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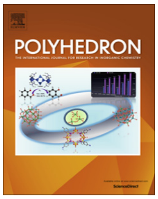

Iron(II) complexes bearing anilido-imine ligands: Synthesis and catalysis on ATRP of methyl methacrylate

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Reactions of the *ortho*-$C_6H_4(NHAr)\text{-}(CH{=}NAr)$ with ^nBuLi and subsequent addition of $FeCl_2$ afford the anilido-aldimine Fe(II) complexes $[(ArN{=}CHC_6H_4\text{-}NAr)Fe]_2(\mu\text{-}Cl)_2$ (Ar = 2,6-$Me_2C_6H_3$ (**1a**); Ar = 2,6-$Et_2C_6H_3$ (**1b**)), and $(ArN{=}CHC_6H_4\text{-}NAr)Fe(\mu\text{-}Cl)_2Li(THF)_2$ (Ar = 2,6-$^iPr_2C_6H_3$ (**1c**)). Similarly, reactions of the 2-$(ArNC(H))C_6H_4\text{-}HNC_9H_6N$ with ^nBuLi and $FeCl_2$ give the N,N,N-tridentate iron complexes $\{[2\text{-}(ArNC(H))C_6H_4\text{-}NC_9H_6N]Fe\}_2(\mu\text{-}Cl)_2$ (Ar = 2,6-$Me_2C_6H_3$ (**2a**), 2,6-$Et_2C_6H_3$ (**2b**), and 2,6-$^iPr_2C_6H_3$ (**2c**)). The X-ray diffraction analysis reveals that **1a** and **1b** are dimeric complexes and **1c** is hetero-binuclear complex. Fe(II) atoms in these complexes are all in a distorted tetrahedral geometry. Complex **2c** was confirmed to be a dimeric complex with the iron atom in a trigonal bipyramidal geometry. Complexes **1a**–**1c** show moderate activities in ATRP of MMA in the presence of benzyl chloride (BnCl). While complexes **2a**–**2c** are inert under the same condition.

1. Introduction

Atom transfer radical polymerization (ATRP), using metal-mediated halogen exchange to control the equilibrium between active and dormant polymer chains, has attracted considerable attentions and was widely used as an important methodology to construct well defined polymers in laboratory and industry [1]. Since its first discovery in 1995, ATRP has become a power tool for preparing new polymers with controlled molecular weights and well-defined microstructures. So far, many kinds of metal complexes such as copper [1c,1e,1h,2], nickel [3], ruthenium [1b,4], and other metals [5] have been tested as pre-catalyst for ATRP, in which the iron complexes have attracted more and more attention due to their low toxicity, low cost, good biocompatibility and potential application in biomaterials [6]. Generally, some ligands were added to these systems to improve the solubility of the metal species in the solution. And it is well also established that the ligands in the complexes play an important role in the catalytic performance, because a suitable ligand can lower the redox potential of the metal and improve both the activity and the controllability of the catalysts [1]. In recent years many works have focus on the investigation on iron complexes in (R)ATRP. Various ligands such as poly-dentate amines [7], phosphines [8], imines [9], carbenes [10], organic acids [11], and thiocarbamates [12] was investigated to support iron complexes, in which the poly-dentate nitrogen ligands have drawn especial attention. For example, the Fe(II) complexes bearing diimine or *N*-alkyl-2-pyridylmethanimine ligands [13] show high efficiency and good controllability in ATRP of styrene and MMA respectively. Some tetradentate N,N,N,N ligands, such as dichloro{[*N*,*N*′-diphenyl-*N*,*N*′-di(quinoline-2-methyl)]-1, 2-ethylene-diamine}, {[*N*,*N*′-dioctyl-*N*,*N*′-di(quinoline-2-methyl)]-1,2-ethylene diamine}, {[*N*,*N*′-dibenzyl-*N*,*N*′-di(quinoline-2-methyl)]-1,2-ethylene diamine}, and (1R,2R)-(-)-*N*,*N*′-di(quinoline-2-methyl) diiminocyclohexane, in combination with Fe(II), were proved to be efficient catalysts for ATRP of methyl methacrylate, in which conversions of 87–43% were obtained in 30–90 min [14].

Recently, our interest has been focused on the anilido-imine ligands and the quinolinyl anilido-imine ligands. These ligands feature easy preparation and fine-tuning of the steric and electronic properties at the metal centers and have been investigated in supporting main group complexes, transition metal complexes, and rare-earth metal complexes [15]. The anilido-imine nickel complexes show moderate activities in olefin polymerization. The quinolinyl anilido-imine rare-earth-metal complexes, aluminum and zinc complexes, and nickel complexes show high activity and good molecular weight controllability in ε-caprolactone polymerization, lactide ring-opening polymerization, and norbornene polymerization respectively [16]. In this paper, we report the synthesis and characterization of several iron(II) complexes supported by

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anilido-imine ligands and quinolinyl anilido-imine ligands. The catalytic behavior of these iron(II) complexes towards the ATRP of MMA were also presented (see Scheme 1).

2. Experimental

2.1. General procedures and methods

All manipulations involving air and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk or dry box techniques. Toluene and hexane were dried over sodium/benzophenone and distilled under nitrogen prior to use. Elemental analyses were performed on a Varian EL miFeoanalyzer. NMR spectra were recorded on a Varian Mercury-300 NMR spectrometer at room temperature in $CDCl_3$ or C_6D_6. The molecular weight and molecular weight distribution of the polymers were measured on a TOSOH HLC 8220 GPC at 40 °C using THF as eluent at a flow rate of 1.0 mL/min. Polystyrene standards were used for calibrations. The ligands were synthesized according to literature procedures [15a,16c].

2.2. Iron complexes preparation and characterization

2.2.1. Preparation of complex **1a**

Under a nitrogen atmosphere, ^{n}BuLi (2.00 M in hexane, 0.50 mL, 1.00 mmol) was added dropwise to *ortho*-C_6H_4(NH-2,6-$Me_2C_6H_3$)-(CH=N-2,6-$Me_2C_6H_3$) (0.33 g, 1.00 mmol) in 25 mL THF at −78 °C. After stirred for 1 h, the reaction mixture was warmed to −40 °C and then $FeCl_2$ (0.13 g, 1.00 mmol) was added in one portion. The reaction mixture was allowed to warm to room temperature gradually and stirred over night. Removal of volatiles in vacuum and crystallization of the residue with toluene afford complex **1a** as red powders (0.37 g, 87.8%). Single crystals for X-ray analysis were grew from THF/hexane at −30 °C within several days as red blocks. *Anal.* Calc. for $C_{46}H_{46}Cl_2N_4Fe_2$ (%): C, 65.97; H, 5.54; N, 6.69. Found: C, 65.91; H, 5.62; N, 6.72. IR(KBr): ν m (cm^{-1}) 1657m, 1600m, 1539s, 1491m, 1455vs, 1369s, 1321m, 1294w, 1172w, 1161s, 812m, 744m (see Scheme 2).

2.2.2. Preparation of complex **1b**

Following the same procedure described for **1a**, treatment of *ortho*-C_6H_4(NH-2,6-$Et_2C_6H_3$)-(CH=N-2,6-$Et_2C_6H_3$) (0.39 g, 1.00 mmol in 25 mL THF) with ^{n}BuLi (2.00 M in hexane, 0.50 mL, 1.00 mmol) and then in situ addition of $FeCl_2$ (0.13 g, 1.00 mmol) gave **1b** in an 85.9% yield (0.41 g). Red crystals for X-ray analysis were grew from the mixture of toluene and hexane at −30 °C within several days. *Anal.* Calc. for $C_{54}H_{62}Cl_2N_4Fe_2$: C, 68.29; H, 6.58; N, 5.90. Found: C, 68.42; H, 6.62; N, 5.84. IR(KBr): ν m (cm^{-1}) 1944w, 1733m, 1705m, 1656m, 1561s,1539s, 1503s, 1372m, 1147m, 819w, 414m.

2.2.3. Preparation of complex **1c**

Following the same procedure described for **1a**, treatment of *ortho*-C_6H_4(NH-2,6-$Et_2C_6H_3$)-(CH=N-2,6-$^{i}Pr_2C_6H_3$) (0.44 g, 1.00 mmol) with ^{n}BuLi (2.00 M in hexane, 0.50 mL, 1.00 mmol) and then in situ addition of $FeCl_2$ (0.13 g, 1.00 mmol) afford **1c** as red powder (0.65 g, 90.4%). Red crystals for X-ray analysis were grew from the mixture of THF and hexane at −30 °C within several days. *Anal.* Calc. for $C_{39}H_{55}Cl_2FeLiN_2O_2$: C, 65.28; H, 7.73; N, 3.90. Found: C, 64.97; H, 7.68; N, 3.98. IR(KBr): ν m (cm^{-1}) 3868w, 3743w, 3629w, 1640m, 1557s, 1457s, 1390s, 1154m, 751m.

2.2.4. Preparation of complex **2a**

Under a nitrogen atmosphere, ^{n}BuLi (2.00 M in hexane, 0.50 mL, 1.00 mmol) was added dropwise to a THF solution (25 mL) of 2-(2,6-$Me_2C_6H_3$NC(H))C_6H_4-HNC_9H_6N (0.35 g, 1.00 mmol) at −78 °C. The reaction solution was warmed to −40 °C and then the $FeCl_2$ (0.13 g, 1.00 mmol) was added. The reaction mixture was allowed to warm to room temperature gradually and stirred overnight. Removal of volatiles under reduced pressure and crystallization of the residue with toluene afford complex **2a** as red powders (0.39 g, 86.4%). *Anal.* Calc. for $C_{48}H_{40}Cl_2N_6Fe_2$ (%): C, 65.26; H, 4.56; N, 9.51. Found: C, 65.54; H, 4.62; N, 9.38. IR(KBr): ν m (cm^{-1}) 3851m, 3674m, 3626m, 1771w, 1735m, 1692s, 1647s, 1555s, 1507s, 1457m, 1423w, 1337w, 766w.

2.2.5. Preparation of complex **2b**

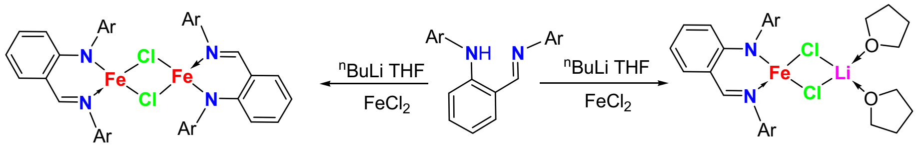
Following the same procedure described for **2a**, treatment of 2-(2,6-$Et_2C_6H_3$NC(H))C_6H_4-HNC_9H_6N (0.38 g, 1.00 mmol in 25 mL THF) with ^{n}BuLi (2.00 M in hexane, 0.50 mL, 1.00 mmol) and then in situ addition of $FeCl_2$ (0.13 g, 1.00 mmol) give **2b** in an 84.7% yield (0.40 g). *Anal.* Calc. for $C_{52}H_{48}Cl_2N_6Fe_2$: C, 66.47; H, 5.15; N, 8.94. Found: C, 66.34; H, 5.32; N, 8.85. IR(KBr): ν m (cm^{-1}) 3852w, 3628w, 3563w, 1648m, 1623s, 1508s, 1453s, 1177w, 745m.

2.2.6. Preparation of complex **2c**

Following the same procedure described for **2a**, treatment of 2-(2,6-$^{i}Pr_2C_6H_3$NC(H))C_6H_4-HNC_9H_6N (0.41 g, 1.00 mmol in 25 mL THF) with ^{n}BuLi (2.00 M in hexane, 0.50 mL, 1.00 mmol) and then in situ addition of $FeCl_2$ (0.13 g, 1.00 mmol) afford **2c** in an 89.5% yield (0.45 g). Red crystals for X-ray analysis were grew from the mixture of toluene and hexane at −30 °C within several days. *Anal.* Calc. for $C_{56}H_{56}Cl_2N_6Fe_2$: C, 67.55; H, 5.67; N, 8.44. Found: C, 67.75; H, 5.84; N, 8.25. IR(KBr): ν m (cm^{-1}) 3854m, 3738m, 3625m, 1730m, 1643s, 1563s, 1515s, 1452m, 744w, 666w.

2.3. Polymerizations

A glass tube was loaded with the catalyst and then corresponding equivalent of MMA, initiator and toluene were added in sequence. The tube was sealed under argon and placed in an oil bath thermostated at the desired temperature. After desired period of time the reaction mixture was poured into 50 mL of ethanol. The polymer was isolated by filtration, washed with ethanol and dried under vacuum at 40 °C for 12 h.



1a, Ar = 2,6-$Me_2C_6H_3$;
1b, Ar = 2,6-$Et_2C_6H_3$

1c, Ar = 2,6-$^{i}Pr_2C_6H_3$

Scheme 1. Synthesis of anilido-imino Fe(II) complexes.