



Synthesis, characterization and catalytic activity of Fe(III) complexes containing Schiff base and triphenylphosphine ligands

Sandya Rani, Badekai Ramachandra Bhat*

Catalysis and Materials Chemistry Division, Department of Chemistry, National Institute of Technology Karnataka, Surathkal, Srinivasanagar-575025, India

ARTICLE INFO

Article history:

Received 6 May 2010

Accepted 14 July 2010

Available online 21 July 2010

Keywords:

Fe(III) complexes

Schiff base

Triphenylphosphine

Oxidation of alcohol

ABSTRACT

The oxidation of alcohols to carbonyls was investigated by an efficient catalyst system comprising of Fe(III)–Schiff base–triphenylphosphine complex. The complex chloroN-(2-mercaptophenyl)salicylideneiminebis (triphenylphosphine)iron(III) showed higher activity for oxidation of various alcohols under relatively mild conditions.

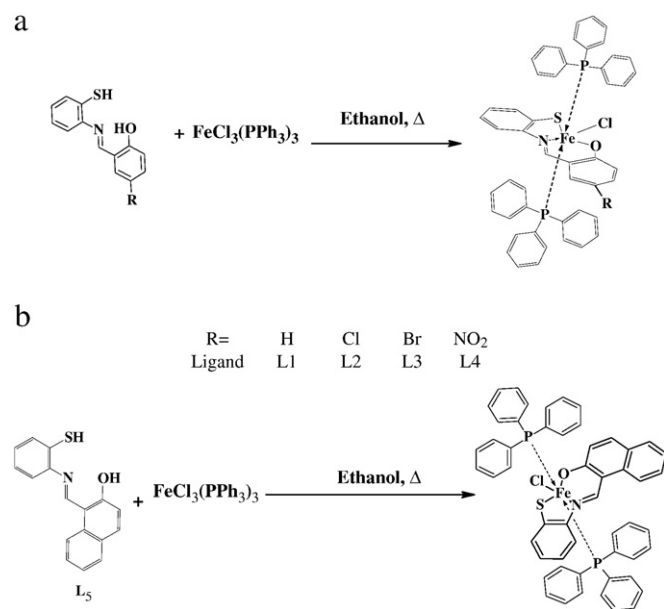
© 2010 Elsevier B.V. All rights reserved.

Optimization of catalytic activities for a given process is typically achieved through the methodical tailoring of the metal–ligand environment. Therefore, ligand frameworks such as the Schiff base that can be sterically and electronically modified with ease are very attractive [1,2]. The use of the Schiff base ligand framework in catalytic reactions has been receiving increasing interest due to the aforementioned advantage and its successes in many newly discovered processes. Most notable is the oxidation of alcohols to carbonyls which is a very important reaction in organic synthesis that involves the use of predominantly Chromium based complexes. Indeed, there are numerous reports where these catalysts have been employed as part of a long synthetic strategy [3,4]. Recently, extensive research efforts have been invested in the development of catalysts based on the Schiff base transition metal complexes of Ru [5–7], Co [8,9], Cu [10], Ni [11] for the oxidation of alcohols to carbonyls.

Among them, less explored iron based Schiff base complexes possess many advantages over traditional catalyst due to iron's copious, non-toxic, and inexpensive nature [12]. In this context, we present the synthesis of a series of novel Schiff base transition metal complexes of iron and their use as potential catalysts for the oxidation of allylic and benzylic alcohols under mild conditions using H_5IO_6 as oxidant.

The starting metal precursor $[FeCl_3(PPh_3)_3]$ was synthesized by reaction between anhydrous $FeCl_3$ and triphenylphosphine in glacial acetic acid [13]. The Schiff base ligands were prepared by the

condensation between salicylaldehyde, its derivatives or 2-hydroxy-1-naphthaldehyde and 2-mercaptoaniline in ethanol [14,15]. Complexes (FeL_1 – FeL_4) containing N-(2-mercaptophenyl)salicylideneimine, and its derivatives were synthesized by stirring the solution of ligands (0.2 mmol) and $[FeCl_3(PPh_3)_3]$ (0.2 mmol) in ethanol (20 ml) for 4 h at room temperature (Scheme 1a). Complex FeL_5 was synthesized in a



Scheme 1. a: Synthesis of FeL_1 – FeL_4 complexes. b: Synthesis of FeL_5 complexes.

* Corresponding author. Tel.: +91 824 2474000x3204; fax: +91 824 2474033.
E-mail address: chandpoorna@yahoo.com (B. Ramachandra Bhat).

Table 1
Analytical and electronic spectral data of Fe(III) complexes.

Complex	Decom. temp (°C)	% Found (theoretical)				UV-vis data, λ_{\max} (nm)	
		C	H	S	N	Intraligand transitions	Charge transfer
FeL ₁	225	69.69(69.80)	4.60(4.66)	3.69(3.80)	1.60(1.66)	248, 294	381
FeL ₂	244	63.61(63.83)	4.12(4.15)	3.39(3.48)	1.49(1.52)	247, 288	388
FeL ₃	240	67.00(67.06)	4.29(4.36)	3.59(3.65)	1.55(1.60)	248, 294	390
FeL ₄	270	66.20(66.26)	4.26(4.31)	3.10(3.15)	3.59(3.61)	246, 288	394
FeL ₅	255	68.67(68.78)	4.72(4.73)	3.60(3.67)	1.58(1.60)	248, 288	419

similar manner using N-(2-mercaptophenyl)naphthylideneimine and [FeCl₃(PPh₃)₃] (Scheme 1b) [16]. The brownish-red colored complexes were washed with diethyl ether and dried in *vacuo*. They were found to be soluble in CH₂Cl₂, CH₃CN, C₆H₆, DMSO and DMF.

The electronic spectra of the ligands and complexes were recorded in acetonitrile. The electronic spectra of the all the complexes showed three bands in the region 240–420 nm (Table 1). The bands appearing in the region 245–295 nm have been assigned to intra ligand transitions [17]. A band in the range of 380–420 nm corresponds to ligand to metal charge transfer transition [18]. A high spin six coordinated Fe(III) complex does not show d–d transitions and hence absorption bands were not observed [19]. Selected IR bands of the ligands and complexes are listed in Table 2. The IR spectra of the ligands exhibit a strong band around 1608–1644 cm⁻¹, which is assigned to ν (CN) vibration. As a result of coordination, this band is red-shifted in the complexes. The band in the region 1265–1315 cm⁻¹ which is assigned to phenolic ν (C–O) in the free ligand, is shifted to a higher wave number in the complexes suggesting the coordination of phenolic oxygen to metal ion [20,21]. A weak band observed in the region 742–765 cm⁻¹, corresponding to ν (C–S) in the ligands, shifts to a lower wave number (721–724 cm⁻¹) which supports sulfur coordination with the iron [22,23]. The bands

around 535 cm⁻¹ and 415–434 cm⁻¹ in the complex is assigned to ν (M–O) and ν (M–N) respectively [24,25]. Three bands due to triphenylphosphine were observed around 1438–1464, 1069–1082 and 688–691 cm⁻¹ as expected [9]. Magnetic susceptibility measurements of all Fe(III) complexes show magnetic moments in the range of 5.80–6.05 B.M, confirming the high spin octahedral structure [26–28]. Thermal behavior of the complexes was determined in nitrogen atmosphere (20 ml min⁻¹) with a heating rate of 10 °C min⁻¹ in the temperature range of 30–400 °C. The thermograms of Fe(III) complexes did not show any decomposition up to 300 °C indicating the absence of coordinated water molecules. The ESR spectrum of the complex shows the broad line with no hyperfine structure [29] supporting the proposed structure. For further confirmation of the structure, efforts are on to get a better single crystal for X-ray analysis.

The oxidation of primary and secondary alcohols catalyzed by the synthesized complexes occurs readily to form the corresponding aldehydes and ketones as major products. The oxidation of benzyl alcohol was studied in more detail to optimize the reaction variables such as solvent, alcohol/oxidant, alcohol/catalyst molar ratio and length of reaction time. We checked first the activity of FeL₁ in different solvents (methanol, acetonitrile, acetone etc.) with periodic acid as the oxidant. The best conversions were observed in acetonitrile. The optimizations of other reaction conditions were studied by taking benzyl alcohol as a substrate with FeL₁ in acetonitrile–H₅IO₆ system (Table 3). The benzaldehyde formed was quantified by GC [30]. In order to study the effect of time on the activity, the product analysis was done at regular intervals of time under similar reaction conditions (Fig. 1). A total reaction time of 90 min at 70 °C gave a constant conversion of 86%. This shows that FeL₁ in acetonitrile–H₅IO₆ system exhibits good efficiency. The catalytic activities of FeL₁–FeL₅ in acetonitrile–H₅IO₆ were carried

Table 2
Infrared spectral data (cm⁻¹) for ligands and its Fe(III) complexes.

Compound	ν (C=N)	ν (C=O)	ν (C-S)	ν (Fe-O)	ν (Fe-N)	Bands due to PPh ₃
L ₁	1608	1270	742	–	–	–
L ₂	1621	1265	754	–	–	–
L ₃	1624	1270	765	–	–	–
L ₄	1644	1277	744	–	–	–
L ₅	1610	1315	746	–	–	–
FeL ₁	1591	1320	724	535	415	1438, 1073, 688
FeL ₂	1597	1318	723	533	427	1440, 1080, 690
FeL ₃	1586	1316	723	537	426	1464, 1082, 690
FeL ₄	1600	1327	724	535	431	1436, 1077, 690
FeL ₅	1593	1322	721	535	434	1437, 1069, 691

Table 3
Optimization of reaction conditions for oxidizing benzyl alcohol to benzaldehyde.

Entry	Amount of FeL ₁ (mmol)	Amount of oxidant (mmol)	Yield (%)
			CH ₃ CN–H ₅ IO ₆ system
1	0	1.0	2.0
2	0.01	1.0	63.0
3	0.02	1.0	69.5
4	0.03	1.0	79.4
5	0.04	1.0	87.3
6	0.05	1.0	87.1
7	0.04	0	3.7
8	0.04	0.25	36.8
9	0.04	0.50	77.6
10	0.04	0.75	86.8

1 mmol benzyl alcohol, 10 ml CH₃CN, 90 min, 70 °C.

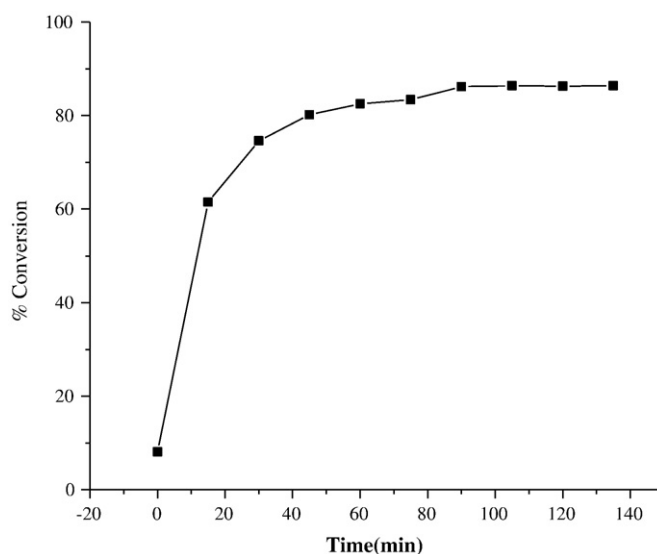
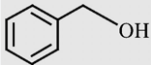
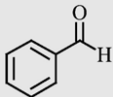
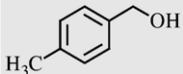
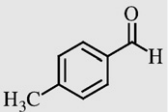
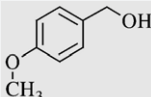
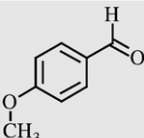
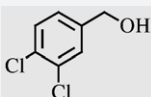
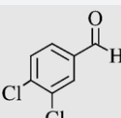
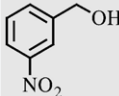
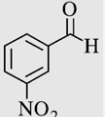
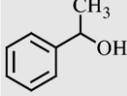
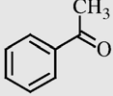
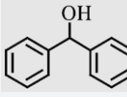
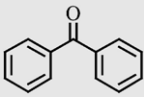
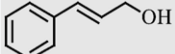
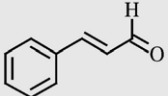


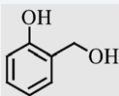
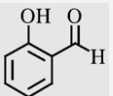
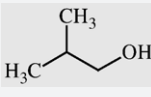
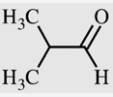
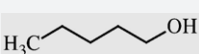
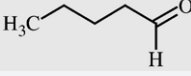
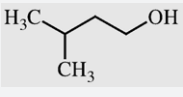
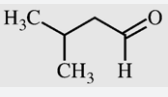

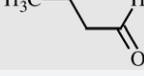
**Fig. 1.** Effect of time on conversion of benzyl alcohol to benzaldehyde.

Table 4
Oxidation of alcohols catalyzed by Fe(III) complexes^a in CH₃CN–H₅IO₆ system^a.

Alcohols	Product	% Yield of carbonyl compound ^b				
		FeL ₁	FeL ₂	FeL ₃	FeL ₄	FeL ₅
		86.1	82.3	83.7	80.8	79.1
		79.5	77.5	78.2	78.6	74.4
		77.5	77.1	74.8	76.2	71.8
		76.5	75.7	73.2	73.8	70.4
		78.8	77.6	75.9	76.7	73.2
		83.4	81.8	78.6	81.2	78.1
		79.7	77.2	74.0	76.1	73.3
		73.2	71.0	68.3	71.5	66.8
		72.6	70.5	67.6	70.1	67.3
		81.4	78.3	72.6	74.9	71.1
		64.8	60.6	56.2	61.1	54.0
		54.3	51.5	49.0	52.6	48.2
		52.1	49.6	45.6	48.1	41.5
		50.6	46.9	41.6	45.1	40.5

^a 1 mmol alcohol, 0.75 mmol H₅IO₆, 0.4 mmol Fe(III) complex, 10 ml CH₃CN, stirring at 70 °C.

^b GC yield, average of 3 trials.

out [31] (Table 4). The catalytic activity varies with the substituent on the Schiff base ligand. It was observed that the activity decreased with an increase in the bulkiness of the substituents.

A substrate to catalyst ratio was varied to determine the effect of concentration of catalyst with respect to substrate. A 0.04 mmol of catalyst was sufficient for the effective transformation of benzyl alcohol to benzaldehyde (Table 3, entry 5). The reaction was also studied in the absence of a catalyst. The yield was insignificant in this case (Table 3, entry 1). This observation reveals the catalytic role of Fe(III) complexes. The reaction was studied at various substrates to oxidant ratios (Table 3). A minimum quantity of 0.75 mmol of the oxidant was sufficient for the effective oxidation of benzyl alcohol to benzaldehyde (Table 3, entry 10).

The oxidation was extended to a variety of alcohols including primary and secondary, aromatic, aliphatic and cyclic alcohols. All the synthesized Fe(III) complexes were found to catalyze the oxidation of alcohols to corresponding carbonyl compounds in good yield (Table 4). All the benzylic primary and secondary alcohols studied were oxidized smoothly to give aldehydes and ketones respectively. Among the various alcohols studied those containing aromatic substituent were found to be more reactive than alicyclic and aliphatic alcohols. Furthermore, cyclohexanol was oxidized relatively better than the linear aliphatic alcohols. All the reactions occurred with complete selectivity for ketones or aldehydes and no other products were detected in the reaction mixture. The over oxidation to carboxylic acid was ruled out by a derivative test.

In conclusion, the octahedral, high spin Fe(III) triphenylphosphine complexes ($\text{FeL}_1\text{--FeL}_5$) containing N-(2-mercaptophenyl)salicylideneimine, its derivatives/ N-(2-mercaptophenyl)naphthylideneimine have proved to be an efficient catalyst in the oxidation of primary and secondary alcohols to carbonyl compounds in the acetonitrile–periodic acid system. The small reaction time and good conversion makes this system useful in synthetic organic chemistry.

References

- [1] E. Ispir, *Dyes Pigments* 82 (2009) 13.
- [2] M.H. Fonseca, E. Eibler, M. Zabel, B. Konig, *Inorg. Chim. Acta* 352 (2003) 136.
- [3] L. Xub, M.L. Trudella, *Tetrahedron Lett.* 44 (2003) 2553.
- [4] J.M. War, *Tetrahedron Lett.* 27 (1986) 3139.
- [5] N. Sathya, A. Manimaran, G. Raja, P. Muthusamy, K. Deivasigamani, C. Jayabalakrishnan, *Transit. Metal Chem.* 34 (2009) 7.
- [6] R. Ramesh, *Inorg. Chem. Commun.* 7 (2004) 274.
- [7] S. Kannan, R. Ramesh, *Polyhedron* 25 (2006) 3095.
- [8] S.J.S. Kalra, T. Punniyamurthy, J. Iqbal, *Tetrahedron Lett.* 35 (1994) 4847.
- [9] D. Ramakrishna, B. Ramachandra Bhat, *Inorg. Chem. Commun.* 13 (2010) 195.
- [10] M. Rong, C. Liu, J. Han, W. Sheng, Y. Zhang, H. Wang, *Catal. Lett.* 125 (2008) 52.
- [11] D. Ramakrishna, B. Ramachandra Bhat, R. Karvembu, *Catal. Commun.* 11 (2010) 498.
- [12] N. Deligonul, M. Tume, *Transit. Metal Chem.* 31 (2006) 920.
- [13] G.N. Rao, C. Janardhana, K. Pasupathy, P.M. Kumar, *Ind. J. Chem.* 39 (2000) 151.
- [14] F. Tisato, F. Refosco, U. Mazzi, G. Bandoli, M. Nicolini, *J. Chem. Soc. Dalton Trans.* (1987) 1693.
- [15] L.D. Albin, M. Jacobson, D.B. Olson, US Patent 5426,085, 1995.
- [16] FeL_1 : yield: 57%; CHNS found (calc.) for $\text{C}_{49}\text{H}_{39}\text{ClNOSP}_2\text{Fe}$, C: 69.69(69.80), H: 4.60(4.66), N: 1.60(1.66), S: 3.69(3.80); IR (KBr, cm^{-1}): 1599, 1439, 1306, 1078, 757, 693, 543, 420. UV–vis: λ_{max} (nm) 248, 294, and 381. μ_{eff} : 6.05 B.M. FeL_2 : yield: 60%. CHNS found (calc.) for $\text{C}_{49}\text{H}_{38}\text{Cl}_2\text{NOSP}_2\text{Fe}$, C: 63.61(63.83), H: 4.115(4.15), N: 1.49(1.52), S: 3.39(3.48); IR (KBr, cm^{-1}): 1599, 1440, 1320, 1087, 752, 692, 542, 428. UV–vis: λ_{max} (nm) 247, 288, 388. μ_{eff} : 5.92 B.M. FeL_3 : yield: 52%. CHNS found (calc.) for $\text{C}_{49}\text{H}_{38}\text{BrClNOSP}_2\text{Fe}$, C: 67.00(67.06), H: 4.29(4.36), N: 1.55(1.60), S: 3.59(3.65); IR (KBr, cm^{-1}): 1597, 1434, 1315, 1084, 758, 696, 540, 498. UV–vis: λ_{max} (nm) 248, 294, 390. μ_{eff} : 5.96 B.M. FeL_4 : yield: 56%. CHNS found (calc.) for $\text{C}_{49}\text{H}_{38}\text{ClN}_2\text{O}_3\text{P}_2\text{SFe}$, C: 66.20(66.26), H: 4.26(4.31), N: 3.10(3.15), S: 3.59(3.61); IR (KBr, cm^{-1}): 1607, 1440, 1310, 1089, 757, 691, 541, 472. UV–vis: λ_{max} (nm) 246, 288, 394. μ_{eff} : 5.82 B.M. FeL_5 : yield: 55%. CHNS found (calc.) for $\text{C}_{53}\text{H}_{41}\text{ClNOSP}_2\text{SFe}$, C: 67.67(68.78), H: 4.72(4.73), N: 1.58(1.60), S: 3.60(3.67); IR (KBr, cm^{-1}): 1607, 1440, 1303, 1073, 752, 693, 541, 451. UV–vis: λ_{max} (nm) 248, 288, 419. μ_{eff} : 6.00 B.M.
- [17] C.A. Sureshan, P.K. Bhattacharya, *J. Mol. Catal. A: Chem.* 136 (1998) 285.
- [18] V. Paredes Garc, R.O. Latorre, E. Spodine, *Polyhedron* 23 (2004) 1869.
- [19] H. Aneetha, J. Padmaja, P.S. Zacharias, *Polyhedron* 15 (1996) 2445.
- [20] S.A.A. Latif, H.B. Hassib, Y.M. Issa, *Spectrochim. Acta A* 67 (2007) 950.
- [21] N. Deligonul, M. Tumer, *Transit. Metal Chem.* 31 (2006) 920.
- [22] A.A. Solimana, W. Linert, *Thermochim. Acta* 338 (1999) 67.
- [23] M.M. Tamizh, K. Mereiter, K. Kirchner, B. Ramachandra Bhat, R. Karvembu, *Polyhedron* 28 (2009) 2157.
- [24] M. Bagherzadeh, L. Tahsini, R. Latifi, V. Amani, A. Ellern, L. Keith Woo, *Inorg. Chem. Commun.* 12 (2009) 476.
- [25] N.T. Madhua, P.K. Radhakrishnan, M. Grunert, P. Weinberger, W. Linert, *Thermochim. Acta* 407 (2003) 73.
- [26] J. Sanmartin, A.M. Garcia Deibe, M. Fondo, D. Navarro, M.R. Bermejo, *Polyhedron* 23 (2004) 963.
- [27] S.A. Sallam, A.S.O. Basheir, A. El-Shetary, A. Lentz, *Transit. Metal Chem.* 27 (2002) 447.
- [28] S.A. AbouEl-Enein, F.A. El-Saied, T.I. Kasher, A.H. El-Wardany, *Spectrochim. Acta A* 67 (2007) 737.
- [29] J.B. Luiz, F.M. Andrade, E.L. Sa, G.R. Friedermann, A.S. Mangrich, J.E. Barclay, D.J. Evans, T. Hasegawa, F.S. Nunes, *J. Br. Chem. Soc.* 15 (2004) 10.
- [30] The reaction product analysis was carried out using gas chromatography (GC) (Shimadzu 2014, Japan); the instrument has a 5% diphenyl and 95% dimethyl siloxane Restek capillary column (30 m length and 0.25 mm diameter) and a flame ionization detector (FID). The initial column temperature was increased from 60 °C to 150 °C at the rate of 10 °C/min and then to 220 °C at the rate of 40 °C/min. Nitrogen gas was used as the carrier gas. The temperatures of the injection port and FID were kept constant at 150 °C and 250 °C, respectively during product analysis. The retention times for different compounds were determined by injecting commercially available compounds under identical gas chromatography conditions. The oxidation products are commercially available, and were identified by GC co-injection with authentic samples.
- [31] A solution of iron(III) complex (0.04 mmol) in acetonitrile was added to the solution of substrate (1 mmol) and H_2IO_6 (1 mmol). The mixture was refluxed for 90 min. At the requisite times aliquots of the reaction mixture were removed and the alcohol and aldehyde/ketone extracted with ether. The ether solution was then analyzed by GC using dichlorobenzene as the internal standard.