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Iron-Catalyzed Reduction

Selective Reduction of Esters to Aldehydes under the Catalysis of Well-Defined NHC–Iron Complexes**

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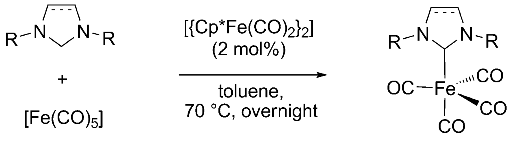
Aldehydes are important building blocks used as reactive intermediates in organic and total synthesis. Their preparation from primary alcohols through oxidative pathways or from carboxylic derivatives by reductive methods is still challenging, as they are usually more reactive than the starting materials towards both oxidation and reduction, and this higher reactivity often leads to chemoselectivity issues.[1] For the specific reduction of esters to aldehydes, bulky reducing agents, such as diisobutylaluminum hydride (DIBAL-H) and lithium tri-*tert*-butoxyaluminum hydride, have been used at low temperature for this transformation.[2] However, such reagents can be difficult to handle in air and are only moderately compatible with other functional groups. Alternative methodologies are reduction reactions catalyzed by transition-metal complexes. In particular, hydrosilylation generally leads to silylacetals, which are stable in situ but converted into aldehydes upon hydrolysis. Indeed, besides hydrogenation, the use of hydrosilanes as reductants is an area of growing interest for the mild and selective reduction of carboxylic acid derivatives.[3] This strategy has been applied to the reduction of esters to alcohols[4–6] or ethers.[5e,7,8] However, examples of selective catalytic hydrosilylation reactions of esters to give aldehydes in the presence of transition-metal[9] or Lewis acid[10] catalysts are scarce. On the other hand, during the last decade, iron[11] has become a useful substitute for precious transition metals, particularly for reduction,[12] and has been studied extensively. Surprisingly, although reduction with iron as the catalyst is well-exemplified for the hydrosilylation of carbonyl derivatives,[13] examples with amides,[14] imines,[15] and carboxylic acids[16] are scarce. Notably, selective iron-catalyzed hydrosilylation reactions of esters to form alcohols[6] or ethers[8] were recently reported. To the best of our knowledge, no iron-catalyzed selective hydrosilylation of esters to give aldehydes has been reported previously. Herein, we report an efficient and selective method for the reduction of esters to aldehydes through hydrosilylation catalyzed by N-heterocyclic-carbene (NHC) iron(0) complexes [(NHC)Fe(CO)$_4$].[17]

We started our investigation with the reduction of methyl phenylacetate (**1a**) as the model substrate with diethylsilane (1.1 equiv). With commercially available [Fe(CO)$_5$] and [Fe$_2$(CO)$_9$] or complexes already developed for the selective hydrosilylation of esters ([CpFe(CO)$_2$(PCy$_3$)][BF$_4$])[6] and carboxylic acids ([(cod)Fe(CO)$_3$] and [(pbo)Fe(CO)$_3$])[16] at room temperature under UV irradiation (350 nm) for 16 h, only moderate conversion and selectivity were observed (see the Supporting Information; cod = 1,5-cyclooctadiene, Cy = cyclohexyl, pbo = (*E*)-4-phenylbut-3-en-2-one). In our search for more reactive and selective catalysts, a new class of tetracarbonyl iron(0) complexes bearing NHC ligands (Scheme 1) showed promising results.[18] The [(NHC)Fe(CO)$_4$] complexes were prepared in one step from [Fe(CO)$_5$] (2 equiv) by treatment with the freshly prepared NHC (1 equiv) in toluene at 70 °C overnight in the presence of [{Cp*Fe(CO)$_2$}$_2$] (2 mol%) as the catalyst and were isolated in moderate to good yields (36–63%).[19] The molecular structures of **4b** and **5** are depicted in Figure 1. The coordination geometry at the iron center is distorted trigonal bipyramidal, with the N-heterocyclic carbene ligand located in an axial position. The Fe–C$_{carbene}$ bond length is 2.007(2) Å for **5** (for **4a**, 1.9988(17) Å and for **4b**, 2.0041(14) Å) and is comparable to those reported previously.[17]



4a, R = Mes, 63%
(unsaturated carbene ring: IMes)
4b, R = 2,6-*i*Pr$_2$C$_6$H$_3$, 59%
(unsaturated carbene ring: DIPP)
5, R = Mes, 36%
(saturated carbene ring: SIMes)

Scheme 1. Synthesis of the [(NHC)Fe(CO)$_4$] complexes. Cp* = pentamethylcyclopentadienyl, Mes = mesityl (2,4,6-trimethylphenyl).

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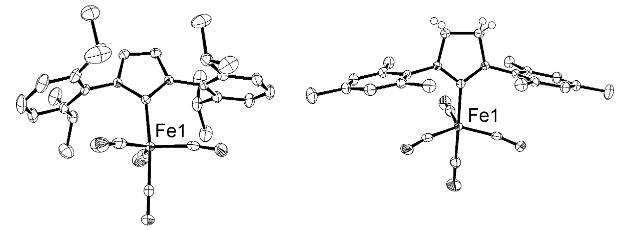
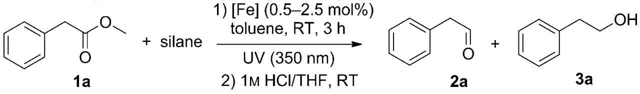


4b **5**

Figure 1. Molecular structures of the complexes **4b** and **5**. Thermal ellipsoids correspond to 50% probability. Hydrogen atoms are omitted for clarity.

Table 1: Optimization of the reaction parameters.[a]

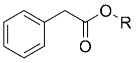
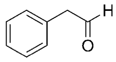
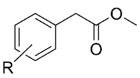
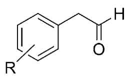
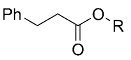
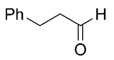
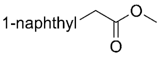
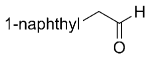
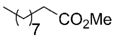
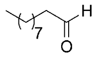
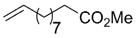
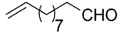
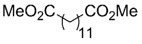
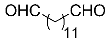
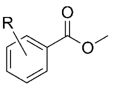
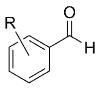
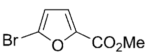
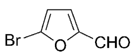


Entry	[Fe] (mol%)	Silane (equiv)	Conv. [%][b]	**2a**/**3a** [%][b]
1	**4a** (2.5)	Et_2SiH_2 (1.1)	98	98:0
2	**4a** (1)	Et_2SiH_2 (1.1)	96	95:1
3[c]	**4a** (1)	Et_2SiH_2 (1.1)	76	72:4
4	**4a** (0.5)	Et_2SiH_2 (1.1)	91	88:3
5[c]	**4b** (1)	Et_2SiH_2 (1.1)	68	65:3
6[c]	**5** (1)	Et_2SiH_2 (1.1)	54	53:1
7	**4a** (2.5)	Ph_2SiH_2 (1.1)	75	75:0
8	**4a** (2.5)	$PhMeSiH_2$ (1.1)	22	18:2
9	**4a** (2.5)	Et_3SiH (1.1)	0	–
10	**4a** (2.5)	$PhSiH_3$ (1.1)	25	0:25
11	**4a** (2.5)	Ph_3SiH (1.1)	0	–
12[d]	**4a** (1)	Et_2SiH_2 (1.1)	0	–

[a] Reaction conditions: 1) methyl phenylacetate (0.5 mmol), silane (0.55 mmol, 1.1 equiv), iron complex (0.5–2.5 mol%), toluene (0.5 mL), room temperature, UV irradiation (350 nm), 1–3 h; 2) hydrolysis with 1 M aqueous HCl (2 mL) and THF (2 mL), room temperature, 2 h. [b] The conversion was determined by GC. [c] The reaction was carried out for 1 h. [d] The reaction was carried out without UV irradiation at room temperature for 72 h.

We tested these complexes **4a**,**b** and **5** as catalysts in the hydrosilylation of esters (Table 1). Notably, with complex **4a** (2.5 mol%) in the presence of Et_2SiH_2 (1.1 equiv), both activity and selectivity were enhanced: full conversion was observed after 3 h at room temperature, and only the aldehyde product was detected (Table 1, entry 1). Although complexes **4b** and **5** gave the aldehyde **2a** selectively under similar conditions, the conversion after reaction for 1 h was lower (compare entries 3, 5, and 6 in Table 1). The superior efficiency of the iron complex **4a** was confirmed by lowering the catalyst loading to 0.5 mol% (Table 1, entry 4). Among a variety of silanes tested, $PhSiH_3$ gave exclusively the alcohol **3a**, albeit with low conversion (25%; Table 1, entry 10), whereas PH_2SiH_2 gave the aldehyde **2a** with 75% conversion (Table 1, entry 7). Thus, the nature of the silane is of crucial importance for the selectivity. Importantly, the role of UV activation (350 nm) was also shown: no reaction was observed with Et_2SiH_2 in the absence of UV irradiation (Table 1, entry 12).

Table 2: Scope of the hydrosilylation of esters to give aldehydes under the catalysis of [(IMes)Fe(CO)$_4$].[a]

Entry	Ester		Aldehyde	Conv. [%]	Yield [%][b]
1		R = Me		96[c]	83
2		R = Et		97[c]	85[d]
3		R = *p*-Me		99[e]	79
4		R = *m*-Me		99[e]	71
5		R = *o*-Me		92[e]	65[f]
6		R = *p*-Br		99[e]	85
7		R = *p*-OMe		83[e]	77
8		R = Me		92[d]	90
9		R = Et		95[c]	95[d]
10		R = Bn		92[c]	83[d]
11[g]				76	65
12				97[e]	90
13	EtOAc		CH_3CHO	95[c]	85[f]
14				75[c]	70[f,h]
15[g]				99[e]	90
16[i]		R = *p*-Br		99[c]	86
17[i]		R = *p*-Me		91[c]	80
18[i]		R = *p*-CF_3		40[e]	–
19[i]		R = H		93[c,j]	83[d]
20				60[c]	55[f]

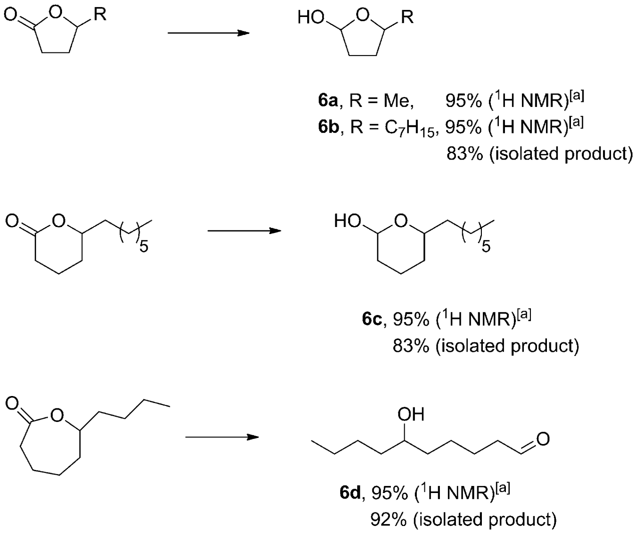
[a] Reaction conditions: 1) ester (0.5 mmol), diethylsilane (0.55 mmol, 1.1 equiv), complex **4a** (1 mol%), toluene (0.5 mL), room temperature, UV irradiation (350 nm), 3 h; 2) hydrolysis with 1 M aqueous HCl (2 mL) and THF (2 mL), room temperature, 2 h. [b] Yield of the isolated product. [c] The conversion was determined by ^1H NMR spectroscopy for the silylacetal intermediate. [d] The yield determined by ^1H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard is given. [e] The yield determined by GC is given. [f] The product was isolated as the 2,4-dinitrophenylhydrazone adduct. [g] Complex **4a** (2 mol%) and diethylsilane (2.2 equiv) were used. [h] 10% conversion into isomerization products was observed. [i] The reaction was carried out with complex **4a** (2.5 mol%) and diphenylsilane (1.5 equiv) at room temperature under UV irradiation (350 nm) for 4 h. [j] The conversion after 5 h is given. Bn = benzyl.

Having optimized the reaction conditions (complex **4a** (1 mol%), Et_2SiH_2 (1.1 equiv), toluene, room temperature, UV irradiation at 350 nm, 3 h), we investigated the scope of this chemoselective reduction of esters to aldehydes (Table 2). Under these conditions, methyl, ethyl, and benzyl esters were converted selectively into the corresponding aldehydes: full conversion was observed after 3 h, and the aldehydes were obtained in good yields (83–95%; Table 2, entries 1, 2, and 8–10). The reaction also proceeded well with methyl acetates substituted with *para*-, *meta*-, and *ortho*-tolyl groups, although *ortho* substitution seemed to inhibit the reactivity slightly (Table 2, entries 3–5). Electronic effects at the *para* position of the aromatic ring of the phenylacetate derivatives were limited, and the corresponding aldehydes were obtained selectively in good yields regardless of the *para* substituent (71–85 %; Table 2, entries 3, 6, and 7). More strikingly, aliphatic esters, such as ethyl acetate or methyl decanoate, could be reduced to the corresponding aliphatic aldehydes in good yields (up to 90 % yield; Table 2, entries 12 and 13). Moreover, methyl 10-undecenoate was transformed into 10-undecenal in 70 % yield; products resulting from the isomerization of the $C{=}C$ bond were obtained in only 10 % yield (Table 2, entry 14). Importantly, the reduction of dimethyl tridecanedioate led selectively to the corresponding dialdehyde, which was isolated in very good yield (90 %; Table 2, entry 15).

Interestingly, this reaction was also successful with aromatic esters. When the reaction was performed with the catalyst **4a** (2.5 mol %) in the presence of Et_2SiH_2 (1.1 equiv) at room temperature under UV irradiation (350 nm) for 4 h, 58 % conversion of methyl *p*-bromobenzoate into the corresponding aldehyde occurred. Indeed, the use of diphenylsilane (1.5 equiv) led to full conversion, and *p*-bromobenzaldehyde was isolated in 86 % yield (Table 2, entry 16). Under similar conditions, *p*-methylbenzaldehyde was also formed in good yield (80 %), whereas the reduction of methyl *p*-trifluoromethylbenzoate occurred with only 40 % conversion, probably because of the strongly electron withdrawing substituent (Table 2, entries 17 and 18). Heteroaromatic esters can be reduced under similar conditions: methyl 5-bromofur-2-yl-methanoate was converted into the corresponding aldehyde, which was isolated as its hydrazone derivative in 55 % yield (Table 2, entry 20).

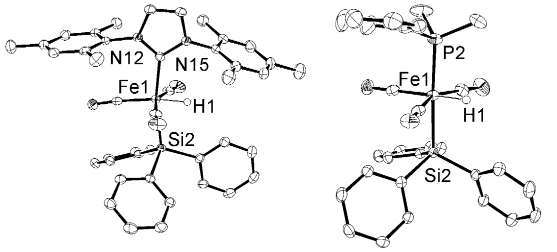
We next focused our attention on the reduction of lactones to lactols (Scheme 2).[9a,20] Such reductions are usually performed with DIBAL-H at low temperature (−78 °C). Under the optimized conditions (complex **4a** (1 mol %), Et_2SiH_2 (1.1 equiv), room temperature, UV irradiation (350 nm), 3 h), the γ-lactones 5-methyltetrahydrofuran-2-one and 5-heptyltetrahydrofuran-2-one were fully converted into the corresponding γ-lactol **6a**,**b**. 5-Heptyltetrahydrofuran-2-ol **6b** was isolated in 83 % yield. Notably, δ-decalactone was converted selectively into δ-decalactol (**6c**), which was isolated in 83 % yield. Similarly, with ε-decalactone as the starting substrate, the reduction proceeded with full conversion, and the hydroxyaldehyde **6d** was obtained selectively in 92 % yield.

To explore the mechanism of this iron-catalyzed hydrosilylation, we first investigated the stoichiometric reaction between **4a** and silanes. The reaction of **4a** with $HSiPh_3$ under UV irradiation (350 nm) led to the formation of the complex $[(IMes)Fe(H)(SiPh_3)(CO)_3]$ (**8a**) resulting from the oxidative addition of the Si–H bond of the silane to unsaturated $[(IMes)Fe(CO)_3]$ (**7**).[21] This complex was fully characterized by elemental analysis, X-ray diffraction studies,[22] and NMR spectroscopy: in the ^1H NMR spectrum, the hydride exhibited a well-resolved singlet at $\delta = -8.74$ ppm,[23b,25] and in the ^{29}Si NMR spectrum, a singlet at $\delta = +28.19$ ppm was observed.[25] The phosphine analogue $[(PMe_2Ph)Fe(H)(SiPh_3)(CO)_3]$ (**9**) was also synthesized. Complex **9** showed similar spectroscopic features to those of **10a**: the hydride proton resonates at $\delta = -9.30$ ppm, and the silicon resonance is at $\delta = +28.4$ ppm.



Scheme 2. $[(IMes)Fe(CO)_4]$-catalyzed hydrosilylation of lactones. Reaction conditions: 1) lactone (0.5 mmol), Et_2SiH_2 (1.1 equiv), complex **4a** (1 mol %), C_6D_6 (solvent), room temperature, UV irradiation (350 nm), 3 h; 2) hydrolysis with 1 M aqueous HCl (2 mL) and THF (2 mL), room temperature, 2 h. [a] Yield determined by ^1H NMR spectroscopy for the silylacetal intermediate.

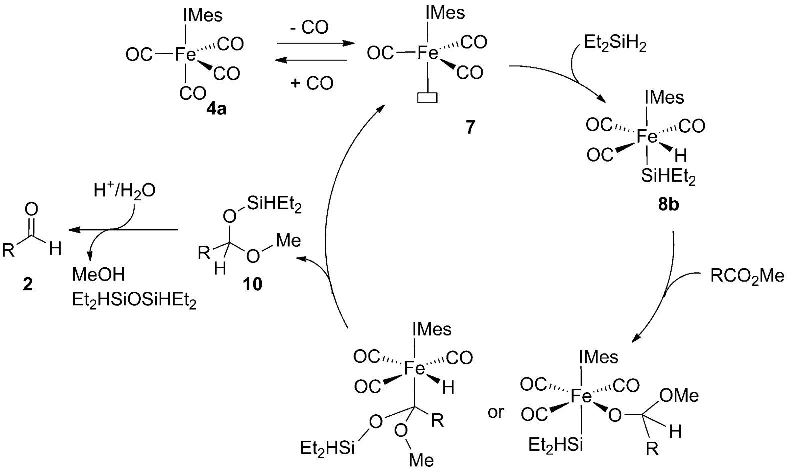
The molecular structures of **8a** and **9** are depicted in Figure 2. The coordination geometry at the iron center is distorted trigonal bipyramidal; the N-heterocyclic carbene ligand (or the phosphine ligand) and the silyl fragment are located in a *trans* axial arrangement with a C_{IMes}-Fe-Si angle of 168.50(6)° (P-Fe-Si, 177.32(2)°). The C_{NHC}–Fe bond length of 1.997(2) Å is similar to that found in the starting complex **4a** (1.9988(17) Å). Furthermore, the Fe–$SiPh_3$ bond lengths (2.3488(9) and 2.3564 (6) Å for **8a** and **9**, respectively) are consistent with those described previously.[22a,23] Notably, the hydride is located in the meridional plane, and the Fe–H distance of 1.43(2) Å for **8a** (1.46(2) Å for **9**) is consistent with an iron–hydride bond.[22a,24]



8a **9**

Figure 2. Molecular structures of the complexes **8a** and **9**. Thermal ellipsoids correspond to 50% probability. One molecule of toluene in **8a** and hydrogen atoms, except the iron hydride ligands, are omitted for clarity.

The reaction of **4a** with Et_2SiH_2 in C_6D_6 led exclusively to the formation of $[(IMes)Fe(H)(CO)_3(SiHEt_2)]$ (**8b**), which was characterized by NMR spectroscopy (hydride signal at



Scheme 3. Proposed catalytic cycle for the iron-catalyzed hydrosilylation of esters to give aldehydes.

$\delta = -9.29$ ppm in the ^{1}H NMR spectrum, silicon resonance at $\delta = +28.2$ ppm with a coupling constant $^1J_{\mathrm{Si,H}} = 178$ Hz in the ^{29}Si NMR spectrum). The addition of a stoichiometric amount of methyl phenylacetate to **8b** under UV irradiation[26] led to the formation of several compounds, including several iron hydride species; as a result, we were unable to distinguish clearly the reactivity of the Fe–H bond or the Fe–Si bond towards the ester.

On the basis of these observations, a plausible catalytic cycle is presented in Scheme 3 for the reduction of esters to aldehydes with Et_2SiH_2 in the presence of [(IMes)Fe(CO)$_4$] as the catalyst precursor. In the initial step, UV activation of [(IMes)Fe(CO)$_4$] generates a 16-electron species [(IMes)-Fe(CO)$_3$] (**7**), which then reacts with the hydrosilane to generate the oxidative-addition complex **8b**. At this stage, the insertion of the carbonyl moiety of the ester into the Fe–Si and/or Fe–H bond is likely. In the final step, reductive elimination affords the silylated acetal **10** and regenerates the active species **7.**

In summary, we have developed simple methodology for the chemoselective reduction of esters to aldehydes with an N-heterocyclic-carbene–iron complex, such as [(IMes)-Fe(CO)$_4$], as the catalyst (1 mol%) in the presence of a secondary silane (diethylsilane or diphenylsilane) as the reducing agent. This reaction occurs at room temperature under UV irradiation with both aromatic and aliphatic esters. Notably, this catalytic system also permitted the efficient and selective reduction of lactones to lactols. We have provided experimental evidence that the hydrosilylation occurs by oxidative addition of the hydrosilane to an unsaturated NHC–Fe species to yield a silyl iron hydride complex.

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Keywords: aldehydes · esters · hydrosilylation · iron catalysis · reduction

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