Catalysis Science & Technology

Iron-Catalyzed Highly Efficient, General Hydrogenation of Aldehydes

Journal:	*Catalysis Science & Technology*
Manuscript ID:	CY-COM-11-2014-001501
Article Type:	Communication
Date Submitted by the Author:	16-Nov-2014
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Journal Name RSCPublishing

COMMUNICATION

Highly Efficient, General Hydrogenation of Aldehydes Catalyzed by PNP Iron Pincer Complexes

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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A general protocol for the synthetically important hydrogenation of aldehydes to alcohols is reported. The reactions are catalyzed by well-defined iron pincer complexes that are capable of hydrogenation of aliphatic and aromatic aldehydes selectively and efficiently under mild conditions, with unprecedented turnover numbers.

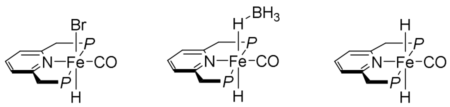
The reduction of carbonyl compounds is a key reaction in organic chemistry and of particular interest for the industrial production of bulk and fine chemicals and pharmaceuticals. The most attractive approach to this end is catalytic hydrogenation using molecular hydrogen, avoiding wasteful use of stoichiometric reductants, or non-atom economical catalytic reactions such as hydrosilylation. Homogenous catalysts often exhibit higher tolerance towards other reducible groups than heterogeneous catalysts. Catalysts for homogenous catalytic hydrogenation reactions usually involve noble metals such as Ru, Rh, Ir and Pt.[1] The substitution of these expensive and potentially toxic noble metals by abundant, inexpensive and environmentally benign metals is very desirable and has prompted significant research efforts. In particular, iron is a very attractive alternative due to its abundance, low cost and low toxicity.

In recent years, there has been significant progress in the development of iron-based catalysts for hydrogenation of various unsaturated substrates, including olefins,[2] alkynes,[2a, 2f, 3] imines,[4] N-heterocycles,[5] CO_2,[6] esters,[7] nitriles,[8] and ketones.[4a, 4c-e, 9] Whereas the iron-catalyzed hydrogenation of ketones is now well documented, iron catalyzed hydrogenation of aldehydes is significantly less investigated.[4a, 4d, 4e, 9f, 10]

In 2007 Casey and Guan reported on the use of Knölker's complex $[\{2,5\text{-}(SiMe_3)_2\text{-}3,4\text{-}(CH_2)_4(\eta^5\text{-}C_4COH)\}Fe(CO)_2H]$ as a bifunctional catalyst for the hydrogenation of ketones.[4a] Notably benzaldehyde was also hydrogenated with a turnover number (TON) of 45 using 2.0 mol% catalyst, 3 atm. of H_2 at 25°C. In the last two years several advancements in this field have been reported. Very recently, cationic analogues of Knölker's complex were synthesized by the Renaud group were applied as catalysts for the hydrogenation of ketones, imines, and aldehydes in water.[4d] For the reported aldehydes, TONs of up to 39 were achieved using 2.5 mol% of iron catalyst, 3.75 mol% Me_3NO in water as solvent employing 10 bar H_2 pressure at 85°C for 14 hours. Similarly, Beller and coworkers reported on a series of modified Knölker complexes and their application as catalysts in hydrogenation reactions of aldehydes and ketones in *iso*-propanol-water mixtures.[9f] In a typical protocol, hydrogenation of aliphatic and aromatic aldehydes resulted in high yields of the corresponding alcohols using 0.1-1.0 mol% of iron catalyst, 0.5-5.0 mol% K_2CO_3, 30 bar of H_2 at 100°C for 17 hours. This corresponds to TONs up to 1000 under these conditions. Furthermore, the Beller group also reported on the development of an *in situ* generated iron catalyst composed of $Fe(BF_4)_2\cdot 6H_2O$ and the tetradentate ligand tris[2-(diphenylphosphino)-phenyl]phosphine.[10] This catalyst system was shown to be very active in the hydrogenation of various aldehydes in the presence of excess trifluoroacetic acid as co-catalyst. Various aldehydes were hydrogenated with excellent conversions using catalyst loadings of 0.2-1.0 mol%, 20 bar of H_2 at 120-140°C in *iso*-propanol as solvent after several hours. Notably, for cinnamaldehyde TONs of up to 2000 were achieved using 40 bar H_2 pressure, which stands as the highest TON reported to date for the iron-catalyzed aldehyde hydrogenation. A somewhat lower TON of 900 was reported by Morris and coworkers for the hydrogenation of benzaldehyde, but this was accomplished under milder reaction conditions.[4e] The authors used a PNP iron pincer precatalyst which required activation by $LiAlH_4$ in *tert*-amyl alcohol. The use of 0.1 mol% precatalyst resulted in a 90% conversion of benzaldehyde to benzyl alcohol with 10 bar H_2 pressure after 2.5 h in THF at 50°C.

Our group has developed a series of iron complexes featuring non-innocent pyridine- or acridine-based pincer ligands and has applied these complexes as efficient catalysts for iron-catalyzed hydrogenation and dehydrogenation reactions.[3b, 6b, 7a, 9d, 9e, 11]

The pincer ligands in these complexes are capable of metal-ligand cooperation by reversible aromatization and dearomatization of the heteroaromatic ligand core caused by protonation and deprotonation of the cooperating ligand site.[12] In 2011, we reported on the application of [(*i*Pr-PNP)Fe(H)(CO)(Br)] (**1**, Scheme 1) as an efficient precatalyst for the hydrogenation of ketones to secondary alcohols.[9d] Whereas **1** needed to be activated by catalytic amounts of strong base, such as KO*t*Bu, the complex [(*i*Pr-PNP)Fe(H)(CO)(BH_4)] (**2**, Scheme 1) is capable of catalyzing this reaction under base free conditions.[9e] Experimental and computational studies on the mechanism revealed the importance of metal ligand cooperation for this catalytic reaction.[9e13] Herein, we report the application of these complexes as efficient catalysts for the hydrogenation of aldehydes with the highest TONs reported to date.



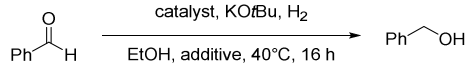
1, with *P* = P*i*Pr$_2$ **2**, with *P* = P*i*Pr$_2$ **3**, with *P* = P*t*Bu$_2$

Scheme 1. Iron pincer complexes used in this study.

In our previous report on the application of complex **1** as precatalyst for the hydrogenation of ketones, we reported that it is less active for the hydrogenation of benzaldehyde to benzyl alcohol. This was presumably due to catalyst deactivation by benzoic acid, which is formed in trace quantities in this reaction via a base mediated Cannizzaro reaction as detected by GC-MS. We observed, however, that the addition of acetophenone increased the activity of the catalyst for the hydrogenation of benzaldehyde. In this reaction, small amounts of the aldol condensation product between benzaldehyde and acetophenone were formed and no benzoic acid was detected.

Encouraged by these preliminary results, we probed the effect of different additives in the hydrogenation of benzaldehyde using 0.05 mol% of **1**, 0.20 mol% KO^{t}Bu and 30 bar H_2 pressure in EtOH[14] at 40 °C and compared the product yields after 16 h (Table 1, entries 1-3). In the presence of 1 mL acetophenone or triethylamine full conversion of benzaldehyde was observed, whereas the reaction without either additive gave only 20% conversion. In the presence of benzaldehyde, minor amounts of 1,3-diphenylpropan-1-one and 1,3-diphenyl-2-propen-1-one were detected (<1%) and, interestingly, no hydrogenation of acetophenone to 1-phenylethanol was observed. Notably, no side products were observed in the reaction with NEt_3. The addition of KO*t*Bu is essential for the reaction, as almost no benzyl alcohol was formed under the same reaction conditions in the absence of KO*t*Bu (entry 4). The borohydride catalyst [(*i*Pr-PNP)Fe(H)(CO)(BH_4)] (**2**) under KO*t*Bu-free conditions resulted in a lower conversion of 62% (entry 5) and the dihydride complex [(*t*Bu-PNP)Fe$(H)_2$(CO)] (**3**) gave a poor conversion of 8% under the same reaction conditions (entry 7). No product was observed in the absence of iron catalyst (entry 8). Testing different amine additives, solvents and temperatures in the reaction (Table S1, S2 and S3, respectively) showed that the highest catalyst activities are achieved with catalyst **1** in the presence of KO*t*Bu, triethylamine or dimethylhexylamine in MeOH or EtOH at 40 °C. Furthermore, we found that the catalyst activity decreases when lower catalyst loadings are used in reactions with a constant catalyst:base ratio of 1:4. When reducing the catalyst loading from 0.050 mol% to 0.025 and 0.010 mol%, the turnover number decreased from 2000 to 1231 and 810, respectively, after 16 h (entries 3, 9, 10). This indicates catalyst deactivation, presumably by benzoic acid formed by base-catalyzed Cannizzaro reaction (vide infra). Next, we checked the effect of hydrogen pressure on the activity of precatalyst **1** in the hydrogenation reaction. In a sequence of reactions in which only the hydrogen pressure was varied in a range of 0 to 70 bar, higher catalytic activity of **1** with rising pressure was observed, as expected (entries 10-14). In the absence of hydrogen no reduction of benzaldehyde was observed (entry 10), ruling out the possibility of a transfer-hydrogenation mechanism.

Table 1. Hydrogenation of benzaldehyde catalyzed by complex 1).[a]



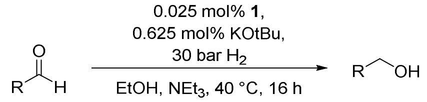
Entry	catalyst ([mol%])	KO*t*Bu [mol%]	$p(H_2)$ [bar]	Additive	Conversion [%][b]	TON
1	**1** (0.050)	0.20	30	-	20	400
2[c]	**1** (0.050)	0.20	30	PhCOMe	>99	2000
3	**1** (0.050)	0.20	30	NEt_3	>99	2000
4	**1** (0.050)	-	30	NEt_3	4	80
5	**2** (0.050)	-	30	NEt_3	62	1240
6	**2** (0.050)	0.20	30	NEt_3	13	260
7	**3** (0.050)	0.20	30	NEt_3	8	160
8	-	0.20	30	NEt_3	<1	0
9	**1** (0.025)	0.10	30	NEt_3	31	1240
10	**1** (0.010)	0.040	30	NEt_3	8	800
11	**1** (0.010)	0.040	0	NEt_3	<1	0
12	**1** (0.010)	0.040	10	NEt_3	3	300
13	**1** (0.010)	0.040	50	NEt_3	15	1500
14	**1** (0.010)	0.040	70	NEt_3	26	2600
15	**1** (0.025)	0.030	30	NEt_3	1	40
16	**1** (0.025)	0.250	30	NEt_3	65	2600
17	**1** (0.025)	0.375	30	NEt_3	91	3640
18	**1** (0.025)	0.625	30	NEt_3	>99	4000
19	**1** (0.025)	1.00	30	NEt_3	16.2	640

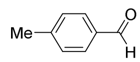
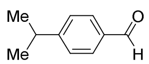
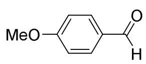
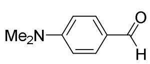
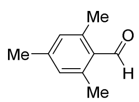
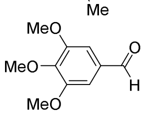
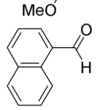
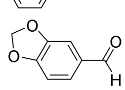
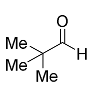
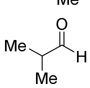
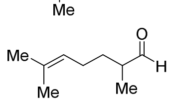
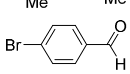
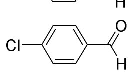
[a] Reaction conditions: Benzaldehyde (5.0 mmol), 40°C, 16 h, EtOH (2 mL), additive (1 mL), performed in a Parr autoclave (45 mL). [b] Based on integration of the ^1H NMR spectra. [c] 1,3-diphenylpropan-1-one and 1,3-diphenyl-2-propen-1-one were detected (<1%).

Interestingly, the catalytic activity of **1** strongly depends on the quantity of KO*t*Bu. A series of hydrogenation reactions of benzaldehyde were performed using complex **1** (0.025 mol%),with varying amounts of KO*t*Bu in EtOH/NEt_3 at 40°C under 30 bar H_2, and the conversions of benzaldehyde were compared after 16 h (entry 5, 15-19). Full conversion of benzaldehyde to benzyl alcohol was achieved using a 25 fold excess of KO*t*Bu with respect to **1** (entry 18). The use of lower, as well as higher KO*t*Bu loadings resulted in lower yields. Ultimately we achieved a TON of 4000, which is significantly higher than reported for other iron catalysts.

Under these conditions various other aldehydes were smoothly hydrogenated to the corresponding alcohols (Table 2). Aromatic as well as secondary and tertiary aliphatic aldehydes were reduced in good to quantitative yields. Notably other functional groups such as acyclic- (entry 3, 6) and cyclic ethers (entry 8), amines (entry 4), and C=C double bonds (entry 12) remained intact during the catalytic hydrogenation, and quantitative conversions were also observed for sterically hindered substrates such as mesitylaldehyde (entry 5), 2-naphthaldeyde (entry 7), and pivaldehyde (entry 9). In the case of 4-bromo- and 4-chlorobenzaldehyde (entry 12, 13) the corresponding ethyl benzoates were formed as side products by base-catalyzed Tishchenko reaction of the substrates with the solvent, and the yields of the corresponding alcohols were low.

Table 2. Substrate scope of hydrogenation reactions catalyzed by complex **1**.[a]

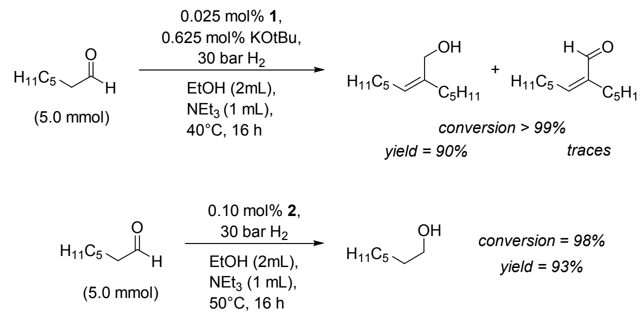


Entry	Aldehyde	Conversion, [%][b]	Yield, [%][c]	TON
1		>99	>99	4000
2		>99	>99	4000
3		>99	>99	4000
4		>99	>99	4000
5		>99	>99	4000
6		>99	95	3800
7		>99	98	3920
8		>99	94	3760
9		>99	98	3920
10		87	74	2960
11		>99	95	3800
12[d]		35	24	960
13[e]		22	15	600

[a] Reaction conditions: Aldehyde (5.0 mmol), p(H_2) = 30 bar, 40 °C, 16 h, EtOH (2 mL), NEt_3 (1 mL), performed in a Parr autoclave (45 mL), average of two runs. [b] Based on integration of the ^{1}H NMR spectra [c] Based on integration of the ^{1}H NMR spectra or determined by GC analysis with mesitylene as standard. [d] 11% of ethyl 4-bromobenzoate were formed. [e] 15% of ethyl 4-chlorobenzoate were formed.

In order to determine if the catalysis is homogeneous, poisoning experiments were conducted in the hydrogenation of cuminaldehyde under the same reaction conditions (Table S5). No poisoning of the catalyst was observed in the presence of an excess of mercury or PMe_3 (30 % with respect to **1**), indicating that catalysis by nanoparticles is unlikely.[15] However, the addition of benzoic acid is detrimental for the catalyst. When a reaction was performed in the presence of 0.25 mol% benzoic acid (10 equiv. with respect to catalyst **1**) a conversion of only 15 % was obtained.

Interestingly, when heptanal, was used as substrate under the same reaction conditions (Z)-2-pentylnon-2-en-1-ol was obtained in 90% yield (Scheme 2). This product is formed via base catalyzed aldol condensation of heptanal to give (Z)-2-pentylnon-2-enal and subsequent hydrogenation of the C=O bond of the product α,β-unsaturated aldehyde. Whereas traces of (Z)-2-pentylnon-2-enal were found in the GC-MS spectrum of the reaction mixture, no evidence for a partial hydrogenation of the C=C bond was observed by NMR and GC-MS spectra. In order to avoid aldehyde condensation catalyzed by the strong base KO*t*Bu, the borohydride complex **2** was used as catalyst in absence of this base. Indeed, under these conditions the selective hydrogenation of primary aldehydes to primary alcohols was possible. Thus hydrogenation of heptanal in the presence of 0.1 mol% catalyst **2** using 30 bar of H_2 pressure at 50°C gave 1-heptanol in 93% yield after 16 h (Scheme 2).



Scheme 2. Hydrogenation reactions of heptanal.

In conclusion, we have developed a general method for the iron-catalyzed hydrogenation of aldehydes to alcohols. The well-defined iron pincer complex [(*i*Pr-PNP)Fe(H)(CO)(Br)] (**1**) is an efficient precatalyst for the hydrogenation and of secondary and tertiary aliphatic aldehydes and aryl aldehydes. These reactions proceed smoothly under mild conditions (30 bar, 40°C) and low catalyst loadings (0.025 mol%) to give the products in good to quantitative yields. This protocol is not suitable for primary aldehydes, as aldol condensation proceeds faster than the hydrogenation of the primary aldehydes so that the corresponding enols are obtained selectively. However, selective hydrogenation of primary aldehydes to primary alcohols is possible by the iron pincer complex [(*i*Pr-PNP)Fe(H)(CO)(BH_4)] (**2**) under KO*t*Bu free conditions. Overall this constitutes the most active system for iron-catalyzed hydrogenation of aldehydes, achieving unprecedented turnover numbers.

This research was supported by the European Research Council under the FP7 framework (ERC No. 246837) and by the MINERVA Foundation. T.Z. received a postdoctoral fellowship from the MINERVA foundation and D.M. holds the Israel Matz Professorial Chair and thanks the Humboldt Foundation for the Meitner-Humboldt Research Award.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details and additional catalytic experiments. See DOI: 10.1039/c000000x/

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