Iron-Catalyzed Hydrosilylation of Esters

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Abstract: The first hydrosilylation of esters catalyzed by a well defined iron complex has been developed. Esters are converted to the corresponding alcohols at 100°C, under solvent-free conditions and visible light activation.

Keywords: alcohols; esters; hydrosilylation; iron catalysis; reduction

Carboxylic acids and their derivatives such as esters are abundant in nature and thus are good raw materials for the production of alcohols. However, the reduction of esters using stoichiometric hydride reagents such as LiAlH$_4$, LiBH$_4$, DIBAL-H is still a difficult reaction.[1] In contrast, metal-catalyzed methodologies are generally more selective and more tolerant towards functional groups.[2] Hydrogenation is indeed the representative methodology for the reduction of esters, although low selectivities have sometimes been observed and the usual drastic conditions employed (high temperature and/or hydrogen pressure) can be a limitation to its utilization.[3] In homogeneous conditions, the hydrogenation of esters is less studied than that of ketones,[4] and ruthenium seems then to be the metal of choice to promote this catalytic reaction.[5] Besides hydrogenation, the use of hydrosilanes as reductants is an area of growing interest for the mild and selective reduction of carboxylic acid derivatives.[2] Following the pioneering reduction of esters catalyzed by the metals of the first transition metal row in 1973 by Tsurugi,[6] Buchwald, in the early 1990s, has described the use of titanium alkoxides or titanocene as efficient catalysts for the reduction of esters using triethoxysilane or PMHS as the hydrosilane source.[7] Interestingly, zinc derivatives were used as catalysts and good selectivities were ob-

served.[8] Transition metals such as rhodium,[9] ruthenium,[10] palladium[11] and molybdenum,[12] were also used. Recently Lewis acids such as B(C$_6$F$_5$)$_3$ have shown moderate to good activities for such reductions.[13] Surprisingly, even if the use of iron as catalyst is well exemplified for the hydrosilylation[14] of aldehydes and ketones,[15] amides,[16] even imines,[17] to the best of our knowledge, no report dealing with the hydrosilylation of esters has been published.

During our recent studies on iron-catalyzed transformations,[18] and particularly on hydrosilylation reactions,[15o–q,16d,17] we have developed well-defined complexes, [CpFe(PR$_3$)(CO)$_2$][X], for the catalytic reduction of aldehydes and ketones.[19] Herein, we describe the first hydrosilylation of esters involving these well defined iron complexes used as the pre-catalysts.

We started our investigation with the reduction of methyl phenylacetate as the model substrate under various conditions and with several complexes (Scheme 1 and Table 1). With the complex [CpFe(CO)$_2$(IMes)][I] **4** {IMes=1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene} as the catalyst (5 mol%) with 4 equivalents of phenylsilane under solvent-free conditions at 100°C and with light irradi-
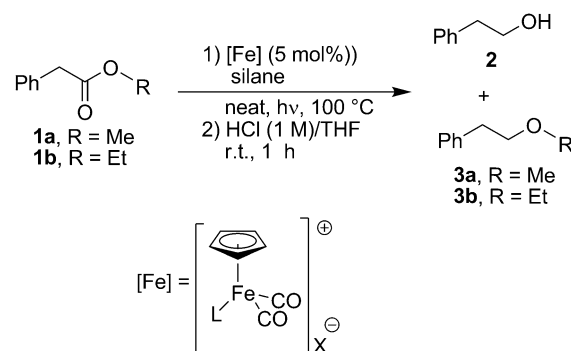
Scheme 1. Reduction of phenylacetate derivatives with piano-stool CpFe(CO)$_2$-type complexes.

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Table 1. Optimization study for the reduction of methyl phenylacetate with piano-stool CpFe(CO)$_2$ type complexes.[a]

Entry	R	Catalyst	Silane (equiv)	Time [h]	Conversion [%][b]	2/3[b]
1	Me	L = IMes, X = I (**4**)	PhSiH$_3$ (4)	24	49	3/2
2	Me	L = PCy$_3$, X = I (**5**)	PhSiH$_3$ (4)	24	85	6/1
3	Me	L = PCy$_3$, X = PF$_6$ (**6**)	PhSiH$_3$ (4)	24	4	100/0
4	Me	L = PCy$_3$, X = BF$_4$ (**7**)	PhSiH$_3$ (4)	24	> 97[d]	100/0
5	Me	L = PPh$_3$, X = BF$_4$ (**8**)	PhSiH$_3$ (4)	24	52	100/0
6	Me	L = PCy$_3$, X = BF$_4$ (**7**)	PhSiH$_3$ (4)	16	> 97	100/0
7	Me	L = PCy$_3$, X = BF$_4$ (**7**)	PhSiH$_3$ (3)	16	95	100/0
8	Me	L = PCy$_3$, X = BF$_4$ (**7**)	PhSiH$_3$ (2)	16	86	100/0
9[c]	Me	L = PCy$_3$, X = BF$_4$ (**7**)	PhSiH$_3$ (4)	24	10	-
10	Me	L = PCy$_3$, X = BF$_4$ (**7**)	Ph$_2$SiH$_2$ (4)	24	14	-
11	Me	L = PCy$_3$, X = BF$_4$ (**7**)	(EtO)$_3$SiH (4)	24	4	-
12	Me	L = PCy$_3$, X = BF$_4$ (**7**)	TMDS (4)	24	4	-
13	Me	L = PCy$_3$, X = BF$_4$ (**7**)	PMHS (5)	24	6	-
14	Me	L = THF, X = BF$_4$	PhSiH$_3$ (4)	72	15	-
15	Et	L = PCy$_3$, X = BF$_4$ (**7**)	PhSiH$_3$ (4)	24	41	11/1
16	Et	L = PCy$_3$, X = BF$_4$ (**7**)	PhSiH$_3$ (4)	66	93	92/8

[a] *Typical conditions:* methyl or ethyl phenylacetate (0.5 mmol), silane (2-5 equiv.), catalyst (5 mol%) were stirred upon visible light irradiation without solvent; the reaction is then hydrolyzed with aqueous 1 M HCl (1 mL) in THF (1 mL) at room temperature for 1 h.
[b] Determined by GC.
[c] Rea0ction performed at 70 °C.
[d] In absence of light irradiation, the conversion was < 5%.

ation, the observed conversion of methyl phenylacetate **1a** was moderate and a mixture of 2-phenylethanol **2** and methyl 2-phenylethyl ether **3a** was obtained in a ratio 3/2.

This reduction was also studied using cationic CpFe(CO)$_2$(phosphine)$^+$ precursors. With the cationic tricyclohexylphosphine iodide complex **5** [CpFe(CO)$_2$(PCy$_3$)][I], 85% conversion was observed, but both alcohol **2** and the ether **3a** were obtained in a 6/1 ratio (Table 1, entry 2). In contrast, with the catalyst **6** [CpFe(CO)$_2$(PCy$_3$)][PF$_6$], only 4% conversion was obtained after 24 h at 100 °C (Table 1, entry 3). As the counterion seems to play a crucial role, we decided to prepare complexes bearing a tetrafluoroborate anion. The cationic complexes **7** and **8** were prepared by analogy to the literature methods.[20]

The molecular structures of the new complex **7**, as well as the complex **8** (see the Supporting Information), were confirmed by X-ray crystallography. ORTEP drawings with the corresponding atom labelling are shown in Figure 1. The structure shows a typical piano-stool geometry.[19,21]

When the complex **7** bearing a tetrafluoroborate counteranion [CpFe(CO)$_2$(PCy$_3$)][BF$_4$] was used as the pre-catalyst, the reduction occurred with full conversion and led selectively to 2-phenylethanol **2**, even in a shorter reaction time (16 h) (Table 1, entries 4 and 6). With the complex **8** [CpFe(CO)$_2$(PPh$_3$)][BF$_4$] under the same conditions, the alcohol **2** was exclusively obtained with 52% conversion (Table 1, entry 5).
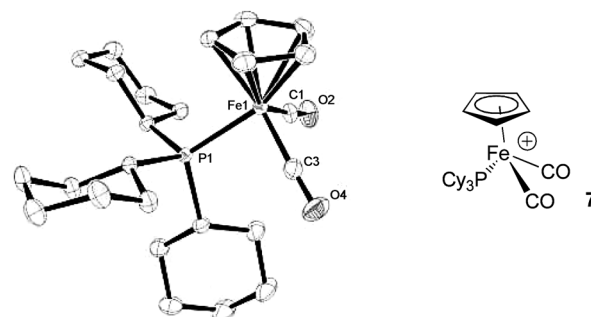

Figure 1. ORTEP view of compound **7** drawn at the 50% probability. Hydrogen atoms and BF$_4$ counterion were omitted for clarity.

When the amount of silane was decreased to 2 equivalents, 86% conversion was obtained (Table 1, entries 7 and 8). The conversion dropped down to 10% when the temperature was lowered to 70 °C (Table 1, entry 9). The importance of the tricyclohexylphosphine ligand for the success of this reduction must be also underlined, as with the precursor [CpFe(CO)$_2$(THF)][BF$_4$], 15% conversion was obtained after 72 h at 100 °C (Table 1, entry 14).[22] Among a variety of silanes tested (Table 1, entries 6, 10–13), optimal conversions were obtained with 4 equivalents of PhSiH$_3$ under solvent-free conditions at 100 °C for 16 h using 5 mol% of the complex **7**. Interestingly, ethyl esters could be reduced using the complex **7** as the catalyst (5 mol%), but longer reac-

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Table 2. Scope of the reduction of methyl esters[a]

Entry	Substrate		Time [h]	Conversion [%][b]	Yield [%][c]
1		R = H	16	95	88
2		R = Me	24	90	70
3		R = Br	24	> 97	83
4		R = OMe	48	> 97	80
5		R = OH	48	> 97	86
6		R = *m*-Me	24	> 97	75
7		R = *o*-Me	24	> 97	73
8			48	> 97	70
9			48	> 97	64
10			16	> 97	83
11			48	> 97	67
12			24	> 97	65
13			45	80	51
14			24	> 97	75[d]

[a] *Typical procedure:* ester (0.5 mmol), PhSiH$_3$ (2 mmol), catalyst **7** (5 mol%) were stirred at 100 °C without solvent upon visible light irradiation for 16-48 h; the reaction is then hydrolyzed with aqueous 1 M HCl in THF (1 mL) at room temperature for 1 h.
[b] Conversion determined by GC.
[c] Isolated yield.
[d] Optical purity = 99%.[23]

tion time (66 h) were necessary to reach a good conversion (93%) with a good selectivity (alcohol **2**/ether **3b** = 92/8) (Table 1, entries 15 and 16).

With this optimized catalytic system in hand, we then explored the scope of the reaction with several methyl esters (Table 2). We have found that the electronic effects at the 4 position of the aromatic ring of phenylacetate derivatives were limited, and the corresponding alcohols were specifically obtained with good isolated yields (70–88%) (Table 2, entries 1–5). Notably, no catalytic dehalogenation occurred during this reaction (Table 2, entry 3). Interestingly, the reaction worked well with methyl 2-(*p*-hydroxyphenyl)-acetate as, after 48 h, the corresponding alcohol was obtained with 86% isolated yield (Table 2, entry 5). In this case, trace amounts of the corresponding 2-(*p*-hydroxyphenyl)ethyl methyl ether (1%) and [2-(*p*-hydroxyphenyl)]ethanal (2%) were detected by GC. The reaction also proceeds well with methyl acetates substituted by *meta*- or *ortho*-substituted phenyl or with 1-naphtyl groups (Table 2, entries 6–8). Methyl 2-phenylbutanoate, which is a more hindered substrate, can be reduced and furnished a moderate yield (64%) of the corresponding 2-phenylbutan-1-ol (Table 2, entry 9). More interestingly, substrates with a heteroaromatic substituent on the methyl acetate such as methyl 2-thienylacetate can be reduced with good yield (83%, Table 2, entry 10). More strikingly, the reaction could be performed with aliphatic esters such as methyl alkanoate derivatives under the same conditions with moderate isolated yields (Table 2, entries 11–13). Moreover, methyl 3-phenylpropanoate can be selectively reduced in the corresponding alcohol with moderate yield (67%, Table 2, entry 11). This iron-catalyzed hydrosilylation of esters is very chemoselective in the presence of a non-conjugated C=C bond as the hydrosilylation of unsaturated esters such as methyl undec-10-enoate and methyl oleate led to

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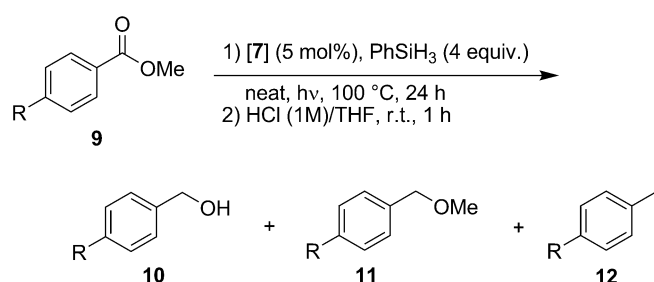
Scheme 2. Reduction of methyl benzoate derivates with $[CpFe(CO)_2(PCy_3)][BF_4]$ **7** as the pre-catalyst.

the corresponding unsaturated alcohols with moderate to good conversions (Table 2, entries 12 and 13).

Surprisingly, the reduction of an α,β-unsaturated ester such as methyl cinnamate under the same conditions proceeds at the C=C bond and leads to a mixture of methyl 3-phenylpropanoate (72% GC yield, 54% isolated yield) and 3-phenylprop-2-enol (14% GC yield), which contrasts with the reactivity observed with an α,β-unsaturated aldehyde.[19]

Of particular interest is the hydrosilylation of (*S*)-methyl mandelate which led after 24 h at 100°C to the corresponding diol with 75% isolated yield and only trace amounts of by-products. It must be underlined that the reduction permits us to obtain an optically active diol[23] (Table 2, entry 14). It must be pointed out that the hydrosilylation of methyl 2-(*p*-nitrophenyl)acetate led to methyl 2-(*p*-aminophenyl)-acetate as the major product with a 52% isolated yield, and a trace amount of the full reduced product, 2-(*p*-aminophenyl)ethanol, which shows that the nitro part was more easily reduced under these conditions.[24]

When performing the hydrosilylation of methyl benzoate derivatives, using the same conditions as above (5 mol% of complex **7**, neat conditions under light activation), we observed the formation of a mixture of three products, the desired benzylic alcohol **10**, the methyl benzyl ether **11** and the substituted tol-

Table 3. Reduction of methyl benzoate derivates with $[CpFe(CO)_2(PCy_3)][BF_4]$ **7** as the pre-catalyst.[a]

Entry		Conversion [%][b]	Ratio **10/11/12**[b]
1	R = H	> 97	65/19/16
2	R = Br	75	1/0/10
3	R = I	> 97	1/0/18
4	R = OMe	53	11/0/42
5	R = Me	38	24/6/8

[a] *Typical procedure:* ester (0.5 mmol), $PhSiH_3$ (2 mmol), catalyst (5 mol%) were stirred at 100°C without solvent upon visible light irradiation for 24 h; the reaction is then hydrolysed with 1 M aqueous HCl in THF (1 mL) at room temperature for 1 h.
[b] Determined by GC.

uene derivate **12** (Scheme 2, Table 3). With methyl benzoate, benzyl alcohol was obtained as the major product, with significant amounts of ether and toluene (Table 3, entry 1). In contrast, with bromo- and iodo-*p*-substituted methyl benzoate, the *p*-halotoluene was the main product with only a trace of a mixture of *p*-halobenzylic alcohol (Table 3, entries 2 and 3). On the other hand, with methoxy- or methyl-*p*-substituted methyl benzoate, the reaction went slower and gave moderate conversions (53 and 38%, respectively), and led to a mixture of alcohol **10** and *p*-substituted toluene derivatives **12** (Table 3, entries 4 and 5).

In summary, we have developed the first catalytic iron-catalyzed hydrosilylation of esters using a well-defined iron complex, $[CpFe(CO)_2(PCy_3)][BF_4]$, as the catalyst. At 100°C, using phenylsilane, under visible light irradiation, the corresponding alcohols were obtained in good to moderate isolated yields in the case of alkanoates or 2-substituted acetates. For benzoates, an overreduction process led mainly to the toluene derivatives. Further investigations into the reactivity of such complexes and directed towards the mechanism of this reaction, especially the role of light and the nature of the active catalytic species, are underway in our laboratory.

Experimental Section

Typical Procedure

In a 20-mL oven-dried Schlenk tube with a stirring bar was loaded the iron complex **7** (15 mg, 0.025 mmol) and the ester (0.5 mmol). The Schlenk tube was then purged on a argon/vacuum system and the silane (1.5–2 mmol) was added. The mixture was stirred at 100°C for 16–48 h under visible light irradiation (24 Watt compact fluorescent lamp). The reaction was quenched by adding 1 mL of HCl (1 M) and 1 mL of THF and stirred during 1 h at room temperature, and then extracted with 2 × 10 mL of Et_2O. The combined organic fractions were washed with brine (3 × 10 mL), dried and concentrated under vacuum. The conversion was determined by ^{1}H NMR and GC. The product was purified by silica gel column chromatography using an ethyl acetate-petroleum ether mixture.

Acknowledgements

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[21] Complex **7** crystallizes in the triclinic space group, P-*1* [$a = 9.723(2)$ Å.; $b = 11.246(3)$ Å.; $c = 11.869(2)$ Å; $\alpha = 89.633(11)°$; $\beta = 83.667(11)°$; $\gamma = 86.318(12)°$; $R = 3.3\%$]. Characteristic bond lengths (Å) about the iron centre are Fe−CO 1.773(2) and 1.784(2), Fe−P 2.2604(6) and Fe−Cp$_{centroid}$ 1.726. Characteristic bond angles (°) about the iron centre are C(1)−Fe−C(3) 97.26(8), C(1)−Fe−P 92.24(6), C(3)−Fe−P 92.15(6). CCDC 873354 and CCDC 873355 contain the supplementary crystallographic data for this paper (complexes **8** and **7**, respectively). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[22] Using salts precursors such as $FeCl_3$, $FeCl_2$, etc. no conversion was observed, see Table S2, in the Supporting Information.

[23] The optical rotation measured for the purified diol is $[\alpha]_D$ observed: $+66.7$ (*c* 1.25, $CHCl_3$); reference: $[\alpha]_D$: $+67$ (*c* 1.0, $CHCl_3$) for (*S*)-(+)-1-phenyl-1,2-ethanediol: D. C. Forbes, S. V. Bettigeri, S. A. Patrawala, S. C. Pischek, M. C. Standen, *Tetrahedron* **2009**, *65*, 70.

[24] The same chemoselectivity was observed for the iron-catalyzed hydrosilylation of nitroarenes into aniline derivatives. See: a) K. Junge, B. Wendt, N. Shaikh, M. Beller, *Chem. Commun.* **2010**, *46*, 1769; b) L. Pehlivan, E. Métay, S. Laval, W. Dayoub, P. Demonchaux, G. Mignani, M. Lemaire, *Tetrahedron Lett.* **2010**, *51*, 1939.

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