EurJOC European Journal of Organic Chemistry

SHORT COMMUNICATION

DOI: 10.1002/ejoc.201300039

Iron-Catalyzed Reduction of Carboxylic Esters to Alcohols

Kathrin Junge,[a] Bianca Wendt,[a] Shaolin Zhou,[b] and Matthias Beller*[a]

Keywords: Synthetic methods / Homogeneous catalysis / Iron / Reduction / Hydrosilanes / Esters / Alcohols

A novel catalytic system formed from Fe(stearate)$_2$/$NH_2CH_2CH_2NH_2$ and polymethylhydrosiloxane was directly developed for the hydrosilylation of carboxylic acid esters to alcohols. The catalytic method exhibits broad substrate scope, including 20 aliphatic, aromatic, and heterocyclic esters. The corresponding alcohols are obtained in moderate to very good yields.

Introduction

Reduction of carbonyl compounds to alcohols is one of the most fundamental transformations in organic synthesis.[1] Here, for the synthesis of special products and on laboratory scale, stoichiometric reactions with boron and aluminum hydrides still prevail.[2] In contrast to these traditional stoichiometric methods, catalysis offers more versatile strategies and might allow for improved selectivities.[3]

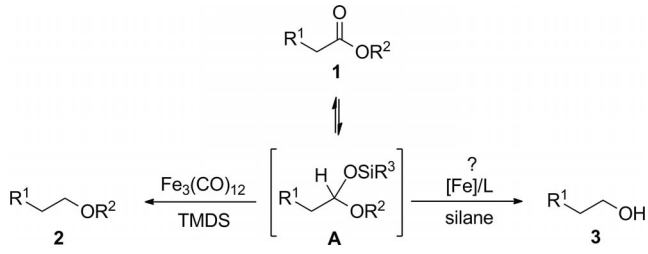
Clearly, catalytic hydrogenation is the ideal method for the reduction of esters. Thus, heterogeneous hydrogenation of fatty esters is realized on bulk scale in industry.[4] However, harsh reaction conditions (200–300 °C and 200–300 atm) are required with the applied catalyst systems, which leads to low functional group tolerance.[5] In contrast, homogeneous hydrogenation of carboxylic esters to alcohols with organometallic complexes is challenging, which is reflected by the limited number of known reports.[6]

Complementary to hydrogenation or transfer hydrogenation, catalytic hydrosilylation is a well-accepted tool that is operationally simple to perform and often allows for high chemoselectivity and regioselectivity under mild conditions.[7] Therefore, over the last decade metal-catalyzed hydrosilylations of esters have received considerable interest. To date, various catalyst systems including Rh,[8] Ru,[9] Mo,[10] Ti,[11] In,[12] Mn,[13] Pd,[14] Zn,[15] and B compounds[16] have proven to be effective for this reduction. Although the majority of the published catalytic systems allow the synthesis of alcohols, only few examples describe the formation of the respective ether.[9b,11–13] Nevertheless, the development of cost-effective, efficient, and highly selective catalysts for this transformation is still desirable, because most of the known protocols either require expensive silanes or have limited functional group tolerance.[17]

[a] Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Straße 29A, 18059 Rostock, Germany
Fax: +49-381-1281-51113
E-mail: Matthias.Beller@catalysis.de
Homepage: www.catalysis.de
[b] College of Chemistry, Central China Normal University Luoyu Road, No. 152, 430079 Wuhan, P. R. China
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201300039.

Results and Discussion

Recently, iron-catalyzed reductions gained increased attention as a result of the economic and ecologic advantages of this metal.[18] Next to its abundance and low toxicity, iron complexes mimic nature, which makes them catalysts of choice.[19] Recently, we published the iron-catalyzed hydrosilylation of carboxylic acid esters to the corresponding ethers by using $Fe_3(CO)_{12}$ and tetramethyldisiloxane (TMDS).[20] Parallel to our work, Darcel described ester reduction by the well-defined iron complex $[CpFe(CO)_2(PCy_3)][BF_4]$ (Cp = cyclopentadienyl, Cy = cyclohexyl) and $PhSiH_3$ to produce a mixture of the corresponding ether and alcohol.[21] This catalytic reaction is supposed to proceed via an *O*-silylated intermediate that is generated by hydrosilylation of the carbonyl group in the ester functionality (Scheme 1). Depending on the reaction conditions, the corresponding ether or alcohol can be formed. On the basis of our experience in the hydrosilylation of carboxylic acid derivatives with non-noble metals,[22] we became interested in developing the first iron catalyst that preferentially transforms esters into alcohols.

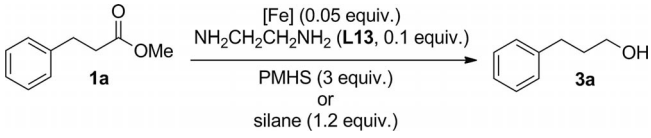


Scheme 1. Iron-catalyzed hydrosilylation of carboxylic acid esters to ethers or alcohols.

In initial experiments, different iron precursors, silanes, and ligands were investigated for the reduction of the model

substrate, methyl 3-phenylpropanoate. In a typical catalytic experiment, the iron salt (5 mol-%), 1,2-diaminoethane (**L13**, 10 mol-%), and polymethylhydrosiloxane (PMHS, 3 equiv.) were used to reduce the carboxylic acid ester (1 mmol). Although most of the iron precursors showed no reactivity at all (Table 1, entries 1–3, 11–17), $Fe(OAc)_2$ and $Fe(stearate)_2$ produced 3-phenylpropanol in up to 86% yield (Table 1, entries 4 and 6). For further optimization, the in situ formed catalyst $Fe(stearate)_2$/**L13** was tested by applying various silanes (Table 1, entries 8–10). Silanes with structural motifs similar to that of PMHS only gave low yields of the desired product (Table 1, entries 8 and 9). Notably, the use of our active catalyst system for ether formation [i.e., $Fe_3(CO)_{12}$] in the presence of N ligands gave no reaction (Table 1, entry 17). As expected by applying $Fe_3(CO)_{12}$ without any ligand, both 3-phenylpropanol and (3-methoxypropyl)benzene were formed (Table 1, entry 18). In addition, no or low reactivity was observed for $Fe(OAc)_2$ and $Fe(stearate)_2$ in the absence of **L13** (Table 1, entries 5 and 7). Clearly, next to the iron precursor, the choice of the ligand has a crucial influence on the formation of the corresponding alcohol or ether.

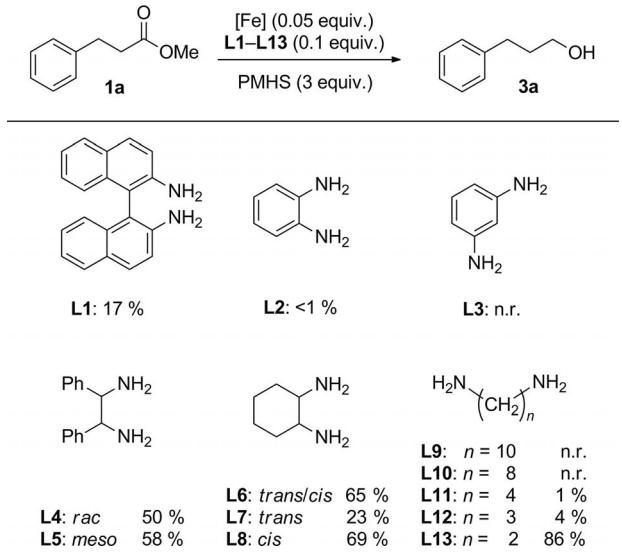
Table 1. Initial screening of iron precursors, silanes, and ligands for reduction of esters.[a]



Entry	[Fe]	Silane	Yield [%][b]
1	$FeBr_2$	PMHS	–
2	$FeCl_2$	PMHS	–
3	$Fe(ClO_4)_2$	PMHS	–
4	$Fe(AcO)_2$	PMHS	63
5[c]	$Fe(AcO)_2$	PMHS	–
6	$Fe(stearate)_2$	PMHS	86
7[c]	$Fe(stearate)_2$	PMHS	5
8	$Fe(stearate)_2$	TMDS	20
9	$Fe(stearate)_2$	$Me_3SiO(Me)Si(H)OSiMe_3$	18
10	$Fe(stearate)_2$	Ph_3SiH	1
11	$Fe(OTf)_2$	PMHS	–
12	Fe_2O_3	PMHS	–
13	Fe_3O_4	PMHS	–
14	$FeCl_3 \cdot 6H_2O$	PMHS	–
15	$FePO_4 \cdot 4H_2O$	PMHS	–
16	$Fe(NO_2)_3 \cdot 9H_2O$	PMHS	–
17	$Fe_3(CO)_{12}$	PMHS	–
18[c,d]	$Fe_3(CO)_{12}$	PMHS	25 (23)
19[d]	$[Et_3NH][HFe_3(CO)_{11}]$	PMHS	24 (17)

[a] Reaction conditions: carboxylic acid ester (1 mmol), [Fe] (5 mol-%), **L13** (10 mol-%), PMHS (3 equiv.) or silane (1.2 equiv.), toluene (2 mL), 20 h, 100 °C. [b] Hexadecane was used as an internal standard. [c] Without ligand **L13**. [d] Yield of ether is given in parentheses. $Fe(stearate)_2 = Fe[CH_3(CH_2)_{16}COO]_2$.

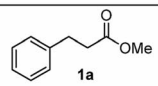
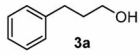
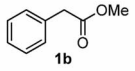
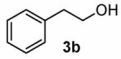
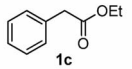
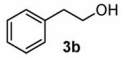
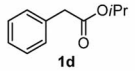
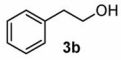
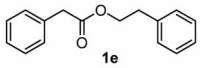
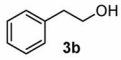
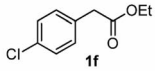
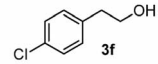
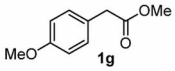
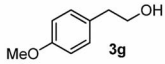
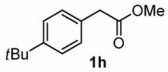
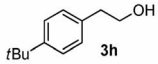
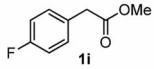
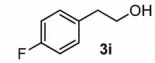
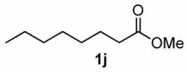
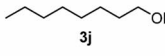
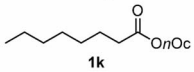
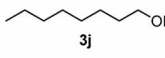
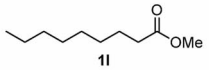
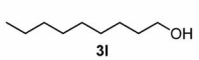
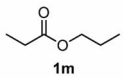
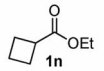
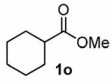
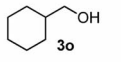
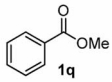
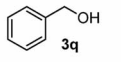
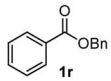
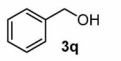
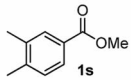
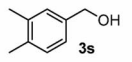
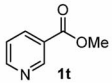
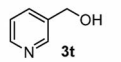
Therefore, different diamino ligands **L1**–**L13** were investigated in the presence of $Fe(stearate)_2$. Here, not only the backbone but also the chain length between the amino functions were varied (Scheme 2). Apparently, an ethylene or C_2 bridge such as in 1,2-diphenylethane-1,2-diamine (**L4**, **L5**), cyclohexane-1,2-diamine (**L6**, **L8**), and 1,2-diaminoethane (**L13**) is beneficial for the catalytic reduction of esters, as they provided good yields of the products (50–86%). Interestingly, for the *trans*/*cis* mixture of cyclohexane-1,2-diamine (**L6**), nearly the same yield (65%) was obtained as that provided by single *cis* isomer **L8** (69%), whereas in the presence of only *trans* ligand **L7**, the yield decreased. A dramatic reduction in catalytic efficiency was observed when the backbone of 1,2-diaminoethane (**L13**) was enlarged by one methylene group (i.e., **L12**).



Scheme 2. Screening of different N-containing ligands for the model reaction. Yields were determined by GC with an internal standard.

Finally, the scope and limitations of the iron-catalyzed hydrosilylation of carboxylic acid esters to alcohols was investigated. Under the optimized conditions [$Fe(stearate)_2$ (5 mol-%), $NH_2(CH_2)_2NH_2$ (**L13**, 10 mol-%), PMHS (3 equiv.), toluene, 20 h, 100 °C], a number of different aliphatic and aromatic esters was reduced (Table 2). In general, aliphatic esters show better results (up to 86% yield) in the catalytic reaction compared to the aromatic substrates (up to 72%). Most of the yields were determined by GC by using an internal standard, but in selected examples the formed alcohols were isolated by column chromatography, and the yields are given in brackets (Table 2, entries 2, 8, 9). There is no significant decrease in the product yield after isolation. For methyl 2-phenylacetate (Table 2, entry 2) the influence of different substituents was investigated in detail. When longer alkyl chains were placed at the ester moiety, higher yields were observed than for the methyl ester (Table 2, entries 3 and 5). In the case of the sterically more demanding isopropyl ester, a slightly lower amount of 2-phenylethanol was formed (Table 2, entry 4). No general trend could be found for *para* substituents on the phenyl ring of methyl-2-phenylacetate. Both, electron-donating and electron-withdrawing groups caused an increase in the product yield (Table 2, entries 8 and 9). In contrast, a reduced yield for the corresponding alcohol was detected for

Table 2. Substrate scope for reduction of esters.[a]

Entry	Ester	Alcohol	Yield [%][b]
1	 1a	 3a	86
2	 1b	 3b	76 (65)
3	 1c	 3b	83
4	 1d	 3b	71
5	 1e	 3b	84[c]
6	 1f	 3f	63[c]
7	 1g	 3g	78[c]
8	 1h	 3h	81 (81)[c]
9	 1i	 3i	75 (72)[c]
10	 1j	 3j	74[d]
11	 1k	 3j	62[d]
12	 1l	 3l	55[e]
13	 1m	 3m	75[c]
14	 1n	 3n	69
15	 1o	 3o	55 62[e]
16	 1p	 3p	64
17	 1q	 3q	59[f]
18	 1r	 3q	72
19	 1s	 3s	62[f]
20	 1t	 3t	35[e]

[a] Reaction conditions: carboxylic acid ester (1 mmol), Fe(stearate)$_2$ (5 mol-%), $NH_2(CH_2)_2NH_2$ (**L13**, 10 mol-%), PMHS (3 equiv.), toluene (2 mL), 20 h, 100 °C. [b] Hexadecane was used as an internal standard; isolated yield is given in parentheses. [c] Carboxylic acid ester (5 mmol), toluene (10 mL). [d] **L8** (10 mol-%). [e] 40 h. [f] Fe(stearate)$_2$ (10 mol-%), $NH_2(CH_2)_2NH_2$ (**L13**, 20 mol-%).

the ester with a chlorine substituent on the phenyl ring (Table 2, entry 6). In addition, linear aliphatic esters could be reduced in good yields (Table 2, entries 10–13). Cyclic carboxylic acid esters form the prevailing alcohols or diol in moderate amounts up to 69% (Table 2, entries 14–16). Moreover, aromatic esters were applied in the iron-catalyzed hydrosilylation to give up to 72% of the alcohol (Table 2, entries 17–19). Regarding heterocyclic acid esters, the efficiency of the catalyst was decreased, and the corresponding alcohol was produced in only 35%, even though the reaction time was extended to 40 h (Table 2, entry 20).

Unfortunately, the functional group tolerance of the aromatic substrates is still limited with this catalytic system (Figure 1). Hence, in methyl 4-(benzylcarbamoyl)benzoate (**1u**) bearing both an ester and an amide group, the amide was preferentially attacked. Furthermore, nitro (in **1v**) and keto groups (in **1w**) were reduced to the amine or the alcohol with our catalyst system, whereas the ester group remained intact.

Figure 1. Aromatic esters showing low functional group tolerance.

Conclusions

The first iron-catalyzed hydrosilylation of carboxylic acid esters to alcohols was described. By using a combination of Fe(stearate)$_2$/$NH_2CH_2CH_2NH_2$ and PMHS, 20 aliphatic, aromatic, and heterocyclic substrates gave the corresponding alcohols in moderate to very good yields (up to 86%).

Experimental Section

General Methods: All chemicals were obtained commercially and were used as received. Fe(OAc)$_2$ was purchased from Aldrich with 99.995% purity on the basis of trace metals analysis. Fe(stearate)$_2$ was available from ABCR (9.57% Fe). With ICP-AES no trace amounts of copper were determined within the detection limit (0.004 mg L^{-1}). PMHS, TMDS, $Me_3SiO(Me)Si(H)OSiMe_3$, and Ph_3SiH were purchased from Aldrich or Merck and were used as received. All isolated compounds were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, HRMS, and HPLC. NMR spectra were recorded with Bruker AV 300 or AV 400 spectrometers. All chemical shifts are related to solvent peaks [chloroform: 7.27 ppm (^{1}H), 77.00 ppm (^{13}C)]. All measurements were carried out at room temperature unless otherwise stated. Mass spectra were generally recorded with a Finnigan MAT 95-XP (Thermo Electron) or a 6210 Time-of-Flight LC/MS (Agilent). GC spectra were measured by using an Agilent GC 7890A.

General Procedure for the Hydrosilylation of Carboxylic Acid Esters: Fe(stearate)$_2$ (0.05 mmol) was placed in an argon-sealed Schlenk tube and dissolved in dry toluene (2 mL). After addition of 1,2-diaminoethane (**L13**, 0.1 mmol), the solution was heated for 15 min at 75 °C. The carboxylic acid ester (1 mmol) was added at room temperature, and the mixture was stirred for 5 min. Finally,

the reaction was initiated by the addition of PMHS (180 μL, 3 equiv.). The reaction mixture was placed in a preheated oil bath (100 °C) for 20 h. Then, hexadecane (GC internal standard, 100 μL per 1 mmol ester) was added at room temperature. The reaction mixture was diluted with THF (4 mL) and carefully quenched with NaOH (25% in MeOH, 300 μL). ***Caution: The reaction mixture bubbles vigorously!*** Conversion and yield were determined by GC analysis without further manipulations and compared with authentic samples. The yield was determined by GC (30 m HP 5 Agilent Technologies 50–300 °C) on the basis of an internal standard (calibration curve). For isolated yields, the catalytic reaction was repeated on a 4–5 mmol substrate scale. After basic quenching of the reaction mixture, the solvents were evaporated. The crude product was purified by column chromatography (pentane/diethyl ether, 4:1→2:1→1:1).

2-Phenylethanol (3b): Yield: 318 mg (4 mmol scale), 65% (isolated). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28–7.20 (m, 2 H, C_6H_5), 7.19–7.11 (m, 3 H, C_6H_5), 3.76 (t, J = 6.6 Hz, 2 H, CH_2), 2.78 (t, J = 6.5 Hz, 2 H, CH_2) 1.57 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.5 (*i*-C_6H_5), 129.1 (*m*-C_6H_5), 128.6 (*o*-C_6H_5), 126.5 (*p*-C_6H_5), 61 (CH_2), 38 (CH_2) ppm. MS (EI): *m*/*z* (%) = 122 (22) $[M]^+$, 103 (3), 91 (100), 77 (6), 65 (23), 63 (9), 51 (10), 39 (12), 31 (7).

2-(4-*tert*-Butylphenyl)ethanol (3h): Yield: 721 mg (5 mmol scale), 81% (isolated). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (d, J = 8.4 Hz, 2 H, C_6H_4), 7.18 (d, J = 8.4 Hz, 2 H, C_6H_4), 3.86 (t, J = 6.7 Hz, 2 H, CH_2), 2.86 (t, J = 6.6 Hz, 2 H, CH_2), 1.65 (s, 1 H, OH), 1.34 (s, 9 H, *t*-C_4H_9) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.4 (*p*-C_6H_4), 135.4 (*i*-C_6H_4), 128.8 (*o*-C_6H_4), 125.6 (*m*-C_6H_4), 63.7 (CH_2), 38.7 (CH_2), 34.5 (*C*-CH_3), 31.4 (C-*C*H_3) ppm. MS (EI): *m*/*z* (%) = 178 (18) $[M]^+$, 163 (100), 147 (14), 132 (11), 117 (30), 143 (8), 105 (15), 91 (19),77 (6), 65 (5), 57 (3), 51 (3), 41 (7), 31 (8).

2-(4-Fluorophenyl)ethanol (3i): Yield: 507 mg (5 mmol scale), 72% (isolated). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22–7.15 (m, 2 H, C_6H_4), 7.04–6.96 (m, 2 H, C_6H_4), 3.82 (t, J = 6.6 Hz, 2 H, CH_2), 2.83 (t, J = 6.5 Hz, 2 H, CH_2), 1.8 (s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 161.5 (d, J = 243.8 Hz, *p*-C_6H_4), 134.2 (d, J = 3.2 Hz, *i*-C_6H_4), 130.4 (d, J = 8.0 Hz, *o*-C_6H_4), 115.3 (d, J = 21.7 Hz, *m*-C_6H_4), 63.6 (CH_2), 38.4 (CH_2) ppm. MS (EI): *m*/*z* (%) = 140 (16) $[M]^+$, 122, (2), 109 (100), 101 (1), 96 (3), 89 (3), 83 (19), 75 (3), 63 (6), 57 (7), 51 (4), 39 (4), 31 (7), 29 (3).

Supporting Information (see footnote on the first page of this article): NMR data and NMR spectra.

Acknowledgments

The authors thank Dr. C. Fischer, S. Buchholz, S. Schareina, K. Fiedler, and S. Rossmeisl (all at the Leibniz-Institut für Katalyse e.V.) for excellent analytical and technical support.

[1] P. G. Andersson, I. J. Munslow (Eds.), *Modern Reduction Methods*, Wiley, New York, **2008**.
[2] J. Seyden-Penne, *Reductions by Alumino and Borohydrides in Organic Synthesis* 2nd ed., Wiley, New York, **1997**.
[3] G. Rothenberg, *Catalysis: Concepts and Green Applications*, Wiley, Weinheim, Germany, **2008**.
[4] Y. Pouilloux, F. Autin, J. Barrault, *Catal. Today* **2000**, *63*, 87–100, and references cited therein.
[5] J. G. de Vries, C. J. Elsevier (Eds.), *Handbook of Homogeneous Hydrogenation*, Wiley-VCH, Weinheim, Germany, **2007**.
[6] For selected references on homogeneous ester reduction, see: a) R. A. Grey, G. P. Pez, A. Wallo, *J. Am. Chem. Soc.* **1981**, *103*, 7536–7542; b) U. Matteoi, M. Bianchi, G. Menchi, P. Frediani, F. Piacenti, *J. Mol. Catal.* **1984**, *22*, 353–362; c) U. Matteoi, G. Menchi, M. Bianchi, P. Frediani, F. Piacenti, *J. Organomet. Chem.* **1986**, *299*, 233–238; d) U. Matteoi, G. Menchi, M. Bianchi, P. Frediani, F. Piacenti, *J. Organomet. Chem.* **1995**, *498*, 177–186; e) H. T. Teunissen, C. J. Elsevier, *Chem. Commun.* **1997**, 667–668; f) H. T. Teunissen, C. J. Elsevier, *Chem. Commun.* **1998**, 1367–1368; g) J. Zhang, G. Leitus, Y. Ben-David, D. Milstein, *Angew. Chem.* **2006**, *118*, 1131–1133; *Angew. Chem. Int. Ed.* **2006**, *45*, 1113–1115; h) L. A. Saudan, C. M. Saudan, C. Debieux, P. Wyss, *Angew. Chem.* **2007**, *119*, 7617–7620; *Angew. Chem. Int. Ed.* **2007**, *46*, 7473–7476; i) W. Kuriyama, Y. Ino, O. Ogata, N. Sayo, T. Saito, *Adv. Synth. Catal.* **2010**, *352*, 92–96; j) Y. Sun, C. Koehler, R. Tan, V. T. Annibale, D. Song, *Chem. Commun.* **2011**, *47*, 8349–8351; k) E. Fogler, E. Balaraman, Y. Ben-David, G. Leitus, L. J. W. Shimon, D. Milstein, *Organometallics* **2011**, *30*, 3826–3833; l) E. Balaraman, E. Fogler, D. Milstein, *Chem. Commun.* **2012**, *48*, 1111–1113; m) I. Carpenter, S. C. Eckelmann, M. T. Kuntz, J. A. Fuentes, M. B. France, M. L. Clarke, *Dalton Trans.* **2012**, *41*, 10136–10140; n) W. Kuriyama, T. Matsumoto, O. Ogata, Y. Ino, K. Aoki, S. Tanaka, K. Ishida, T. Kobayashi, N. Sayo, T. Saito, *Org. Process Res. Dev.* **2012**, *16*, 166–171; o) K. Junge, B. Wendt, F. A. Westerhaus, A. Spannenberg, H. Jiao, M. Beller, *Chem. Eur. J.* **2012**, *18*, 9011–9018; p) D. Spasyuk, S. Smith, D. G. Gusev, *Angew. Chem.* **2012**, *124*, 2826–2829; *Angew. Chem. Int. Ed.* **2012**, *51*, 2772–2775; q) D. Spasyuk, D. G. Gusev, *Organometallics* **2012**, *31*, 5239–5242; r) M. L. Clarke, *Catal. Sci. Technol.* **2012**, *2*, 2418–2423; s) C. Cheng, M. Brookhart, *Angew. Chem.* **2012**, *124*, 9556–9558; *Angew. Chem. Int. Ed.* **2012**, *51*, 9422–9424.
[7] a) I. Ojima, in: *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rapport), Wiley-VCH, Chichester, UK, **1989**, vol. 1; b) B. Marciniec, J. Gulinsky, W. Urbaniak, Z. W. Kornetka, in: *Comprehensive Handbook on Hydrosilylation* (Ed.: B. Marciniec), Pergamon Press, Oxford, **1992**; c) V. B. Pukhnarevich, E. Lukevics, L. T. Kopylova, M. G. Voronkov, in: *Perspectives of Hydrosilylation* (Ed.: E. Lukevics), Institute of Organic Synthesis Riga, **1992**; d) M. A. Brook, in: *Silicon in Organic, Organometallic and Polymer Chemistry*, Wiley, New York, **2000**; e) B. Marciniec, *Coord. Chem. Rev.* **2005**, *249*, 2374–2390.
[8] T. Ohta, M. Kamiya, K. Kusui, T. Michibata, M. Nobutomo, I. Furukawa, *Tetrahedron Lett.* **1999**, *40*, 6963–6966.
[9] a) M. Igarashi, R. Mizuno, T. Fuchikami, *Tetrahedron Lett.* **2001**, *42*, 2149–2151; b) K. Matsubara, T. Iura, T. Maki, H. Nagashima, *J. Org. Chem.* **2002**, *67*, 4985–4988.
[10] A. C. Fernanades, C. C. Romao, *J. Mol. Catal. A* **2006**, *253*, 96–98.
[11] a) S. C. Berk, K. A. Kreutzer, S. L. Buchwald, *J. Am. Chem. Soc.* **1991**, *113*, 5093–5095; b) S. C. Berk, S. L. Buchwald, *J. Org. Chem.* **1992**, *57*, 3751–3753; c) K. J. Barr, S. C. Berk, S. L. Buchwald, *J. Org. Chem.* **1994**, *59*, 4323–4326; d) M. T. Reding, S. L. Buchwald, *J. Org. Chem.* **1995**, *60*, 7884–7890; e) X. Verdaguer, M. C. Hansen, S. C. Berk, S. L. Buchwald, *J. Org. Chem.* **1997**, *62*, 8522–8528.
[12] N. Sakai, T. Moriya, T. Konakahara, *J. Org. Chem.* **2007**, *72*, 5920–5922.
[13] Z. Mao, B. T. Gregg, A. R. Cutler, *J. Am. Chem. Soc.* **1995**, *117*, 10139–10140.
[14] J. Nakanishi, H. Tatamidani, Y. Fukumoto, N. Chatani, *Synlett* **2006**, 869–872.
[15] a) H. Mimoun, *J. Org. Chem.* **1999**, *64*, 2582–2589; b) S. Das, K. Möller, K. Junge, M. Beller, *Chem. Eur. J.* **2011**, *17*, 7414–7417.
[16] D. J. Parks, W. E. Piers, *J. Am. Chem. Soc.* **1996**, *118*, 9440–9441.
[17] For a review on the hydrosilylation of carboxylic esters, see: D. Addis, S. Das, K. Junge, M. Beller, *Angew. Chem.* **2011**, *123*, 6128–6135; *Angew. Chem. Int. Ed.* **2011**, *50*, 6004–6011.

[18] For selected reviews on iron catalysis, see: a) C. Bolm, J. Legros, J. Le Paih, L. Zani, *Chem. Rev.* **2004**, *104*, 6217–6254; b) R. M. Bullock, *Angew. Chem.* **2007**, *119*, 7504–7507; *Angew. Chem. Int. Ed.* **2007**, *46*, 7360–7363; c) S. Enthaler, K. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 3363–3367; *Angew. Chem. Int. Ed.* **2008**, *47*, 3317–3321; d) S. Gaillard, J.-L. Renaud, *ChemSusChem* **2008**, *1*, 505–509; e) R. H. Morris, *Chem. Soc. Rev.* **2009**, *38*, 2282–2291; f) W. M. Czaplik, M. Mayer, J. Cvengroš, A. Jacobi v. Wangelin, *ChemSusChem* **2009**, *2*, 396–417; g) M. Zhang, A. Zhang, *Appl. Organomet. Chem.* **2010**, *24*, 751–757; h) K. Junge, K. Schröder, M. Beller, *Chem. Commun.* **2011**, *47*, 4849–4859; for books on iron catalysis, see: i) B. Plietker (Ed.), *Iron Catalysis in Organic Chemistry*, 1st ed., Wiley-VCH, Weinheim, Germany, **2008**; j) M. Bullock (Ed.), *Catalysis without Precious Metals*, 1st ed., Wiley-VCH, Weinheim, Germany, **2010**; k) B. Plietker (Ed.), *Iron Catalysis: Fundamental and Applications*, Springer, Heidelberg, **2011**.

[19] For selected Fe-catalyzed hydrosilylations, see: a) N. S. Shaikh, K. Junge, M. Beller, *Org. Lett.* **2007**, *9*, 5429–5432; b) H. Nishiyama, A. Furuta, *Chem. Commun.* **2007**, 760–762; c) N. S. Shaikh, S. Enthaler, K. Junge, M. Beller, *Angew. Chem.* **2008**, *120*, 2531–2535; *Angew. Chem. Int. Ed.* **2008**, *47*, 2497–2501; d) A. M. Tondreau, E. Lobkovsky, P. J. Chirik, *Org. Lett.* **2008**, *10*, 2789–2792; e) A. Furuta, H. Nishiyama, *Tetrahedron Lett.* **2008**, *49*, 110–113; f) B. K. Langlotz, H. Wadepohl, L. H. Gade, *Angew. Chem.* **2008**, *120*, 4748–4752; *Angew. Chem. Int. Ed.* **2008**, *47*, 4670–4674; g) A. M. Tondreau, J. M. Darmon, B. M. Wile, S. K. Floyd, E. Lobkovsky, P. J. Chirik, *Organometallics* **2009**, *28*, 3928–3940; h) Y. Sunada, H. Kawakami, T. Imaoka, Y. Motoyama, H. Nagashima, *Angew. Chem.* **2009**, *121*, 9675–9678; *Angew. Chem. Int. Ed.* **2009**, *48*, 9511–9514; i) S. Zhou, K. Junge, D. Addis, S. Das, M. Beller, *Angew. Chem.* **2009**, *121*, 9671–9674; *Angew. Chem. Int. Ed.* **2009**, *48*, 9507–9510; j) T. Inagaki, L. Thanh Phong, A. Furuta, J.-i. Ito, H. Nishiyama, *Chem. Eur. J.* **2010**, *16*, 3090–3096; k) T. Inagaki, A. Ito, J.-i. Ito, H. Nishiyama, *Angew. Chem.* **2010**, *122*, 9574–9577; *Angew. Chem. Int. Ed.* **2010**, *49*, 9384–9387; l) S. Hosokawa, J.-i. Ito, H. Nishiyama, *Organometallics* **2010**, *29*, 5773–5775; m) F. Jiang, D. Bézier, J.-B. Sortais, C. Darcel, *Adv. Synth. Catal.* **2011**, *353*, 239–244; n) L. C. Misal Castro, D. Bézier, J.-B. Sortais, C. Darcel, *Adv. Synth. Catal.* **2011**, *353*, 1279–1824; o) S. Enthaler, *ChemCatChem* **2011**, *3*, 666–670; p) H. Tsutsumi, Y. Sunada, H. Nagashima, *Chem. Commun.* **2011**, *47*, 6581–6583; q) S. Enthaler, *Eur. J. Org. Chem.* **2011**, 4760–4763; r) D. Bezier, G. T. Venkanna, J.-B. Sortais, C. Darcel, *ChemCatChem* **2011**, *3*, 1747–1750; s) M. Haberberger, E. Irran, S. Enthaler, *Eur. J. Inorg. Chem.* **2011**, 2797–2802; t) L. C. Misal Castro, J.-B. Sortais, C. Darcel, *Chem. Commun.* **2012**, *48*, 151–153; u) E. Buitrago, F. Tinnis, H. Adolfsson, *Adv. Synth. Catal.* **2012**, *354*, 217–222; v) C. Belger, B. Plietker, *Chem. Commun.* **2012**, *48*, 5419–5421.

[20] S. Das, Y. Li, K. Junge, M. Beller, *Chem. Commun.* **2012**, *48*, 10742–10744.

[21] D. Bezier, G. T. Venkana, L. C. Misal Castro, J. Zheng, T. Roisnel, J.-B. Sortais, C. Darcel, *Adv. Synth. Catal.* **2012**, *354*, 1879–1884.

[22] a) S. Zhou, K. Junge, D. Addis, S. Das, M. Beller, *Org. Lett.* **2009**, *11*, 2461–2464; b) S. Zhou, K. Junge, D. Addis, S. Das, M. Beller, *Angew. Chem.* **2009**, *121*, 9671–9674; *Angew. Chem. Int. Ed.* **2009**, *48*, 9507–9510; c) S. Zhou, D. Addis, S. Das, K. Junge, M. Beller, *Chem. Commun.* **2009**, 4883–4885; d) S. Das, D. Addis, S. Zhou, K. Junge, M. Beller, *J. Am. Chem. Soc.* **2010**, *132*, 1770–1771; e) S. Das, S. Zhou, D. Addis, S. Enthaler, K. Junge, M. Beller, *Top. Catal.* **2010**, *53*, 979–984; f) S. Das, D. Addis, K. Junge, M. Beller, *Chem. Eur. J.* **2011**, *17*, 12186–12192; g) S. Das, D. Addis, L. R. Knöpke, U. Bentrup, K. Junge, A. Brückner, M. Beller, *Angew. Chem.* **2011**, *123*, 9346–9350; *Angew. Chem. Int. Ed.* **2011**, *50*, 9180–9184.

Received: January 10, 2013
Published Online: March 1, 2013

