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# Iron(II) Complexes for the Efficient Catalytic Asymmetric Transfer Hydrogenation of Ketones

**Nils Meyer, Alan J. Lough, and Robert H. Morris*[a]**

**Abstract:** Iron(II) carbonyl compounds of the type *trans*-[Fe(NCMe)(CO)(P-N-N-P)][$BF_4$]$_2$ bearing the ethylenediamine-derived diiminodiphosphine ligands (*R,R*)- or (*S,S*)-1,2-diphenyl-1,2-diaminoethane were synthesized and characterized, including by their crystal structures. The new complexes are suitable precatalysts for the transfer hydrogenation of ketones at room temperature, giving turnover frequencies of up to 2600 $h^{-1}$ with low catalyst loadings (0.025–0.17 %). Screening experiments showed that the precatalysts are able to produce alcohols from a wide range of simple ketones. For sterically demanding prochiral ketones, excellent enantioselectivities were obtained (up to 96 % *ee*).

**Keywords:** asymmetric catalysis · carbonyl ligands · hydrogenation · iron · ketones

## Introduction

The reduction of carbonyl compounds to alcohols is an industrially relevant reaction for the preparation of fine chemicals, perfumes, agrochemicals and pharmaceuticals.[1] Metal-catalysed pathways to these kinds of alcohols include $H_2$ hydrogenation, hydrosilation or transfer hydrogenation, and use catalysts based on the precious metals palladium, rhodium, iridium and ruthenium.[2] There have been several attempts to develop iron catalysts for these kinds of reactions, because these would be cheaper and non-toxic.[3,4] In this regard, Chirik's, Beller's and Nishiyama's groups have recently reported useful iron catalysts for the hydrosilation of aldehydes and ketones[3a,b,g] and their transfer hydrogenation.[5]

Our group has shown that iron(II) compounds with diiminodiphosphine and diaminodiphosphine ligands are effective for the $H_2$ hydrogenation and transfer hydrogenation of ketones and an aldimine.[6] The enantiopure iron(II) complex *trans*-(*R,R*)-[Fe(NCMe)(L)(cy$P_2N_2$)][$BF_4$]$_2$ with L = $CH_3CN$ (see Figure 1) was found to be a moderately active precatalyst for the $H_2$ hydrogenation of acetophenone to afford enantioenriched (*S*)-1-phenylethanol, in 27 % *ee* In contrast, the complex with the ligand L = CO is not an $H_2$ hydrogenation catalyst but is a highly active and moderately enantioselective transfer hydrogenation catalyst at room temperature, converting a variety of aromatic ketones into the corresponding alcohols. The enantioselectivity was somewhat increased, but the activity was decreased, in the complex in which L = *t*BuNC.[6a]

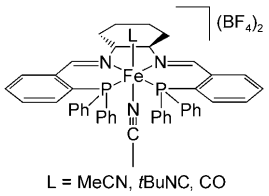


Figure 1. Structures of the *trans*-(*R,R*)-[Fe(NCMe)(L)(cy$P_2N_2$)][$BF_4$]$_2$ complexes.

This contribution reports the synthesis and characterisation of iron(II) carbonyl complexes in which the diamine precursors to the diiminodiphosphine ligands have been varied in order to study the effect of the ligand structure on the activities and enantioselectivities of iron-based transfer hydrogenation catalysts. The achiral and chiral tetradentate diiminodiphosphine ligands eth$P_2N_2$ ({$PPh_2$(2-$C_6H_4$)CH=N-($CH_2$)$_2$N=CH(2-$C_6H_4$)$PPh_2$})[7] and (*R,R*)- and (*S,S*)-diph-eth$P_2N_2$ ({$PPh_2$(2-$C_6H_4$)CH=N(CHPh)$_2$N=CH(2-$C_6H_4$)-$PPh_2$})[8] have thus been employed.

## Results and Discussion

**Synthesis and characterization of the complexes**: The iron complexes *trans*-[Fe(NCMe)(CO)(eth$P_2N_2$)][$BF_4$]$_2$ (**1**) and

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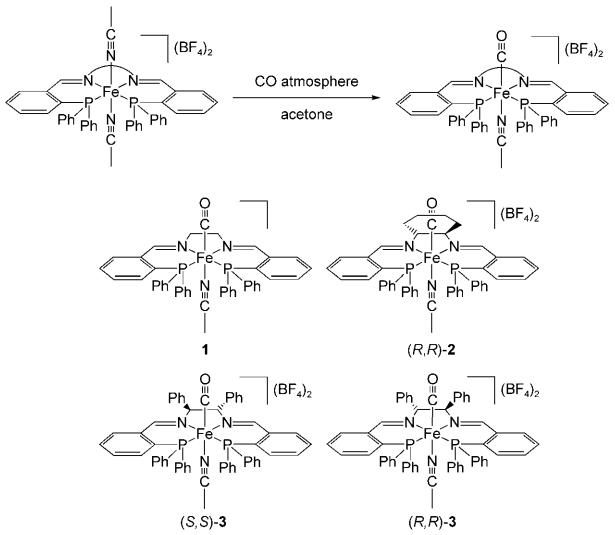
(*R,R*)- and (*S,S*)-*trans*-[Fe(NCMe)(CO)(diph-eth$P_2N_2$)]-[$BF_4$]$_2$ [(*S,S*)-**3** and (*R,R*)-**3**] were obtained as orange solids in good yields when the corresponding bis-acetonitrile compounds *trans*-[Fe(NCMe)$_2$(eth$P_2N_2$)][$BF_4$]$_2$[6b] and (*R,R*)- and (*S,S*)-*trans*-[Fe(NCMe)$_2$(diph-eth$P_2N_2$)][$BF_4$]$_2$[6b] were stirred under CO in acetone (Scheme 1). The similar synthesis of (*R,R*)-[Fe(NCMe)(CO)(cy$P_2N_2$)][$BF_4$]$_2$ (**2**) has been described previously.[6a] The new compounds are fairly air-stable, both as solids and in solution. They are soluble in acetonitrile and methylene chloride, slightly soluble in acetone, chloroform and propan-2-ol and insoluble in tetrahydrofuran, ether and hydrocarbons. When dissolved in acetonitrile, they react over the course of several hours to give back the starting bis-acetonitrile complexes, a reaction that is easily followed by $^{31}P\{^1H\}$ NMR spectroscopy.




Scheme 1. Preparation of the carbonyl complexes **1**, (*R,R*)-**2** and (*S,S*)- and (*R,R*)-**3**.

The new compounds were characterized by NMR techniques, elemental analysis, mass spectrometry, IR spectroscopy and single-crystal X-ray crystallography. The $^1H$, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra are consistent with the solid-state structures shown in Figure 2. A broadening of the signals relative to those of the starting materials is observed, especially in the $^1H$ NMR spectra. Complex **1** in $CD_2Cl_2$ produces a singlet at 50.8 ppm in the $^{31}P\{^1H\}$ NMR spectrum (vs. 54.4 ppm for the starting complex), whereas for **3** two doublets at 49.9 and 53.0 ppm were observed (vs. a singlet for the starting material at 51.8 ppm). The $^{13}C\{^1H\}$ NMR spectra show the expected signals, but no signals for the CO carbon nuclei could be observed. Characteristic IR absorptions for $\nu_{C\equiv O}$ were found for both compounds: at 2002 cm$^{-1}$ in **1** and 2004 cm$^{-1}$ in **3**. These are typical values for dicationic iron(II)-coordinated carbonyl ligands:[10] $\nu_{C\equiv O}$ in (*R,R*)-**2**, for example, is 2000 cm$^{-1}$, whereas $\nu_{C\equiv O}$ in the $Fe^{II}$ complex *cis*-[Fe(CO)(NCMe)($PEt_2CH_2NMeCH_2PEt_2$)($PMe_2CH_2PMe_2$)][$BF_4$]$_2$ is 1991 cm$^{-1}$.[10c] Mass spectra (ESI$^+$) show the dicationic fragments without the acetonitrile and carbonyl ligands ([$M$−MeCN−CO]$^{2+}$).

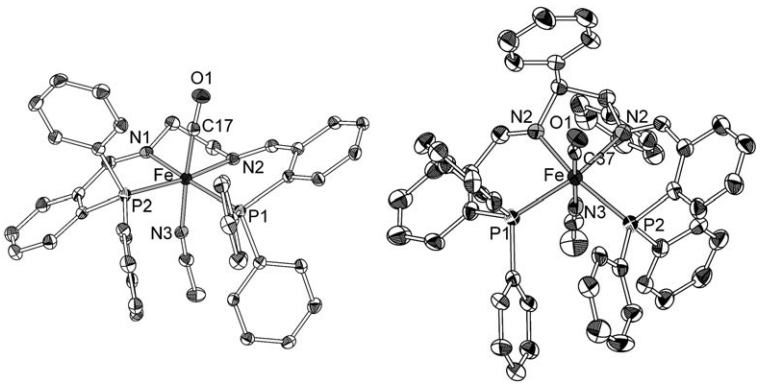



Figure 2. ORTEP views of the molecular structures of **1** (left) and (*S,S*)-**3** (right). Thermal ellipsoids are drawn to encompass 30% probability. Hydrogen atoms, $BF_4^-$ anions and solvent molecules are omitted for clarity. Only one of the two independent molecules of **3** is shown. Selected interatomic distances [Å] and angles [°]: **1**) Fe−P1 2.2882(11), Fe−P2 2.2809(11), Fe−N1 2.012(4), Fe−N2 2.027(5), Fe−N3 1.953(6), Fe−C17 1.775(4), O1−C17 1.144(4); P1-Fe-P2 102.98(4), P1-Fe-N1 168.88(9), P1-Fe-N2 87.29(9), P1-Fe-N3 89.13(9), P1-Fe-C37 91.1(1), P2-Fe-N1 86.93(8), P2-Fe-N2 169.72(9), P2-Fe-N3 92.52(9), P2-Fe-C17 92.8(1), N1-Fe-N2 82.8(1), N1-Fe-N3 85.4(1), N1-Fe-C17 93.40(2), N2-Fe-N3 87.7(1), N2-Fe-C17 86.76(2), N3-Fe-C17 174.46(2), Fe-C17-O1 175.01(4). (*S,S*)-**3**) Fe−P1 2.2791(2), Fe−P2 2.2725(2), Fe−N1 2.012(4), Fe−N2 2.027(5), Fe−N3 1.953(6), Fe−C37 1.828(7), O1−C37 1.122(7); P1-Fe-P2 102.61(6), P1-Fe-N1 88.6(1), P1-Fe-N2 169.7(1), P1-Fe-N3 88.7(1), P1-Fe-C37 90.23(2), P2-Fe-N1 167.5(1), P2-Fe-N2 87.4(1), P2-Fe-N3 90.0(1), P2-Fe-C37 88.37(2), N1-Fe-N2 81.67(2), N1-Fe-N3 84.73(2), N1-Fe-C37 97.14(2), N2-Fe-N3 93.72(2), N2-Fe-C37 87.66(3), N3-Fe-C37 177.83(3), Fe-C37-O1 174.89(6).

The solid-state structures and selected bond lengths and angles are shown in Figure 2. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. The iron is coordinated in a distorted octahedral fashion, with the nitrogen and phosphorus atoms of the PNNP ligand forming the equatorial plane and the acetonitrile and carbonyl ligand located in axial positions (Figure 2). Interatomic distances and angles are in ranges similar to those seen in the previously described starting material [Fe(NCMe)$_2$(eth$P_2N_2$)][$BF_4$]$_2$.[6b] The iron–carbon distance is 1.755(4) Å, and the CO is bound in an almost linear fashion with respect to the iron [Fe-C-O 175.01(4)].

Complex (*S,S*)-**3** crystallizes in the monoclinic space group $P2_1$ with four molecules in the unit cell and two independent molecules in the asymmetric unit. The independent molecules are quite similar, so only one is discussed here. As in **1**, a distorted octahedral coordination of the iron with the PNNP ligand in the equatorial plane is observed. The phenyl rings of the chiral bridge are found in axial positions

on the Fe-N-C-C-N ring, with a ($C_{Ph}$)-C-C-($C_{Ph}$) torsion angle of 169.92(6)°. The P–Fe and N–Fe distances are comparable to those in related $Fe^{II}$ compounds bearing tetradentate PNNP ligands.[6,9] The Fe–C distance is 1.775(4) Å and the Fe-C-O angle is 174.89(6)°, both of which are typical for $Fe^{II}$ carbonyl compounds.[10] All of the other bond distances and angles are very similar to those in the starting material, (*R,R*)-*trans*-[Fe(NCMe)$_2$(diph-eth$P_2N_2$)][$BF_4$]$_2$.[10b]

**Transfer hydrogenation**: To investigate the catalytic activity of **1** and (*R,R*)-**3**,[1] we first tried acetophenone as the substrate. We were pleased to find that these are highly active precatalysts for the transformation of acetophenone into 1-phenylethanol at room temperature, in propan-2-ol as the hydrogen source and solvent. Figure 3 shows comparable runs of **1**, (*R,R*)-**2** and (*R,R*)-**3**, each with a catalyst/base/substrate ratio of 1:8:600 (base = KO*t*Bu, $c_{acetophenone}$ = 0.5 mol L$^{-1}$). The complexes all show very similar activities, indicating that the steric influences of the ligands, which are increasing from **1** to **2** to **3**, have only a minor effect on the reactivity (Figure 3). In each case the reaction starts off at a constant rate until the equilibrium is approached. Thus, after 10 min, complex (*R,R*)-**2** had produced the most 1-phenylethanol [72% conv., TOF[11] = 2600 h$^{-1}$, 35% *ee* (*S*)], followed by **1** (62% conv., TOF = 2200 h$^{-1}$) and then (*R,R*)-**3** [57% conv., TOF = 2000 h$^{-1}$, 63% *ee* (*S*)]; the TOFs were determined from the degrees of conversion after 10 min. The maximum conversion in each case is 88–90% even after stirring overnight. It should be mentioned that the turnover frequency of (*R,R*)-**2** is significantly increased under these reaction conditions in relation to those previously reported.[6a] A TOF of 907 h$^{-1}$ was reported for (*R,R*)-**2** when the C/B/S ratio was 1:8:200.

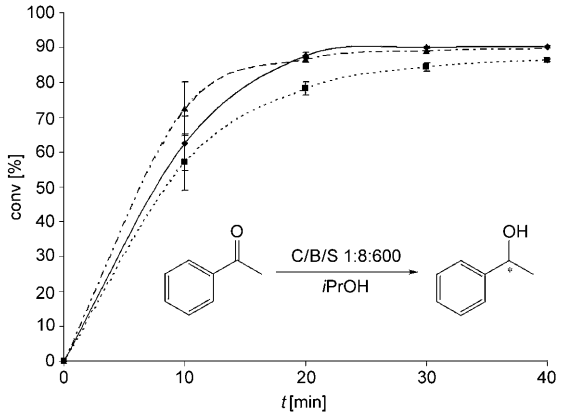



Figure 3. Asymmetric transfer hydrogenation of acetophenone in the presence of **1** (◆), (*R,R*)-**2** (▲) or (*R,R*)-**3** (■) as precatalysts in basic propan-2-ol at 24 °C.

When the substrate loadings are further increased, the reactions stop before reaching 90% conversion. As an example, 73% conversion was achieved with (*R,R*)-**3** when a C/B/S ratio of 1:8:4000 was used ($c_{acetophenone}$ = 3.3 mol L$^{-1}$). When the same C/B/S ratio but a larger amount of propan-2-ol was used ($c_{acetophenone}$ = 1.7 mol L$^{-1}$), a slightly higher turnover frequency was observed. However, the overall yield of 1-phenylethanol did not increase significantly (75%). The turnover frequencies determined after 1 h are 1300 h$^{-1}$ and 1600 h$^{-1}$, respectively.

To reach complete conversion, the acetone formed during the reaction has to be removed from the mixture.[12,13] Complete (*R,R*)-**3**-catalysed conversion (99%) of acetophenone into 1-phenylethanol [60% *ee* (*S*)] was achieved when propan-2-ol and acetone were removed in vacuo from the mixture after 15 min of reaction and replaced by fresh propan-2-ol.

The fact that the compound (*R,R*)-**3** gave 1-phenylethanol in significantly higher enantiomeric excess (63% *S*) than (*R,R*)-**2** (35% *S*) is evidence that the active catalytic iron species is still bound to the ligand. At the end of the reaction, racemisation is observed when the reaction is not stopped after reaching the equilibrium. After 12 h, the *ee* of the alcohol product had dropped to 25% when (*R,R*)-**2** was used and to 44% when (*R,R*)-**3** was used.

So far we have not been able to identify the catalytically active species. On following the reaction by $^{31}P\{^1H\}$ NMR, we noted that the signals for the precatalyst **3** disappeared, and two doublets at 82.5 and 65.9 ppm ($J_{P,P}$ = 24 Hz) appeared, but further study is required to identify the catalytic active species. We also observed several peaks between −7.4 and −17.3 ppm, suggesting the presence of noncoordinated phosphorus atoms.

The results of the screening of several substrates (Figure 4) in the presence of (*R,R*)-**3** as the precatalyst are summarized in Table 1. For comparison we also show the conversion after 15 or 30 min. Almost complete conversion (86–96%) had been achieved after 1 h for all of the substrates, except for **16**. We first increased the steric bulk of acetophenone by replacing the methyl group with ethyl, isopropyl or *tert*-butyl groups (entries 1–4, Table 1). The sterically more demanding substrates caused decreases in the activity of the catalyst [TOF **4** (2000 h$^{-1}$) > **5** (900 h$^{-1}$) > **6** ≈ **7** (700 h$^{-1}$)], whereas on the other hand the enantioselectivities increased (*ee* **4** < **5** < **6** < **7**). Alcohols with *ee*s of up to 96% were thus obtained. Interestingly, another transfer hydrogenation catalyst system that displays similar trends in activity and selectivity is a mixture of [$Ru_3(CO)_{12}$] and the (*S,S*)-diph-eth$P_2N_2$ ligand.[14] Here it was proposed that the mechanism involved a ruthenium cluster catalyst.

Use of acetophenone derivatives with chloro substituents in the *ortho* or *para* positions of their phenyl rings seems to have no significant influence on the reactivities of the substrates (entries 5, 7). This result is the opposite of the generally observed trend for the transfer hydrogenation catalysts reported by Noyori and co-workers, in which *ortho*-Cl substitution, for example, decreases the rate of the reduction.[15]

[1] The (*R,R*) enantiomer of **3** was used exclusively for all catalytic reaction. Test reactions showed no difference in the catalytic activity and enantioselectivity of (*R,R*)- and (*S,S*)-**3**, except that (*S,S*)-**3** yields the alcohol in the opposite configuration to that from (*R,R*)-**3**.

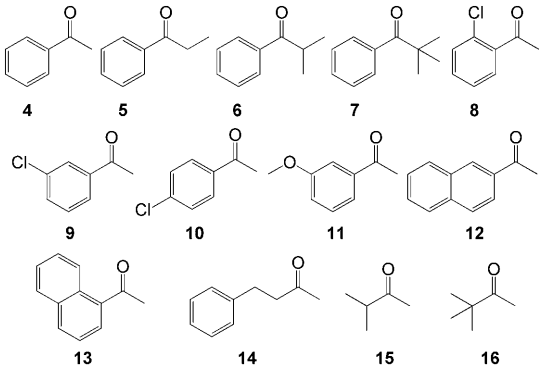



Figure 4. Ketone substrates that are reduced to the corresponding alcohols under the transfer-hydrogenation conditions described in Table 1.

Table 1. Asymmetric transfer hydrogenation catalysed by (*R*,*R*)-**3** at room temperature.

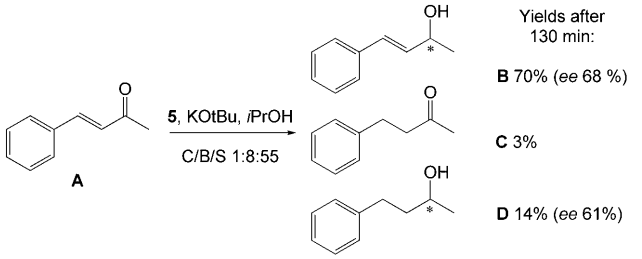
| Entry | Substrate (Figure 4) | *t* [min] | Yield [%] | *ee S* [%] |
|---|---|---|---|---|
| 1[a] | **4** | 15 | 68 | 63 |
| 2[a] | **5** | 30 | 75 | 70 |
| 3[a] | **6** | 30 | 58 | 94 |
| 4[b] | **7** | 15 | 93 | 96 |
| 5[a] | **8** | 30 | 93 | 29 |
| 6[a] | **9** | 30 | 68 | 45 |
| 7[a] | **10** | 30 | 81 | 38 |
| 8[a] | **11** | 30 | 86 | 52 |
| 9[a] | **12** | 30 | 61 | 52 |
| 10[b] | **13** | 30 | 73 | 61 |
| 11[b] | **14** | 15 | 91 | 57 |
| 12[a] | **15** | 15 | 63 | 12 |
| 13[b] | **16** | 60 | 48 | 21 |

The reactions were carried out at 24 °C in the presence of (*R*,*R*)-**3** (0.005 mmol) and KO*t*Bu (0.04 mmol) in *i*PrOH (6 mL). [a] C/B/S 1:8:600 [b] C/B/S 1:8:200.

In contrast, chloro substitution in the *meta* position caused a slight decrease in the activity (entry 6), whereas a methoxy group in the *meta* position showed no significant influence (entry 8). This trend is also the opposite of the activity trend observed for a $[RuCl_2(PNN)(PPh_3)]$ catalyst system.[16]

The complex **3** was also found to be an active catalyst for the reduction of 1- and 2-acetonaphthone (entries 9, 10). Good activities were observed, but only moderate enantioselectivities. We were pleased to find that **3** is also able to catalyse the reduction of non-aromatic ketones (entries 11–13). Thus, for the substrates **14** and **15**, excellent activities and moderate enantioselectivities could be achieved, whereas for the sterically more demanding 2,2-dimethylbutan-2-one (**16**) only very low activity was observed. Examples of the enantioselective reduction of **14**–**16** are rare: a solution of a binol-derived diphosphinite ruthenium complex in propan-2-ol and base at 40 °C was reported to catalyse the transfer hydrogenation of **15** to afford the alcohol in 99 % *ee*,[17] whereas an iron carbonyl/porphyrin mixture produced an 11 % conversion of **16**, but only at 100 °C.[5]

The iron-catalysed transfer hydrogenation of an α,β-unsaturated substrate—(*E*)-4-phenylbut-3-en-2-one (**A**, Scheme 2)—was also examined. Only low levels of conversion could be achieved, so a C/B/S ratio of 1:8:55 was chosen. The relative amounts of the possible products phenylbut-3-en-2-ol (**B**), 4-phenylbutan-2-one (**C**), 4-phenylbutan-2-ol (**D**) and the starting ketone **A** were monitored during the reaction, and the results are summarized in Scheme 2 and Figure 5. The main product was the allyl alcohol **B**, obtained in 70 % yield (68 % *ee*) after 130 min. It was formed immediately after the reaction had started. After 420 min, a 75 % yield of **B** had been produced. A small amount of **C** (5 %) resulting from the reduction of the double bond was observed during the first 50 min, but almost complete conversion into the completely reduced alcohol **D** had occurred after 130 min and only traces of **C** were detected after longer reaction times. Compound **D** was obtained in 14 % yield (61 % *ee*) after 130 min. It first appeared after a short induction period, indicating that it is formed almost entirely from **C**. It should be mentioned that no more significant changes were observed when the mixture was allowed to react for longer periods, even for days. The yields after 23 h were **B** 71 %, **C** < 1 % and **D** 27 %. Interestingly, these results are in contrast with the outcomes of the same reaction catalysed by **2**, in which **D** was the main product.[6a] We suggest that the sterically more demanding ligand system of **3** hinders the hydrogenation of the C=C double bond.




Scheme 2. (*R*,*R*)-**3**-catalysed transfer hydrogenation of the α,β-unsaturated ketone **A**.

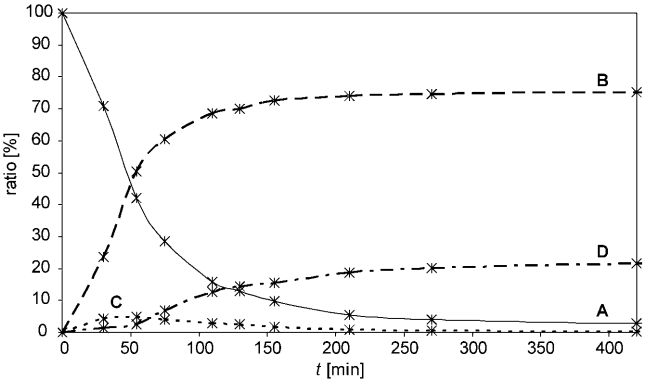



Figure 5. Asymmetric transfer hydrogenation of (*E*)-4-phenylbut-3-en-2-one catalysed by (*R*,*R*)-**3** in *i*PrOH with C/B/S 1:8:55.

## Conclusions

In summary, we have described highly active and well-defined iron precatalysts **1** and **3** for the transfer hydrogenation of aromatic and non-aromatic ketones. The iron complexes were fully characterized, including by their crystal structures. They have excellent catalytic activities at room temperature, competitive with those of the best-established ruthenium catalysts.[18] With bulky substrates, excellent enantiomeric selectivities were observed when **3** was used as the precatalyst. This is the only iron catalyst so far reported to give such high *ee* values at high levels of conversion. In addition, we have further optimized our recently reported catalytic iron system involving **2**, now achieving high turnover frequencies (up to 2600 $h^{-1}$), high turnover numbers and high enantiomeric excesses. This is an important step in the journey to replace precious and toxic platinum metal catalysts with cheap and environmentally friendly iron compounds. Further mechanistic work is required to explain the unique selectivities of the ketone reductions described in this work.

## Experimental Section

**General procedures**: All reactions were carried out under $N_2$ by standard Schlenk or drybox techniques. Dry, oxygen-free solvents were prepared by distillation from appropriate drying reagents and employed throughout. Substrates **4**–**11** and **14**–**16** were distilled from $P_2O_5$. All other commercially available reagents were used without further purification. The complexes *trans*-(*R,R*)-[Fe(NCMe)(CO)(cy$P_2N_2$)][$BF_4$]$_2$ (**2**),[6a] *trans*-[Fe(NCMe)$_2$(eth$P_2N_2$)][$BF_4$]$_2$[6b] and *trans*-(*R,R*)-[Fe(NCMe)$_2$(diph-eth$P_2N_2$)][$BF_4$]$_2$[6b] have been described previously. Varian Gemini 400 MHz and 300 MHz spectrometers were employed for recording $^1$H (400 MHz and 300 MHz), $^{13}$C{$^1$H} (100 MHz and 75 MHz) and $^{31}$P{$^1$H} (121 MHz) NMR spectra at ambient temperature. The $^1$H and $^{13}$C{$^1$H} NMR spectra were referenced to solvent resonances. The $^{31}$P{$^1$H} NMR spectra were referenced to 85% $H_3PO_4$ (0 ppm). Gas chromatography was carried out on a Perkin–Elmer Autosystem XL instrument. All infrared spectra were recorded on a Nicolet 550 Magna-IR spectrometer. The elemental analysis were performed on a Perkin–Elmer 2400 CHN elemental analyser. Samples were handled under argon when appropriate.

**General procedure for the synthesis of *trans*-[Fe(NCMe)(CO)(eth$P_2N_2$)][$BF_4$]$_2$ (1) and *trans*-(*R,R*)-[Fe(NCMe)$_2$(diph-eth$P_2N_2$)][$BF_4$]$_2$ [(*R,R*)-3]**: A solution either of *trans*-[Fe(NCMe)$_2$(eth$P_2N_2$)][$BF_4$]$_2$ (1.31 g, 1.5 mmol) or *trans*-(*R,R*)-[Fe(NCMe)$_2$(diph-eth$P_2N_2$)][$BF_4$]$_2$ (0.51 g, 0.5 mmol) in acetone was stirred under CO for 2 h. The reaction mixture was concentrated to dryness to give an orange solid. The whole procedure was repeated three times. The solution was concentrated to dryness and the remaining orange residue was washed with toluene and ether. Crystallization from $CH_2Cl_2$/$Et_2O$ or acetone/$Et_2O$ gave the analytically pure compounds.

**Compound 1**: Yield: 1.14 g (1.3 mmol, 87%); $^1$H NMR ($CD_2Cl_2$): $\delta$ = 1.86 (s, 3H; MeCN), 4.09 (br s, 2H; $CH_2$), 4.25 (br s; $CH_2$), 6.46–8.06 (several br s, 18H; Ar), 9.30 ppm (s, 2H; CH=N); $^{13}$C NMR ($CD_2Cl_2$): $\delta$ = 65.6 ($CH_2$), 129.5–138.6 (several m, Ar), 175.3 ppm (CH=N); $^{31}$P NMR ($CD_2Cl_2$): $\delta$ = 50.8 (s); IR (KBr): $\tilde{\nu}$ = 2002 $cm^{-1}$ ($\nu_{C\equiv O}$); MS (ESI$^+$): *m/z* (%): 330.1 [*M*−MeCN−CO]$^{2+}$; elemental analysis (%) calcd for $C_{43}H_{37}B_2F_8N_3P_2Fe_1$: C 57.18, H 4.13, N 4.65; found: C 56.12, H 4.15, N, 4.83. Crystals of **1** for the X-ray diffraction study were obtained by diffusion of ether into a $CH_2Cl_2$ solution.

**Compound (*R,R*)-3**: Yield: 0.47 g (0.4 mmol, 80%); $^1$H NMR ($CD_2Cl_2$): $\delta$ = 1.20 (br s, 3H; MeCN), 5.28 (br s, 2H; CH), 5.81–8.07 (several br s, 28H; Ar), 9.33 ppm (br s, 2H; CH=N); $^{13}$C NMR ($CD_2Cl_2$): $\delta$ = 76.3 (CH), 77.8 (CH), 127.6–139.2 (several m, Ar), 176.9 (CH=N), 178.1 ppm (CH=N); $^{31}$P NMR ($CD_2Cl_2$, 121 MHz): 51.6 (d, $J_{P,P}$ = 31 Hz), 49.2 ppm (d, $J_{P,P}$ = 31 Hz); IR (KBr): $\tilde{\nu}$ = 2004 $cm^{-1}$ ($\nu_{C\equiv O}$); MS (ESI$^+$): *m/z* (%): 406.1 [*M*−MeCN−CO]$^{2+}$; elemental analysis (%) calcd for $C_{55}H_{45}B_2F_8N_3P_2Fe_1$: C 62.59, H 4.30, N 3.98; found: C 61.93, H 4.96, N 3.67.

The complex (*S,S*)-**3** was also prepared with similar yield and properties. Crystals of this complex for the X-ray diffraction study were obtained by diffusion of ether into an acetone solution.

**Transfer hydrogenation**: A solution of substrate (1, 3 or 20 mmol) in propan-2-ol (6 mL) was added to a mixture of solid precatalyst [**1**, (*R,R*)-**2** or (*R,R*)-**3**, 0.005 mmol] and KO*t*Bu (0.04 mmol). The immediately formed dark solution was stirred vigorously. Samples were taken from the mixture, quenched by exposure to air and analysed by gas chromatography. When the samples are exposed to air the solutions turn yellow and the reaction stops immediately. The alcohol/ketone concentrations do not change in these solutions, even after several days. The GC retention times were obtained by comparison of the GC retention times for product mixtures with known literature values. All of the catalytic results were reproduced.

**Structural determination of 1 and (*S,S*)-3**: X-ray crystallographic data for **1** and (*S,S*)-**3** were collected on a Bruker–Nonius Kappa-CCD diffractometer with use of monochromated $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å) and were measured with a combination of $\phi$ scans and ω scans with κ offsets, to fill the Ewald sphere. Data collection parameters and crystallographic information are given in Table 2. The data were processed by use of the Denzo-SMN package. Absorption corrections were carried out with SORTAV. The structures were solved and refined with SHELXTL V6.1 for full-matrix, least-squares refinement based on $F^2$. All H atoms were included in calculated positions and allowed to refine in riding-motion approximation with $U_{iso}$ tied to the carrier atom.

Table 2. Summary of crystal data and details of intensity collection and least-squares refinement parameters for **1** and (*S,S*)-**3**.

| | **1** | (*S,S*)-**3** |
|---|---|---|
| empirical formula | $C_{43}H_{37}B_2F_8FeOP_2$ | $C_{58}H_{51}B_2F_8FeN_3O_2P_2$ |
| $F_w$ | 903.17 | 1113.43 |
| $T$ [K] | 150(2) | 150(2) |
| space group | $P\bar{1}$ | $P2_1$ |
| $a$ [Å] | 9.9487(4) | 11.4484(3) |
| $b$ [Å] | 14.2587(4) | 23.0724(6) |
| $c$ [Å] | 14.4888(4) | 22.4850(6) |
| $\alpha$ [°] | 92.1580(2) | 90 |
| $\beta$ [°] | 94.0940(2) | 91.941(1) |
| $\gamma$ [°[ | 100.3860(2) | 90 |
| $V$ [Å$^3$] | 2013.8(1) | 5935.8(3) |
| $Z$ | 2 | 4 |
| $\rho$ [mg $cm^{-3}$] | 1.489 | 1.246 |
| reflections collected | 22594 | 45379 |
| unique reflections | 9142 [$R_{int}$ = 0.0656] | 20334 [$R_{int}$ = 0.075] |
| data; parameters | 9142; 542 | 20334; 1369 |
| $R1$;[a] $wR2$[b] | 0.0622; 0.1737 | 0.0661; 0.18116 |

[a] $R1 = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

CCDC-710194 (**1**) and CCDC-710195 [(*S,S*)-**3**] contain 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.

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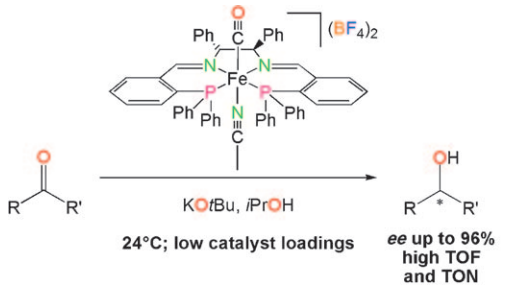


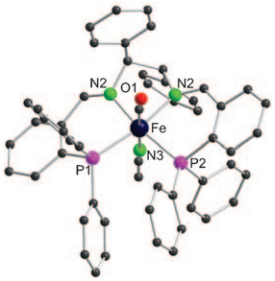


**Ferrous efficiency**: New achiral and chiral iron complexes containing P-N-N-P diiminodiphosphine ligands display high activity—and in the case of the catalyst shown, high enantioselectivity—in the catalytic transfer hydrogenation of ketones. This is an important step in the journey to replace precious and toxic platinum metal catalysts with cheap and environmentally friendly iron compounds.

**Hydrogenation**

*N. Meyer, A. J. Lough, R. H. Morris** ..... ▮▮▮▮–▮▮▮▮

**Iron(II) Complexes for the Efficient Catalytic Asymmetric Transfer Hydrogenation of Ketones**