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Expanding the catalytic scope of (cyclopentadienone)iron complexes to the hydrogenation of activated esters to alcohols

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Abstract: Herein, we report the application of the easy-to-make and bench-stable (cyclopentadienone)iron complexes (such as **1**) as pre-catalysts for the hydrogenation of esters. After optimization of the reaction conditions (solvent, temperature, pressure), complex **1** was tested in the hydrogenation of a range of esters. With most of the activated trifluoroacetate esters, a quantitative formation of TFE was obtained at low catalyst loadings. For non-activated esters, no reaction was observed. Trifluoroacetic acid, a common impurity in hydrolytically labile trifluroacetate esters, was shown to act as a poison for the catalyst. However, the simple addition of Et_3N allowed to restore the catalyst activity. Our study constitutes the first example of ester hydrogenation with an Fe complex based on a non-pincer ligand.

Catalytic hydrogenations (CHs) are a reaction class of key importance in the sustainable manufacture of both bulk commodities and fine chemicals for several reasons. Firstly, H_2 is a cheap and clean reductant, which allows to achieve a perfect atom economy and to minimize the generation of waste. Secondly, CHs are operationally simple and generally require minimal workup operations for the isolation of the product. Last but not least, as CHs are a very mature research field, countless heterogeneous[1] and homogeneous[2] catalysts have been developed, which allow to carry out these reactions with high chemo-, regio- and/or stereoselectivity. However, most of these catalysts rely on precious metals (e.g., Ru, Rh, Ir, Pd, Pt), with associated problems of toxicity, high cost and limited stock which prevent, in some cases, their industrial use. Therefore, replacing precious metals with cheap base metals such as Fe, Co or Ni is currently considered a task of primary scientific and industrial relevance.[3] From the point of view of sustainability, Fe is certainly the most appealing of these metals, owing to its wide availability (2nd most abundant metal in the Earth's crust), low cost and scarce toxicity.[4] Accordingly, numerous Fe-based catalysts have been developed in the last decade for the hydrogenation of olefins,[5] ketones,[6] imines,[6c,7] and carbon dioxide/sodium bicarbonate,[7a, 8] including several enantioselective versions.[6i-m,7e,f] The more difficult ester hydrogenation[9] was only recently reported for the first time by Milstein and co-workers (Figure 1 A).[10]

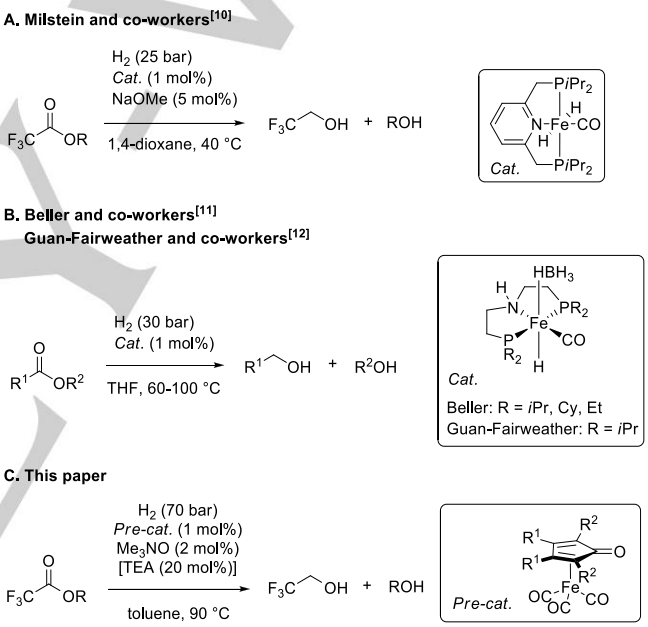

Figure 1. Previous examples of Fe-catalyzed ester hydrogenation (A, B), and the new methodology described in this paper (C).

Shortly after the Milstein's report, other examples of Fe-catalyzed ester hydrogenation were described by the groups of Beller[11] and Guan-Fairweather[12] (Figure 1 B), expanding the substrate scope to non-trifluoroacetate esters.[13] However, all these methodologies rely on costly and air-sensitive PNP pincer ligand Fe-complexes,[10-12] which hampers their possible industrial use. In sharp contrast, (cyclopentadienone)iron complexes[14] (Figure 1 C, Figure 2) are ideal pre-catalysts for industrial applications, as they are easy-to-make and stable compounds.[15] Under suitable experimental conditions, these complexes can be converted in situ into catalysts for the hydrogenation of ketones,[6g,h,k-m] imines[7a-d] and carbon dioxide/sodium bicarbonate.[7a,8a] However, to the best of our knowledge, no application of (cyclopentadienone)iron complexes in ester CH has been reported so far.

Building on our expertise in the synthesis and catalytic use of (cyclopentadienone)iron complexes,[6k,l] we set to investigate whether they could be employed as pre-catalysts for the hydrogenation of esters. Thus, the "classical" complex **1** (Figure

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2) was tested, after in situ activation with Me_3NO,[6i-m,7a-d] in the hydrogenation of activated trifluoroacetate substrates **S1-S3** (Table 1). The first experiments were carried out under 70 bar of H_2 at 110 °C for 17 h.

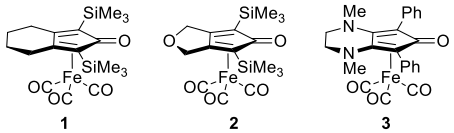
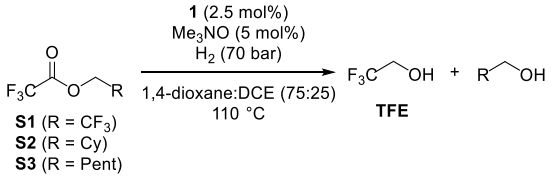


Figure 2. Examples of (cyclopentadienone)iron complex.

As in the Fe-catalyzed hydrogenation of **S1** reported by Milstein and co-workers,[10] we intended to use 1,4-dioxane as solvent. However, Me_3NO – i.e. the catalyst activator – was poorly soluble in 1,4-dioxane. Therefore, it was added to the catalytic mixture from a 1,2-dichloroethane (DCE) stock solution. Consequently our initial trials were done using a 1,4-dioxane/DCE solvent mixture.

Table 1. Test of pre-catalyst **1** in the hydrogenation of trifluoroacetate esters **S1-S3**.[a]



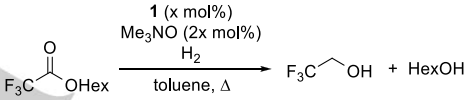
Entry	Sub.	Deviation from above	Yield TFE (%)[b]
1	**S1**	-	100[c]
2	**S1**	without **1**	7[d]
3	**S1**	without Me_3NO	17[d]
4	**S1**	+ Hg(0) [38 mol%]	100
5	**S1**	+ $P(OMe)_3$ [1.3 mol%]	100
6	**S1**	+ $P(OMe)_3$ [2.5 mol%]	36
7	**S1**	+ $P(OMe)_3$ [5.0 mol%]	16
8	**S2**	-	77
9	**S3**	-	82[e]
10	**S2**	1,4-dioxane	100
11	**S2**	DCE	89
12	**S2**	toluene	100
13	**S3**	toluene	100

[a] Reaction conditions: substrate (1 mmol), **1** (2.5 mol%), Me_3NO (5 mol%), P_{H2} = 70 bar, solvent (0.75 mL), *T* = 110 °C, reaction time = 17 h. DCE = 1,2-dichloroethane; TFE = 2,2,2-trifluoroethanol. [b] Determined by $^{19}F\{^1H\}$-NMR analysis of the reaction crude.[10] [c] Mole balance (by $^{19}F\{^1H\}$-NMR, using α,α,α-trifluorotoluene as internal standard) = 89%, due to the low boiling point of **S1** and consequent loss during handling. [d] Formed by hydrolysis of **S1**, together with an equimolar amount of trifluoroacetic acid (TFA). [e] Mole balance = 99%.

As shown in Table 1 (entry 1), substrate **S1** was quantitatively hydrogenated to 2,2,2-trifluoroethanol (TFE) with no sign of hydrolysis to trifluoroacetic acid (TFA). In the absence of either complex **1** or Me_3NO, no reduction took place (Table 1, entries 2 and 3), but TFE was detected due to hydrolysis of **S1**, as confirmed by the presence of equimolar amounts of TFA. Catalyst poisoning experiments were carried out *in operando*:[16] while the addition of an excess of Hg(0) did not affect the hydrogenation of **S1** (Table 1, entry 4), $P(OMe)_3$ led to a drop of conversion only when its amount was ≥ 1 equiv. to **1** (Table 1, entries 5-7). These data are consistent with a homogeneous catalyst being operating. With the less activated substrates **S2** and **S3**, full conversion was not obtained (Table 1, entries 8, 9). However, when using pure 1,4-dioxane as a solvent and therefore adding Me_3NO as a solid, **S2** was fully hydrogenated (Table 1, entry 10). Uncomplete conversion was obtained in pure DCE (Table 1, entry 11), indicating that this solvent may have been the cause of the previously observed catalyst stalling. Toluene also allowed to obtain 100% yield for both **S2** and **S3** (Table 1, entries 12-13) and was selected as solvent for the rest of our study.

Further optimization of the reaction parameters was performed with substrate **S3** in toluene (Table 2). Decreasing the amount of pre-catalyst **1** from 2.5 to 1 mol% did not affect the yield, which remained quantitative both at 110 °C (Table 2, entry 2) and at 90 °C (Table 2, entry 3), corresponding to a TON of 100. Nearly quantitative yields were obtained also when temperature (Table 2, entry 4) or pressure (Table 2, entry 5) were further decreased to 70 °C and 35 bar, respectively. At 90 °C and under 70 bar of H_2, the catalyst loading could be further reduced (Table 2, entries 6-8), leading to a decrease in conversion but an increase in TON.

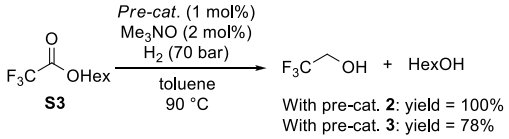
Table 2. Optimization of reaction parameters in the hydrogenation of *n*-hexyl trifluoroacetate **S3** promoted by complex **1**.[a]



Entry	mol% **1**	*T* (°C)	*P* (bar)	Yield (%)[b]	TON
1	2.5	110	70	100	40
2	1	110	70	100	100
3	1	90	70	100	100
4	1	70	70	99	99
5	1	90	35	98	98
6	0.5	90	70	97	194
7	0.25	90	70	84	336
8	0.2	90	70	62	310

[a] Reaction conditions: substrate (1 mmol), **1** (x mol%), Me_3NO (2x mol%), toluene (0.75 mL), reaction time = 17 h. [b] Determined by $^{19}F\{^1H\}$-NMR analysis of the reaction crude. No substrate hydrolysis observed in any case.

The known (cyclopentadienone)iron complexes **2** and **3** (Figure 2), screened in the hydrogenation of substrate **S3** under the optimized conditions, also showed catalytic activity (Scheme 1).



Scheme 1. Screening of (cyclopentadienone)iron complexes **2** and **3** in the hydrogenation of *n*-hexyl trifluoroacetate (**S3**).

The 3,4-ethylenediamino-substituted (cyclopentadienone)iron complex **3**, recently reported as very active in the hydrogenation of imines and $NaHCO_3$,[7a] appeared to be slightly less active than pre-catalysts **1** and **2**.

Trifluoroacetates are prone to undergo hydrolysis with adventitious water, releasing TFA. Thus, before determining the substrate scope of pre-catalyst **1**, we decided to investigate

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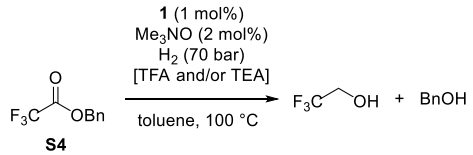
whether traces of TFA could exert a detrimental effect on the catalytic reaction (Table 3).

Table 3. Study of effect of TFA on the hydrogenation activity of **1**.[a]



S4

Entry	mol% TFA	mol% TEA	Yield (%)[b]
1	-	-	100
2	1.3	-	4
3	5	-	0
4	-	5	100
5	5	1	0
6	5	5	7
7	5	20	85

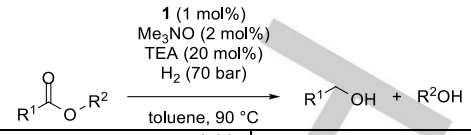
Reaction conditions: substrate **S4** (1 mmol), **1** (1 mol%), Me_3NO (2 mol%), toluene (0.25 mL), reaction time = 17 h. [b] Determined by $^{19}F\{^1H\}$-NMR analysis of the reaction crude.

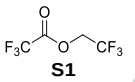
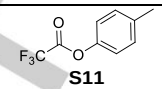
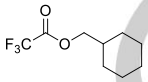
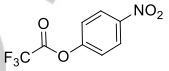
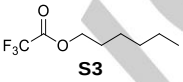
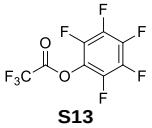
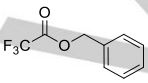
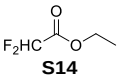
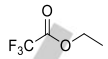
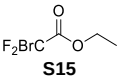
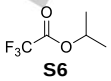
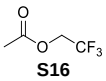
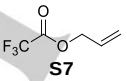
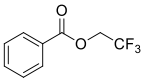
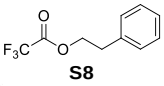
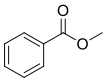
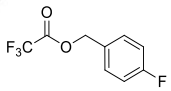
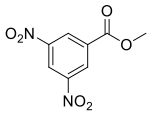
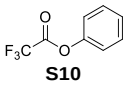
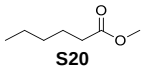
For this purpose, a fresh batch of benzyl trifluoroacetate **S4**, totally exempt from TFA (as verified by $^{19}F\{^1H\}$-NMR), was prepared. As shown in Table 3, the hydrogenation of **S4** proceeded smoothly in the absence of any additive (Table 3, entry 1). The addition of 1.3 mol% of TFA (Table 3, entry 2) caused an almost complete deactivation of the catalyst – further confirmed when 5 mol% of TFA was used (Table 3, entry 3). We considered that addition of a base such as triethylamine (TEA) could prevent catalyst poisoning by neutralizing TFA. First, it was verified that TEA alone (5 mol%) does not impair the reaction (Table 3, entry 4). Gratifyingly, the addition of an excess of TEA restored to a large extent the activity of the catalyst (Table 3, entries 5-7).

A substrate screening with 20 different esters was carried out under optimized reaction conditions (Table 4). When traces of TFA were detected in the starting material, TEA (20 mol%) was added prior to the hydrogenation. With the exception of **S12** and **S13** – bearing electron-poor aryl groups – all trifluoroacetates **S1-11** gave full conversion (entries 1-13). In contrary to the seminal report of Milstein and co-workers on the Fe-catalyzed hydrogenation of trifluoroacetate esters,[10] the yields were scarcely influenced by the steric bulk of the substituents at the alkoxy group, and relatively bulky substrates such as **S2**, **S6** and **S8** were quantitatively hydrogenated. Unfortunately, all the non-trifluoroacetate substrates **S14-20** (Table 4, entries 14-20) turned out to be totally unreactive, including $CF_2HCOOEt$ (**S14**) and $CF_2BrCOOEt$ (**S15**) which were expected to be only slightly "less activated" than CF_3COOEt (**S5**).

We elaborated a tentative mechanism (Scheme 2) which, similarly to the mechanisms proposed for other catalytic ester hydrogenation methodologies,[9-12] involves two steps performed by the same catalyst: i) reduction of the ester C=O group leading to the hemiacetal **A** (catalytic Cycle A); ii) reduction of the aldehyde **B** (catalytic Cycle B), formed by hydrolysis of the hemiacetal **A**.

Table 4. Substrate screening for the hydrogenation of esters in the presence of pre-catalyst **1**.[a]



#	Substrate	Yield (%)[b]	#	Substrate	Yield (%)[b]
1	 **S1**	100[c]	11	 **S11**	100[d]
2	 **S2**	100	12	 **S12**	0[d]
3	 **S3**	100	13	 **S13**	0[d]
4	 **S4**	100	14	 **S14**	0[d]
5	 **S5**	100	15	 **S15**	0[d]
6	 **S6**	87, 100[d]	16	 **S16**	0
7	 **S7**	50, 100[d,e]	17	 **S17**	0[d]
8	 **S8**	100	18	 **S18**	0[f]
9	 **S9**	60, 100[d]	19	 **S19**	0[f]
10	 **S10**	0, 100[d]	20	 **S20**	0[f]

Reaction conditions: substrate (1 mmol), **1** (1 mol%), Me_3NO (2 mol%), toluene (0.25 mL), reaction time = 17 h. [b] Determined by $^{19}F\{^1H\}$-NMR analysis of the reaction crude. [c] Pre-treatment with TEA (20 mol%) was necessary at this stage due to the formation of TFA in our ageing batch of **S1**. [d] Substrate pre-treated with TEA (20 mol%) before hydrogenation. [e] Our analytical method did not allow us to determine whether the olefin was hydrogenated or not. [f] Determined by GC with dodecane as internal standard.

In both cycles A and B, the active complex ***act*-1a** (initially generated from **1** in the presence of Me_3NO) splits H_2 forming the (hydroxycyclopentadienyl)iron hydride ***act*-1b**, which was firstly isolated and characterized by Knölker et al.[17] The two above-mentioned C=O reduction steps are sequentially performed by ***act*-1b** through the pericyclic transition states **TS-A** and **TS-B**, similar to those commonly accepted for the hydrogenation of aldehydes and ketones.[6e,f,18] As esters are much less reactive towards hydride attack compared to aldehydes, the formation of the hemiacetal **A** should be the rate-limiting step of the process. This expectation is supported by the

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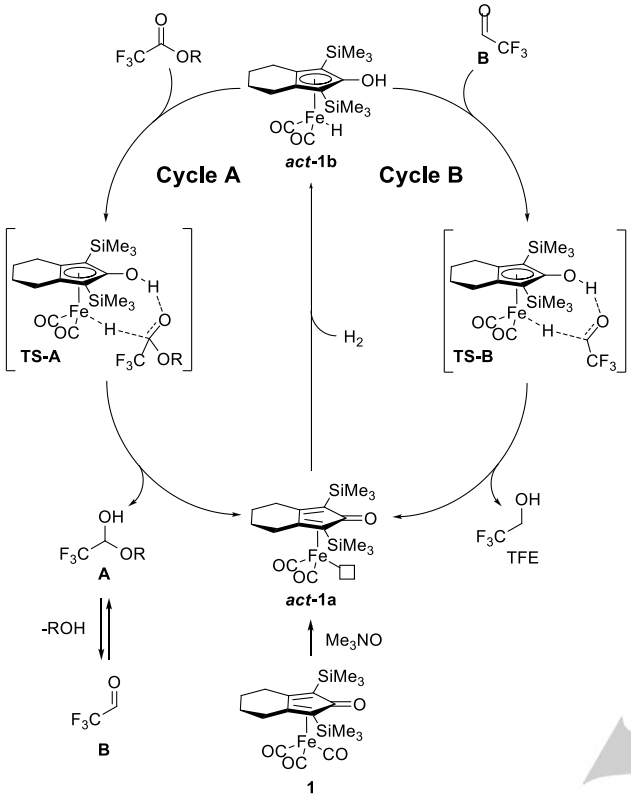
fact that conversion is observed only with trifluoroacetate esters, possessing the strongly electron-withdrawing group CF_3.



Scheme 2. Tentative mechanism for the hydrogenation of trifluoroacetate esters promoted by pre-catalyst **1** upon activation with Me_3NO.

In conclusion, we have demonstrated that air-stable and easy-to-make (cyclopentadienone)iron complexes such as **1** can be used as pre-catalysts for the hydrogenation of trifluoroacetate esters. The reaction, which occurs quantitatively at low catalyst loading (TON up to 336), has a broad substrate scope in terms of alkoxy residues, and bulky substituents are also tolerated. This study represents a remarkable expansion of the application scope of (cyclopentadienone)metal complexes in general (metal = Fe or Ru, in most cases), which did not include so far any ester substrate.[14,19] Moreover, to the best of our knowledge, this is the first example of Fe-catalyzed ester hydrogenation involving a cheap and stable pre-catalyst instead of costly and air-sensitive pincer complexes.[9,11b]

Experimental Section

General procedure for the ester hydrogenation screening. In a nitrogen-filled mBraun glovebox, a solution of pre-catalyst (0.01 mmol, 1 mol% in 0.25 mL solvent) was dispensed to a glass vial containing solid Me_3NO (0.02 mmol, 2 mol%). The vials were capped and the obtained solutions were stirred for 1 h at 30 °C. After this time, each vial was opened and a mixture of substrate (1 mmol) and TEA (0.2 mmol, 20 mol%) was added. The vials were capped again and put inside the Premex 96er Multireactor. The system was purged three times with nitrogen (10 bar) and three times with hydrogen (10 bar). The reaction vessels were pressurized at 70 bar, heated at 90 °C and stirred overnight. The reactions were cooled down and then, after releasing hydrogen, they were flushed with nitrogen (10 bar). After adding α,α,α-trifluorotoluene (about 0.5 mmol), the crudes were analyzed by $^{19}F\{1H\}$ NMR.

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Keywords: iron • hydrogenation • homogeneous catalysis • ester reduction • (cyclopentadienone)iron complexes

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