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Aerobic oxidation of hydrocarbons catalyzed by electronegative iron salen complexes

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Abstract

A number of salen derivatives bearing electronegative substituents and their corresponding iron(III) chloro complexes have been prepared. Several of the complexes catalyze aerobic oxidation of cyclohexene, primarily to allylic oxidation products. Evidence supports a radical chain autoxidation mechanism, with the complex functioning to decompose intermediate alkyl hydroperoxides. Activity is observed only for complexes with relatively high Fe(III/II) reduction potentials, but the incomplete correlation of activity with potential indicates that more subtle structural and electronic effects also play an important role in determining the rates of the catalytic reactions.

Keywords: Iron; Salen complexes; Oxidation; Olefins; Epoxidation

1. Introduction

The selective oxidation of petroleum feedstocks to industrially useful organic molecules using dioxygen would be a major accomplishment in the management and use of our natural resources. Perhalogenated metal porphyrins, such as Fe(TFPPBr$_8$)Cl, are remarkably active and robust catalysts for the oxidation of alkanes and alkenes by O_2 under mild conditions [1]. Recent results suggest that the oxygenation mechanism is not biomimetic, but rather radical chain autoxidation, in which the role of the metal complex is to catalytically decompose hydroperoxides formed from the hydrocarbons and dioxygen [2,3]. Indeed, perhalogenated iron(III) porphyrin complexes are very active catalysts for the decomposition of organic peroxides [4,5].

The high catalytic activity of these porphyrin complexes is attributed to (i) substitution of the ligand hydrogen atoms by halogens, which inhibits oxidative destruction of the catalyst; and especially (ii) stabilization of lower oxidation states (i.e., Fe(II)) by the electron-withdrawing halogen substituents, which disfavors the Fe(II) complex reaction with dioxygen and permits the Fe(III) complex to oxidize peroxides (normally the slow step in catalyzed peroxide decomposition) much more rapidly than other catalysts [5].

However, for practical implementation these complexes have severe disadvantages: they are

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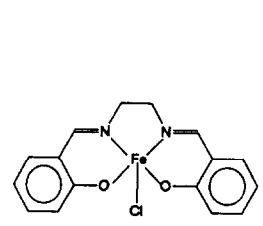
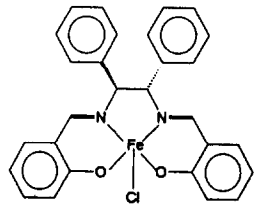


I (- 0.36 V)



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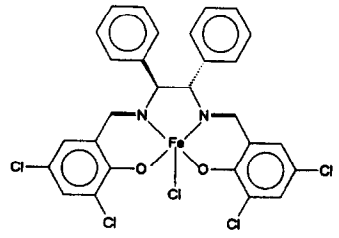
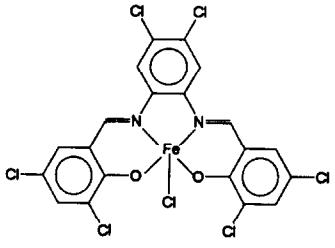
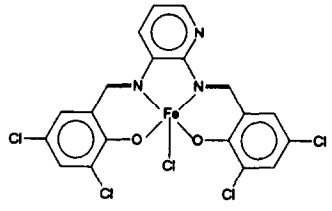


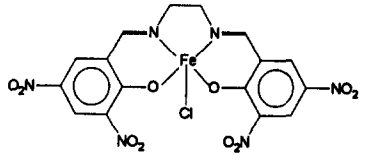
III (-0.11 V)



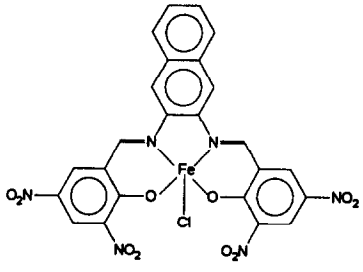
IV (- 0.03 V)



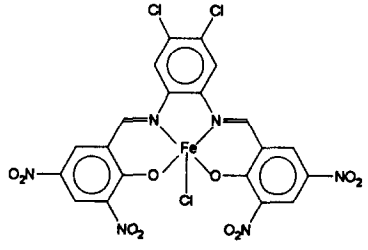
V (0.01 V)



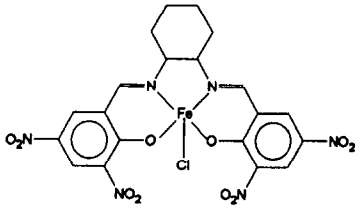
VI (0.07 V)*



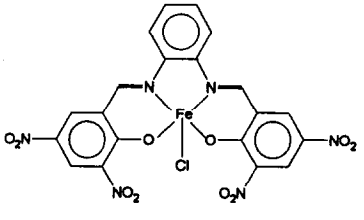
VII (0.115 V)



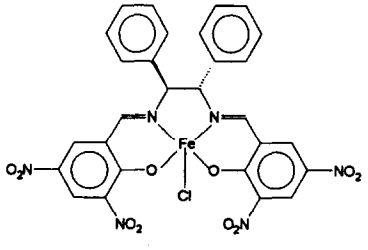
VIII (0.13 V)*



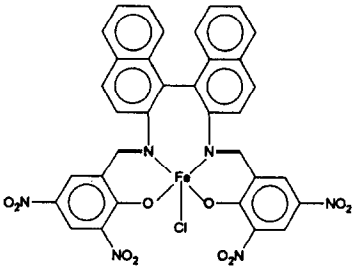
IX (0.13 V)



X (0.16 V)*



XI (0.195 V)+



XII (0.23 V)

Fig. 1. Structures of the electronegative iron salen complexes synthesized, and their iron(III/II) reduction potentials (V vs. AgCl/Ag) measured in 0.1 M tetra-n-butylammonium tetrafluoroborate/CH_3CN. * In DMF. + In CH_2Cl_2.

difficult to synthesize and purify, and hence quite costly. Despite their unprecedented high catalytic activities for aerobic hydrocarbon oxidation, they fall short (by perhaps 1–2 orders of magnitude) of the activity needed for commercialization. Extrapolation of the quantitative model used to validate the radical chain mechanism [3] suggests that it is improbable that such increases in activity will be achievable [5]. There is therefore a clear need for catalysts based on simpler, more easily synthesized and cheaper ligands, that exhibit reactivity equal to or greater than perhalogenated porphyrins, and preferably subject to facile structural and electronic variability.

The use of simpler analogs to mimic the behavior of porphyrin complexes is well established. The salen tetradentate (but not macrocyclic) ligands consist of two nitrogen and two oxygen rather than four nitrogen donors. However, they have been shown to form complexes that mimic porphyrin chemistry [6]. Iron(III) salen complexes are similar to iron(III) porphyrins in that in both, the tetradentate ligands take up a square planar coordination geometry, often with a fifth ligand (e.g., chloro) in an apical position and an open sixth coordination site [7]. Most importantly, salens are relatively easy to synthesize from readily available precursors, by condensation of derivatives of salicylaldehyde and ethylenediamine.

Metal salen complexes have been investigated as oxidation catalysts for some time. Oxo-chromium(V) salen complexes have been used as catalysts for the epoxidation of alkenes using iodosylbenzene or *m*-chloroperbenzoic acid [8]; more recently, manganese complexes of chiral salen derivatives have proven highly useful for enantioselective epoxidation, using bleach as an oxidant [9]. Herein, we report the first use of iron salen complexes for hydrocarbon oxidation with dioxygen. We have prepared a series of novel iron(III) salen complexes containing electron-withdrawing substituents [10], and describe the relationship between their catalytic activities and electronic properties.

2. Results

A series of electronegatively substituted salen ligands were synthesized by standard methods – Schiff base condensation of 2 moles of the appropriate salicylaldehyde derivative with 1 mole of a diamine [11] – starting with commercially available materials. Ligands were characterized by ^{1}H NMR spectroscopy. Their iron(III) complexes were obtained by reacting the respective ligand with iron(III) chloride in alcoholic solution [12]. The overall yield was usually greater than 90%. The structures of all complexes prepared are shown in Fig. 1.

Complexes were characterized by elemental analysis, mass spectrometry and ^{1}H NMR spectroscopy. In addition, the X-ray crystal structure of one complex, the tetranitro derivative **VI**, was determined. The ORTEP of **VI** is shown in Fig. 2. The local geometry about the iron differs somewhat from that of the parent Fe(salen)Cl (**I**), in that the salen ligand is slightly twisted out of planarity, and a water molecule occupies the sixth position. (The complex Fe(salen)Cl can exist both in a monomeric, pentacoordinate as well as in a dimeric, hexacoordinate structure in the solid state. However, in solution the complex is monomeric [7].) Complete crystallographic details will be published separately [13].

Electrochemical studies were generally carried out in acetonitrile solution. Some of the complexes are too insoluble in that solvent, and dimethylformamide was used instead. Several compounds were examined in both CH_3CN and

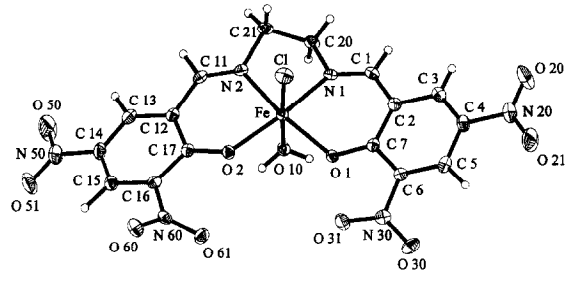


Fig. 2. ORTEP diagram of **VI**, with ellipsoids drawn at the 30% probability level.

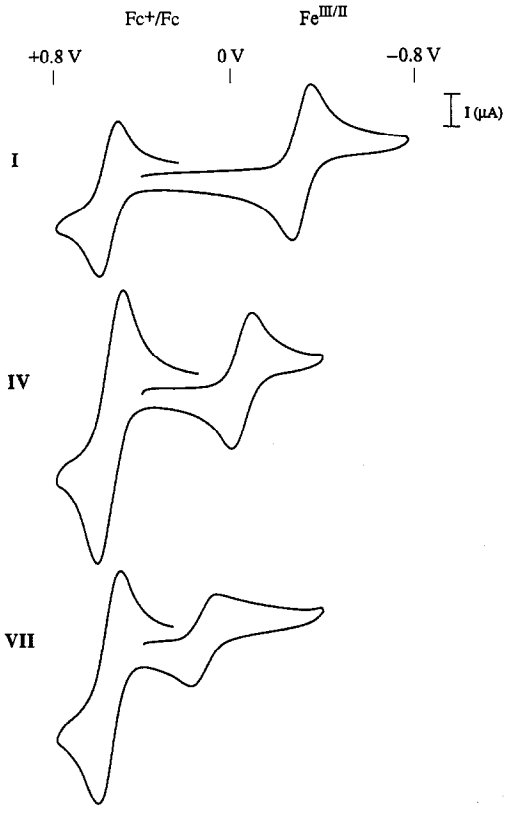


Fig. 3. Cyclic voltammograms of iron salen complexes **I**, **IV** and **VII**, recorded in 0.1 M tetra-n-butylammonium tetrafluoroborate/DMF (V vs. AgCl/Ag).

DMF, showing only a small shift in potential between solvents (e.g., 0.04 V for **I** and 0.005 V for **VII**). The iron complexes exhibit clean and quasireversible electrochemistry; typical cyclic voltammograms are illustrated in Fig. 3. Potentials for the various complexes are shown in Fig. 1. There is a rather systematic anodic shift of the iron (III/II) redox couple with increasing electron-withdrawing substitution of the ligand framework. The shifts in iron (III/II) redox potential seem generally more sensitive to substitution on the salicylaldehyde portion of the ligand than on the diamine – for example, compare the 0.2 V shift from **II** to **III**, with the < 0.1 V shift from **III** to **IV** – and nitro groups exert a considerably greater effect than chlorides. Overall, the iron (III/II) potential shifts by more than 500 mV from **I**, Fe(salen)Cl, to the tetranitro derivatives (**X–XII**). This range is similar to that observed on going from the perhalogenated iron porphyrins [5] to the parent Fe(TPP)Cl [14], a change of about 0.6 V. Irreversible oxidation of the salen complexes occurs only at quite positive potentials (e.g. for **XI**: > 1.5 V), suggesting that these complexes will be oxidatively robust.

The iron salen complexes were tested as catalysts for aerobic oxidation of hydrocarbons. Most experiments utilized cyclohexene as substrate, with some limited studies on the less reactive alkane, 3-methylpentane. Typical catalytic reaction conditions involve acetonitrile solutions at 25°C, stirred under 1 atm of O_2, with periodic product sampling by gas chromatography. Under these conditions, complexes **I–V** are essentially inactive while **VI**, **VII**, **VIII** and **X** are nearly insoluble. It was found that incorporation of large nonpolar groups into the diamine 'bridge' increases solubility, so tetranitro derivatives **IX**, **XI** and **XII** were sufficiently soluble to test. Complex **XI** is the most active; its performance is shown in Table 1 and compared to those of other salen derivatives, and of halogenated iron porphyrin complexes, as a function of redox potential in Fig. 4. It should be noted that **IX**, which is less oxidizing than **XI**, is only 20% as active; whereas **XII**, which is *more* oxidizing, is virtually inactive.

The product distributions for oxidation of cyclohexene catalyzed by **IX** and **XI** are shown in Fig. 5, and compared to those obtained using the halogenated iron porphyrins, Fe(TFPP)Cl and Fe(TFPPBr$_8$)Cl. For all four catalysts,

Table 1
Catalytic oxidation of cyclohexene by XI and dioxygen (1 atm)

Reaction conditions	Catalytic Turnovers	
	3 h	24 h
Standard (in CH_3CN, 25°C)	4	162
+ *t*-BuOOH	45	151
+ BHT	0	0.4
+ H_2O	2	56
in CH_2Cl_2 (25°C)	3	46
in DMF (25°C)	4	5
in CH_3CN ((55°C)	127	196

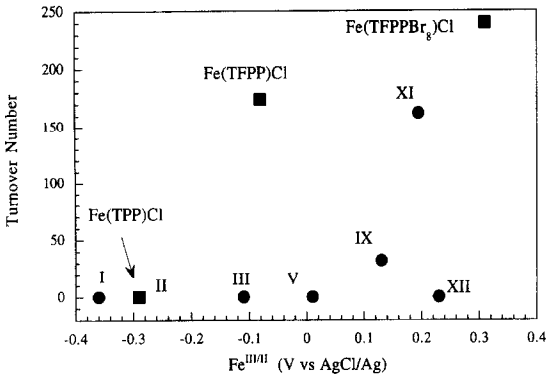


Fig. 4. Plot of activity for catalytic cyclohexene oxidation vs. iron(III/II) reduction potential (V) for halogenated porphyrin (squares) and salen (circles) complexes of Fe(III).

nearly all oxidation takes place at allylic positions to give cyclohexanol and cyclohexanone (in about a 1:2 ratio), with only a few percent of epoxide observed. Radical initiators and inhibitors are also observed to have an effect on the catalytic reaction with compound **XI** (Table 1). Addition of *t*-BuOOH substantially accelerates oxidation during early stages, although after longer reaction times this effect vanishes, indicating that the peroxide serves only to shorten the induction period (during which peroxides begin to be produced via the autoxidation mechanism). Conversely, the radical inhibitor BHT shuts down oxidation essentially completely. Reaction is somewhat inhibited by the potential ligand H_2O, and slowed considerably in the better coordinating solvent DMF.

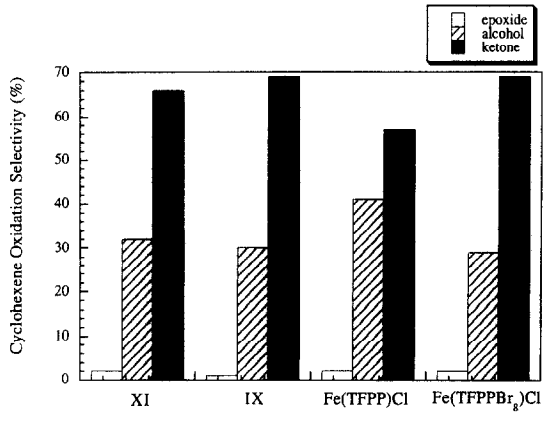


Fig. 5. Product selectivity for the oxidation of cyclohexene with dioxygen catalyzed by electronegative iron salen and iron porphyrin complexes.

Complex **XI** also catalyzes the oxidation of 3-methylpentane. After 24 hours in CH_3CN at 25°C under 1 atm of O_2, in the presence of one equivalent of t-butyl hydroperoxide, two catalytic turnovers are observed, giving primarily 3-methyl-3-pentanol (41%) and 3-methyl-2-pentanone (51%). This catalytic activity, although very low, is in fact comparable to that of $Fe(TFPPBr_8)Cl$ under similar conditions [2]. (Oxidation reactions with halogenated iron porphyrins were performed in CH_2Cl_2; no activity was observed in CH_3CN.) The selectivity for secondary oxidation is considerably higher for **XI** (51% 3-methyl-2-pentanone) than for $Fe(TFPPBr_8)Cl$ (16%).

Several control experiments were performed. Catalysis is not affected by the presence or absence of light. In the presence of the ligand alone no oxidation occurs; while autoxidation by simple transition metal salts, such as iron(III) chloride, is about two orders of magnitude slower. Use of iodosylbenzene as an oxidant affords only a small amount of substrate oxidation. The salen catalysts are very stable to oxidative degradation under reaction conditions, in spite of the fact that (in contrast to perhalogenated porphyrins) they do possess carbon–hydrogen bonds which might be expected to provide sites for attack by intermediate radicals.

3. Discussion

Our work suggests that the unusual catalytic properties observed with perhalogenated metalloporphyrins can indeed be reproduced with simpler ligand systems by the use of electronegative substituents, best demonstrated by the tetranitro derivative **XI**. All the observations for this catalyst point to the same radical chain autoxidation mechanism (Fig. 6) previously established for the metalloporphyrin-catalyzed oxidation of isobutane [2,3], where the primary (only?) role of the metal is to catalytically de-

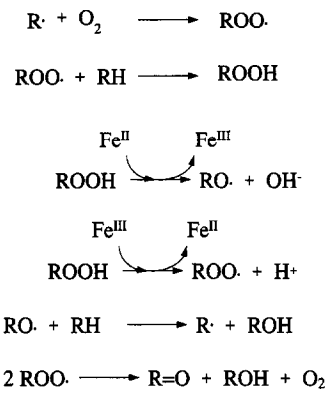


Fig. 6. Key steps in the proposed radical chain mechanism for oxidation of cyclohexene.

compose the hydroperoxide by alternate reduction and oxidation. This is indicated by the high selectivity for allylic oxidation rather than epoxidation, as well as the sensitivity to radical initiators and inhibitors. Moreover, the chloro- and nitro-substituted salen complexes show good resistance to oxidative deactivation. This is an important consideration, as deactivation appears to be a significant problem in other practical applications of salen derivatives as oxidation catalysts [9].

A striking feature of the halogenated metalloporphyrin catalysts is the correlation of catalytic activity with redox potential. This is interpreted in the context of the radical chain mechanism, with the key parameter being the rate of oxidation of hydroperoxide by Fe(III) – the slow step of hydroperoxide decomposition via the Haber–Weiss cycle. The latter in turn is governed by the Fe(III)/Fe(II) potential, with an approximately linear relationship between the log of the rate constant and the potential [3].

The activity data for salen complexes exhibit roughly similar behavior, in that no activity is observed for the least oxidizing complexes, and **XI** is more active than **IX**. However, Fig. 4 shows important anomalies. First, the entire activity–potential curve is shifted to higher potential, by some 0.3 V, for the salen systems. Second, and more strikingly, the most oxidizing complex studied, **XII**, is completely *inactive*. We propose that hydroperoxide oxidation is most probably an *inner-sphere* process, requiring prior coordination of the peroxide to the metal center, to account for both of these observations. In that case the fine structural details of the complex would play an important role, along with redox potential, in determining the rate of oxidation. The most obvious effect would be on the ability of the peroxide to coordinate, which would directly impact an inner-sphere mechanism. In addition, ligand distortions caused by substitution may strongly influence the reorganization energy of the redox reaction. For example, the severe departures from planarity found for iron (and other) complexes of perhalogenated porphyrins [5] may reduce the reorganization energy by distorting the structure of the ground state towards that of the transition state, and thus lower the overall activation energy, relative to the less distorted salen system.

As for complexes **XI** and **XII**, which have very different activities in spite of their similar iron(III/II) potentials (0.195 V and 0.23 V, respectively), preliminary data suggest that the two complexes have different electronic structures. **XI** appears to be high-spin iron(III). SQUID measurements show μ_{eff} to be 4.7 at 300 K, while the ^{1}H NMR shows broad, widely dispersed resonances at about 70 and 50 ppm, consistent with those of previously reported high-spin iron(III) salen complexes [15]. On the other hand, complex **XII** shows much less dispersed NMR resonances at about 10 and 15 ppm, and a μ_{eff} of 3.7 at 300 K, suggesting it is an intermediate-spin state. It is tempting to ascribe the lack of observed catalytic activity with **XII** to this electronic structure difference; perhaps ligand exchange is slower, so that the hydroperoxide does not enter the coordination sphere as rapidly as in a high-spin complex. It may be noted that the active halogenated iron porphyrin complexes are high-spin at room temperature [5]. More extensive experiments that may shed light on the role of the electronic structures of these electronegative iron salen complexes are in progress.

In conclusion, we have succeeded in designing an active and robust catalyst for cyclohexene oxidation by dioxygen using readily and cheaply available derivatives of the salen ligand. We have already achieved about 2/3 of the activity of the best iron porphyrin catalyst, using a complex that (unlike the latter) is not completely substituted with electron-withdrawing groups. Hence, it should be possible to further increase the electronegativity and the redox potential. The correlation between potential and activity seems to be subject to subtle structural effects that were not readily apparent in the porphyrin system; but this may in fact offer additional possibilities for manipulating reactivity, so that both factors (electronic and steric) can be controlled independently and simultaneously. Such a situation provides an unusually intriguing opportunity for connecting the results of basic research to development of practical catalysts, which we are currently attempting to exploit.

4. Experimental

4.1. Materials and methods

All chemicals used for the synthesis of the ligands and complexes were reagent grade. Salicylaldehyde, 3,5-dichlorosalicylaldehyde and 3,5-dinitrosalicylaldehyde as well as 1,2-diaminoethane, 1,2-diaminobenzene, 2,3-diaminonaphthalene, 1,2-diamino-4,5-dichlorobenzene, 2,3-diaminopyridine, (1*R*, 2*R*)-1,2-diamino-1,2-diphenylethane, 1,2-diaminocyclohexane, 2,2′-diamino-(*R*)-1,1′-binaphthyl and triethylamine were obtained from Aldrich; anhydrous iron(III) chloride from EM Science; and tetra-n-butylammonium tetrafluoroborate (electrochemical grade) from SACHEM. Acetonitrile (Omnisolv solvent) was purchased from EM Science, nitromethane from Fluka and absolute ethanol from Quantum Chemical Corp. Cyclohexene, 3-methylpentane (Aldrich) and the solvents used for the catalytic experiments were distilled under argon prior to use.

Electronic absorption spectra were recorded on a Hewlett Packard HP 8452 diode array spectrophotometer. ^{1}H NMR spectra were obtained on a GE QE 300 MHz NMR spectrometer in acetonitrile-d_3 or DMSO-d_6 with the solvent as internal reference. IR spectra were recorded as KBr pellets on a Perkin Elmer Model 1600 FT-IR spectrometer. CI and FAB mass spectra were obtained at the UC Riverside mass spectrometry facility and elemental analyses were obtained at the Caltech analytical facility. Magnetic measurements were performed on a SQUID magnetometer (Quantum Design, MPMS). Cyclic voltammetry was performed using an EG and G Princeton Applied Research Model 173 potentiostat/galvanostat driven by a Model 175 universal programmer and using a standard three electrode configuration. A AgCl/Ag electrode containing 3 M NaCl (BAS MF 2063) served as reference electrode, a Pt wire as counter electrode and a glassy carbon electrode as working electrode. Cyclic voltammetric measurements were performed at 25°C under argon in acetonitrile, dimethylformamide or dichloromethane with 0.1 M tetra-n-butylammonium tetrafluoroborate as the supporting electrolyte. The solvent was passed through activated alumina prior to use. Potentials are reported vs. AgCl/Ag in 3 M NaCl. Ferrocene was added after each run as an internal standard. The Fe(III/II) couple of ferrocene was observed at 0.450 V (acetonitrile), 0.550 V (dimethylformamide) and 0.435 V (dichloromethane) under these experimental conditions (scan rate = 0.1 V/s). The complex concentration was $\approx$ 1 mM.

Catalytic oxidations were performed in stirred flasks. In a typical experiment 5 μmol of the iron salen complex were dissolved in 15 ml freshly distilled acetonitrile. After saturation of the solution with dioxygen, 1 ml hydrocarbon was injected. The reaction products were monitored at periodic time intervals using gas chromatography. Control oxidation experiments

showed no substrate (cyclohexene or 3-methylpentane) oxygenation in the absence of catalyst.

4.2. Synthesis of the ligands and complexes

General procedure for ligands [11]: A solution of diamine (1 mmol) in 25 ml absolute ethanol was slowly added to a stirred solution of the salicylaldehyde (2 mmol) derivative in 100 ml of absolute ethanol. The reaction mixture was then refluxed for 30 min, during which time the yellow–orange Schiff base ligand precipitated. After cooling the ligand was filtered, washed with cold methanol and dried. Yields were > 90%. The Schiff base ligands were characterized by ^{1}H NMR spectroscopy.

General procedure for iron complexes [12]: The desired Schiff base ligand (0.5 mmol) was dissolved in 200 ml hot absolute ethanol. Next, anhydrous iron(III) chloride (0.6 mmol) dissolved in 20 ml of ethanol was slowly added to the warmed stirred solution. Then triethylamine (1 mmol) in 20 ml ethanol was added dropwise. The reaction mixture was heated with stirring for an additional 30 min and then concentrated and cooled. Crystals formed, which were then separated by filtration, washed with cold methanol and dried. Yields were > 85%. The iron salen complexes were characterized by elemental analysis and mass spectrometry. Several of the complexes were obtained with one or two equivalents of water or ethanol.

A modification of the above method, for the synthesis of Schiff base ligands and complexes bearing nitro substituents, was found to lead to analytically purer products. A typical procedure is as follows: 3,5-dinitrosalicylaldehyde (2 mmol) was dissolved in 20 ml warm absolute ethanol. Triethylamine (2 mmol) in 5 ml of ethanol was next added while stirring. Finally, the diamine (1 mmol) in 30 ml ethanol was added slowly. The resulting yellow–orange reaction mixture was refluxed for an additional 20 min, during which time the Schiff base ligand precipitated as the bis(triethylammonium) salt, which was subsequently filtered, washed with cold methanol and dried. Yield was > 90%. The free ligand (as the bis(triethylammonium) salt, 0.5 mmol) was dissolved in 50 ml hot ethanol. Anhydrous iron(III) chloride (0.6 mmol) in 20 ml ethanol was then added slowly to the warmed solution. The reaction mixture was refluxed for 30 min and then concentrated. Crystals of the desired product formed after cooling and were subsequently filtered, washed with cold methanol and dried. Yield was > 80%.

The following entries list the ^{1}H NMR spectral data (300 MHz, DMSO-d_6) for the free ligands, and the mass spectral and elemental analytic data for the corresponding Fe(ligand)Cl complexes. For the catalytically most active complex **XI**, the mass spectral and elemental analytic data for the free ligand are also given.

II: Ligand: NMR: δ 5.11 (s, 2 H; CH), 6.85 (m, 4 H; aryl-H), 7.20 (m, 4 H; aryl-H), 7.30 (m, 10 H, aryl-H), 8.55 (s, 2 H; CH), 13.35 (s, 2 H; OH). Complex: MS(FAB$^-$): 509 (M^-). Anal.: Calcd for $C_{28}H_{22}N_2O_2FeCl$: C, 65.97; H, 4.35; N, 5.49. Found: C, 65.61; H, 4.44; N, 5.30.

III: Ligand: NMR: δ 4.8 (s, 2 H; CH), 7.15–7.45 (m, 14 H, aryl-H), 8.32 (s, 2 H; CH), 14.7 (s, 2 H; OH). Complex: MS(FAB$^-$): 647 (M^-). Anal.: Calcd for $C_{28}H_{18}N_2O_2FeCl_5$: C, 51.93; H, 2.80; N, 4.32. Found: C, 51.66; H, 2.83; N, 4.23.

IV: Ligand: NMR: δ 7.80–7.92 (m, 6 H; aryl-H), 9.1 (s, 2 H; CH). Complex: MS(CI): 611 (M^+), 576 ($[M - Cl]^+$). NMR of the complex revealed the presence of triethylamine, and the analytical data appear most compatible with 1 Et_3N and 2 H_2O molecules of crystallization per complex. Anal.: Calcd for $C_{26}H_{27}N_3O_4FeCl_7$: C, 41.67; H, 3.63; N, 5.61. Found: C, 41.50; H, 3.08; N, 5.27.

V: Ligand: NMR: δ 7.5–8.05 (m, 6 H; aryl-H), 8.5 (m, 1 H; aryl-H), 8.9 (s, 1 H; CH), 9.1 (s, 1 H; CH). Complex: MS(FAB$^-$): 544 (M^-). Anal.: Calcd for $C_{19}H_9N_3O_2FeCl_5 \cdot H_2O$: C, 40.58; H, 1.97; N, 7.46. Found: C, 40.51; H, 2.26; N, 7.60.

VI: Ligand: NMR: δ 4.10 (s, 4 H; CH_2),

8.65–8.73 (m, 4 H; aryl-H), 8.86 (s, 2 H; CH). Complex: MS(FAB$^-$): 537 (M^-). Anal.: Calcd for $C_{16}H_{10}N_6O_{10}FeCl \cdot 2\ H_2O$: C, 33.50; H, 2.46; N, 14.64. Found: C, 33.57; H, 2.24; N, 14.85.

VII: Ligand: NMR: δ 7.4–8.9 (m, 10 H; aryl-H), 8.8 (s, 2 H; CH). Complex: MS(FAB$^-$): 635 (M^-), 600 ($[M - Cl]^-$). Anal.: Calcd for $C_{24}H_{12}N_6O_{10}FeCl \cdot C_2H_5OH$: C, 45.81; H, 2.66; N, 12.32. Found: C, 46.93; H, 3.27; N, 12.52.

VIII: Ligand: NMR: δ 7.45–7.90 (m, 2 H; aryl-H), 8.35–8.9 (m, 4 H; aryl-H), 8.6 (s, 2 H; CH), 13.3 (s, 2 H; OH). Complex: MS(FAB$^-$): 653 (M^-). Anal.: Calcd for $C_{20}H_8N_6O_{10}FeCl_3 \cdot C_2H_5OH$: C, 37.72; H, 2.01; N, 11.99. Found: C, 37.07; H, 2.10; N, 12.17.

IX: Ligand: NMR: δ 1.4–1.5 (m, 4 H; CH_2), 1.8–1.9 (m, 4 H; CH_2), 4.3 (s, 2 H; CH), 8.67–8.74 (m, 4 H; aryl-H), 8.92 (s, 2 H; CH). Complex: MS(FAB$^-$): 591 (M^-). Anal.: Calcd for $C_{20}H_{16}N_6O_{10}FeCl$: C, 40.60; H, 2.73; N, 14.20. Found: C, 40.81; H, 3.40; N, 14.16.

X: Ligand: NMR: δ 7.5–7.9 (m, 4 H; aryl-H), 8.5–8.75 (m, 4 H; aryl-H), 9.16 (s, 2 H; CH). Complex: MS(FAB$^-$): 585 (M^-). Anal.: Calcd for $C_{20}H_{10}N_6O_{10}FeCl \cdot C_2H_5OH$: C, 41.83; H, 2.55; N, 13.29. Found: C, 41.87; H, 2.76; N, 13.61.

XI: Ligand: NMR: δ 5.31 (s, 2 H; CH), 7.30–7.5 (m, 10 H, aryl-H), 8.72–8.8 (m, 4 H, aryl-H), 9.11 (s, 2 H, CH). IR (cm^{-1}, KBr): 1629 (ν(C=N)). MS (FAB$^+$): 601 (MH^+). Anal.: Calcd for $C_{28}H_{20}N_6O_{10} \cdot H_2O$: C, 54.38; H, 3.59; N, 13.59. Found: C, 54.06; H, 3.75; N, 13.48. Complex: MS(FAB$^+$): 690 (MH^+), 655 ($[M - Cl]^+$). Anal.: Calcd for $C_{28}H_{18}N_6O_{10}FeCl \cdot C_2H_5OH$: C, 48.97; H, 3.29; N, 11.42. Found: C, 48.31; H, 3.23; N, 11.51. IR (KBr): 1636 cm^{-1} (ν(C=N)).

XII: Ligand: NMR: δ 6.55–8.4 (m, 12 H; naphthyl-H), 8.7–8.8 (m, 4 H; aryl-H), 9.76 (s, 2 H; CH). Complex: MS(FAB$^+$): 727 ($[M - Cl]^+$), FAB$^-$: 761 (M^-). Anal.: Calcd for $C_{34}H_{18}N_6O_{10}FeCl \cdot C_2H_5OH$: C, 53.52; H, 2.99; N, 10.40. Found: C, 55.67; H, 3.34; N, 10.70.

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