



Synthesis, crystal structure and reactivity studies of iron complexes with pybox ligands



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ABSTRACT

Iron(II) complexes, [Fe(2,6-bis(4,4-dimethyl-1,3-oxazolin-2-yl)pyridine)Cl₂] ((Fe(Me₂-pybox)Cl₂), **3**) and [Fe(2,6-bis(4,4-diphenyl-1,3-oxazolin-2-yl)pyridine)Cl₂] ((Fe(Ph₂-pybox)Cl₂), **4**), have been synthesized and characterized by X-ray crystallographic analysis. Upon treatment of complex **3** with silver triflate and **4** with acetonitrile, [Fe(Me₂-pybox)(CH₃CN)OTf₂] (**5**) and [Fe(Ph₂-pybox)(CH₃CN)₂Cl][FeCl₃] (**6**) were obtained, respectively. The bulkier phenyl substitutes were found not only to cause the elongation of the N–Fe bonds but also influence the reactivity of the Fe center.

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1. Introduction

Since Nishiyama's first report on the tridentate nitrogen ligand pybox in 1989 [1], the use of chiral pybox ligands derived from aminoalcohols in transition metal catalysis has received considerable attention due to the convenient preparation, ready availability of the chiral precursors, and their excellent performance [2–9]. The pybox usually serves as a tridentate ligand [10,11], although a few examples as bidentate ligands (involving pyridine and one of the two oxazoline nitrogen atoms) [12–15], and as monodentate ligands have been reported [16,17]. These observations make the synthesis and structural characterization of pybox transition metal complexes highly interesting and useful as they may allow one to understand the factors that influence the coordination nature of ligands, and therefore the reactivity of the corresponding complexes [18–23].

The development of iron-based catalysts has recently become an active research area due to their low cost and low toxicity, as well as benign environmental impact [24–28]. A number of Fe/pybox catalyst systems were developed for various organic transformations such as the asymmetric Nazarov cyclization of divinyl ketones [29], the asymmetric aziridine formation reaction [30], Mukaiyama–Aldol reaction [31,32], the enantioselective conjugate addition [33,34], olefin polymerization [35,36], etc. Despite the wide applications of these catalysts, structural studies of well-defined iron–pybox complexes are scarce [30,36,37]. Herein, we report the synthesis, crystal structure and reactivity studies of two iron(II)–pybox complexes with different steric hindrance.

2. Experimental

2.1. Materials and methods

Commercially available reagents were used without further purification. 2-Amino-2,2-diphenylethanol was prepared by reduction of 2,2-diphenylglycine according to the literature procedure [38]. Column chromatographic purifications were performed using Merck silica gel 60. ¹H, and ¹³C{¹H} NMR spectra were recorded using Bruker AVIII 400 or AVIII 500 spectrometer. Chemical shifts in ¹H NMR and ¹³C{¹H} NMR were reported in parts per million

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(ppm). The residual solvent peak was used as an internal reference: ^1H NMR (CHCl_3 in chloroform-*d* δ 7.26) and $^{13}\text{C}\{^1\text{H}\}$ NMR (chloroform-*d* δ 77.0). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). Coupling constants were reported in Hertz (Hz). The NMR data of iron complexes are not available due to the paramagnetic properties of the Fe(II) complexes. Mass spectra were recorded on an Accela-LCQ Fleet mass chromatograph, using Electro Spray Ionization (ESI) mode. HRMS analysis was carried out using a LTQ-Orbitrap-MS (LTQ Orbitrap Velos, Thermo Scientific) with ESI in positive ionization mode. Elemental analysis was performed using a Flash 2000 – Thermo Scientific CHNO Analyzer. MW of PE was determined by a PL-GPC 220 type high-temperature chromatograph equipped with three Pgel 10 μm Mixed-B LS type columns.

2.2. Synthesis of ligands and iron complexes

2.2.1. Ligand L1

To a solution of 2-amino-2-methyl-1-propanol (0.979 g, 11 mmol) and triethylamine (3.03 g, 30 mmol) in chloroform (25 mL), 2,6-pyridinedicarbonyl dichloride (1.02 g, 5 mmol) solution in chloroform (10 mL) was slowly added at 0 °C with continuous stirring. The mixture was stirred for 16 h at room temperature. To the reaction mixture, thionyl chloride (3.7 mL, 50 mmol) was added, and the mixture was heated at reflux for 5 h. The solvent and excess thionyl chloride were removed *in vacuo* to give the crude dichloride compound as a colorless oil. The oil was treated with a solution of NaOH (0.8 g) in water (20 mL) and methanol (40 mL) at room temperature for 3 days. The mixture was extracted with dichloromethane (30 mL \times 3). The combined organic extracts were washed with brine and dried over MgSO_4 . The crude product was purified by column chromatography on silica gel (hexanes:ethyl acetate = 1:2 as eluent) to afford a white solid (0.69 g, 49%). ^1H NMR (500 MHz, CDCl_3): 8.19 (d, 2H, $J = 7.8$ Hz), 7.84 (t, ^1H , $J = 7.8$ Hz), 4.21 (s, 4H), 1.39 (s, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): 160.83, 146.94, 137.20, 125.68, 79.71, 67.99, 28.41.

2.2.2. Compound 1

To a solution of 2-amino-2,2-diphenylethanol (2.0 g, 9.4 mmol) and triethylamine (2.8 g, 28.2 mmol) in chloroform (30 mL), 2,6-pyridinedicarbonyl dichloride (0.96 g, 4.7 mmol) solution in chloroform (10 mL) was slowly added at 0 °C with continuous stirring. The mixture was stirred for 16 h at room temperature. Water (50 mL) was added and the reaction mixture was extracted with dichloromethane (30 mL \times 3). The combined organic extracts were washed with brine and dried over MgSO_4 . The crude product was purified by column chromatography on silica gel (hexanes:ethyl acetate = 1:1 as eluent) to afford a white solid (1.88 g, 72%). ^1H NMR (500 MHz, d^6 -DMSO): 9.08 (s, 2H), 8.20–8.17 (m, 3H), 7.42–7.40 (m, 8H), 7.31–7.29 (m, 8H), 7.27–7.22 (m, 4H), 5.36 (t, 2H, $J = 5.4$ Hz), 4.40 (d, 4H, $J = 5.4$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): 162.23, 149.41, 142.85, 139.91, 128.05, 127.27, 126.80, 124.57, 66.17, 65.99. HRMS (ESI): calcd for $\text{C}_{35}\text{H}_{32}\text{N}_3\text{O}_4$ m/z 558.23928 ($\text{M}+\text{H}^+$). Found 558.23934.

2.2.3. Ligand L2

To a solution of compound 1 (220 mg, 0.4 mmol) in chloroform (5 mL), thionyl chloride (240 μL) was added. The mixture was stirred at reflux for 2 h. Water (10 mL) was added to quench the reaction. The mixture was extracted with dichloromethane (10 mL \times 3). The combined organic extracts were washed with brine and dried over MgSO_4 . The crude product was purified by column chromatography on silica gel (hexanes:ethyl acetate = 8:1 as eluent) to afford a white solid, which is a mixture of compounds

2 and L2, that have Rf similar values. The white solid was treated with a solution of NaOH (0.2 g) in water (6 mL), methanol (12 mL) and dichloromethane (12 mL) at room temperature for 24 h. The mixture was extracted with dichloromethane (10 mL \times 3). The combined organic extracts were washed with brine and dried over MgSO_4 . The crude product was purified by column chromatography on silica gel (hexanes:ethyl acetate = 4:1 as eluent) to afford a white solid in 41% overall yield. ^1H NMR (500 MHz, CDCl_3): 8.47 (d, 2H, $J = 7.8$ Hz), 7.92 (t, ^1H , $J = 7.8$ Hz), 7.41–7.39 (m, 8H), 7.35–7.31 (m, 8H), 7.28–7.24 (m, 4H), 5.08 (s, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): 161.71, 146.95, 145.71, 137.29, 128.53, 127.30, 126.78, 126.70, 80.53, 79.85. HRMS (ESI): calcd for $\text{C}_{35}\text{H}_{28}\text{N}_3\text{O}_2$ m/z 522.21815 ($\text{M}+\text{H}^+$). Found 522.21822.

2.2.4. Iron complex 3

Under nitrogen atmosphere, to a 100 mL Schlenk flash charged with the L1 (273 mg, 1.0 mmol) and iron(II) chloride tetrahydrate (199 mg, 1.0 mmol), tetrahydrofuran (20 mL) was added. The mixture was stirred at room temperature for 4 h. The solvent was removed *in vacuo*, and the purple powder was washed with cold ether (15 mL \times 3) to provide the iron(II) pincer complex in nearly quantitative yield (390 mg). The crystal suitable for a single-crystal X-ray diffraction was obtained by diffusion of diethyl ether into a dichloromethane solution of 3. MS (ESI, MeOH): 364.04 (100%, ($\text{M}-\text{Cl}$) $^+$). Elemental analysis (%) for $\text{C}_{15}\text{H}_{19}\text{Cl}_2\text{FeN}_3\text{O}_2$: Calc. C, 45.03; H, 4.79; N, 10.50. Found: C, 44.87; H, 4.92; N, 10.22.

2.2.5. Iron complex 4

The synthetic procedure is same to that of iron complex 3. Iron complex 4 was obtained as a light purple powder. The single crystal suitable for X-ray diffraction studies was obtained by diffusion of diethyl ether into a tetrahydrofuran solution of 4. MS (ESI, MeOH): 612.13 (100%, ($\text{M}-\text{Cl}$) $^+$). Elemental analysis (%) for $\text{C}_{35}\text{H}_{27}\text{Cl}_2\text{FeN}_3\text{O}_2 \cdot 1\text{Et}_2\text{O}$: Calc. C, 64.83; H, 5.16; N, 5.82. Found: C, 64.55; H, 4.88; N, 6.11.

2.2.6. Iron complex 5

Under nitrogen atmosphere, to a 25 mL Schlenk flash charged with iron complex 3 (20 mg, 0.05 mmol) and silver triflate (30 mg, 0.12 mmol), acetonitrile (2 mL) was added. The mixture was stirred at dark for 1 h and then stirred under light for another 20 min to decompose surplus silver triflate. Filtration was carried out, and diethyl ether was added to precipitate 5 as an orange solid. The single crystal of 5 suitable for X-ray diffraction studies was grown by vapor diffusion of *n*-hexane into an acetonitrile solution of 5. MS (ESI, MeOH): 477.98 (100%, ($\text{M}-\text{OTf}-\text{CH}_3\text{CN}$) $^+$). Elemental analysis (%) for $\text{C}_{19}\text{H}_{22}\text{F}_6\text{FeN}_4\text{O}_8\text{S}_2$: Calc. C, 34.14; H, 3.32; N, 8.38. Found: C, 33.87; H, 3.50; N, 8.64.

2.2.7. Iron complex 6

Iron complex 6 was obtained by vapor diffusion of diethyl ether into acetonitrile solution of 4 under nitrogen atmosphere. MS (ESI, MeOH): 694.12 (100%, ($\text{M}-\text{FeCl}_3$) $^+$). Elemental analysis (%) for $\text{C}_{39}\text{H}_{33}\text{Cl}_4\text{Fe}_2\text{N}_5\text{O}_2$: Calc. C, 54.64; H, 3.88; N, 8.17. Found: C, 54.37; H, 4.02; N, 8.43.

2.3. General ethylene polymerization procedure

Ethylene polymerizations were performed in a 100 mL glass reactor equipped with a septum adapter and a magnetic stir bar. Iron complex (5 μmol) was added to the reactor and kept under vacuum for 30 min and then purged with N_2 . The reactor was then charged with toluene (50 mL) under N_2 and then pressurized with ethylene (18 bar) at the 50 °C with stirring. The polymerization was started by the addition of MAO ($\text{Al}/\text{Fe} = 1000$). After 1 h, the reaction was quenched by the addition of acidified methanol fol-

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