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Cationic manganese(III) porphyrins bound to a novel bis-functionalised silica as catalysts for hydrocarbons oxygenation by iodosylbenzene and hydrogen peroxide

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Abstract

The cationic manganese porphyrins: manganese(III) 5,10,15-tris(2,6-dichlorophenyl)-20-(4-*N*-methylpyridyl)porphyrin ([Mn{M(4-*N*-MePy)TDCPP}]$^{2+}$), 5,10,15,20-tetra(2,3,5,6-tetrafluoro-4-trimethylammoniumphenyl)porphyrin ([Mn(TF4TMAPP)]$^{5+}$) and 5,10,15,20-tetra(4-*N*-methylpyridyl)porphyrin ([Mn{T(4-*N*-MePy)P}]$^{5+}$) supported on silica modified with propylimidazole (IPG), sulfonatophenyl (SiSO$_3^-$) and both propylimidazole and sulfonatophenyl (SiSO$_3^-$(IPG)) have been studied as catalysts in the epoxidation of (*Z*)-cyclooctene and oxidation of cyclohexane. High yields of products were obtained using PhIO as oxidant without leaching, except for the IPG, of the catalyst from the surface of the support. The catalysts also have been used with H_2O_2 in the epoxidation of (*Z*)-cyclooctene with and without a co-catalyst (imidazole or ammonium acetate). The best catalyst [Mn{T(F4TMAPP)}]-SiSO$_3$(IPG) achieved almost 200 turnovers of the product *cis*-epoxycyclooctane using ammonium acetate as co-catalyst. The analogous homogeneous systems have been studied for comparison, but they did not reach the same efficiency. With these studies the two-fold role of imidazole in oxygenations of hydrocarbons by H_2O_2 and Mn(III) porphyrins was confirmed. The characterisation of supported metalloporphyrins by UV–VIS spectroscopy is reported too. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Manganese(III) porphyrin; Hydrocarbons oxygenation; Role of co-catalyst; Bis-functional support; Hydrogen peroxide

1. Introduction

In the search of versatile catalytic systems that mimic the action of cytochrome P-450-dependent monooxygenases, some synthetic metalloporphyrins have been found to be highly efficient homogeneous catalysts for alkene epoxidation and alkane hydroxylation, using oxygen atom donors such as iodosylbenzene (PhIO), HSO_5^- or H_2O_2. However, these homogeneous catalysts have some drawbacks: (i) they can be easily destroyed during the reaction and (ii) it is not easy to recover the catalyst at the end of the reaction for re-use [1–3].

In recent publications it has been argued that these limitations might be avoided by binding the metalloporphyrins to solid materials [4]. The support can also provide steric and electronic effects, which, in some respects, are analogous to the influence of the protein matrix of hemoproteins [5,6]. There are reports using metalloporphyrins, bound to silica [7], ion exchange resins [8] and clays [9] as catalysts in reactions of hydrocarbons oxygenation by PhIO with some systems reaching high yields of products and improved regioselectivity [9]. Within this context it would be

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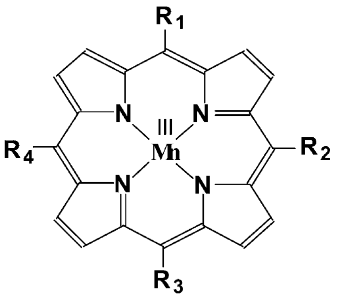
interesting to extend the applications of these supported catalysts to include the use of the cheap and clean oxidant H_2O_2 [10–12]. In this respect it is important to promote the heterolytic cleavage of the O–O bond of H_2O_2 at the expense of its homolysis. In solution this can be achieved with a co-catalyst (commonly a heterocyclic nitrogen base [13] or an ammonium salt, such as ammonium acetate [14] or a combination of a carboxylic acid and a heterocyclic base [15]) added to the reaction. The role of the co-catalyst in such systems is to facilitate the formation of the active oxygen species Mn(V)=O from the reaction of Mn(III) porphyrin with H_2O_2 [13].

This paper describes the development of catalytic systems based on a silica support modified with two functional groups; propylimidazole, to act as a ligand to the Mn(III) and an acid/base co-catalyst, and sulfonatophenyl groups, to anchor cationic metalloporphyrins to the support by electrostatic interactions. The catalysts used were $[Mn\{M(4\text{-}N\text{-}MePy)TDCPP\}]^{2+}$, $[Mn\{T(F4TMAPP)\}]^{5+}$ and $[Mn\{T(4\text{-}N\text{-}MePy)P\}]^{5+}$ (Fig. 1). These were bound to supports modified with the two groups described above and, for control experiments, to supports with only propylimidazole (IPG) or only sulfonatophenyl groups ($SiSO_3^-$). These catalysts were used for (*Z*)-cyclooctene epoxidation and the hydroxylation of cyclohexane using PhIO and for the epoxidation of (*Z*)-cyclooctene with H_2O_2 as the oxygen donor.

2. Experimental

2.1. Materials

$[Mn\{T(4\text{-}N\text{-}MePy)P\}]Cl_5$ was obtained from Midcentury. All solvents and reagents were of commercial grade unless otherwise stated and were purchased from Merck, Fluka and Aldrich. Dichloromethane (DCM), dichloroethane (DCE), methanol (MeOH) and acetonitrile (ACN) HPLC grade were used as received. Cyclohexane and (*Z*)-cyclooctene were purified by column chromatography on basic alumina prior to use and their purities were checked by gas chromatographic analysis. Hydrogen peroxide (H_2O_2 30% in H_2O, Fluka) was stored at 5°C and checked



R_1=R_2=R_3	R_4	$Mn^{III}P$
2,6-dichlorophenyl	4-N-methylpyridyl	$[Mn\{M(4\text{-}N\text{-}MePy)TDCPP\}]^{2+}$
R_1=R_2=R_3=R_4=		
Tetrafluoro-4-trimethylammonium		$[Mn(TF4TMAPP)]^{5+}$
4-N-methypyridyl		$[Mn(T(4\text{-}N\text{-}Me)PyP)]^{5+}$

Fig. 1. Synthetic metalloporphyrins.

by titration every 3 months [16]. Iodosylbenzene was prepared as described previously [17]. Samples were stored in a freezer and analysed every 6 months by iodometric assay.

2.1.1. Manganese(III) porphyrins

2.1.1.1. [Mn{M(4-N-MePy)TDCPP}]$^{2+}$. The synthesis of the M(4-*N*-Py)TDCPPH$_2$ was carried out according to previously reported procedure [18]. This compound was characterised by UV–VIS spectroscopy, thin layer chromatography (TLC) on silica gel, FAB MS and ^{1}H NMR spectroscopy confirming the structure and the purity of the porphyrin. Manganese insertion into M(4-*N*-Py)TDCPPH$_2$ was achieved by heating the free-base porphyrin and $MnCl_2 \cdot 4H_2O$ at reflux in *N,N*-dimethylformamide (DMF) [19]. At the end of the reaction, the solvent was removed under vacuum and the Mn porphyrin obtained was separated from the free-base by column chromatography on alumina. The separation was monitored by UV–VIS spectroscopy and by TLC on alumina. The Mn porphyrin obtained (80% yield) gave a single spot by TLC (3%, v/v MeOH/DCM).

[Mn{M(4-*N*-Py)TDCPP]$^+$ was methylated by reaction with a large excess of CH_3I in DMF at room temperature, under argon [20]. The unreacted CH_3I and DMF were removed under vacuum. The iodide anion was exchanged quantitatively for chloride using a Dowex 1 × 2-200 1-chloride ion exchange resin with 1%, v/v H_2O/MeOH as eluent. The product gave one spot by TLC on alumina (5%, v/v MeOH/DCM).

$$\text{UV–VIS}: \ (\text{DCM})\ \lambda_{\text{max}},\ \text{nm}\ (\varepsilon,\ \text{mol}^{-1}\,\text{l}\,\text{cm}^{-1})\ 368,\ 480\ (4.3\times10^4),\ 580$$

ESI MS: (*m/z* 924 [$M - \text{Cl}^-$]$^+$, calc. av. *m/z* 925), (*m/z* 889 [$M - 2\text{Cl}^-$]$^+$, calc. av. *m/z* 889), (*m/z* 445 [$M - 2\text{Cl}^-$]$^{2+}$, calc. av. *m/z* 444).

2.1.1.2. [Mn{T(F4TMAPP)}]$^{5+}$. [Mn{T(F4TMAPP)}]$^{5+}$ was obtained by a modification of the method of La et al. [21] as reported recently [22].

2.1.2. Solid supports

IPG was obtained previously [18] and had elemental analysis: C = 4.00%, H = 1.37% and N = 0.20%, which corresponds to 7.1×10^{-5} mol of propylimidazole/g of IPG. $SiSO_3^-$ was prepared by refluxing a suspension of silica gel with 2-(4-chlorosulfonylphenyl)ethyltrichlorosilane in toluene, according to the method of Leal et al. [23]. After hydrolysis and neutralisation with $NaHCO_3$, the excess of salt was eliminated after washing with H_2O, the material was dried under vacuum at 100°C for 8 h. Elemental analysis: C = 4.40%, H = 1.37% and S = 1.74% indicates that the material had 5.0×10^{-4} mol of sulfonatophenyl per gram of $SiSO_3^-$. $SiSO_3^-$(IPG) was prepared by refluxing a suspension of $SiSO_3^-$ with 3-chloropropyltrimethoxysilane and imidazole in toluene for 45 min. The solid obtained was dried under vacuum at 100°C. Elemental analysis: C = 6.73%, H = 1.40%, S = 1.60% and N = 0.82% shows that the material had 2.9×10^{-4} mol of propylimidazole/g of $SiSO_3^-$(IPG). A scheme representing the functionalisation of the silica is shown in the Fig. 2.

2.1.3. Preparation of supported manganese(III) porphyrins

Mn(III) porphyrin ligation to the solid supports was achieved by stirring a solution of Mn(III) porphyrin, [Mn{M(4-*N*-MePy)TDCPP}]Cl_2 in DCM, [Mn{T(F4TMAPP)}]$(PF_6)_5$ in ACN or [Mn{T(4-*N*-MePy)P}]Cl_5 in H_2O with a suspension of support for 10–20 min. The resulting catalysts [Mn{T(F4TMAPP)}]-support and [Mn{T(4-*N*-MePy)P}]-support were washed with MeOH and the [Mn{M(4-*N*-MePy)TDCPP}]-support was washed with DCE in a Soxhlet extractor overnight to remove unbound and weakly bound Mn(III) porphyrin. The solids were dried for 3 h at 100°C.

2.2. UV–VIS spectra

The UV–VIS spectra were recorded on a Hewlett-Packard 8453 Diode Array UV–VIS spectrophotometer. In the case of supported Mn(III) porphyrins, spectra were recorded in a 2 mm path length quartz cell, using a mixture of the supported catalyst and the support in a suspension in CCl_4.

2.3. ESI MS spectra and FAB MS

ESI and FAB MS spectra were recorded on a VG Analytical Autospec mass (University of York) spectrometer and ESI mass spectra were run by the

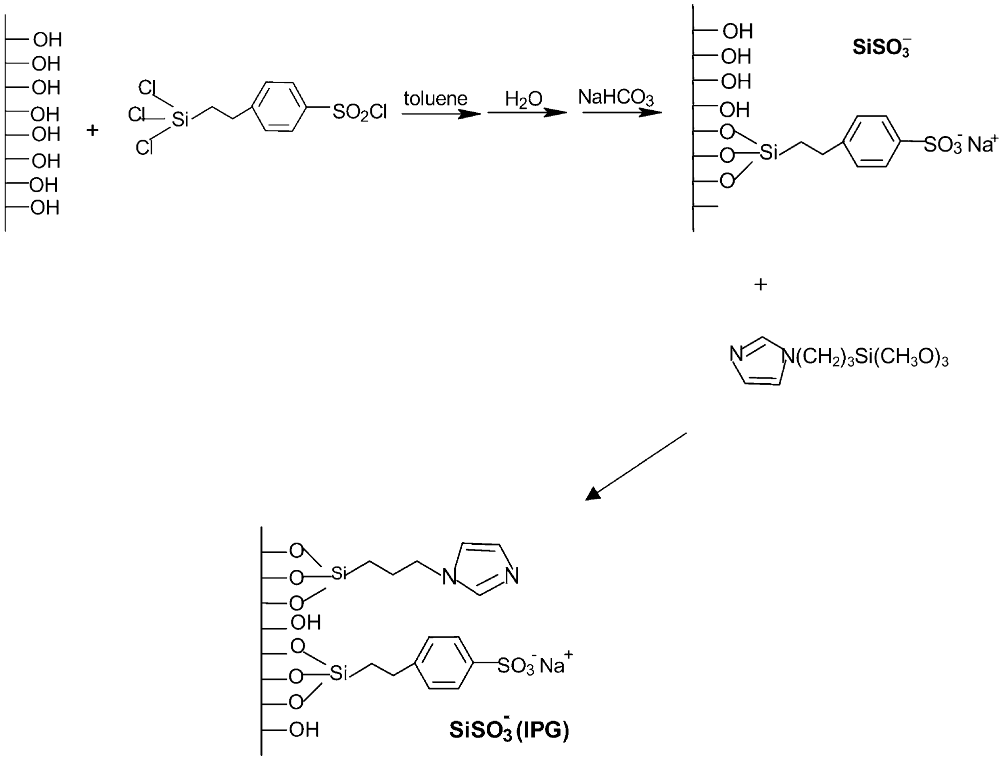


Fig. 2. Functionalisation of surface silica with sulfonatophenyl and propylimidazole groups.

EPRSC Mass Spectrometry Service Centre (University of Wales, Swansea).

2.4. Product analysis by gas chromatography

Gas chromatographic analyses were performed on a Hewlett Packard HP 6890 Series GC System, coupled to a flame ionisation detector, using a capillary column (HP-INNOWAX, cross-linked poly(ethylene glycol), length 30 m; i.d. 0.25 mm, film thickness 0.25 μm) and nitrogen as the carrier gas.

2.5. Procedure for catalytic oxygenations

All substrates were checked prior to use, by gas chromatography, to ensure that they were free from oxidation products. Reactions were carried out in a 2 ml vial sealed with a teflon-coated silicone septum and stirred at room temperature. Catalyst, co-catalyst (for reactions with H_2O_2), substrate and internal standard (cyclohexanone for (*Z*)-cyclooctene epoxidation, octan-1-ol for cyclohexane oxidation) were dissolved in DCE (DCE/ACN 1:1 for reactions with H_2O_2) and the oxidant was added. Yields based on the oxidant added, were determined by removing aliquots of the reaction mixture and analysing them by gas chromatography. No reaction occurred in control reactions in the absence of the Mn(III) porphyrin.

3. Results and discussion

3.1. Characterisation of supported manganese(III) porphyrins by UV–VIS spectroscopy

The presence of the Mn(III) porphyrin was confirmed by UV–VIS spectroscopy for all the Mn(III) porphyrin-supported catalysts studied. A typical spectrum is shown in the Fig. 3. This study shows that no detectable demetallation or exchange of the metal ion occurred during the preparation procedure, since

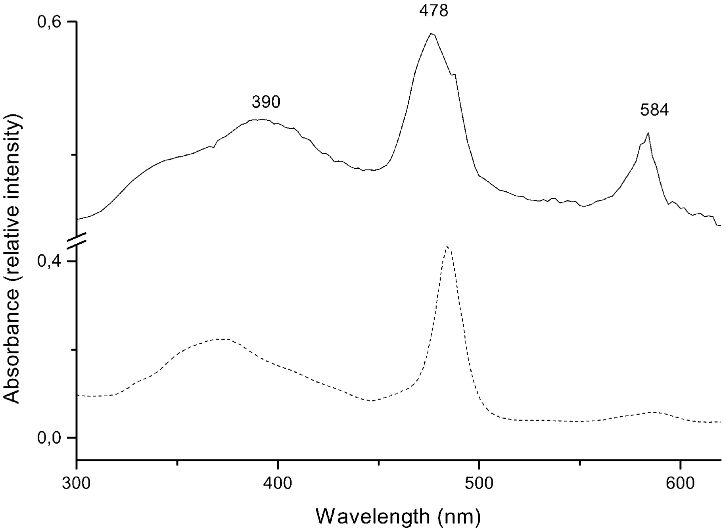


Fig. 3. UV–VIS spectra of dash: solution of [Mn{M(4-*N*-MePy)TDCPP}]Cl_2 and solid: suspension of [Mn{M(4-*N*-MePy)TDCPP}]-$SiSO_3$(IPG) in CCl_4.

all bands observed for the supported manganese porphyrins are characteristic of a Mn(III) porphyrin [24].

The loadings were quantified by measuring the amount of unloaded Mn(III) porphyrin, in the combined reaction solvent and washings, by UV–VIS spectroscopy (Table 1).

The data reveal that the Mn(III) porphyrins linked to ionic supports $SiSO_3^-$ and $SiSO_3^-$(IPG) have the highest loadings. With IPG the coordinative bond to the Mn(III) porphyrins is reversible [25], allowing competitive coordination solvents such as acetonitrile and methanol to displace the Mn(III) porphyrin. The cationic Mn(III) porphyrins used in this study can also be bound directly to unmodified silica, as has been noted before for metallo-tetra(*N*-methylpyridyl)porphyrins [9]. However, this binding is weaker than that to $SiSO_3^-$ and the catalysts obtained are less efficient. The results from these systems are not included in this paper.

3.2. Catalytic oxygenations with PhIO

3.2.1. Epoxidation of (Z)-cyclooctene

The epoxidation of (*Z*)-cyclooctene with PhIO catalysed by the manganese porphyrins which is an easy oxidation that gives only one product

Table 1
Amounts of cationic Mn(III) porphyrins bound to the supports

Support	Metalloporphyrin	Solvent used in Soxhlet extraction	Loading (%)
IPG	[Mn{M(4-*N*-MePy)TDCPP}]$^{2+}$	DCM	74
IPG	[Mn{TF4TMAPP}]$^{5+}$	ACN/MeOH	85
IPG	[Mn{T(4-*N*-MePy)P}]$^{5+}$	MeOH	95
$SiSO_3^-$	[Mn{M(4-*N*-MePy)TDCPP}]$^{2+}$	DCM	94
$SiSO_3^-$	[Mn{TF4TMAPP}]$^{5+}$ [a]	ACN/MeOH	97
$SiSO_3^-$	[Mn{T(4-*N*-MePy)P}]$^{5+}$	MeOH	98
$SiSO_3^-$(IPG)	[Mn{M(4-*N*-MePy)TDCPP}]$^{2+}$	DCM	95
$SiSO_3^-$(IPG)	[Mn{TF4TMAPP}]$^{5+}$	ACN/MeOH	100
$SiSO_3^-$(IPG)	[Mn{T(4-*N*-MePy)P}]$^{5+}$	MeOH	99

[a] From [22].

Table 2
Oxidation of (*Z*)-cyclooctene by PhIO catalysed by cationic Mn(III) porphyrins

Catalyst	*Cis*-epoxycyclooctane (%)[a]	Leaching (%)
[Mn{M(4-*N*-MePy)TDCPP}]Cl_2	80	–
[Mn{M(4-*N*-MePy)TDCPP}]-IPG	92	15
[Mn{M(4-*N*-MePy)TDCPP}]-$SiSO_3$	78	0
[Mn{M(4-*N*-MePy)TDCPP}]-$SiSO_3$(IPG)	100	0
[Mn{TF4TMAPP}]$(PF_6)_5$[b,c]	97	–
[Mn{TF4TMAPP}]-IPG[b]	94	20
[Mn{TF4TMAPP}]-$SiSO_3$[b,c]	92	0
[Mn{TF4TMAPP}]-$SiSO_3$(IPG)[b]	94	0
[Mn{T(4-*N*-MePy)P}]Cl_5[d,e]	44	–
[Mn{T(4-*N*-MePy)P}]-IPG[f]	77	0
[Mn{T(4-*N*-MePy)P}]-$SiSO_3$	53	0
[Mn{T(4-*N*-MePy)P}]-$SiSO_3$(IPG)	63	0

[a] Yields based on starting PhIO after 24 h in DCE, magnetic stirring and room temperature. Amounts: Mn(III)P, 2.3×10^{-7} mol or equivalent of supported catalyst; alkene, 200 μl; PhIO, 5.5 mg; DCE, 800 μl.

[b] In CAN.

[c] From [22].

[d] From [28].

[e] In ACN/DCM/MeOH 6:3:1.

[f] From [25].

cis-epoxycyclooctane, was first studied to obtain information about the accessibility of the Mn(III) centres of the supported catalysts towards substrates and oxidants. All the reactions were carried out in DCE, since this is a good solvent for several oxygenation reactions catalysed by metalloporphyrins [26,27].

The results obtained with the cationic Mn(III) porphyrins in homogeneous and supported systems reveal that the catalysts bearing halogen substituents on the *meso*-aryl positions are more efficient than the others in the oxygenations (Table 2).

Catalyst filtration after reactions with manganese porphyrins ligated to IPG, followed by UV–VIS spectroscopy of the filtrates, showed that ~15% of [Mn{M(4-*N*-MePy)TDCPP}]$^{2+}$, 20% of [Mn{T(F4TMAPP)}]$^{5+}$ and 0% of [Mn{T(4-*N*-MePy)P}]$^{5+}$ was leached from the support. In contrast, no leaching was detected with the cationic catalysts electrostatically bound to the anionic supports. The latter observation was confirmed by filtering the catalyst before the end of the reaction; the filtrate, with fresh oxidant, showed no catalytic activity [29].

It is noteworthy that control reactions, using the supports under identical conditions but without Mn(III) porphyrins, gave low epoxidation yields ~ 5%.

3.2.2. Oxidation of cyclohexane

To obtain further information about the effectiveness of the supported catalysts, they were compared using the hydroxylation of alkanes, which are less reactive than alkenes. The substrate chosen was the cyclohexane and the selectivities of the reactions for cyclohexanol and cyclohexanone formation were determined. The best yields, as above, were obtained with the catalysts bearing the electron-withdrawing –Cl and –F substituents (Table 3). The presence of these substituents, make the active intermediate Mn(V)=O more electrophilic and hence more reactive toward hydrocarbons. Although leaching was observed for [Mn{M(4-*N*-MePy)TDCPP}]$^{2+}$ and [Mn{T(F4TMAPP)}]$^{5+}$ on IPG (10 and 5%, respectively), it is clear by comparison of the reactivity of [Mn{M(4-*N*-MePy)TDCPP}]$^{2+}$ and [Mn{M(4-*N*-MePy)TDCPP}]-IPG that the imidazole groups of the support improve the catalyst's efficiency presumably by coordination to the Mn(III) porphyrin. They also increase the alcohol/ketone selectivity. Imidazole groups are known to favour the formation of the active oxidant Mn(V)=O [13,30] relative to Mn(IV)–O in these systems. The former active intermediate Mn-oxo transfer oxygen to the

Table 3
Oxidation of cyclohexane by PhIO catalysed by cationic Mn(III) porphyrins

Catalyst	Cyclohexanol (%)[a]	Cyclohexanone (%)[a]	Leaching (%)
[Mn{M(4-*N*-MePy)TDCPP}]$\mathrm{Cl_2}$	22	6	–
[Mn{M(4-*N*-MePy)TDCPP}]-IPG	70	<1	10
[Mn{M(4-*N*-MePy)TDCPP}]-$\mathrm{SiSO_3}$	38	<1	0
[Mn{M(4-*N*-MePy)TDCPP}]-$\mathrm{SiSO_3}$(IPG)	69	<1	0
[Mn{T(F4TMAPP)}]$\mathrm{(PF_6)_5}$	70	15	–
[Mn{TF4TMAPP}]-IPG	74	9	5
[Mn{TF4TMAPP}]-$\mathrm{SiSO_3}$[b]	48	23	0
[Mn{TF4TMAPP}]-$\mathrm{SiSO_3}$(IPG)[c]	79	13	0
[Mn{T(4-*N*-MePy)P}]$\mathrm{Cl_5}$[d,e]	4	2	–
[Mn{T(4-*N*-MePy)P}]-IPG	40	5	0
[Mn{T(4-*N*-MePy)P}]-$\mathrm{SiSO_3}$	44	7	0
[Mn{T(4-*N*-MePy)P}]-$\mathrm{SiSO_3}$(IPG)	43	6	0

[a] Yields based on starting PhIO after 24 h in DCE, magnetic stirring and room temperature. Amounts: Mn(III)P, 2.3×10^{-7} mol or equivalent of supported catalyst; alkane, 200 μl; PhIO, 1.1 mg; DCE, 800 μl.

[b] In ACN, from [22].

[c] In CAN.

[d] In ACN/DCM/MeOH 6:3:1.

[e] From [9].

substrates faster and more selective than the latter [31–33].

3.3. Catalytic oxygenations with H_2O_2

Iodosylbenzene is a convenient source of oxygen for use in small scale epoxidations since it gives good conversions and does not normally react with hydrocarbons without catalysis. However, its expense, low oxygen content (7.3% w/w) and polymeric nature are significant disadvantages that limit its use [25]. By contrast hydrogen peroxide is an important oxidant since it is inexpensive, has high oxygen content and is clean. For these reasons H_2O_2 was examined as an oxidant with the supported Mn(III) porphyrins catalysts in this study. The results from the epoxidation

Table 4
Oxidation of (*Z*)-cyclooctene by H_2O_2 catalysed by cationic Mn(III) porphyrins in the presence or absence of added imidazole (Im)[a]

Catalyst	*Cis*-epoxycyclooctane (%)*		Leaching (%)
	Without Im	With Im	
[Mn{M(4-*N*-MePy)TDCPP}]$\mathrm{Cl_2}$	6	51	–
[Mn{M(4-*N*-MePy)TDCPP}]-IPG	11	45	25
[Mn{M(4-*N*-MePy)TDCPP}]-$\mathrm{SiSO_3^-}$	5	38	0
[Mn{M(4-*N*-MePy)TDCPP}]-$\mathrm{SiSO_3}$(IPG)	11	45	0
[Mn{T(F4TMAPP)}]$\mathrm{(PF_6)_5}$	4	25	–
[Mn{TF4TMAPP}]-IPG	13	37	
[Mn{TF4TMAPP}]-$\mathrm{SiSO_3}$	6	28	
[Mn{TF4TMAPP}]-$\mathrm{SiSO_3}$(IPG)	7	38	
[Mn{T(4-*N*-MePy)P}]$\mathrm{(PF_6)_5}$	3	10	–
[Mn{T(4-*N*-MePy)P}]-IPG	7	13	
[Mn{T(4-*N*-MePy)P}-$\mathrm{SiSO_3^-}$	3	10	
[Mn{T(4-*N*-MePy)P}]-$\mathrm{SiSO_3}$(IPG)	4	17	

* Yields based on starting H_2O_2 after 24 h in DCE/ACN (1:1), magnetic stirring and room temperature.

[a] Amounts: Mn(III)P, 2.3×10^{-7} mol or equivalent of supported catalyst; alkene, 200 μl; H_2O_2, 2.4 μl; imidazole, 4.6×10^{-6} mol; DCE/ACN 1:1, 800 μl.

of (*Z*)-cyclooctene catalysed by supported cationic Mn(III) porphyrins are presented in the Table 4 and show that moderate yields of epoxide were obtained in the presence of imidazole co-catalyst.

The data in the Table 4 show two main trends:

1. [Mn{M(4-*N*-MePy)TDCPP}]$^{2+}$ and [Mn{T(F4T-MAPP)}]$^{5+}$ in homogeneous and heterogeneous systems give the highest yields of *cis*-epoxycyclooctane, due to the electron-withdrawing halogen substituents on the *meso*-aryl positions, which increase the electrophilicity of the Mn(V)=O active oxidant.
2. The best yields of *cis*-epoxycyclooctane occur on addition of free imidazole. It has been reported previously that Mn(III) porphyrin-catalysed oxidations of hydrocarbons by H_2O_2 in homogeneous solution are dramatically improved by the addition of a co-catalyst (e.g. heterocyclic nitrogen bases or ammonium acetate), which, by acting as an acid/base catalyst and as an axial ligand for the manganese, favours the formation of Mn(V)=O through the heterolytic cleavage of peroxide bond O–O [13]. The higher yields of *cis*-epoxycyclooctane when imidazole was added to reactions catalysed by Mn(III) porphyrins-$SiSO_3$(IPG) indicate that the imidazole bound to the support is unable to exert the two-fold role of co-catalyst in oxygenations of hydrocarbons by H_2O_2 catalysed by Mn(III) porphyrins. In the supported system, the co-catalyst may act as a Mn ligand in *trans*-position of the OOH ligand, but it is unable to act as acid/base catalyst, which is necessary for formation of intermediate Mn(III)–OOH [13]. This two-fold role of imidazole was evidenced previously for homogeneous systems [34,35].

We also observed that most efficient catalysts are bound to the *bis*-functional support $SiSO_3^-$(IPG). Presumably these have the benefit of both the sulfonate and imidazole groups. The former ensures the metalloporphyrin is securely anchored to the support and the latter by axial ligation to the manganese act as proximal ligand, facilitating the formation of active species, as occurs in natural peroxidases. Furthermore, the co-catalyst imidazole attached on the silica surface is protected and is unable to undergo the competitive oxidation with the substrate as reported by Collman et al. [36].

In another experiment with a large excess of the H_2O_2, the more efficient catalysts [Mn{M(4-*N*-MePy)-

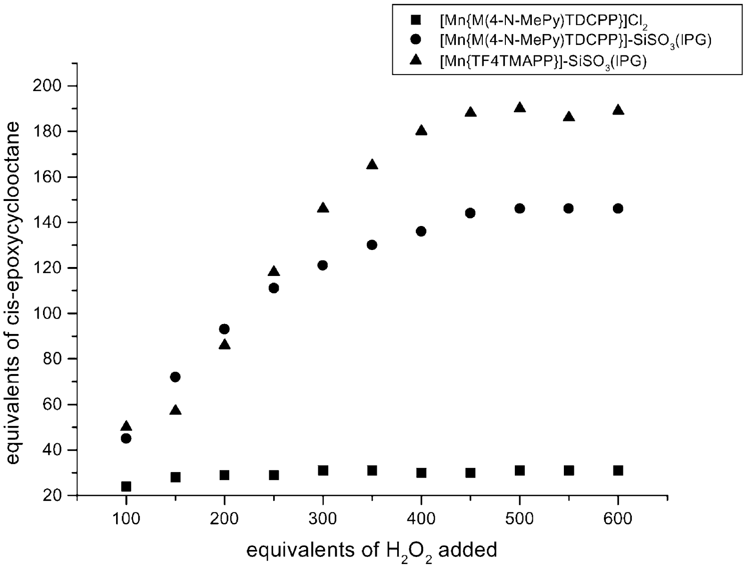


Fig. 4. Epoxidation of (*Z*)-cyclooctene upon successive addition of H_2O_2 to a CH_3COONH_4/catalyst mixture. Conditions: successive addition of H_2O_2 (50 eq. relative to the catalyst every 45 min) to a (*Z*)-cyclooctene: CH_3COONH_4: catalyst (3500:100:1) mixture in ACN/DCE (5:4).

TDCPP}]-$SiSO_3$(IPG) and [Mn{T(F4TMAPP)}]-$SiSO_3$(IPG) gave 155 and 190 catalyst turnovers, respectively, in the epoxidation of (*Z*)-cyclooctene (Fig. 4).

However, when the [Mn{M(4-*N*-MePy)TDCPP}]-$SiSO_3$(IPG) catalyst was recycled in another oxidation of (*Z*)-cyclooctene with H_2O_2 (molar ratio catalyst:oxdant 1:100) a low yield of *cis*-epoxycyclooctane (∼7%) was obtained due, probably, to the oxidative destruction of the catalyst. This conclusion was supported by a UV–VIS study of the homogeneous reaction using [Mn{M(4-*N*-MePy)TDCPP}]Cl_2 and H_2O_2 which showed the bleaching of the Mn porphyrin. Product analysis showed that only 30 turnovers of *cis*-epoxycyclooctane were obtained with the homogeneous catalyst (Fig. 4).

In the recycling studies using a large excess of H_2O_2, the co-catalyst added was the CH_3COONH_4. In this condition high amount of co-catalyst is required, if imidazole were used could result in an oxidative competition between co-catalyst and substrate [36].

It is important to emphasise that the supported systems reported in this paper are moderately efficient catalysts for the epoxidation of (*Z*)-cyclooctene by H_2O_2 (Table 4), reaching yields of *cis*-epoxycyclooctane comparable to those reported for manganese(III) 5,10,15,20-tetra(2,6-dichloro-3-acetylaminophenyl) porphyrin, linked by a covalent bond to silica [10]. The catalysts used in the present study are, however, easier to anchor to the support since the attachment is achieved mainly by electrostatic binding and does not involve the formation of a covalent linkage.

4. Conclusion

1. Concerning to the use of hydrogen peroxide, a cleaner and cheap oxidant, in oxygenations of hydrocarbons catalysed by Mn(III) porphyrins supported on rigid and the easy way obtained systems, it can be stated that: (i) none of the supported Mn porphyrins are efficient catalysts for hydrocarbon oxygenation without an added co-catalyst, because imidazole on the support surface coordinated to the Mn is unable to act as an acid/base catalyst; (ii) the two-fold role of imidazole, as *trans*-ligand to the Mn(III) porphyrins and as an added acid/base co-catalyst was evidenced for these rigid systems.
2. The best catalysts in this study have halogenated *meso*-aryl groups.
3. The cationic Mn(III) porphyrins studied, mainly the halogenated [Mn{M(4-*N*-MePy)TDCPP}]$^{2+}$ and [Mn{T(F4TMAPP)}]$^{5+}$, linked to the bis-functional support $SiSO_3^-$(IPG) are efficient catalysts for (*Z*)-cyclooctene epoxidation by PhIO and H_2O_2 and cyclohexane oxygenation by PhIO. This support provides two important benefits: the sulfonatophenyl groups ensure the metalloporphyrin is securely anchored to the support and the propilimidazole groups by axial ligation to the Mn(III) act as proximal ligand, reflecting the role of histidine in some enzymes. Moreover, there is the advantage that the method to anchor the Mn(III) porphyrin on the support is very simple since it is by electrostatic and coordinative binding.

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