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Iron-Catalyzed Oxidation of Thioethers by Iodosylarenes: Stereoselectivity and Reaction Mechanism

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Abstract: Catalytic properties of a series of iron(III)–salen (salen = *N*,*N*′-bis(salicylidene)ethylenediamine dianion) and related complexes in asymmetric sulfoxidation reactions, with iodosylarenes as terminal oxidants, have been explored. These catalysts have been found to efficiently catalyze oxidation of alkyl aryl sulfides to sulfoxides with high chemoselectivity (up to 100%) and moderate-to-high enantioselectivity (up to 84% with isopropylthiobenzene and iodosylmesitylene), the TON (TON = turnover number) approaching 500. The influence of the ligand (electronic and steric effects of the substituents), oxidant, and substrate structures on the oxidation stereoselectivity has been investigated systematically. The structure of the reactive intermediates (complexes of the type [Fe^{III}(ArIO)(salen)] and the reaction mechanism have been revealed by both mechanistic studies with different iodosylarenes and direct in situ ^{1}H NMR observation of the formation of the reactive species and its reaction with the substrate.

Keywords: asymmetric catalysis · iron · oxidation · reaction mechanisms · sulfoxides

Introduction

The enantioselective catalytic oxofunctionalization of prochiral substrates is of evident interest and in recent years has continued to stimulate significant efforts towards this goal.[1a,b] The development of new catalysts remains a continuing challenge reflecting the growing needs for new, cheap, effective, selective, and environmentally benign catalytic processes for pharmaceutical, food, and agricultural industries.[1c]

In this paper, the problem of catalytic asymmetric sulfoxidation will be touched upon. Chiral sulfoxides can be obtained by catalytic oxidation of prochiral sulfides either in enzymatic processes or from transition-metal-based catalysts;[1a,b,2a–c] in this work, enzymatic oxidations will be excluded from consideration. Historically, the first catalytic systems for asymmetric oxidation of sulfides were Kagan–Modena type ones (based on a Ti(O*i*Pr)$_4$/dialkyl tartrate combination and alkylhydroperoxides as oxidants).[3a–c] Although those are currently the most developed and applied systems, they have certain disadvantages (low turnover numbers, the need to precisely control the reaction conditions and water content) that stimulates the search for other transition-metal-based catalytic systems.

Among such catalytic systems, those that make use of chiral complexes of abundant, nontoxic, and environmentally benign iron complexes are regarded as underrepresented. Indeed, despite the broad range of iron-catalyzed reactions in organic synthesis,[4] until recently only iron–porphyrins were known to catalyze asymmetric sulfoxidations with iodosylarenes or alkylhydroperoxides (with *ee*'s in general $<55\%$).[5a–e] In the late 1990 s, Fontecave et al. explored the binuclear iron complex [$Fe_2O(pb)_4(H_2O)_2$][ClO_4]$_4$ (pb = (−)-4,5-pinene-2,2′-bipyridine) as a catalyst in sulfide oxidation with H_2O_2, but the *ee*'s were low ($<40\%$), and preparative oxidations had never been performed with that system (iron/substrate/oxidant ratio of 1:600:10 was applied).[5f–h] Later, Legros and Bolm reported the systems based on iron(III) complexes generated in situ from iron acetylacetonate- and β-aminoalcohol-derived Schiff bases, which, despite the generally low yields (15–44%), showed remarkable enantioselectivities of up to 96%[6a–c] and was employed in the synthesis of an anti-inflammatory drug Sulindac.[6d]

In 2002, Rajagopal and co-workers published a mechanistic study of non-stereoselective [Fe^{III}Cl(salen)]-catalyzed

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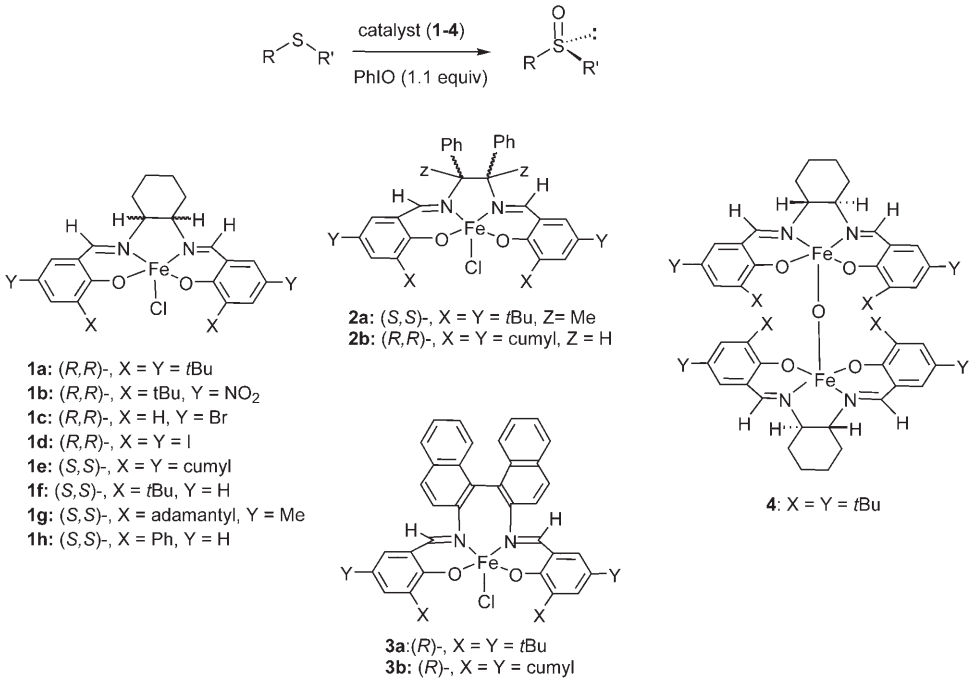
Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. It includes ^{1}H NMR data of the paramagnetic complexes **1**–**4**, measurement of antiferromagnetic coupling constant for **4**, selected NMR data for the compounds involved and so forth.

(salen = *N*,*N*′-bis(salicylidene)ethylenediamine dianion) oxidation of sulfides with iodosylbenzene.[7a] Two years later, Bryliakov and Talsi published an asymmetric version of this system: using chiral iron(III)–salen complexes **1a** and **2a** (Scheme 1), they claimed the oxidation of sulfides with high



Scheme 1. Reaction scheme and the catalysts considered.

efficiency (up to 500 turnovers) and chemoselectivity (mostly over 90%), and with *ee*'s up to 62%.[7b] The initial findings on the reaction mechanism and active intermediates were presented.[7b] We now report the catalytic properties (in oxidation of thioethers with iodosylarenes) of a family of related chiral iron(III)–salen complexes, detail the influence of the ligand, substrate, and oxidant structures and reaction conditions on the sulfoxidation enantioselectivity, and establish the nature of the reactive intermediates on the basis of mechanistic and NMR spectroscopic data.

Results and Discussion

In addition to the previously reported[7b] complexes **1a** and **2a**, series of complexes **1**–**4** (Scheme 1) derived from readily available chiral diamines and substituted salicylaldehydes have been synthesized and screened in asymmetric oxidation of alkyl aryl sulfides by iodosylbenzene. The results of room temperature asymmetric oxidations of benzyl phenyl sulfide with iodosylbenzene are presented in Table 1. The effect of the reaction conditions on the oxidation chemo- and stereoselectivity was examined in previous work.[7b] The optimized conditions found in the previous paper were applied (CH_3CN, room temperature, 150 rpm stirring, [oxidant]/[substrate]/[catalyst] = 55:50:1) unless otherwise stated.[7b] Most complexes showed very high conversions and chemoselectivities (90–98%). As expected, the best results (enantioselectivities) were achieved with complexes **1a** and **2a** (Table 1, entries 1, 2, 11). We note that catalyst **1a** was capable of performing at least 500 turnovers without loss of enantioselectivity (Table 1, entries 2 and 3). It was found that bulky X substituent was necessary for high enantioselectivity (e.g., complex **1c** displayed zero *ee*: Table 1, entry 5). Removal of the Y substituent (**1f**) or substitution of Y = alkyl with Y = NO_2 (**1b**) resulted in poorer *ee*'s, indicating that the structure of the salicylidene moieties with X = Y = *t*Bu is optimized both in terms of electronic and steric factors (Table 1, entries 8 and 4). Replacement of the 3-*t*Bu groups with other bulky ones (cumyl or adamantyl substituents in **1e** and **1g**, Table 1, entries 7 and 9, respectively) led to worse optical yields. The influence of the diamine moiety is not straightforward: while complexes **1a**

Table 1. Enantioselective oxidation of benzyl phenyl sulfide with PhIO catalyzed by iron complexes **1**–**4**.[a]

	Catalyst	*T* [°C]	Conversion [%][b]	Selectivity [%][c]	*ee* [%][d]	Config.[e]
1	**1a**	0	95	91	62	*(S)*-(−)
2	**1a**	20	92	91	55	*(S)*-(−)
3	**1a**	20[f]	96	72	55	*(S)*-(−)
4	**1b**	20	99	98.5	25	*(S)*-(−)
5	**1c**	20[g]	70	95	≈0	–
6	**1d**	20[h]	92	94	8	*(R)*-(−)
7	**1e**	20	87	96	37	*(R)*-(−)
8	**1f**	20	91	93	39	*(R)*-(−)
9	**1g**	20	79	95	3	*(R)*-(−)
10	**1h**	20	97	88	4	*(R)*-(−)
11	**2a**	0	91	85	62	*(R)*-(−)
12	**2b**	20	86	96	12	*(S)*-(−)
13	**3a**	20[i]	42	100	≈0	–
14	**3b**	20[h]	52	100	≈0	–
15	**4**	20	87	97	64	*(S)*-(−)
16	**4**	-21	95	97	65	*(S)*-(−)

[a] Reaction conditions (unless otherwise stated): Fe complex (0.002 mmol), CH_3CN (1 mL), sulfide (0.1 mmol), PhIO (0.11 mmol), 150 rpm stirring for 2 h. [b] Conversion = ([RSOR′] + [RSO_2R'])/([RSR′] + [RSOR′] + [RSO_2R']). [c] Selectivity = [RSOR′]/([RSOR′] + [RSO_2R']). [d] Determined by ^1H NMR spectroscopy with the [Eu(hfc)$_3$] chiral shift reagent in CCl_4. [e] Determined by comparing [Eu(hfc)$_3$]-shifted NMR patterns of sulfoxides with those of the sulfoxides with known absolute configuration. [f] Fe (0.0001 mmol), solvent (0.4 mL), substrate (0.05 mmol; thus substrate/catalyst ratio of 500), reaction time 7 h. [g] Reaction time 4 h. [h] Overnight. [i] Reaction time 6 h.

and **2a** display nearly equal enantioselectivities (to afford sulfoxides with opposite absolute configurations), catalysts **1e** and **2b** gave rather different results (Table 1, entries 7 and 13, respectively). Interestingly, the use of (*R*)-(+)-2,2′-diamino-1,1′-binaphthalene as the chiral diamine (for the synthesis of complexes **3**) does not seem to be fruitful: the resulting catalysts did not demonstrate measurable enantioselectivities (Table 1, entries 13 and 14). In all cases the oxidation occurred with reversal of the absolute configuration, that is, (*R*,*R*)-catalysts gave (*S*)-sulfoxides and vice versa. Interestingly, antiferromagnetically coupled binuclear iron(III) complex **4**[8] (see Supporting Information), prepared by dimerization of catalyst **1a**, appeared to be a better catalyst than the parent monomer (Table 1, entries 15 and 16).

The other points of major interest were the elucidation of the substituent effects (in the substrates) and the reaction temperature on the oxidation enantioselectivity. One can see that reduction of the temperature from 20 to 0 °C resulted in an increase of enantioselectivity of $PhSCH_2Ph$ oxidation over complex **1a** (Table 1, cf. entries 1 and 2). Similar data obtained with other substrates are collected in Table 2. *p*-BrPhSMe was oxidized with lower *ee*'s than $PhSCH_2Ph$; however, one can see that introduction of an electron-withdrawing substituents in the aromatic ring of PhSMe raised the enantioselectivity (Table 2, cf. entries 1, 2 and 5). *p*-NO_2PhSMe gave more encouraging results, the oxidation *ee* demonstrating weaker dependence on the reaction temperature (Table 2, entries 5–7). Complexes **1e** and **1g** did not demonstrate such high *ee*s and conversions with *p*-NO_2PhSMe; an experiment with complex **2a** (at substrate/catalyst ratio of 1000) showed very low conversion even after 20 h stirring at room temperature (Table 2, entry 9). Complex **4** gave quite nice results with both $PhSCH_2Ph$ (Table 1, entries 15 and 16) and *p*-NO_2PhSMe (Table 2, entry 10). Interestingly, PhS*i*Pr appeared to be a good substrate for enantioselective oxidation over complex **1a** (Table 2, entry 11). Thus, it is apparent that introduction of both electron-withdrawing and bulky substituents in the structure of the sulfide increases the oxidation selectivity.

The nature of the oxidizing species: The first data on the nature of the oxygen-transferring species were obtained in the preceding communication.[7b] In particular, we ruled out the intermediacy of the oxoferryl π radical cation[7a] $[Fe^{IV}{=}O(Cl)(salen)]^{\bullet+}$ similar to previously detected $[Fe^{IV}{=}O(porphyrin)]^{\bullet+}$ in iron–porphyrin/iodosylarene systems.[9] First of all, oxoferryl π radical cations are expected to have typical $S=3/2$ spectra with resonances at $g_{eff}\approx4$ and $g_{eff}\approx2$.[9a–c] However, treatment of complexes **1a** and **2a** with PhIO and *m*-CPBA (which had been reported to generate oxoferrylporphyrin π radical cations[9]) did not lead to formation of any $S=3/2$-type spectra. Secondly, according to the ^{1}H NMR spectra (Figure 1), the interaction of complex **1a** with iodosylbenzene at −20 °C resulted in the formation of a new iron(III) species that was identified as the $[Fe^{III}Cl(PhIO)(salen)]$ complex (**1a**(PhIO)).[7b]

This new species **1a**(PhIO) was obtained in concentrations up to 40% of the total observable Fe^{III} concentration (Figure 1a); no PhIO was observed at this stage of the interaction. The addition of the substrate (Figure 1b–d) and warming the sample to 0 °C lead to the simultaneous formation of the corresponding sulfoxide (peak at $\delta=2.73$ ppm) and PhI (peak at $\delta=7.71$ ppm), the concentration of **1a**-(PhIO) decreasing. The latter can be restored by shaking with additional PhIO (Figure 1e). Thus, we proposed the following reaction cycle for the reported catalytic system (Scheme 2), including the Lewis acid activation of iodosylbenzene to form the oxygen-transferring species **1a**-(PhIO).[9d,e,10]

To corroborate our conclusions on the nature of the active intermediate, we applied the approach previously exploited by others;[9e,10b,d] namely, different iodosylarenes (ArIO = PhIO, *p*-NO_2PhIO, MesIO) were used as terminal oxidants in stereoselective oxidations. Indeed, if the oxygen-transferring species did not contain the coordinated iodozylarene (e.g., $[Fe^{IV}{=}O(Cl)(salen)]^{\bullet+}$ or $[Fe^{V}{=}O(Cl)(salen)]$),[7a] the oxidation chemo- and stereoselectivities would be independent of the particular terminal oxidant taken. Otherwise, the selectivities should vary with different iodosylarenes in asymmetric oxidation of sulfides catalyzed by iron–salen complexes of the families **1**–**4**. The results obtained are presented in Table 3.

The oxidation of $PhSCH_2Ph$ mediated by complex **1a** displayed rather weak dependence on the iodosylarenes: the enantioselectivities were in the

Table 2. Enantioselective oxidation of sulfides with PhIO catalyzed by iron complexes **1**–**2**, **4**.[a]

	Catalyst	*T* [°C]	Sulfide	Conversion [%][b]	Selectivity [%][c]	*ee* [%][d]	Config.[e]
1	**1a**	0	PhSMe	96	83	22	*(S)*-(−)
2	**1a**	0	*p*-BrPhSMe	95	96	41	*(S)*-(−)
3	**2a**	0	*p*-BrPhSMe	90	90	43	*(R)*-(−)
4	**1a**	20	*p*-NO_2PhSMe	90	95	58	*(S)*-(−)
5	**1a**	0	*p*-NO_2PhSMe	82	96	59	*(S)*-(−)
6	**1a**	−21[f]	*p*-NO_2PhSMe	64	97	62	*(S)*-(−)
7	**1e**	20	*p*-NO_2PhSMe	66	94	26	*(R)*-(−)
8	**1g**	20	*p*-NO_2PhSMe	49	97	7	*(R)*-(−)
9	**2a**	20[g]	*p*-NO_2PhSMe	10	≈100	53	*(R)*-(−)
10	**4**	0	*p*-NO_2PhSMe	86	96	66	*(S)*-(−)
11	**1a**	20	PhS*i*Pr	≈100	93	69	*(S)*-(−)

[a] Reaction conditions (unless otherwise stated): Fe complex (0.002 mmol), CH_3CN (1 mL), sulfide (0.1 mmol), PhIO (0.11 mmol), 150 rpm stirring for 2 h. [b] Conversion = ([RSOR′]+[RSO_2R′])/([RSR′]+[RSOR′]+[RSO_2R′]).[c] Selectivity = [RSOR′]/([RSOR′]+[RSO_2R′]). [d] Determined by ^{1}H NMR spectroscopy with [Eu(hfc)$_3$] chiral shift reagent in CCl_4. [e] Determined by comparing [Eu(hfc)$_3$]-shifted NMR patterns of sulfoxides with those of the sulfoxides with known absolute configuration. [f] Reaction time 4 h. [g] Reaction conditions: Fe complex (0.0001 mmol), CH_3CN (0.5 mL), sulfide (0.1 mmol), PhIO (0.11 mmol), 150 rpm stirring for 20 h.

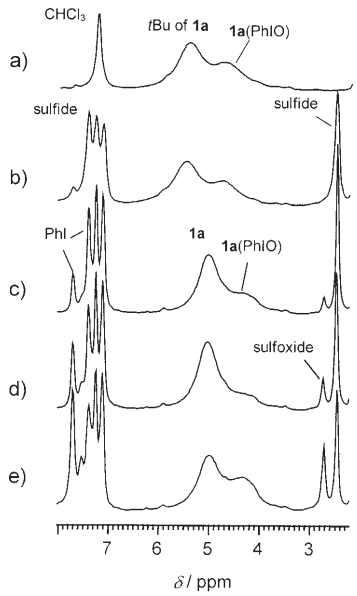
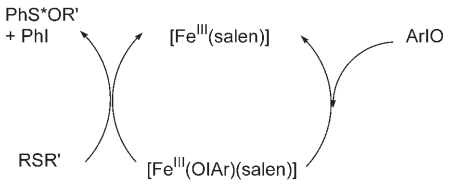


Figure 1. ^{1}H NMR spectra (in the range of 8 to 2 ppm) of a) complex **1a** (0.02 M in $CDCl_3$) shaken for 5 min with 2 equiv of PhIO at cooling, −20 °C; b) after addition of 5 equiv of *p*-Br-PhSMe; c) after warming up to 0 °C; d) after storing for 5 min at 0 °C C; e) after shaking with an additional 1 equiv of PhIO without cooling, recorded at 0 °C. In the range of 7.1 to 7.6 ppm, ^{1}H resonances of aromatic protons of PhI, sulfide, and sulfoxide are overlapped. From reference [7b].



Scheme 2. Proposed catalytic cycle for iron-catalyzed asymmetric oxidation of sulfides.

range of 55–63 % *ee* for the oxidation of $PhSCH_2Ph$ (Table 3, entries 1–3) and 56 to 60 % *ee* for the oxidation of *p*-NO_2PhSMe (Table 3, entries 4–6). The most spectacular difference was observed in the case of *p*-NO_2PhIO, which showed very low conversion and very high chemoselectivity in the oxidation of *p*-NO_2PhSO (Table 3, entry 5). However, when complex **1e** was chosen as the catalyst, the observed enantioselectivity dependence on the iodosylarene was more pronounced (Table 3, entries 7–12). In all cases, *p*-NO_2PhIO gave the lowest *ee*'s and conversions, whereas both PhIO and MesIO demonstrated significantly higher conversions and *ee*'s. It was found that the oxidation of PhS*i*Pr catalyzed by **1a** was more sensitive to the nature of iodosylarene (Table 3, entries 13 and 14). Namely, the oxidation with MesIO resulted in the sulfoxide with much higher chemo- and stereoselectivity. A similar *ee* was achieved with **4** as the catalyst (Table 3, entry 15).[11] Decreasing the oxidation temperature to −21 °C led to the increase of enantioselectivity: the highest *ee* of 84 % was observed in the oxidation of PhS*i*Pr with MesIO catalyzed by **1a** (Table 3, entry 16).

The dependence of the observed enantioselectivities confirm unambiguously the key role of the observed intermediates of the type $[Fe^{III}(ArIO)(salen)]$ in the stereoselective oxidation of thioethers. In most cases, introduction of the electron-withdrawing substituent (*p*-NO_2) in iodosylbenzene resulted in lower *ee*'s and lower conversions (the latter could be explained by the lower reactivity of the *p*-NO_2PhIO). The use of the more bulky iodosylmesitylene in most cases resulted in higher *ee*'s (relative to PhIO).

We mark that the oxidation enantioselectivity can probably be further improved by introducing additional elements of chirality into 3,3′-positions of the salicylidene rings of salen ligands to obtain the so-called second-generation salen complexes.[12]

Possible impact of kinetic resolution: We evaluated the possible role of kinetic resolution that was found to be the case in other sulfoxidation systems.[6c,13a–d] In a particular experiment, $PhSOCH_2Ph$ (42.6 μmol) was oxidized by MesIO (21.3 μmol) over complex **1a** (20 °C, reaction time 1.5 h, [SO] concentration 0.061 M). The resulting sulfone was obtained in 63 % yield (yield = 100 %·$[SO_2]/{}^1/_2([SO_2]+[SO])$), the remaining sulfoxide displaying *ee* of 9 % (*S* configura-

Table 3. Enantioselective oxidation of sulfides with different iodosylarenes catalyzed by iron(III) complexes.[a]

	Catalyst	*T* [°C]	Sulfide	ArIO	Conversion [%][b]	Selectivity [%][c]	*ee* [%][d]	Config.[e]
1	**1a**	20	$PhSCH_2Ph$	PhIO	92	91	55	*(S)*-(−)
2	**1a**	20	$PhSCH_2Ph$	*p*-NO_2PhIO	90	100	56	*(S)*-(−)
3	**1a**	20	$PhSCH_2Ph$	MesIO	93	98	63	*(S)*-(−)
4	**1a**	20	*p*-NO_2PhSMe	PhIO	90	95	58	*(S)*-(−)
5	**1a**	20	*p*-NO_2PhSMe	*p*-NO_2PhIO	42	100	56	*(S)*-(−)
6	**1a**	20	*p*-NO_2PhSMe	MesIO	75	84	60	*(S)*-(−)
7	**1e**	20	$PhSCH_2Ph$	PhIO	87	96	37	*(R)*-(−)
8	**1e**	20	$PhSCH_2Ph$	*p*-NO_2PhIO	60	100	18	*(R)*-(−)
9	**1e**	20	$PhSCH_2Ph$	MesIO	93	95	33	*(R)*-(−)
10	**1e**	20	*p*-NO_2PhSMe	PhIO	66	94	26	*(R)*-(−)
11	**1e**	20	*p*-NO_2PhSMe	*p*-NO_2PhIO	31	100	21	*(R)*-(−)
12	**1e**	20	*p*-NO_2PhSMe	MesIO	93	95	33	*(R)*-(−)
13	**1a**	20	PhS*i*Pr	PhIO	≈100	93	69	*(S)*-(−)
14	**1a**	20	PhS*i*Pr	MesIO	≈100	≈100	77	*(S)*-(−)
15	**4**	20	PhS*i*Pr	MesIO	94	97	77	*(S)*-(−)
16	**1a**	−21	PhS*i*Pr	MesIO	69	94	84	*(S)*-(−)

[a] Reaction conditions (unless otherwise stated): Fe complex (0.002 mmol), CH_3CN (1 mL), sulfide (0.1 mmol), ArIO (0.11 mmol), 150 rpm stirring for 2 h. [b] Conversion = ([RSOR′] + [RSO_2R′])/([RSR′] + [RSOR′] + [RSO_2R′]). [c] Selectivity = [RSOR′]/([RSOR′] + [RSO_2R′]). [d] Determined by ^{1}H NMR spectroscopy with [Eu(hfc)$_3$] chiral shift reagent in CCl_4. [e] Determined by comparing [Eu(hfc)$_3$]-shifted NMR patterns of sulfoxides with those of the sulfoxides with known absolute configuration.

tion). This corresponds to the stereoselection factor[13e] of 1.12 that could hardly exert significant impact on the enantioselectivity under the adopted optimal oxidation conditions. However, such a possibility was checked by the oxidation with differing amounts of the iodosylarene (Table 4). One can see that varying the amount of the oxidant results in significant differences in the conversion and selectivity, but does not measurably affect the oxidation enantioselectivity.

Table 4. Enantioselective oxidation of benzyl phenyl sulfide with MesIO catalyzed by iron complexes **1**–**3**.[a]

	Catalyst	T [°C]	Oxidant/ substrate	Conversion [%][b]	Selectivity [%][c]	*ee* [%][d]	Config.[e]
1	**1a**	20	32:50	59	98	64	*(S)*-(−)
2	**1a**	20	56:50	93	98	63	*(S)*-(−)
3	**1a**	20	80:50	100	87	63	*(S)*-(−)

[a] Reaction conditions (unless otherwise stated): Fe complex (0.002 mmol), CH_3CN (1 mL), sulfide (0.1 mmol), 150 rpm stirring for 2 h. [b] Conversion = ([RSOR′] + [RSO_2R'])/([RSR′] + [RSOR′] + [RSO_2R']). [c] Selectivity = [RSOR′]/([RSOR′] + [RSO_2R']). [d] Determined by ^{1}H NMR spectroscopy with [Eu(hfc)$_3$] chiral shift reagent in CCl_4. [e] Determined by comparing [Eu(hfc)$_3$]-shifted NMR patterns of sulfoxides with those of the sulfoxides with known absolute configuration.

Conclusion

In conclusion, we have presented a series of iron(III)–salen and related complexes capable of enantioselective oxidation of alkyl aryl sulfides with iodosylarenes as terminal oxidants. Highly enantioselective oxidation (up to 84% *ee*) can be performed with low catalyst loading (2.0–0.2 mol%). The enantioselectivity originates directly from the oxidation step, while under- or overoxidation has negligible effect on the observed *ee*'s. The influence of the ligand (electronic and steric effects of the substituents) and substrate structures of on the oxidation stereoselectivity has been investigated systematically. The active intermediate was detected by ^{1}H NMR spectroscopy and was shown to be a [Fe^{III}(ArIO)(salen)] complex. The key role of the intermediate of this type in the enantioselective sulfoxidations was confirmed by mechanistic studies with different iodosylarenes: the observed chemo- and enantioselectivities showed the dependence on the nature of the iodosylarene (used); a catalytic cycle is proposed.

Experimental Section

General methods: CCl_4 and CH_2Cl_2 (analytical grade) were stored over molecular sieves and used without further purification. Ethyl acetate and hexane (reagent grade) were used for column chromatography without purification. H_2O_2 was used as analytical grade 30% aqueous solution. Silica gel 40 (0.063–0.200 mm) for column chromatography was purchased from Merck. All other chemicals (diacetoxyiodo(benzene), mesityl iodide, *p*-nitroiodobenzene, sulfides, $CDCl_3$, *(R,R)*-(−)-*N,N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine, (1*R*,2*R*)-(−)-1,2-diaminocyclohexane, (*R*)-(−)-2,2′-diamino-1,1′-binaphthalene, (1*R*,2*R*)-(−)-diphenyl-1,2-ethanediamine etc.) were Aldrich, Lancaster, or Acros commercial reagents. Iodosylbenzene (PhIO) was prepared according to reference [14a] Iodosylmesitylene (MesIO) was synthesized according to the modified procedure in reference [14b] (see below), and *p*-NO_2PhIO was obtained in two stages (from *p*-NO_2PhI via *p*-NO_2PhICl_2) according to references [14c,d]. 2-Hydroxy-3-isopropyl-5-nitro-benzaldehyde was prepared according to reference [15a]; 3,5-dicumyl-2-hydroxybenzaldehyde, 3-phenyl-2-hydroxybenzaldehyde and 3-adamantyl-5-methyl-2-hydroxybenzaldehyde were prepared by formylation of the corresponding phenols by Casiraghi method.[15b] Complex **4** was prepared according to a modified procedure in reference [8b] (see below).

^{1}H NMR spectra were recorded on a Bruker DPX-250 spectrometer at 250.13 MHz, in 5 mm cylindrical glass tubes. Chemical shifts were referenced to added tetramethylsilane. Typical operation conditions for ^{1}H measurements were the following: spectral width 5000 Hz, spectrum accumulation frequency 0.5 Hz, number of scans 16–64, 2 μs radio-frequency pulse, 16K–32K data points. ^{1}H NMR spectra of paramagnetic complexes **1**–**4** were recorded with the following conditions: spectral width 125000 Hz, spectrum accumulation frequency 2 Hz, number of scans 1K–4K, 3 μs radio-frequency pulse, 64K data points (for ^{1}H NMR spectra of paramagnetic iron(III)–salen complexes see the Supporting Information).

Typical procedure for catalytic oxidation of sulfides: The Fe complex (**1**–**4**) (0.002 mmol) in CH_3CN (1 mL) was placed in a flask with magnetic stirrer, the temperature was stabilized (−21, 0, or 20°C), then sulfide (0.1 mmol) was added, followed by the oxidant (0.11 mmol of ArIO). The flask was capped and the mixture was stirred at 150 rpm for 2 h.

After the reaction was complete, the solvent was removed and the product was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate). Conversions and selectivities were calculated based on ^{1}H NMR measurements of the sulfide, sulfoxide, and sulfone relative concentrations. Selected ^{1}H NMR data (20°C, CCl_4/$CDCl_3$ 1:1): $\delta = 2.55$ (*p*-NO_2PhSCH_3), 2.77 (*p*-$NO_2PhSOCH_3$), 3.08 ppm (*p*-$NO_2PhSO_2CH_3$); selected ^{1}H NMR data (20°C, CCl_4): $\delta = 4.16$ ($PhSCH_2Ph$) 3.90 (m; $PhSOCH_2Ph$), 4.05 ppm ($PhSO_2CH_2Ph$); selected ^{1}H NMR data (20°C, CCl_4): $\delta = 3.30$ (m; $PhSCHMe_2$), 2.65 (m; $PhSOCHMe_2$), 3.01 ppm (m; $PhSO_2CHMe_2$); selected ^{1}H NMR data (20°C, CCl_4): $\delta = 2.45$ (*p*-$BrPhSCH_3$), 2.62 (*p*-$BrPhSOCH_3$), 2.94 (*p*-$BrPhSO_2CH_3$).[7b,13a]

The *ee*'s were measured by ^{1}H NMR spectra with [Eu(hfc)$_3$] chiral shift reagent in CCl_4. The absolute configuration was determined by comparing [Eu(hfc)$_3$]-shifted NMR patterns of sulfoxides with those of the sulfoxides with known absolute configuration (for details see the Supporting Information for reference [7b]).

Iodosylmesytilene MesIO: $NaBO_3 \cdot 4H_2O$ (10 equiv) was added slowly to a solution of mesityl iodide (4 mmol) in glacial acetic acid (40 mL) at 60°C, and the mixture was stirred for 4 h at this temperature. Then, volatiles were removed in vacuo, the residue was extracted with CH_2Cl_2 (2 × 20 mL), and the solvent was removed to afford a white residue, which was further hydrolyzed by NaOH for 1 h as detailed in reference [14a], washed with H_2O (2 × 10 mL) and CH_2Cl_2 (1 × 10 mL), and dried in vacuo.

Typical procedure of tetradentate Schiff bases syntheses: Tetradentate chiral ligands for complexes **1b**–**h**, **2b**, **3a**,**b** were prepared according to the following common procedure adopted from the literature:[16] the corresponding aldehyde (1.5 mmol) and diamine (0.6 mmol) were dissolved in dry methanol (10 mL; if necessary, $CHCl_3$ (5 mL) was added for better solubility of the reagents: this was the case while preparing the ligands for complexes **1c**, **1d**, **3a**, **3b**) and refluxed for 2–3 h. Then the mixtures were allowed to cool down to RT. If precipitation of the Schiff base was observed, the solid was filtered off, washed with hexane, and dried in vacuo. Otherwise, the reaction mixture was evaporated in the flow of air and the tetradentate Schiff base was separated and purified by column chromatography on SiO_2 (eluent: hexane/ethyl acetate).

Complexes 1a and 2a: These compounds were prepared either following the procedure given in reference [8b] or as follows: $Fe(OAc)_3$ (1.2 mmol) was dissolved in ethanol (20 mL) and added to the solution of the Schiff base ligand (1 mmol) in toluene (20 mL) at 80°C. After refluxing for 1 h, a saturated aqueous solution of NaCl (10 mL) was added under stirring

and the mixture was allowed to cool down to room temperature. The mixture was washed with water (2×40 mL) and dried over $CaSO_4$. Volatiles were removed and the desired complex was crystallized from CH_3CN/Et_2O mixture. ^1H spectra of complexes **1a** and **1b** synthesized according to this procedure and according to the literature[8b] were identical.

Complexes 1b, 1h: $FeCl_3$ (0.55 mmol) was added to the ligand (0.5 mmol) in MeOH (10 mL); the mixture was refluxed for 2 h and then stirred at room temperature overnight. The solid formed was filtered off and dried in vacuo.

Complexes 1c, 1d, 1f: $FeCl_3$ (0.55 mmol) was added to the ligand (0.5 mmol) in $MeOH/CH_2Cl_2$ mixture (1:1, 10 mL); the mixture was stirred at room temperature for 8 h and then stored at −10 °C overnight. The solid formed was filtered off and dried in vacuo.

Complexes 1e, 1g, 2b: $FeCl_3$ (0.55 mmol) was added to the ligand (0.5 mmol) in $MeOH/CH_2Cl_2$ mixture (2:1, 10 mL); the mixture was refluxed 2 h and stirred at room temperature for 8 h. The reaction mixture was concentrated to 1 mL and the target product was purified by column chromatography on SiO_2 (eluent: hexane/ethyl acetate).

Complexes 3a, 3b: $FeCl_3$ (0.50 mmol) was added to the ligand (0.5 mmol) in $MeOH/CH_2Cl_2$ mixture (1:1, 10 mL); the mixture was refluxed for 2 h, was concentrated to 5 mL at boiling temperature, and was evaporated at room temperature in vacuo. The target products were separated on a column with SiO_2 (eluent: hexane/ethyl acetate).

Complex 4: Water (1 drop) and Et_2NH (0.2 mmol, 20 μL) were added to a solution of complex **1a** (0.2 mmol) in CH_2Cl_2 (3 mL) and the mixture was stirred at room temperature overnight. The solution was washed with water (5 mL) and dried over $CaSO_4$, and volatiles were removed. The residue was extracted with CH_3CN, and the extract was diluted with THF and Et_2O, and allowed to evaporate slowly at room temperature to give crystals of **4**.

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