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

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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 corresponding complexes [18–23].

ABSTRACT

Iron(II) complexes, $[Fe(2,6-bis(4,4-dimethyl-1,3-oxazolin-2-yl)pyridine)Cl_2]$ ((Fe(Me₂-pybox)Cl₂), **3**) and $[Fe(2,6-bis(4,4-diphenyl-1,3-oxazolin-2-yl)pyridine)Cl_2]$ ((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, $[Fe(Me_2-pybox)(CH_3CN)OTf_2]$ (**5**) and $[Fe(Ph_2-pybox)(CH_3CN)_2CI][FeCl_3]$ (**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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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 welldefined 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





Inorganica Chimica Acta

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(ppm). The residual solvent peak was used as an internal reference: ¹H NMR (CHCl₃ in chloroform-*d* δ 7.26) and ¹³C{¹H} 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 Plgel 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 $(30 \text{ mL} \times 3)$. The combined organic extracts were washed with brine and dried over MgSO₄. 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, CDCl₃): 8.19 (d, 2H, J = 7.8 Hz), 7.84 (t, ¹H, J = 7.8 Hz), 4.21 (s, 4H), 1.39 (s, 12H). ¹³C{¹H} NMR (125 MHz, CDCl₂): 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), 2,6pyridinedicarbonyl 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 MgSO₄. 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%). 1 H NMR (500 MHz, d⁶-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). ¹³C{¹H} NMR (125 MHz, CDCl₃): 162.23, 149.41, 142.85, 139.91, 128.05, 127.27, 126.80, 124.57, 66.17, 65.99. HRMS (ESI): calcd for C₃₅H₃₂N₃O₄ m/z 558.23928 (M+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 μ L) 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 MgSO₄. 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 × 3). The combined organic extracts were washed with brine and dried over MgSO₄. 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, CDCl₃): 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). ¹³C{¹H} NMR (100 MHz, CDCl₃): 161.71, 146.95, 145.71, 137.29, 128.53, 127.30, 126.78, 126.70, 80.53, 79.85. HRMS (ESI): calcd for C₃₅H₂₈N₃O₂ *m/z* 522.21815 (M+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 cacuo*, and the purple powder was washed with cold ether (15 mL × 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%, (M–Cl)⁺). Elemental analysis (%) for C₁₅H₁₉Cl₂FeN₃O₂: 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): $612.13 (100\%, (M-Cl)^{+})$. Elemental analysis (%) for C₃₅H₂₇-Cl₂FeN₃O₂·1Et₂O: 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%, (M–OTf–CH₃CN)⁺). Elemental analysis (%) for C₁₉H₂₂F₆FeN₄O₈S₂: 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%, $(M-FeCl_3)^+$). Elemental analysis (%) for C₃₉₋ H₃₃Cl₄Fe₂N₅O₂: 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 μ mol) was added to the reactor and kept under vacuum for 30 min and then purged with N₂. The reactor was then charged with toluene (50 mL) under N₂ and then pressurized with ethylene (18 bar) at the 50 °C with stirring. The polymerization was started by the addition of MAO (Al/Fe = 1000). After 1 h, the reaction was quenched by the addition of acidified methanol fol-

lowed by precipitation in methanol. The polymer was then washed 3 times with methanol and dried in a vacuum oven to constant weight.

2.4. X-ray diffraction studies

Single-crystal X-ray diffraction data were collected with a Bruker SMART diffractometer equipped with a CCD area detector (Mo K α , λ = 0.71073 Å). The crystals were mounted on a glass fiber and coated with paratone-N oil. Data collection was carried out at 100(2) K or 223(2) K to minimize solvent loss, possible structural disorder and thermal motion effects. Structure was solved using SHELXS-86 (Patterson) and refined using SHELXL-97 (full-matrix least-squares on F2). All non-hydrogen atoms were anisotropically refined. Hydrogen atoms on carbon atoms were placed in idealized positions and refined as riding atoms, with C–H 0.93 Å and Uiso (H) = 1.2 Ueq (C). The program SHELXTL was used to prepare molecular graphics images. Data collection and structures refinement parameters are presented in Table 1.

3. Results and discussion

3.1. Ligand synthesis

L1 (Me₂-pybox) and L2 (Ph₂-pybox) were prepared according to the literature procedure with some modification (Scheme 1) [39], which allows the use of pyridine-2,6-dicarbonyl dichloride and the corresponding amino alcohol as the starting materials. Pyridine-2,6-dicarbonyl dichloride was synthesized by mixing pyridine-2,6-dicarboxylic acid in SOCl₂ at reflux. Condensation with 2-amino-2-methyl-1-propanol in the presence of Et₃N was then carried out, followed by cyclization using SOCl₂. All the crude intermediates were used without purification, and final product L1 was obtained in 49% yield after recrystallization in hexane-EtOAc as a white solid. Synthesis of L2 started with the condensation of pyridine-2,6-dicarbonyl dichloride and 2-amino-2,2-diphenylethanol using Et₂N as base to afford diamide 1 as a white solid in 72% yield. 2-Amino-2,2-diphenylethanol was readily derived from 2,2diphenylglycine by the LiAlH₄ reduction [38]. Heating diamide 1 and SOCl₂ in CHCl₃ at reflux for 2 h afforded a mixture of 2 and L2, which have similar R_f values. The mixture was treated with a

Table 1

Crystallographic data and structure refinement parameters for complexes L2, 3-6.

solution of NaOH in a mixture of solvent $(H_2O/MeOH/CH_2Cl_2)$ at room temperature for 24 h to afford the pure **L2** as a white solid in 42% overall yield.

The crystal of L2 suitable for a single-crystal X-ray diffraction was obtained by slowly evaporation of solvent of its dichloromethane solution. The molecular structure of L2 shows a twisted conformation with the N atoms of the two oxazoline rings rotating away from the central pyridine (Fig. 1). The oxazoline rings are nearly planar with a dihedral angle of 50.89° between them. The dihedral angles between the two phenyl rings are 76.73° for $Plane_{C1}/Plane_{C7}$ and 67.05° for $Plane_{C30}/Plane_{C24}$.

3.2. Iron complexes synthesis and crystallographic studies

Iron complexes **3** and **4** were prepared by stirring iron (II) chloride tetrahydrate and the corresponding pybox ligand at a ratio of 1:1 in THF at room temperature (Scheme 2). During the preparation of the Me₂-pybox complex **3**, the resultant solution turned dark blue-violet instantly. Upon removal of the solvent *in vacuo*, iron complex **3** was achieved in almost quantitative yield. In the case of the Ph₂-pybox complex **4**, a light violet solution was observed and **4** was obtained as a light purple solid in a slightly lower yield of 65%, presumably due to the larger steric hindrance of the **L2** ligand making its coordination to the iron center less favorable.

¹H NMR analysis results of the iron complexes **3** and **4** were similar to those of analogous compound in the literature [30]. Only highly shifted resonances appearing as broad singlet peaks were observed, indicating that they are paramagnetic complexes. The structures of complexes **3** and **4** were elucidated by X-ray crystallography. The crystals suitable for single-crystal X-ray diffraction were obtained by diffusion of diethyl ether into their solutions (CH₂Cl₂ in case of **3**, THF in the case of **4**). Both of these complexes exhibit distorted trigonal bipyramidal geometry (Fig. 2 and Fig. 3).

As expected, in complex **3** the **L1** ligand is coordinated in a tridentate fashion to the iron center via three N atoms, with bond distances of N–Fe being 2.240, 2.145 and 2.212 Å. The two Fe–Cl bond distances are both 2.3488 Å. Similar to the (R,R)-Et–pybox Zinc complex [40], the atoms of N(2), Cl(1), Cl(2), Fe(1) are approximately coplanar with N(1) and N(3) in the axial orientation to complete the trigonal bipyramidal coordination. The pyridine and two oxazoline rings were found to be nearly planar and the dihedral

Compound	L2	3	4	5	6
Compound Empirical formula Formula weight Crystal system Space group a (Å) b (Å) c (Å) α (°) β (°) γ (°) V (Å3) Z T (K) Density (calc.) (Mg m ⁻³) Absorption coefficient (mm ⁻¹) Crystal habit, colour	L2 $C_{35}H_{27}N_3O_2$ 521.60 Monoclinic P2(1)/C 10.8032(17) 12.1835(19) 20.626(3) 90.00 102.317(4) 90.00 2652.3(7) 4 100(2) 1.306 0.082 block, colorless 000 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	3 C ₁₅ H ₁₉ Cl ₂ FeN ₃ O ₂ 400.08 Monoclinic P2(1)/C 10.0639(11) 15.7554(19) 11.2901(13) 90.00 98.515(2) 90.00 1770.4(4) 4 100(2) 1.501 1.164 block, dark-red	4 C ₃₉ H ₃₇ Cl ₂ FeN ₃ O ₃ 722.47 Monoclinic P2(1)/C 9.0563(4) 28.3096(14) 13.8556(7) 90.00 93.2330(10) 90.00 3546.6(3) 4 223(2) 1.353 0.617 block, colorless	5 C ₁₉ H ₂₂ F ₆ FeN ₄ O ₈ S ₂ 668.38 Monoclinic Cc 15.3382(18) 9.8899(11) 17.930(2) 90.00 98.143(3) 90.00 2692.4(5) 4 223(2) 1.649 0.807 block, orange	6 C ₃₉ H ₃₃ Cl ₄ Fe ₂ N ₅ O ₂ 857.20 Monoclinic P2(1)/C 16.4907(7) 8.7045(4) 27.1368(11) 90.00 95.8110(10) 90.00 3875.3(3) 4 223(2) 1.469 1.066 rod, orange 0.02 0.01
Crystal size (mm) θ Range (°) Independent reflections R_{int} Final <i>R</i> , Rw ^a	0.60 × 0.34 × 0.30 1.93–27.50 6076 0.0303 0.0502, 0.1275	$0.38 \times 0.10 \times 0.04$ 2.05-27.50 4095 0.0496 0.0484, 0.1025	0.58 × 0.36 × 0.20 1.44-27.50 8142 0.0518 0.0578, 0.1378	$0.18 \times 0.10 \times 0.08$ 2.29–25.00 3894 0.0486 0.0599, 0.1413	$0.28 \times 0.06 \times 0.04$ 1.24–25.00 6835 0.0694 0.0617, 0.1476

^a $R = \Sigma ||F_0| - |F_c|| \Sigma ||F_0|$ for "observed" reflections having $F2 > 2\delta$ (F2). Rw = $[\Sigma w(F_0^2 - F_c^2)^2 / \Sigma w(F_0^2)^2]^{1/2}$ for all data.



Scheme 1. Synthesis of pybox ligands L1 and L2.



Fig. 1. Ellipsoid plot of L2. Thermal ellipsoids are drawn at the 30% probability level. All hydrogen atoms are omitted for clarity.



Scheme 2. Synthesis of iron complexes 3 and 4.



Scheme 3. Synthesis of iron complex 5.

angle between two oxazoline rings is 6.20°, while the dihedral angles between pyridine ring and two oxazoline rings are 4.55° and 6.51°, respectively. The **L2** ligand in complex **4** is also coordinated to the iron center in a tridentate mode, although the N–Fe bonds between the oxazoline rings and Fe are elongated compared



Scheme 4. Synthesis of iron complex 6.



Fig. 2. Ellipsoid plot of **3**. Thermal ellipsoids are drawn at the 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1-N1 2.240(2), Fe1-N2 2.145(2), Fe1-N3 2.212(2), Fe1-Cl1 2.3488(8), Fe1-Cl2 2.3488(8); N2-Fe1-N3 73.51(9), N2-Fe1-N1 73.08(8), N3-Fe1-N1 146.06(8), N2-Fe1-Cl2 139.63(7), N3-Fe1-Cl2 99.49(6), N1-Fe1-Cl2 101.96(6), N2-Fe1-Cl1 98.83(6), N3-Fe1-Cl1 98.04(6), N1-Fe1-Cl1 92.78(6), Cl2-Fe1-Cl1 121.54(3).

to those of complex **3** (2.3370 and 2.510 Å in **4** vs. 2.240 and 2.212 Å in **3**). It is noteworthy that the two N–Fe bonds distances are considerably different, 2.510 of N(3)–Fe(1) is significantly longer than the other one. This may be caused by the steric repulsions between the phenyl groups. The dihedral angles between the two oxazoline rings, pyridine ring and two oxazoline rings are 16.07°, 11.40° and 12.00° respectively, indicating that the planar structure was greatly distorted because of the phenyl substituents.



Fig. 3. Ellipsoid plot of **4**. Thermal ellipsoids are drawn at the 30% probability level. Solvent and all hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1–N1 2.3370(19), Fe1–N2 2.120(2), Fe1–Cl1 2.2560(7), Fe1–Cl2 2.2573(7); N2–Fe1–Cl1 110.81(6), N2–Fe1–Cl2 124.82(6), Cl1–Fe1–Cl2 124.11(3), N2–Fe1–N1 74.79(7), Cl1–Fe1–N1 100.51(5), Cl2–Fe1–N1 98.53(5).

3.3. Reactivity studies

Iron complex **3** is stable both as a solid and in solution under inert atmosphere. To test its reactivity, it was treated with silver triflate in acetonitrile in the absence of light. An instant color change from dark blue-violet to orange was observed. After exposure to light for 20 min, the unreacted silver reagent and AgCl were removed by filtration. Complex **5** was obtained as a light orange solid (Scheme 3). The single crystal of **5** suitable for X-ray diffraction studies was grown by vapor diffusion of diethyl ether into the acetonitrile solution of **5** (Fig. 4). The X-ray structure shows that the two chloride ligands were replaced by two triflate ligands and one acetonitrile molecule was coordinated to the iron center forming a distorted octahedral iron(II) complex. Two O and the S atoms of one of the OTf were found to be disordered at two positions with occupancy ratio of approx. 72:28. The bond lengths of



Fig. 4. Ellipsoid plot of **5**. Thermal ellipsoids are drawn at the 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Fe1–N1 2.214(6), Fe1–N2 2.143(5), Fe1–N3 2.208(6), Fe1–N4 2.168(7), Fe1–O3 2.091(4), Fe1–O6 2.181(5); O3–Fe1–N2 170.5(2), O3–Fe1–N4 87.9(2), N2–Fe1–N4 97.5(2), O3–Fe1–O6 84.3(2), N2–Fe1–O6 90.4(2), N4–Fe1–O6 172.1(2), O3–Fe1–N3 99.4(2), N2–Fe1–N3 73.1(2), N4–Fe1–N3 88.4(2), O6–Fe1–N3 94.5(2), O3–Fe1–N1 114.1(2), N2–Fe1–N1 73.6(2), N4–Fe1–N1 91.7(2), O6–Fe1–N1 90.0(2), N3–Fe1–N1 146.4(2).



Fig. 5. Ellipsoid plot of **6**. Thermal ellipsoids are drawn at the 30% probability level. $[FeCl_3]^-$ and all hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles $[\circ]$: Fe1-N1 2.288(3), Fe1-N2 2.183(3), Fe1-N3 2.406(3), Fe1-N4 2.143(4), Fe1-N5 2.249(4), Fe1-Cl1 2.2885(13); N2-Fe1-N1 72.80(13), N2-Fe1-N3 71.66(12), N2-Fe1-N4 85.80(13), N2-Fe1-N5 84.10(13), N3-Fe1-N1 144.35(12), N4-Fe1-N5 169.90(14), N1-Fe1-Cl1 105.06(10), N2-Fe1-Cl1 177.02(10), N3-Fe1-Cl1 110.56(9), N4-Fe1-Cl1 96.15(11), N5-Fe1-Cl1 93.95(11).

Fe(1)–N(1) 2.214 Å, Fe(1)–N(2) 2.143 Å, Fe(1)–N(3) 2.208 Å and the trans angle of N(3)–Fe(1)–N(1) 146.4° are similar to those in complex **3**.

In contrast to **3**, iron complex **4** decomposed in the similar reaction conditions, which may be explained by the weak coordination between more steric Ph₂-pybox ligand with the iron center. The Fe-Cl bond of iron complex 4 could be cleaved in mild conditions (Scheme 4). In the absence of silver triflate, diffusion of ether into the solution of 4 in acetonitrile afforded complex 6 (Fig. 5). It was speculated that one of the Fe-Cl bonds on complex 4 was cleaved, and the released chloride reacted with FeCl₂ to form the FeCl₃ counter anion in solution. Two molecules of acetonitrile were then coordinated to the iron center to afford a hexa-coordinated complex with an octahedral geometry. It appears that the geometrical change from trigonal bipyramid to octahedron leads to a smaller steric repulsion: the Fe(1)-N(1) and Fe(1)-N(3) bonds distances of 2.288 and 2.406 Å respectively, are now considerably shorter than those in complex **4**; and the dihedral angle between the two oxazoline rings, pyridine ring and two oxazoline become 10.09°, 3.65° and 7.25° respectively, also smaller than those in complex 4.

As iron complexes have displayed some moderate to good activities for ethylene polymerization [41–45], preliminary investigations to apply iron complex **3** and **4** as ethylene polymerization catalysts were carried out. They were both found to be effective towards ethylene polymerization in the presence of MAO (Al/ Fe = 1000) at 50 °C under 18 bar. Iron complex **4** shows a higher catalytic activity (1.01 kg/mol (Fe)·h) than **3** (0.51 kg/mol (Fe)·h) and the resultant polymer obtained from **4** possesses a higher molecular weight (8.9×10^4) than that from **3** (5.9×10^4), indicating bulky phenyl groups are beneficial to the catalytic activity and favoring the higher molecular weight. These results are comparable to those with the reported isopropyl analogue [**35**]. However, the catalytic activities are still considered low, presumably due to the alkylation of the pybox ligand in the presence of co-catalyst MAO [**46**].

4. Conclusions

We have successfully synthesized the iron (II) complexes $[Fe(Me_2-pybox)Cl_2]$ (**3**) and $[Fe(Ph_2-pybox)Cl_2]$ (**4**) by the reaction

of iron (II) chloride tetrahydrate with the corresponding pybox ligands. X-ray crystallographic analysis and reactivity studies of these pybox-Fe complexes were performed. The results indicate that the coordination abilities of pybox ligands to the iron center as well as the reactivity of the pybox-Fe complexes are dependent on the structure of the pybox ligand employed.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2014.08.050.

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