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Syntheses of manganese and iron tetraspirobifluorene porphyrins as new catalysts for oxidation of alkenes by hydrogen peroxide and iodosylbenzene

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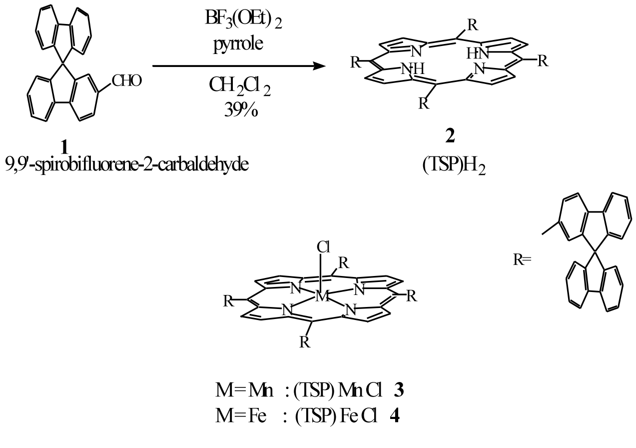
Abstract—The condensation of pyrrole with 9,9′-spirobifluorene aldehyde yields new the 5,10,15,20-tetra(spirobifluorene) porphyrins; epoxidation of cyclooctene and styrene derivatives catalyzed by the manganese and iron complexes is reported using H_2O_2 and PhIO as oxygen atom donors. © 2003 Elsevier Science Ltd. All rights reserved.

The synthetic versatility of the porphyrins makes them especially attractive for the construction of enzyme analogues through the elaboration of superstructure of the macrocycle.[1,2] A similar approach in concept involves replacement of the protein structure by an organic polymer.[3,4] In principle, we think that spiroporphyrins will be very promising and nice precursors to create heterogeneous catalysts for shape selective oxidation since metalloporphyrins have been used as catalysts in a variety of reactions including olefin epoxidation and alkane hydroxylation.[5,6]



Scheme 1.

Spirobifluorene compounds consist of two mutually perpendicular π-systems connected via a common insulating tetracoordinate atom. In addition to model receptors for chiral recognition,[7] spiro derivatives provide a potentially useful stereochemistry that makes the molecules suitable for interconnection in future molecular devices.[8] Three-dimensional polymers can also be prepared by anodic oxidation of spirobifluorenes.[9,10] Herein we report the efficient synthesis of tetraspirobifluorene porphyrin and preliminary catalytic properties of the manganese and iron complexes of this new ligand. The test reactions used are the epoxidation of styrene derivatives and cyclooctene using H_2O_2 and PhIO as oxygen atom donors.

Following the Lindsey procedure,[11] pyrrole reacts with the desired aromatic aldehydes to form tetrasubstituted porphyrins. The mono-aromatic aldehyde **1** derivative is synthesized (Scheme 1) by treatment of 9,9′-spirobifluorene with $TiCl_4$ and Cl_2CHOCH_3 by a modified procedure of that previously reported by Mattiello[12]. Thus porphyrin **2**, illustrated in the upper scheme, was prepared from the corresponding 9,9′-spirobifluorene aldehyde and pyrrole in 39% yields.

In a typical experimental procedure, pyrrole (524 μL, 7.5 mmol) and 9,9′-spirobifluorene-2-carbaldehyde (2.5 g, 7.5 mmol) dissolved in 725 mL of distilled dichloromethane were stirred in the presence of 197 μL of $BF_3(OEt)_2$ (48%) for 3.5 h. After the addition of chloranil (1.54 g, 6.25 mmol), and a further 1 h stirring, several drops of triethylamine were added. The solvent

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was removed and the residue was purified by two subsequent column chromatographies on silica gel: first dichloromethane and then 3:1 dichloromethane: cyclohexane. The crystallization in toluene gave the 5,10,15,20-tetra(spirobifluorene)porphyrin (called tetraspiroporphyrin for simplification, $TSPH_2$) in 39% yield.

Although atropisomers are not expected when the *meso*-aryl groups are substituted in the *meta* position, there are few examples such as porphyrin carborane system,[13] *meta*-aryl fullerene porphyrins[14,15] and multimetallic porphyrin monomers.[16] Thus the large size of the 9,9′-spirobifluorene group may also hinder rotation around the C_{meso}–C_{aryl} bond.[17] Actually, we previously observed such a situation with dispiroporphyrins.[17] Indeed, the ^1H NMR spectrum of compound **2** displayed several peaks for the pyrrole resonances between 8.74 and 8.68 ppm, and four resonances at highfield position (−2.43, −2.52, −2.54 and −2.56 ppm) assigned to internal NH. For example, the presence of four atropisomers in statistical proportion was observed by ^1H NMR after ruthenium complexion of $(TSP)H_2$ **2**.[18]

For the purpose of catalysis, the manganese $(TSP)Mn^{III}Cl$ **3** and $(TSP)Fe^{III}Cl$ **4** complexes were prepared by treatment of **2** with $MnCl_2$ (30 h, 83% yield), and $FeCl_2$ (2 h, 80% yield), respectively, at room temperature, following a method recently reported.[19] Table 1 shows the results obtained for the oxidation of styrene and cyclooctene by H_2O_2 catalyzed by Mn(III)-*meso*-tetraspiroporphyrin **3**, two Mn(III)-*meso*-tetraarylporphyrins bearing no halogen substituents, (TPP)MnCl and (TMP)MnCl, and two halogenated porphyrins, with Cl substituents at the *ortho* positions of the *meso*-aryl rings, (TDCPP)MnCl, and F substituents at all positions of the *meso*-phenyl rings, (TFPP)MnCl, for comparison. Reactions were performed over a 2 h period at 20°C with the molar ratio: catalyst/oxidant/substrate = 1:20:800 in a CH_2Cl_2: CH_3CN (1:1) mixture. In all reactions, was used a co-catalyst (imidazole) as it has been shown to have a beneficial effect.[20] The epoxidation reaction was monitored by gas chromatography (GC) and styrene epoxide (or cyclooctene epoxide) was found to be the major product in all cases, but aldehydes were also detected as byproducts and identified by GC–MS. The yields obtained are upper than those previously reported for (TFPP)MnCl but lower than (TDCPP)MnCl.[20] Under these conditions (condition A), half of (TPP)MnCl was destroyed after 2 h of reaction whereas (TSP)MnCl **3** is found almost unchanged as Mn-*meso*-tetraarylporphyrins bearing *ortho* substituents on phenyl groups. This may also be related to the absence of aliphatic C–H bonds on the spiro groups.

Table 1. Influence of the nature of porphyrin catalyst on the oxidation of cyclooctene (C) or styrene (S) by hydrogen peroxide in the presence of imidazole[a]

Catalyst	Alkene	Yield (%)[b]	Catalyst destruction (%)
(TSP)MnCl	C	70	<5
	S	57	<5
(TPP)MnCl	C	46	50
	S	30	50
(TMP)MnCl	C	45	<5
	S	40	<5
(TFPP)MnCl	C	58	<5
	S	43	<5
(TDCPP)MnCl	C	97	<5
	S	93	<5

[a] *Condition A*: Using an excess of alkene (40 equiv. versus hydrogen peroxide): addition of hydrogen peroxide (35% wt in water, 20 equiv. relative to catalyst) to a mixture of (P)MnCl/imidazole/alkene (1/10/800) in dichloromethane/acetonitrile (1:1) under anaerobic conditions. Concentration of (P)MnCl = 3 mM. The reaction was monitored by gas chromatography using a CP-Chirasil-Dex column.

[b] Yield based on starting olefin after 2 h at room temperature (unchanged after 12 h).

Table 2. Epoxidation of alkenes by Mn or Fe(TSP)Cl using iodosylbenzene or hydrogen peroxide

Catalyst	Oxidant	Alkene	Yield (%)[a]	Epoxide aldehyde
(TSP)MnCl[b]	H_2O_2	Cyclooctene	70	–
		Styrene	57	1.3
		4-Chlorostyrene	95	3.1
(TSP)MnCl[c]	PhIO	Cyclooctene	96	–
		Styrene	75	1.9
		4-Chlorostyrene	73	4
(TSP)FeCl[d]	PhIO	Cyclooctene	67	–
		Styrene	65	1.5
		4-Chlorostyrene	98	3

[a] Yield based on starting olefin after 1 h (for experiments with PHIO) and 2 h (for experiments with H_2O_2) at room temperature.

[b] *Condition A* (see Table 1).

[c] *Condition B*: Using an excess of alkene (10 equiv. versus iodosylbenzene): addition of iodosylbenzene (100 equiv. relative to catalyst) to a mixture of (P)MnCl/imidazole/alkene (1/10/1000) in dichloromethane under anaerobic conditions. Concentration of (P)MnCl = 0.5 mM.

[d] Condition B without imidazole.

For the novel $(TSP)H_2$ **2**, the investigation was extended to the epoxidation of different aromatic and aliphatic alkenes with iodosylbenzene as oxidant using both (TSP)MnCl **3** and (TSP)FeCl **4**. The results obtained are shown in Table 2. In the presence of excess of alkene, the oxidation yield based on starting olefin consumed varied from 67 to about 100% with both manganese and iron complexes (**3** and **4**). There is only a small decrease in epoxide yield when the olefin, is not in excess with respect to the oxidant. Thus the yield decreases from 75 to 61% with (TSP)MnCl/PhIO and from 65 to 50% with (TSP)FeCl/PhIO. It should be mentioned, however, that formation of aldehydes was observed with 20–40% yield, in some cases.

Cyclic voltammetry (CH_2Cl_2, 0.2 M Bu_4NPF_6 versus SCE) was also used to characterize the two complexes (TSP)MnCl **3** and (TSP)FeCl **4**. The ring- and metal-centered oxidations of **3** ($E_{1/2} = 1.05$ and 1.52 V) and **4** (1.01 and 1.50 V) are slightly lower than their (TPP)MnCl (1.16 and 1.55 V) and (TPP)FeCl (1.24 and 1.55 V) analogs.[21] As established also by cyclic voltammetry, the two compounds **3** and **4** undergo a third reversible one-electron oxidation of the fluorene group at 1.76 V leading to the formation of π-cation radicals. This last behavior was previously observed with organic 9,9′-spirobifluorene monomer before electropolymerization.[9]

In conclusion, we have developed new efficient syntheses of free base tetraspiroporphyrin **2** with high yield[22] and demonstrated the effectiveness and the resistance of the $Mn^{III}Cl$ and $Fe^{III}Cl$ derivatives as catalysts for alkene epoxidation. Detailed alkene epoxidation employing heterogenized metalloporphyrin catalysts after electropolymerization of these precursors will be reported in due course.

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22. *Spectroscopic data for selected compounds*:
    9,9′-Spirobifluorene-2-carbaldehyde ***1***: ^1H NMR (300 MHz, $CDCl_3$): δ 9.84 (CHO, s, 1H), 8.04 (dd, 1H), 7.96 (ddd, 1H), 7.94 (dd, 1H), 7.91 (ddd, 2H), 7.47 (td, 1H), 7.43 (td, 2H), 7.30 (sdd, 1H), 7.22 (td, 1H), 7.14 (td, 2H), 6.82 (ddd, 1H), 6.74 (ddd, 2H); ^{13}C NMR ($CDCl_3$): δ 191.6 (C=O), 150, 149.7, 147.8, 147.4, 141.8, 140.1, 135.9, 130.2, 129.5, 128, 127.9, 125.2, 124.3, 124.3, 123.8, 121.1, 120.3, 120.2 (C aromatic), 65.6 (C_9); FAB MS ($M = C_{26}H_{16}O)^{\bullet+}$: 344.1199; UV–vis ($CH_2Cl_2$): $\lambda_{max/nm}$ (log ε): 328 (4.08), 303 (4.38), 292 (4.32), 282 (4.31), 225 (4.59); mp 209°C.
    (TSP)H$_2$ ***2***: ^1H NMR (500 MHz, toluene-d_8): δ 8.69 (*H*-β-pyrrole, m, 8H), 8.1 (t, 1H), 8.04 (d, 2H), 7.95–7.86 (m, 11H), 7.6–7.54 (m, 14H), 7.36 (t, 5H), 7.15–7.03 (m, 9H), 7.21 (t, 5H), 6.96 (m, 9H), 6.78 (d, 2H), 6.75 (d, 2H); FAB MS ($M = C_{120}H_{70}N_4+H)^+$: 1567.5600; UV–vis ($CH_2Cl_2$): $\lambda_{max/nm}$ (log ε): 652 (3.44), 594 (3.42), 556 (3.84), 520 (3.98), 427 (5.39), 342 (4.07), 309 (4.53), 297 (4.5), 228 (5.21).
    (TSP)Mn^{III}Cl ***3***: ESI MS ($M = C_{120}H_{68}ClN_4Mn-Cl)^+$: 1620.4874; UV–vis ($CH_2Cl_2$): $\lambda_{max/nm}$ (log ε): 625 (4.11), 587 (3.92), 481 (5.04), 407 (4.67), 382 (4.67), 336 (4.63), 309 (4.79), 297 (4.74), 228 (5.21).
    (TSP)Fe^{III}Cl ***4***: ^1H NMR (300 MHz, $CDCl_3$): δ 80.8 (*H*-β-pyrrole, m br, 8H), 8.81–6.66 (*H*-9,9′-spirobifluorene, m, 60H); FAB MS ($M = C_{120}H_{68}ClFeN_4)^{\bullet+}$: 1656.4408; UV–vis ($CH_2Cl_2$): $\lambda_{max/nm}$ (log ε): 523 (3.29), 511 (3.88), 426 (4.84), 335 (4.42), 309 (4.61), 297 (4.56), 228 (4.98).