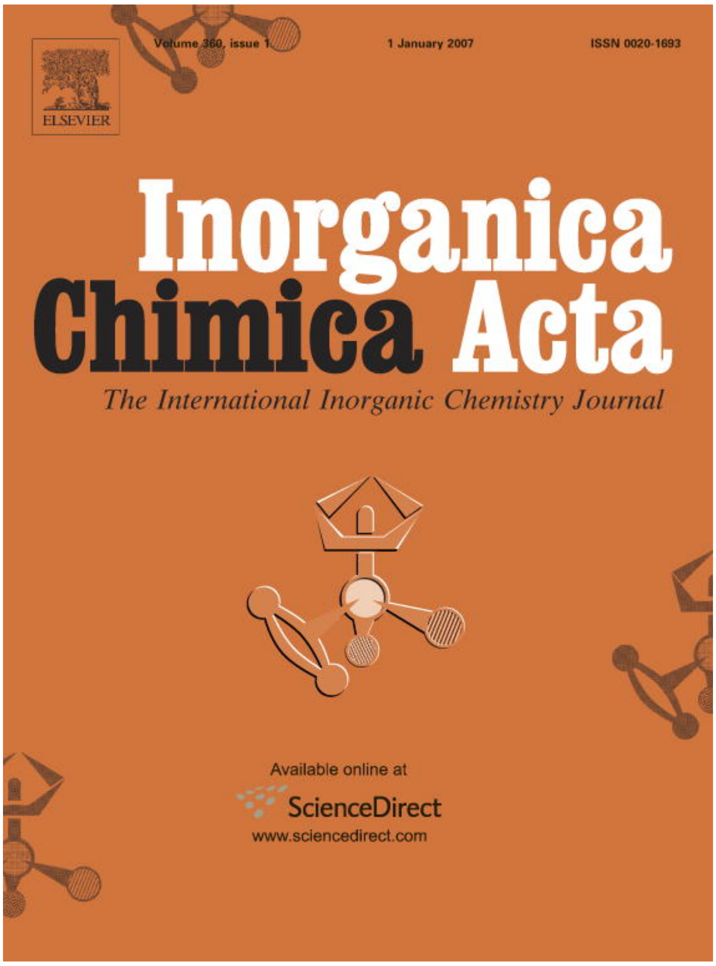
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Mononuclear diastereopure non-heme Fe(II) complexes of pentadentate ligands with pyrrolidinyl moieties: Structural studies, and alkene and sulfide oxidation

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Abstract

Mononuclear iron(II) complexes of enantiopure Py(ProOH)$_2$ (**2**) and Py(ProPh$_2$OH)$_2$(**3**) ligands have been prepared with FeCl$_2$ and Fe(OTf)$_2 \cdot$ 2MeCN. Both ligands coordinate to the metal in a pentadentate fashion. Next to the meridional *N*,*N*′,*N*-coordination of the ligand, additional coordination of the oxygen atoms of both hydroxyl groups to the metal is found in complexes **4**–**7**. Complex [FeCl(**2**)](Cl) (**4**) shows an octahedral geometry as determined by X-ray diffraction and is formed as a single diastereoisomer. The solution structures of complexes **4**–**7** were characterized by means of UV–Vis, IR, ESI-MS, conductivity and CD measurements. The catalytic potential of these complexes in the oxidation of alkenes and sulfides in the presence of H$_2$O$_2$ is presented.

Keywords: Amino acids; Iron; Ligand design; Oxidation; Peroxides

1. Introduction

The selective oxidation of organic molecules using environmentally friendly oxidants like dioxygen or hydrogen peroxide is a topic of continuing interest [1]. Metalloenzymes capable of activating dioxygen in order to oxidize exogenous substrates play an important and inspirational role in the design of new oxidation catalysts [2]. Particularly, non-heme iron oxygenases have become attractive targets for extensive research efforts toward the synthesis of small-molecule analogues of their active sites [3]. Some of these model complexes based on multidentate nitrogen donors have proven to be very efficient catalysts for the epoxidation [4] and *cis*-dihydroxylation [5] of alkenes and stereoselective hydroxylation of alkanes [6]. Furthermore, several non-cyclic pentadentate *N*-ligands with an octahedral geometry around iron(II) centers were recently developed as models for bleomycin [7a], a non-heme iron glycopeptide system which catalyzes stereoselective oxo-transfer to olefinic substrates [7b]. Interesting results were obtained with these systems in terms of catalytic activities and mechanistic insight in alkane and alkene oxidation [8–12]. Next to some of the structural models, also functional models based on simple nitrogen ligands like phenanthroline in combination with iron salts show high activities in some of these alkene oxidation reactions [13]. However, none of these pentadentate ligands contain stereogenic centers.

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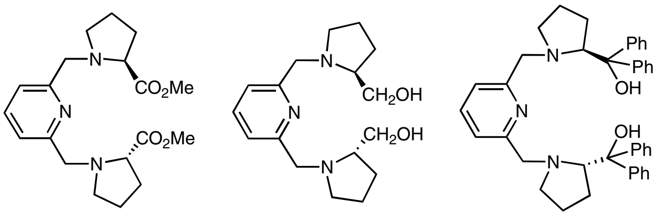

Py(ProMe)$_2$ (**1**) Py(ProOH)$_2$ (**2**) Py(ProPh$_2$OH)$_2$ (**3**)

Fig. 1. Chiral pentadentate ligands Py(ProMe)$_2$ (**1**), Py(ProOH)$_2$ (**2**) and Py(ProPh$_2$OH)$_2$ (**3**).

Previously, we have reported the synthesis of iron(II) complexes with the chiral ligand Py(ProMe)$_2$ (**1**) (Fig. 1) built from pyridyl and prolinate ester building blocks. In these complexes, a η^3-meridional $NN'N$ coordination of the Py(ProMe)$_2$ ligand was observed, which in combination with strongly coordinating anions yielded penta-coordinate iron(II) complexes [14]. In the presence of weakly coordinating anions, **1** acts as a pentadentate ligand with additional coordination of the carbonyl oxygen atoms of both ester moieties, forming iron(II) complexes with a seven-coordinate geometry. The different coordination modes of the ligand in these iron complexes found in the solid state are preserved in solution, providing a well-defined coordination environment around the metal and resulting in diastereopure iron complexes. In addition, the [Fe(OTf)$_2$(**1**)] complex forms a relatively stable high-spin alkyl peroxo [Fe(OO*t*-Bu)(X)(**1**)](OTf)$_y$ (X = OH$_2$, MeCN, OH$^-$, $y = 2$ or 1) intermediate upon treatment with *t*-BuOOH at temperatures below −40 °C. This intermediate was found to be able to activate C–H bonds of non-activated alkanes such as cyclohexane and adamantane [15].

In the chiral pentadentate ligands Py(ProOH)$_2$ (**2**) and Py(ProPh$_2$OH)$_2$ (**3**), the prolinate esters on the stereogenic C-atoms have been replaced by pyrrolidinyl moieties bearing either CH$_2$OH (**2**) or bulkier CPh$_2$OH groups (**3**) (Fig. 1). Our expectation was that these ligands, especially the bulkier ligand **3**, would impose an octahedral coordination geometry on the iron center leaving one vacant site which could potentially be occupied by an oxidant. This coordination geometry was observed in the X-ray crystal structure of metal complexes with a similar ligand, which contains a phenyl instead of a pyridine group, yielding C_2 symmetrical complexes where the diphenylhydroxymethyl groups are pointing above and below the NCN-metal plane, predisposed for non-linear pentadentate coordination [16].

In this paper, we describe the synthesis and coordination behavior of ligands **2** and **3** toward iron(II) salts in the solid state and in solution. In addition, the structure of complex **4**, [FeCl(**2**)]Cl, was characterized by X-ray crystal structure determination. The catalytic potential of complexes **4**, [Fe(OTf)(**2**)](OTf) (**5**), [FeCl(**3**)]Cl (**6**) and [Fe(OTf)(**3**)](OTf) (**7**) derived from ligands **2** and **3** was investigated in alkene and sulfide oxidation with hydrogen peroxide as an oxidant.

2. Experimental

2.1. General details

Reactions with metal salts were carried out using standard Schlenk techniques. The solvents were dried and freshly distilled prior to use. (*S*)-prolinol [17], 2,6-bis(chloromethyl)-pyridine [18], Fe(OTf)$_2 \cdot$ 2MeCN [19] and 2,6-bis[[(*S*)-2-(methyloxycarbonyl)-1-pyrrolidinyl]methyl]-pyridine (Py(ProMe)$_2$) [14] were prepared according to the previously published procedures. ^{1}H (300.1 MHz) and ^{13}C {^{1}H} (75.5 MHz) NMR spectra were recorded on a Varian Inova 300 spectrometer. Optical rotations ($[\alpha]_D^{21}$) were measured with a Perkin polarimeter 241. Elemental microanalyses were carried out by Microanalytisches Laboratorium Dornis und Kolbe, Mulheim a.d. Ruhr, Germany. ESI-MS spectra were recorded on a Micromass LS-TOF mass spectrometer at the Bijvoet Institute, Biomolecular Mass Spectrometry, Utrecht University. Solid state infrared spectra were recorded on a Perkin–Elmer Spectrum One FT-IR instrument. Solution IR spectra were recorded with a Mettler Toledo ReactIR™ 1000 spectrometer with a SiComp™ probe, which was fitted in a reaction vessel under a N$_2$ atmosphere. Acetonitrile was subtracted as a background. UV–Vis spectra were recorded on a Cary 50 Varian spectrometer. CD spectra were recorded on Jasco J810 instrument (Radboud University Nijmegen). Gas chromatography analyses were performed with a Perkin–Elmer Autosystem XL GC using a 30 m, PE-17 capillary column with a FID detector. HPLC analyses were performed with a Perkin–Elmer Series 200 machine, equipped with Diode Array II detector and LC pump using a Daicel Chiracel OD column.

2.2. Synthesis of ligands and complexes

2.2.1. 2,6-Bis[[(S)-2-(hydroxymethyl)-1- pyrrolidinyl]-methyl]pyridine (Py(ProOH)$_2$) (2)

2,6-Bis(chloromethyl)pyridine (14.8 mmol, 2.6 g) and (*S*)-prolinol (4 equiv., 59 mmol, 6 g) were dissolved in CH$_2$Cl$_2$ (70 mL). Subsequently, K$_2$CO$_3$ (6 equiv., 96 mmol, 13.3 g) dissolved in water (70 mL) was added to the reaction mixture followed by the addition of [*n*Bu$_4$N]Cl (10 mol%, 1.48 mmol, 0.41 g). The resulting mixture was vigorously stirred at reflux temperature for 16 h. The layers were separated and the water layer was washed with CH$_2$Cl$_2$ (2 × 40 mL). The organic layers were collected and evaporated *in vacuo*. The remaining crude oil was purified via column chromatography (SiO$_2$, ethylacetate:methanol = 1:1 (v/v)). A pale yellow solid was obtained in 66% yield (3 g). *Anal.* Calc. for C$_{17}$H$_{27}$N$_3$O$_4$: C, 66.85; H, 8.91; N, 13.76. Found: C, 66.74; H, 8.76; N, 13.67%. ESI-MS *m/z*: 306.15 ((M+H)$^+$, calc. 306.22); $[\alpha]_D^{21} = -88.6$ deg cm^3 g^{-1} dm^{-1} (*c* 0.625, MeOH). IR (solid) nu(tilde) (cm^{-1}): 3386 (s), 3184 (br), 2952 (s), 2943 (s), 2878 (s), 2794 (s), 2739 (m), 1595 (m), 1575 (m), 1460 (m), 1418 (w), 1376 (w), 1360 (w), 1340 (w), 1290 (w), 1272 (w), 1219 (w), 1208 (w), 1183 (w), 1162 (w), 1147 (w), 1124 (m), 1103 (w), 1077 (s), 1042 (m), 1029 (w), 1020 (w), 1005 (w), 962 (w), 936 (w), 925 (w), 905 (w), 824 (w), 768 (m), 664 (w). ^{1}H NMR (CD_3OD) δ: 7.75 [1H, t, $^3J_{H,H} = 8.1$ Hz, H_{pyr}], 7.38 [2H, d, $^3J_{H,H} = 7.8$ Hz, H_{pyr}], 4.16 [2H, d, AX, $^2J_{H,H} = 13.8$ Hz, ArCH_2N], 3.61 [2H, d, AX, $^2J_{H,H} =$ 13.8 Hz, ArCH_2N], 3.54 [4H, d, $^2J_{H,H} = 5.1$ Hz, CH_2OH], 2.95 [2H, quintet, $^3J_{H,H} = 4.5$ Hz, C*H], 2.71–2.77 [2H, m, NCHH ring], 2.37 [2H, q, $^2J_{H,H} = 9$ Hz, NCHH ring], 1.89–1.97 [2H, m, CHHC*H ring], 1.67–1.78 [6H, m, CH_2CH_2N and CHHC*H ring] ppm. ^{13}C{^{1}H} NMR (CD_3OD) δ: 159.99 (Pyr C(2,6)), 138.86 (Pyr C(4)), 123.26 (Pyr C(3,5)), 66.78 (C-OH), 64.92 (C*), 61.30 (ArCH_2N), 55.93 (NCH_2 ring), 28.67 (CH_2C*H ring), 23.86 (CH_2CH_2N) ppm. UV–Vis (acetonitrile) [λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$)]: 213 (7652), 265 (3791).

2.2.2. 2,6-Bis[[(S)-2-(diphenylhydroxymethyl)-1-pyrrolidinyl]methyl]pyridine Py(ProPh$_2$OH)$_2$(**3**)

A THF solution of phenyl magnesium bromide (0.67 M, 55 mmol, 82 mL) was added via a cannula into a solution of Py(ProMe)$_2$ (6.9 mmol, 2.5 g) in dry THF (20 mL). The resulting yellow solution was stirred at ambient temperature for 16 h. The reaction mixture was quenched with NH_4Cl (33 mL). The two layers were separated and the organic layer was extracted with water (2 × 30 mL), washed with brine (30 mL), dried with $MgSO_4$, filtered and evaporated *in vacuo*. The resulting crude oil was purified via column chromatography (SiO_2, first hexane:ethylacetate = 2:1 (v/v), then hexane:ethylacetate = 1:2 (v/v)). The product was isolated as a white solid in 25% yield (1.05 g). *Anal.* Calc. for $C_{41}H_{43}N_3O_2$: C, 80.75; H, 7.11; N, 6.89. Found: C, 80.78; H, 6.98; N, 6.77%. ESI-MS *m*/*z*: 610.31 ((M+H)$^+$, calc. 610.34); $[\alpha]_D^{21} = +42$ (*c* 0.365, THF). IR (solid) nu(tilde) (cm^{-1}): 3292 (br), 3063 (w), 3026 (w), 2973 (m), 2942 (m), 2832 (m), 2815 (m), 2797 (m), 1589 (m), 1574 (w), 1491 (m), 1458 (s), 1449 (s), 1376 (m), 1355 (m), 1300 (w), 1286 (w), 1209 (w), 1185 (m), 1170 (m), 1112 (s), 1084 (m), 1062 (m), 1037 (m), 1002 (w), 939 (w), 921 (w), 897 (w), 872 (m), 821 (w), 799 (w), 763 (w), 746 (s), 710 (s), 705 (s), 694 (s). ^{1}H NMR ($CDCl_3$) δ: 7.67 (4H, d, $^3J_{H,H} = 7.5$ Hz, H_{ortho} of Ph), 7.58 (4H, d, $^3J_{H,H} = 7.2$ Hz, H_{ortho} of Ph), 7.46 (1H, t, $^3J_{H,H} = 8.1$ Hz, H_{pyr}), 7.03–7.31 (12H, m, $H_{m,p}$ of Ph), 6.85 (2H, d, $^3J_{H,H} = 7.5$ Hz, H_{pyr}), 4.10 (2H, dd, $^3J_{H,H} = 3.6$ and 5.7 Hz, C*H), 3.36 (2H, d, AB, $^2J_{H,H} = 14.1$ Hz, ArCH_2N), 2.92–2.95 (2H, m, NCHH ring), 3.29 (2H, d, AB, $^2J_{H,H} = 14.1$ Hz, ArCH_2N), 2.49 (2H, q, $^2J_{H,H} = 8.1$ Hz, NCHH ring), 1.91–1.98 (2H, m, CHHC*H ring), 1.72–1.76 (2H, m, CHHC*H ring), 1.60–1.67 (4H, m, CH_2CH_2N) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 158.92 [Pyr C(2,6)], 148.01 [Pyr C(3,5)], 146.74 [Pyr C(4)], 136.62 [C_{ipso} of Ph], 128.18 [C_{meta} of Ph], 126.38 [C_{para} of Ph], 125.88 [C_{ortho} of Ph], 78.20 [C-OH], 70.82 [C*], 61.78 [ArCH_2N], 55.71 [NCH_2 ring], 29.89 [CH_2C*H ring], 24.55 [CH_2CH_2N] ppm. UV–Vis (acetonitrile) [λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$)]: 225 (23 252), 263 (5464).

2.2.3. [FeCl(Py(ProOH)$_2$)]Cl (**4**)

A colorless solution of anhydrous $FeCl_2$ (0.98 mmol, 125 mg) in dry MeCN (10 mL) was added to a yellowish solution of **2** (0.98 mmol, 0.3 g) in dry MeCN (20 mL). The reaction mixture was stirred for 1 h at ambient temperature during which a yellow precipitate formed. The solvent was removed via a cannula and the remaining crude product was redissolved in a minimum amount of dry MeOH and precipitated with dry Et_2O (60 mL). The product was obtained as a yellow solid in 88% yield (0.376 g). Crystals suitable for X-ray analysis were obtained by vapor diffusion of dry Et_2O into a saturated methanolic solution of **4**. *Anal.* Calc. for $C_{17}H_{27}Cl_2FeN_3O_2$: C, 47.25; H, 6.30; N, 9.72. Found: C, 47.30; H, 6.38; N, 9.70%. ESI-MS *m*/*z*: 396.05 ((M−Cl)$^+$, calc. 396.11), 360.11 ((M−2Cl,−H)$^+$, calc. 360.14). $[\alpha]_D^{21} = +116$ deg cm^3 g^{-1} dm^{-1} (*c* 0.425, MeOH). IR (solid) nu(tilde) (cm^{-1}): 3011 (s), 2953 (s), 2888 (m), 2801 (m), 1608 (m), 1582 (m), 1469 (m), 1439 (m), 1408 (w), 1349 (w), 1334 (w), 1271 (w), 1209 (w), 1156 (w), 1098 (w), 1081 (w), 1061 (m), 1025 (m), 1010 (w), 993 (w), 983 (w), 928 (w), 913 (w), 806 (w), 755 (w). UV–Vis (acetonitrile) [λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$)]: 212 (8025), 264 (4259), 301 (1568).

2.2.4. [Fe(OTf)(Py(ProOH)$_2$)](OTf) (**5**)

A colorless solution of Fe(OTf)$_2$ · 2MeCN (1 mmol, 438 mg) in MeCN (15 mL) was added to a yellowish solution of **2** (1 mmol, 300 mg) in dry MeOH (15 mL). Immediately after addition, the color of the reaction mixture turned to light orange. The reaction mixture was stirred for 1 h at ambient temperature, followed by evaporation of the solvent *in vacuo*. The remaining brown oil was dissolved in a minimal amount of dry MeCN and washed with dry Et_2O (50 mL). After removal of the solvent, the brown oil was dried *in vacuo* to yield the product as a yellowish solid in 85% yield (560 mg). *Anal.* Calc. for $C_{17}H_{27}F_6FeN_3O_8S_2$: C, 34.61; H, 4.13; N, 6.37. Found: C, 34.68; H, 4.21; N, 6.30%. ESI-MS *m*/*z*: 510.06 ((M−OTf)$^+$, calc. 510.10), 360.091 ((M−2OTf,−H)$^+$, calc. 360.14), 180.55 ((M−2OTf)$^{2+}$, calc. 180.57) $[\alpha]_D^{21} = +112$ deg cm^3 g^{-1} dm^{-1} (*c* 0.615, MeOH). IR (solid) nu(tilde) (cm^{-1}): 3257 (br), 2971 (m), 2891 (m), 1609 (w), 1584 (w), 1472 (w), 1441 (m), 1277 (s), 1237 (s), 1224 (s), 1163 (s), 1097 (w), 1081 (w), 1027 (s), 927 (w), 802 (w), 759 (w). UV–Vis (acetonitrile) [λ_{max}, nm (ε, $M^{-1}\,cm^{-1}$)]: 213 (6539), 264 (5200), 301 (1322).

2.2.5. [FeCl(Py(ProPh$_2$OH)$_2$)]Cl (**6**)

A colorless solution of anhydrous $FeCl_2$(0.49 mmol, 63 mg) in dry MeOH (10 mL) was added to a colorless solution of **3** (0.49 mmol, 300 mg) in dry CH_2Cl_2 (15 mL). Immediately after addition, the color of the reaction mixture turned to yellow. The reaction mixture was stirred for 1 h at ambient temperature, followed by evaporation of the solvent *in vacuo*. The remaining yellow oil was dissolved in a minimal amount of dry MeOH and precipitated by addition of dry Et_2O (50 mL). The product was isolated as a beige solid in 83% yield (300 mg). *Anal.* Calc. for $C_{41}H_{43}Cl_2FeN_3O_2$: C, 66.86; H, 5.88; N, 5.70. Found: C, 66.74; H, 5.87; N, 5.59%. ESI-MS *m/z*: 663.21 ($(M-2Cl-1H)^+$, calc. 663.25); $[\alpha]_D^{21} = +60$ deg cm^3 g^{-1} dm^{-1} (*c* 0.42, MeCN). IR (solid) nu(tilde) (cm^{-1}): 3094 (s), 3056 (s), 2957 (s), 2901 (s), 2871 (s), 1611 (m), 1598 (m), 1591 (m), 1494 (m), 1472 (m), 1449 (m), 1439 (m), 1393 (w), 1350 (m), 1312 (m), 1272 (m), 1216 (w), 1191 (w), 1161 (m), 1105 (m), 1090 (m), 1061 (s), 1032 (m), 996 (m), 966 (w), 922 (m), 888 (m), 786 (m), 751 (s), 708 (m), 697 (m), 663 (w). UV–Vis (acetonitrile) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 218 (24594), 263 (10777), 302 (5477), 354 (2297).

2.2.6. *[Fe(OTf)(Py(ProPh$_2$OH)$_2$)](OTf) (7)*

A colorless solution of $Fe(OTf)_2 \cdot 2MeCN$ (0.45 mmol, 273 mg) in MeCN (10 mL) was added to a colorless solution of **3** (0.45 mmol, 195 mg) in dry CH_2Cl_2 (15 mL). Immediately after addition, the color of the reaction mixture turned to bright yellow. The reaction mixture was stirred for 1 h at ambient temperature, followed by evaporation of the solvent *in vacuo*. The remaining yellow oil was dissolved in a minimal amount of dry MeCN and precipitated by addition of dry Et_2O (50 mL). The product was isolated as a yellow solid in 81% yield (347 mg). *Anal.* Calc. for $C_{43}H_{43}F_6FeN_3O_8S_2$: C, 53.59; H, 4.50; N, 4.36. Found: C, 53.70; H, 4.65; N, 4.37%. ESI-MS *m/z*: 663.21 ($(M-2OTf-2H)^+$, calc. 663.25); $[\alpha]_D^{21} = +82$ deg cm^3 g^{-1} dm^{-1} (*c* 0.58, MeCN). IR (solid) nu(tilde) (cm^{-1}): 3350 (br), 3063 (m), 2972 (m), 2891 (w), 1656 (w), 1610 (w), 1598 (w), 1583 (w), 1494 (w), 1472 (w), 1450 (w), 1429 (w), 1274 (s), 1237 (s), 1224 (s), 1162 (s), 1113 (w), 1072 (w), 1057 (w), 1027 (s), 999 (m), 915 (w), 885 (w), 852 (w), 779 (w), 746 (m), 706 (m). UV–Vis (acetonitrile) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 221 (23147), 264 (11177), 301 (5588), 351 (2323).

2.2.7. *[ZnCl(Py(ProOH)$_2$)]Cl*

A similar synthetic route as described for iron complex **4** was used, by reacting anhydrous $ZnCl_2$ (0.54 mmol, 74 mg) and **2** (0.54 mmol, 0.16 g) in MeOH (15 mL). A white powder was obtained in 67% yield (160 mg). Crystals suitable for X-ray crystallographic analysis were obtained by vapor diffusion of dry Et_2O into a saturated methanolic solution of the complex. *Anal.* Calc. for $C_{17}H_{27}Cl_2ZnN_3O_2$: C, 46.23; H, 6.16; N, 9.51. Found: C, 46.12; H, 6.20; N, 9.61%. $[\alpha]_D^{21} = +65$ deg cm^3 g^{-1} dm^{-1} (*c* 0.55, MeOH). IR (solid) nu(tilde) (cm^{-1}): 3015 (s), 2958 (s), 2886 (m), 2806 (m), 1608 (m), 1586 (m), 1469 (m), 1456 (m), 1415 (w), 1350 (w), 1335 (w), 1273 (w), 1209 (w), 1156 (w), 1099 (w), 1082 (w), 1062 (m), 1026 (m), 1010 (w), 994 (w), 983 (w), 930 (w), 912 (w), 805 (w), 777 (w), 666 (w). ^{1}H NMR (CD_3OD) δ: 8.03 (1H, t, $^3J_{H,H} = 7.8$ Hz, H_{pyr}), 7.44 (2H, d, $^3J_{H,H} = 7.5$ Hz, H_{pyr}), 4.10 (2H, d, AB, $^2J_{H,H} = 16.2$ Hz, ArCH_2N), 4.05 (2H, d, AB, $^2J_{H,H} = 16.2$ Hz, ArCH_2N), 3.62 (1H, d, AX, $^3J_{H,H} = 7.2$ Hz, C*H*HOH), 3.02 (1H, d, AX, $^3J_{H,H} = 3$ Hz, CH*H*OH), 3.58 (1H, d, AX, $^3J_{H,H} = 7.2$ Hz, C*H*HOH), 3.06 (1H, d, AX, $^3J_{H,H} = 3$ Hz, CH*H*OH), 3.02–2.96 (2H, m, NCH*H* ring), 2.89–2.83 (2H, m, C∗*H*), 2.22–2.16 (2H, m, C*H*HCH$_2$N), 2.10–1.98 (4H, m, CH*H*CH$_2$N and C*H*HC∗H ring), 1.92–1.83 (2H, m, CH*H*C∗H ring) ppm. ^{13}C{^{1}H} NMR (CD_3OD) δ: 154.54 [Pyr *C*(2,6)], 142.29 [Pyr *C*(4)], 123.16 [Pyr *C*(3,5)], 61.35 [*C*-OH], 69.71 [*C*∗], 60.44 [Ar*C*H$_2$N], 56.46 [N*C*H$_2$ ring], 26.98 [*C*H$_2$C∗H ring], 23.88 [*C*H$_2$CH$_2$N] ppm.

2.3. *Catalytic procedures*

2.3.1. *General oxidation procedure 1*

To a solution of catalyst (3.5 μmol) in acetonitrile (2.8 mL) was added alkene (1.75 mmol, 500 equiv.) followed by slow, dropwise addition of 0.5 mL of 70 mM H_2O_2 solution in acetonitrile (35 μmol, 10 equiv., diluted from 35% aqueous H_2O_2) over 30 min. The reaction mixture was stirred at ambient temperature for another 30 min, followed by the addition of a known amount of internal standard (PhBr for styrene and PhSMe, pentadecane for cyclohexene, *cis*-stilbene and 1-decene, 1,2-dichlorobenzene for cyclooctene). To an aliquot (1 mL) taken from the reaction mixture was added Et_2O and it was analyzed by GC. The products were identified by comparison of the retention times with those of authentic compounds in GC and GC/MS spectra.

2.3.2. *General oxidation procedure 2 (for sulfides)*

To a solution of a catalyst (3.5 μmol) in acetonitrile (4 mL) was added a substrate (1.75 mmol, 50 equiv.) followed by slow addition of the H_2O_2 (0.3 mL of 700 mM in acetonitrile, 2.1 mmol, 60 equiv. diluted from 35% aqueous H_2O_2) over 30 min. The reaction mixture was stirred at ambient temperature. A sample for GC or NMR was taken after 1 h or as otherwise stated. When an additive was used, the particular additive (0.035 mmol, 10 equiv.) was added to a solution of catalyst (3.5 μmol) in acetonitrile (4 mL). The solution was stirred at ambient temperature for 10 min followed by the addition of a substrate and the oxidant. In the case of sulfide oxidation, the solvent was evaporated in vacuo and the crude product was purified by column chromatography (SiO_2, pentane/Et_2O = 1:2 (v/v), then ethyl acetate). Enantiomeric excesses were determined by HPLC using a chiral stationary phase, Daicel CHIRACEL OD, UV detector 210 nm, hexane:*i*-PrOH.

2.3.2.1. (R)-(+)-2-Methoxyphenyl methyl sulfoxide. Purification via column chromatography afforded the product as a yellow oil. $[\alpha]_D = +72.6$ (*c* 1.16, acetone). ^{1}H NMR ($CDCl_3$) δ: 2.77 (3H, s), 3.89 (3H, s), 6.92 (1H, d, $^3J_{H,H} = 8.1$ Hz), 7.19 (1H, t, $^3J_{H,H} = 7.5$ Hz), 7.45 (1H, t, $^3J_{H,H} = 8.2$ Hz), 7.82 (1H, d, $^3J_{H,H} = 7.8$ Hz) ppm. HPLC: $t_r(S) = 18.81$ min, $t_r(R) = 22.43$ min (Chiracel OD; flow rate 1 mL min^{-1}; hexane/*i*-PrOH = 95:5).

2.3.2.2. (R)-(+)-4-Methoxyphenyl methyl sulfoxide. Purification via column chromatography afforded the product as a yellow oil. $[\alpha]_D = +17$ (c 0.93, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 2.69 (3H, s), 3.84 (3H, s), 7.03 (2H, d, $^3J_{H,H} = 8.7$ Hz), 7.60 (2H, d, $^3J_{H,H} = 8.7$ Hz) ppm. HPLC: $t_r(R) = 34.05$ min, $t_r(S) = 37.65$ min (Chiracel OD; flow rate 1 mL min^{-1}; hexane/i-PrOH = 95:5).

2.3.2.3. (R)-(+)-4-Bromophenyl methyl sulfoxide. Purification via column chromatography afforded the product as a white solid. $[\alpha]_D = +21$ (c 1.21, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 2.72 (3H, s), 7.52 (2H, d, $^3J_{H,H} = 8.4$ Hz), 7.67 (2H, d, $^3J_{H,H} = 8.7$ Hz) ppm. HPLC: $t_r(R) = 38.49$ min, $t_r(S) = 40.40$ min (Chiracel OD; flow rate 1 mL min^{-1}; hexane/i-PrOH = 98:2).

2.3.2.4. (R)-(+)-4-Nitrophenyl methyl sulfoxide. Purification via column chromatography afforded the product as a white solid. $[\alpha]_D = +14$ (c 1.08, $CHCl_3$). ^1H NMR ($CDCl_3$) δ: 2.79 (3H, s), 7.84 (2H, d, $^3J_{H,H} = 8.7$ Hz,), 8.40 (2H, d, $^3J_{H,H} = 9.3$ Hz) ppm.

2.4. Conductivity measurements

The conductivity measurements were performed using a Consort C832 Multimeter analyzer at ambient temperature. The conductometer was calibrated using an aqueous solution of potassium chloride. Procedure followed: first the relative conductivity (κ in S cm^{-1}) of the solvent was measured ($V = 10$ mL) and then the relative conductivity of the samples ($V = 10$ mL). The conductivity of the compound is obtained by substraction of the blank conductivity from the conductivity of the sample. The molar conductivities (Λ_M in S cm^2 mol^{-1}) of the compounds were calculated using the following equation: $\Lambda_M = 1000*\kappa/c$ [20].

2.5. X-ray crystal structure determinations

X-ray intensities were measured on a Nonius Kappa CCD diffractometer with rotating anode (graphite monochromator, $\lambda = 0.71073$ Å) up to a resolution of $(\sin\theta/\lambda)_{max} = 0.65$ Å^{-1} at a temperature of 150 K. The structures were refined with SHELXL-97 [21] against F^2 of all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. OH hydrogen atoms were refined freely with isotropic displacement parameters, CH hydrogen atoms were refined as rigid groups. Geometry calculations and checking for higher symmetry were performed with the PLATON [22] program.

*2.5.1. X-ray crystal structure determination of **4***

Crystals of compound **4** suitable for X-ray crystallographic analysis were obtained as described in Section 2 (*vide supra*). $[C_{17}H_{27}ClFeN_3O_2]Cl$, Fw = 432.17, yellow plate, $0.36 \times 0.24 \times 0.12$ mm^3, orthorhombic, $P2_12_12_1$ (no. 19), $a = 9.9579(1)$, $b = 10.8650(1)$, $c = 17.4125(2)$ Å, $V = 1883.90(3)$ Å^3, $Z = 4$, $D_x = 1.524$ g/cm^3. 37750 reflections were measured. An absorption correction based on multiple measured reflections was applied ($\mu = 1.10$ mm^{-1}, 0.64–0.87 correction range). 4316 reflections were unique ($R_{int} = 0.0692$). The initial coordinates were taken from the isostructural [ZnCl(**2**)]Cl. 234 parameters were refined with no restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0294/0.0691. R_1/wR_2 [all refl.]: 0.0321/0.0709. $S = 1.054$. Flack parameter [23] $x = -0.008(12)$. Residual electron density between −0.42 and 0.41 e/Å^3.

*2.5.2. X-ray crystal structure determination of [ZnCl(**2**)]Cl*

$[C_{17}H_{27}ClN_3O_2Zn]Cl$, Fw = 441.69, colorless/yellowish block, $0.27 \times 0.12 \times 0.12$ mm^3, orthorhombic, $P2_12_12_1$ (no. 19), $a = 9.9450(1)$, $b = 10.8403(1)$, $c = 17.3876(2)$ Å, $V = 1874.50(3)$ Å^3, $Z = 4$, $D_x = 1.565$ g/cm^3. 38060 reflections were measured. An absorption correction based on multiple measured reflections was applied ($\mu = 1.61$ mm^{-1}, 0.64–0.82 correction range). 4283 reflections were unique ($R_{int} = 0.0496$). The structure was solved by Direct Methods [49]. 234 parameters were refined with no restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0245/0.0555. R_1/wR_2 [all refl.]: 0.0265/0.0566. $S = 1.043$. Flack parameter [23] $x = -0.007(8)$. Residual electron density between −0.61 and 0.55 e/Å^3.

3. Results and discussion

3.1. Synthesis

Ligand $Py(ProOH)_2$ (**2**) was synthesized in a one step procedure using 4 equiv. of (S)-prolinol with respect to 2,6-bis(chloromethyl)pyridine in a biphasic CH_2Cl_2/H_2O system with 10% of $[n\text{-}Bu_4N]Cl$ as a phase transfer catalyst and K_2CO_3 as base (Scheme 1). Using this procedure, the desired ligand **2** was obtained in 66% yield after purification by column chromatography. An excess of (S)-prolinol was used to obtain the ligand in a higher yield at the expense of monosubstituted by-product. When only 2.5 equiv. of (S)-prolinol was used, the yield dropped to 32%. The synthesis of **2** was earlier reported by Bernauer et al. [24] using a rather time consuming purification procedure.[2]

The bulkier ligand $Py(ProPh_2OH)_2$ (**3**) could not be obtained via this one step procedure. The reaction using 2,6-bis(chloromethyl)pyridine and 2.5 equiv. of 2,2-(diphenyl)-(1S)-hydroxymethylpyrrolidine yielded a rather complex mixture of products [25]. A Grignard reaction of bismethyl ester ligand **1** ($Py(ProMe)_2$) with excess of PhMgBr gave the desired ligand **3**, however in a low 25% yield and after purification by column chromatography

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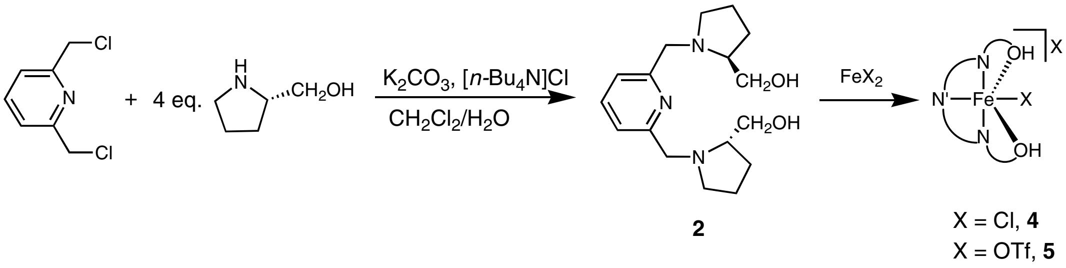
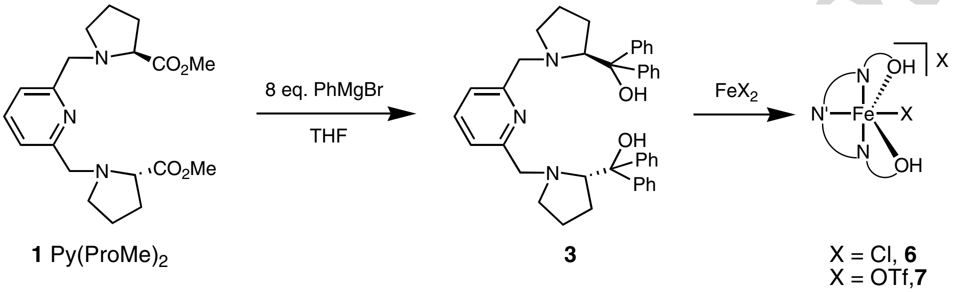
[2] Complexation of crude **2** with $Cu(ClO_4)_2 \cdot 6H_2O$ and crystallization of the $[CuCl(\mathbf{2})](ClO_4)$ complex, followed by decomplexation with Na_2H_2edta and two subsequent purification steps via ion-exchange chromatography.



Scheme 1. Synthesis of ligand Py(ProOH)$_2$ (**2**) and the corresponding iron(II) complexes **4** and **5**.



Scheme 2. Synthesis of ligand Py(ProPh$_2$OH)$_2$ (**3**) and the corresponding iron(II) complexes **6** and **7**.

(Scheme 2). Both ligands **2** and **3** were synthesized and isolated in enantiopure form (*vide infra*).

Iron(II) complexes **4**–**7** were synthesized by mixing equimolar amounts of ligand, either **2** or **3**, with FeCl$_2$ or Fe(OTf)$_2$ · 2MeCN. The reaction of anhydrous iron dichloride with **2** or **3** afforded [FeCl(**2**)]Cl (**4**, yellow) and [FeCl(**3**)]Cl (**6**, yellowish), respectively. The reaction of either **2** or **3** with an iron salt containing the weakly coordinating triflate anion resulted in the formation of [Fe(OTf)(**2**)]OTf (**5**, yellowish) and [Fe(OTf)(**3**)](OTf) (**7**, yellow), respectively. All complexes are relatively stable toward O$_2$ and moisture, but were kept under a nitrogen atmosphere for storage. All complexes were characterized by UV–Vis, solid and solution IR spectroscopy, ESI-MS, elemental analysis, conductivity and CD measurements. In addition, the molecular structure of [FeCl(**2**)]Cl (**4**) was obtained by X-ray crystal structure determination.

3.2. Solid state structure of 4

Crystals of [FeCl(**2**)]Cl (**4**) suitable for X-ray diffraction were obtained via vapor diffusion of Et$_2$O into a concentrated MeOH solution of **4**. The molecular geometry of **4** is shown in Fig. 2. Selected bond distances and angles are listed in Table 1 and the relevant crystallographic data are given in Section 2. The crystal structure of **4** is isostructural with [ZnCl(**2**)]Cl.[3] The iron(II) center in **4** is in a distorted octahedral geometry because of the coordination of all five donor atoms of ligand **2** and of a chloride anion, which is positioned *trans* to the pyridine nitrogen. The *NN′NOO*-pentacoordination of the Py(ProOH)$_2$ ligand results in the formation of a single diastereoisomer of **4** with $R_NR_NS_CS_C$ configuration. The R_N configuration of the nitrogen stereogenic centers is created upon coordination of the pyrrolidinyl N-donor atoms of the ligand to iron, while the given S_C configuration of the C stereogenic centers is retained. This results in an overall Λ-configuration at the metal center.

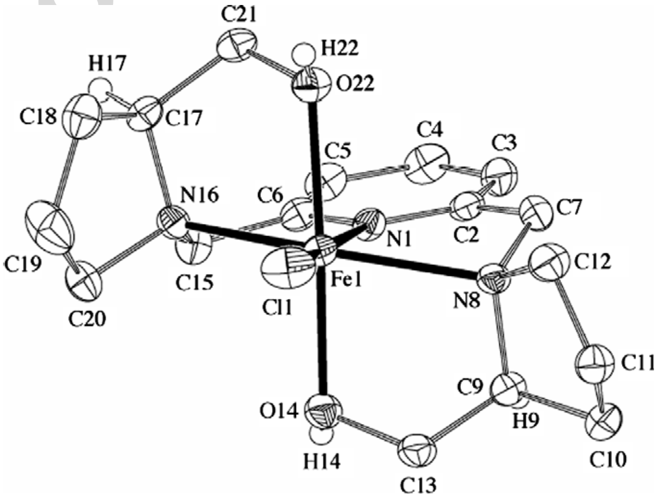


Fig. 2. Displacement ellipsoid plot (50% probability) of the cation of **4**. The hydrogen atoms at both stereogenic carbon atoms and hydroxyl groups are shown, while the remaining hydrogen atoms and the non-coordinated chloride are omitted for clarity.

In order to define the equatorial plane around iron, the deviations of the least-squares planes of the NN′NClFe and N$_2$O$_2$Fe arrangements were compared. Deviations for all atoms in the range of 0.1486(15)–(−0.3126(15)) Å were found for the N$_2$O$_2$Fe least-squares plane, whereas the

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[3] For further crystallographic details on [ZnCl(**2**)]Cl see Section 2 of this paper.

Table 1
Selected bond distances (Å) and angles (°) of complex **4**

Distances			
Fe–N(1)	2.1385(16)	Fe–O(14)	2.1594(15)
Fe–N(8)	2.3108(17)	Fe–O(22)	2.1832(16)
Fe–N(16)	2.2761(17)	H(14)···Cl(2)	2.11(3)
Fe–Cl(1)	2.3187(6)	H(22)···Cl(2)^{i}	2.28(3)
Angles			
N(8)–Fe–N(16)	149.46(6)	O(14)–Fe–N(1)	88.75(6)
N(1)–Fe–N(8)	73.92(6)	O(22)–Fe–N(1)	84.29(6)
N(1)–Fe–N(16)	75.96(6)	O(14)–Fe–N(8)	79.71(6)
N(1)–Fe–Cl(1)	172.01(5)	O(22)–Fe–N(16)	79.30(6)
N(8)–Fe–Cl(1)	99.85(5)	O(14)–H(14)···Cl(2)	171(3)
N(16)–Fe–Cl(1)	110.59(5)	O(22)–H(22)···Cl(2)^{i}	171(3)
O(14)–Fe–O(22)	171.77(6)		

Symmetry operation i: 0.5 − *x*, 1 − *y*, *z* − 0.5.

NN′NCl arrangement and the iron center are essentially all in one plane with a maximum deviation of −0.1054(17) Å for the pyridine nitrogen. Consequently, the equatorial plane is defined by the *mer* η^3-*N*,*N′*,*N* coordination of the three nitrogen atoms and the chloride anion, which is in agreement with the ligand field enforced by these ligands.The two axial positions are then occupied by the oxygen atoms of the hydroxyl groups of the ligand. The second chloride anion is a non-coordinated counteranion. Only this free chloride is involved as an acceptor in a hydrogen bonding network with the hydroxyl groups as donors, thereby forming infinite chains of cations and anions (Fig. 3).

The octahedral geometry of **4** is rather distorted as reflected by the *cisoid* (73.96(6)–110.59(5)°) and *transoid* (149.46(6)°, 171.77(6)° and 172.01(5)°) angles around the iron atom. In particular, the larger N(8,16)–Fe–Cl angles (99.85(5) and 110.59(5)°, respectively) deviate considerably from the ideal value of 90° and are a consequence of the *mer* η^3-*N*,*N′*,*N* coordination of the ligand. This also results in N–Fe–N transoid angles (N(8)–Fe–N(16) = 149.46(6)°) strongly deviating from the ideal value of 180° [14,26]. The Fe–N distances reflect the different chemical nature of the donor atoms with the Fe–N(pyr) distance, Fe–N(1) = 2.1385(16)Å being noticeably shorter than the Fe–N (pro) distances, Fe–N(8) = 2.3107(17)Å and Fe–N(16) = 2.2762(17) Å. Overall, these distances have typical values expected for such Fe–N bonds in high-spin Fe(II) complexes [9c,9d,10b,10d]. The longer Fe–N(8) (2.3108(17) Å) distance is compensated by a shorter Fe–O(14) distance (2.1594(15) Å) of the same pyrrodinyl ring, whereas the shorter Fe–N(16) 2.2761(17) bond of the other ring is combined with a longer Fe–O(22) (2.1832(16) Å) distance of the hydroxyl group. Similar Fe–N bond lengths differences were reported for structurally related pincer-type *N*,*N′*,*N*-iron(II) Py(ProMe)$_2$ complexes [14]. The torsional twist of the pyridyl ring from the FeNN′NCl equatorial plane is 19.22(7)°. The five-membered chelate rings of the FeNN′NCl equatorial plane have different conformations; whereas the Fe(1)–N(1)–C(6)–C(15)–N(16)-ring has an half-chair conformation twisted around the C(15)···N(16) bond, an envelope conformation with N(8) out of the plane is observed for the Fe(1)–N(1)–C(2)–C(7)–N(8) chelate. The pyrrolidinyl chelate rings also have different conformations; the ring containing N(8) has an envelope conformation with C(10) positioned out of the plane, while the other ring containing N(16) has an half-chair conformation twisted around C(20)–N(16). Due to these conformational differences, the overall C_2 symmetry of the complex in solution is lost in the solid state. Regrettably, attempts to grow single crystals for complexes **5**–**7** have failed.

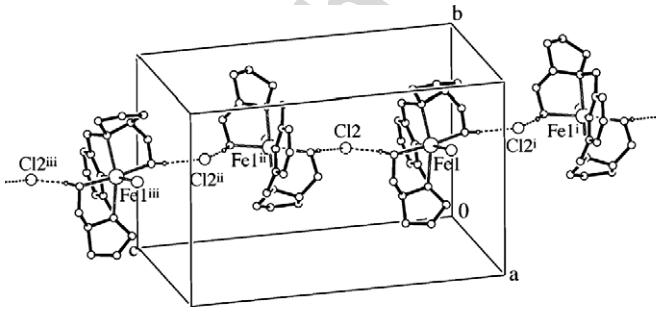

Fig. 3. Infinite one-dimensional chain of **4** formed by hydrogen bonds in the direction of the crystallographic *c*-axis. Dashed lines indicate hydrogen bonds between the hydroxyl groups as donors and the non-coordinated chloride anions as acceptors. C–H hydrogen atoms are omitted for clarity. Symmetry operations i: 0.5 − *x*, 1 − *y*, *z* − 0.5; ii: 0.5 − *x*, 1 − *y*, z + 0.5; iii: *x*, *y*, *z* + 1.

3.3. Structures of complexes 4–7 in solution

The ESI mass spectra of samples of solutions of **4**–**7** in MeOH or MeCN point to the presence of a single mononuclear species in solution. For complex **4**, peaks at *m*/*z* 396.05 and 180.58 correspond to [FeCl(**2**)]$^+$ (parent peak) and [Fe(**2**)]$^{2+}$ ions, respectively. A similar ionization pattern was detected for **5** with peaks at *m*/*z* 510.06 [Fe(OTf)(**2**)]$^+$ and 180.58 [Fe(**2**)]$^{2+}$, respectively. The observed isotope distribution pattern is in good agreement with the calculated one. In contrast, the ESI mass data recorded for **6** and **7** displayed two identical parent cation peaks at *m*/*z* 663.25 and 610.39. The latter peak corresponds to the ligand protonated [(**3**)H]$^+$, while the former *m*/*z* 663.25 is in agreement with a calculated ion of formulation [Fe(**3**)-2(H)]$^+$ containing a doubly deprotonated ligand.[4]

UV–Vis, conductivity, and solution IR measurements were carried out on solutions of the respective complexes **4**–**7** in acetonitrile. UV–Vis absorption spectra showed strong ligand-based absorptions around 215 and 265 nm. The extinction coefficients obtained for the iron complexes derived from ligand **3** having four phenyl rings were much higher than the ones obtained for complexes derived from ligand **2** (Table 2). In addition, all metal complexes exhibit metal-to-ligand charge transfer (MLCT) bands at 301 nm,

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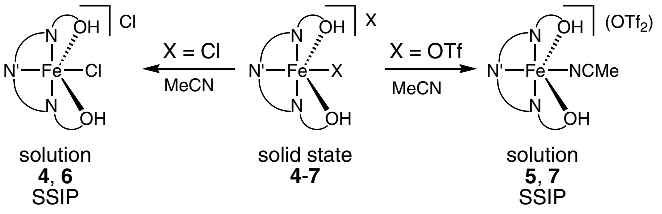
[4] The oxidation of Fe(II) to Fe(III) most probably occurred during the electrospray ionization, as other characterization techniques support the presence of an iron(II) center in both **6** and **7**.

Table 2
Selected properties of **4**–**7** in acetonitrile

Complex	UV–Vis[a] (nm)	Molar conductivity (S cm^{2}mol^{-1})	Type of electrolyte
[FeCl(**2**)]Cl (**4**)	212 (8025), 264 (4259), 301 (1568)	78 (0.6 mM)	1:1
[Fe(OTf)(**2**)](OTf) (**5**)	213 (6539), 264 (5200), 301 (1322)	254 (1.4 mM)	2:1
[FeCl(**3**)]Cl (**6**)	218 (24 594), 263 (10 777), 302 (5477), 354 (2297)	83 (0.5 mM)	1:1
[Fe(OTf)(**3**)](OTf) (**7**)	221 (23 147), 264 (11 177), 301 (5588), 351 (2323)	268 (1.1 mM)	2:1

[a] Extinction coefficients (M^{-1} cm^{-1}) are given in parentheses after each feature.



Scheme 3. Structures of complexes **4**–**7** in the solid state and in acetonitrile solution (SSIP = solvent separated ion pair).

while complexes **6** and **7** derived from ligand **3** show an additional feature at 354 nm ($\varepsilon = 2297$ M^{-1} cm^{-1}) and at 351 ($\varepsilon = 2323$ M^{-1} cm^{-1}), respectively.

Molar conductivities were measured at concentrations around 1 mM for **5** and **7** (1.4 mM and 1.1 mM, respectively). The concentrations of chloride derivatives **4** and **6** (0.6 mM and 0.5 mM, respectively) had to be chosen slightly lower because of their low solubility in acetonitrile (Table 2). Molar conductivities obtained for **4** (78 S cm^2 mol^{-1}) and **6** (83 S cm^2 mol^{-1}) are too high for non-electrolytes and are close to the literature values of 120–160 S cm^2 mol^{-1}for 1:1 electrolytes [27,28]. These findings indicate that the [FeCl(**L**)]Cl complexes exist in solution as solvent separated ion pairs. The higher molar conductivities found for complexes **5** and **7** are in agreement with a 2:1 electrolyte behavior [29], most likely indicating that a solvent molecule has replaced the coordinated triflate anion, *i.e.* these complexes exist in solution as [Fe(**L**)(MeCN)]$^{2+}$ and OTf$^-$ solvent separated ion pairs (Scheme 3). Similar conclusions were drawn from the solution IR analysis of **5** and **7**. Four sharp single vibrations[5] at 1275 ($\nu_{as}SO_3$), 1224 (ν_sCF_3), 1161 ($\nu_{as}CF_3$), and 1032 (ν_sSO_3) cm^{-1} were observed, which are typical for non-coordinated triflate anions [30]. Moreover, the appearance of a new vibration at 2248 cm^{-1}(ν(C≡N)) further supports the replacement of a OTf anion by a neutral acetonitrile ligand. The replacement of a coordinated triflate anion by coordinating solvents is commonly observed in iron complexes with weakly coordinated anions [31].

Solution CD spectra of complexes **4**–**7** in MeCN in the range of 250–450 nm all show very similar CD curves with a positive Cotton effect around 260 nm (Fig. 4). These observations point to an identical configuration at the metal center in all four complexes. On the basis of the stereochemistry found for **4** in the solid state and using the sector rules [32] for C_2 symmetric pyridine metal complexes, an absolute Λ-configuration at the iron center in **4**–**7** was assigned [33]. This assignment is unambiguous because of the presence of the (given) S_C configuration of the stereogenic C atoms of the pyrrolidinyl moieties and by the octahedral *NN′NOO* coordination of the pentacoordinate ligands **2** and **3** to the Fe(II) center.[6] This pentacoordination mode results in the formation of C_2 symmetrical complexes, which is further corroborated by the NMR analysis of [ZnCl(**2**)]Cl, a complex isostructural to **4** in the crystal.[7] The retention of the ligand pentacoordination with a Λ-configuration at the metal furthermore points to the presence of **4**–**7** in solution as single diastereoisomers with $R_NR_NS_CS_C$ configuration.

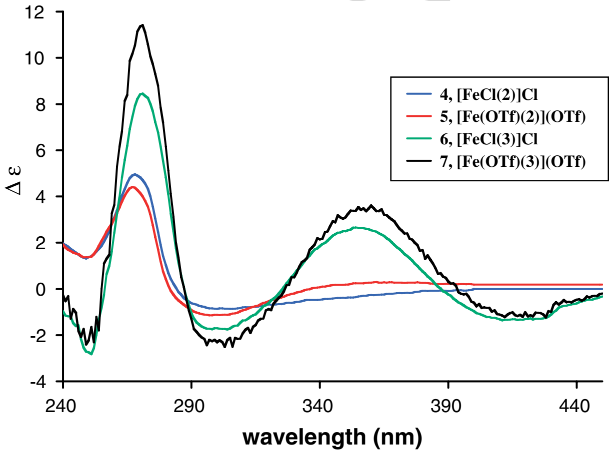


Fig. 4. CD spectra in acetonitrile of complexes **4**–**7**.

3.4. Catalysis

Iron(II) complexes **4**–**7** were tested as catalysts for the oxidation of unfunctionalized hydrocarbons, e.g. alkanes and alkenes, and eventually sulfide substrates. Initial oxidation tests in acetonitrile under ambient conditions using

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[5] Detailed analysis of the vibrations of coordinated and non-coordinated triflate anions of structurally related iron complexes is presented in Ref. [14].

[6] In the case where octahedral metal complexes of penta-coordinate ligands with an R_C configuration of the C atom of pyrrolidinyl moieties [33b] or when metal complexes with pentagonal bipyramidal geometries with all five donor atoms of the ligand forming a pentagonal plane around the metal center would have formed [14], a Δ-configuration would have resulted at the metal.

[7] The ^{1}H and ^{13}C{1H} NMR spectra of [ZnCl(**2**)]Cl showed the presence of a single species with an overall C_2 symmetry. For ^{1}H and ^{13}C{1H} NMR data see Section 2.

a catalyst:oxidant:substrate ratio of 1:10:500 revealed that none of the complexes is capable of oxidizing alkane substrates like cyclohexane or adamantane in the presence of H_2O_2. However, complexes **5**–**7** were active in the oxidation of alkenes and sulfides under these conditions. Since complexes **6** and **7** displayed higher TON's in the oxidation of cyclooctene and cyclohexene than complex **5** (results not shown), further catalytic tests were performed using only these complexes derived from ligand **3** (Table 3).

3.4.1. Alkene oxidation

In general, the highest total TON's were obtained in the oxidation reaction of cyclohexene with H_2O_2 (Table 3, 8.4 for **6** and 7.7 for **7**, entry 1), whereas the oxidation of other olefinic substrates yielded total TON's numbers lower than five (Table 3, entries 2–5). Both catalysts afforded the corresponding allylic alcohol and ketone (A/K = 1.6 (**6**) and 1.1 (**7**)) as the main products in similar yields and with very little epoxide formation (Table 3, entry 1). In the case of cyclooctene, which is less susceptible to allylic oxidation [34], catalyst **6** yielded the epoxide as the only product while with catalyst **7** both the epoxide and *cis*-diol product were formed albeit with low TON's (Table 3, entry 2). Oxidation of styrene yielded benzaldehyde in substantial amounts besides styrene oxide and some unidentified products. Benzaldehyde was the main product in addition to small amounts of *cis*- and *trans*-epoxide and also *trans*-stilbene in the oxidation of *cis*-stilbene with both catalysts. The oxidation of α-alkenes like 1-decene afforded only traces of epoxide product with both **6** and **7**.

Catalysts **6** and **7** provided different product ratios in the oxidation reactions of cyclooctene and *cis*-stilbene. This might indicate that these catalysts operate via different oxidation mechanisms. The formation of (small) amounts of epoxide and diol products may point to a metal-based mechanism, while the formation of benzaldehyde in the oxidation of styrene and *cis*-stilbene as well as the formation of mainly allylic oxidation products in the oxidation of cyclohexene strongly suggests the formation of the C-centered radicals in the alkene oxidations with both complexes [1]. Furthermore, the alkene oxidation observed with these complexes is most probably not resulting from the oxidation initiated by the free hydroxyl radicals, since also alkanes would be expected to undergo oxidation, which is, however, not the case for complexes **6** and **7**.

Table 3
Oxidation of alkenes catalyzed by [FeCl(**3**)]Cl (**6**) and [Fe(OTf)(**3**)](OTf) (**7**) with H_2O_2[a]

Entry	Substrate	Product	TON[b]		Conversion of oxidant (%)	
			6	**7**	**6**	**7**
1	cyclohexene	epoxide	0.7	0.6	84	77
		2-cyclohexen-1-ol	4.7	3.7		
		2-cyclohexen-1-one	3.0	3.4		
2	cyclooctene	epoxide	2.4	0.6	24	17
		diol	n.o.	1.1		
3	1-decene	epoxide	trace	trace		
4	styrene[c]	styrene oxide	2.5	0.28	43	23
		benzaldehyde	1.8	2.0		
5	*cis*-stilbene[d]	*cis*-epoxide	0.4	0.5	11	22
		benzaldehyde	0.7	1.7		

[a] Reaction conditions: 0.5 mL of 70 mM H_2O_2 solution in MeCN (diluted from 35% H_2O_2 solution in water) was added slowly over 30 min at ambient temperature to a stirred solution of 2.8 mL MeCN containing Fe-complex (3.5 μmol) and substrate (1.75 mmol). The resulting mixture was stirred further for 30 min at ambient temperature. Ratio of catalyst:oxidant:substrate = 1:10:500.

[b] Moles of product/moles of catalyst.

[c] Also some unidentified products were detected by GC.

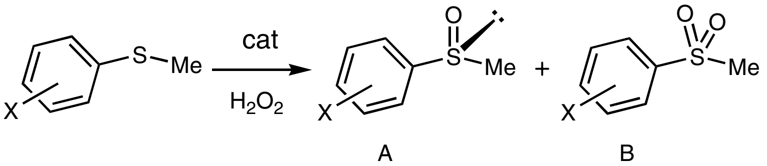
[d] *trans*-Stilbene and *trans*-stilbene oxide were detected as products by GC, but were not quantified.

3.4.2. Sulfide oxidation

Chiral sulfoxides are important compounds in medicinal and pharmaceutical chemistry [35] and find increasing use as chiral auxiliaries in asymmetric synthesis and as ligands in enantioselective catalysis [36]. Several methods for the asymmetric oxidation of prochiral sulfides have been reported [37], but the oxidation by chiral metal complexes is one of the most attractive routes [1c,38]. Catalysts based on titanium, manganese, and vanadium have been widely applied [39–41]. Only few systems based on iron have, however, been developed for the enantioselective oxidation of sulfides. Most of them involve structurally complex iron porphyrines as catalysts and iodosyl benzene or alkyl hydroperoxides as the terminal oxidant [42]. Fontecave et al. studied the catalytic and spectroscopic properties of mono- and dinuclear iron complexes of (−)-4,5-pinene-2,2′-bipyridine ligands using H_2O_2 as an oxidant [43]. The enantioselectivity obtained with these iron catalysts did not surpass 55% ee. However, very good selectivities up to 96% ee were reported recently by Bolm et al. combining either $Fe(acac)_3$ or vanadium salts with Schiff base ligands in the presence of H_2O_2 [44].

The results of the selective oxidation of sulfides to sulfoxides mediated by the chiral complexes **6** and **7** as catalysts are shown in Table 4. The oxidation of aryl methyl sulfides to sulfoxides using H_2O_2 as the oxidant at ambient temperature (ratio of catalyst:oxidant:substrate = 1:10:500) is catalyzed by both complexes. High conversion of the oxidant was observed in the reactions of aryl methyl sulfide with H_2O_2 within 1 h (Table 4, entries 1 and 2). No overoxidation of the sulfoxide product to the corresponding sulfone occurred. To optimize the conversion of the substrate, the reactions were carried out with a slight excess (1.2 equiv.) of the oxidant toward the substrate (ratio of catalyst:oxidant:substrate = 1:60:50). Under these conditions, catalyst **6** (Table 4, entry 3) showed an improved activity as compared with that of complex **7** (Table 4, entry 4). Phenyl methyl sulfoxide (TON = 44.3) was formed in 88% yield within 1 h with very little overoxidation to the sulfone (<5%). The reaction appeared to be dependent on the nature and the position of the substituent on the aryl ring of the substrate. The reactions of aryl methyl sulfides with electron-donating substituents (*o*- and

Table 4
Oxidation of aryl methyl sulfides catalyzed by [FeCl(**3**)]Cl (**6**) and [Fe(OTf)(**3**)](OTf) (**7**) with H_2O_2[a]



Entry	Compound	X=	Additive	Yield (%)		ee (%)[c]	Configuration	Time (h)
				A[b]	B[b]			
1[d]	**6**	H		(7.2)[e]	n.o.	11	*R*	1
2[d]	**7**	H		(9.4)[e]	n.o.	4	*R*	1
3	**6**	H		88(44.3)[e]	4	13	*R*	1
4	**7**	H		34(19)[e]	2	7	*R*	1
5	**6**	*o*-MeO		87[g]	<5[h]	20	*R*	3
6	**6**	*p*-MeO		84[g]	9[h]	17	*R*	16
7	**6**	*p*-NO_2		56[g]	14[h]	9[i]	*R*	16
8	**6**	*p*-Br		87[g]	9[h]	10	*R*	16
9	**6**	H	acetic acid	81	9	21	*R*	1
10	**6**	H	anisic acid	85(87)[f]	6(4)[f]	27(16)[f]	*R*	1
11	**6**	*o*-MeO	anisic acid	91[g]	<5[h]	25	*R*	3
12	**6**	*p*-MeO	anisic acid	93[g]	7[h]	26	*R*	3
13	**6**	*p*-NO_2	anisic acid	62[g]	16[h]	11[i]	*R*	16
14	**6**	*p*-Br	anisic acid	89[g]	8[h]	19	*R*	3

[a] Reaction conditions: see Procedure 2 in Section 2 (ratio cat:oxid:substrate = 1:60:50); n.o. = not observed.
[b] Yield of PhSOMe and $PhSO_2Me$ was determined by GC using bromobenzene as an internal standard.
[c] Determined via HPLC (Daicel CHIRACEL OD, for hexane:*i*-PrOH ratio for each of the products see Section 2).
[d] Reaction conditions: see Procedure 1 in Section 2 (ratio cat:oxid:substrate = 1:10:500).
[e] TON in parentheses (moles of product/moles of catalyst).
[f] The values in parentheses were calculated with 0.5 equiv. of anisic acid.
[g] Isolated yield after column chromatography.
[h] Yield determined by ^1H NMR analysis.
[i] The ee% was calculated from the optical rotation of the sample compared to the optical rotation of the pure stereoisomer [38d].

p-methoxy) provided yields of 87% and 84% (Table 4, entries 5 and 6), although longer reaction times were required in the case of the *p*-substituted aryl sulfide to obtain the product in high yield. Longer reaction times were also necessary for substrates with electron-withdrawing substituents (Br and NO_2) in the aryl *p*-position. In the case of *p*-nitro phenyl sulfide, even after 16 h about 30% of the starting material remained unreacted.[8] A significant amount of sulfone (10–13%) was formed when longer reaction times had to be applied. As both catalysts were applied in diastereopure form, it was disappointing to find that in all reactions the corresponding sulfoxides were formed with low ee's.

The use of additives has been reported in several cases to have a beneficial effect on the efficiency and selectivity in metal-catalyzed reactions [1b,45]. However, the search for the right additive often follows a trial and error strategy especially in reactions of which mechanistic details are still unknown, e.g. iron-mediated sulfide oxidations. Jacobsen et al. have found that the presence of an excess of acetic acid (ratio of catalyst:additive = 1:10) could improve the efficiency of alkene epoxidation with H_2O_2 and an iron catalyst [4a]. Recently, Bolm et al. reported enhanced reactivities and selectivities in sulfide oxidation using benzoic acids as additives in sub-stoichiometric amounts (ratio catalyst:additive = 1:0.5) [44]. Following these findings we chose to test two additives, acetic acid and *p*-anisic acid, for an investigation of their effect on the oxidation of phenyl methyl sulfide (entries 9 and 10). Indeed, the reactions using either one of these additives gave the sulfoxide in higher yields and with slightly improved enantioselectivities (up to 21% and 27%, respectively), while only small amounts of sulfone by-product were formed. The highest selectivity and the lowest amount of sulfone was obtained when *p*-anisic acid was used as an additive in excess to the amount of iron catalyst (catalyst:additive = 1:10). Better yields (~90%) with shorter reaction times and improved enantioselectivities (up to 26% ee) were found with *p*-anisic acid as an additive for *o*- and *p*-substituted aryl methyl sulfides (entries 11–14).

The formation of sulfone next to the sulfoxide might imply the existence of a kinetic resolution process during the oxidation reaction [39d,39f,46]. To examine whether such a process is operative in the case of catalyst **6**, the oxidation of racemic phenyl methyl sulfoxide with H_2O_2 was performed in the absence and presence of acetic

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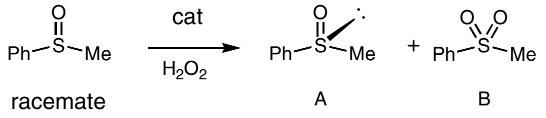
[8] Low yields (21-41%) of sulfoxide with *p*-nitrophenyl methyl sulfide were reported also with other iron catalyzed systems, see Ref. [35,42].

Table 5
Oxidation of aryl methyl sulfoxide catalyzed by [FeCl(**3**)]Cl (**6**) with H_2O_2[a]



Entry	Additive	Yield B (%)[b]	ee (%)[c]	Configuration	Time (h)
1		14	11	*R*	3
2		15	12	*R*	16
3	acetic acid	19	11	*R*	3
4	acetic acid	23	9	*R*	16
5	anisic acid	13	26	*R*	3
6	anisic acid	16	22	*R*	16

[a] Reaction conditions: see Procedure 2 in Section 2 (ratio cat:oxid:substrate = 1:60:50).

[b] Yield of PhSOMe and $PhSO_2Me$ was determined by GC using bromobenzene as an internal standard.

[c] Ee in recovered sulfoxide; determined via HPLC (Daicel CHIRACEL OD, hexane:*i*-PrOH = 95:5).

and *p*-anisic acid and conversions and ee values were measured after 3 and 16 h (Table 5). The conversion of sulfoxide to sulfone was rather low for reactions without an additive (Table 5, entries 1 and 2) and in the presence of *p*-anisic acid (Table 5, entries 5 and 6). Higher conversions were observed in the presence of acetic acid (Table 5, entries 3 and 4). The ee values of the recovered sulfoxides show kinetic resolution to some extent. The oxidation of *S*-sulfoxide ($k_S > k_R$) occurs predominantly with stereoselective factors (*s*) [47] of 4.8 without an additive, 2.03 for acetic acid and 7.2 for *p*-anisic acid. The ee of the recovered sulfoxides remained constant in time; only in the presence of *p*-anisic acid was a slight decrease observed. Apparently, the same catalyst favors the oxidation of sulfide to yield *R*-sulfoxide and catalyzes predominantly the oxidation of *S*-sulfoxide to sulfone. Such a dual selectivity of the same catalyst is not uncommon [41h,48].

Even though the kinetic resolution of sulfoxides in the presence of complex **6** can take place, the amount of sulfone formed in the oxidation of sulfides (Table 4) stayed below 10%, except for the reaction of sulfide with the *p*-nitro substituent (Table 4, entries 7 and 13), and the ee values of the sulfoxides did not change significantly during the course of the reaction. These observations indicate that the ee values of sulfoxides originate from the enantioselective oxidation of sulfide substrate rather than from kinetic resolution of the chiral sulfoxides formed in the course of the reaction [44c,48].

4. Conclusions

We have shown that the ligands $Py(ProOH)_2$ and $Py(ProPh_2OH)_2$ are obtained in an enantiomerically pure form and their corresponding iron(II) complexes are formed as single diastereoisomers which retain their structural integrity and stereochemistry in solution. Overall, the reactions of complexes **4**–**7** with H_2O_2 under ambient conditions generate poorly defined metal-based oxidants for alkane and alkene oxidation. Complex **6** showed very high activity in the oxidation of various *o*- and *p*-substituted sulfides with and without an additive, comparable with the most active catalysts reported in the literature [37] albeit with low ee's. The use of additives showed a slight improvement of the ee's, which is promising for further optimization of thes reaction conditions (i.e. lower temperatures). The ligands presented here together with the $Py(ProMe)_2$ ligand can be seen as members of a bigger family of ligands built on the same framework which can be easily modified by organic synthetic methods. This class of ligands and their iron complexes are therefore an interesting lead for the development of more active and selective oxidation catalysts.

5. Supplementary material

CCDC Nos. 609009 (**4**) and 609010 ([ZnCl(**2**)]Cl) 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 [or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: int. code +44(1223)336 033; e-mail: deposit@ccdc.cam.ac.uk].

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