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Because of relevance to H_2 storage^{1–10} and hydrogenation catalysis,^{11–15} metal amine-borane complexes^{16–18} and their dehydrogenated forms, such as amino-boranes^{20–22} and imino-boranes⁴ 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 essential to dehydrogenation and the consequent transformations.^{16–20} Specifically, amino-borane complexes containing a $M-H_2B=NR_2$ 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 $M-BH_2=NR_2$ platform could provide a strategy with which to design efficient catalysts capable of operating sustainable syntheses.

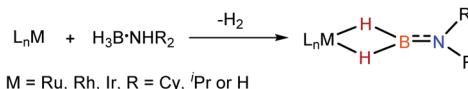
Wider exploration of metal amino-borane chemistry is challenging since $M-H_2B=NH_2$ species are very reactive toward H_2 release. In 2010, Aldridge *et al.* reported the isolation of $[(IMes)_2Rh(H)_2(\eta^2-H_2B=NR_2)]$ and $[(IMes)_2Ir(H)_2(\eta^2-H_2B=NR_2)]$ from the metal-catalyzed dehydrogenation of $R_2-HN\cdot BH_3$.^{21a} At the same time, Alcaraz and Sabo-Etienne reported the preparation of $(PCy_3)_2Ru(H)_2(\eta^2-H_2B=NH_nMe_{2-n})$ ($n = 0–2$) complexes^{22a} 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

$Cp^*Fe(\eta^2-H_2B=NC_6H_4PPh_2)$ 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.

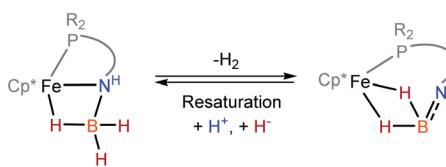
$[CpRu(PR_3)_2]^+$ fragments was developed.^{21b,22b} Turculet *et al.* have shown that the ruthenium-alkoxide complex is able to activate $H_3B\cdot NHR_2$ producing hydrido ruthenium complex.²³ Notably, Weller and Macgregor found that dehydrocoupling of ammonia-borane by $[Ph_2P(CH_2)_3PPh_2Rh(\eta^6-C_6H_5F)]$ affords a μ -amino-borane bimetallic Rh complex, in which the simplest $H_2B=NH_2$ 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 $(PNP)Fe(H)(\eta^2-BH_4)$ with ammonium salts.³⁰ Inspired by earlier research on $M-H_2B=NR_2$ 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 $Cp^*Fe(\eta^1-H_3B-NHC_6H_4PPh_2)$ (2) ($Cp^* = Me_5C_5^-$) to the imino-borane complex $Cp^*Fe(\eta^2-H_2B=NC_6H_4PPh_2)$ (3), and

a) Fundamental step involved in catalytic amine-borane dehydrogenation



b) Hypothetical dehydrogenation-regeneration of iron amido-borane



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

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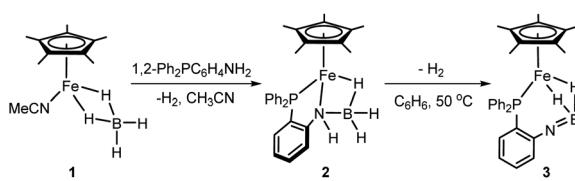


resaturation of the imino-borane by stepwise protonation and hydride transfer (Scheme 1b). This new class of iron species is capable of catalyzing 1,2-selective transfer hydrogenation of quinolines with $\text{H}_3\text{N}^+\text{BH}_3$.

To synthesize the iron amido-borane complex, a new monomer, the iron tetrahydridoborate precursor $\text{Cp}^*\text{Fe}(\eta^2\text{-BH}_4)(\text{NCMe})$ (**1**), was prepared *in situ* by the reaction of $[\text{Cp}^*\text{Fe}(\text{NCMe})_3]\text{PF}_6$ with Bu_4NBH_4 in acetonitrile at room temperature for 5 min. Such ferrous borohydrides have been documented only rarely,³¹ since they are prone to form poly-nuclear iron borate clusters.^{32,33} The ^{11}B NMR spectrum of the reaction solution shows a quintet at δ 15.4 ($J_{\text{BH}} = 88$ Hz) for the BH_4^- ligand of **1**, and this stands in contrast to the signal at δ -32.0 observed for Bu_4NBH_4 . 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- $\text{Ph}_2\text{PC}_6\text{H}_4\text{NH}_2$ 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 $\text{Fe}-\text{H}-\text{B}$. Owing to exchange between the hydrogen atoms at the boron,³⁴ the terminal $\text{B}-\text{H}$ resonances in the ^1H NMR spectrum are very broad and are obscured by the distinct Cp^* signals. To assign the $\text{B}-\text{H}$ hydride signals, the deuterated compound $\text{Cp}^*\text{Fe}(\text{D}_3\text{B}-\text{NHC}_6\text{H}_4\text{PPh}_2)$ (**d-2**) was synthesized from $\text{Cp}^*\text{Fe}(\text{BD}_4)(\text{NCMe})$. In addition to the $\text{Fe}-\text{D}-\text{B}$ 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 $\text{B}-\text{D}$ hydrides (Fig. 1).

When a C_6H_6 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 H_2 nearly quantitatively (see Fig. S4†). In solution, the ^{31}P NMR spectrum of **3** displays a sharp signal at δ 71.9, in contrast to the peak at δ 85.9 for **2**. The ^{11}B 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 $\text{B}=\text{N}$



Scheme 2 Synthetic route to imino-borane complex.

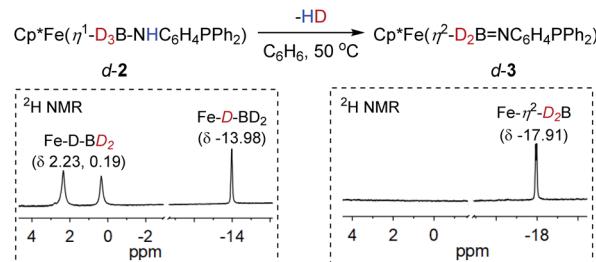


Fig. 1 ^2H NMR spectra for dehydrogenation of **d-2** to **d-3**.

double bond character in the dehydrogenated form of the amido-borane complex. In the ^1H NMR spectrum, the $\text{Fe}-\text{H}-\text{B}$ signal was observed at δ -17.91 with the integral of 2H, and no characteristic signal for a terminal $\text{B}-\text{H}$ 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 $\text{Fe}-\text{D}-\text{B}$, indicating the formation of **d-3** (Fig. 1). When the dehydrogenation was conducted in a J-Young tube in C_6D_6 , a characteristic triplet corresponding to HD appeared at δ 4.43 ($J_{\text{HD}} = 45$ 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 BH_3 moiety in **2** is stabilized by one of the $\text{B}-\text{H}$ bonds binding at the $\text{Fe}-\text{NH}$ unit to form an $\text{Fe}-\text{H}-\text{B}-\text{N}$ four-membered metallacycle. This metal-ligand cooperative binding mode increased the $\text{B}-\text{H}$ bond length in the bridging $\text{B}-\text{H}(1)$ bond to 1.362 Å vs. 1.129 Å and 1.121 Å for the two terminal $\text{B}-\text{H}$ bonds. The $\text{B}-\text{N}$ bond length of 1.545(3) Å in **2** is slightly shorter than that in $\text{H}_3\text{B}-\text{NH}_3$ ($d_{\text{B}-\text{N}} = 1.58(2)$ Å).³⁷ Crystallographic analysis of **3** confirmed an imino-borane complex with a $\text{Cp}^*\text{Fe}(\eta^2\text{-H}_2\text{B}=\text{NC}_6\text{H}_4\text{PPh}_2)$ framework. After dehydrogenation of **2**, striking structural changes were observed. The N atom

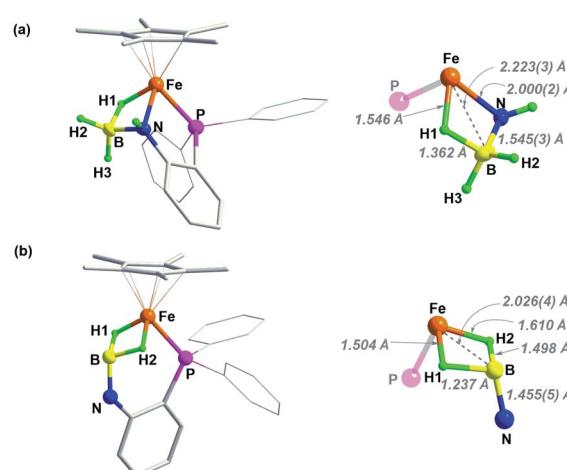


Fig. 2 Solid-state structure (50% probability thermal ellipsoids) of (a) complex **2** and (b) **3**. For clarity, hydrogen atoms of Cp^* and phenyl rings are omitted.



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 quasi-tetrahedral geometry, and the B–N bond appears to be partially sp^3 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 $\text{H}(\text{Et}_2\text{O})_2\text{BAr}_4^{\text{F}}$ in $\text{C}_6\text{H}_5\text{F}$. 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 $[\text{3H}]^+$. Alternatively, the reaction of complex 2 with $\text{H}(\text{Et}_2\text{O})_2\text{BAr}_4^{\text{F}}$ unambiguously provides $[\text{3H}]^+$ and produces H_2 . X-ray crystallographic analysis reveals that the resulting cationic complex $[\text{3H}]^+$ exhibits a similar framework to its imino-borane precursor (3). In contrast, the B–N distance in $[\text{3H}]^+$ (1.586(6) Å) is extended by 0.13 Å and the $[\text{3H}]^+$ 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 $[\text{3H}][\text{BAr}_4^{\text{F}}]$ 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 $[\text{3H}]^+$, the boron is coordinatively unsaturated, as manifested by its interaction with a σ -donor. For instance, treatment of 2 with $[\text{HPPh}_3][\text{BAr}_4^{\text{F}}]$ ($\text{p}K_a^{\text{MeCN}} = 7.6$)³⁹ provides a Ph_3P -stabilized borane complex, $[\text{3H}(\text{PPh}_3)]^+$ ($m/z = 742.2620$, calcd $m/z = 742.2626$). The ^1H NMR spectrum of $[\text{3H}(\text{PPh}_3)]^+$ exhibits

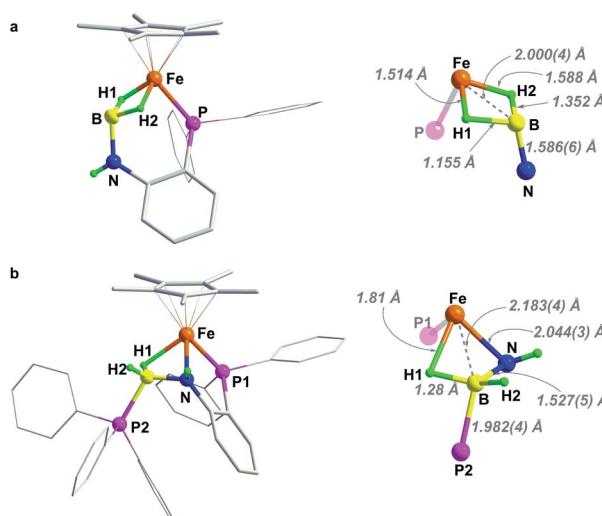
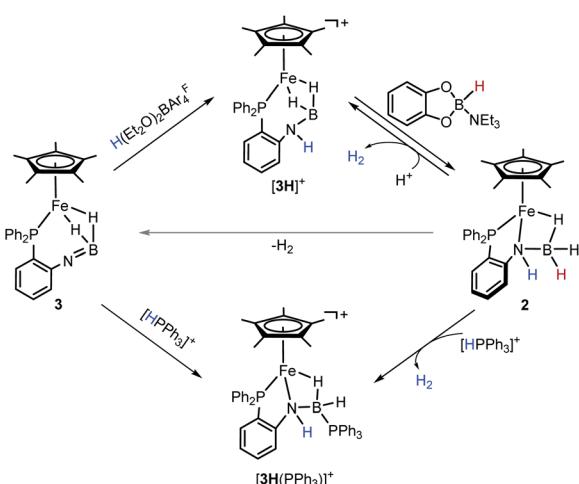


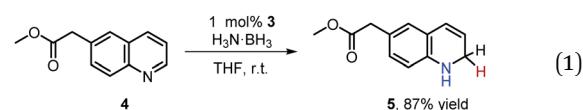
Fig. 3 Solid-state structures of (a) complex $[\text{3H}]^+$ and (b) $[\text{3H}(\text{PPh}_3)]^+$. For clarity, counterion $[\text{BAr}_4^{\text{F}}]^-$, hydrogen atoms of Cp^* and phenyl rings have been omitted.

an NH resonance at δ 4.68, suggesting that protonation occurred at the N site. The distinctive upfield hydride signal for $\text{Fe}-\text{H}-\text{B}$ is observed at δ -15.58 . In the ^{31}P NMR spectrum, two phosphorus signals at δ 78.90 and -1.26 correspond to the $\text{Fe}-\text{P}$ and the $\text{B}-\text{P}$ resonances, respectively. The ^{11}B signal at δ -13.72 indicates a tetracoordinated boron, which is further confirmed by crystallographic analysis of $[\text{3H}(\text{PPh}_3)]^+$ (Fig. 3). In the solid-state structure, a Ph_3P molecule is bound to the B center ($d_{\text{B}-\text{P}} = 1.982(4)$ Å), leading to the formation of a new $\text{Fe}-\text{H}-\text{B}-\text{N}$ four-membered metallacycle. As a amido-borane complex, $[\text{3H}(\text{PPh}_3)]^+$ 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 $[\text{3H}][\text{BAr}_4^{\text{F}}]$ in fluorobenzene with catecholborane- NEt_3 adduct ($\delta_{\text{B}} = 10.56$, $J_{\text{HB}} = 142.4$ 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 ($\delta_{\text{B}} = 13.86$) was also observed in the ^{11}B NMR spectrum, which agrees with the hydride transfer from the organohydride reagent to $[\text{3H}]^+$. It was interesting that the ion $[\text{3H}]^+$ is stable towards 5,6-dihydrophenanthridine and Hantsch ester. These results indicate that the hydride-donating ability (ΔG_{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 $[\text{HPPh}_3][\text{BAr}_4^{\text{F}}]$, which produces $[\text{3H}(\text{PPh}_3)]^+$ and releases H_2 (Scheme 3).



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



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 $\text{H}_3\text{N}\cdot\text{BH}_3$ dehydrogenation at room temperature. In the presence of 1 mol% catalyst, a THF solution of $\text{H}_3\text{N}\cdot\text{BH}_3$ (1.0 mmol) generates about 2.2 equivalent of H_2 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-quinoloneacetate (**4**) to the catalytic system containing one equiv. of $\text{H}_3\text{N}\cdot\text{BH}_3$ and 1 mol% of **3** gave 1,2-dihydro-methyl-6-quinoloneacetate (**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) complex isolated from dehydrogenation of its phosphinoamido-borane precursor, and have realized the regeneration of an $\text{Fe}-\text{H}_3\text{B}-\text{N}(\text{H})\text{Ar}$ 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.

Acknowledgements

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