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# Isonitrile Iron(II) Complexes with Chiral $N_2P_2$ Macrocycles in the Enantioselective Transfer Hydrogenation of Ketones

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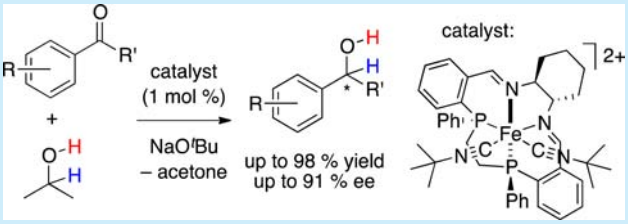
Supporting Information

**ABSTRACT:** Bis(isonitrile) iron(II) complexes bearing a $C_2$-symmetric $N_2P_2$ macrocyclic ligand, which are easily prepared from the corresponding bis(acetonitrile) analogue, catalyze the asymmetric transfer hydrogenation (ATH) of a broad scope of ketones in excellent yields (up to 98%) and with high enantioselectivity (up to 91% ee).




Enantiopure alcohols are important in pharmaceutical and fragrance chemistry and are easily accessed by asymmetric reduction of the corresponding ketones using a plethora of chiral ruthenium, iridium, or rhodium catalysts.[1] However, the high cost and toxicity of the involved transition metals have hampered their use in industry.[2] Recently, nontoxic and cheap, but achiral, iron catalysts[3] have been mainly used in hydrogenation, hydrosilylation, and cross-coupling reactions.[4] In contrast, only a handful of chiral catalysts have been developed for enantioselective transformations such as hydrosilylation,[5] direct $H_2$-hydrogenation[6] (AH), and transfer hydrogenation[7−11] of ketones (ATH). Despite spectacular advances, the stability of iron catalysts is still a major issue. For example, Morris has shown that the iron catalysts with an open-chain tetradentate PNNP ligand **A** (Figure 1) decompose to iron(0) nanoparticles during catalysis,[7c] whereas the less bulky ligand **B** gives robust, highly active, and enantioselective catalysts when combined with a strong $\pi$-acceptor (such as carbon monoxide).[8]

In an alternative approach, Gao has combined a chiral $N_4P_2$ macrocycle with $[Fe_3(CO)_{12}]$ in situ, but the resulting catalyst has been found to be heterogeneous.[6a,10] As large rings are unsuitable to unleash a strong macrocyclic effect,[12] we decided to prepare $N_2P_2$ macrocycles with a ring size between 14 and 16. It should be noted that most previously reported macrocycles of this kind are achiral and have not been used in catalysis[13] or have a *pseudo meso* configuration.[14] We have recently reported the first examples of enantiopure $C_2$-symmetric $N_2P_2$ macrocycles (**1a−c**, Figure 1).[15] Ligands **1a−c** form the mononuclear, stable, diamagnetic bis(acetonitrile) complexes $[Fe(MeCN)_2(N_2P_2)](BF_4)_2$ (**2a−c**) and the bromocarbonyl derivatives $[FeBr(CO)(N_2P_2)]BPh_4$ (**3a**, **3c**) (Figure 2).[15] In this paper, we report the application of these complexes in the ATH of acetophenone in basic isopropanol.[16]

However, in a preliminary screening, the bis(acetonitrile) complex **2a** gave irreproducible results; its diamino analogue **2b** was essentially inactive, and **2c** gave low enantioselectivity (Table S1). The $^{31}P\{^1H\}$ NMR spectrum of the reaction

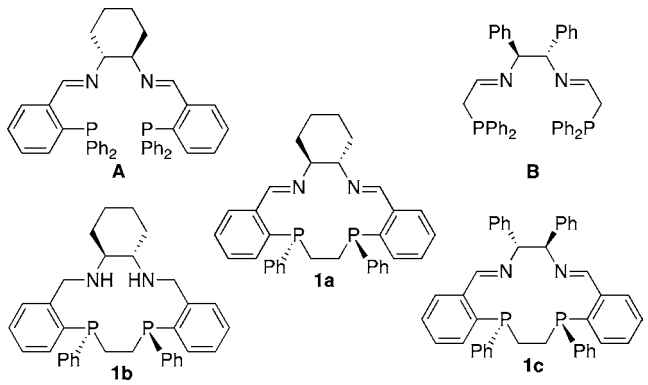



**Figure 1.** Open-chain PNNP ligands **A** and **B** and macrocyclic analogues **1a−c**.

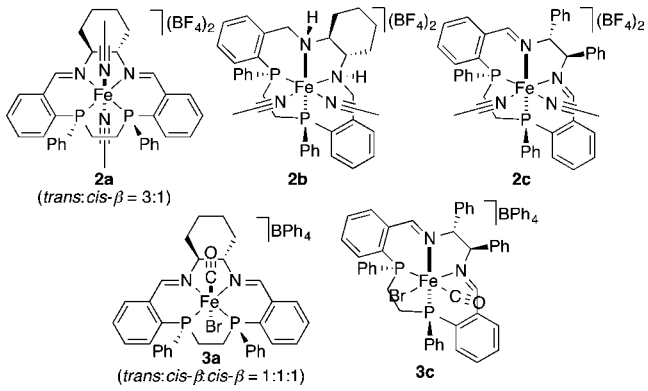



**Figure 2.** Bis(acetonitrile) complexes **2a−c** and bromocarbonyl complexes **3a** and **3c**.

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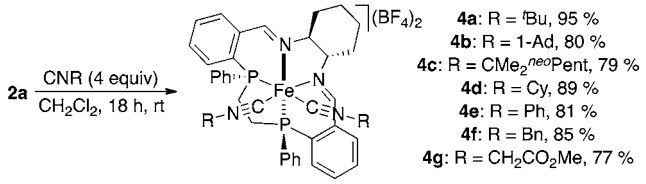
solution with complex **2a** showed the presence of free ligand, which we attribute to partial complex decomposition under catalysis conditions. Therefore, we sought to further stabilize the system by using strongly binding ancillary ligands in combination with the best performing cyclohexane-based ligand **1a**. As carbonyl ligands were not effective (Table S1, Supporting Information),[17] we focused on isonitriles, which are sterically and electronically tunable ligands and have previously been applied in the iron-catalyzed (asymmetric) transfer hydrogenation of ketones.[7a,11,18]

The acetonitrile ligands of $[Fe(MeCN)_2(\mathbf{1a})](BF_4)_2$ (**2a**) were smoothly substituted by *tert*-butyl isocyanide (4 equiv) to give the bright yellow/orange complex Λ-*cis*-*β*-$[Fe(CN^tBu)_2(\mathbf{1a})](BF_4)_2$ (**4a**),[19] which was isolated as a stable, diamagnetic solid in 95% yield (Scheme 1). Using the same protocol, a small library of bis(isonitrile) complexes **4a**–**g** was prepared with different isonitriles, all of which are commercially available.

**Scheme 1. Synthesis of Bis(isonitrile) Complexes 4a–g**




The bis(isonitrile) complexes **4a**–**g** preferentially adopt a Λ-*cis*-*β* configuration (Λ-*cis*-*β*:trans ≈ 93:7). The $^{31}P\{^1H\}$ NMR AX spin systems (**4a**: $\delta$ 91.7 and 84.1 ($^2J_{P,P'}$ = 42.0 Hz)) indicates that one phosphine is *trans* to isonitrile and one *trans* to imine. The IR spectrum of **4a** shows two new bands at 2165 and 2142 $cm^{-1}$, in agreement with the mutual *cis* arrangement of the isonitrile ligands. Complex **4e** bearing two phenyl isocyanide ligands was structurally characterized by X-ray diffraction (Figure 3). Despite the different overall structure

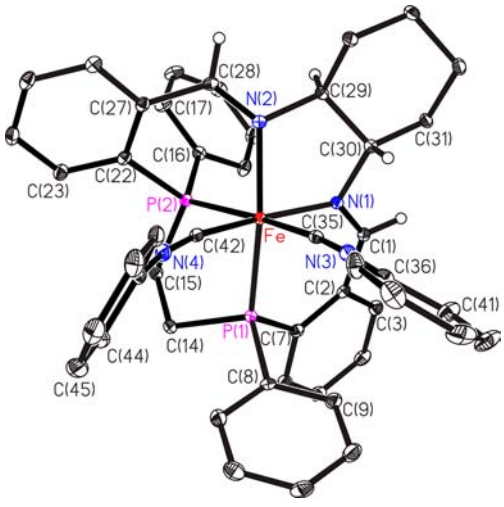
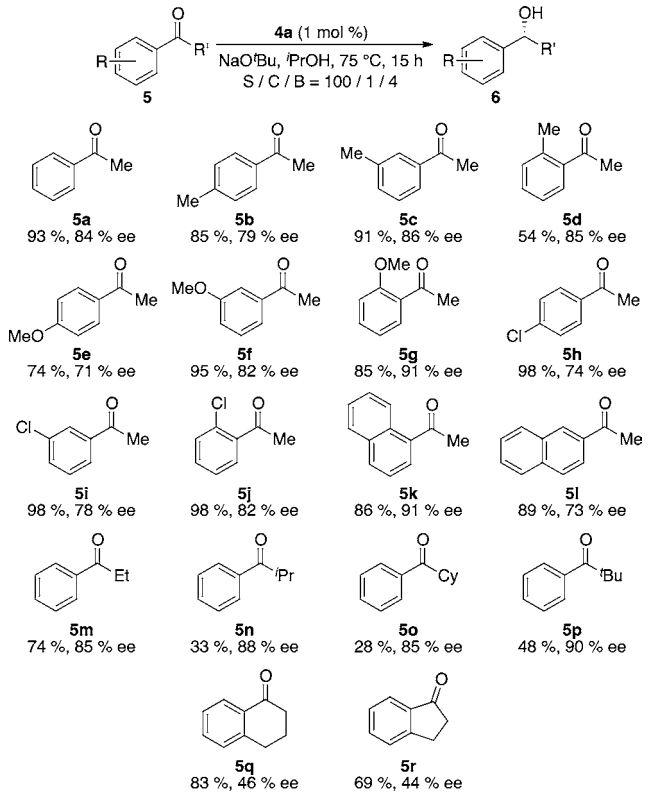



**Figure 3.** ORTEP plot of the dication of **4e** (thermal ellipsoids at 30% probability). Selected bond lengths (Å) and angles (deg): P(1)–Fe 2.1710(5), P(2)–Fe 2.2280(4), N(1)–Fe 1.9797(14), N(2)–Fe 1.9987(13), C(35)–Fe 1.8856(17), C(42)–Fe 1.8433(17), C(35)–Fe–C(42) 79.95(7), P(2)–Fe–N(1) 101.95(4), Fe–C(35)–N(3) 173.14(15), Fe–C(42)–N(4) 168.01(16), C(35)–N(3)–C(36) 176.05(17), C(42)–N(4)–C(43) 164.00(19).

(*cis*-*β* vs *trans*), the compression of the Fe–P and Fe–N distances in **4e** with respect to the open-chain analogue[7a] $[Fe(MeCN)_2(\mathbf{A})]^{2+}$ can be taken as an indication of a significant macrocylic effect.

A screening of the bis(isonitrile) complexes **4a**–**g** in the ATH of acetophenone in basic isopropanol showed that the *tert*-butyl isocyanide derivative **4a** is the catalyst of choice (Table S2). Complex **4a** (1 mol %) reduced a broad scope of aromatic ketones with high to excellent enantioselectivity in the presence of $NaO^tBu$ (4 mol %) (Scheme 2).

**Scheme 2. ATH of Aromatic Ketones with Catalyst 4a**[a]




[a]Reactions were performed on a 1.0 mmol scale in $^i$PrOH (0.25 M). Yields and ee's were determined by GC.

Substitution by methyl, methoxy, and chloro groups showed a trend toward higher selectivity for *ortho*-substituted acetophenones. Thus, 91% ee was obtained for 1-(2-methoxyphenyl)ethan-1-ol (**6g**). Similarly, 1-acetonaphthone gave superior results as compared to 2-acetonaphthone (**5k** vs **5l**), and the corresponding alcohol **6k** was obtained with 91% ee. Overall, the hydrogenation of standard acetophenone derivatives is efficient, reproducible, and highly enantioselective. More hindered ketones **5m**-**5p** are also hydrogenated with high enantioselectivity albeit, not surprisingly, the corresponding alcohols **6m**–**p** were obtained in lower yields. Thus, the *tert*-butyl-substituted ketone **5p** gave 2,2-dimethyl-1-phenylpropan-1-ol (**6p**) in 48% yield and with 90% ee (Scheme 2). This is a remarkable result because few well-defined chiral catalysts give high enantioselectivity with phenyl alkyl ketones PhC(O)R that bear bulky R groups, and with the notable exception of $[FeBr(CO)(\mathbf{B})]^+$,[8] most of them are based on precious metals.[20] We also tested cyclic aromatic ketones, but the corresponding alcohols **6q** and **6r** were obtained with modest enantioselectivity (46% and 44% ee, respectively).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Overall, complex **4a** is less active but considerably more enantioselective in the ATH of acetophenone than Morris' first-generation catalysts (PNNP = **A**, Figure 1).[7] In addition, the observed enantioselectivity is in the range of the second-generation complexes with ligand **B**.[8] The moderate activity of **4a** is in line with analogous observations made with open-chain PNNP derivatives bearing isonitrile ligands.[7a]

A series of homogeneity tests were performed by adding mercury, 1,10-phenanthroline, or triphenylphosphine[6a] to the reaction solution with catalyst **4a** and acetophenone. No effect on the outcome of the reaction was observed, which supports a mechanism involving a homogeneous catalyst.

We also carried out preliminary experiments to elucidate the nature of the active species and the reaction mechanism. Upon addition of 2-propanol and sodium *tert*-butoxide (4 equiv) to **4a**, followed by heating at 75 °C, the initially insoluble complex dissolves and a deep blue color evolves. The $^1$H NMR spectrum of this mixture is sharp, and both imine signals have disappeared (Figure S62, Supporting Information) indicating that the active catalyst bears a reduced diamino ligand. The $^{31}$P{$^1$H} NMR spectrum shows that a single species is formed, which features an AB spin system at $\delta$ 89.3 and 87.5 ($^2J_{P,P'}$ = 38.6 Hz, Figure S60, Supporting Information). In 2-propanol-$d_8$, these signals appear as multiplets (Figure S61, Supporting Information), which clearly indicates incorporation of deuterium. No free macrocycle (or oxide thereof) was detected in solution, which rules out significant complex decomposition. The IR spectrum of the reaction mixture shows a band at 2142 cm$^{-1}$, which we assign to a single coordinated isonitrile, and a second absorbance at 1647 cm$^{-1}$, which suggests that the other isonitrile ligand is reduced to a C═N-containing species. The same complex is also observed when a stoichiometric amount of sodium *tert*-butoxide (1 equiv) is used, but this mixture is inactive in catalysis. We are presently investigating the nature of the observed species and its relationship to the active catalyst.

In this paper, we have reported an iron(II) catalyst for the predictable and reliable transfer hydrogenation of a broad scope of ketones with high yield and high enantioselectivity that is based on well-defined, fully characterized iron(II) complexes of a $N_2P_2$ macrocycle in combination with isonitriles as ancillary ligands. As standard tests indicate a homogeneous mechanism, we conclude that the use of chiral $N_2P_2$ macrocyclic ligands is a promising strategy to prepare well-defined, robust, and highly enantioselective Fe(II) catalysts that withstand harsh reaction conditions.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental procedures and characterization of all new products. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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(16) The complexes bearing ligand **1a** exist as mixtures of *trans*- and *cis*-$\beta$ isomers, whereas those of ligands **1b** and **1c** adopt the *cis*-$\beta$ structure exclusively; see also ref 15.
(17) Complexes $[Fe(CO)(MeCN)(N_2P_2)](BF_4)_2$, which were prepared by stirring under CO atmosphere in acetone and used without purification (see ref 7a), gave similar or inferior results as compared to the corresponding bis(acetonitrile) complexes (Table S1, entries 6 and 7, Supporting Information).
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