Letter

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Efficient and selective iron complex-catalyzed hydroboration of aldehydes

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ABSTRACT: An imine-coupled [Fe-N_2S_2]$_2$ complex, prepared from a readily-available benzothiazolidine ligand, catalyzes selectively the hydroboration of aliphatic and aromatic aldehydes at low catalyst loadings (0.1 mol %) using pinacolborane. Both mono- and disubstituted aromatic and aliphatic aldehydes are hydroborated selectively in the presence of ketones, nitriles, alkenes, amines, and halides. Reaction of the [Fe-N_2S_2]$_2$ complex with CO and preliminary reaction progress kinetic studies point to a complex mechanism.

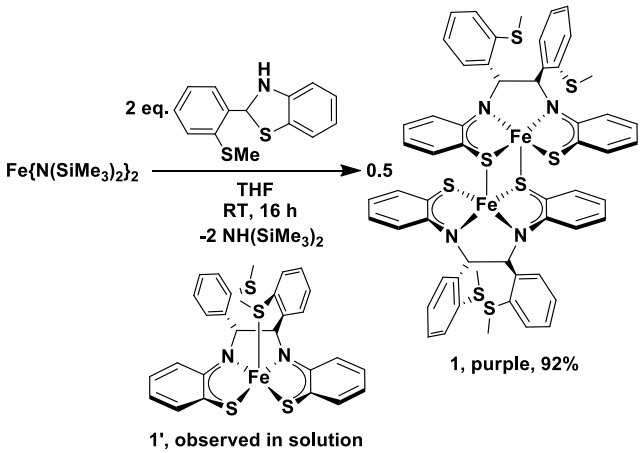
Keywords. Iron, aldehyde hydroboration, pinacolborane, selectivity, reaction progress kinetic analysis

Catalytic hydroboration of carbonyl compounds using pinacolborane (HBpin) represents an attractive strategy in organic synthesis[1] not only for synthesizing widely used borate ester intermediates,[2,3] but also for conversion into the corresponding alcohols.[4] Since the Bpin group can serve as a versatile directing and protecting group, this catalytic process enjoys further advancement in synthetic chemistry.[5-8] Intrigued by recent reports from C. Gunanathan and co-workers of selective aldehyde (*vs.* ketone) hydroboration catalysed by a simple Ru precursor,[9] we disclose herein an efficient and strictly selective iron-based catalyst containing an imine-coupled, redox-active N_2S_2 ligand.

To date, hydroboration catalysts for carbonyl compounds based on transition metals (Ti,[10-14] Mo,[15] Fe,[16] Ru,[9] Co,[17] and Cu[18]), main group metals (Li,[19] Mg,[20-22] Ca,[23] Al,[24,25] Ga,[26] Zn,[27-30] Ge and Sn[31]), and main group elements (P),[32] are known. Recently, rare-earth metal catalysts,[33,34] and a silica-supported Zr catalyst[35] have also been reported. Selective hydroboration of aldehyde over ketone, however, has only recently been reported using Fe(acac)$_3$,[16] aluminum monohydride,[25] diazaphosphine,[32] and [(*p*-cymene)$RuCl_2$]$_2$[9] catalysts. In these cases, ketones can also be hydroborated by increasing either the catalyst loading, reaction temperature or reaction time.

Herein we report the synthesis of a paramagnetic, imine-coupled Fe(II) complex, [Fe(N_2S_2)]$_2$ **1** and its application to selective hydroboration catalysis of various aliphatic and aromatic aldehydes at low catalyst loading (0.1 mol %) at room temperature using HBpin. In this unique example of iron-catalysed carbonyl hydroboration, the reaction tolerates a variety of reducible functional groups, including nitriles, amines, alkenes, halides, and ketones even at elevated temperatures.

We recently reported an easily-prepared benzothiazolidine ligand, [$S^{Me}N^{H}S$] containing a potentially labile thioether donor, that undergoes facile ring-opening to afford a series of mono-, di- and trinuclear Fe(II) complexes containing the anionic thioether-imine-thiolate [$S^{Me}NS$] ligand.[36] During the course of this study, we observed that treatment of the low-coordinate iron complex, [Fe{N(SiMe$_3$)$_2$}$_2$] with two eq. of [$S^{Me}N^{H}S$] in THF at room temperature afforded the title complex, 1 as a purple solid in 92% yield (Scheme 1). Complex 1 was characterized by ^{1}H NMR and UV-vis spectroscopy, ESI-MS, and single-crystal X-ray diffraction. The ^{1}H NMR spectrum shows broadened and shifted resonances spanning the range from δ 88.03 to −14.42, indicative of a paramagnetic complex.



Scheme 1. Synthesis of [Fe(N_2S_2)]$_2$, 1

Single crystals of **1** for X-ray diffraction were grown from a saturated THF solution. Interestingly, the solid-state structure of **1** shows formation of a thiolate-bridged dimer containing imine-coupled N_2S_2 ligands (Figure S7 in the Supporting Information). One of the two thiolates in each monomer binds to an iron centre in the other, linking the two. Moreover, the imine groups of two tridentate $S^{Me}NS$ ligands have been transformed into a diamido unit,

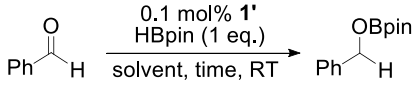
forming the redox-active $(N_2S_2)^{2-}$ ligand with two uncoordinated thioether groups.

While **1** is dimeric in the solid-state, in solution (CD_2Cl_2, THF-d_8 and C_6D_6; Figures S1-S3) it exists solely as a monomer that retains the square pyramidal coordination about iron (**Scheme 1**). The monomeric structure in solution is confirmed by a broad paramagnetic singlet (3H) at δ 88.03 in the ^{1}H NMR spectrum due to coordination of one of the thioether groups to the paramagnetic iron centre; the methyl resonance of the uncoordinated S-Me is observed at δ 2.21. The dimeric structure of **1** was not observed in any solvent. The identity of **1'** [Fe(N_2S_3)] was further confirmed by electrospray mass spectrometry (Figures S5-S6). The solution magnetic moment of **1'** at room temperature (measured by Evans' method[37]) is 2.7 μ_B, consistent with two unpaired spins. Detailed analysis of the magnetic properties and electronic interactions between the high-spin, square pyramidal iron centre and the redox active $(N_2S_2)^{2-}$ ligand of **1'** will be published elsewhere.

We commenced our catalytic study using complex **1'** as a catalyst for the reduction of carbonyl compounds. While poor results were obtained using H_2 or Et_3SiH, treatment of 1 eq. of benzaldehyde, with 1 eq. of HBpin and 10 mol % of **1'** in C_6D_6 at room temperature gave the hydroboration product in quantitative yield in one hour (**Table 1**, entry 1) as observed by both ^{1}H and ^{11}B NMR spectroscopy. While the purple solution of **1'** was unchanged upon addition of benzaldehyde, once HBpin was added, the colour changed quickly to light beige or colorless, showing that complex **1'** acts as a precatalyst. Reducing the catalyst loading to 0.1 mol % still gave excellent yields (> 80%) within 15 minutes (entry 2) that were essentially quantitative after 30 minutes (entry 3) at room temperature. In contrast, use of alternate Fe(II) precatalysts (*i.e.*, $FeCl_2$, $Fe(OTf)_2$, and $Fe\{N(SiMe_3)_2\}_2$) gave much lower yields of the hydroboration product along with dark precipitates (entries 4-6), underscoring the uniqueness of **1'**.

A similar test with the [$S^{Me}N^HS$] ligand alone (entry 7) failed to give more than 5% hydroboration product. Surprisingly, reaction of equimolar acetophenone and HBpin using 0.1 mol % of **1'** at room temperature afforded less than 5% of the hydroboration product. Even with high catalyst loading (10 mol %) at 60 °C for 16 h, less than 10% of the corresponding borate ester was detected, indicating that precatalyst **1'** is selective toward aldehydes (vs. ketones). A brief screening of solvents showed that both tetrahydrofuran and acetonitrile gave comparable yields of the hydroboration product (Table 1, entries 8 and 9). Without precatalyst **1'** less than 5% of the hydroboration product was formed in two hours (entry 10).

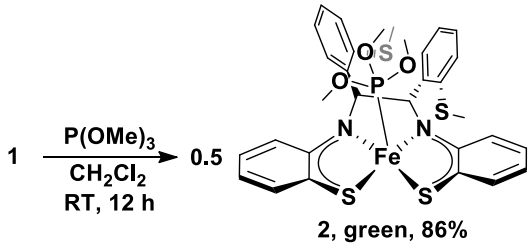
Table 1. Optimization of reaction conditions[a]



Entry	Catalyst (mol %)	Solvent	Time (h)	Yield (%)[b]
1	**1'** (10)	C_6D_6	1	> 99
2	**1'** (0.1)	C_6D_6	0.25	> 80
3	**1' (0.1)**	**C_6D_6**	**0.5**	**> 99**
4	$Fe\{N(TMS)_2\}_2$ (0.5)	C_6D_6	0.5	20
5	$FeCl_2$ (0.5)	C_6D_6	0.5	35
6	$Fe(OTf)_2$ (0.5)	C_6D_6	0.5	51
7	[$S^{Me}N^HS$] ligand (1)	C_6D_6	0.5	< 5
8	**1'** (0.1)	THF-d_8	0.5	95
9	**1'** (0.1)	CD_3CN	0.5	> 99
10	None	C_6D_6	2	< 5
11	**2** (0.1)	C_6D_6	0.5	86

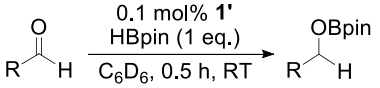
[a]Reaction conditions: benzaldehyde (0.436 mmol), HBpin (0.436 mmol), solvent (0.3 ml), catalyst loading relative to benzaldehyde. [b]Yields were determined by ^{1}H NMR spectroscopy using mesitylene as an internal standard.

With the optimized reaction conditions in hand, the scope of the hydroboration was examined with a variety of aldehydes. Precatalyst **1'** showed remarkable efficiency with excellent selectivity in hydroboration reactions of both aliphatic and aromatic aldehydes (**Table 2**). Cyclic aliphatic aldehyde, electron-rich 1-pentanal and 2-(methylthio) benzaldehyde all afforded high yields of their corresponding borate esters (entries 1, 2 and 15). The α, β-unsaturated aldehyde yielded a single product (entry 3). Aromatic aldehydes containing electron-withdrawing as well as reducible functional groups showed excellent tolerance (entries 7-12, 14) yielding > 99% of the hydroboration products under these conditions. Interestingly, electron-donating aromatic aldehydes gave low to moderate yields (entries 5 and 13), in contrast to 1-pentanal, suggesting that both steric and electronic factors are at play in this system. Significantly, terephthalaldehyde was cleanly converted into the bis(borate ester) derivative with 2 eq. of HBpin (entry 16). However, when 1 eq. of HBpin was treated with equimolar terephthalaldehyde at room temperature, as well as heating at 50 °C for 4 h, only the monohydroborated product was observed, indicating insignificant activation by the para-CH_2OBpin group. Importantly, 4-acetylbenzaldehyde underwent selective hydroboration only at the aldehyde group (entry 17) demonstrating the synthetic utility of this system. As ketone substrates are not hydroborated even at elevated temperatures, this is a rare example of exclusive aldehyde selectivity over ketone when compared, for example, to $Fe(acac)_3$-catalyzed chemoselective hydroboration of aldehydes over ketones in which poor selectivity was achieved with 3-acetylbenzaldehyde.[16] To compare the efficiency of **1'** with a closely related derivative, we prepared and fully characterized the diamagnetic phosphite complex, [Fe(N_2S_2)P(OMe)$_3$], **2** (**Scheme 2**).[38] Treatment of 1 eq. of benzaldehyde with 1 eq. of HBpin catalyzed by 0.1 mol % of **2** afforded 86% of the corresponding borate ester in 30 minutes (**Table 1**, entry 11).

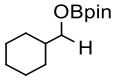
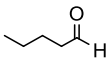
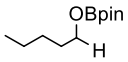
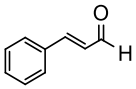
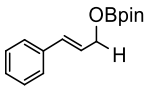
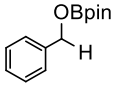
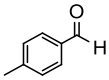
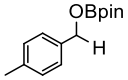
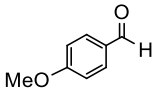
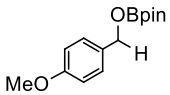
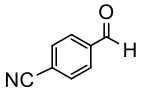
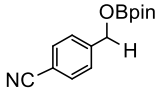
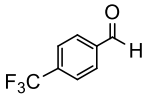
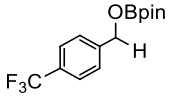
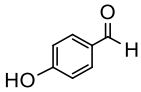
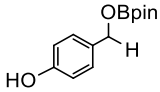
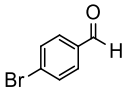
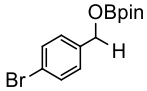
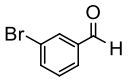
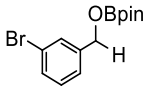
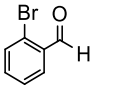
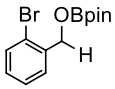
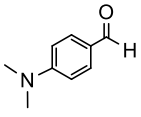
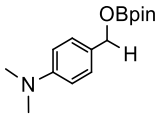
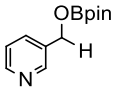
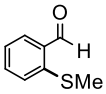
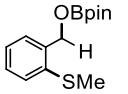
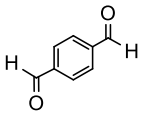
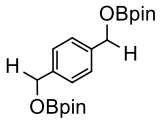
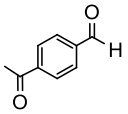
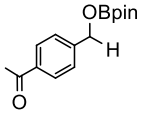


Scheme 2. Synthesis of [Fe(N_2S_2)P(OMe)$_3$], 2

Table 2. Scope of hydroboration of aldehydes



Entry	Aldehyde	Product	Yield (%)[a]

1			> 99
2			> 99
3			85
4			> 99
5			70
6			> 99
7			> 99
8			> 99 (87)
9[b]			39
10			> 99
11			> 99
12			> 99
13			26
14			> 99
15			> 99
16[c]			> 99
17			> 99

[a]Conditions: Aldehyde (0.436 mmol) was added to **1'** (0.1 mol %) in C_6D_6 (0.3 ml) followed by HBpin (0.436 mmol) at room temperature. All reactions afforded a single product and yields were calculated *vs.* mesitylene internal standard (0.058 mmol), average of at least 2 runs. [b]CD_3CN (0.4 ml) was used. [c]2 equiv. of HBpin were used. Isolated yield in parentheses using 1 mol % of **1'**.

In order to gain insight about potential catalytic intermediates or resting states in this hydroboration system, catalytic hydroboration of 4-(trifluoromethyl) benzaldehyde was scaled up using 1 mol % of **1'**, and of benzaldehyde using 2.5 mol % of **2**. The remaining brown liquid of the catalytic species, obtained from catalytic hydroboration using 1 mol % of **1'**,[39] showed a mix of diamagnetic and paramagnetic resonances in the ^{1}H NMR spectrum due to unidentified species with no evidence of precatalyst **1'** (Figure S38). Nonetheless, this mixture further efficiently converted a portion of fresh substrate/HBpin mixture into the borate ester product, confirming the presence of active catalyst. Likewise, the ^{1}H NMR spectrum of the remaining green solid resulting from catalytic hydroboration using 2.5 mol % of diamagnetic species **2** was also inconclusive, showing a mix of resonances from both diamagnetic and paramagnetic species (Figure S39). The ^{31}P{^{1}H} NMR spectrum taken during the reaction displays two singlets due to free $P(OMe)_3$ and an unidentified species along with a broad singlet due to precatalyst **2** (Figure S40). The stoichiometric reaction of **2** with excess HBpin at room temperature also provided little insight into the catalyst resting state, affording small amounts of borohydride, observed previously in reactions of catecholborane and phosphorus ligands[40] (Figures S41-S42).

To gain further mechanistic insight into this efficient iron catalysis, we performed kinetic studies to identify the resting state and substrate dependence of the catalytic process. We initially carried out analysis using the Reaction Progress Kinetic Analysis (RPKA) technique.[41,42] Using this technique, the kinetic order of the aldehyde and HBpin can be solved by carrying out a series of experiments in which the initial concentrations of each component are varied.

Using less reactive 4-methylbenzaldehyde, we were able to validate that the observed reaction rate is indeed sensitive to both the initial concentration of aldehyde and HBpin. Increasing initial concentration of either aldehyde or HBpin results in a commensurate increase in the observed rate of reaction, suggesting that the catalytic system bears a positive order in both components. However, extracting a meaningful integer value for the order in each component was not straightforward, as both the percent conversion and shape of the reaction progress curve changed dramatically depending on if the reaction was performed with equimolar (blue) or excess (red and yellow) starting materials (Figure 1).

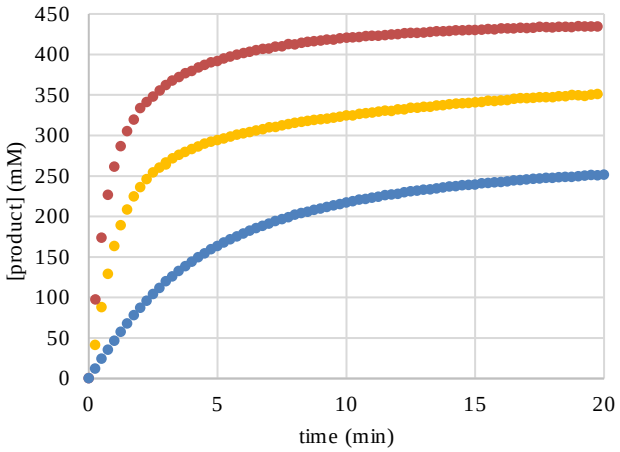


Figure 1. Effect of concentration on rate of formation of product in the hydroboration of 4-methylbenzaldehyde by precatalyst **1'** ([**1'**] = 0.44 mM, 23 °C, C_6H_6; blue [CHO] = [HBpin] = 450 mM; red [CHO] = 450 mM, [HBpin] = 675 mM; yellow [CHO] = 675 mM, [HBpin] = 450 mM).

When utilizing the RPKA method to extract information, analysis of the data is simplified because the difference in initial concentration of the two components (designated the reaction excess) is maintained for each experiment. However, for hydroboration using Fe precatalyst **1'**, analysis by ReactIR revealed that in a typical experiment, the rate of consumption of HBpin was greater than that for the aldehyde (Figure 2). This results in incomplete reduction of the aldehyde at short reaction times, unless more than one equivalent of HBpin is present.

Analysis of the reaction revealed no obvious by-products to account for the extra consumption of HBpin.[43] Due to this observation, we hypothesized that HBpin was being utilized to activate the initial iron catalyst. Consistent with this, a dramatic colour change was observed upon addition of substrates to a solution of **1'** (from deep purple to either beige or colourless). Kinetic evidence for catalyst activation could be gleaned

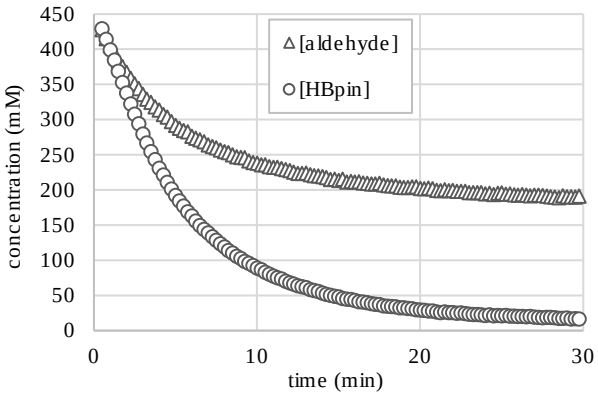


Figure 2. Unequal rates of consumption of aldehyde and HBpin in the hydroboration of *p*-methylbenzaldehyde by precatalyst **1'** ([**1'**] = 0.44 mM, 23 °C, C_6H_6, [CHO] = [HBpin] = 450 mM).

by carrying out a series of reductions where aliquots of both aldehyde and HBpin are added, allowing the reaction to proceed to completion between each subsequent addition. These experiments revealed several key features. First, conversion to product is lowest after the first equimolar addition of aldehyde and HBpin, and increases in all subsequent doses (~65% conversion *cf.* ~90% for latter cycles; Figure 3). In addition, the rate of reaction appears to increase after the first aliquot addition. This is observed from the reaction profile for the concentration of HBpin for a series of sequential additions (Figure 3, cycle 1 vs. 2-4).

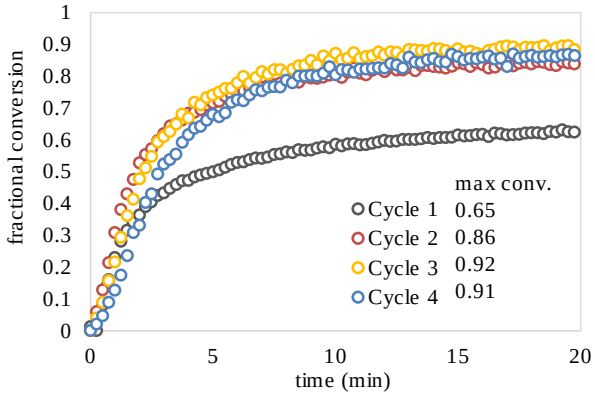


Figure 3. Comparing process efficiency for the first substrate addition and subsequent additions. See also Figure 4, and SI, Figure S44 for concentration profiles.

These observations revealed conclusively that the iron catalyst needs to undergo irreversible activation through reaction with HBpin to form the active complex. Furthermore, once activated, this catalyst is both exceptionally active (capable of producing ca. 40 mmol product/min) and very long-lived. In our studies, we demonstrated that a TON of ca. 5200 was easily achieved; note that this is by no means the limit of the activity. Importantly, reaction of the iron complex with HBpin in the absence of aldehyde appears to be detrimental. In experiments where the order of reagent addition was reversed, that is HBpin was added before aldehyde (Figure 4, cycle 5), we see a net decrease in the rate of reduction in the subsequent experiment (Figure 4, cycle 6).

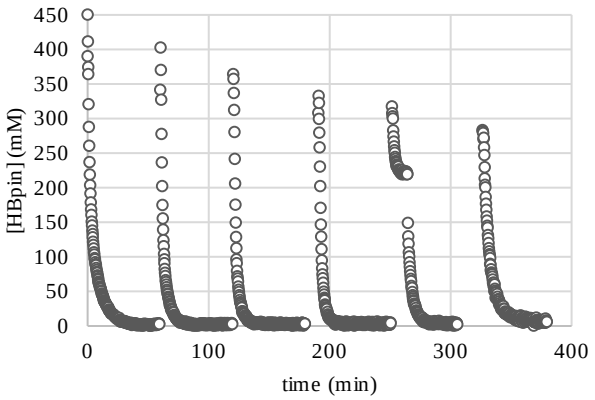
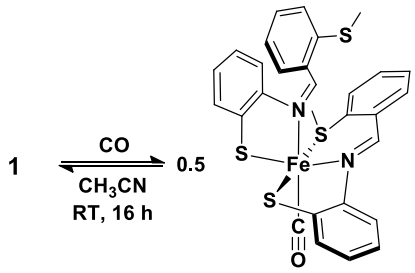


Figure 4. Concentration of HBpin throughout the multi-dose experiment. The experiment was initiated by the addition of HBpin (0.45 mmol), and aldehyde (0.45 mmol) to a solution of **1'** (0.44 µmol) in C_6H_6 at 23 °C. Cycles (2-4, 6) were triggered by the addition of HBpin (0.45 mmol), followed by aldehyde (0.45 mmol), ca. 15 s later. In Cycle 5, the order of addition of the reagents was reversed.

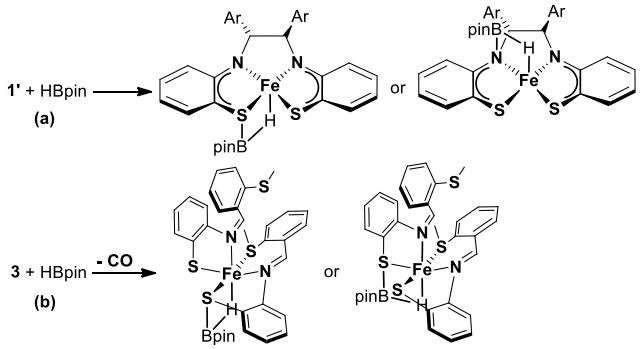
As no reaction of precatalyst **1'** was observed with aldehydes, we investigated its reaction with the more reactive carbonyl moiety, carbon monoxide. Treatment of complex **1** with CO in acetonitrile afforded an iron complex, [Fe(κ^3-SNS)(κ^2-SNS)CO], **3** (**Scheme 3**) which was characterized by IR, ^{1}H NMR and X-ray crystallography. The IR spectrum (Figure S13) of **3** in the solid state shows a strong and sharp CO stretching vibration at 1952 cm^{-1}, confirming the addition of a CO ligand to the iron centre. The X-ray data show that car-

bonylation of **1'** cleaves the diamido C-C bond, generating a pseudooctahedral iron centre occupied by one CO and two SNS ligands (Figure S14). Interestingly, the ^{1}H NMR spectrum of diamagnetic complex **3** dissolved in CD_2Cl_2 shows also the paramagnetic resonances of complex **1'**, indicating that CO addition to iron is reversible in solution.



Scheme 3. Synthesis of [Fe(κ^3-SNS)(κ^2-SNS)CO], 3

Metal-catalyzed hydroboration of carbonyl compounds typically proceeds through either Lewis acid substrate activation or B-H bond activation.[4] In the latter case formation of an iron hydride could be accompanied by boryl transfer to either the nitrogen or sulphur (**Scheme 4a**).[44-46] In light of the reversible reaction of precatalyst **1'** with CO, however, one may also have to consider reaction pathways that involve bifunctional Fe SNS catalysts (**Scheme 4b**).



Scheme 4. Potential B-H bond activation pathways for aldehyde hydroboration catalysis using 1' (a, top) and 3 (b, bottom)

Finally, our observations highlighting the robust and efficient nature of the iron catalyst led us to push the limits of stability for this system. Thus, we could demonstrate that this catalyst is tolerant of many common species that would typically deactivate such a metal catalyst. This includes running the reaction with crude aldehyde (contaminated with 5% 4-methylbenzoic acid) and even performing the reduction in open air (see SI, Figures S45–S46). Further kinetic studies are ongoing with catalysts **1** and **2** and their stable redox partners, i.e., $(\mathbf{1'})^+$ and $(\mathbf{1'})^-$.

In summary, we have prepared and characterized a five-coordinate, paramagnetic imine-coupled iron complex, $[Fe(N_2S_2)]_2$ that demonstrates excellent efficiency and selectivity in hydroboration catalysis of various aldehydes. The key advantages of this process are its exclusive aldehyde selectivity over ketone, wide reducible functional group tolerance, mild reaction conditions and catalyst lifetime. This simple iron catalysed hydroboration system will therefore be attractive for synthetic, medicinal and fine chemical catalysis.

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Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org. Detailed experimental procedures, characterization of the Fe(II) complexes, crystallographic details of Fe(II) complexes, and copies of ^{1}H, ^{11}B, and ^{31}P{^{1}H} NMR spectra.

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SYNOPSIS

An imine-coupled [Fe-N_2S_2]$_2$ complex, catalyzes selectively the hydroboration of aliphatic and aromatic aldehydes at low catalyst loadings (0.1 mol %) using pinacolborane.

Table of Contents