VIP Catalytic Hydrogenation

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Efficient Hydrogenation of Ketones Catalyzed by an Iron Pincer Complex**

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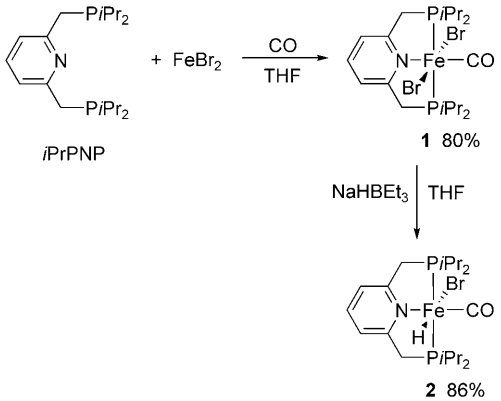
The catalytic reduction of ketones to the corresponding alcohols is an important reaction in organic chemistry, which is usually catalyzed by complexes of precious metals (e.g. Rh, Ir, Ru) using either H_2 or *i*PrOH as hydrogen source.[1] In particular, the reduction of ketones with gaseous hydrogen provides an atom-economical synthetic method. The development of iron-based catalysts with similar activity is desirable due to their low toxicity, lower price, and the benign environmental impact of iron compounds.[2]

Although considerable progress has been made in iron-catalyzed transfer hydrogenations and hydrosilylations,[3] only a few studies have been published on iron-catalyzed hydrogenations.[4–7] Chirik and co-workers recently described the synthesis of the well-defined catalyst [(*i*PrPDI)Fe$(N_2)_2$] (*i*PrPDI = ((2,6-CHMe$_2$)$_2$C$_6$H$_3$N=CMe)$_2$C$_5$H$_3$N), which was capable of hydrogenating alkenes and alkynes with 0.3 mol% catalyst loading and 4 atm hydrogen pressure at ambient temperature. Turnover frequencies of up to 1814 h^{-1} were reached with this system for the hydrogenation of 1-hexene.[4] We are aware of only two iron complex systems that are capable of catalyzing the hydrogenation of ketones to alcohols. Casey et al. described the bifunctional complex [{2,5-(SiMe$_3$)$_2$-3,4-(CH$_2$)$_4$(η^5-C$_4$COH)}Fe(CO)$_2$H], which catalyzes hydrogenation of ketones under mild conditions with high chemo- and diastereoselectivity, resulting in 50 turnovers.[5] The diiminodiphosphine and diaminodiphosphine iron complexes described by Morris and co-workers were studied in the catalytic hydrogenation of acetophenone, leading to high conversion at high pressure and excess of base ($T = 50\,°C$, $p(H_2) = 25$ atm, TON 225; catalyst:base = 15).[6]

We recently reported reactions catalyzed by pyridine-based pincer complexes of ruthenium,[8] including hydrogenation of esters to alcohols[9a] and hydrogenation of amides to amines and alcohols under mild conditions.[9b] A new mode of cooperation between the ligand and the metal center, involving aromatization–dearomatization of the ligand, plays a key role in these reactions. To develop corresponding iron catalysts with similar reactivity would be desirable. The preparation of the paramagnetic Fe^{II} complexes [(PNN)FeCl$_2$][10a] (PNN = 2-((di-*tert*-butylphosphinomethyl)-6-diethylaminomethyl)pyridine) and [(*t*BuPNP)FeCl$_2$] (*t*BuPNP = 2,6-bis(di-*tert*-butylphosphinomethyl)pyridine),[10a,b] as well as the formation of the cationic complex [(PNN)FeCl(thf)](PF$_6$)[10a] has already been reported. The dinitrogen hydride complex [(*i*PrPNP)Fe(H)$_2$(N$_2$)], described by Trovitch et al., catalyzes the hydrogenation of 1-hexene, but showed only poor activity in the hydrogenation of cyclohexene, while the complex [(*i*PrPNP)FeH$_2$(SiH$_2$Ph)(N$_2$)] was not effective in the hydrosilylation of alkenes.[7] Based on the unusual reactivity of pyridine pincer based hydrido carbonyl Ru^{II} complexes, we started to investigate the synthesis of analogous iron complexes.

Herein we report the synthesis and characterization of the new iron pincer complexes [(*i*PrPNP)Fe(CO)Br$_2$] (**1**) and [(*i*PrPNP)FeH(CO)Br] (**2**) (*i*PrPNP = 2,6-bis(diisopropylphosphinomethyl)pyridine). The iron hydride complex **2** is the most efficient iron complex catalyst reported to date for the hydrogenation of ketones. The reaction takes place under very mild conditions, with turnover numbers of up to 1880 using 4.1 atm hydrogen pressure at ambient temperature (26–28 °C). The two dearomatized complexes [(*i*PrPNP^{-H})FeH(CO)(NCPh)] (**3**) and [(*i*PrPNP^{-H})FeH(CO)(PhCOPh)] (**4**) were characterized by multinuclear NMR spectroscopy and their reactivity was investigated. Based on these results a mechanism for this reaction is proposed.



Scheme 1. Synthesis of the Fe^{II} complexes **1** and **2**.

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The reaction of $FeBr_2$ with *i*PrPNP in THF under an atmosphere of CO resulted in the formation of the blue complex **1** in good yield (Scheme 1). The IR spectrum of **1** exhibits a strong absorption at 1944 cm^{-1} assignable to coordinated CO. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at $\delta = 72.8$ ppm, indicating that the two phosphorus atoms of the PNP ligand are equivalent. The ^1H NMR spectrum exhibits one doublet of doublets at $\delta = 1.44$ ppm for the methyl protons of the *i*Pr groups, one multiplet at $\delta =$ 2.87 ppm for the CH protons of the *i*Pr groups and one doublet at $\delta = 4.05$ ppm for the methylene protons, indicating a C_S or C_2 symmetry of the complex and thus a *trans* orientation of the two bromide ligands. The crystal structure of **1** (Figure 1) displays a distorted octahedral geometry

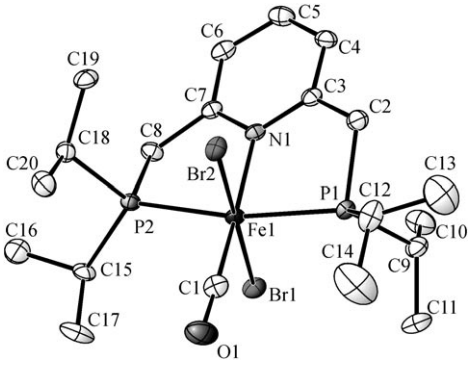


Figure 1. Molecular structure of complex **1** with the thermal ellipsoids set at 50% probability. Selected bond lengths [Å] and angles [°]: Fe1–Br1 2.484(1), Fe1–N1 2.046(4), Fe1–C1 1.746(5), Fe1–P1 2.302(1), C1–O1 1.160(6); C1-Fe1-N1 177.4(2), Fe1-C1-O1 177.6(5), P1-Fe1-P2 166.71(5), Br1-Fe1-Br2 178.09(3), Br1-Fe1-P1 94.35(4), Br1-Fe1-N1 91.75(11).

around the metal center, with the CO ligand *trans* to the pyridine nitrogen and the two bromine atoms in the apical positions.

The hydrido complex [(*i*PrPNP)FeH(CO)Br] (**2**) was prepared by treating **1** in THF with one equivalent of $NaHBEt_3$ (Scheme 1) and was isolated as a brown solid in 86% yield. The carbonyl vibration in the IR spectrum is shifted to 1892 cm^{-1}. The equivalence of both phosphorus atoms is reflected in the observation of a singlet peak at $\delta =$ 90.43 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The ^1H NMR spectrum shows a triplet at $\delta = -20.47$ ppm ($^2J_{PH} = 53.5$ Hz) for the hydrido ligand, four doublets of doublets for the methyl protons, and two multiplets for the CH protons of the *i*Pr groups, indicating lack of symmetry in comparison with **1**.

According to the crystal structure of complex **2** the Fe^{II} center has a distorted octahedral environment including the *i*PrPNP, hydride, carbon monoxide, and bromide ligands (Figure 2). The CO ligand is coordinated *trans* to the pyridine nitrogen, while the hydride is *trans* to the bromide ligand (Fe1–H1 1.42(4) Å).

Complex **2** was investigated as a catalyst for the hydrogenation of ketones. In preliminary experiments various solvents were tested for the hydrogenation of acetophenone, using 0.05 mol% **2**, 0.1 mol% KO*t*Bu and 4.1 atm hydrogen

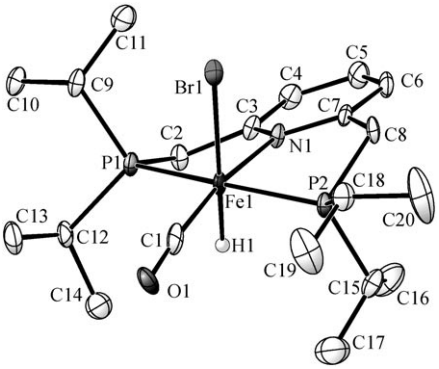
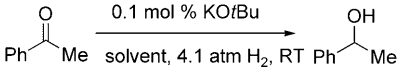


Figure 2. Molecular structure of complex **2** with the thermal ellipsoids set at 50% probability. Selected bond lengths [Å] and angles [°]: Fe1–Br1 2.547(11), Fe1–P1 2.218(1), Fe1–N1 2.045(3), Fe1–C1 1.730(5), Fe1–H1 1.42(4), C1–O1 1.145(5); Br1-Fe1-P1 100.7(4), Br1-Fe1-N1 93.0(1), Fe1-C1-O1 173.7(4), P1-Fe1-P2 163.75(5), N1-Fe1-C1 168.7(19), Br1-Fe1-H1 179.7(19).

Table 1: Iron-catalyzed hydrogenation of acetophenone.[a]



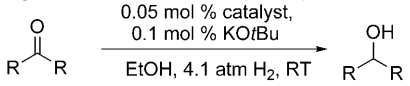
Solvent	*t* [h]	Yield [%] (conversion [%])[b]	TON	TOF/h^{-1}
MeOH	23	13 (23)	260	11
EtOH	21.5	94 (94)	1880	87
EtOH[c]	4	85 (86)	1720	430
*n*PrOH	21	30 (35)	600	29
*i*PrOH	20	9 (21)	180	9
THF	24	0	–	–
–	22	0	–	–

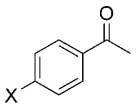
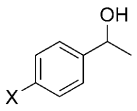
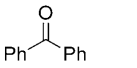
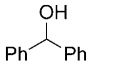
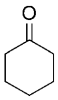
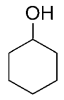
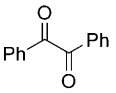
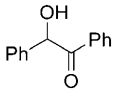
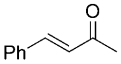
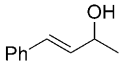
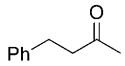
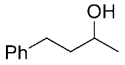
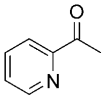
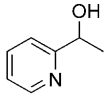
[a] Reaction conditions: **2** (0.0025 mmol), KO*t*Bu (0.005 mmol), substrate (5 mmol), *m*-xylene (1 mmol), ethanol (3 mL), H_2 (4.1 atm). [b] Determined by GC analysis with *m*-xylene as internal standard [c] $T =$ 40 °C.

pressure at ambient temperature (26–28 °C). Selected experiments for the catalytic hydrogenation of acetophenone are outlined in Table 1. It became apparent that catalytic hydrogenation could only be facilitated in alcoholic solvents, with ethanol giving the highest activity by complex **2**. No hydrogenation was observed in THF or neat acetophenone. In MeOH and *i*PrOH *rac*-1-phenylethanol was obtained only in poor yields of 13% and 9%, respectively (Table 1). The hydrogenation of acetophenone in *n*PrOH gives *rac*-1-phenylethanol in 30% yield, while in EtOH the best yield is 94%. Interestingly, slight heating of the reaction mixture to 40 °C gives after only 4 h *rac*-2-phenylethanol in 85% yield with a turnover number of 1720 and a turnover frequency of 430 h^{-1}. This is the highest reported catalytic activity for ketone hydrogenation by iron complexes. It should be noted that both base and H_2 are necessary for the reaction to occur. The strong dependency of the yield on the solvent suggest that an equilibrium with the alcoholic solvent might be involved, as observed previously for ruthenium complexes.[11]

Based on these results the scope and limitations of catalyst **2** were explored, using EtOH as solvent and 4.1 atm hydrogen

Table 2: Hydrogenation of ketones catalyzed by **2**.[a]

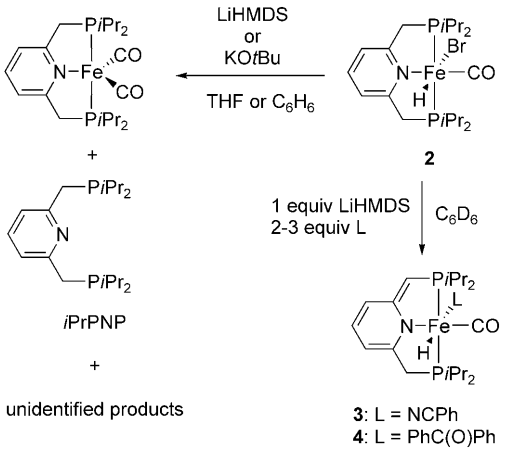


Entry	Substrate	Product	*t* [h]	Yield [%][b]	TON
1			21.5	94 (94)	1880
2	X = Cl		18	86 (89)	1720
3	X = Br		22	78 (78)	1560
4	X = Me		22	72 (73)	1440
5	X = NH_2		24	0 (0)	0
6	X = CN		24	0 (0)	0
7			24	70 (74)	1400
8			24	64 (67)	1280
9			20	67	1340
10			15	54 (54)	1080
11[c]			17	20 (95)	1220
				44	
				29	
12[c]			21	2 (97)	
				10	
				42	
13			15	87 (88)	1740
14[d]			24	36 (39)	288

[a] Reaction conditions: **2** (0.0025 mmol), KO*t*Bu (0.005 mmol), substrate (5 mmol), ethanol (3 mL), *m*-xylene (1 mmol), H_2 (4.1 atm). [b] Yield of alcohol, determined by GC analysis with *m*-xylene as internal standard (conversion of alcohol is in parenthesis). [c] 0.005 mmol **2** and 0.01 mmol KO*t*Bu were used. [d] 2 mmol of PhCHO in 4 mL EtOH were used

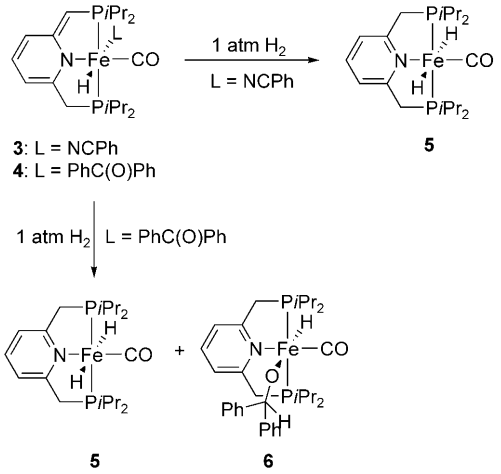
pressure at room temperature. Halogen or methyl substituents on the aromatic system had a small impact on the yield (72–86% yield, Table 2, entry 2–4). Interestingly, no hydrogenolysis of the C–Cl or CBr bonds took place. In the presence of a nitrile or a primary amine group no catalytic activity of complex **2** was observed (Table 2, entries 5 and 6), probably as a result of preferential coordination of these groups. Simple ketones such as benzophenone and cyclohexanone were reduced in good yield of 74% and 67%, respectively (Table 2, entries 7 and 8). Although the diketone benzil was not completely soluble under the reaction conditions, it showed good reactivity as well, resulting in selective hydrogenation to yield the monohydrogenation product benzoin, which quantitatively precipitated during the reaction (67% yield, Table 2, entry 9). The trifluoro-substituted acetophenone, which mainly forms the hemiacetal under the reaction conditions,[12] thus lowering the effective concentration of the ketone, was reduced to the corresponding alcohol in moderate yield of 54% (Table 2, entry 10). The reduction of α,β-unsaturated ketones such as *trans*-4-phenyl-3-buten-2-one or 2-cyclohexenone resulted in mixtures, where reduction of the double bond also took place. 2-Acetylpyridine, which can potentially bind to the iron center, was hydrogenated in very good yield (Table 2, entry 13). Benzaldehyde was hydrogenated only at lower substrate concentrations and with higher catalyst loading (Table 2, entry 14). The reason for the low activity of **2** in the hydrogenation of benzaldehyde is not clear.[13,14]

In order to develop a mechanistic understanding of the catalytic hydrogenation of ketones the reactivity of complex **2** was investigated in stoichiometric reactions. Treatment of **2** with one or two equivalents of base (LiHMDS or KO*t*Bu) in an aprotic solvent (e.g. THF, C_6H_6, toluene) results in immediate decomposition to the Fe^0 complex [(*i*PrPNP)-$Fe(CO)_2$], free ligand (*i*PrPNP), and unidentified paramagnetic products.[15] In contrast to that, no change in ^{31}P NMR spectrum was observed, when two equivalents of KO*t*Bu were added to an EtOH solution of complex **2**.[16] Nevertheless, deprotonation to a dearomatized complex takes place in the presence of 2–3 equivalents of an ancillary ligand like benzonitrile (**3**)[14] or benzophenone (**4**),[14] which probably stabilize the Fe^{II} center by binding at the vacant coordination site (Scheme 2). The $^{31}P\{^1H\}$ NMR spectra of complexes **3** and **4** show AB-systems with doublet signals at $\delta = 83.17$ and 90.70 ppm in case of **3** ($^2J_{PP} = 112.6$ Hz), and doublet signals at



Scheme 2. Reactivity of **2** towards base.

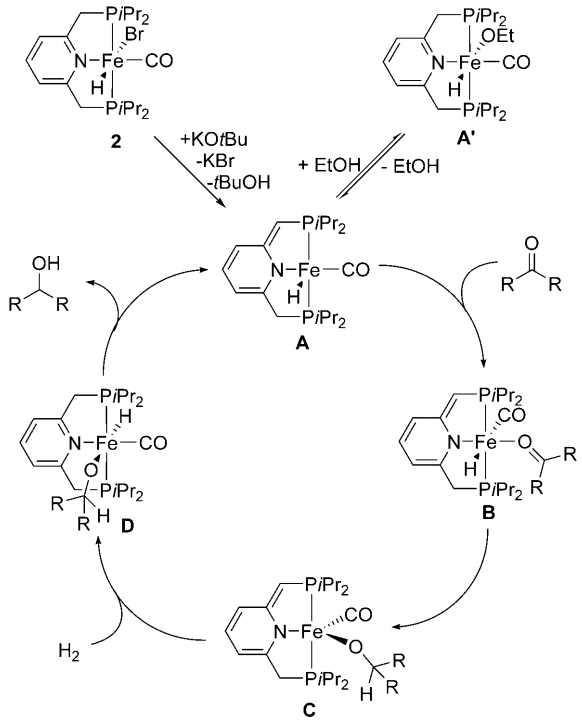
$\delta = 82.73$ and 89.82 ppm in case of **4** ($^2J_{PP} = 102.7$ Hz), corresponding to two inequivalent phosphorus centers, respectively. The hydride ligand exhibits a virtual triplet at $\delta = -15.92$ ppm for complex **3** and a doublet of doublets at $\delta = -14.95$ ppm for complex **4**, indicating that the ancillary ligands are *trans* to the hydride, respectively. A broadened singlet at $\delta = 3.89$ ppm in the ^{1}H NMR spectrum of **3**, which integrates to one and a doublet resonance at $\delta = 64.8$ ppm ($^1J_{PC} = 51.1$ Hz) in the ^{13}C-DEPTQ spectrum suggest the formation of an anionic PNP system (confirmed by ^{1}H-^{13}C-HSQC NMR).



Scheme 3. Reactivity **3** and **4** towards H_2.

Complex **4** reacts rapidly with hydrogen. NMR studies indicate the formation of a hydrido alkoxo complex **6**[14] together with a *trans* dihydride complex **5** (Scheme 3).[14] The selectively decoupled ^{31}P{^{1}H} NMR spectrum of the mixture shows a triplet signal at $\delta = 118.3$ ppm for complex **5**, suggesting that a symmetric dihydride complex was formed, and a doublet signal at $\delta = 90.01$ ppm for complex **6**. The hydride ligands of complex **5** exhibit a triplet at $\delta = -7.36$ ppm ($^2J_{PH} = 39.4$ Hz) in the ^{1}H NMR spectrum, while the hydride ligand in **6** shows a triplet resonance at $\delta = -19.94$ ppm ($^2J_{PH} = 52.5$ Hz). The appearance of triplet signals for both complexes in the ^{1}H NMR spectrum is in agreement with re-aromatized complexes. The three equivalents of benzophenone that were employed to stabilize the dearomatized species were fully converted to the corresponding alkoxide. In contrast to the reactivity of **4**, complex **3** reacts slowly under one atmosphere of hydrogen to give the *trans* dihydride complex **5** (Scheme 3).[14] This observation is in agreement with the low catalytic activity of **2** towards *para*-cyanoacetophenone in the hydrogenation reaction. Thus, it is unlikely that the ketone can be reduced directly by *trans*-[(*i*PrPNP)Fe(H)$_2$(CO)] without pre-coordination. Opening of the phosphorus arm at room temperature to generate a vacant coordination site is not reasonable.

Based on these results a possible reaction mechanism for the hydrogenation of ketones catalyzed by **2** might involve intermediate formation of a reactive dearomatized species, which is stabilized by reversible addition of ethanol to



Scheme 4. Proposed reaction mechanism for the hydrogenation of ketones catalyzed by **2**.

generate the aromatic complex **A′** (Scheme 4). Ketone coordination to **A** followed by isomerization to intermediate **B** makes insertion of the ketone into the Fe–H bond possible. The pentacoordinated alkoxo carbonyl complex **C** can react with hydrogen to give the aromatic hydrido alkoxy complex **D**. Elimination of the product alcohol would regenerate the dearomatized species **A**.

In conclusion, we have developed an efficient iron catalyst for the hydrogenation of ketones under mild conditions. Our NMR studies suggest that the reaction proceeds through a dearomatized intermediate. Ketone coordination, insertion of the ketone into the Fe–H bond of the dearomatized intermediate, followed by addition of hydrogen with re-aromatization likely play key roles in this mechanism. We are currently aiming at expanding the scope of this novel ketone hydrogenation reaction, as well studying its mechanistic implications.

Experimental Section

General procedure for catalytic hydrogenation: A 90 mL Fischer-Porter tube was charged under nitrogen with the catalyst **2** (0.0025 mmol), KO*t*Bu (0.005 mmol), ketone (5 mmol), *m*-xylene (1 mmol), ethanol (3 mL), and 4.1 atm hydrogen. The solution was stirred at ambient temperature (26–28 °C) for the specified time and the product alcohols were determined by GC with *m*-xylene as internal standard, using a Carboxen 1000 column on a HP 690 series GC system.

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Keywords: homogeneous catalysis · hydrogenation · iron complexes · ketones · pincer ligands

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[13] It is possible that this is a result of trace benzoic acid formation (by a Canizzaro-type reaction), which can potentially inhibit the catalytic activity of **2**. Benzene was not observed, negating the possibility of deactivation by CO, that might have been generated by decarbonylation of benzaldehyde.

[14] For details see Supporting Information.

[15] The complex [(*i*PrPNP)Fe(CO)$_2$] was found to be inactive for hydrogenation of ketones under the standard reaction conditions.

[16] While no change in the $^{31}P\{^1H\}$ NMR spectrum was observed, it is possible that the corresponding hydrido ethoxy complex [(*i*PrPNP)FeH(CO)OEt] is formed, as it is expected to have a very similar $^{31}P\{^1H\}$ NMR spectrum to that of **2**. Note that complexes **2** and **6** are very similar in their $^{31}P\{^1H\}$ and ^1H NMR spectra.

