Reduction

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General and Highly Efficient Iron-Catalyzed Hydrogenation of Aldehydes, Ketones, and α,β-Unsaturated Aldehydes**

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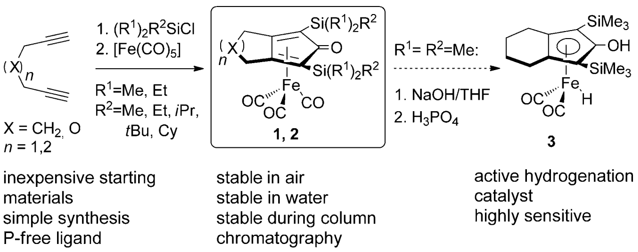
The reduction of carbonyl compounds constitutes one of the most important catalytic methods in synthetic organic chemistry both on laboratory and industry scale.[1] The products of this transformation, namely primary, secondary, and allylic alcohols, represent key building blocks in the pharmaceutical, agrochemical, fine-chemicals, and fragrance industry.[2]

To date metal hydride reagents, hydrosilylation reactions, and transfer hydrogenations are frequently employed for such reductions. However, the stoichiometric formation of undesired by-products does not meet the requirements for sustainable synthesis. On the contrary, catalytic hydrogenation represents a 100 % atom-efficient methodology.[3] Often, heterogeneous catalysts are used in industry because of their facile separation and potential recyclability. However, their major drawback is the limited tolerance towards functional groups, especially towards other reducible moieties such as olefins, alkynes, and nitro-, ester-, and amide functional groups. Therefore, easily tuneable homogeneous hydrogenation catalysts have attracted great interest during the last decades. The majority of the known homogeneous and heterogeneous catalyst systems are based on precious metals such as ruthenium, rhodium, iridium, and palladium.[4] As a result of their restricted availability, high price, and potential toxicity, the search for more economical and environmentally friendly catalysts based on nonprecious analogues (Fe, Cu, Zn, Mn) is a real and challenging goal.

Clearly, a state-of-the-art hydrogenation catalyst should be based on inexpensive materials (metal, ligand, or support) and should be easy to synthesize and convenient to handle. Additionally, it should be highly active and show excellent selectivity towards a broad range of functional groups.

Even though reduction catalysts based on iron are highly attractive candidates to meet these criteria, the field of iron-catalyzed hydrogenation of carbonyl compounds still remains underrepresented.[5–7] Notably, Casey and Guan developed the first efficient iron system for hydrogenation of carbonyl compounds in 2007.[8] By using the highly air-sensitive complex **3** (Scheme 1), various simple aldehydes and ketones were reduced under mild reaction conditions. Unfortunately, industrially important α,β-unsaturated carbonyl compounds showed very low chemoselectivity with this system. In 2011, Milstein and co-workers developed a defined iron pincer complex[9] based on their elegant work on similar ruthenium complexes.[10] To date, this catalyst represents the most efficient iron-based system for the reduction of ketones [turnover number (TON) = 1880]. However, benzaldehyde was reduced in only 36 % yield even with increased catalyst loading, while α,β-unsaturated substrates gave mixtures of hydrogenated products with moderate yields.



Scheme 1. Synthesis of the tricarbonyl(η^4-cyclopentadienone)iron complexes **1** and **2**.

Based on our interest in iron-catalyzed reductions,[11] we recently set out to develop improved iron complexes for the reduction of different kinds of carbonyl compounds. First, we synthesized eight different tricarbonyl(η^4-cyclopentadienone)iron complexes (**1a**–**f** and **2a**–**b**) in a straightforward two-step procedure starting from either commercially available 1,6-heptadyines or 1,7-octadiynes, iron pentacarbonyl, and chlorotrialkylsilanes in excellent yield (Scheme 1 and Table 1).[12]

In contrast to the known complex **3**,[13] and Milstein's pincer complex,[9] all synthesized iron complexes can be handled without special precautions. In fact, they are stable in air and water, and can be purified by column chromatography on silica gel. Next, we wondered if the hydrogenation of carbonyl compounds would be possible by using an in situ Hieber base reaction to activate the tricarbonyl(η^4-cyclopentadienone)iron complexes.[13,14]

Considering the industrial importance of 1-arylethanols, our initial catalytic investigations were carried out using the hydrogenation of acetophenone (**4a**) as a benchmark reaction (Table 1). As expected the blank reaction without the iron

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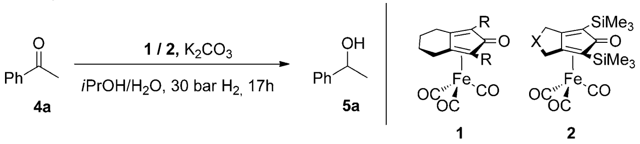
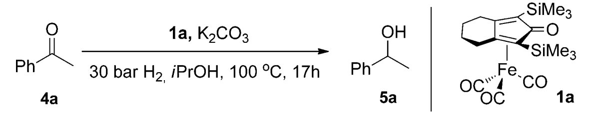
Table 1: Different iron complexes for the catalytic hydrogenation of acetophenone.[a]



Entry	Fe catalyst (mol %)	Yield[b] [%]	TON
1	–	<1	–
2[c]	**1a**: R = $SiMe_3$ (1)	<1	–
3	**1a**: R = $SiMe_3$ (0.01)	37	3700
4	**1b**: R = $SiEtMe_2$ (0.01)	34	3400
5	**1c**: R = $Si\textit{i}PrMe_2$ (0.01)	<1	–
6	**1d**: R = $Si\textit{t}BuMe_2$ (0.01)	38	3800
7	**1e**: R = $SiCyMe_2$ (0.01)	22	2200
8	**1f**: R = $SiEt_3$ (0.01)	21	2100
9	**2a**: X = CH_2 (0.01)	21	2100
10	**2b**: X = O (0.01)	<1	–
11	$[Fe(Cp^*)_2]$ (1)	<1	–
12	$[\{CpFe(CO)_2\}_2]$ (0.5)	<1	–

[a] General reaction conditions: acetophenone (1.0 mmol), Fe complex **1/2** (0.01 mol %), K_2CO_3 (0.05 mol %), *i*PrOH/H_2O (0.5 mL/0.2 mL), H_2 (30 bar), at 100 °C for 17 h. [b] Determined by GC analysis using hexadecane as an internal standard. [c] Reaction without base. Cp = C_5H_5, Cp* = C_5Me_5, Cy = cyclohexyl.

Table 2: Influence of different reaction parameters on the iron-catalyzed hydrogenation of acetophenone.[a]



Entry	Solvent	**1a** (mol %)/ K_2CO_3 (mol %)	*T* [°C]	*p* (bar)	Yield[b] [%]
1	EtOH/H_2O	1:2	80	10	>99
2	*i*PrOH/H_2O	1:2	80	10	>99
3	DME/H_2O	1:2	80	10	>99
4	THF/H_2O	1:2	80	10	>99
5	DMF/H_2O	1:2	80	10	51
6	DMSO/H_2O	1:2	80	10	3
7	tol/H_2O	1:2	80	10	<1
8	*i*PrOH/H_2O	0.1:0.5	60	10	8
9	*i*PrOH/H_2O	0.1:0.5	80	10	77
10	*i*PrOH/H_2O	0.1:0.5	100	10	60
11	*i*PrOH/H_2O	0.1:0.5	130	10	63
12	*i*PrOH/H_2O	0.1:0.5	100	30	>99
13	*i*PrOH/H_2O	0.1:0.5	100	50	92
14	*i*PrOH/H_2O	0.05:0.25	100	30	>99
15	*i*PrOH/H_2O	0.01:0.05	100	30	37

[a] General reaction conditions: acetophenone (1.0 mmol), **1a** (0.01–1 mol %) K_2CO_3 (0.05–2 mol %), organic solvent/H_2O (0.5 mL/0.2 mL), H_2 (10–30 bar) for 17 h. [b] Determined by GC analysis using hexadecane as an internal standard. DME = dimethoxyethane, DMF = *N*,*N*-dimethylformamide, DMSO = dimethylsulfoxide, THF = tetrahydrofuran.

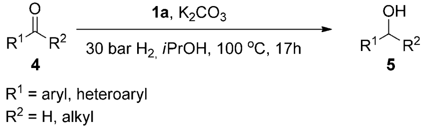
catalyst did not show any activity (Table 1, entry 1). When **1a** was used in a mixture of *i*PrOH and H_2O without base no product formation was observed (Table 1, entry 2). To our delight adding a tiny amount of K_2CO_3 (0.05 mol %) to the reaction mixture led to the smooth hydrogenation of acetophenone even with a catalyst loading as low as 0.01 mol % (Table 1, entry 3; TON = 3700). This result represents the highest TON for the hydrogenation of carbonyl compounds with any iron-based catalysts to date. Comparable high TONs of up to 3800 were observed when **1b** and **1d** were used as catalyst precursors (Table 1, entries 4 and 6). While **1e**, **1f**, and **2a** gave lower TONs (Table 1, entries 7–9), **1c** and **2b** did not yield any product at all (Table 1, entries 5 and 10). When the cyclopentadienone moiety was displaced by Cp and Cp* no reaction occurred, and thus indicates the importance of the non-innocent character of the ligand (Table 1, entry 11 and 12).

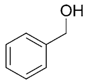
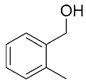
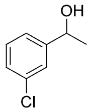
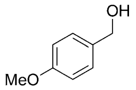
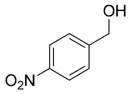
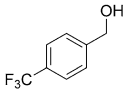
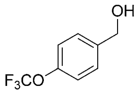
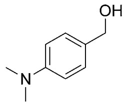
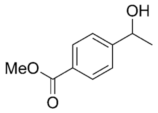
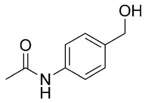
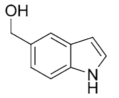
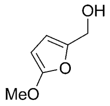
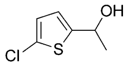
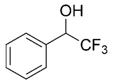
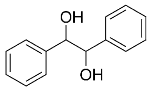
Next, the influence of critical reaction parameters such as solvent, temperature, pressure, and catalyst loading were investigated. The hydrogenation of **3a** showed full conversion and excellent yields of greater than 99 % when aqueous alcoholic solutions such as EtOH and *i*PrOH as well as aqueous ethereal solutions as DME and THF were used as solvents (Table 2, entries 1–4). In a DMF/water mixture a moderate yield of 51 % was obtained (Table 2, entry 5), whereas DMSO gave only trace amounts of **5a** (Table 2, entry 6). When a nonpolar solvent such as toluene was used in combination with H_2O no product is formed (Table 2, entry 7). The observations that reductions are possible in ethereal solvent mixtures of DME and THF, as well as in DMF, and that no reduction occurred in the absence of hydrogen gas, clearly indicate a hydrogenation mechanism.

Next, the influence of temperature and pressure were investigated. In the range of 80–130 °C the hydrogenation of **4a** with a low hydrogen pressure of 10 bar gave good yields of **5a** in the range of 60–77 % even with a low catalyst loading of 0.1 mol % **1a** (Table 2, entries 9–11). When 60 °C was applied as reaction temperature the yield drops down to 8 % (Table 2, entry 8). Increasing the pressure from 10 bar to 30 bar led to full conversion and an excellent yield of greater than 99 % (Table 2, entry 12). Finally, the catalyst loading was decreased to 0.05 mol % and to our delight, the yield remained as high as greater than 99 % (Table 2, entry 14). Further lowering to 0.01 mol % of **1a** yielded the product in a 37 % yield (Table 2, entry 15).

With the optimized reaction conditions in hand, we investigated the scope and limitations of the iron-catalyzed hydrogenation protocol. First, we considered the hydrogenation of different benzaldehydes and aromatic ketones. Besides the hydrogenation of acetophenone, benzaldehyde was also hydrogenated smoothly in high yield (94 %; Table 3, entry 1). We then focused our attention on the influence of different functional groups. Remarkably, different aryl aldehydes and ketones bearing various electron-withdrawing and electron-donating groups in the *ortho*-, *meta*-, and *para*-positions showed high reactivity with excellent yields in the range of 94–99 % with catalyst loadings of 0.1–0.5 mol % (Table 3, entries 2–5). Furthermore, we investigated substrates with pharmaceutically relevant trifluoromethyl, trifluoromethoxy, amino, ester, and amide substituents as well as heterocycles. To the best of our knowledge, there is no iron-catalyzed hydrogenation reaction of carbonyl compounds reported which tolerates these functional groups. We were pleased to find that all these compounds were hydrogenated smoothly and **5g**–**5k** were obtained with good to excellent

Table 3: Iron-catalyzed hydrogenation of aromatic/heteroaromatic aldehydes and ketones to primary and secondary alcohols.[a]

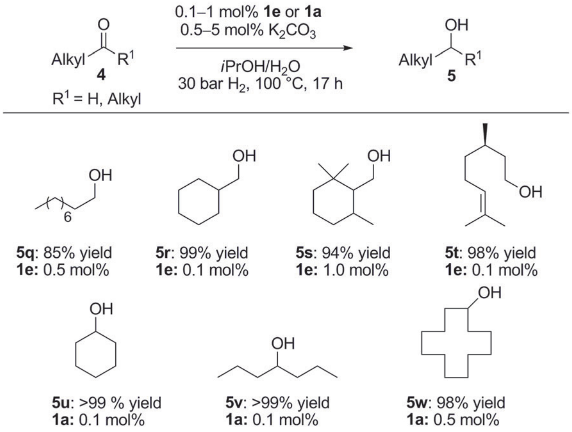


Entry	Product		**1a** (mol %)	Yield[c] [%]
1		**5b**	0.1	94 (89)
2		**5c**	0.5	99
3		**5d**	0.1	98
4		**5e**	0.1	99 (96)
5		**5f**	0.1	99 (96)
6		**5g**	1	98
7		**5h**	1	>99
8		**5i**	0.1	>99
9		**5j**	0.5	76
10		**5k**	0.1	99 (92)
11		**5l**	0.5	95
12		**5m**	0.1	>99 (97)
13		**5n**	0.5	82
14		**5o**	0.5	>99
15		**5p**	0.5	>99[c]

[a] General reaction conditions: aldehyde or ketone **4** (1.0 mmol), **1a** (0.01–1 mol%), 5-fold excess K_2CO_3 (0.05–5 mol%), iPrOH/H_2O (0.5 mL/0.2 mL), H_2 (10–30 bar) for 17 h. [b] Determined by GC analysis using hexadecane as an internal. Yield of isolated product given within parentheses. [c] *cis/trans* ratio 4:1.

yields (60–>99%). Similarly, different substituted N-, O- and S-heteroaromatic aldehydes and ketones gave high yields of (Table 3, entries 11–13). Notably, α-trifluoroacetophenone was hydrogenated with excellent yield (>99%) to the corresponding alcohol **5o** (Table 3, entry 14). In the hydrogenation of the α-diketone benzil both keto functionalities were reduced and the industrially important α-diol hydrobenzoin is produced in 95% yield (Table 3, entry 15).

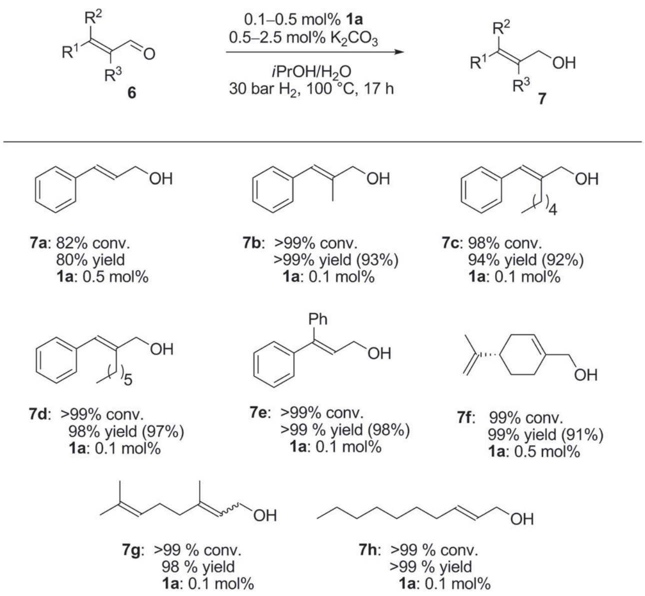
The hydrogenation of aliphatic aldehydes and ketones using iron catalysts is only scarcely investigated. Therefore, seven different aliphatic aldehydes as well as cyclic and aliphatic ketones (**4q–w**) were explored. Again all substrates were hydrogenated with good to excellent yields (85–<99%) to the corresponding alcohols **5q–w** (Scheme 2). Sterically demanding substrates, for example, **4s**, did not lead to a drop in catalyst activity. Moreover, citronellal (**4t**) is selectively reduced to citronellol (**5t**), which is an important compound for the fragrance industry, in excellent yield of 98%. Notably, the catalytic system leaves the double bonds untouched.



Scheme 2. Iron-catalyzed hydrogenation of aliphatic aldehydes and ketones into allylic and secondary alcohols.

Finally, we were interested in the hydrogenation of α,β-unsaturated aldehydes. In principle three different products are possible resulting from either the hydrogenation of the double bond, the carbonyl group, or the hydrogenation of both functionalities. Therefore, product mixtures are often observed. Gratifyingly, our catalyst system selectively reduces the C=O bond, thus yielding allylic alcohol **7** as the only product (Scheme 3). The further transformation of allylic alcohols into key building blocks of complex molecular architectures is well established in organic synthesis.[15]

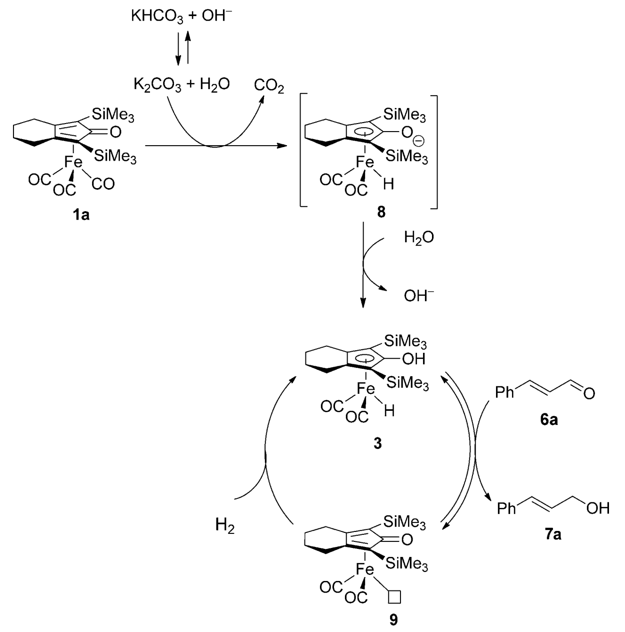
Cinnamyl alcohol (**7a**), as well as the α- and β-substituted cinnamyl alcohols **7b–e** were also obtained in good to excellent yields (90–>99%). The industrially important perillyl alcohol (**7f**) and geraniol (**7g**) were delivered in 98–99% yields, and again no hydrogenation of the double bonds was observed. Simple aliphatic *trans*-2-decenal (**6h**) was also reduced nicely and the corresponding allylic alcohols **7h** was obtained with excellent yield. We also wanted to investigate the scale-up of the reaction procedure to a synthetically applicable scale of 5 grams of starting material. Gratifyingly,



Scheme 3. Iron-catalyzed hydrogenation of α,β-unsaturated aldehydes into allylic alcohols.

the hydrogenation of 5 grams of **6c** with a catalyst loading of 0.5 mol% **1a** yielded **7c** in 96% after distillation (for ^{1}H NMR spectrum of the crude reaction mixture, see the Supporting Information).

On the basis of previous work of the groups of Casey[8] and Knölker,[13] as well as our own findings, we propose the following mechanism (Scheme 4). As no hydrogenation occurs in the absence of K_2CO_3, first the base has to activate the 18-electron iron(0) precatalyst **1a**. Hydroxide adds to one carbon monoxide, which is coordinated to the iron center of **1a** and the hydride complex **8** is formed with the release of CO_2 by a Hieber base reaction. After protonation, the 18-electron iron(II) species **3** is formed, and **3** can transfer one hydride and one proton to reduce **6a** and the 16-electron iron(0) species **9** is formed. Oxidative addition of hydrogen closes the catalytic cycle by formation of the iron(II) hydride complex **3**.



Scheme 4. Postulated mechanism.

In conclusion, we have demonstrated that easy-to-synthesize, air- and water-stable iron complexes such as **1a** can be used for the efficient hydrogenation of carbonyl compounds. The compound **1a** is conveniently activated in alcohol/water solutions using inexpensive K_2CO_3 as a base. Notably, the catalyst system shows a high tolerance towards a variety of functional groups such as halides, methoxy, nitro, trifluoromethyl, trifluoromethoxy, amines, esters, amides, and N-, O-, and S-heterocycles. High yields, up to greater than 99%, were observed in the hydrogenation of aromatic and aliphatic aldehydes and ketones as well as α,β-unsaturated aldehydes to primary, secondary, and allylic alcohols. TONs of up to 3800 are obtained and the catalytic procedure can be easily scaled up. All this makes the new protocol highly attractive for the selective reduction of various carbonyl compounds.

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