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Oxidation of alkanes and alkenes by iodosylbenzene and hydrogen peroxide catalysed by halogenated manganese porphyrins in homogeneous solution and covalently bound to silica

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Abstract

Manganese(III) 5-(pentafluorophenyl)-10,15,20-tri(2,6-dichlorophenyl)porphyrin, Mn(PFTDCPP), and manganese(II) 2,3,7,8,12,13,17,18-octachloro-5-(pentafluorophenyl)-10,15-20-tri(2,6-dichlorophenyl)porphyrin, Mn(PFTDCCl$_8$PP), have been synthesised and used as catalysts in hydrocarbon oxidations by iodosylbenzene and hydrogen peroxide both in solution and covalently bound to aminopropylated silica. The former shows higher efficiency in the epoxidation of alkenes by iodosylbenzene, whereas the perchlorinated manganese porphyrin is more efficient in the hydroxylation of alkanes by this oxidant. The supported manganese(III) porphyrin show the same activity as its homogeneous analogue. With hydrogen peroxide as oxygen donor, Mn(PFTDCPP) is a stable and effective catalyst in the presence of imidazole. The perchlorinated analogue is a poor catalyst with this oxidant. The eight additional chlorine atoms on the porphyrin ring stabilise Mn(II) and unfavour the formation of the active species, Mn^{V}=O.

Keywords: Porphyrins; Manganese porphyrins; Catalysis; Supported catalysts; Hydrocarbon oxidation

1. Introduction

Metalloporphyrins are versatile oxidation catalysts which have been used as models for monooxygenases based on cytochrome P-450 [1–4]. In recent years, part of this research has been directed towards the manufacturing of fine chemicals and oxidation of drugs and pollutants [5–7]. The most efficient systems involve iron and manganese tetraaylporphyrins bearing electron-withdrawing substituents on the aryl group [8–12]. The improved catalytic efficiency of metalloporphyrins due to the presence of halogen atoms attached to tetrapyrrolic macrocycle prompted much research on the synthesis of β-substituted porphyrins [11,13,14]. The resultant β-octahalogenated metalloporphyrins, the so-called 'third generation catalysts'

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[3], have been reported to be much more active and significantly more stable than their β-unsubstituted analogous [11,15], although this is not always true as can be seen from this work and other reported metalloporphyrins [16–18].

In metalloporphyrin-based systems, a variety of oxygen donors have been used such as iodosylbenzene (PhIO) [3,19–21], ROOH [22], NaOCl [23], $KHSO_5$ [24,25] and hydrogen peroxide [26,27]. Iodosylbenzene was the first oxidant used [16,19,20] and it is still widely used today since it is a single-oxygen donor which is able to perform metalloporphyrin-catalysed oxidations with high turnovers and high yields [21,28–32]. The major problem with oxidants containing an O–O bond, such as hydrogen peroxide, is to avoid the homolytic cleavage of this bond with the resultant formation and reactions of oxy radicals [27]. However, the presence of nitrogen bases, such as imidazole, as axial ligand, induces the heterolytic cleavage of the O–O bond with the formation of high-valent oxo-iron or manganese species and efficient oxygen transfer to hydrocarbons [27]. This effect makes it possible to use this cheap and clean oxidant which gives water and dioxygen as by-products to oxidise organic compounds.

A problem associated with hydrocarbon oxidations catalysed by metalloporphyrins is the oxidative self-destruction of the catalyst under the very strong oxidising medium. One approach to reduce the metalloporphyrin degradation is to immobilise the catalyst by attachment to an organic or inorganic polymer. This strategy can prevent μ-oxo dimer formation and give the benefit of easy catalyst recovery [33].

In this paper, we report the catalytic results of hydrocarbon oxidations using hydrogen peroxide with systems which attempt to combine robust catalysts, halogenated and per-halogenated manganese porphyrins (manganese 5-(pentafluorophenyl)-10,15-20-tri(2,6-dichlorophenyl)porphyrin, Mn(PFTDCPP), and the corresponding β-octachlorinated Mn(PFTDCCl$_8$PP), (Fig. 1), with the advantage that these porphyrins can be covalently grafted on to inert supports. In order to explore the catalytic activities of these manganese porphyrins and to compare them with others from the literature, iodosylbenzene was used as the initial oxygen donor, and subsequently, this was replaced by hydrogen peroxide.

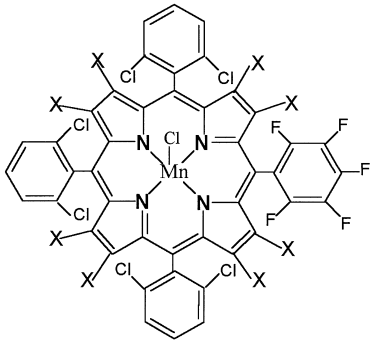

Fig. 1. Manganese 5-(pentafluorophenyl)-10,15-20-tri(2,6-dichlorophenyl)porphyrin, Mn(PFTDCPP) and manganese 2,3,7,8,12,13, 17,18-octachloro, 5-(pentafluorophenyl)-10,15-20-tri(2,6-dichlorophenyl) porphyrin, Mn(PFTDCCl$_8$PP).

2. Experimental

2.1. Physical measurements

GC analyses were performed on a Varian Star 3400CX chromatograph with a flame ionisation detector using a DB-wax (1 μm thickness) megabore column (30 m × 0.538 mm) and the results were analysed on a Varian Workstation. FAB^+ mass spectra were obtained on a V.G. Analytical Autospec instrument using 4-nitrobenzyl alcohol as the matrix. ^1H and ^{19}F NMR spectra were recorded on a Bruker DRX400 instrument using $CDCl_3$ as solvent at ambient temperature (293 ± 4 K) and referenced to $SiMe_4$ and CF_3COOH for ^1H and ^{19}F, respectively. UV–VIS spectra were obtained with a Hewlett-Packard 8452A diode array spectrometer.

2.2. Materials

All compounds used were purchased from Aldrich or Merck and were analytical grade. Methanol was refluxed over a magnesium and iodine mixture and after distillation stored over 4 Å molecular sieves. Iodosylbenzene was prepared in two steps from iodobenzene following the methods described by Saltzmann and Sharefkin [34,35] and the purity was shown to be 97% as determined by iodometric titration [36]. Aminopropyl modified silica was prepared according to a lit-

erature procedure [37] using Kieselgel 60 Merck (surface area 500 $m^2\ g^{-1}$; pore size 60 Å and particle size 40–63 μm) and had a loading of 30% based on nitrogen content (CNH analysis) assuming an average of two bonds between silane and silica and five silanol groups per nm^{-2} [38]. The alkenes were purified on a short basic alumina (150 type T) column immediately before using them in an oxidation. Silica gel used for column chromatography was Kiesegel 60 Merck (230–400 mesh). TLC used aluminium-backed silica gel 60 F_{254} plates (Merck).

2.3. Synthesis of manganese porphyrin, Mn(PFTDCPP)

Manganese porphyrin, Mn(PFTDCPP), was obtained by metallation of the free ligand H_2(PFTDCPP) [30] (0.040 g, 0.044 mmol) with manganese(II) acetate tetrahydrate (0.098 g, 0.4 mmol) in acetonitrile (40 ml) following the method described by Kadish et al. [39]. At the end of the reaction, the solvent was evaporated under vacuum and the resulting manganese(III) porphyrin was purified by chromatography on a silica column. Elution with dichloromethane gave a small amount of free base porphyrin and methanol:dichloromethane (1:1) mixture gave the desired compound. Hydrogen chloride was bubbled through the solution to ensure that chloride was the axial ligand. The solution was evaporated to dryness and 0.039 g (0.040 mol) of Mn(PFTDCPP)Cl were obtained (90% yield).

UV–VIS data for Mn(PFTDCPP)Cl (CH_2Cl_2): λ, nm (ε, $l\,mmol^{-1}\,cm^{-1}$) 370 (55), 394 sh (34), 478 (110), 580 (10). *m/z* (FAB^+): 962.9.

2.4. Synthesis of 2,3,7,8,12,13,17,18-octachloro,5-(pentafluorophenyl)10,15,20-tri(2,6-dichlorophenyl) porphyrin, H_2(PFTDCCl_8PP)

This porphyrin was prepared by chlorination of Zn(PFTDCPP) with *N*-chlorosuccinimide (NCS) [14]. Metallation of H_2(PFTDCPP) (0.055 g, 0.061 mmol) with zinc acetate dihydrate (0.097 g, 0.44 mmol) was carried out in acetonitrile in a similar way as previously described for metallation with manganese. After metallation, the crude product obtained was purified by chromatography on a silica column with a dichloromethane:hexane (1:1) mixture as eluent. The pink fraction containing Zn(PFTDCPP) was collected and evaporated to dryness (0.048 g, 86% yield).

Zn(PFTDCPP) (0.048 g, 0.053 mmol) in freshly distilled methanol (35 ml) was heated to reflux and NCS (0.189 g, 1.41 mmol) was added. Extra portions of NCS were added during the reaction period and the chlorination was monitored by UV–VIS spectroscopy through the red shift of Soret band from 424 to 448 nm; this corresponds to 3 nm per introduced chlorine atom. The crude Zn(PFTDCCl_8PP) was demetallated with trifluoroacetic acid (0.8 ml) in DCM (80 ml); H_2O was added and the organic layer was separated and neutralised with saturated aqueous $NaHCO_3$ solution. H_2(PFTDCCl_8PP) was purified by chromatography on a silica column with hexane:dichloromethane (3:1) as eluent and 51 mg (0.043 mmol) of H_2(PFTDCCl_8PP) was recovered (37% overall yield).

UV–VIS (CH_2Cl_2): λ, nm (ε, $l\,mmol^{-1}\,cm^{-1}$) 444 (210), 542 (22), 628 (4), 692 (1). *m/z* (HR-FAB^+): 1181.65254, calculated for $C_{44}H_{11}N_4F_5Cl_{13}{}^{37}Cl$: 1181.65138. ^1H NMR ($CDCl_3$), δ (ppm): 7.69–7.72 (9H, m, *meta*- and *para*-phenyl), −1.89 (2H, bs, pyrrole N–H). ^{19}F NMR ($CDCl_3$), δ (ppm): −139.25 (dd, F_{ortho}), −153.18 (t, F_{para}), −164.19 (td, F_{meta}).

2.5. Synthesis of Mn(PFTDCCl_8PP)

The metallation of H_2(PFTDCCl_8PP) was carried out as described for H_2(PFTDCPP). Purification with silica column, using dichloromethane:hexane (1:3) followed by dichloromethane:methanol (1:1), two main fractions were recovered, one manganese(II) complex (Soret band at 452 nm) and the other a mixture of manganese(II) and manganese(III) (Soret band at 498 nm) complexes. Starting from 0.030 g (0.025 mmol) of free ligand, 0.028 g (0.021 mmol) of both manganese porphyrins was recovered (85% total yield).

UV–VIS (CH_2Cl_2), Mn^{II}(PFTDCCl_8PP): λ, nm (ε, $l\,mmol^{-1}\,cm^{-1}$): 378 (21), 452 (87), 578 (8). *m/z* (FAB^+), Mn(PFTDCCl_8PP): 1238.7.

2.6. Synthesis of supported catalysts

Supported catalysts were prepared through reaction of Mn(PFTDCPP)Cl (15.6 μmol) or Mn(PFTD-

CCl_8PP) (6.2 μmol) with aminopropylated silica (0.75 and 0.30 g, respectively) in diglyme at 140°C under argon for 6 h, following the method described by Mansuy et al. [40]. The resulting solid was filtered and extracted with CH_2Cl_2 (24 h) and then CH_3OH (24 h) by a Soxhlet procedure. The solid was then dried at 80°C for 24 h. The manganese porphyrin loading was obtained by elemental analysis (CNH) as 12.5 and 19.0 μmol g^{-1} silica for Mn(PFTDCPP) and Mn(PFTDCCl_8PP), respectively.

2.7. Alkene and alkane oxidations

2.7.1. Iodosylbenzene

All reactions were performed at room temperature in small conical vessels (3 ml) with magnetic stirring. The manganese porphyrin or supported manganese porphyrin (0.25 μmol) was stirred with the desired substrate (500 μmol) in dichloromethane (1.5 ml) before the oxidant (25 μmol) was added. Recycling of the supported catalyst was carried out with the solid recovered after oxidation reaction by filtration, washing with methanol and drying. For reactions in the presence of co-catalysts (imidazole and pyridine), the heterocyclic base was added as a solution in dichloromethane (see Tables 2–4 for concentrations). The formation of reaction products was monitored by removing aliquots (0.5 μl) for GC analysis.

2.7.2. Hydrogen peroxide

The reactions were performed in a way similar to those described above. Metalloporphyrins and co-catalysts were stirred in a dichloromethane:acetonitrile (1:1) solvent mixture. The substrate was then added and followed few minutes later by hydrogen peroxide (30% w/v) using a microsyringe. The reaction was monitored by GC analysis.

3. Results and discussion

3.1. Synthesis of manganese(III) 5-(pentafluorophenyl)-10,15,20-tri(2,6-dichlorophenyl)porphyrin and manganese(II) (and manganese(III)) 2,3,7,8,12,13,17,18-octachoro-5-(pentafluorophenyl)-10,15,20-tri(2,6-dichlorophenyl)porphyrin

The required porphyrin ligand, H_2(PFTDCPP), was prepared as described previously [30] and metallated using standard procedures to give the desired manganese(III) porphyrin, Mn(PFTDCPP), or zinc(II) porphyrin, Zn(PFTDCPP).

The β-pyrrole chlorination of H_2(PFTDCPP) was performed on the zinc complex using a molar excess of NCS in refluxing methanol, using a procedure described in the literature [14]. Demetallation by triflouroacetic acid gave the free chlorinated ligand, H_2(PFTDCCl_8PP), in moderate yield (37% of overall yield from H_2(PFTDCPP)). The 24 nm red shift of the Soret band corresponds to 3 nm per introduced chlorine atom at the β-pyrrole positions as previously observed for chlorination of H_2(TDCPP) [14,41]. The red shift of the absorptions results from the stabilisation of HOMO ($a_{1u}\pi$ and $a_{2u}\pi$) and LUMO ($e_g\pi^*$) orbitals by the electron-withdrawing substituents on the β-pyrrole positions: both the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) energies decrease, but the LUMO orbital is slightly more stabilised than the HOMO. Thus, the net result is a decrease in the energy gap between the HOMO and LUMO [42,43].

The ^{1}H NMR chemical shifts of the aromatic protons of H_2(PFTDCCl_8PP) reflect the electron-withdrawing inductive effect of chlorine atoms which reduce the ring charge density, and consequently, the anisotropic effect. The same effect and nonplanarity of H_2(PFTDCCl_8PP) are responsible for the downfield shift of NH protons in H_2(PFTDCCl_8PP) ($\delta_{NH} = -1.89$ ppm) compared to H_2(PFTDCPP) ($\delta_{NH} = -2.63$ ppm) [30]. The β-pyrrole proton signals are absent in the NMR spectrum of H_2(PFTDCCl_8PP) which indicates total substitution of these hydrogens by chlorine atoms. The ^{19}F NMR chemical shifts of H_2(PFTDCCl_8PP) are similar to those of H_2(PFTDCPP), indicating that the chlorine substitution on β-pyrrole position does not have a major effect on the fluorine environments in this porphyrin.

The halogenated porphyrin was metallated with manganese(II) acetate in refluxing acetonitrile to give a mixture of both the manganese(II) (Soret band at 452 nm) [21] and the manganese(III) (Soret band at 498 nm) porphyrins. The presence of a large number of electron-withdrawing chlorines at the periphery of porphyrin is able to stabilise the manganese(II) oxidation state in air, as has already been observed by Meunier et al. with the perhalogenated manganese

tetramesitylporphyrin [44] and Mansuy et al. with manganese β-heptanitro, tetra-(2,6-dichlorophenyl) porphyrin [21].

3.2. Synthesis of the supported manganese porphyrins, Si-Mn(PFTDCPP) and Si-Mn(PFTDCCl$_8$PP)

The manganese porphyrin was grafted on to aminopropylated silica by nucleophilic aromatic substitution of the *para*-fluorine in the pentafluorophenyl group [40] to give a catalyst loading of 12.5 μmol g^{-1} of support and 19.0 μmol g^{-1} of support, respectively, for Si-Mn(PFTDCPP) and Si-Mn(PFTDCCl$_8$PP). The UV–VIS spectrum of Si-Mn(PFTDCPP) showed a Soret band at 478 nm, similar to that of the starting Mn^{III}(PFTDCPP)Cl, indicating that the porphyrin ring was not significantly affected by anchoring it to the support. However, Si-Mn^{II}(PFTDCCl$_8$PP) showed a red shifted Soret band (462 nm) reflecting, probably, further distortion of the hindered non-planar macrocycle due to the covalently attachment to the solid surface. Contrary to the effect of electron-withdrawing substituents, the changes in porphyrin ring planarity lead to a destabilisation of the HOMO but not of the LUMO orbitals thus leading to the decrease in the HOMO–LUMO energy gap, responsible for the red shift of the Soret band. These effects have been reported for other β-pyrrole substituted porphyrins studied by Kadish et al. ([43] and references [9,13,14] therein).

3.3. Catalytic activities of manganese porphyrins

3.3.1. Alkene epoxidation and alkane hydroxilation by iodosylbenzene catalysed by Mn^{III}(PFTDCPP) and Mn^{II}(PFTDCCl$_8$PP) in solution and supported on silica

The efficiencies and stabilities of the manganese porphyrins as catalyst for hydrocarbon oxidation in free solution and supported on silica were examined first using cyclooctene as the substrate. Table 1 shows the epoxide yields from the oxidation catalysed by the manganese porphyrins prepared in this study. Mn^{III}(TDCPP)[1] and Mn^{III}(TDCPP)(NO$_2$)$_7$P[1] were also included for comparison since the former is one of the most efficient and most widely used catalyst [13,26] and the Mn^{III}(TDCPP)(NO$_2$)$_7$P have been reported recently as a very good catalyst for hydrocarbon oxidations [21]. The manganese(III) 5-(pentafluorophenyl)tri(2, 6 - dichlorophenyl)porphyrin is as good a catalyst for cyclooctene epoxidation by iodosylbenzene as the already established Mn(TDCPP). This result shows that substitution of one 2,6-dichlorophenyl group by pentafluorophenyl does not change the catalytic efficiency of the manganese porphyrin, at least toward very reactive substrates such as cyclooctene, and it has the advantage that it is possible to anchor this new manganese porphyrin to solid supports covalently through the fluorinated phenyl group. The catalytic activity of the resulting supported porphyrin is similar to that of the homogeneous system (Table 1).

Table 1
Epoxidation of cyclooctene by iodosylbenzene catalysed by homogeneous and supported manganese porphyrins in dichloromethane[a]

Catalyst	Epoxide yield (%)[b]
Mn(PFTDCPP)	93
Si-Mn(PFTDCPP)	95
Mn(PFTDCCl$_8$PP)	87
Si-Mn(PFTDCCl$_8$PP)	67
Mn(TDCPP)	90[c]
Mn(TDCPP)(NO$_2$)$_7$P	90[c]

[a] MnP: 2.5×10^{-7} mol; PhIO: 3.0×10^{-5} mol; cyclooctene: 5.0×10^{-4} mol; CH_2Cl_2: 1.5 cm^3.
[b] Based on PhIO.
[c] Data from [21].

No degradation of the catalyst was observed when Mn^{III}(PFTDCPP) was used in homogeneous reactions after five additions of the oxidant (each with catalyst:oxidant, 1:300, added at 2 h intervals), giving a total of 745 catalytic turnovers. Recycling the supported Mn^{III}(PFTDCPP)Cl gave a reproducible yield of cyclooctene epoxide (70%). These results are good if compared to other systems reported before [30]. In order to prove that the catalysis was performed by heterogeneous catalyst and not by leached manganese porphyrin from the support, the supernatant was filtered at the end of reaction and allowed to react further in the same conditions. No additional epoxide was produced indicating that the catalytic activity of this supported porphyrin is truly heterogeneous in nature.

[1] Mn(TDCPP) is manganese(III) meso-tetrakis-(2,6-dichlorophenyl)porphyrin and Mn(TDCPP) (NO$_2$)$_7$P is the Mn(TDCPP) with nitro group substituents on the β-pyrrole positions.

Interestingly, the perhalogenated manganese porphyrin is not a better catalyst for epoxidation of cyclooctene than the unsubstituted analogue, specially when it is grafted on aminopropylsilica (Table 1). With this metalloporphyrin, the manganese(II) oxidation state is stabilised as discussed before. We have not investigated the electrochemistry of these metalloporphyrins yet but it is expected that the additional halogenation will give a positive shift of the redox potentials of this complex as observed by Kadish et al. with halogenated iron(III) and manganese(III) tetrakis(3,5-dichloro-2,6-dimethoxyphenyl)porphyrin [43]; by Mansuy et al. with nitrated manganese(II) tetra(2,6-dichlorophenyl)porphyrin [21] and by others with related compounds [14,45]. It is likely that this stabilisation makes it harder to oxidise the Mn(II) to form the catalytic species O=Mn(V), which may account for why this perhalogenated manganese porphyrin does not show the expected high efficiency arising from the increased electrophilicity of the macrocycle due to the electron-withdrawing Cl groups. Mansuy et al [21] have made a similar observation with the manganese(II) tetra-(2,6-dichlorophenyl)-β-heptanitro porphyrin and manganese(III) tetra(2,6-dichlorophenyl)porphyrin for cyclooctene epoxidation although the first complex is a much better catalyst for alkane hydroxylation. Furthermore, Gonsalves et al. [41] have reported that the complex manganese(III) tetrakis(2,6-dichlorophenyl)-β-octachloro porphyrin is less stable than the corresponding Mn^{III}TDCPP in oxidations of hydrocarbons with H_2O_2 and NaOCl. They explain their results based on studies by Ghosh who used density functional theory (DFT), through which β-chlorinated and β-brominated porphyrins are estimated to have first ionisation potentials (IP) not much different from those of the corresponding non-β-halogenated compounds. These DFT results confirm what was suggested by the catalytic studies ([15] and references therein). The perhalogenated catalyst is 20% less efficient when it is supported on aminopropylsilica (Table 1). Based on the Soret band red shift in the UV–VIS spectrum of the Si-Mn(PFTDCCl_8PP) this manganese porphyrin is more distorted on the support than in solution, probably due to stereochemical crowding provoking a loss of aromatic stability of the porphyrin. This steric crowding will make interaction with the substrate more difficult and low the catalytic efficiency.

Table 2
Yields of products from the oxidation of cyclohexene with PhIO catalysed by homogeneous and supported manganese porphyrins in dichloromethane[a]

Catalyst	Yield (%)		
	Epoxide[b]	Cyclohex-2-en-1-one[b]	Cyclohex-2-en-1-ol[b]
Mn(PFTDCPP)	77	8	8
Si-Mn(PFTDCPP)	80	10	9
Mn(PFTDCCl_8PP)[c]	73	5	13
Si-Mn(PFTDCCl_8PP)	49	17	19

[a] MnP: 2.5×10^{-7} mol; PhIO: 3.0×10^{-5} mol; cyclohexene: 5.0×10^{-4} mol; CH_2Cl_2: 1.5 cm^3.
[b] Based on PhIO after constant yield (3 h).
[c] Presence of 7.5×10^{-6} mol of imidazole.

The oxidation of cyclohexene catalysed by these manganese porphyrins gave cyclohexene epoxide as the main product and two allylic oxidation products, cyclohex-2-en-1-ol and cyclohex-2-en-1-one in small yields (Table 2). Although the reactions were carried out in the presence of air, the product yields did not exceed 100% unlike the corresponding reactions of Fe(PFTDCPP) [30] and Mn(TDCPP) [46,47] which were attributed to dioxygen trapping cyclohexyl radicals in a contributory autooxidation process.

In alkene oxidations by iodosylbenzene–manganese porphyrin systems, the active oxidant is considered to be the oxomanganese(v) porphyrin, OMn^V(P) [3,7,48–51]. The small amounts of allylic alcohol and ketone probably originate from reactions involving H-atom abstraction from the relatively reactive allylic C–H bond followed by hydroxyl transfer from metal to carbon (oxygen rebound mechanism) ([46,47] and references therein) or by electron transfer, to give the allylic cation, and ion-pair collapse [47,52–54]. High level of epoxidation and low level of allylic oxidation as observed with studied manganese porphyrins confirm a O=Mn^V(P) as a predominant active species (type 1 intermediate as designed by Gunter and Turner) [51].

As observed for cyclooctene, the catalytic efficiency of the supported perhalogenated manganese porphyrin is decreased by comparison with the homogeneous reaction. This, as discussed above, arises from the greater steric hindrance around the active ox-

Table 3
Yields of products from the oxidation of cyclohexane with PhIO catalysed by homogeneous and supported manganese porphyrins in dichloromethane[a]

Catalyst	Co-catalyst	Yield (%)[b]		Ratio of alcohol to ketone
		Cyclohexanol	Cyclohexanone	
Mn^{III}(PFTDCPP)	–	7	2	3.5
	Pyridine[c]	11	1	11
	Imidazole[d]	37	4	9.2
Mn^{II}(PFTDCCl$_8$PP)	–	1	0	1
	Imidazole[e]	42	2	21
Si-MnPFTDCPP	–	13	2	6.5
Si-MnPFTDCCl$_8$PP	Imidazole[e]	37	1	37

[a] MnP: 2.5×10^{-7} mol; PhIO: 2.5×10^{-5} mol; cyclohexane: 5.0×10^{-4} mol; CH_2Cl_2: 1.5 cm^3.
[b] Based on PhIO.
[c] 6.2×10^{-5} mol.
[d] 5×10^{-6} mol.
[e] 7.5×10^{-6} mol.

idant which make interaction with the substrate more difficult. Thus, comparing both the supported catalysts indicates that the presence of eight β-chlorine atoms is a disadvantage for catalytic epoxidation, as observed by Gonsalves et al. for perhalogenated manganese porphyrins using NaOCl as oxidant [18].

It is well known that the catalytic ability of manganese porphyrins is improved by the use of nitrogen bases as co-catalysts [3,55,56]. In order to study the abilities of the manganese porphyrin/PhIO systems to hydroxylate less reactive aliphatic C–H bonds two nitrogen bases were investigated with the aim of improving the efficiency of these catalysts. The results are reported in Tables 3 and 4 for cyclohexane and adamantane oxidation, respectively.

It is clear that the yield of oxidation products and the selectivity for the hydroxylation are improved by the presence of the co-catalysts for both substrates. This is because the ligand favours the formation of the high-valent oxo-manganese species, OMn^{V}(P), which is responsible for oxygen insertion into the substrates.

Imidazole is more efficient as co-catalyst than pyridine (Tables 3 and 4). The lower yields observed with pyridine could be due to its weaker ligand affinity for

Table 4
Yields of products from the oxidation of adamantane with PhIO catalysed by homogeneous and supported manganese porphyrins in dichloromethane[a]

Catalyst	Co-catalyst	Yield (%)[b]			*Tert* to *sec* relative reactivity
		1-ol[c]	2-ol[c]	2-one[c]	
Mn^{III}(PFTDCPP)	–	37	10	5	7
	Pyridine[d]	45	7	1	16
	Imidazole[e]	52	13	1	11
Mn^{II}(PFTDCCl$_8$PP)	Imidazole[f]	61	14	1	12
Si-MnPFTDCPP	–	58	11	2	13
Si-MnPFTDCCl$_8$PP	Imidazole[f]	48	8	1	16

[a] MnP: 2.5×10^{-7} mol; PhIO: 2.5×10^{-5} mol; adamantane: 5.0×10^{-4} mol; CH_2Cl_2: 1.5 cm^3.
[b] Based on PhIO.
[c] 1-ol: 1-adamantanol; 2-ol: 2-adamantanol and 2-one: 2-adamantanone.
[d] 6.2×10^{-5} mol.
[e] 5×10^{-6} mol.
[f] 7.5×10^{-6} mol.

Mn^{III} porphyrins [26]. The differences in reactivities and product distributions in epoxidation reactions with different axial ligands have been explained by Gunter and Turner [55]. The donor strength of the *trans*-axial ligand influences the electron density in the metal-oxo moiety of the active complex, either through σ- or π-charge donation, and is responsible for the differences in activities observed with different cocatalyst. σ-Donation is expected to increase the rate of oxygen loss from the catalyst. Conversely, significant axial π-donation would decrease the ability of the catalyst to epoxidise a given substrate, by raising the energy of the critical acceptor orbital of the catalyst [55]. Pyridine is a better π-donor than imidazole which may account for the poorer results obtained when pyridine is the co-catalyst.

The results show the moderate efficiency of these systems for the hydroxylation of cyclohexane, with yields up to 42% for cyclohexanol (with small amounts of cyclohexanone) (Table 3) and of adamantane, with formation of adamantan-1-ol, -2-ol, and -2-one (Table 4). The yields of hydroxylation with the Mn^{II}PFTDCCl_8PP, unlike those of epoxidation, are higher than those with Mn^{III}PFTDCPP, and the supported perhalogenated catalyst shows yields similar to those from the homogeneous system. These results were not expected because this perhalogenated manganese porphyrin is Mn(II). To our knowledge, there is only one report in the literature which shows good catalytic yields for hydroxylation using manganese(II) porphyrin [21] and supplementary experiments are necessary in order to investigate the catalytic species and to explore the catalytic potentiality of these systems for hydroxylation of linear alkanes.

As is normally observed in oxidations of adamantane, there is a preference for the tertiary centre (yield of 1-ol versus 2-ol + 2-one) (Table 4). However, the selectivity of the oxidation is determined mainly by the presence of the co-catalyst rather than the increased number of electron-withdrawing halogens on the porphyrin ring (cf. the reactions of Mn^{III}PFTDCPP/imidazole and Mn^{II}PFTDCCl_8PP/imidazole and of Mn^{III}PFTDCPP in the presence and absence of co-catalyst). It is observed that the support improves the selectivity of the cyclohexane and adamantane oxidations (Tables 3 and 4). This was not expected, specially for adamantane, since increased steric hindrance at the active site by the presence of the support, would result in a decrease in selectivity for the 1-position, as observed previously for FePFTDCPP [30].

3.3.2. Alkene epoxidation and alkane hydroxylation by hydrogen peroxide catalysed by Mn(PFTDCPP) and Mn(PFTDCCl_8PP) in solution and supported on silica

Hydrogen peroxide is an important oxidant for the catalytic oxidation of hydrocarbons because it is inexpensive, readily available and produces water and oxygen as the only by-products. The epoxidation of alkenes and oxidation of alkanes by H_2O_2 with manganese porphyrin complexes has been studied by Mansuy [57–59]. It was proposed that, in the absence of a co-catalyst such as imidazole, manganese(III) porphyrins catalyse the homolytic cleavage of the O–O bond, resulting in the generation of Mn(IV) and hydroxyl radicals. With the co-catalyst present, heterolytic cleavage which leads to oxo-Mn(V) and hydroxide is favoured [21,26,38]. Imidazole may also

Table 5
Epoxidation of cyclooctene by hydrogen peroxide catalysed by homogeneous and supported manganese porphyrins in CH_2Cl_2:CH_3CN[a]

Catalyst	Co-catalyst	Epoxyde yield (%)[b]
Mn^{III}(PFTDCPP)	–	–
	Pyridine[c]	34
	Imidazole[d]	81
	$NH_4(O_2CCH_3)$[d]	94 (100)[e]
Si-MnPFTDCPP	–	8
	Imidazole[f]	30
	$NH_4(O_2CCH_3)$	31
Mn^{II}(PFTDCCl_8PP)	–	–
	Imidazole[f]	7
	$NH_4(O_2CCH_3)$[f]	6
Si-MnPFTDCCl_8PP	–	–
	Imidazole[d]	7

[a] MnP: 2.5×10^{-7} mol; H_2O_2: 2.5×10^{-5} mol; cyclooctene: 5.0×10^{-4} mol; CH_2Cl_2: 0.75 cm^3; CH_3CN: 0.75 cm^{-3}.
[b] Based on H_2O_2.
[c] 6.2×10^{-6} mol.
[d] 5.0×10^{-6} mol.
[e] This yield correspond to substrate conversion for equivalent ratio H_2O_2:substrate = 1.
[f] 7.5×10^{-6} mol.

Table 6
Yields of products from the oxidation of cyclohexane with hydrogen peroxide catalysed by homogeneous manganese porphyrins in CH_2Cl_2:CH_3CN[a]

Catalyst	Co-catalyst	Yield (%)[b]	
		Cyclohexanol	Cyclohexanone
Mn^{III}(PFTDCPP)	–	–	–
	Pyridine[c]	15	1
	Imidazole[d]	27	1
	$NH_4(O_2CCH_3$[d]	28 (12)[e]	5
Mn^{II}(PFTDCCl_8PP)	–	–	–
	Imidazole[f]	8	–
	$NH_4(O_2CCH_3$[f]	6	–

[a] MnP: 2.5×10^{-7} mol; H_2O_2: 2.5×10^{-5} mol; cyclohexane: 5.0×10^{-4} mol; CH_2Cl_2: 1.5 cm^3.
[b] Based on H_2O_2.
[c] 6.2×10^{-6} mol.
[d] 5×10^{-6} mol.
[e] % Conversion — MnP: 2.5×10^{-7}; H_2O_2: 200 eq; cyclohexane: 200 eq.
[f] 7.5×10^{-6} mol.

serve as a general base catalyst for the O–O bond heterolysis [60,61].

The manganese mono-(pentafluorophenyl)-tri-(2,6-dichlorophenyl)porphyrin's ability to catalyse the epoxidation of alkenes and hydroxylation of alkanes by hydrogen peroxide has been investigated. The reactions were carried out in the absence and presence of a co-catalyst. The systems Mn(III)PFTDCPP/H_2O_2/co-catalyst/CH_2Cl_2,ACN and SiNH-Mn(III)PFTDCPP/H_2O_2/co-catalyst/CH_2Cl_2,ACN were found to epoxidise cyclooctene with moderate–good yields (Table 5). The homogeneous system showed a moderate activity in the hydroxylation of cyclohexane with good selectivity for cyclohexanol (Table 6). The presence of co-catalyst is clearly necessary presumably to favour the heterolytic cleavage of the O–O bond of H_2O_2 and to stabilise the (P)Mn(V)=O complex. The homogeneous system is much more efficient than the supported analogue, leading to complete conversion of the cyclooctene to epoxide by one equivalent of H_2O_2 using ammonium acetate as the co-catalyst. The advantage of this co-catalyst over the others is that it is not consumed during reaction and it is likely that it catalyses the formation of Mn^{V}=O via formation of an Mn^{III}-OOCOCH$_3$ species which favours the cleavage of the O–O bond as proposed by Mansuy et al. ([62,63] and references therein).

The cyclooctene epoxide yield was reproducible in recycling experiments with the homogeneous catalyst provided the co-catalyst (imidazole) concentration was maintained through new additions with the oxidant. The turnovers of 686 were obtained after eight additions of oxidant, which is excellent compared to the 800 maximum possible for the total amount of H_2O_2 added (Fig. 2). However, the manganese porphyrin was almost completed bleached (84%) after these reactions, partly because the large decrease in the substrate concentration leads to catalyst self-oxidation. The yields of epoxide from cyclooctene using the supported manganese porphyrin catalyst in this study lie between those two other similar covalently supported systems described by Mansuy et al. for the same oxidant:Mn(TDC-mNHCOCH$_3$PP)-Si[2] (60–70% of epoxide) and Mn(TDCSPP-K10) (15% of epoxide) [63]. Since these manganese porphyrins have similar structures, comparison of all these systems suggests that silica may be a better support than montmorillonite when hydrogen peroxide is the oxidant.

The manganese porphyrin having chloro substituents on the β-pyrrole positions is a poor catalyst for the oxidation of alkenes and alkanes with hydrogen peroxide (Tables 5 and 6). UV–VIS analysis of

[2] Mn(TDC-mNHCOCH$_3$)-Si* and Mn(TDCSPP-K10)* are manganese(III) meso-tetrakis-(2,6-dichlorophenyl)porphyrin derivatives bearing NH_2 (covalently bound to silica CBA bearing-CH_2COOH groups) and SO_3H (covalently bound to montmorillonite K10 bearing –NH_2 groups), respectively.

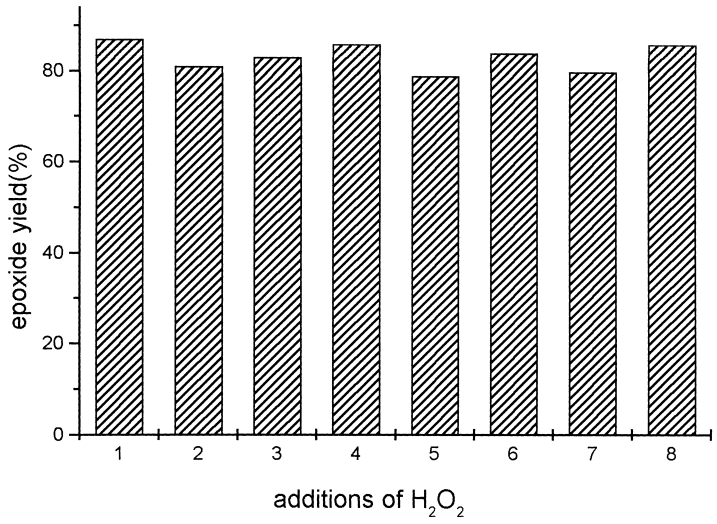

Fig. 2. Recycling of Mn(PFTDCPP) in the epoxidation of (*Z*)-cyclooctene by H_2O_2 in CH_2Cl_2. 2.5×10^{-7} mol de MnP; MnP:H_2O_2:Im = 1:100:20. A new charge of co-catalyst (imidazole) was added with each fresh aliquot of oxidant.

the solution after reaction showed that the catalyst was completely recovered indicating that the presence of eight β-chlorine atoms provides stability to the catalyst, even in solution, contrary to that observed for reactions with $MnTDCCl_8PP$ [55]. The poor yields may be attributed to the stabilisation of the $Mn^{II}P$ which unfavours the formation of the required intermediate oxidation state, Mn^{V}=O, and leads to an alternative mechanism. The active intermediate could be a Mn^{II}–O–OH species, generated by the reaction of $Mn^{II}P$ with hydrogen peroxide. Porphyrin peroxo complexes have been studied by Valentine et al. as catalysts in hydrocarbon oxidations [64]. These species have been shown to be nucleophilic rather than eletrophilic, with poor reactivities to hydroxylation of hydrocarbons or epoxidation of electron-rich olefins. Clearly, a better understanding of the reactivities of these manganese porphyrins and mechanisms to account for their reactions are needed. To this aim, further work is now in progress in our laboratory.

4. Conclusions

The most important challenge in the metalloporphyrin based catalysts for oxidation remains the need to design complexes that are stable and can be recovered at the end of the process. With this aim, we have synthesised and characterised two robust manganese porphyrins which can be classified as second and third generation catalysts and anchored them to amino functionalised silica. In general, these systems are efficient at catalysing alkene epoxidation and/or alkane hydroxylation by iodosylbenzene and by hydrogen peroxide in the presence of a co-catalyst.

With iodosylbenzene as oxygen donor, the second generation manganese porphyrin, Mn(PFTDCPP)Cl, is more efficient at epoxidising alkenes whereas the perchlorinated analogue is more effective at catalysing alkane hydroxylation. The supported Mn(PFTDCPP) shows good stability in recycling experiments and the same activity as the homogeneous catalyst, with the advantage that it can be recovered at the end of the reaction. Anchoring the catalyst with a covalent bond appears to be a good strategy for supporting the porphyrin since the porphyrin is not leached into solution even in the strong oxidising conditions.

The system Mn(PFTDCPP)Cl/H_2O_2/ammonium acetate seems promising in alkene oxidations since both the co-catalyst and the oxidant are cheap, clean and readily available. The perchlorinated manganese porphyrin, however, is a poor catalyst with hydrogen peroxide. The eight additional chlorine atoms on the porphyrin ring lead to the stabilisation of the metal

as Mn(II) and the formation of the catalytic species, Mn^{V}=O, from this oxidation state seems unfavourable. Further work is now in progress in our laboratory in order to investigate the mechanism of these reactions.

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