2 fragment acts as a bis(σ -borane) ligand coordinated to the metal center.^{21–23} The B–N bond distance of 1.455(5) Å in 3 is shorter by 0.09 Å than that in 2, and is close to that reported for the cyclic trimer borazine (1.4355(21) Å).³⁸ Combined with the NMR results, the B–N bond length in 3 suggests some double bond character.^{21,22} As the imino-borane fragment is tethered in the coordination sphere, the boron center adopts a quasitetrahedral geometry, and the B–N bond appears to be partially sp³ hybridized. Dehydrogenation of the amido-borane complex also caused the decrease of the Fe…B distances from 2.223(3) Å to 2.026(4) Å which is shorter than the sum of the covalent radii of Fe and B atom (2.16 Å), indicating that the borane and the metal are bonded.

Notably, the amido-borane compound 2 can be regenerated by stepwise protonation of 3 and transfer of a hydride (Scheme 3). Complex 3 reacts readily with $H(Et_2O)_2BAr_4^F$ in C_6H_5F . The reaction solution was analyzed by ESI-MS spectroscopy, which showed an ionic peak at m/z = 480.1726 (calcd m/z = 480.1715), suggesting the formation of $[3H]^+$. Alternatively, the reaction of complex 2 with $H(Et_2O)_2BAr_4^F$ unambiguously provides $[3H]^+$ and produces H₂. X-ray crystallographic analysis reveals that the resulting cationic complex [3H]⁺ exhibits a similar framework to its imino-borane precursor (3). The BH₂ moiety retains a binding mode of the $bis(\sigma-BH_2)$ fashion (Fig. 3). In contrast, the B–N distance in $[3H]^+$ (1.586(6) Å) is extended by 0.13 Å and the $[3H]^+$ framework becomes much less compact than that of 3. Probably due to the fluxional structure of the seven-membered Fe-P-C-C-N-B(H) ring, the solution of $[3H][BAr_4^F]$ gives broad ¹H NMR resonances even at -60 °C. The phosphorus resonance arose at δ 72.0 as a singlet when the solution sample was cooled to -40 °C (Fig. S20 and S21[†]).

In $[3H]^+$, the boron is coordinatively unsaturated, as manifested by its interaction with a σ -donor. For instance, treatment of 2 with $[\text{HPPh}_3][\text{BAr}_4^{\text{F}}]$ ($pK_a^{\text{MeCN}} = 7.6$)³⁹ provides a Ph₃Pstabilized borane complex, $[3H(\text{PPh}_3)]^+$ (m/z = 742.2620, calcd m/z = 742.2626). The ¹H NMR spectrum of $[3H(\text{PPh}_3)]^+$ exhibits

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Scheme 3 Conversions of iron imino-borane, amino-borane and amido-borane complexes.



Fig. 3 Solid-state structures of (a) complex $[\mathbf{3H}]^+$ and (b) $[\mathbf{3H}(\text{PPh}_3)]^+$. For clarity, counterion $[\text{BAr}_4^{\text{F}}]^-$, hydrogen atoms of Cp* and phenyl rings have been omitted.

an N*H* resonance at δ 4.68, suggesting that protonation occurred at the N site. The distinctive upfield hydride signal for Fe–*H*–B is observed at δ –15.58. In the ³¹P NMR spectrum, two phosphorus signals at δ 78.90 and –1.26 correspond to the Fe–*P* and the B–*P* resonances, respectively. The ¹¹B signal at δ –13.72 indicates a tetracoordinated boron, which is further confirmed by crystallographic analysis of [**3H**(PPh₃)]⁺ (Fig. 3). In the solid-sate structure, a Ph₃P molecule is bound to the B center ($d_{\rm B-P}$ = 1.982(4) Å), leading to the formation of a new Fe–H–B–N fourmembered metallacycle. As a amido-borane complex, [**3H**(PPh₃)]⁺ has a B–N bond length of 1.527(5) Å, somewhat shorter than 1.545(3) Å in **2**.

After attaching a proton at the N atom, we subsequently explored restoration of the original borane moiety. Treatment of freshly prepared [3H][BAr4] in fluorobenzene with catecholborane-NEt₃ adduct ($\delta_{\rm B} = 10.56, J_{\rm HB} = 142.4 \text{ Hz}$)⁴⁰ results in the regeneration of 2, as evidenced by the NMR spectra (Fig. S29 and S30[†]). The ¹H NMR spectrum of the reaction mixture displays a characteristic hydride signal at -13.97 ppm, indicating the recovery of the iron amido-borane complex. On the other side, concomitant formation of the borenium ion ($\delta_{\rm B} =$ 13.86) was also observed in the ¹¹B NMR spectrum, which agrees with the hydride transfer from the organohydride reagent to $[3H]^+$. It was interesting that the ion $[3H]^+$ is stable towards 5,6-dihydrophenanthridine and Hantszch ester. These results indicate that the hydride-donating ability $(\Delta G_{\rm H}^{-})$ of 2 is in the range of 55–59 kcal mol⁻¹.⁴¹ The reactive nature of the hydride in 2 was demonstrated by the reaction with [HPPh₃] $[BAr_4^F]$, which produces $[3H(PPh_3)]^+$ and releases H₂ (Scheme 3).

$$\xrightarrow{0}_{V \to V} \xrightarrow{1 \mod \% 3}_{H_3 N \cdot BH_3} \xrightarrow{0}_{V \to V} \xrightarrow{H}_{H} \xrightarrow{H} (1)$$

$$4 \qquad 5, 87\% \text{ yield}$$

The metal amine-borane complexes and their dehydrogenated derivatives are implicated throughout the catalytic cycle of amine-borane dehydrogenation. We found both the iron complexes 2 and 3 are efficient catalysts for H₃N·BH₃ dehydrogenation at room temperature. In the presence of 1 mol% catalyst, a THF solution of $H_3N \cdot BH_3$ (1.0 mmol) generates about 2.2 equivalent of H₂ within 6 h based on GC quantification (Fig. S33[†]). More importantly, such catalytic dehydrocoupling systems allow for selective transfer hydrogenation of quinolines to dihydroquinolines, which are valuable synthons leading to many bio-active compounds.42 For instance, addition of methyl-6-quinolineacetate (4) to the catalytic system containing one equiv. of H₃N·BH₃ and 1 mol% of 3 gave 1,2dihydro-methyl-6-quinolineacetate (5) in excellent yield within 6 h (eqn (1)). The outcome of this reaction was unaffected by switching the catalyst from 3 to 2, or by use of excess reducing agent or by an increase in the reaction temperature (Table S1⁺).

Conclusions

By tethering the N-B unit within the coordination sphere, we have demonstrated an example of imino-borane iron(II) dehydrogenation complex isolated from of its phosphinoamido-borane precursor, and have realized the regeneration of an Fe-H₃B-N(H)Ar fragment by submitting the dehydrogenated imino-borane to sequential protonation and hydride transfer reactions. Based on the dehydrogenation of ammonia-borane catalyzed by the two iron species, the catalytic reduction of quinoline to 1,2-dihydroquinoline was established. This work provides a new perspective for the studies of reversible conversions between amine-borane complexes and the dehydrogenated forms, and exploration of iron-based catalysis for important organic transformations.

Conflicts of interest

There are no conflicts to declare.

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