Asymmetric Catalysis

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Highly Enantioselective Transfer Hydrogenation of Ketones with Chiral $(NH)_2P_2$ Macrocyclic Iron(II) Complexes**

*Raphael Bigler, Raffael Huber, and Antonio Mezzetti**

Abstract: *Bis(isonitrile) iron(II) complexes bearing a C_2-symmetric diamino $(NH)_2P_2$ macrocyclic ligand efficiently catalyze the hydrogenation of polar bonds of a broad scope of substrates (ketones, enones, and imines) in high yield (up to 99.5 %), excellent enantioselectivity (up to 99 % ee), and with low catalyst loading (generally 0.1 mol %). The catalyst can be easily tuned by modifying the substituents of the isonitrile ligand.*

The asymmetric transfer hydrogenation (ATH) and direct hydrogenation of polar bonds and alkenes are among the most investigated reactions in catalysis, and a plethora of chiral and achiral catalysts has been developed to this end.[1] However, most systems are based on precious metals, whose high cost has hampered industrial application.[2] More recently, base (3d) metals have been found to be efficient substitutes, and in some cases even to outperform precious metals.[3] The hydrogenation of polar double bonds with homogeneous iron catalysts has been pioneered by Gao,[4] Morris,[5] and Beller.[6] Currently, the most active ATH system is Morris' catalyst $[FeCl(CO)(\mathbf{A})]BF_4$ (Figure 1), which hydrogenates ketones with a TOF of more than 200 s^{-1}, but the enantioselectivity (between 24 and 99 % *ee*) is modest for most substrates.[7]

Gao's heterogeneous system that combines macrocycle **B** with $[Fe_3(CO)_{12}]$ hydrogenates aryl alkyl ketones and β-ketoesters using H_2 with high selectivity (usually > 95 % *ee*),[4,8] but modest activity (TOF up to 40 h^{-1}) as compared to Morris' catalyst.[7] Gade has reported a highly enantioselective Fe^{II} catalyst with an anionic boxmi ligand for the hydrosilylation of aryl alkyl ketones, but with a relatively high catalyst loading (5 mol %).[9] Therefore, a system that is both highly active and selective has still to be found.

We have recently prepared the enantiopure C_2-symmetric N_2P_2 macrocycles **1a–c** (Figure 1), which form the mononuclear, stable, diamagnetic bis(acetonitrile) complexes $[Fe(MeCN)_2(\mathbf{1a–c})](BF_4)_2$ (**2a–c**).[10] The rationale was to exploit the macrocyclic effect[11] to stabilize the metal complexes and to prevent their decomposition to nanoparticles, which is often observed in iron catalysis.[12] Although the bis(acetonitrile) complexes **2a–c** performed poorly in the ATH of ketones, the bis(isonitrile) analogue $[Fe(CNtBu)_2(\mathbf{1b})](BF_4)_2$ hydrogenated aryl alkyl ketones with up to 98 % yield and 91 % *ee*.[13] As preliminary NMR studies showed that both imines are reduced during catalysis, we decided to investigate the corresponding derivatives bearing the diamino ligand **1a**, which is easily prepared by $LiAlH_4$ reduction of **1b**. Herein, we show that the corresponding complexes are highly active and enantioselective in the ATH of a broad scope of ketones in basic isopropanol.

The bis(isonitrile) complexes $[Fe(CNR)_2(\mathbf{1a})](BF_4)_2$ (R = *t*Bu, **3a**; 1-Ad, **3b**; Ph, **3c**; 2,6-Xyl, **3d**; $CMe_2^{neo}Pent$, **3e**) were obtained from $[Fe(MeCN)_2(\mathbf{1a})](BF_4)_2$ (**2a**), which was prepared from **1a** and $[Fe(OH_2)_6](BF_4)_2$ in CH_2Cl_2/MeCN in the presence of DBU (see the Supporting Information for details).[14] The acetonitrile ligands in **2a** are easily displaced by commercially available isonitriles at 50 °C to afford **3a–e** in good yield as yellow, stable, diamagnetic solids (Scheme 1). The $^{31}P\{^1H\}$ NMR spectra of **3a–e** show that they adopt the Λ-*cis*-β configuration only, as confirmed by X-ray studies of **3a–c** (Figure 2; Supporting Information, Figures S23 and S33). The various isonitrile ligands induce subtle conformational changes in the macrocycle (Supporting Information, Table S9).[15]

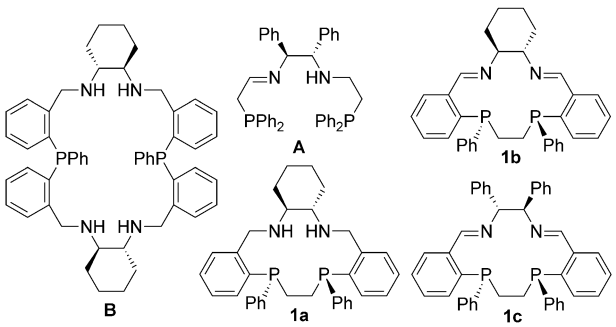
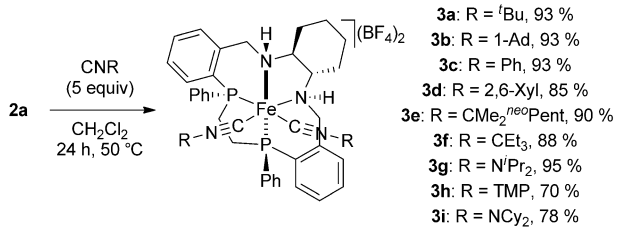


Figure 1. Open-chain PNNP ligand **A** and macrocyclic analogues.



Scheme 1. Synthesis of bis(isonitrile) complexes **3a–i**.

[*] R. Bigler, R. Huber, Prof. Dr. A. Mezzetti
Departement Chemie und Angewandte Biowissenschaften
Eidgenössische Technische Hochschule (ETH) Zürich
8093 Zürich (Switzerland)
E-mail: mezzetti@inorg.chem.ethz.ch

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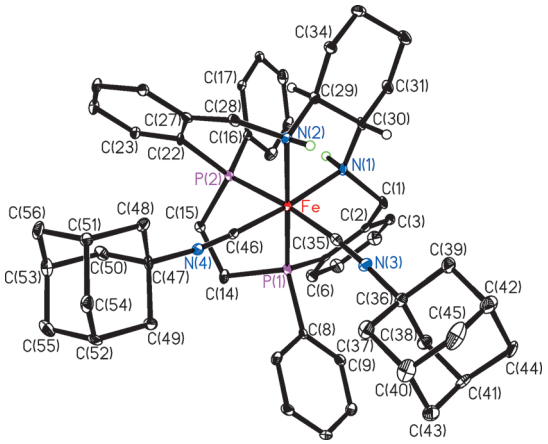
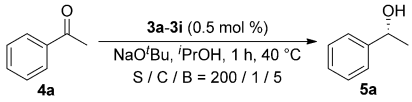


Figure 2. ORTEP of the dication of **3b** (ellipsoids are set at 30% probability). Selected bond lengths [Å] and angles [°]: P1–Fe 2.1899(17), P2–Fe 2.2169(17), N1–Fe 2.042(4), N2–Fe 2.053(5), C35–Fe 1.889(6), C46–Fe 1.842(6); C35-Fe-C46 89.0(2), P2-Fe-N1 92.15(14).

Table 1: Catalyst screening in the asymmetric transfer hydrogenation of acetophenone **4a**.



Entry[a]	Catalyst	Yield[b]	*ee*[b]
1	**3a** (R = *t*Bu)	91	79
2	**3b** (R = 1-Ad)	90	82
3	**3c** (R = Ph)	9	65
4	**3d** (R = 2,6-Xyl)	6	76
5	**3e** (R = $CMe_2{}^{neo}Pent$)	86	88
6	**3f** (R = CEt_3)	88	96
7	**3g** (R = N*i*Pr$_2$)	69	98
8	**3h** (R = NCy_2)	33	98
9	**3i** (R = TMP)	39	98

[a] Reactions were performed on a 1.0 mmol scale in *i*PrOH (0.25 M). [b] Yield and *ee* values were determined by GC.

A preliminary screening in the ATH of acetophenone (**4a**) in basic isopropanol at 40 °C (S/C/B = 200/1/5; under argon) showed that **3a**, **3b**, and **3e** are very active, but the enantioselectivity was moderate (79 to 88% *ee*, Tables 1; Supporting Information, Table S1). Complexes **3c** and **3d** bearing aryl-substituted isonitriles were barely active (< 10% yield). The significant influence of the isonitrile substituents on the enantioselectivity was exploited for optimization.

With 3-ethylpentyl isonitrile,[16] $[Fe(CNCEt_3)_2(\mathbf{1a})](BF_4)_2$ (**3f**) gave (*S*)-1-phenylethan-1-ol with 96% *ee* and 88% yield after 1 h when all other conditions were the same (Table 1, entry 6). Possibly, the ethyl groups of **3f** protrude more toward the metal center than the adamantyl groups of **3b**, which are constrained in the *syn*-pentane conformation (Figure 2), thus increasing the enantioselectivity.

Furthermore, the bulky *N*-isocyanides CNR (R is N*i*Pr$_2$, TMP, or NCy_2)[16,17] gave the complexes $[Fe(CNR)_2(\mathbf{1a})](BF_4)_2$ (R = N*i*Pr$_2$, **3g**; TMP, **3h**; NCy_2, **3i**) as diamagnetic, orange solids (Scheme 1) as a single Λ-*cis*-β isomer (by $^{31}P\{^1H\}$ NMR spectroscopy). Although the free *N*-isocyanides are unstable,[17] their iron(II) complexes show no signs of decomposition over several months at room temperature. As compared to **3f**, **3g–i** are slightly less active in the ATH of acetophenone (**4a**), but the enantioselectivity reached 98% *ee* under otherwise identical conditions (Table 1, entries 7–9). This is, to the best of our knowledge, the highest enantioselectivity ever observed in the ATH of acetophenone with well-defined iron catalysts.

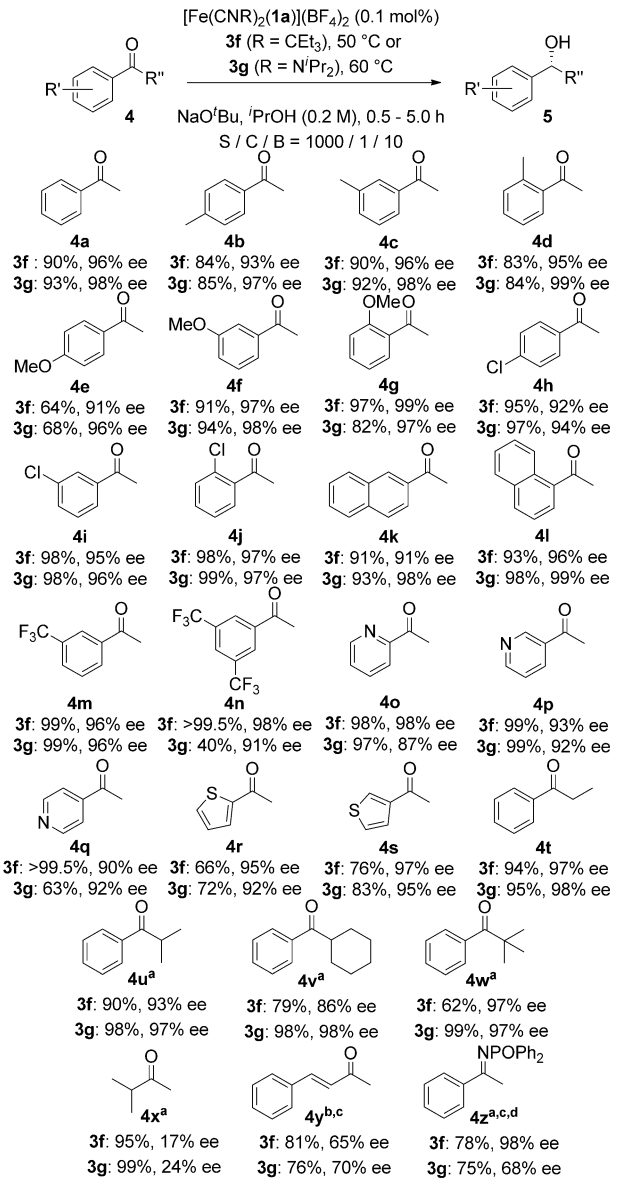
When the loading was lowered to 0.1 mol%, the most promising catalysts **3f** and **3g** hydrogenated **4a** with the same enantioselectivity, even at higher temperatures (50 and 60 °C for **3f** and **3g**, respectively) to maintain high activity (Supporting Information, Tables S2 and S3). Under optimized conditions, **3f** gave **5a** with 96% *ee* and 90% yield within 1.5 h at 50 °C. Catalyst **3g** gave **5a** with 98% *ee* and higher yield (93%) after 2.0 h at 60 °C. Periodical sampling of the reaction solutions showed that *ee* erosion approaching equilibrium was marginal (see the Supporting Information).

A broad scope of aryl alkyl ketones **4a–w** was reduced with high yield and excellent enantioselectivity (Scheme 2; Supporting Information, Chart S1). Substitution by methyl, methoxy, or chloro is well tolerated, and the corresponding products were obtained in high yield and with excellent enantioselectivity. With the exception of 2′-methoxyacetophenone **4g**, for which the *C*-isonitrile catalyst **3f** was more selective (99% *ee*), the *N*-isonitrile derivative **3g** was superior and afforded the corresponding alcohols **5b–g** with 94 to 99% *ee*. Challenging substrates such as *ortho*-substituted acetophenones **4d** and **4g** gave the lowest rates, but were hydrogenated in more than 80% yield with up to 99% *ee* within 2.5 to 5 h (TOF > 160 h^{-1}).

Ketones with larger aryl groups, such as 2- and 1-acetonaphthone (**4k** and **4l**), were easily reduced by **3g** to give the corresponding alcohols **5k** and **5l** in high yield (93 and 98%) and with 98 and 99% *ee*, respectively. Catalyst **3f** gave the trifluoromethyl-substituted alcohols **5m** and **5n**, which are important synthons for fungicides[18] and NK1 antagonists,[19] in quantitative yield and with 96% and 98% *ee*, respectively.

Acyl-substituted heterocycles were also investigated. Although pyridine- or thiophene-substituted ketones tend to coordinate to the metal center and thus poison it, **3f** hydrogenated acyl pyridines **4o–q** rapidly (the TOF was up to 1960 h^{-1} in the case of **4o**) and with enantioselectivities between 90 and 98% *ee*. The conversion of acyl thiophenes **4r** and **4s** was modest (66% for **4r** and 76% for **4s**), but the products were obtained with 95 and 97% *ee*, respectively. The low conversions are not attributed to catalyst poisoning, but rather to the electron-rich nature of these aromatics that stabilizes the ketone with respect to the alcohol and shifts the equilibrium toward the former.

An aryl alkyl ketone of the type BzR″ containing bulkier alkyl groups such as propiophenone **4t** was hydrogenated with high enantioselectivity (97% and 98% *ee* for **3f** and **3g**, respectively) within 1.5 to 2.5 h, whereas substrates with secondary or tertiary alkyl substituents (**4u–w**) reacted sluggishly under standard conditions. However, at higher temperature (75 °C) and catalyst loading (0.4 mol%), **3g** gave



Scheme 2. Asymmetric transfer hydrogenation with catalyst **3 f** and **3 g**. Reaction conditions: substrate (2.5 mmol) in *i*PrOH (0.2 M), see the Supporting Information, Chart S1 for reaction times. Yields and *ee* values were determined by GC. [a] The reaction was performed with 0.625 mmol of the substrate at 75 °C with S/C/B = 250/1/10. [b] Complete chemoselectivity for the allylic alcohol (saturated alcohol/ketone < 1%). [c] The *ee* values were determined by HPLC. [d] Yield of isolated product.

alcohols **4 u**–**w** in excellent yield (≥ 98%) and enantioselectivity (≥ 97% *ee*). Cyclohexyl phenyl ketone **4 v** was hydrogenated with an impressive 98% *ee* within 1 h, and the bulky *tert*-butyl phenyl ketone **4 w** gave similar results, which is remarkable as only very few well-defined systems (and mostly based on precious metals) give high *ee* with such substrates.[5b,d,13,20]

As for substrates bearing other polar double bonds (**4 x**–**z**), the dialkyl ketone **4 x** gave the corresponding alcohol **5 x** with high yield, but low enantioselectivity (≤ 24% *ee*). The hydrogenation of enone **4 y** to the corresponding allylic alcohol was completely chemoselective, fast (TOF up to 1610 h^{-1}), and gave 65 and 70% *ee* with **3 f** and **3 g**, respectively. Albeit only moderate, this enantioselectivity is, to the best of our knowledge, the highest ever obtained in the iron-catalyzed hydrogenation of benzylideneacetone.[5a,b,d,7a] Finally, **3 f** hydrogenated phosphoryl imine **4 z**,[5i,6c] a chiral amine percursor, in good yield and with 98% *ee*.

Preliminary tests support a homogeneous mechanism. The reaction solutions are clear yellow without turbidity, and the addition of PPh_3 and 1,10-phenanthroline according to Gao's method[8] had no influence on either yield or enantioselectivity. Further mechanistic studies are underway.

In conclusion, we have presented well-defined, highly active Fe^{II} catalysts for the transfer hydrogenation of a broad scope of ketones with excellent enantioselectivity. The change from the previously reported[13] diimino macrocycle **1 b** to its diamino analogue **1 a** leads to a substantial increase in activity, and the isonitrile ligands strongly influence both the enantioselectivity and the activity. As the isonitrile ligands are introduced in the final step of the catalyst synthesis and can be easily modified, the system is highly modular and tunable. Therefore, these iron(II) catalysts are a valuable alternative to the best current systems, as they are applicable to a broad scope of ketones, give high activity and enantioselectivity, and can be easily optimized for specific substrates.

Keywords: alcohols · asymmetric catalysis · hydrogen transfer · iron · macrocyclic ligands

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[15] Details of the crystallographic analyses are given in the Supporting Information. CCDC 1051053 (**3a**), 1051054 (**3b**), and 1051055 (**3c**) 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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