Homogeneous Catalysis

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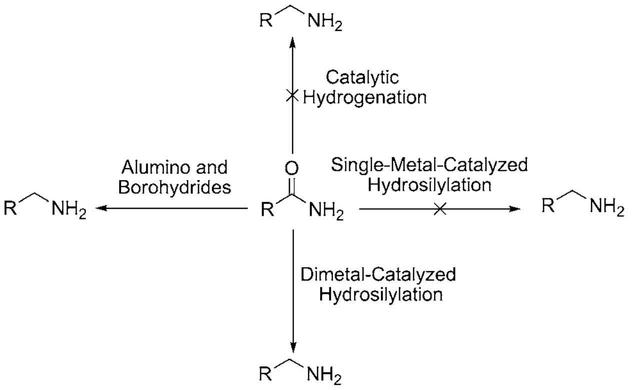
Two Iron Catalysts are Better than One: A General and Convenient Reduction of Aromatic and Aliphatic Primary Amides[**]

*Shoubhik Das, Bianca Wendt, Konstanze Möller, Kathrin Junge, and Matthias Beller**

Substituted amines and their derivatives are of significant importance for the synthesis of numerous products of the pharmaceutical and agrochemical industry. Furthermore, they represent building blocks for fine and bulk chemicals as well as polymers and dyes.[1] In particular, primary amines are useful intermediates for further derivatizations. Owing to their importance, the development of novel methods for the synthesis of primary amines continues to be an active area of research.[2] The most common approaches for their synthesis include reduction of nitriles,[3] reductive amination of aldehydes and ketones,[4] reduction of carboxylic acids in the presence of ammonia,[5] alkylation of organic halides with ammonia or ammonia equivalents,[6] borrowing hydrogenation methodologies,[7] and hydroamination of alkynes.[8] In addition to all these achievements, the selective reduction of primary amides represents a straightforward route to this class of compounds because of the availability of carboxylic acid amides.

So far, for the reduction of primary amides traditional metal hydride-mediated reduction reactions still prevail (Scheme 1).[9] Because of the air and moisture sensitivity of these reagents and the costly purification of the products, selective catalytic methods,[10] especially hydrogenations, are highly desired.[11] Unfortunately, until to date no general catalytic hydrogenation of amides to amines exists.[5]

Complementary to reductions with molecular hydrogen, catalytic hydrosilylations are increasingly often applied in organic synthesis because of their operational simplicity and often improved chemo- and regioselectivity under mild conditions.[12] More specifically, metal-catalyzed hydrosilylations of amides have received considerable interest in the last decade and various catalyst systems have proven to be effective for this reduction.[13] Notably, the vast majority of the known noble metal-based catalysts can be used only for the reduction of more active tertiary or secondary amides. In fact, there is only one report by Igarashi and Fuchikami,[13b] who showed the possibility for the reduction of primary amides. Normally, primary amides are dehydrated to the corresponding nitriles under hydrosilylation conditions.[14]



Scheme 1. Different processes for the reduction of primary amides.

In recent years, iron-based complexes allowed for considerable inventions in organometallic catalysis.[15] Apart from the abundant availability of iron, the often low toxicity and biomimetic pre-catalysts make iron an ideal metal for catalysis.[16] Based on our previous studies using biocatalysts for the reduction of secondary and tertiary amides, herein we report the first general and convenient iron-based catalytic reduction of primary amides.[17]

At the start of our work we investigated the reaction of benzamide (**1**) with inexpensive methyldiethoxysilane in toluene as a model system to identify and optimize critical reaction parameters (Table 1). As expected no reaction occurred in the absence of any catalyst (Table 1, entry 1). In agreement with previously reported results, in the presence of ammonium hydridotriironundecarbonylate benzonitrile was the major product instead of the desired benzyl amine (Table 1, entry 4).[14b,c] Also applying other iron pre-catalysts benzonitrile is formed or no reactivity was observed. In addition, we investigated the influence of several nitrogen-based ligands (Scheme 2) together with different iron salts, for example, $Fe(OAc)_2$ as catalyst precursor in the presence of methyldiethoxysilane to improve the desired reaction (see the Supporting Information). Unfortunately, no progress was achieved.

However, using benzonitrile as a substrate, which is formed from benzamide as shown in Table 1, the latter catalysts proved to be active and provided benzylamine in 85 % yield.[18] The best results are observed in the presence of phenanthroline ligands, which provided high yields of benzylamine. Phenanthrolines substituted with electron-donating groups showed the best activity (Table 2, entries 10–12).

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[*] Dr. S. Das, B. Wendt, Dr. K. Möller, Dr. K. Junge, Prof. Dr. M. Beller
Leibniz-Institut für Katalyse e.V. an der Universität Rostock
Albert-Einstein-Str. 29a, 18059 Rostock (Germany)
E-mail: matthias.beller@catalysis.de
Homepage: http://www.catalysis.de

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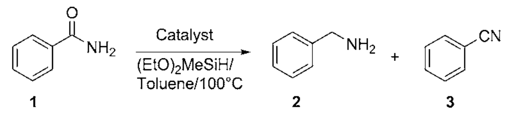
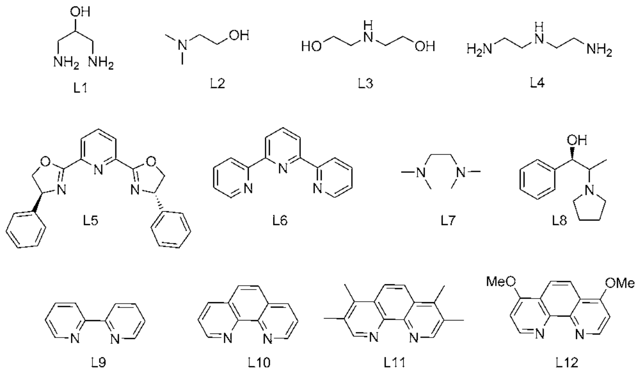
Table 1: Catalytic reduction of benzamide in the presence of iron catalysts.[a]



Entry	Catalyst [mol%]	Solvent	Yield of **2**[b] [%]	Yield of **3**[b] [%]
1	–	toluene	–	–
2	$Fe(OAc)_2$ (10)	toluene	3	83
3	$Fe_3(CO)_{12}$ (10)	toluene	1	83
4	$[Et_3NH][HFe_3(CO)_{11}]$ (5)	toluene	4	90
5	$Fe(acac)_2$ (10)	toluene	–	–
6	FeO (10)	toluene	–	–
7	$Fe(OTf)_2$ (10)	toluene	–	–
8	$Fe(NO_3)_2$ (10)	toluene	–	–
9	$Fe(acac)_3$ (10)	toluene	–	65
10	$FeBr_3$ (10)	toluene	–	–
11	$Fe(OAc)_2$ (10)	dioxane	–	–

[a] Reaction conditions: Benzamide (1.0 mmol), silane (3.0 mmol), solvent (3 mL), 24 h. [b] Determined by GC with hexadecane as an internal standard.



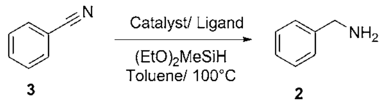
Scheme 2. Structures of different ligands for hydrosilylation of primary amides.

Surprisingly, oxazoline and terpyridine ligands did not show any activity at all (Table 2, entries 5–6). Furthermore, other iron precursors were also not active including ammonium hydridotriironundecarbonylate (Table 2, entries 15–22).

Next, we tried to combine the two different iron-catalyzed reactions. To our delight, the chemoselective reduction to benzylamine is possible in a consecutive manner in the same solvent and with the same silane. As shown in Table 3, this diiron catalysis is performed with 2 mol% of $[Et_3NH][HFe_3(CO)_{11}]$ and 10 mol% of $Fe(OAc)_2$ in the presence of nitrogen-based ligands. Again, the best result (70% of benzylamine) is obtained applying ligand **L11** (Table 3, entry 11). The use of other iron precursors did not increase the yield (Table 3, entries 15–21).

In addition to $(EtO)_2MeSiH$, other silanes such as $PhSiH_3$, Ph_2SiH_2, $(EtO)_3SiH$, PMHS, and TMDS were also tested for this reduction. However, in none of the cases appreciable activity was found (see the Supporting Information). The reaction can be performed also in 1,4-dioxane or di-*n*-

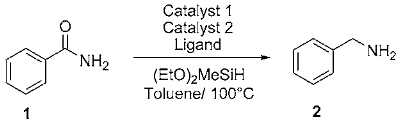
Table 2: Iron-catalyzed reduction of benzonitrile.



Entry	Catalyst [mol%]	Ligand [mol%]	Yield[a] [%]
1	$Fe(OAc)_2$ (10)	L1 (20)	5
2	$Fe(OAc)_2$ (10)	L2 (20)	7
3	$Fe(OAc)_2$ (10)	L3 (20)	–
4	$Fe(OAc)_2$ (10)	L4 (20)	–
5	$Fe(OAc)_2$ (10)	L5 (20)	–
6	$Fe(OAc)_2$ (10)	L6 (20)	–
7	$Fe(OAc)_2$ (10)	L7 (20)	25
8	$Fe(OAc)_2$ (10)	L8 (20)	4
9	$Fe(OAc)_2$ (10)	L9 (20)	40
10	$Fe(OAc)_2$ (10)	L10 (20)	50
11	**$Fe(OAc)_2$ (10)**	**L11 (20)**	**85**
12	$Fe(OAc)_2$ (10)	L12 (20)	75
13	$Fe(OAc)_2$ (10)	L11 (15)	62
14	$Fe(OAc)_2$ (7.5)	L11 (20)	50
15	$Fe(acac)_2$ (10)	L11 (20)	–
16	FeO (10)	L11 (20)	–
17	$Fe(BF_4)_2$ (10)	L11 (20)	10
18	FeF_2 (10)	L11 (20)	15
19	$Fe_3(CO)_{12}$ (10)	L11 (20)	10
20	$Fe(OTf)_2$ (10)	L11 (20)	5
21	$Fe(NO_3)_2$ (10)	L11 (20)	6
22	$[Et_3NH][HFe_3(CO)_{11}]$ (2)	L11 (20)	4

[a] Determined by GC with hexadecane as an internal standard.

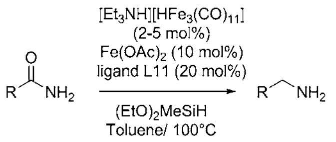
Table 3: Diiron-catalyzed reduction of benzamide.

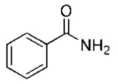
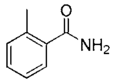
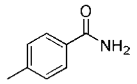
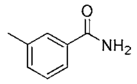
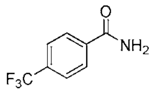
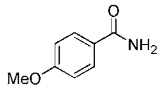
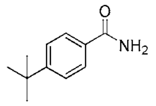
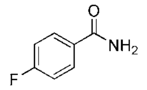
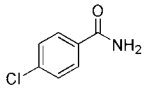
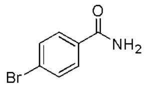
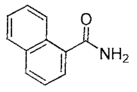
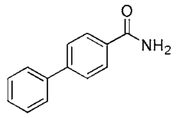
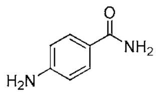
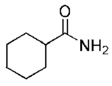
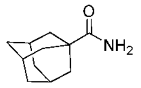


Entry	Fe Catalyst 1 [2 mol%]	Fe Catalyst 2 [mol%]	Ligand [mol%]	Yield[a] [%]
1	$[Et_3NH][HFe_3(CO)_{11}]$	$Fe(OAc)_2$ (10)	L1 (20)	1
2	$[Et_3NH][HFe_3(CO)_{11}]$	$Fe(OAc)_2$ (10)	L2 (20)	3
3	$[Et_3NH][HFe_3(CO)_{11}]$	$Fe(OAc)_2$ (10)	L3 (20)	–
4	$[Et_3NH[HFe_3(CO)_{11}]$	$Fe(OAc)_2$ (10)	L4 (20)	–
5	$[Et_3NH][HFe_3(CO)_{11}]$	$Fe(OAc)_2$ (10)	L5 (20)	–
6	$[Et_3NH][HFe_3(CO)_{11}]$	$Fe(OAc)_2$ (10)	L6 (20)	–
7	$[Et_3NH][HFe_3(CO)_{11}]$	$Fe(OAc)_2$ (10)	L7 (20)	15
8	$[Et_3NH][HFe_3(CO)_{11}]$	$Fe(OAc)_2$ (10)	L8 (20)	2
9	$[Et_3NH][HFe_3(CO)_{11}]$	$Fe(OAc)_2$ (10)	L9 (20)	15
10	$[Et_3NH][HFe_3(CO)_{11}]$	$Fe(OAc)_2$ (10)	L10 (20)	35
11	$[Et_3NH][HFe_3(CO)_{11}]$	**$Fe(OAc)_2$ (10)**	**L11 (20)**	**70**
12	$[Et_3NH][HFe_3(CO)_{11}]$	$Fe(OAc)_2$ (10)	L12 (20)	60
13	$[Et_3NH][HFe_3(CO)_{11}]$	$Fe(OAc)_2$ (10)	L11 (15)	45
14	$[Et_3NH][HFe_3(CO)_{11}]$	$Fe(OAc)_2$ (7.5)	L11 (20)	42
15	$[Et_3NH][HFe_3(CO)_{11}]$	$Fe(acac)_2$ (10)	L11 (20)	–
16	$[Et_3NH][HFe_3(CO)_{11}]$	FeO (10)	L11 (20)	–
17	$[Et_3NH][HFe_3(CO)_{11}]$	$Fe(BF_4)_2$ (10)	L11 (20)	5
18	$[Et_3NH][HFe_3(CO)_{11}]$	FeF_2 (10)	L11 (20)	2
19	$[Et_3NH][HFe_3(CO)_{11}]$	$Fe_3(CO)_{12}$ (10)	L11 (20)	6
20	$[Et_3NH][HFe_3(CO)_{11}]$	$Fe(OTf)_2$ (10)	L11 (20)	5
21	$[Et_3NH][HFe_3(CO)_{11}]$	$Fe(NO_3)_2$ (10)	L11 (20)	4

[a] Determined by GC with hexadecane as an internal standard.

Table 4: Diiron-catalyzed hydrosilylation of primary amides: substrate scope.



Entry	Substrates	$[Et_3NH][HFe_3(CO)_{11}]$ [mol%]	Yield[b] [%]
1		2	70
2		2	70
3		2	68
4		2	68
5		5	65 (59)[a]
6		2	68 (60)[a]
7		2	62 (58)[a]
8		5	63
9		4	60
10		5	65
11		5	60
12		5	60
13		4	58
14		5	52
15	$CH_3(CH_2)_7CONH_2$	4	48
16	$CH_3(CH_2)_4CONH_2$	4	51
17	$CH_3(CH_2)_8CONH_2$	4	49
18		4	53

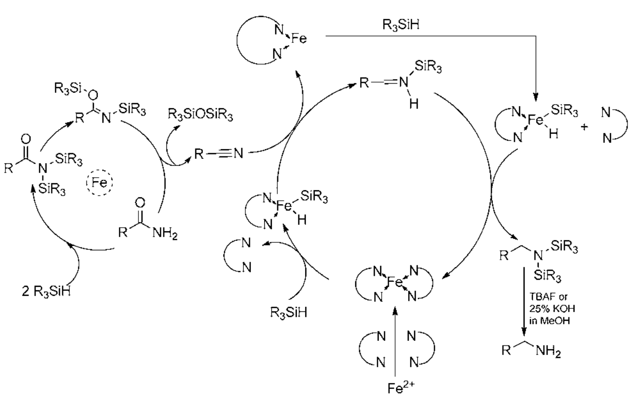
[a] Isolated yields are given in parenthesis for entries 5, 6, and 7. In all other cases GC yields are reported. [b] After the end of the reaction, the mixture was stirred with 4 mL of a 1 M TBAF solution for 3 h and then measured with GC using hexadecane as a standard (for 1 mmol substrate we added 1 mmol of hexadecane).

butylether; however a slower reaction took place in the latter solvents.

Regarding the mechanism (Scheme 3), we propose an initial dehydration of benzamide to benzonitrile with subsequent reduction. Clearly, the different reactivity of the two iron species for the dehydration of benzamide and for hydrosilylation of the corresponding nitrile is surprising. Obviously, benzonitrile is not efficiently hydrosilylated by the iron carbonyl complex (see Table 2, entry 22), which might be explained by the lower coordination ability compared to the Fe^{II} complex. On the other hand, the amide is not activated by $Fe(OAc)_2$.

Next, the scope and limitations of this first iron-catalyzed reduction of primary amides with methyldiethoxysilane were explored. As shown in Table 4, 18 different carboxylic acid amides were reduced smoothly to the corresponding amines. Substrates included various substituted benzamides and higher aromatic amides as well as linear and cyclic aliphatic amides.

In none of the cases any secondary or tertiary amines were observed as side products. With respect to benzamides, both electron-donating and electron-withdrawing substituents behaved in the same manner (Table 4, entries 5–6). In addition, the hydrosilylation took place in case of *ortho*-substituted benzamide (Table 4, entry 2). Noteworthy, the reaction tolerated different halides and amine substituents (Table 4, entries 8–10, and 13). Expediently, several aliphatic amides including adamantanecarboxamide were also reduced to the amines in moderate yield (Table 4, entry 18).



Scheme 3. Proposed mechanism for the diiron-catalyzed reduction of benzamide.

In conclusion, we developed the first iron-catalyzed reductions of primary amides to amines. Notably, the desired transformation does not proceed in the presence of a single metal catalyst, but using two different iron complexes in a consecutive manner allowed for the formation of the primary amine. The generality of this protocol is shown in the hydrosilylation of 18 different primary amides with inexpensive $(EtO)_2MeSiH$. Notable features of our protocol are the selectivity, operational simplicity, and safe and mild reaction conditions.

Experimental Section

General procedure for the reduction of amides: A 25 mL dried Schlenk tube containing a stirring bar was charged with $[Et_3NH][HFe_3(CO)_{11}]$ (2–5 mol %) and the amide (1 mmol). Anhydrous toluene (2 mL) and $(EtO)_2MeSiH$ (3.5 mmol) were added respectively after purging the Schlenk tube with argon. The mixture was stirred at 100 °C and monitored by TLC. After complete disappearance of the substrates, the reaction mixture was cooled to room temperature. At the same time, another 25 mL Schlenk tube containing a stirring bar was charged with $Fe(OAc)_2$ (10 mol %) and ligand (20 mol %). Anhydrous toluene (2 mL) was added and stirred at room temperature for 15 min. Then, 3.5 mmol of $(EtO)_2MeSiH$ was added to the mixture and stirred at room temperature. After 10 min, the reaction mixture from the first Schlenk tube was transferred to the second Schlenk tube under argon atmosphere, washed with a minimum amount of toluene (2 mL). The reaction mixture was stirred at 100 °C for 28 h. After cooling to room temperature, hexadecane was added as a standard to the reaction mixture and washed with THF followed by the addition of 5 mL of 25 % solution of KOH in methanol. The mixture was stirred for 3 h and the yield was determined by GC using hexadecane as an internal standard (for 1 mmol of substrate 1 mmol of hexadecane was added). For isolation of the products the reaction mixture was concentrated to dryness. After addition of diethyl ether, subsequent filtration and concentration in vacuum, the pure product was purified by column chromatography using ethyl acetate and triethylamine.

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Keywords: amides · amines · homogeneous catalysis · iron · reduction

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