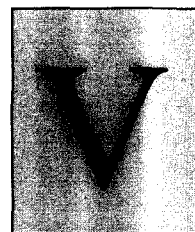

CHAPTER



Oxidation of Hydrocarbons Catalyzed by Chiral Iron(III) and Manganese(III) Salens: A Comparative Study

CHAPTER V

Oxidation of Hydrocarbons Catalyzed by Chiral Iron(III) and Manganese(III) Salens: A Comparative Study*

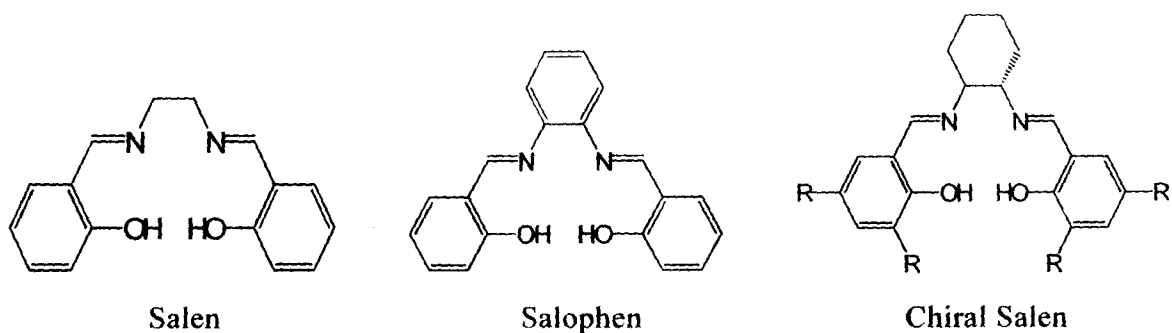
Abstract

A group of chiral iron(III)-salen and manganese(III)-salen complexes were employed as catalysts in the oxidation of hydrocarbons at room temperature, using pentafluoroiodosylbenzene as the source of oxygen. A comparison has been drawn between these two sets of catalysts. The reactions were carried out in acetonitrile and dichloromethane. Iron(III)-salen catalyzed oxygenation reactions were found to be dependent upon the reaction media whereas no distinct solvent effect had been noticed in the corresponding manganese(III) catalysts.

* The part of this work has been published in *Catalysis Communication*, 2009, **10**, 708.

V.1 Introduction

The selective oxidation and functionalization of alkanes and alkenes under mild conditions is an important scientific and economic goal¹. It sustains extensive research and interest worldwide with systems mimicking the dioxygen activation induced by iron containing biological system such as bleomycin², cytochrome P-450³ and methane monooxygenase⁴ receiving particular attention. Oxygen activation and transfer by cytochrome P-450 is of interest in both biomimetic and synthetic chemistry. The P-450 catalyzed oxygen transfer reaction was proposed to proceed through an oxohaem catalytic intermediate.³ Metalloporphyrins have always enjoyed a special preference as synthetic models for the reaction site of cytochrome P-450.^{3d,5} Apart from the porphyrins, the another important ligand systems, especially in the context of catalysis for the asymmetric oxidation of organic substrates, are the Schiff base derivatives, salens [salen= 1,6-bis(2-hydroxyphenyl)-2,5-diazahexa-1,5-diene] and its derivatives.⁶⁻¹¹ Hugo Schiff described the condensation between an aldehyde and an amine leading to a Schiff base as early as in 1864.¹² Schiff base ligands are capable of coordinating metal ions through imine nitrogen and another donor group, usually linked to the aldehyde. Because of their diverse coordination chemistry and various applicabilities in different fields, there has been a tremendous amount of interest on this class of compounds and nowadays active and well designed Schiff base ligands are considered "privileged ligands". In fact, Schiff bases are able to stabilize many different metals in various oxidation states, controlling the performance of metals in various oxidation states. Salen ligands, on the other hand, are regarded as special type of chelating Schiff base and they are formed when two equivalents of salicylaldehyde are combined with a diamine. The metal complexes of the salen ligands, with four coordinating sites and two axial sites open to ancillary ligands are catalytically potent like metalloporphyrins, but their preparation is considerably simple than the porphyrins. Although the term Salen was used originally only to describe the tetradentate Schiff bases derived from ethylenediamine, the more general term Salen-type is used in the literature to describe the class of [O,N,N,O] tetradentate Schiff base ligands (Scheme V.1).



Scheme V.1 Different Salen ligands.

The metallosalen derivatives, most notably those of manganese,^{13,14} chromium¹⁵ and vanadium¹⁶ have emerged as efficient catalysts in various reactions. An increase in the enantioselectivities for the substrates has been achieved by modulating the steric and electronic properties of metallosalens.¹⁴ Although iron(III) dominates the oxygenation chemistry of metalloporphyrins, studies on the oxidation of organic substrates using iron(III)-salen complexes are sparsely reported in literature. Several substituted iron(III)-salen complexes have been investigated as model for catechol dioxygenase¹⁷, catalytic role of iron(III)-salen remains rather unexplored.¹⁹⁻²⁵ In contrast, several chiral manganese salen complexes, reported by Jacobsen¹³ and Katsuki¹⁴ were shown to be efficient catalysts for the asymmetric epoxidation of *cis*-olefins with oxidants like iodosylarenes, NaOCl, H₂O₂, NaIO₄, peracids, etc. Infact, the Jacobsen-Katsuki reaction is universally recognized as one of the most powerful methods for the epoxidation of unfunctionalized prochiral olefins.

Herein, we report the use of chiral iron(III)-salen and manganese(III)-salen complexes as catalysts for hydrocarbon oxidation using pentafluoriodosylbenzene as terminal oxidant. The electronic properties of the metallosalens used have been tuned by variation of different electron-withdrawing and electron donating substituents on the salen ligand frame, which in turn modulate the catalytic behavior of metallosalens in oxygenation reactions. A comparative study between the iron(III) and manganese(III) salens as catalysts towards various types of C-H bonds of hydrocarbons has been presented here.

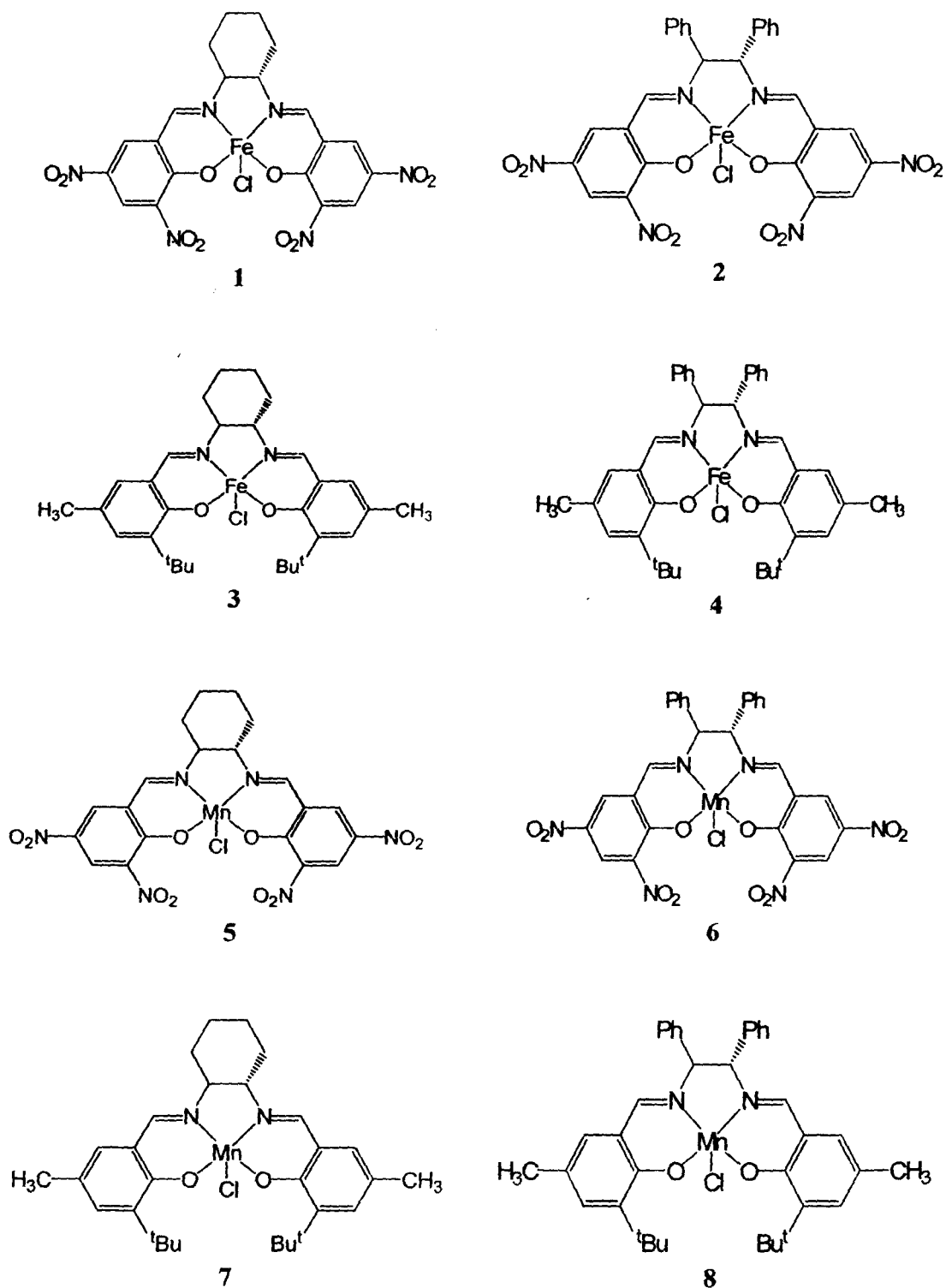


Figure V.1 Metallosalen catalysts used in the study

V.2 Results and discussions

V.2.1 *Synthesis of the catalysts*

Four tetradentate chiral salen ligands and eight complexes derived from them were synthesized (Figure V.1). Among them, four complexes have not been reported earlier. 3, 5-disubstituted salen ligands were prepared according to the known procedure.^{13g, 19} The mononuclear iron(III) complexes (1-4) were prepared from anhydrous FeCl₃ and corresponding 3,5-disubstituted salen ligands.¹⁹ Manganese analogs (5-8) were prepared from Mn(OAc)₂ · 4H₂O and the corresponding ligands in the presence of LiCl.^{13g}

V.2.2 *Characterization of the complexes*

The known complexes (1, 2, 7, 8) were characterized by elemental analysis, MS and IR; all the data matched well with the reported ones. The four new complexes (3, 4, 5, 6) were characterized by elemental analysis, MS and IR.

V.2.3 *Oxygenation of hydrocarbons catalyzed by metallosalens*

V.2.3.1 *Cyclohexene oxidation by metallosalens with C₆F₅IO*

In order to make a comparison among the various metallosalen catalysts, cyclohexene has been chosen as a model substrate. Reactions were performed at room temperature in both acetonitrile and dichloromethane media. Typical catalytic reactions involve acetonitrile/dichloromethane solutions at 25⁰C, stirred under pentafluoroiodosylbenzene (C₆F₅IO) with periodic product sampling by gas chromatography. The results obtained were summarized in Table V.1.

Among the iron(III) salen complexes, electronegatively substituted complexes (catalyst 1 and 2) emerged as better catalysts. With catalysts 1 and 2, cyclohexene has been oxidized in very high yield under suitable reaction condition; overall conversion being 98% for catalyst 1 and 80% for catalyst 2 respectively (entry 1 & 3, Table V.1). The alkyl substituted iron(III) salen complexes showed lesser catalytic activity in bringing about cyclohexene oxidation (entry 5-8, Table V.1). The electronegative iron(III) salen catalysts, like their porphyrin counterparts have been found much more effective in catalytic oxidation of cyclohexene by C₆F₅IO at ambient condition.

Table V.1 Metallosalen catalyzed oxidation of Cyclohexene by C₆F₅IO at 25°C

Entry	Catalyst	Solvent	Conversion (%)	Product (% yields) ^a		
				1-ol	1-one	epoxide
1	1	CH ₃ CN	98	37	36	25
2	1	CH ₂ Cl ₂	58	10	05	43
3	2	CH ₃ CN	80	35	32	13
4	2	CH ₂ Cl ₂	33	08	04	21
5	3	CH ₃ CN	10	04	02	03
6	3	CH ₂ Cl ₂	16	07	04	05
7	4	CH ₃ CN	44	20	19	05
8	4	CH ₂ Cl ₂	30	13	09	08
9	5	CH ₃ CN	46	06	02	38
10	5	CH ₂ Cl ₂	44	07	02	35
11	6	CH ₃ CN	43	05	01	37
12	6	CH ₂ Cl ₂	42	07	01	34
13	7	CH ₃ CN	31	07	03	21
14	7	CH ₂ Cl ₂	31	07	03	21
15	8	CH ₃ CN	65	16	10	39
16	8	CH ₂ Cl ₂	62	20	15	27

^ayields are with respect to total oxidant concentration

Solvent plays an important role in the catalytic reactions studied. The reactions were performed in acetonitrile and dichloromethane. The choice of the solvents was governed by the urge to know and understand the behaviour pattern of the iron(III)-salen complexes in coordinating as well as in non-coordinating solvents. It was found that acetonitrile as a solvent exhibit good activity under the conditions employed. In contrast overall conversion in dichloromethane is always lower (Table V.1). But interestingly there is a complete turn around in product profile as can be evidenced from the bar-diagram for the catalytic oxygenation of cyclohexene by catalyst (1) in those two solvents (Figure V.2). In dichloromethane there is a definite predominance of epoxide among the oxygenated products.

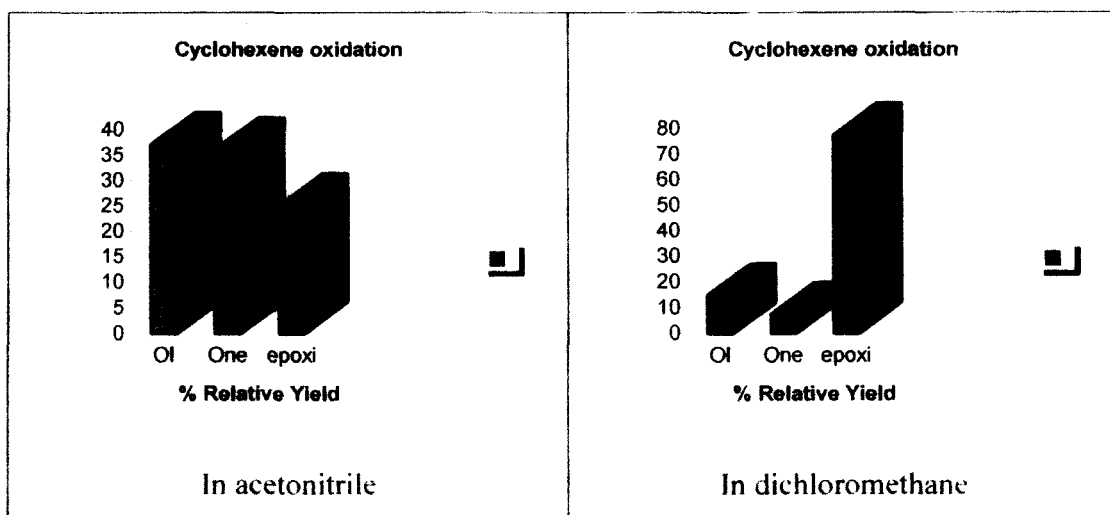


Figure V.2 Relative yields of oxidized products of cyclohexene in acetonitrile (left) and dichloromethane (right) in case of catalyst **1**.

For the corresponding manganese(III)-salen catalysts cyclohexene was mainly converted to epoxides by C_6F_5IO at room temperature. Interestingly, manganese(III)-salen catalysed oxygenation of cyclohexene does not depend a large extent on the substituent at the salicylidine moiety and reaction medium: percentage conversion of cyclohexene by C_6F_5IO remained almost same in both acetonitrile and dichloromethane (entry 9-16, Table V.1). In all these cases yield is not quantitative and for catalyst **8** highest percentage conversion (65%) of cyclohexene was obtained. Another distinct feature of these reactions is that allylic oxidation is less favoured over epoxidation (unlike the iron(III) salen- C_6F_5IO system).

V.2.3.2 Norbornene oxidation by metallosalens with C_6F_5IO

Norbornene and its oxidized products like epoxy norbornane, diol, etc. have wide applications in polymer synthesis, pharmaceutical intermediates, general organic synthesis, etc.²⁶ Oxidation of norbornene has been carried out by many catalytic systems but in most of the cases, the selectivity and yield of the epoxide is moderate²⁷⁻³³. Patel *et al.* have carried out oxidation of norbornene with tert-butyl hydroperoxide (TBHP) using a polymer-supported manganese catalyst at 40°C²⁸. After 24 hours the observed selectivity of the epoxide was only 45%. Koner *et al.* also carried out the oxidation of norbornene with TBHP over Cr(salen) catalyst immobilized in MCM-41, where *exo* and *endo* norborneols were the major products²⁹. There have been many reports on the epoxidation of norbornene using iodosylbenzene as the oxidant over different catalysts³⁰. But the epoxide yield was found to be low in most of the cases. Epoxidation of norbornene using CsCl-promoted Ag/Al₂O₃ catalyst was carried out with air as an oxidant with high selectivity, but at a temperature of

225°C³¹ Epoxidation using Co(III) acetylacetonate³² at temperature ranging from 60 to 130°C under 10 kg cm⁻² pressure of O₂ afforded a selectivity of 43% to the epoxide after 18 h.

Table V.2 Metallosalen catalyzed oxidation of Norbornene by C₆F₅IO at 25°C

Entry	Catalyst	Solvent	% Yield of <i>exo</i> -epoxide
1	1	CH ₃ CN	35
2	1	CH ₂ Cl ₂	45
3	2	CH ₃ CN	22
4	2	CH ₂ Cl ₂	15
5	3	CH ₃ CN	22
6	3	CH ₂ Cl ₂	34
7	4	CH ₃ CN	21
8	4	CH ₂ Cl ₂	45
9	5	CH ₃ CN	45
10	5	CH ₂ Cl ₂	45
11	6	CH ₃ CN	52
12	6	CH ₂ Cl ₂	52
13	7	CH ₃ CN	77
14	7	CH ₂ Cl ₂	72
15	8	CH ₃ CN	80
16	8	CH ₂ Cl ₂	85

^ayields are with respect to total oxidant concentration

Kamata *et al.*³³ have recently reported the epoxidation of various olefins including norbornene with hydrogen peroxide using a lacunary silicotungstate, $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$, with high selectivity based on the oxidant. However, the yield based on the substrate was low. With the difference in reactivity of the iron(III) and manganese(III)-salen catalysts towards cyclohexene established we extended our study to other hydrocarbons. Norbornene was regiospecifically oxidized to its *exo* epoxide under identical reaction condition. Results have been presented in Table V.2. A cursory glance at Table V.2 indicates that among the metallosalens, alkyl substituted Mn(III) salen complexes (catalyst 7 and 8) are most active catalysts affording *exo*-epoxynorbornanes in 75-85% yield (entry 13-16, Table V.2). Presence of electron withdrawing nitro groups in salen moiety gave poorer conversion. No

solvent dependence has been observed in manganese(III) salen catalyzed epoxidation reaction of norbornene. Iron(III) salen complexes were also found active in converting norbornene to *exo*-epoxynorbornanes but the conversion is less impressive (entry 1-8, Table V.2). Among the iron(III)-salens, nitro substituted catalysts, **1** and **2** gave slightly better results than the corresponding alkyl substituted catalysts. Here again, appreciable solvent effect was observed in iron(III)-catalysed epoxidation of norbornene, yields of epoxide being higher in less polar dichloromethane than in acetonitrile.

V.2.3.3 Oxidation of cyclooctene and 1-octene by metallosalens with C₆F₅IO.

The eight metallosalen complexes were also found effective in epoxidation of cyclooctene and 1-octene, the results are summarized in table 3 and table 4 respectively. In both the cases, alkyl substituted manganese(III) salen complexes seemed better catalysts than others (entry 9-16 in both Table V.3 and Table V.4). Solvent again played some role, akin to what we observed in case of other olefinic compounds discussed earlier.

Table V.3 Metallosalen catalyzed oxidation of Cyclooctene by C₆F₅IO at 25°C

Entry	Catalyst	Solvent	% Yield of epoxide
1	1	CH ₃ CN	28
2	1	CH ₂ Cl ₂	37
3	2	CH ₃ CN	18
4	2	CH ₂ Cl ₂	25
5	3	CH ₃ CN	05
6	3	CH ₂ Cl ₂	10
7	4	CH ₃ CN	05
8	4	CH ₂ Cl ₂	Nil
9	5	CH ₃ CN	42
10	5	CH ₂ Cl ₂	43
11	6	CH ₃ CN	44
12	6	CH ₂ Cl ₂	48
13	7	CH ₃ CN	55
14	7	CH ₂ Cl ₂	39
15	8	CH ₃ CN	59
16	8	CH ₂ Cl ₂	42

^ayields are with respect to total oxidant concentration

Table V.4 Metallosalen catalyzed oxidation of 1-octene by C₆F₅IO at 25°C

Entry	Catalyst	Solvent	% Yield of epoxide
1	1	CH ₃ CN	18
2	1	CH ₂ Cl ₂	13
3	2	CH ₃ CN	12
4	2	CH ₂ Cl ₂	08
5	3	CH ₃ CN	Nil
6	3	CH ₂ Cl ₂	Nil
7	4	CH ₃ CN	Nil
8	4	CH ₂ Cl ₂	Nil
9	5	CH ₃ CN	34
10	5	CH ₂ Cl ₂	32
11	6	CH ₃ CN	38
12	6	CH ₂ Cl ₂	43
13	7	CH ₃ CN	10
14	7	CH ₂ Cl ₂	05
15	8	CH ₃ CN	12
16	8	CH ₂ Cl ₂	05

V.2.3.4 Oxidation of cyclohexane by metallosalens with C₆F₅IO

The catalytic oxidation of unactivated sp³ hybridized C-H bonds of cyclohexane at ambient condition poses an interesting challenge to chemists. It might be noted that the oxidation of cyclohexane is an industrial process and it is important from both economical and environmental points of view. Cyclohexane's oxidized products are raw materials in the adipic synthesis, i.e., precursors of Nylon 6 and Nylon 66. In the present industrial process, cyclohexane is oxidized at drastic conditions using cobalt naphthenate or octoate as catalysts affording conversion in the range of 3-8%.³⁴ Only one report of iron-salen catalyzed oxidation of cyclohexane up to 10.2% appeared in the literature.²³ In our endeavour, only complexes **1**, **2** and **6** were found to be effective in catalyzing cyclohexane at room temperature in acetonitrile medium. The best result was obtained for the complex **1**, which showed 23% yield of cyclohexanol and cyclohexanone (entry 1, Table V.5). In this conversion, the turnover frequency (TOF) is 4.6 per hour. However the TOF for the oxidation of cyclohexene is 19.6 per hour. These lower turnover numbers are to be

improved before the catalyst has industrial application, but the results have indeed demonstrated the role of solvent and catalyst structure on the possible improvement of the oxidative conversions of the substrate.

Table V.5 Metallosalen catalyzed oxidation of Cyclohexane by C_6F_5IO at $25^\circ C$

Entry	Catalyst	Solvent	Conversion (%)	Product (% yields)	
				Alcohol	Ketone
1	1	CH_3CN	23	13	10
2	2	CH_3CN	07	05	02
3	3	CH_3CN	Nil	Nil	Nil
4	4	CH_3CN	Nil	Nil	Nil
5	5	CH_3CN	Nil	Nil	Nil
6	6	CH_3CN	14	06	08
7	7	CH_3CN	Nil	Nil	Nil
8	8	CH_3CN	Nil	Nil	Nil

^ayields are with respect to total oxidant concentration

V.2.4 Nature of reactive intermediates

Complexes 1-8 generate active species capable of transferring oxygen to the substrates with C_6F_5IO , because these complexes can participate in hydrocarbon oxygenation reactions as described earlier. Most of the previously reported studies about the oxidation reactions catalyzed by manganese complexes have emphasized on the formation of an oxo-manganese intermediate by the reaction of manganese complexes with iodosylbenzene^{14, 35}. The Mn(III) salen compounds studied by us, showed similar reaction trend towards various olefinic substrates and the involvement of oxo-manganese species as a key intermediate can be predicted.

On the other hand, there exists considerable debate on the reactive intermediate formed during the catalytic transformation of organic substrates by iodosylarenes-iron(III)-salen combination. Rajagopal and Ramraj²¹ reported a mechanistic study on oxygenation of organic sulfides by iron (III)-salen complexes and proposed $[Fe^{IV}=O(salen)]^{+}$ species as the key intermediate. However, recent studies of Bryliakov²² and Fujii²⁴ on the similar systems provided evidence in favour of more complex intermediate, namely iodosylbenzene(salen)-iron(III) complex. Upon addition of C_6F_5IO to iron(III)-salens we got similar similar electronic spectral pattern supporting the formation of oxometal species as the key intermediate,²¹ we believe the system can reveal a system of far grater complexity than initially believed. Formation of substantial amount of epoxides together with allylic C-H oxidized product (for cyclohexene) ruled out the possibility of the involvement of radical chain autoxidation process.¹⁹ Again almost complete reversal of product profile in the non-

coordinating solvent methylene chloride indicated that a complete different chemistry altogether is going on. Studies of our laboratory are now focused on understanding the nature of the intermediates in iron(III) salen catalyzed oxygenation reactions of C-H bonds by C_6F_5IO .

V.3 Conclusion

1. To achieve catalytic C-H bond activation and functionalization at room temperature, a useful reaction condition for hydrocarbon oxidation using metal complexes with readily and cheaply available chiral derivatives of the salen ligand has been successfully designed. Catalytic activities of iron(III) and manganese(III)-salen complexes towards various types of hydrocarbons have been compared.
2. Catalytic reactivity of the metallosalens has been found to be dependent on the substitution pattern at salicylidine moiety, the chiral diamine fragment and reaction media.
3. Iron(III)-salen complexes with electron withdrawing substituents are found to be more efficient in oxygenation reaction of hydrocarbons by C_6F_5IO . Catalytic oxygenation reactions have been found to be dependent on the reaction medium. In polar acetonitrile, overall conversion of the substrates to the oxidized products is always higher than that in dichloromethane. Dichloromethane medium favours epoxidation.
4. On the other hand, manganese(III)-salens with electron donating alkyl substituents emerged as better catalyst in epoxidizing norbornene, cyclooctene and 1-octene. No distinct solvent effect has been observed in manganese(III)-salen catalyzed oxygenation reactions.
5. Both the metallosalens catalyze regiospecific oxidation of norbornene to its *exo* epoxide.
6. At room temperature, the unactivated C-H bond of cyclohexane has been catalytically oxidized in reasonably good yield by chiral iron(III)-salens, whereas manganese(III) salens appear to be less effective.

V.4 Experimental

V.4.1 Instruments and reagents

Electronic absorption spectra were recorded with a Perkin Elmer Lambda-2S spectrophotometer. IR spectra were recorded in KBr palate with Nicolet 460 protégé IR spectrophotometer. Reactions were monitored in Perkin Elmer Autosystem XL Gas Chromatograph. Mass spectra were taken in Jeol SX-102 (FAB). Elemental Analyses were carried out in Perkin Elmer Series II, CHNS/O Analyzer.

All chemicals used for the synthesis of the ligands and metal complexes were reagent grade. 3,5-dinitrosalicylaldehyde, (1R, 2R)-(+)-1,2-diaminocyclohexane, (1R,2R)-(+)-1,2-diphenylethylenediamine, 2-tert butyl -4-methylphenol, Tin (IV) chloride and triethylamine were obtained from Aldrich and used as received. Anhydrous iron(III) chloride was obtained from S.D. Fine Chemicals Ltd (India). Cyclohexene and the solvents used for the catalytic experiments were distilled under argon prior to use.

V.4.2 Synthesis of the ligands and the catalysts

Nitro substituted and the alkyl substituted salen ligands and the corresponding iron(III) and manganese(III) complexes were prepared by literature method.^{13g, 19} Catalysts **1**, **2**, **7** and **8** were characterized by mass, spectral and analytical data which corresponded to the reported data.^{13g, 19} For the other metallosalen catalysts the characterization data is given below.

3. MS(FAB): 551 (M^+), 516 ($[M-35]^+$). Anal.: Calcd for $C_{30}H_{40}N_2O_2FeCl$: C, 65.3; H, 7.2; N, 5.1. Found: C, 65.8; H, 7.4; N, 5.2. IR (KBr) $\nu(C=N)/cm^{-1}$: 1612.

4. MS(FAB): 649 (M^+), 614 ($[M-35]^+$). Anal.: Calcd for $C_{38}H_{42}N_2O_2FeCl$: C, 70.2; H, 6.5; N, 4.3. Found: C, 70.4; H, 6.4; N, 4.4. IR (KBr) $\nu(C=N)/cm^{-1}$: 1612.

5. MS(FAB): 591 (M^+). Anal.: Calcd for $C_{20}H_{16}N_6O_{10}MnCl \cdot H_2O$: C, 39.4; H, 2.9; N, 13.8. Found: C, 39.8; H, 3.1; N, 14.0. IR (KBr) $\nu(C=N)/cm^{-1}$: 1643.

6. MS(FAB): 689 (M^+). Anal.: Calcd for $C_{28}H_{18}N_6O_{10}MnCl$: C, 48.80; H, 2.6; N, 12.2. Found: C, 48.9; H, 2.8; N, 12.2. IR (KBr) $\nu(C=N)/cm^{-1}$: 1635.

V.4.3 Catalytic oxidations

Catalytic reactions were carried out in small screw capped vials fitted with PTFE septa. In a typical reaction 100 μ M of catalyst and 100-200 mM of substrate were dissolved in 2 mL of argon saturated solvent. The oxidation reaction was initiated by adding 2 mM of C_6F_5IO and the contents were magnetically stirred for one hour. The standard solution of dodecane was added to this reaction mixture and an aliquot was injected into a capillary column (carbowax, 30 meter) of a preheated GC. The identification and the quantitation of the products were done from the response factors of standard product samples as usual (Internal standard: Dodecane, 2mM).

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