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Iron(II) complexes featuring chiral PNNP diferrocene: Synthesis and characterization of potential hydrogenation catalysts

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ABSTRACT

Chiral non-racemic PNNP biferrocene with either imine or amine nitrogen coordination sites were synthesized. Only the imine-type formed dicationic iron complexes of the type $[Fe(PNNP)(NCMe)_2][BF_4]_2$ and $[Fe(PNNP)(NCMe)(CO)][BF_4]_2$. Some of these complexes were found to be active in hydrogenation and transfer hydrogenation reactions but their applicability is limited by moderate-to-low conversion and enantioselectivity.

1. Introduction

Platinum metal-based asymmetric catalysis, in particular asymmetric hydrogenation, is one of the most established standard methodologies for the synthesis of enantiopure alcohols and amines [1–3]. Recently, not only for economic reasons, but also driven by the ideas of 'Green and environmentally friendly chemistry', iron-based catalysis has attracted significant attention from chemists [4–12]. In particular, the group of Morris reported several highly efficient iron-based catalytic systems [13–21]. For example, complexes of the tetradentate PNNP ligands L1–L6 (Chart 1) and their use in asymmetric hydrogenations were described [13–15]. It was found that this type of ligand in the hydrogenation of acetophenone only led to high conversion at elevated temperatures and with the achiral ligands L2 and L6 (complexes C1 and C2, Chart 2), both of which have an unsubstituted ethylene bridge.

When chiral ligands bearing substituents at the ethylene unit were used (e.g., ligand L1, Chart 1), the conversion dropped to very low values (e.g., ligand L1: 4% conversion) [14]. Based on these findings, we envisaged that for enantioselective hydrogenations also higher conversion could be achieved with chiral ligands bearing an unsubstituted rather than a substituted ethylene bridge. It is clear that for chiral ligands with an unsubstituted ethylene bridge the chirality has to be introduced at a different position of the ligand. Therefore, we replaced the aryl rings of L2 and L6 by homochiral ferrocene units. This structural change resulted in the well-defined chiral non-racemic ligands (S_{Fc},S_{Fc})-**1** [22] and (S_{Fc},S_{Fc})-**2** [23] (Chart 3), both of which contain an unsubstituted ethylene bridge.

The synthesis of (S_{Fc},S_{Fc})-**1a** and analogs has been described previously by Kagan and co-workers [22], while the preparation of (S_{Fc},S_{Fc})-**2a** has been reported by Hou and co-workers [23]. Ligands of the type (S_{Fc},S_{Fc})-**1** and (S_{Fc},S_{Fc})-**2** were used in a few cases in conjunction with noble metals in the hydrogenation and transfer hydrogenation of ketones. In addition to **1a** and **2a**, in this study we synthesized the new compounds (S_{Fc},S_{Fc})-**1b** and (S_{Fc},S_{Fc})-**2b**, which contain P^iPr_2 instead of PPh_2 substituents. The coordination behavior of **1** and **2** towards iron(II) was investigated and catalyst precursors were prepared. Several hydrogenation and transfer hydrogenation reactions were also carried out.

2. Results and discussion

Synthesis of (S_{Fc},S_{Fc})-1 and (S_{Fc},S_{Fc})-2. As outlined in Scheme 1, condensation of enantiopure aldehydes (S_{Fc})-**5**, which were prepared by applying Kagan's methodology [22,24], with 0.5

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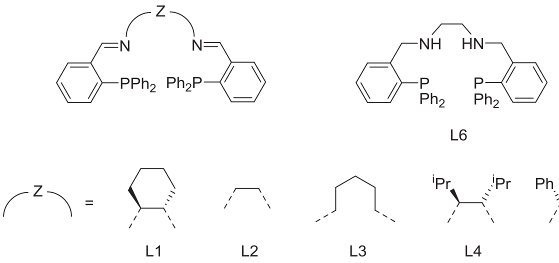


Chart 1. Examples of well-defined tetradentate PNNP ligands.

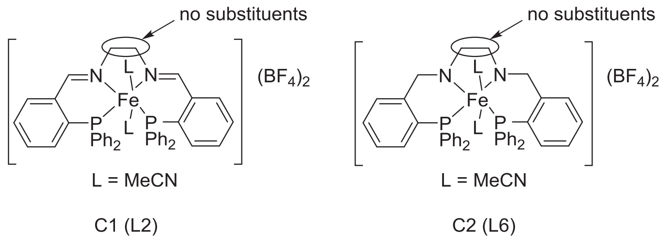


Chart 2. Examples of well-defined iron-based asymmetric transfer hydrogenation precatalysts.

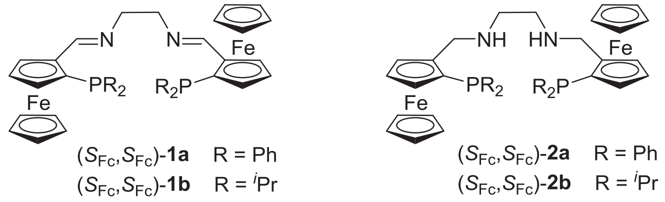


Chart 3. Structures of chiral non-racemic tetradentate ferrocene-based ligands.

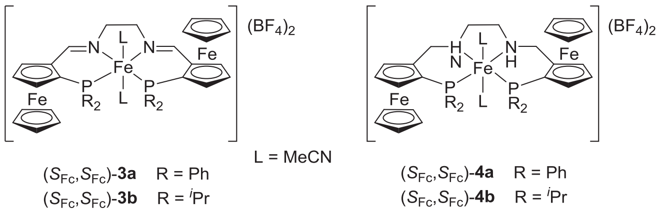


Chart 4. Structures of the *trans*-$(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-[Fe(PNNP)(NCMe)$_2$][BF$_4$]$_2$ and *trans*-$(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-[Fe(PNHNHP)(NCMe)$_2$][BF$_4$]$_2$ complexes.

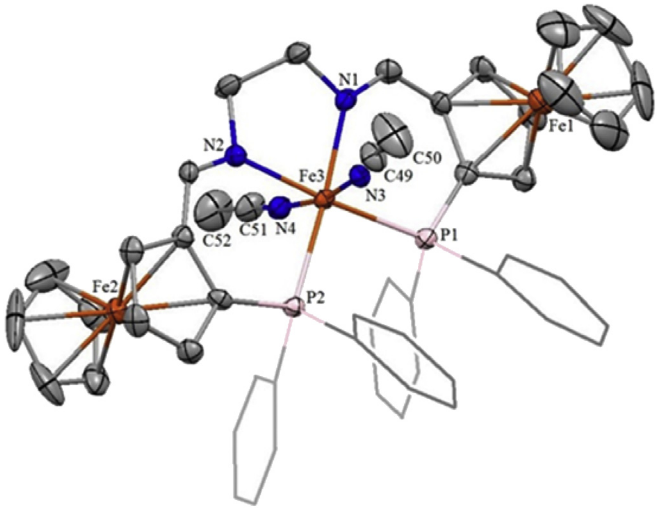
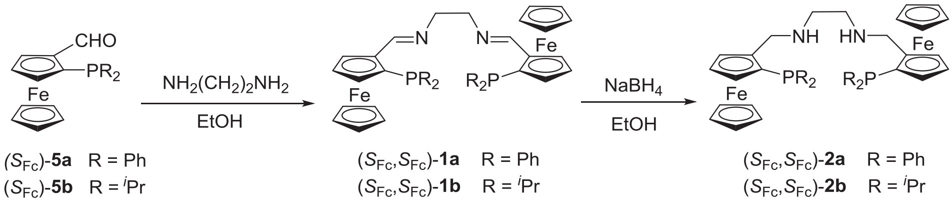


Fig. 1. Structural view of $(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-**3a** showing 50% thermal ellipsoids (H atoms, BF_4^- anions and solvent molecules are omitted for clarity). Selected bond lengths (Å) and bond angles (°): N1-C11 1.292(5), N1-C47 1.469(5), N2-C34 1.283(5), N2-C48 1.474(5), N3-C49 1.131(5), N4-C51 1.142(5), N1-Fe3 2.045(3), N2-Fe3 2.026(3), N3-Fe3 1.930(3), N4-Fe3 1.916(4), P1-Fe3 2.324(1), P2-Fe3 2.334(1), N1-Fe3-N2 81.3(1), P1-Fe3-P2 93.56(4), P1-Fe3-N1 92.7(1), P2-Fe3-N2 92.9(1), P1-Fe3-N2 172.4(1), P2-Fe3-N1 172.1(1), N3-Fe3-N4 169.7(1).

equivalents of ethylenediamine gave the desired compound $(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-**1**. Treatment of $(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-**1** with NaBH$_4$ in ethanol gave $(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-**2** in quantitative yield (Scheme 1).

Synthesis of iron complexes. The coordination behavior with iron was investigated by using [Fe(H$_2$O)$_6$][BF$_4$]$_2$ in acetonitrile under ambient conditions and an inert atmosphere to generate the corresponding [Fe(L)(NCMe)$_2$][BF$_4$]$_2$ complexes (Chart 4). The reaction of $(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-**1a** with imine functionalities was very clean and quantitative and $(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-**3a** was isolated in 93% yield as a red powder. The molecular structure of $(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-**3a** was determined by X-ray crystallography and selected bond distances and angles are given in the caption (Fig. 1, for a discussion see below). In order to prepare $(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-**3b**, the same reaction conditions were used but a longer reaction time was required. However, the product was more difficult to extract and purify because unidentified side products were also formed. Complex $(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-**3b** was isolated as a red powder in 59% yield. Under analogous reaction conditions the ligands $(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-**2a** and $(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-**2b** did not react with the iron salt used and coordination did not take place. The reason for this behavior is not clear but it could be due to the larger bite angles in these ligands. We recently described a biferrocene-based Fe(II) PNP pincer complex that showed similar behavior [24]. The following discussion is therefore focused on complexes obtained from $(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-**1a** and $(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-**1b.**

Reactivity towards CO. In order to obtain active iron-based hydrogenation catalysts it seems to be important to have the strong field ligand CO coordinated to iron, which appears to maintain a low spin configuration throughout the catalytic cycle [22,25–31]. Therefore, $(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-**3a** and $(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-**3b** were stirred overnight in acetone under a CO atmosphere (1 bar) in an autoclave to obtain mono-CO complexes $(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-**6a** and $(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-**6b** in respective isolated yields of 91% and 64% (Scheme 2). The ^{31}P{^{1}H} NMR spectrum of $(S_{\mathrm{Fc}},S_{\mathrm{Fc}})$-**6a** contained one pair of doublets with a $^2J_{\mathrm{PP}}$ value of 45.8 Hz. These signals are indicative of a single isomer



Scheme 1. Synthesis of chiral non-racemic tetradentate ferrocene-based ligands.