# Discrete Iron Complexes for the Selective Catalytic Reduction of Aromatic, Aliphatic, and α,β-Unsaturated Aldehydes under Water–Gas Shift Conditions

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The water–gas shift reaction (WGSR) of carbon monoxide and water to give carbon dioxide and hydrogen [Eq. (1)] is a very important industrial process.[1] For instance, it plays a major role in steam reforming of alkanes to produce hydrogen. Therefore, it is the basis of important bulk hydrogenation processes, most notably the catalytic reduction of molecular nitrogen to form ammonia in the Haber-Bosch process.[2]

$$CO + H_2O \overset{cat.}{\rightleftharpoons} CO_2 + H_2 \qquad (1)$$
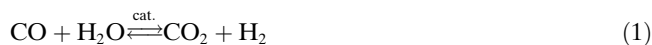
In general, WGSRs are performed in the presence of stable heterogeneous catalysts at high temperatures and pressures. As an example, Fe_3O_4 or copper metal are employed as catalysts at temperatures up to 350 °C.[3] However, since the early 1970s, the development of homogenous catalysts based on Ru, Rh, Ir, and Pt has also been investigated in order to perform the WGSR under milder reaction conditions, typically at temperatures around 100 °C.[1] In addition to noble-metal catalysts, less expensive discrete molecular iron complexes have also been investigated for use in this reaction. Hence, as early as 1978, King and co-workers demonstrated that simple iron pentacarbonyl catalyzes the WGSR,[4] although temperatures as high as 180 °C were required.

From a conceptual point of view, the WGSR allows the use of carbon monoxide and water as a source of hydrogen. Therefore, catalytic hydrogenations might be performed with a mixture of CO and water as the reductant. Surprisingly, this approach has not been widely studied.[5] Based on our general interest in developing selective iron-catalyzed reductions,[6] we started to investigate the reduction of unsaturated compounds with the WGSR as a source of hydrogen in the presence of discrete iron complexes.[7] During the last decade, several elegant iron-catalyzed hydrogenations, transfer hydrogenations and hydrosilylations, especially of carbonyl compounds (Scheme 1), have been developed.[7,8] However, to the best of our knowledge, no iron-catalyzed reductions under WGSR conditions have been reported to date.[9] Herein, we demonstrate that it is possible to selec-
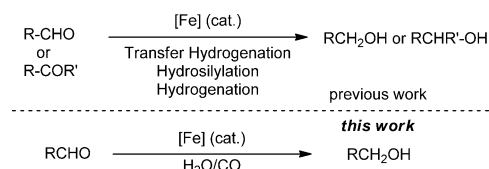
Scheme 1. Iron-catalyzed reduction of carbonyl compounds with various reductants.
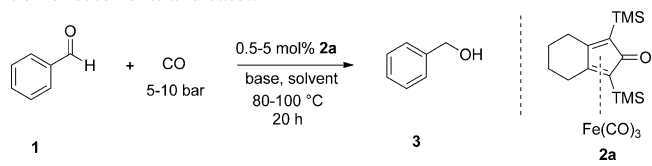
tively reduce a variety of aldehydes by using cheap carbon monoxide and water as the source of hydrogen in the presence of discrete cyclopentadienyliron–tricarbonyl complexes. Previously, this type of complex had been synthesized by Knölker and co-workers. Later, Casey and co-workers elegantly demonstrated that such iron complexes can be used for the reduction of ketones under a low pressure of molecular hydrogen.[10,11,12]

Initial experiments were carried out with benzaldehyde as a model substrate, 10 bar of carbon monoxide in the presence of various bases and solvents, and the stable cyclopentadienyliron–tricarbonyl complex **2a**. It is noteworthy that **2a** is the precursor of the "Knölker iron complex" (**2b**), which has mainly been applied to ketone hydrogenations, but is also significantly more sensitive to oxygen than **2a** and therefore difficult to handle. In the presence of potassium carbonate in pure water, benzyl alcohol was obtained in 24 % yield (Table 1, entry 1). Addition of THF as a cosolvent improved the reactivity significantly and the desired product was observed in 77 % yield (Table 1, entry 3). Benzyl alcohol was formed in an even better yield (95 %) when DMF was employed as the cosolvent (Table 1, entry 4). Interestingly, in the case of DMF, a byproduct resulting from the reductive amination of the decomposed DMF and benzaldehyde was also observed (5 % yield). The most efficient and selective system is formed when the reaction is carried out in DMSO and an excellent yield of 99 % was achieved (Table 1, entry 5).

To investigate the role of the base in our system, various inorganic bases (Cs_2CO_3, KOH, and LiOtBu) and one organic base (NEt_3) were tested in the model system (Table 1, entries 6–9). From these experiments, it can be concluded that K_2CO_3 is the base of choice for this system. Control experiments showed that the iron catalyst and base are necessary for the reduction (Table 1, entries 10 and 11). The catalyst showed good activity (94 % yield) even when lower cat-

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Table 1. Iron-catalyzed reduction of benzaldehyde by the WGSR: Variation of cosolvents and bases.[a]

	Solvent [1 M]	Base [2 equiv]	2a [mol%]	Yield[b] [%]
1	H_2O	K_2CO_3	5	24
2	PhMe/H_2O 1:1	K_2CO_3	5	0
3	THF/H_2O 1:1	K_2CO_3	5	77
4	DMF/H_2O 1:1	K_2CO_3	5	95
5	DMSO/H_2O 1:1	K_2CO_3	5	99
6	DMSO/H_2O 1:1	Cs_2CO_3	5	85
7	DMSO/H_2O 1:1	KOH	5	45
8	DMSO/H_2O 1:1	LiOtBu	5	49
9	DMSO/H_2O 1:1	Et_3N	5	9
10	DMSO/H_2O 1:1	–	5	0
11	DMSO/H_2O 1:1	K_2CO_3	–	0
12	DMSO/H_2O 1:1	K_2CO_3	1	99
13	DMSO/H_2O 1:1	K_2CO_3	0.5	94
14	DMSO/H_2O 1:1	K_2CO_3 (1 equiv)	1	99, 70[c], 89[d]

[a] Reactions performed with benzaldehyde (1 mmol), base (2 mmol), **2a** and CO (10 bar) unless otherwise noted. [b] GC yields calculated with hexadecane as internal standard, average of two runs. [c] Reactions performed with 5 bar of CO. [d] Reaction performed at 80 °C.

alyst loadings (as little as 0.5 mol% of **2a**) were tested. Similarly, high yields were obtained when 1 equivalent of K_2CO_3 was used or when the reaction was performed under 5 bar of CO or at lower reaction temperatures. As shown in Scheme 2, different iron carbonyl complexes were evaluated in the model reaction (1 mol% catalyst loading). In addition to the air- and moisture-stable complex **2a**, application of the more sensitive complex **2b** also resulted in a quantitative yield. Only disappointing results are obtained with other commercially available iron carbonyl complexes, such
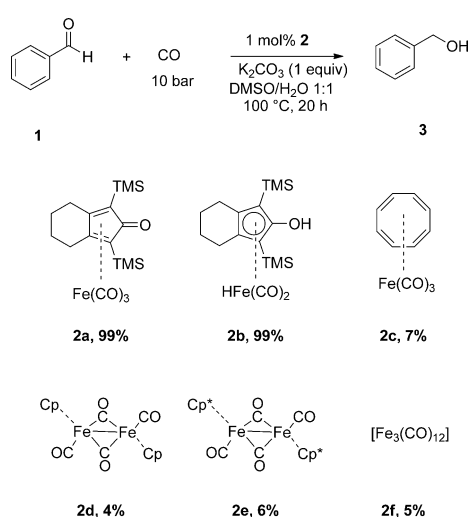
Scheme 2. Testing different iron–carbonyl complexes for the reduction of benzaldehyde to benzyl alcohol. Cp = Cyclopentadienyl, Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl.

as **2c**, **2d** and **2e**. It is worth noting that higher catalyst loadings (5–10 mol%) did not lead to increased yields in these cases. Finally, only very low conversion was detected by using simple iron dodecacarbonyl (**2f**) as a precatalyst.

Regarding the mechanism of this reduction, we believe that hydroxide will attack the carbonyl coordinated to the iron center. Subsequently, carbon dioxide will be eliminated and an active iron hydride species is formed, which should be responsible for the reduction.[1]

The substrate scope and potential limitations of the reaction were also explored (Table 2). With aromatic aldehydes that bear either electron-donating (Table 2, entries 1–6) or electron-withdrawing groups (Table 2, entries 9–13), the corresponding benzylic alcohols were obtained in excellent yields in most cases. It is noteworthy that *ortho*-substituted derivatives also gave nearly quantitative yields of the desired products (Table 2, entries 2 and 4). Nitrile, chloro, trifluoromethyl, methoxy, and trifluoromethoxy substituents were tolerated under these conditions. In contrast, nitriles completely inhibited the hydrogenation of C=O bonds by the iron system developed by Casey and Guan[10] and the authors explain the observed inhibition by postulating that the nitrile group of 4-acetylbenzonitrile is trapped by the unsaturated iron intermediate. In addition, we found that several heterocyclic aldehydes were reduced smoothly in good to excellent yields (Table 2, entries 14–18). It should be noted that the iron catalyst system shown here is highly selective towards the reduction of aldehydes under the reaction conditions described. When similar reactions were performed with nitrobenzene, methyl benzoate, benzonitrile, styrene, or phenylacetylene, no reduction occurred. However, in the case of acetophenone a 5% yield of the corresponding benzylic alcohol is obtained in the presence of 1 mol% of **2a**.

After observing general activity with aromatic aldehydes, we turned our attention to more challenging aliphatic aldehydes. The first substrate tested, citronellal, was reduced to citronellol in excellent yield (99%) in the presence of 5 mol% of **2a** (Table 3, entry 1). Several cyclic and branched aliphatic aldehydes were converted into the corresponding alcohols in quantitative yields with only 1 mol% of the iron catalyst (Table 2, entries 2–5). Exemplarily, the reduction of nonanal was carried out with 5 mol% of **2a** and 2 mmol of base, leading to the formation of 1-nonanol in 62% yield (Table 3, entry 6).

Four different α,β-unsaturated aldehydes were then tested as substrates.[13] In general, the iron catalyst reduces both the carbonyl group and the α,β-double bond. When the double bond is activated by an additional aryl group, an approximately 1:1 mixture of the allylic alcohol and the saturated alcohol was obtained. However, in the case of aliphatic α,β-unsaturated aldehydes the major product was the allylic alcohol (Scheme 3).

Finally, scale-up experiments in the presence of 1 mol% of the iron catalyst **2a** were carried out to demonstrate the applicability of the procedure developed. Benzaldehyde (20 mmol) was converted to the desired product with full

Table 2. Iron-catalyzed reduction of aromatic aldehydes: Substrate scope.[a]

	Aromatic aldehyde	Product	2a [mol %]	Yield[b] [%]
1			1	99 (96)
2			1	99
3			1	99
4			1	99
5			1	97 (92)
6			1	99
7			1	99 (95)
8			1	99
9			1	99
10			1	99 (94)
11			1	82
12			2	76
13			1	96
14			1	66 (59)
15			2	78 (76)
16			1	92

Table 2. (Continued)

	Aromatic aldehyde	Product	2a [mol %]	Yield[b] [%]
17			1	96
18			1	59

[a] Reactions performed with aldehyde (1 mmol), base (1 mmol), **2a** and CO (10 bar). [b] GC yield calculated with hexadecane as internal standard. Yields of the isolated product are in brackets.

Table 3. Iron-catalyzed reductions of aliphatic aldehydes under WGSR conditions.[a]

	Aliphatic aldehydes	Products	2a [mol %]	Yield[b] [%]
1			5	99 (95)
2			1	99
3			1	99
4			1	99 (96)
5			1	92
6			5	62[c]

[a] Reactions performed with aldehyde (1 mmol), base (1 mmol), **2a** and CO (10 bar). [b] GC yields calculated with hexadecane as internal standard. Yields of the isolated product are in brackets. [c] Reaction performed with 2 mmol of base. Isolated yields in brackets.

conversion and an isolated yield of 86%. When the reaction was run on a 10 g scale with 20 bar of carbon monoxide, the product was isolated in 87% yield.

In conclusion, we have developed a selective iron-catalyzed reduction of aldehydes with carbon monoxide as the reductant in the presence of base and water. The generality of this approach is demonstrated by the efficient reduction of 18 aromatic and six aliphatic aldehydes. Furthermore, α,β-unsaturated aldehydes could also be reduced with the catalyst. It is also worth noting that the reaction is easily scaled-up. Currently, further studies into this methodology with other unsaturated compounds are under way in our laboratory.
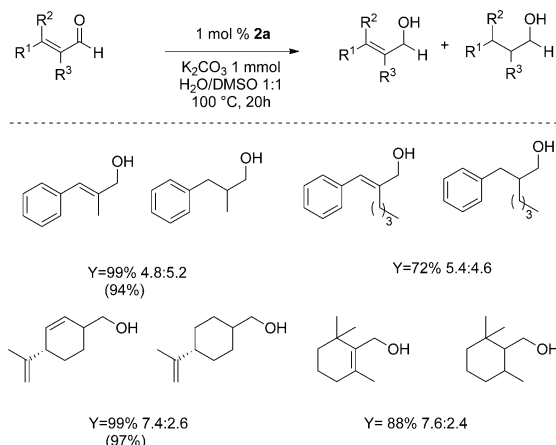
Scheme 3. Iron-catalyzed reduction of α,β-unsaturated aldehydes. Reactions performed with of aldehyde(1 mmol), of base (1 mmol), **2a** (1 mol%) and CO (10 bar). GC yields calculated with hexadecane as the internal standard. Yields of the isolated product are in brackets.

Experimental Section

General comments: All reactions were carried out under an Argon atmosphere. All substrates were purchased from Sigma–Aldrich, Alfa Aesar and Acros Organics and were used as received. Gas chromatographic analysis was performed on an Agilent HP-5890 instrument with an FID detector and an HP-5 capillary column (poly(dimethylsiloxane) with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 mm film thickness) with argon as the carrier gas. Gas chromatography–mass spectroscopic analysis was carried out on an Agilent HP-5890 instrument with an Agilent HP-5973 mass selective detector (EI) and an HP-5 capillary column (poly(dimethylsiloxane) with 5% phenyl groups, 30 m, 0.25 mm i.d., 0.25 mm film thickness) with helium as the carrier gas.

General procedure for the reduction of benzaldehyde: Six glass vials (4 mL) were charged with the precursor of the Knölker iron complex (1 mol%, 4.2 mg), K$_2$CO$_3$ (1 mmol, 138.2 mg), and a stirring bar. All vials were placed into an alloy plate, equipped with a septum and an inlet needle, and then flushed with argon. DMSO (0.5 mL), degassed water (0.5 mL), and benzaldehyde (1 mmol, 102 μL) were injected into each vial. The alloy plate with six vials was then placed in an autoclave (300 mL, Parr Instruments 4560 series). At room temperature, the autoclave was flushed with CO and finally pressurized to 10 bar with CO. The autoclave was then heated to 100°C for 20 h, cooled to room temperature, and the remaining CO was released slowly. After discharging the CO, hexadecane (100 μL) was added to the reaction mixture as the internal standard, and HCl (1 mL, 1 M) was also added. The mixture was stirred for 1 h and the yield determined by GC and GC-MS were also acquired and compared to analyze potential side products. The isolated products were purified by column chromatography.

General procedure for scale-up experiments for the reduction of benzaldehyde: A Teflon sleeve (250 mL) was charged with the precursor of the Knölker iron complex (1 mol%, 393.8 mg), K$_2$CO$_3$ (1 equiv, 13.02 g), were placed in an autoclave (300 mL, Parr Instruments 4560 series, equipped with an impeller) and then flushed three times with argon. DMSO (50 mL), degassed water (50 mL), and benzaldehyde (94.2 mmol, 9.57 mL) were injected into the Teflon sleeve. At room temperature, the autoclave was flushed with CO and pressurized with CO to 20 bar. Afterwards, the autoclave was heated to 100°C for 20 h, then cooled to room temperature, and the remaining CO was released slowly. The reaction mixture was neutralized with HCl (1 M) and stirred for 1 h. After extraction (five times with EtOAc), the combined organic layers were dried over MgSO$_4$. The crude product was purified by column chromatography (Heptane/EtOAc: 80:20).

[1] For some selected reviews on the WGSR see : a) A. J. Esswein, D. G. Nocera, *Chem. Rev.* **2007**, *107*, 4022; b) R. B. King, *J. Organomet. Chem.* **1999**, *586*, 2; c) P. C. Ford, *Acc. Chem. Res.* **1981**, *14*, 31.

[2] a) *Catalytic Ammonia Synthesis: Fundamentals and Practice* (Ed.: J. R. Jennings), Plenum, New York, **1991**; b) R. Schlögl, *Angew. Chem.* **2003**, *115*, 2050; *Angew. Chem. Int. Ed.* **2003**, *42*, 2004; c) M. Appel, *Ullmann's Encyclopedia of Industrial Chemistry: Ammonia*, Wiley-VCH, Weinheim, **2011**.

[3] C. L. Thomas, *Catalytic Process and Proven Catalyst*, Academic Press, New York, **1970**.

[4] R. B. King, C. C. Frazier, R. M. Hanes, A. D. King Jr., *J. Am. Chem. Soc.* **1978**, *100*, 2925.

[5] a) L. He, F.-J. Yu, X.-B. Lou, Y. Cao, H.-Y. He, K.-N. Fan, *Chem. Commun.* **2010**, *46*, 1553; b) L. He, L.-C. Wang, H. Sun, J. Ni, Y. Cao, H.-Y. He, K.-N. Fan, *Angew. Chem.* **2009**, *121*, 9702; *Angew. Chem. Int. Ed.* **2009**, *48*, 9538; c) F. Ragaini, S. Cenini, *J. Mol. Catal. A: Chem.* **1996**, *105*, 145; d) K. Nomura, M. Ishino, M. Hazama, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2624; e) A. J. Pardey, M. Fernandez, A. B. Rivas, M. C. Ortega, C. Urbina, D. Moronta, C. Longo, M. Mediavilla, P. J. Baricelli, S. A. Moya, *Inorg. Chim. Acta* **2002**, *329*, 22; f) S. Moya, R. Sariego, P. Aguirre, R. Sartori, P. Dixneuf, *Bull. Soc. Chim. Belg.* **1995**, *104*, 19; g) J. Y. Jiang, J. T. Mei, Y. H. Wang, F. Wen, Z. L. Jin, *Appl. Catal. A* **2002**, *224*, 21.

[6] For recent selected examples of our results on iron in catalysis, see: a) K. M. Driller, S. Prateeptongkum, R. Jackstell, M. Beller, *Angew. Chem.* **2011**, *123*, 558; *Angew. Chem. Int. Ed.* **2011**, *50*, 537; b) A. Boddien, D. Mellmann, F. Gärtner, R. Jackstell, H. Junge, P. J. Dyson, G. Laurenczy, R. Ludwig, M. Beller, *Science* **2011**, *333*, 1733; c) S. Das, B. Wendt, K. Möller, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2012**, *51*, 1662; *Angew. Chem.* **2012**, *124*, 1694; d) G. Wienhöfer, I. Sorribes, A. Boddien, F. Westerhaus, K. Junge, H. Junge, R. Llusar, M. Beller, *J. Am. Chem. Soc.* **2011**, *133*, 12875; e) K. Junge, B. Wendt, N. Shaikh, M. Beller, *Chem. Commun.* **2010**, *46*, 1769.

[7] For selected recent reviews on and highlights of iron in catalysis, see : a) C. Bolm, J. Legros, J. L. Paith, L. Zani, *Chem. Rev.* **2004**, *104*, 6217; b) S. Enthaler, K. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 3363; *Angew. Chem. Int. Ed.* **2008**, *47*, 3317; c) A. Correa, O. G. Mancheño, C. Bolm, *Chem. Soc. Rev.* **2008**, *37*, 1108; d) E. B. Bauer, *Curr. Org. chem.* **2008**, *12*, 1341; e) W. M. Czaplik, M. Mayer, A. J. von Wangelin, *Angew. Chem.* **2009**, *121*, 616; *Angew. Chem. Int. Ed.* **2009**, *48*, 607; f) K. Junge, K. Schröder, M. Beller, *Chem. Commun.* **2011**, *47*, 4849; g) W. M. Czaplik, M. Mayer, J. Cvengros, A. Jacobi von Wangelin, *ChemSusChem* **2009**, *2*, 396; h) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Rev.* **2011**, *111*, 1293; i) H. Nakazawa, M. Itazaki, *Top. Organomet. Chem.* **2011**, *33*, 27; j) R. H. Morris, *Chem. Soc. Rev.* **2009**, *38*, 2282.

[8] For selected recent examples, see: a) D. Bézier, F. Jiang, T. Roisnel, J.-B. Sortais, C. Darcel, *Eur. J. Inorg. Chem.* **2012**, 1333; b) F. Jiang, D. Bézier, J.-B. Sortais, C. Darcel, *Adv. Synth. Catal.* **2011**, *353*, 239; c) L. C. Misal Castro, D. Bézier, J.-B. Sortais, C. Darcel, *Adv. Synth. Catal.* **2011**, *353*, 1279; d) A. P. Dieskau, J.-M. Begouin, B. Plietker, *Eur. J. Inorg. Chem.* **2011**, 5291; e) R. Langer, G. Leitus, Y. Ben-David, D. Milstein, *Angew. Chem.* **2011**, *123*, 2168; *Angew. Chem. Int. Ed.* **2011**, *50*, 2120; f) P. Bhattacharya, J. Krause, H. Guan, *Organometallics* **2011**, *30*, 4720; g) T. N. Plank, J. L. Drake, D. K. Kim,

T. W. Funk, *Adv. Synth. Catal.* **2012**, *354*, 597; h) E. Buitrago, F. Tinnis, H. Adolfsson, *Adv. Synth. Catal.* **2012**, *354*, 217; i) A. Mikhailine, R. H. Morris, *Inorg. Chem.* **2010**, *49*, 11039.

[9] In 1988, Brunet and Taillefer reported that aryl iodides could be reduced with catalytic amounts of iron pentacarbonyl under 1 bar of CO: J.-J. Brunet, M. Taillefer, *J. Organomet. Chem.* **1988**, *348*, C5.

[10] C. P. Casey, H. Guan, *J. Am. Chem. Soc.* **2007**, *129*, 5816.

[11] For selected reports on the Knölker iron complex in reduction reactions, see: a) C. P. Casey, H. Guan, *J. Am. Chem. Soc.* **2009**, *131*, 2499; b) S. Zhou, S. Fleischer, K. Junge, M. Beller, *Angew. Chem.* **2011**, *123*, 5226; *Angew. Chem. Int. Ed.* **2011**, *50*, 5120; c) A. Pagnoux-Ozherelyeva, N. Pannetier, M. D. Mbaye, S. Gaillard, J. L. Renaud, *Angew. Chem.* **2012**, *124*, 5060; *Angew. Chem. Int. Ed.* **2012**, *51*, 4976.

[12] For enantioselective reductions of C=O bonds, see: a) A. Berkessel, S. Reichau, A. van der Höh, N. Leconte, J.-M. Neuddörfl, *Organometallics* **2011**, *30*, 3880; b) J. P. Hopewell, J. E. D. Martins, T. C. Johnson, J. Godfrey, M. Wills, *Org. Biomol. Chem.* **2012**, *10*, 134; c) J. F. Sonnenberg, N. Coombs, P. A. Dube, R. H. Morris, *J. Am. Chem. Soc.* **2012**, *134*, 5893; d) P. E. Sues, A. J. Lough, R. H. Morris, *Organometallics* **2011**, *30*, 4418; e) P. O. Lagaditis, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **2011**, *133*, 9662; f) T. Inagaki, A. Ito, J.-I. Ito, H. Nishiyama, *Angew. Chem.* **2010**, *122*, 9574; *Angew. Chem. Int. Ed.* **2010**, *49*, 9384; g) T. Inagaki, L. T. Phong, A. Furuta, J. Ito, H. Nishiyama, *Chem. Eur. J.* **2010**, *16*, 3090; h) D. Addis, N. Shaikh, S. Zhou, S. Das, K. Junge, M. Beller, *Chem. Asian J.* **2010**, *5*, 1687;

i) A. Furuta, H. Nishiyama, *Tetrahedron Lett.* **2008**, *49*, 110; j) N. S. Shaikh, S. Enthaler, K. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 2531; *Angew. Chem. Int. Ed.* **2008**, *47*, 2497; k) B. K. Langlotz, H. Wadepohl, L. H. Gade, *Angew. Chem.* **2008**, *120*, 4748; *Angew. Chem. Int. Ed.* **2008**, *47*, 4670; l) H. Nishiyama, A. Furuta, *Chem. Commun.* **2007**, 760.

[13] For a general review, see: a) R. Noyori, T. Ohkuma, *Angew. Chem.* **2001**, *113*, 40; *Angew. Chem. Int. Ed.* **2001**, *40*, 40; for reactions involving Ru or Rh, see: b) T. Ohkuma, H. Ooka, T. Ikariya, R. Noyori, *J. Am. Chem. Soc.* **1995**, *117*, 10417; c) J. M. Grosselin, C. Mercier, G. Allmang, F. Glass, *Organometallics* **1991**, *10*, 2126; for reactions involving Cu, see: d) J.-X. Chen, J. F. Daeuble, D. M. Brestensky, J. M. Stryker, *Tetrahedron* **2000**, *56*, 2153; e) J.-X. Chen, J. F. Daeuble, J. M. Stryker, *Tetrahedron* **2000**, *56*, 2789; f) H. Shimizu, N. Sayo, T. Saito, *Synlett* **2009**, 1295; for a reaction involving gold supported on iron oxide, see: g) C. Milone, M. L. Tropeano, G. Gulino, G. Neri, R. Ingoglia, S. Galvagno, *Chem. Commun.* **2002**, 868; for reactions involving poly(aniline) supported platinum catalysts, see: h) M. Steffan, F. Klasovsky, J. Arras, C. Roth, J. Radnik, H. Hofmeister, P. Claus, *Adv. Synth. Catal.* **2008**, *350*, 1337; i) P. Claus, *Top. Catal.* **1998**, *5*, 51; for mechanistic studies with silver as the catalyst see: j) K. H. Lim, A. B. Mohammad, I. V. Yudanov, K. M. Neyman, M. Bron, P. Claus, N. Rösch, *J. Phys. Chem. C* **2009**, *113*, 13231.