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Iron-Catalyzed 1,2-Selective Hydroboration of *N*-Heteroarenes

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Supporting Information

ABSTRACT: A N_2-bridged diiron complex $[Cp^*(Ph_2PC_6H_4S)Fe]_2(\mu\text{-}N_2)$ (**1**) has been found to catalyze the hydroboration of *N*-heteroarenes with pinacolborane, giving *N*-borylated 1,2-reduced products with high regioselectivity. The catalysis is initiated by coordination of *N*-heteroarenes to the iron center, while the B−H bond cleavage is the rate-determining step.

Reduction of *N*-heteroarenes provides valuable dearomatized *N*-heterocycles, such as dihydropyridines, which constitute an important family in organic chemistry, the pharmaceutical industry, and biological transformations.[1] For example, 1,4-dihydropyridine and its analogues are known to be organohydride donors and serve as mild reducing agents in organocatalysis and sustainable synthesis.[2] 1,2-Dihydropyridines are important building blocks in the construction of natural products and drug molecules containing *N*-heterocycles.[3] Although catalytic hydrogenation of pyridines was considered to be a straightforward strategy for the synthesis of dihydropyridines,[4] the reactions usually are carried out under harsh conditions and sometimes suffer from poor chemo- or regioselectivity. Consequently, exploration of alternative methods for the reduction of pyridines is highly desirable. Catalytic hydrosilylation[5] or hydroboration[6] of pyridines enables selective reduction of *N*-heteroarenes.[7] In this context, 1,4-reduced products have been obtained using Mg,[6] Ru,[8] and organoborane[9] catalysts for hydrosilylation or hydroboration of pyridines. Systems that achieve 1,2-reduction of pyridines include $[RhCl(cod)]_2/PCy_3$/HBpin,[10] $[Cp^*_2LaH]_2$/HBpin,[11] [(DIPPnacnac)CaH·THF]/$PhSiH_3$,[12] and $[IrCl(coe)_2Cl]_2/Et_2SiH_2$.[13]

Establishing catalysis based on the most inexpensive metal, iron, for regioselective reduction of *N*-heteroarenes is significant and of interest. In the past two decades, considerable progress has been made in iron-catalyzed reduction of unsaturated hydrocarbons such as ketones,[14] imines,[15] esters,[16] amides,[17] nitriles,[18] and alkynes.[19] However, iron-catalyzed dearomative reduction of pyridines has been rarely documented. An example of this is the iron(II) complex supported by a bis(phosphino)amine pincer ligand for catalytic hydrogenation of *N*-heteroarenes to the tetrahydro products rather than to dihydropyridines.[20] In previous studies, we investigated the stoichiometric reduction of *N*-benzylpyridinium cations (BNA^+) to BNAH by iron(II) hydrides of Cp*(P−P)FeH-type (P−P = chelating diphosphine).[21] However, these iron(II) hydrides are inactive toward catalytic hydroboration or hydrosilylation of pyridines. It is noteworthy that synergism of ruthenium-thiolate reactivity enabled the catalysis of 1,4-hydrosilylation of pyridines and its benzannulated congeners.[8c,22] In this communication, we present a dinitrogen-bridged diiron compound $[Cp^*(Ph_2PC_6H_4S)Fe]_2(\mu\text{-}N_2)$ (**1**), which achieves the regioselective 1,2-hydroboration of *N*-heteroarenes with good to excellent yields. The initial step of the catalysis involves coordination of *N*-heteroarenes to the iron center rather than activation of the B−H bond.

Compound **1** was synthesized in straightforward fashion by the reaction of $[Cp^*Fe(NCMe)_3]PF_6$ with $Ph_2PC_6H_4SNa$ in THF at room temperature (yield: 75%). Recrystallization was accomplished by slow diffusion of pentane into a toluene solution of **1** at −30 °C. X-ray crystallographic analysis of **1** revealed the structure of a μ-N_2 diiron complex with the formula of $[Cp^*(Ph_2PC_6H_4S)Fe]_2(\mu\text{-}N_2)$ (Figure 1).

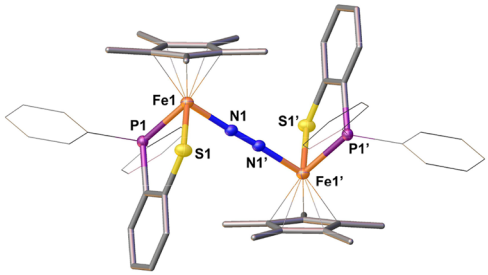

Figure 1. Structure of **1** (50% probability thermal ellipsoids).

Compound **1** has a centrosymmetric arrangement in which the two $Cp^*Fe(Ph_2PC_6H_4S)$ moieties are bridged essentially linearly by an N≡N ligand (∠Fe−N−N = 177.3(4)°). Each iron atom adopts typical three-legged piano-stool geometry. The N≡N moiety is weakly coordinated between two Fe centers and minimally activated, as indicated by the short N−N distance of 1.130(6) Å. Such N−N separation is close to that of a free N_2 molecule (1.0977 Å)[23] and comparable to the N−N distance reported for a bridging dinitrogen diiron complex.[24] In Raman spectroscopy, the N−N stretching frequency of **1** was displayed at 2016 cm^{-1} as a medium-strong band (Supporting Information, Figure S1). Although N_2-bridged diferrous complexes are known,[25] only a few of them have been structurally identified.[24a,26]

We began by examining the role of **1** in the catalytic hydroboration of pyridine (**2a**) with HBpin. At a loading of 1 mol % of **1** in benzene at room temperature, pyridine was hydroborated to afford *N*-borylated 1,2-dihydropyridine (**3a**). The conversion was only 39% after 24 h, but the yield of hydroborated product increased to 61% at 50 °C. No reaction took place in 36 h in the absence of **1** showing that the iron compound is responsible for this conversion. When 9-borabicyclo[3.3.1]-

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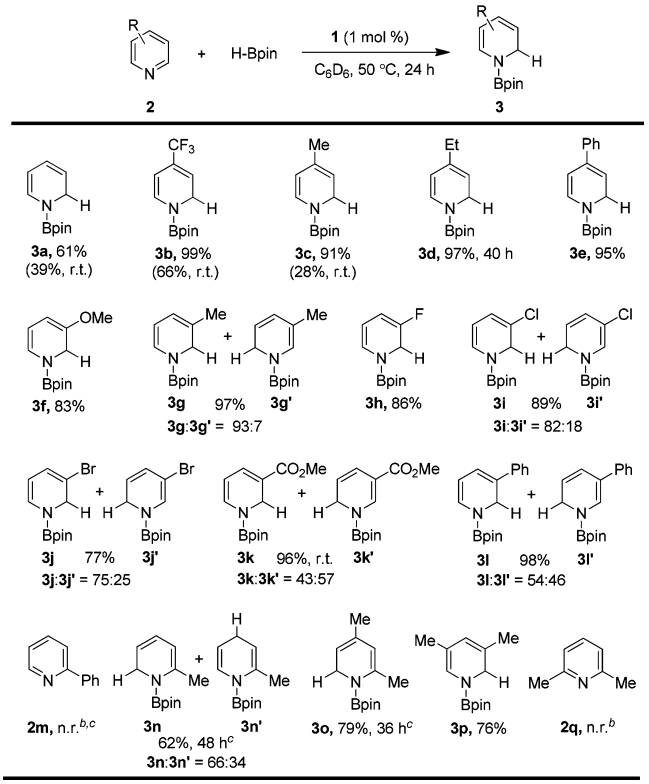
nonane (9-BBN) or catecholborane (HBcat) was employed as the reducing agent, hydroboration of pyridine was not observed even at 50 °C.

The substrate scope of the hydroboration reaction was further explored. Pyridines with both electron-donating and electron-withdrawing groups undergo hydroboration efficiently affording the corresponding 1,2-dearomatized products. Functional groups such as CF_3, phenyl, OMe, and COOMe were all found to be tolerated under the reaction conditions (Table 1). In *para*-

Table 1. Iron(II)-Catalyzed 1,2-Hydroboration of Pyridines[a]



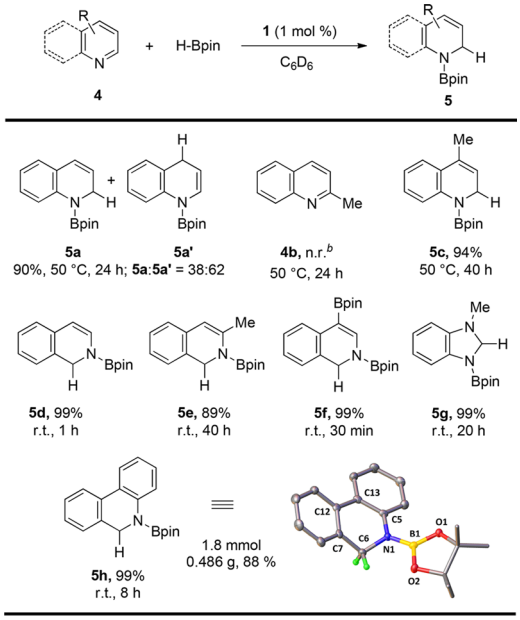
[a]Reaction conditions: **2** (0.24 mmol), HBpin (0.48 mmol, 2 equiv), **1** (1 mol %, 0.0024 mmol), and tetraethylsilane (internal standard, 0.053 mmol) in 0.6 mL of C_6D_6 at 50 °C for 24 h. Yields were determined by ^{1}H NMR analysis based on **2**. [b]No reaction. [c]2.5 mol % of **1**, 0.06 mmol.

substituted pyridines, it is more likely that the electron-withdrawing group accelerates the hydroboration (**3b**–**3e**). For example, at room-temperature, hydroboration of 4-trifluoromethylpyridine gave **3b** in 66% yield, compared to 28% yield of **3c** obtained for 4-methylpyridine. In the hydroboration of *meta*-substituted pyridines, the H atom was delivered to the C2-position, providing the *N*-boryl-3-substituted-1,2-dihydropyridine as the major product. Even halides were compatible with the 1,2-regioslective hydroborations (**3h**–**3j**), and no dehalogenation was observed.[8b,c,27]

Interestingly, 2-phenylpyridine failed to undergo hydroboration under the catalytic conditions even using 2.5 mol % of **1**, while the reaction with 2-picoline resulted in the formation of a 66:34 mixture of 1,2- and 1,4-dihydropyridine in 62% yield (**3n** and **3n′**) after 48 h. The ratio of **3n**/**3n′** retains ca. 65:35 during the reaction as monitored by ^{1}H NMR spectrum with time. Especially, this ratio is also independent of the amount of **1** used (Table S3–S4). Blocking C4 of 2-methylpyridine with a methyl group protected 2,4-lutidine from 1,4-hydroboration affording **3o** in 79% yield with a reaction time prolonged to 40 h. The reaction with 3,5-lutidine gave the 1,2-hydroborated product (**3p**, 76% yield) exclusively.

The substrate scope is not limited to pyridines. The iron compound also displayed excellent activity in hydroboration of benzofused *N*-heterocycles including quinolines, isoquinolines/phenanthridine and 1-methyl-1*H*-benzo[*d*]imidazole (Table 2).

Table 2. Catalytic 1,2-Hydroboration of Benzofused *N*-Heterocycles[a]



[a]Reaction conditions: **4** (0.24 mmol), HBpin (0.48 mmol, 2 equiv), **1** (1 mol %, 0.0024 mmol), and tetraethylsilane (internal standard, 0.053 mmol) in 0.6 mL of C_6D_6. Yields were determined by ^{1}H NMR analysis based on **4**. [b]No reaction.

In the reaction of quinoline, a mixture of 1,2- and 1,4-dihydroquinoline (**5a**/**5a′** = 38:62) was obtained. Hydroboration was not observed for 2-methylquinoline (**4b**) but 4-methylquinoline was reduced selectively to give 4-methyl-1,2-dihydroquinoline (**5c**).

The reactions of isoquinolines proceeded smoothly at room temperature to afford 1,2-hydroborated products in good to excellent yields (**5d**–**5f**). In particular, the C–B bond in **5f** was tolerated in this protocol, which facilitates further functionalization of the dearomatized products. Selective reduction of isoquinolines to dihydroisoquinolines is challenging because of the possibility of overreduction.[28] When methyl-1*H*-benzo[*d*]-imidazole was subjected to catalytic hydroboration, the 1,2-reduced product (**5g**) was obtained in quantitative yield. The iron-catalyzed hydroboration can be scaled up successfully without significant loss in efficiency. As indicated by hydroboration of phenanthridine, the 1,2-dearomatized product (**5h**) was isolated in 88% yield after recrystallization. The structure of **5h** was unequivocally established by single-crystal X-ray analysis.

To gain further insight into the initial step of the iron-catalyzed hydroboration, several stoichiometric reactions were carefully examined. We found that **1** reacted preferentially with *N*-heteroarenes rather than activating HBpin. Judging from the NMR and ESI-MS spectra, compound **1** is stable toward HBpin. This result is consistent with our previous findings that addition of HBpin across the iron–thiolate bond is thermodynamically unfavorable.[29] Unlike HBpin, *N*-heteroarenes can replace the N_2

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ligand in **1** to afford the mononuclear iron(II) complex [Cp*($Ph_2PC_6H_4S$)Fe(*N*-heteroarene)].

Treating a brown solution of **1** in benzene with isoquinoline led to a rapid color change to black. The resulting mononuclear complex [Cp*($Ph_2PC_6H_4S$)Fe(C_9H_7N)] (**6**) was characterized by X-ray crystallographic analysis (Figure 2). Moreover, the

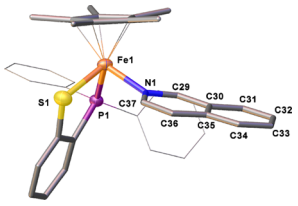
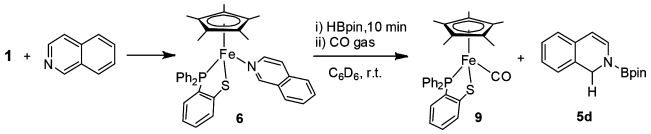


Figure 2. Structure of **6** (50% probability of thermal ellipsoids).

intermediate [Cp*($Ph_2PC_6H_4S$)Fe(C_5H_5N)] (**7**, Figure S6) was isolated from the reaction mixture of pyridine, HBpin, and **1** at −30 °C. In both **6** and **7**, the substrates were coordinated to the iron center through an N atom. Such iron−substrate complex [Cp*($Ph_2PC_6H_4S$)Fe(C_6H_7N)] (**8**, Figure S7) was also isolated for 3-methylpyridine. However, binding of 2-phenylpyridine (**2m**) to the iron center seems to be unfavorable. The compound crystallized from the reaction mixture of **1** and **2m** in all cases was **1**. Catalytic reduction of 2-phenylpyridine by hydrosilylation or hydroboration was found to be difficult,[8c,9a,11] which is probably due to the steric and electronic effects arising from the phenyl group.

A stoichiometric reaction of **6** with HBpin at room temperature gave **5d** exclusively within 10 min (Scheme 1). The generated

Scheme 1. Reaction of 6 with HBpin, Then with CO



organoiron species was trapped by CO giving [Cp*($Ph_2PC_6H_4S$)-Fe(CO)] (**9**) (Figures S9−10).[29] The isoquinoline ligand in **7** can be replaced by a more Lewis acidic borane 9-BBN, producing the stable monomeric ferrous-borane adduct **10** (Figures S11−12).[29] This is consistent with our observation that the hydroboration of pyridine by 9-BBN was unsuccessful.

Notably, both **6** and **7** showed activity comparable to that of **1** in the catalytic hydroboration of pyridine and isoquinoline, indicating intermediacy of [Cp*($Ph_2PC_6H_4S$)Fe(*N*-heteroarene)] in the catalysis. The kinetic analysis was performed for the catalytic hydroboration of isoquinoline by HBpin. A plot of the initial rate (v_i) for the formation of **5d** vs [**1**] indicated the reaction was first-order in [**1**], while v_i was found to be independent of the concentration of isoquinoline (Figures S13−S14). The zero order for [isoquinoline] suggests that binding of substrate to the iron center is not rate-limiting. Notably, further kinetic studies showed that the reaction rate is first order in [HBpin], and no inhibition was observed at high initial concentrations of HBpin (Figure S15).[11,30] In particular, a kinetic isotope effect (KIE) of 2.33 was obtained using DBpin (Figure 3), indicating that the B−H bond cleavage is the rate-determining step in the catalytic reaction.[31]

In the case of the hydroboration of quinoline catalyzed by the Mg−H complex,[32] formation of a 1,4-addition product was suggested by direct hydride transfer to the C4 position of

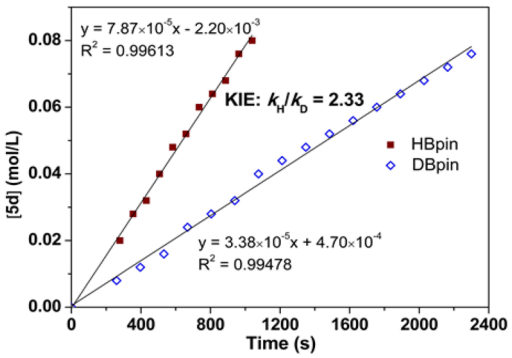
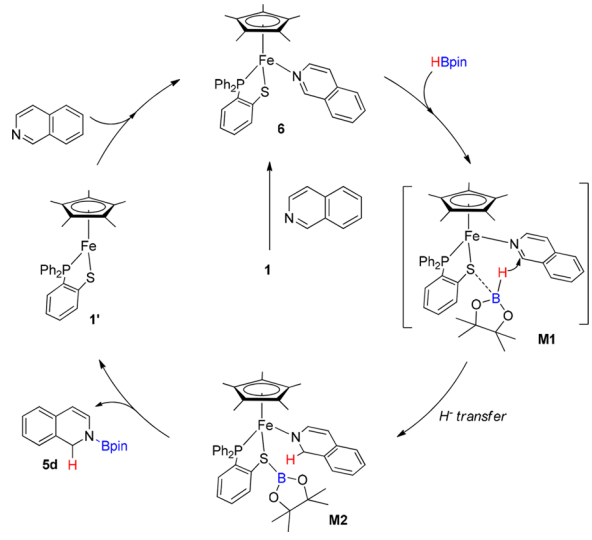


Figure 3. Initial rates of reduction of isoquinoline by HBpin and DBpin in the presence of **1**.

quinoline.[33] However, **1** is stable toward HBpin, and in our catalysis, the generation of Fe(II)−H species has not been detected by ^{1}H NMR spectroscopic analysis. Formation of 1,2-hydroborated products might be due to the *ortho*-position of the *N*-heterocycle in [Cp*($Ph_2PC_6H_4S$)Fe(*N*-heteroarene)] favoring the nucleophilic attack by the hydride of HBpin. Blocking all the C2 positions of pyridine with substituents, as in 2,6-lutidine (**2q**) or 2-methylquinoline (**4b**), failed to steer the 1,4-hydroboration. However, substituents in the para-position of pyridine allow the 1,2-hydroboration.

The phosphinothiolate ligand in **1** is crucial to the catalysis. In contrast, piano-stool iron(II) complexes with chelating diphosphine ligands such as Cp*($Ph_2PN^{tBu}PPh_2$)FeH, Cp*(1,2-$Ph_2PC_6H_4PPh_2$)FeH, and [Cp*($Ph_2PN^{tBu}PPh_2$)Fe(N_2)]$^+$ are inactive in the hydroboration of *N*-heteroarenes. On the basis of experimental results, the catalytic mechanism is proposed in Scheme 2. Catalytic generation of borenium ions from HBpin has

Scheme 2. Proposed Catalytic Cycle for Hydroboration of Isoquinoline by 1



been described for the ruthenium(II)−thiolate system.[34] The thiolate site in **6** could facilitate the hydride transfer from HBpin to **6** through S → B interaction (**M1**) and capture the borenium ion after the B−H bond cleavage (**M2**). Subsequent transferring of the borenium to the reduced *N*-heterocycle provides the final product and regenerates the 16-electron iron(II) active species **1′**.[29] Note that the regioselectivity of the dihydropyridine products is

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sensitive to the substituent of the precursor.[1d] The regioisomeric *N*-boryl-1,4-product for 2-picoline and quinoline could be formed by the hydride transfer to the *para*-position of the *N*-heterocycle.[32]

In summary, we have developed a N_2-bridged diiron complex as an efficient precatalyst for regioselective 1,2-hydroboration of *N*-heteroarenes with HBpin. This catalysis exhibits excellent regioselectivity and broad functional group compatibility and enables the large scale synthesis of 1,2-dihydropyridines. Mechanistic studies reveal that coordination of the substrate to the iron center initiates the catalysis and that the B−H bond cleavage is the rate-determining step. Future work will focus on a detailed mechanistic analysis and an expansion of catalytic reactions based on such iron−thiolate compound.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b11416.

Experimental details and characterization of the products (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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