APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2004; **18**: 277–281
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.634

Preparation, characterization and catalytic oxidation properties of tris[2-(2-pyridyl)benzimidazole]iron(II) complexes

Mei Wang*, Hongfei Sun, Yu Wang, Xiuna Wang, Fei Li and Licheng Sun**

State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, P.R. China

Received 22 January 2004; Accepted 1 February 2004

Complexes $[Fe(Hpbi)_3](ClO_4)_2$ (1) and $[Fe(Hpbi)_3](SbF_6)_2$ (2) (Hpbi = 2-(2-pyridyl)benzimidazole) were prepared by a modified method and characterized by IR, ^1H and ^{13}C NMR, mass spectrometry, electron paramagnetic resonance spectra and elemental analysis. The catalytic activities of 1 and 2 were evaluated for the oxidation of cyclohexene, cyclohexane, ethylbenzene and adamantane with *tert*-butylhydroperoxide or H_2O_2 as oxidant, and the results were compared with the properties of their analogue $[Fe(bpy)_3](SbF_6)_2$ (3). Complexes 1 and 2 both afforded the ketonization product for the oxidation of ethylbenzene and the hydroxylation product for adamantane. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: iron complexes; biomimetic oxidation; pyridylbenzimidazole ligand; hydroxylation; ketonization

INTRODUCTION

Iron complexes are widely known in nature and essential to many biological redox catalysts as active sites of diverse enzymes. In recent years, the study of iron complexes with multidentate nitrogen ligands has gained greater momentum, partially due to their ability to catalyze or promote oxidation of alkanes and alkenes under ambient conditions so as to mimic the admirable functions of some nonheme metalloenzymes.[1–7] The iron complexes with ligands featuring an imidazole moiety have attracted much attention because of the biological significance of imidazole and its derivatives as essential components of various metalloenzymes.[8–17] Although the synthesis and the structures of ionic iron(II) complexes $[L_3Fe]X_2$ with imidazole derivatives 2-(2-pyridyl)imidazole (L^1 = Hpi) and 2-(2-pyridyl)benzimidazole (L^2 = Hpbi) have been reported (Fig. 1),[18,19] the investigations of these iron(II) complexes have been focused on spin-crossover, magnetic properties and Mössbauer spectra,[18,20–26] and the catalytic oxidation properties of the complexes remain to be studied yet. We are currently engaged in the synthesis of iron(II) complexes having an Hpbi ligand and sequentially exploring the catalytic performances of the complexes in the oxidation of methylenic carbon atoms. Here, we describe the spectroscopic properties of ionic iron(II) complexes $[Fe(Hpbi)_3](ClO_4)_2$ (**1**), $[Fe(Hpbi)_3](SbF_6)_2$ (**2**) and $[Fe(bpy)_3](SbF_6)_2$ (**3**) and their catalytic activities with either TBHP or H_2O_2 as oxidant for mild oxidation of cyclohexane, cyclohexene, ethylbenzene and adamantane.

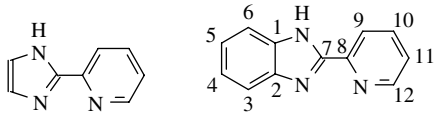
*Correspondence to: Mei Wang, State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, People's Republic of China.
E-mail: symbueno@vip.sina.com
**Correspondence to: Licheng Sun, State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian 116012, People's Republic of China.
E-mail: symbueno@vip.sina.com
Contract/grant sponsor: Ministry of Science and Technology of China.
Contract/grant sponsor: Chinese National Natural Science Foundation; Contract/grant numbers: 20128005; 20173006.

EXPERIMENTAL

Materials and instruments

All reactions and operations related to organometallic complexes were carried out under a dry, oxygen-free dinitrogen atmosphere with standard Schlenk techniques. Solvents were distilled prior to use with routine drying agents. The Hpbi ligand was prepared by the literature procedure.[20] Other commercially available chemical reagents were used as received. **Caution:** perchlorate salts are potentially explosive and should be handled with care!

IR spectra were recorded from KBr pellets on a JASCO FT/IR 430 spectrophotometer. ^1H and ^{13}C NMR spectra



L^1 = Hpi L^2 = Hpbi

Figure 1. Structures of ligands Hpi and Hpbi.

were collected on a Varian INOVA 400NMR spectrometer. Mass spectra of iron complexes **1** and **2** were recorded on an HP1100 MSD instrument. Elemental analyses were performed on a Carlo Erba MOD-1106 elemental analyzer. Electron paramagnetic resonance (EPR) spectra were obtained using a JES-FE1XG EPR spectrometer and 2,2-diphenyl-1-picrylhydrazyl was used as standard. Gas chromatography (GC) analyses were performed on a Hewlett-Packard instrument equipped with a flame ionization detector and an HP-5 column (30 m × 0.32 mm) and GC–mass spectrometry (MS) analyses were carried out on an HP6890GC/5973MS apparatus.

Preparation of complexes 1–3

Complexes **1** and **2** were prepared by a modified procedure.[20] Upon addition of Hpbi (0.59 g, 3.0 mmol) in CH_3CN/toluene (v/v, 10/2) to the CH_3CN (10 ml) solution of $FeCl_2{\cdot}H_2O$ (0.15 g, 1.0 mmol), a large amount of deep-purple precipitant appeared. After removal of all solvent, the residue was suspended in CH_3CN (30 ml). Two equivalents of silver salt ($AgClO_4$ or $AgSbF_6$) was added to the vigorously stirred suspension sheltered with aluminum foil. The red–purple solution was filtered through a 0.5 μm filter paper. The solvent was removed *in vacuo* and the re-dissolved solution of the residue was subject to the filtration/concentration procedure twice more. The red–purple product **1** was dried *in vacuo* and recrystallized in CH_3CN–$(CH_3)_2CO$–Et_2O. Yield: 360 mg (42%). IR (KBr): ν 3100-2500 (br, N–H), 1605 (m, C═N) cm^{-1}. ^1H NMR (Me_2SO-d_6): δ 12.60 (br, 3H, N*H*), 8.71, 8.34, 7.99, 7.50 (4s, each for 3H, C*H* of Py), 7.62, 7.22 (2s, each for 6H, C*H* of Ph). ^{13}C NMR (DMSO-d_6, the carbon atoms are numbered as in fig. 1 for L^2): δ 149.16 (C7), 147.96 (C12), 146.71 (C8), 137.57 (C1), 136.12 (C10), 126.34 (C2), 123.41 (C11), 121.30 (C4 and C5), 120.16 (C9), 116.27 (C6), 114.25 (C3). MS (API-ES): $m/z = 320.7\ M^{2+}$, 640.1 $[M^{2+} - H^+]^+$. Anal. Found: C, 51.29, H, 3.43, N, 14.61. Calc. for $C_{36}H_{27}Cl_2FeN_9O_8{\cdot}H_2O$: C, 50.37, H, 3.40, N, 14.68%.

Complex **2** was prepared by a similar procedure. Yield: 668 mg (59%). ^1H NMR (Me_2SO-d_6): δ 52.90, 47.57, 27.85, 11.27 (4s, br, each for 3H, C*H* of Py), 7.65 (br, 3H, N*H*), 5.89, 5.20 (2s, br, each for 6H, C*H* of Ph). The IR and MS spectra of **2** are quite similar with those of **1**. Anal. Found: C, 37.97, H, 2.60, N, 11.08. Calc. for $C_{36}H_{27}N_9F_{12}Sb_2Fe{\cdot}H_2O$: C, 38.16, H, 2.58, N, 11.13%.

Preparation of **3** was carried out in the same manner as in the literature.[27] ^1H NMR (Me_2SO-d_6): δ 8.86 and 7.58 (2d, each for 3H, C*H* of Py), 8.23 and 7.54 (2t, each for 3H, C*H* of Py). MS (API-ES): $m/z = 262.1\ M^{2+}$.

General procedure for hydrocarbon oxidation by iron(II)-based catalysts (1–3)

An acetonitrile solution (1 ml) of cyclohexane, cyclohexene, ethylbenzene or adamantane (1.0 mmol) and the precatalyst (**1**, **2** or **3**, 5 mol%, 0.05 mmol) was cooled to 0 °C. One or two equivalents of pre-cooled (0 °C) *tert*-butylhydroperoxide (TBHP; 65 wt% in H_2O) or H_2O_2 (30 wt% in H_2O) was added dropwise in 2 min with rapid stirring under a dinitrogen atmosphere. After 2 h, conversion and selectivity were determined by GC analysis of the resulting solution using 1,2-dichlorobenzene as internal standard. The organic products were identified by GC–MS analysis.

RESULTS AND DISCUSSION

Synthesis and characterization of 1–3

Complexes **1**–**3** were characterized by IR, ^1H and ^{13}C NMR, MS, EPR and elemental analysis. In the API-ES positive mode mass spectra, the ionic iron(II) complexes $[Fe(Hpbi)_3]^{2+}$ exhibit the parent ion peak at $m/z = 320.7$ and the peak for the species $[Fe(Hpbi)_2(pbi)]^+$ at $m/z = 640.1$, which is formed by deprotonation of one of the NH groups in the Hpbi ligands of complex **1** or **2**. Complexes **1** and **2** each display a sawtoothed broad band in the region 2500–3100 cm^{-1}, assigned to the N–H stretching frequency, and a characteristic band of ν(C═N) at 1605 cm^{-1} for ligand Hpbi. The ^1H NMR spectra of complexes **1** and **2** each exhibit four singlets for the protons of pyridyl groups and two singlets for those of the phenylene groups, suggesting a symmetric nature of the three Hpbi ligands in the coordination sphere of the iron(II) center. The signals of the carbon atoms of the imidazole and pyridine rings in the ^{13}C NMR spectrum of **1** are more or less shifted upfield relative to the corresponding signals of the free ligand.

There is a noticeable difference in the ^1H NMR spectra between complex **2** and complexes **1** and **3**. The ^1H NMR spectrum of **2** in Me_2SO-d_6 is paramagnetic, as is apparent from the broad ^1H NMR resonances of Hpbi ligands appearing in the wide region of 5–53 ppm. The protons of the pyridyl rings of the Hpbi ligands are found at 11–53 ppm in the ^1H NMR spectrum of **2** and those of the phenylene rings are at 5–6 ppm, shifting to high field. The broad single signal at 7.65 ppm is tentatively assigned to the protons of the NH groups of the ligands. In contrast, complexes **1** and **3** exhibit normal ^1H NMR spectra in the region δ 7–13 ppm, with the chemical shifts of all signals very similar to those of the corresponding signals in the free ligand. Six strong and sharp signals along with multiple weak signals of hyperfine splitting were observed in the EPR spectrum of complex **2**, and these are typical for high-spin antimony(V) ($I = 5/2$ for ^{121}Sb and 7/2 for ^{123}Sb; Fig. 2). Interestingly, both complexes **1** and **3** (the former with the same cation $[Fe(Hpbi)_3]^{2+}$ and the

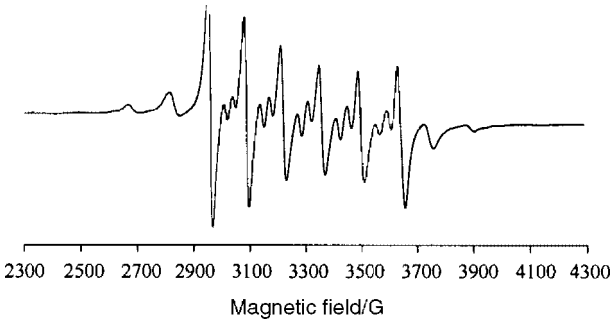


Figure 2. EPR spectra of **2** in the solid state at 20 °C. Receiver power, 5.0 mW; frequency, 9.443 GHz; modulation frequency, 100 kHz; modulation amplitude, 2.0 G.

latter with the same counter anion $[SbF_6]^-$ as **2**) are EPR silent in the solid state at 20 °C.[22] The strong signals of high-spin antimony(V) might submerge the EPR signal arising from the iron(II) center of complex **2**. The ^1H NMR and EPR spectra of **1**–**3** show that the magnetic properties of a series of cationic complexes vary not only with different counter anions, but also with the interaction of the ligand and the counter anion, either by a mediating metal center or through space. It is assumed that the changes in the ligand sphere symmetry and the ligand field strength result in the distinct magnetic properties of the analogous complexes **2**.

Catalytic oxidation of cyclohexane, cyclohexene, ethylbenzene and adamantane by complexes 1–3

The salts of the iron(II) complexes **1** and **2** with $[ClO_4]^-$ or $[SbF_6]^-$ counter anion were used as precatalysts in the present research, and the results were compared with that of the bipyridine iron(II) complex, $[Fe(bpy)_3](SbF_6)_2$ (**3**). The catalytic activities of complexes **1** and **2** for oxidation of cyclohexane, cyclohexene, ethylbenzene and adamantane were explored under mild conditions with 20-fold excess of the substrate. The preliminary results are summarized in Tables 1 and 2, together with the results with the analogous iron(II) complex **3** for comparison. The results for entries 1 and 2 show that TBHP is a better oxidant than H_2O_2 for the model catalysts. Thus, TBHP was used for the rest of the reactions.

Dihydroxylation and epoxidation products were not detected by GC–MS from the resulting solution of cyclohexene oxidation by **1** and **2** with TBHP as oxidant. A large amount of 2-cyclohexenone and a minor amount of 2-cyclohexenol were formed (entries 2 and 3). The alcohol/ketone (A/K) value is 0.18 for **1** and 0.22 for **2**. In comparison, the ratio of 2-cyclohexenol to 2-cyclohexenone (A/K) is 0.76 for catalyst **3** under identical conditions (entry 4). Similarly, the oxidation of cyclohexane gave cyclohexanol and cyclohexanone as detectable products in an A/K ratio of 0.54–0.58 (entries 5 and 6). When ethylbenzene was used as a substrate, acetophenone was detected as the only product. No hydroxylation product was found even in the initial period of the oxidation reaction of ethylbenzene by complex **1**, **2** or **3** with one equivalent of TBHP at 0 °C (entries 8–10). In contrast, the oxidation of adamantane yielded only hydroxylation products. The ratio of tertiary adamantanol to

Table 2. The results of oxidation of adamantane by complexes **1**–**3**[a]

Entry	Catalyst	TN (2°ol[b])	TN (3°ol[b])	3°/2°[c]	Conversion (%)
1	**1**	5.3	16.4	9.3	81
2	**2**	4.9	18.0	11.0	86
3	**3**	4.6	15.7	10.2	76

[a] Oxidant TBHP, two equivalents. The other reaction conditions are the same as those in Table 1.
[b] 2°ol = 2-adamantanol, 3°ol = 1-adamantanol.
[c] 3°/2° = 3°ol/2°ol multiplied by 3.

Table 1. The results of oxidation of cyclohexene, cyclohexane and ethylbenzene catalyzed by complexes **1**–**3**[a]

Entry	Catalyst	Substrate/equiv. (oxidant)	TN (-ol[b])	TN (-one[b])	A/K	Conversion (%)
1	**2**	Cyclohexene/2 (H_2O_2)	1.5	4.8	0.31	31
2	**2**	Cyclohexene/2 (TBHP)	2.3	10.4	0.22	64
3	**1**	Cyclohexene/2 (TBHP)	1.9	10.7	0.18	63
4	**3**	Cyclohexene/2 (TBHP)	4.4	5.8	0.76	51
5	**2**	Cyclohexane/2 (TBHP)	2.1	3.9	0.54	30
6	**1**	Cyclohexane/2 (TBHP)	1.8	3.1	0.58	25
7	**3**	Cyclohexane/2 (TBHP)	1.9	2.7	0.70	23
8	**2**	Ethylbenzene/1 (TBHP)	—	20.0		>99
9	**1**	Ethylbenzene/1 (TBHP)	—	20.0		>99
10	**3**	Ethylbenzene/1 (TBHP)	—	19.9		>99

[a] Reaction conditions: catalyst 0.05 mmol (5 mol%); reaction temperature 0–5 °C (2 h); solvent CH_3CN 1 mL.
[b] -ol: cyclohexenol for entries 1–4 and cyclohexanol for entries 5–7. -one: cyclohexenone for entries 1–4 and cyclohexanone for entries 5–7. TN: moles of product per mole of catalyst, determined by GC and GC–MS analysis with *o*-dichlorobenzene as an internal standard.

secondary adamantanol multiplied by three (to correct for the threefold higher number of 2° C–H bonds in adamantane) is around 9–11 for catalysts **1**–**3** (Table 2), which is in line with the typical value for the oxidation reaction of adamantane initiated by *tert*-butoxy radical.[1] The distinct ketonization and hydroxylation selectivities for the oxidation of ethylbenzene and adamantane suggest that the oxidation reactions might proceed via different mechanisms. The allylic carbon atoms in linear alkenes, either terminal or internal, cannot be oxidized by complexes **1** and **2** even with four equivalents of TBHP or H_2O_2. Iron(II) complexes containing Hpbi ligand act as an effective model for the selective oxidation of hydrocarbons at the reactive secondary and tertiary carbon atoms, being analogous to oxygenated Fenton chemistry.[28]

The oxidation rates of the three substrates in Table 1 catalyzed by complex **2** were monitored by GC analysis (Figure 3). Ethylbenzene was completely converted to acetophenone in 20 min with two equivalents of TBHP, whereas a moderate conversion for cyclohexene (64%) and a low conversion for cyclohexane (30%) were observed after 2 h.

The conversions of the substrates catalyzed by $[(Hpbi)_3Fe][SbF_6]_2$ (**2**) are higher than those from the corresponding reactions by $[(bpy)_3Fe][SbF_6]_2$ (**3**) (entries 2, 5 versus 4, 7). Complexes **1** and **2**, bearing the different counter anions $[ClO_4]^-$ and $[SbF_6]^-$, exhibited comparable catalytic activities for oxidation of cyclohexene and ethylbenzene, whereas for the less reactive cyclic hydrocarbons, like cyclohexane and adamantane, the conversions by **2** were higher than those by complex **1** (entry 5 versus 6 in Table 1 and entry 2 versus 1 in Table 2). The positive effect of $[SbF_6]^-$ is identical with the reported methane monooxygenase mimic catalysts $[(mep)FeCH_3CN]_2]X_2$ (mep = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-pyridylmethyl)ethane-1,2-diamine, X = ClO_4, SbF_6) for alkene epoxidation.[2]

In conclusion, the different EPR properties of the analogous complexes **1**–**3** might be induced by counter anions, as observed for **1** and **2**, and by the replacement of one of the pyridyl groups in the bipyridine ligand with a benzimidazolyl group, as seen for **2** and **3**. Complexes **1** and **2** act as effective catalysts in oxygenated Fenton chemistry to oxidize the reactive methylenic and methinic centers of hydrocarbons selectively in the presence of TBHP or H_2O_2 under mild conditions. Both complexes displayed high activities for ketonization of ethylbenzene and a moderate activity for hydroxylation of adamantane. The oxidation of cyclohexene mainly afforded ketonization product with a considerable activity, and both ketonization and hydroxylation products were formed in comparable amounts with a low activity for the oxidation of cyclohexane.

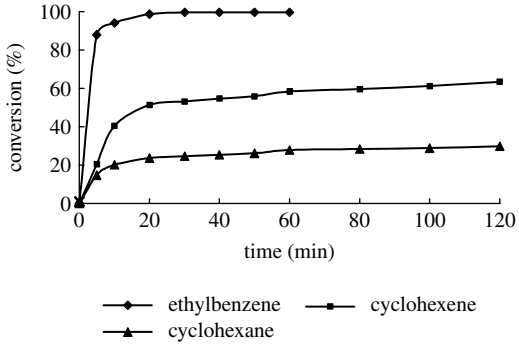


Figure 3. Conversion versus time plots of the oxidation with ethylbenzene, cyclohexene and cyclohexane. Oxidant, two equivalents of TBHP. Other conditions are the same as those in Table 1.

Acknowledgements

We gratefully acknowledge the Ministry of Science and Technology of China and the Chinese National Natural Science Foundation (grant nos 20128005 and 20173006) for financial support.

REFERENCES

1. Costas M, Chen K, Que Jr L. *Coord. Chem. Rev.* 2000; **200–202**: 517 and references cited therein.
2. White MC, Doyle AG, Jacobsen EN. *J. Am. Chem. Soc.* 2001; **123**: 7194.
3. Costas M, Tipton AK, Chen K, Jo D, Que Jr L. *J. Am. Chem. Soc.* 2001; **123**: 6722.
4. Wang Z, Martell AE, Motekaitis RJ, Reibenspies JH. *Inorg. Chim. Acta* 2000; **300–302**: 378.
5. Kodera M, Taniike Y, Itoh M, Tanahashi Y, Shimakoshi H, Kano K, Hirota S, Iijima S, Ohba M, Okawa H. *Inorg. Chem.* 2001; **40**: 4821.
6. Wada A, Ogo S, Nagatomo S, Kitagawa T, Watanabe Y, Jitsukawa K, Masuda H. *Inorg. Chem.* 2002; **41**: 616.
7. Fazio O, Gnida M, Meyer-Klaucke W, Frank W, Kläui W. *Eur. J. Inorg. Chem.* 2002; 2891.
8. Brennan BA, Chen Q, Juarez-Garcia C, True AE, O'Connor CJ, Que Jr L. *Inorg. Chem.* 1991; **30**: 1937.
9. Buchanan RM, O'Brien RJ, Richardson JF, Latour J. *Inorg. Chim. Acta* 1993; **214**: 33.
10. Buchanan RM, Chen S, Richardson JF, Bressan M, Forti L, Morvillo A, Fish RH. *Inorg. Chem.* 1994; **33**: 3208.
11. Wang S, Luo Q, Wang X, Wang L, Yu K. *J. Chem. Soc. Dalton Trans.* 1995; 2045.
12. Wang J, Mashuta MS, Sun Z, Richardson JF, Hendrickson DN, Buchanan RM. *Inorg. Chem.* 1996; **35**: 6642.
13. Brewer CT, Brewer G, Shang M, Scheidt WR, Muller I. *Inorg. Chim. Acta* 1998; **278**: 197.
14. Kwak B, Cho KW, Pyo M, Lah MS. *Inorg. Chim. Acta* 1999; **290**: 21.
15. Pascaly M, Duda M, Schweppe F, Zurlinden K, Müller FK, Krebs B. *J. Chem. Soc. Dalton Trans.* 2001; 828.
16. Moon D, Lah MS, Del Sesto RE, Miller JS. *Inorg. Chem.* 2002; **41**: 4708.
17. Benisvy L, Blake AJ, Collison D, Davies ES, Garner CD, McInnes EJL, McMaster J, Whittaker G, Wilson C. *J. Chem. Soc. Dalton Trans.* 2003; 1975.
18. Sams JR, Tsin TB. *J. Chem. Soc. Dalton Trans.* 1976; 488.
19. Peng SM, Hua HF. *Bull. Inst. Chem. Acad. Sin.* 1990; **37**: 49.
20. Baker AT, Goodwin HA. *Aust. J. Chem.* 1977; **30**: 771.
21. Martin RL, Roos IAG, Goodgame DML, Machado AASC. *Aust. J. Chem.* 1978; **31**: 487.
22. Reeder KA, Dose EV, Wilson LJ. *Inorg. Chem.* 1978; **17**: 1071.

23. Boča R, Baran P, Dlháň L, Šima J, Wiesinger G, Renz F, El-Ayaan U, Linert W. *Polyhedron* 1997; **16**: 47.
24. Boca R, Vrbova M, Werner R, Haase W. *Chem. Phys. Lett.* 2000; **328**: 188.
25. Enamullah M, Uddin MN, Hossain D, Kabir M, Awwal A, Linert W. *J. Coord. Chem.* 2000; **49**: 171.
26. Charbonnière LJ, Williams AF, Piguet C, Bernardinelli G, Rivara-Minten E. *Chem. Eur. J.* 1998; **4**: 485.
27. Posse MEG, Juri MA, Aymonino PJ, Piro OE, Negri HA, Castellano EE. *Inorg. Chem.* 1984; **23**: 948.
28. Sawyer DT. *Coord. Chem. Rev.* 1997; **165**: 297.