Very Important Publication

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Improved Second Generation Iron Pincer Complexes for Effective Ester Hydrogenation

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Abstract: Hydrogenation of esters to alcohols with a well-defined iron ^{iPr2}PNP pincer complex has been recently reported by us and other groups. We now introduce a novel and sterically less hindered ^{Et2}PNP congener that provides superior catalytic activity in the hydrogenation of various carboxylic acid esters and lactones compared to the known complex. Successful hydrogenation proceeds under relatively mild conditions (60 °C) with lower catalyst loadings.

Keywords: alcohols; catalytic hydrogenation; esters; iron; pincer complexes

The catalytic hydrogenation of esters to the corresponding alcohols represents an interesting methodology of paramount importance for organic synthesis and fine chemical processes.[1] In the past, this transformation relied on the use of stoichiometric amounts of inorganic metal hydrides such as $LiAlH_4$, $NaBH_4$ and related compounds resulting in the formation of stoichiometric amounts of waste products followed by complex work-up procedures.[2] In contrast, catalytic hydrogenation of esters and lactones employing H_2 constitutes a completely atom economic, waste-free and environmentally benign transformation. Heterogeneous catalysts are applied in the hydrogenation of fatty esters but these catalysts require high temperature and pressure.[3] Hence, the development of milder and more selective catalytic protocols for ester hydrogenation facilitated by well-defined homogeneous complexes constitutes an actual and highly desired research goal.[4]

In the early 2000s a variety of seminal reports on homogeneous catalysts for the hydrogenation of esters appeared in the literature.[5–7] Major developments in this field were made by the groups of Milstein,[8] Saudan,[9] Kuriyama,[10] and Gusev.[11] In addition, very recently a highly active bis-NHC amino pincer Ru complex has been developed for ester hydrogenation.[12]

Despite the recent progress with these Ru-based materials, the development of inexpensive, earth-abundant metal catalysts is desirable. In this context, iron-based catalysts are of special interest due to their low cost, low toxicity and high abundance.[13] In the past year, significant advances have been achieved in our group[14] and others[15] using well-defined iron-based pincer complexes (Figure 1), which were successfully applied in selective hydrogenation and dehydrogenation reactions.[16] Based on our experience in this redox catalysis,[17] we became interested in the development of similar applications using an iron-based catalyst.

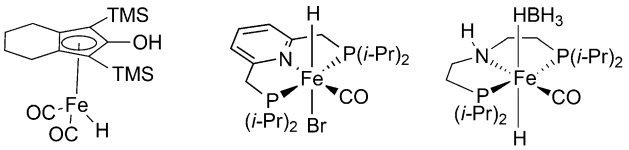


Figure 1. Recently developed iron complexes for catalytic hydrogenation.

Inspired by our recent work on the hydrogenation of esters to alcohols[14b] conducted with the isopropyl-tagged iron-PNP pincer complex **1**, we focused on the preparation of two novel congeners **2** and **3** bearing phosphine motifs with different steric demands (Figure 2). Herein, we address the influence of the alkyl substituents at the phosphorus binding site on

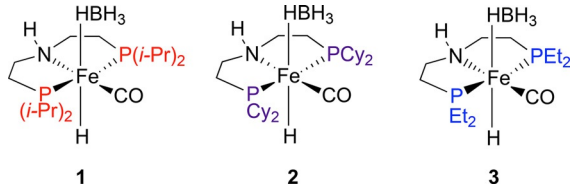


Figure 2. Iron pincer complexes investigated in this work.

the catalytic performance of the complexes in the hydrogenation of esters and lactones.

The preparation of complexes **2** and **3** was guided by previous work in this field.[14a] The precursor of complex **3** was prepared from the reaction of $FeBr_2 \cdot 2THF$ with bis(2-diethylphosphinoethyl)amine under an atmosphere of CO (see **1b** in the Supporting Information).

The hydridoborato complex **3** was prepared in 56% yield by treating the complex $\{FeBr_2(CO)[HN(CH_2CH_2P(CH_2CH_3)_2)_2]\}$ (**7**) with excess of $NaBH_4$ (for details see the Supporting Information). The bright yellow complex **3** has been well characterized by multinuclear NMR spectroscopy, high resolution mass spectrometry, IR spectroscopy (ATR), X-ray[18] and elemental analysis (Figure 3). In the ^1H NMR spectrum, the hydride ligand resonates at $\delta = -19.6$ ppm ($J_{H,P} = 50.0$ Hz) as a sharp triplet, whereas the BH_4 ligand appears as a broad signal at $\delta = -3.0$ ppm. In the IR spectrum bands at 1898 cm^{-1} indicate the coordination of CO to the metal centre.

For the catalytic benchmark reaction, we chose the hydrogenation of methyl benzoate by applying 1 mol% of catalysts **1**–**3** at 30 bar H_2 and 60 °C. To our delight, complex **3** produced a 99% yield of benzyl alcohol (Table 1, entry 3) whereas under the same reaction conditions complexes **1** and **2** only gave 50 and 30% yields of the product, respectively (Table 1, entries 1, 2). Noteworthy, complex **3** also facilitates the hydrogenation of methyl benzoate even at 40 °C albeit with a significant lower yield of 44% of **5a** (Table 1, entry 4). These experimental findings indicate the strong temperature dependence of this catalytic transformation. We assume that complex **3** readily losses borane at 60 °C to form the active catalytic species. Lowering the catalyst loading by a factor of 2 necessitates a prolongation of the reaction time to 16 h in order to achieve a reasonable yield of 86% (Table 1, entry 5). On the contrary, only 52% benzyl alcohol is obtained when the reaction is aborted after 6 h (Table 1, entry 6). Gratifyingly, decreasing the H_2 pressure to 10 bar still resulted in a good yield (82%) of benzyl alcohol after 6 h (Table 1, entry 7). The hydrogenation even proceeded smoothly at low pressure (2 bar), resulting in 58% of the desired product (Table 1, entry 8).

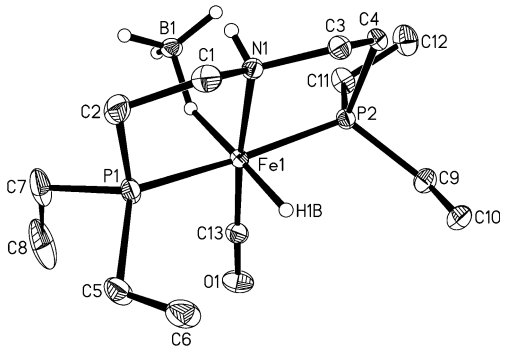
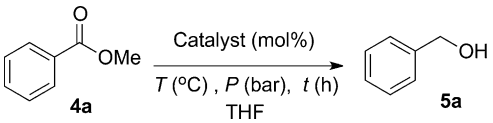


Figure 3. Molecular structure of complex **3** in the crystal. Only one of the two molecules of the asymmetric unit is depicted. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms except those on Fe, N and B are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Fe1–N1 2.070(2), Fe1–P2 2.1964(6), Fe1–P1 2.1967 (6), Fe1–H1B 1.50(3), Fe1–C13 1.725(2), C13–O1 1.162(3); P2–Fe1–P1 168.69(3), C13–Fe1–H1B 86.3 (12), C13–Fe1–N1 172.16(10), C13–Fe1–P1 95.51(8).

Table 1. Optimization of the reaction conditions for hydrogenation of methyl benzoate.[a]



Entry	Catalyst [mol%]	P [bar]	T [°C]	t [h]	Yield[b] [%]
1	**1** (1)	30	60	6	50
2	**2** (1)	30	60	6	30
3	**3** (1)	30	60	6	99
4	**3** (1)	30	40	16	44
5	**3** (0.5)	30	60	16	86
6	**3** (0.5)	30	60	6	52
7	**3** (1)	10	60	6	82
8	**3** (1)	2	60	6	58

[a] Methyl benzoate (0.5 mmol), **1**–**3** (0.005 mmol), THF (1 mL), 6–16 h, 40–60 °C, 2–30 bar H_2.
[b] Yield determined by GC analysis using hexadecane as an internal standard.

To evaluate the most active catalyst, we studied the performance of complexes **1**–**3** in the hydrogenation of methyl benzoate at 60 °C and 30 bar H_2 applying different interval times (Figure 4). The hydrogenation of methyl benzoate performed with complex **3** afforded benzyl alcohol in 90% yield within 4 h reaction time. However, the deployment of complexes **1** and **2** under the same reaction conditions resulted in significantly lower yields of 20% and 18%, respectively. Hence, we conclude that complex **3** represents the most efficient iron catalyst for ester hydrogenation known to date. In our previous studies on methyl benzoate hydrogenation[14b] using catalyst **1A** at the B3PW91/TZVP DFT level, we found that the reaction follows an outer-sphere mechanism in two suc-

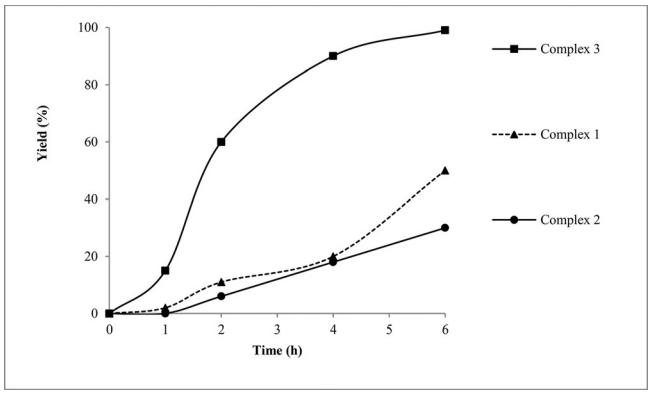


Figure 4. Hydrogenation of methyl benzoate using iron pincer complexes **1–3** at different interval times. *Reaction conditions:* methyl benzoate (0.5 mmol), **1–3** (0.005 mmol), 1 mL of THF (1 mL), 60 °C, 30 bar H_2. Yield determined by GC analysis using hexadecane as an internal standard.

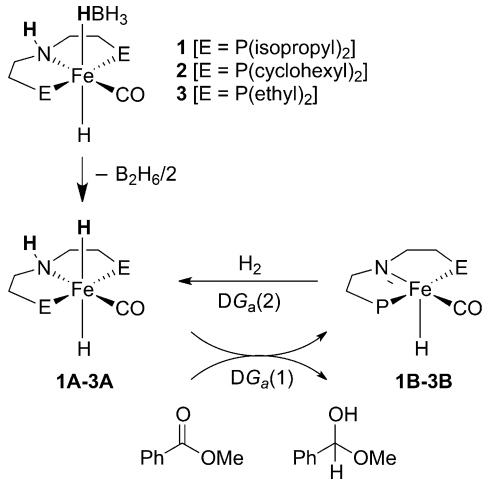


Figure 5. First step of methyl benzoate hydrogenation.

cessive cycles (Figure 5). The first one is the formation of the corresponding hemiacetal followed by the dissociation into benzaldehyde and methanol; and the second one is benzaldehyde hydrogenation to benzyl alcohol. After each step, the active catalyst **1A** is regenerated by H_2 addition from the amido intermediate **1B** (Figure 5).

On the basis of the computed Gibbs free energy barriers, hemiacetal formation has the highest barrier and therefore represents the rate-determining step. To compare the hydrogenation activity of catalysts **1A**–**3A**, we computed only the first step reaction by using the same method (B3PW91/TZVP) and procedure. All these data are summarized in the Supporting Information.

As reported previously, the Gibbs free energy barrier [$\Delta G_a(1)$] for hemiacetal formation by using catalyst **1A** is 21.51 kcal mol^{-1}. Using catalysts **2A** and **3A**, the free energy barrier is 24.12 and 20.15 kcal mol^{-1}, respectively. This shows that the catalyst **3A** has the lowest free energy barrier, while the barrier of catalyst **2A** is the highest. Our computed order of free energy barriers is in line with the observed activity shown in Figure 4. This can be ascribed to the steric effect of the substituents at the P centres.

In addition to the hydrogenation barriers, it is also interesting to compare the Gibbs free energy barrier [$\Delta G_a(2)$] of the catalyst regeneration. Moving from **1B** to **1A**, the reaction has a Gibbs free energy barrier of 17.14 kcal mol^{-1} and is slightly exergonic by 0.33 kcal mol^{-1}. Moving from **2B** to **2A**, the reaction has a Gibbs free energy barrier of 16.46 kcal mol^{-1} and is exergonic by 3.86 kcal mol^{-1}. Moving from **3B** to **3A**, the Gibbs free energy barrier is 18.12 kcal mol^{-1} and the reaction is slightly exergonic by 0.37 kcal mol^{-1}.

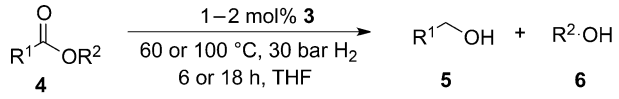
Next, we examined the scope of the hydrogenation reaction with the diethylphosphine-tagged complex **3**. Various aromatic and aliphatic esters (Table 2 and Table 3) as well as lactones (Table 3) were hydrogenated to their corresponding alcohols/diols with excellent yield at 30 bar H_2 and 60–100 °C applying 1–2 mol% catalyst loadings. Esters with both electron-donating (**4b**) and electron-withdrawing (**4c**, **4d**) substituents were converted into the corresponding alcohols with excellent yields under relatively mild conditions (Table 2, entries 2–4).

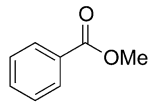
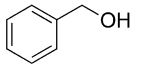
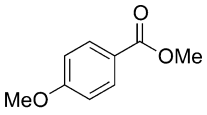
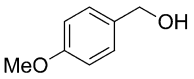
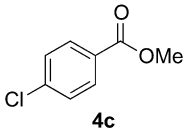
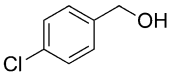
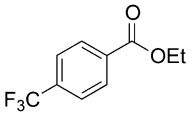
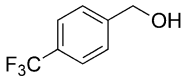
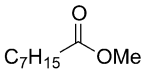
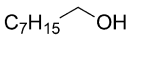
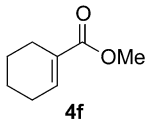
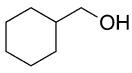
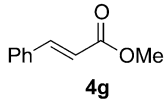
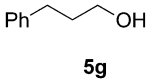
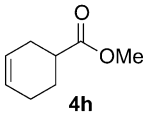
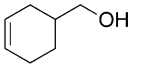
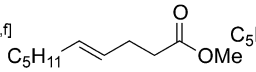
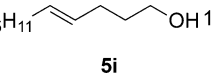
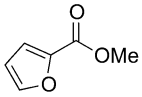
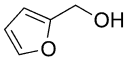
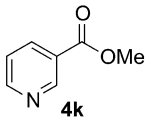
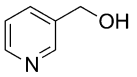
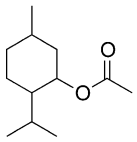
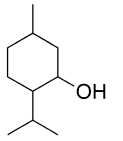
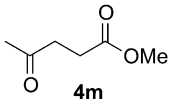
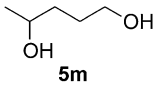
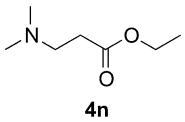
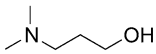
Rewardingly, the homogeneous hydrogenation of the long-chain aliphatic ester methyl octanoate (**4e**) produced 1-octanol in quantitative yield. Then, we proceeded with a chemoselectivity study utilizing ester substrates containing C=C bonds (Table 2, entries 6–9). Conjugated double bonds such as 1-cyclohexene methyl ester (**4f**) or methyl cinnamate (**4g**) were reduced in addition to the carboxyl functionality and the corresponding saturated alcohols were obtained in excellent yields. More interestingly, the isolated C=C motifs both in 3-cyclohexene-1-carboxylate (**4h**) and the aliphatic unsaturated ester (**4i**) remained intact after the catalytic transformation and the corresponding unsaturated alcohols were observed as the sole reaction product. Furthermore, heteroaromatic esters (**4j** and **4k**) were smoothly reduced to the desired alcohols with good yields (Table 2, entries 10 and 11).

Hydrogenation of menthyl acetate (**4l**) led to menthol with 63% yield and the conversion of methyl levulinate readily afforded 1,4-pentanediol (**5m**) after isolation. Moreover, an ethyl carboxylate featuring a dimethylamino group at the β-position underwent the desired catalytic transformation to the amino alcohol (**5n**). Note that the well described Ru-MACHO-BH catalyst does not facilitate the homogeneous hydrogenation of substrate **4n** to **5n**.[10]

The versatility of complex **3** as efficient and selective homogeneous hydrogenation catalyst was further

Table 2. Catalytic hydrogenation of aromatic and aliphatic esters using iron complex **3**.[a]



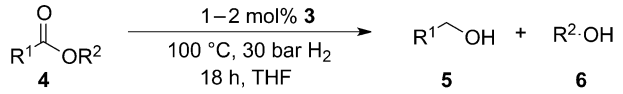
Entry	Ester	Alcohol	T [°C]	Conv. (Yield [%][b])
1[c]	 **4a**	 **5a**	60	>99 (99)[d]
2	 **4b**	 **5b**	60	>99 (90)
3	 **4c**	 **5c**	60	>99 (99)
4[e]	 **4d**	 **5d**	60	>99 (88)
5	 **4e**	 **5e**	100	>99 (95)
6[c]	 **4f**	 **5f**	100	>99 (98)
7	 **4g**	 **5g**	60	>99 (95)[d]
8	 **4h**	 **5h**	100	>99 (92)
9[c,f]	 **4i**	 **5i**	100	>99 (98)
10[e]	 **4j**	 **5j**	100	>99 (95)
11[e]	 **4k**	 **5k**	100	>99 (92)
12[c,e]	 **4l**	 **5l**	100	65 (63)
13	 **4m**	 **5m**	100	>99 (90)
14[c]	 **4n**	 **5n**	100	>99 (86)

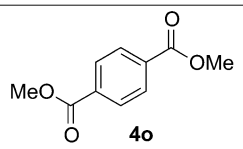
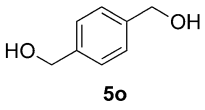
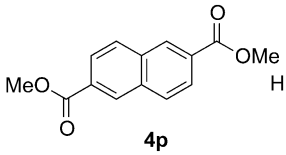
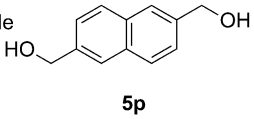
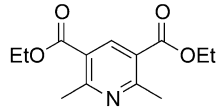
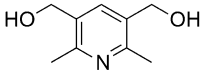
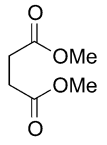
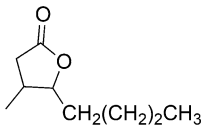
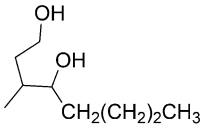
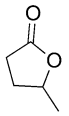
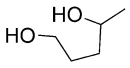
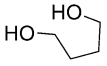
[a] Substrate (1 mmol), **3** (0.01 mmol), THF (1 mL), 60 or 100 °C, 30 bar H_2, 18 h.
[b] Conversion was determined by GC analysis using hexadecane as an internal standard (isolated yield in parentheses).
[c] Substrate (0.5 mmol), **3** (0.005 mmol), yield was determined GC analysis using hexadecane as an internal standard.
[d] 6 h reaction time.
[e] 2 mol% **3**.
[f] *cis*-4-Decen-1-ol was used for product calibration.

demonstrated in the preparation of diols from diesters and lactones, respectively. Aromatic diesters such as dimethyl terephthalate (**4o**) and naphthalene 2,6-dimethyl carboxylate (**4p**) were cleanly reduced to form the diols in good yields. Interestingly, the catalytic system is tolerant towards the pyridine ring in compound **4q** and almost quantitative product formation was observed upon reaction with H_2 gas (Table 3, entry 3). Comparable results were found with the aliphatic dimethyl succinate (Table 3, entry 4). The mixture of *cis* and *trans* isomers of whiskey lactone (important ingredient in the aroma of whiskey) was hydrogenated to **5s** with 90% isolated yield (mixture of stereoisomers). The important bio-mass derived γ-valerolactone (GVL) successfully formed the branched alcohol **5t** in a yield of 98%. Additionally, the sterically less demanding γ-butyrolactone was converted quantitatively into 1,4-butanediol even at 60 °C.

In conclusion, we demonstrated the effective ester hydrogenation by means of the second generation

Table 3. Hydrogenation of diesters and lactones.[a]



Entry	Ester	Alcohol	Conv. (Yield [%][b])
1	 **4o**	 **5o**	>99 (96)
2	 **4p**	 **5p**	>99 (89)
3[d]	 **4q**	 **5q**	>99 (91)
4[c]	 **4r**	 **5r**	>99 (97)
5[d]	 **4s**	 **5s**	>99 (97)
6[d]	 **4t**	 **5t**	>99 (98)
7[c,e]	 **4u**	 **5u**	>99 (99)

[a] Substrate (1 mmol), **3** (0.01 mmol), THF (1 mL), 100 °C, 30 bar H_2, 18 h.
[b] Conversion was determined by GC analysis using hexadecane as an internal standard (isolated yield in parentheses).
[c] Substrate (0.5 mmol), **3** (0.005 mmol), yield was determined GC analysis using hexadecane as an internal standard.
[d] 2 mol% **3**.
[e] 60 °C.

iron PNP pincer complex **3**. This catalytic system gave improved results for the selective hydrogenation of various aromatic and aliphatic esters including diester motifs and lactones.

Experimental Section

General Procedure

The catalytic transformations were performed in a 300-mL autoclave equipped with an internal aluminium plate to include seven uniform reaction glass vials (4 mL) sealed with cap, septum and needle. The autoclave was placed into an aluminium block as heating system to perform the reactions. The general procedure for the catalytic hydrogenation is as follows: In a reaction vial (4 mL), iron complex **3** (0.01 mmol) was mixed with 1 mL of THF and the resulting solution was stirred briefly. After that the ester (1 mmol) was added and the reaction vials were placed into a 300-mL autoclave. The autoclave was flushed thrice with hydrogen, pressurized to 30 bar H_2, placed into an aluminium block, heated up to reaction temperature (60 or 100 °C) and the reaction mixtures were stirred for 6 or 18 h, respectively. After completion of the reaction time, the autoclave was cooled to room temperature and hydrogen was released. The reaction mixtures were analyzed by GC-FID and GC-MS. Product isolation was performed *via* column chromatography using silica gel as stationary phase and an *n*-pentane/ethyl acetate mixture (2:1) as eluent.

The computational methodology as well as the energetic data and the optimized Cartesian coordinates are comparatively given in the Supporting Information.

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[18] CCDC 1421516 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

