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Alkene epoxidation with iodosylbenzene catalysed by polyionic manganese porphyrins electrostatically bound to counter-charged supports

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Manganese(III) complexes of tetra-anionic and tetra-cationic porphyrins have been immobilised on counter-charged, surface-modified silica supports and on organic ion-exchange resins. The reactions of these supported manganese(III) porphyrin systems and analogous uncharged homogeneous systems have been examined using cyclooctene and (*E*)- and (*Z*)-4-methylpent-2-ene epoxidations, with iodosylbenzene (PhIO) as the oxygen donor.

Comparisons using the manganese porphyrin systems as catalysts for the epoxidation of cyclooctene in acetonitrile reveal that, in low turnover reactions (maximum 136 turnovers), they all give an essentially quantitative yield of epoxide although the heterogeneous reactions are significantly slower than the homogeneous analogues. In large scale repeat-use experiments, however, the supported catalysts are clearly superior, giving markedly better yields.

The epoxidations of (*E*)- and (*Z*)-4-methylpent-2-ene with all the catalysts show a very high stereoretention, with the (*Z*)-alkene reacting faster than the (*E*)-isomer. The sterically hindered manganese(III) 5,10,15,20-tetrakis-(2,6-dichloro-3-sulfonatophenyl)porphyrin (MnTDCSPP) shows the highest selectivity for the (*Z*)-isomer; by contrast the supported manganese(III) 5,10,15,20-tetrakis[2,3,5,6-tetrafluoro-4-(trimethylammonio)phenyl]-porphyrin on Dowex ($MnTF_4TMAPP$–Dowex) reacts with the two alkenes at effectively the same rate.

The mechanism of the epoxidations and the influence of the porphyrin ligand and support on the substrate selectivity are discussed.

Introduction

Over the last decade modelling cytochrome P450 with soluble tetraarylmetalloporphyrins using a range of different oxygen atom donors has received much attention.[1] The main thrust of this work has been concerned with the mechanisms of these reactions, the nature of the active oxidant and with factors that control the selectivity of the oxidations. The two major drawbacks that have prevented the practical application of metalloporphyrin catalysts in synthesis are, first, the instability of the metalloporphyrins towards intermolecular self-destruction, and secondly, the difficulty in recovering the expensive catalyst for use in further reactions. The first can be reduced by the use of sterically hindered metallotetraarylporphyrins, which prevent the close approach of catalyst molecules.[2] However, recovery of the catalyst remains a problem. An approach that has the potential to overcome both problems in the cytochrome P450 models is the use of supported metalloporphyrin catalysts.[3] The site-isolation of catalysts on solids can prevent intermolecular self-oxidation and can in principle, through the local environment of the support, provide oxidation catalysts with unique activities and selectivities. Furthermore, the supported catalysts can be readily recovered and recycled or could be used in catalytic filters in flow reactors. These heterogenised systems would reduce the waste-discharge of metals employed as catalysts in industrial processes, a factor that is becoming increasingly important due to stringent environmental regulations.

Different methods have been employed to attach porphyrin catalysts to solids,[3,4] namely, electrostatic binding of charged porphyrins to counter-charged supports, intercalation of charged porphyrins between the layers of clays, entrapment within the pores or matrices of solids, covalent binding to the support, axial ligation to surface-bound ligands and the synthesis of hybrid materials such as metalloporphyrinosilica through sol–gel processes.[1,4c] In previous work involving the immobilisation of metalloporphyrins by ligation to functional groups attached to the surface of a solid support, it was observed that even though these materials are efficient catalysts, the coordinative bonding is reversible.[5] This requires careful control of the solvent to minimize catalyst leaching or the advantages of the support catalyst will be lost.[6]

In this paper we report the use of the robust charged manganese(III) porphyrins, MnTDCSPP or $MnTF_4TMAPP$ (Fig. 1) as oxidation catalysts when supported on counter-charged, surface-modified silica or ion-exchange resins, $SiNMe_3^+$ and Amberlyst A27 or $SiSO_3^-$ and Dowex MSC1 (Fig. 1), through electrostatic interactions. These heterogeneous manganese(III) porphyrin systems and their respective homogeneous analogues have been used to bring about epoxidation with PhIO as the oxygen donor. The stability and activity of these catalytic systems are reported.

Results

Supports for charged porphyrins

Two modified silica gel supports have been prepared: one with surface anionic groups ($SiSO_3^-$) and the other with cationic functionality ($SiNMe_3^+$) (Fig. 1). These were obtained by reacting silica gel with 2-(4-chlorosulfonatophenyl)ethyltrichlorosilane and trimethoxy-3-(trimethylammonio)propylsilane, respectively, following a general procedure of Basolo and co-workers.[7] Preliminary experiments showed that it is import-

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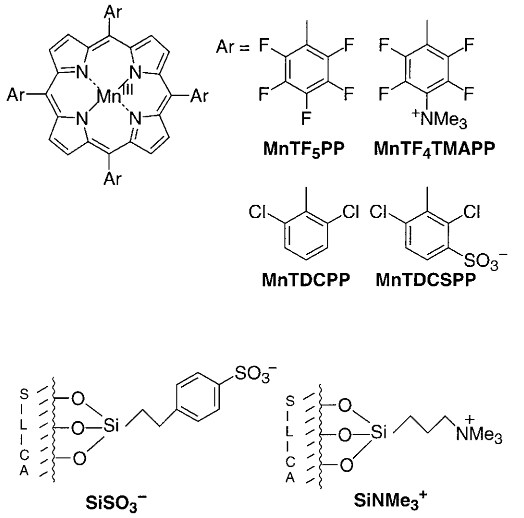


Fig. 1 The structures of the porphyrin catalysts and supports.

ant to ensure that all the sulfonic acid groups are converted to sulfonates since acidity can lead to the demetallation of porphyrins when these materials are used as supports.

The extent of surface reaction for the modified silica gels were obtained by elemental analysis. This showed that the surface loading for $SiSO_3^-$ was 5.5×10^{-4} mol g^{-1} and for $SiNMe_3^+$ 1.0×10^{-3} mol g^{-1}. Assuming 5 silanol groups nm^{-3} and an average of two links between the organosilane and the surface,[7] these loadings correspond to 27% and 48% coverage of the silica surface.

For comparison with the modified silica gel supports, two highly cross-linked, polystyrene–divinylbenzene based, ion-exchange resins were also used in this study: the cation exchanger Dowex MSC1 with phenylsulfonate groups (20% cross-linked) and the anion exchanger Amberlyst A27 with benzyltrimethylammonium functionality (20% cross-linked).

Manganese(III) porphyrins

Two charged manganese porphyrins were used as catalysts in this investigation: manganese(III) 5,10,15,20-tetrakis[2,3,5,6-tetrafluoro-4-(trimethylammonio)phenyl]porphyrin ($MnTF_4TMAPP$) and manganese(III) 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphyrin (MnTDCSPP) (Fig. 1). These were prepared from 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (H_2TF_5PP) and 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (H_2TDCPP) by modifications of literature methods.[8–11]

Two uncharged manganese porphyrins, $MnTF_5PP$ and MnTDCPP, were also prepared and used as catalytic comparators for $MnTF_4TMAPP$ and MnTDCSPP respectively.

Preparation of supported catalysts

The immobilisation of the charged metalloporphyrins on the counter-charged supports was achieved by stirring an acetonitrile ($MnTF_4TMAPP$) or methanol (MnTDCSPP) solution of the catalyst with a suspension of the support using the mass ratio 1:100. With the resins care had to be taken to prevent the fracturing of the particles by avoiding vigorous stirring. The resulting material was filtered and thoroughly extracted in a Soxhlet apparatus with methanol, followed by acetonitrile to remove any weakly bound MnP. The loading was quantified by measuring the amount of unloaded MnP, in the combined reaction solvent and washings, by UV–Vis spectroscopy. For all the supports the loadings were quantitative (10 mg g^{-1} support).

The UV–Vis spectra of the homogeneous and supported catalysts are shown in Figs. 2 and 3. To make the comparisons easier the main Soret peaks in each spectrum have been scaled to approximately equal intensities.

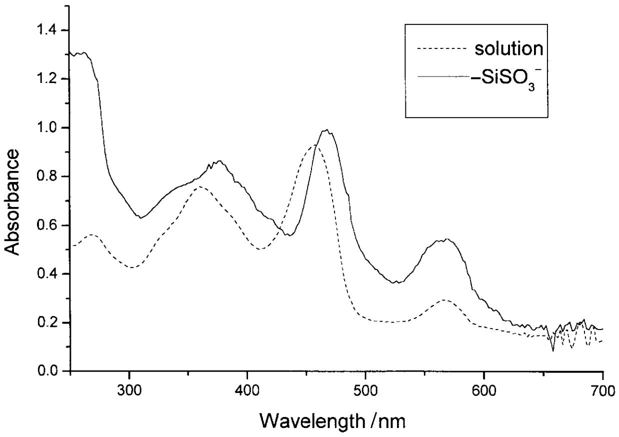


Fig. 2 The UV–Vis spectra of a solution of $MnTF_4TMAPP$ and a suspension of $MnTF_4TMAPP–SiSO_3^-$ in acetonitrile. They are scaled to give approximately equivalent absorptions of the Soret peak at ~470 nm.

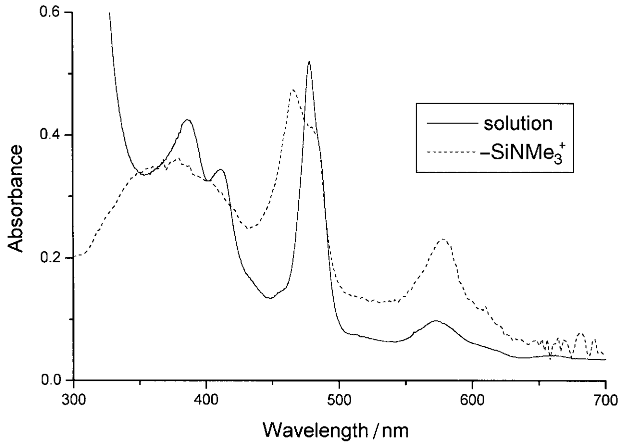


Fig. 3 The UV–Vis spectra of a solution of MnTDCSPP and a suspension of $MnTDCSPP–SiNMe_3^+$ in methanol.

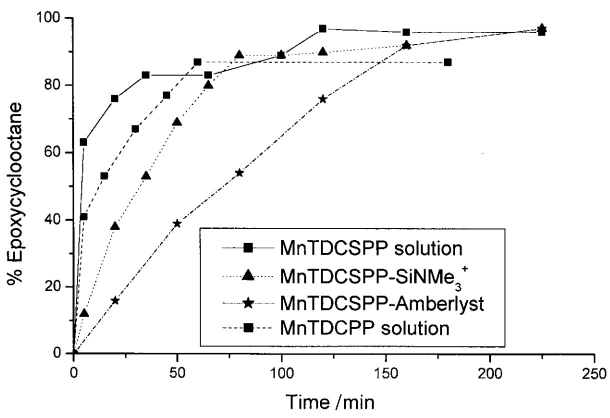


Fig. 4 The growth of epoxycyclooctane with time in the reaction of cyclooctene with PhIO catalysed by homogeneous and supported MnTDCSPP and MnTDCPP in acetonitrile (5.0×10^{-7} mol MnP; MnP:PhIO:cyclooctene, 1:136:2300).

Cyclooctene epoxidation using a single addition of iodosylbenzene

The standard conditions used for the epoxidations of cyclooctene, with both the homogeneous and heterogeneous systems, employed the catalyst, oxidant and substrate in the molar ratios 1:136:2300. The production of epoxide during the reaction was monitored by GC analysis (Figs. 4 and 5).

Initially the epoxidations of cyclooctene catalysed by MnTDCSPP, $MnTDCSPP–SiNMe_3^+$ and $MnTF_4TMAPP–$

Table 1 Product yields from cyclooctene epoxidation catalysed by homogeneous and supported manganese porphyrins in different solvents[a]

Catalyst	Solvent	Epoxide (%)[b]	PhI (%)[c]
MnTDCSPP[c]	MeOH	16	51
MnTDCSPP[c]	MeCN–MeOH[f]	72	80
MnTDCSPP[d]	CH_2Cl_2	67	88
MnTDCSPP[d]	MeCN	96	100
MnTDCSPP–$SiNMe_3^+$	CH_2Cl_2	77	96
MnTDCSPP–$SiNMe_3^+$	MeCN	91	103
$MnTF_4TMAPP$[e]	MeCN	97	100
$MnTF_4TMAPP$–$SiSO_3^-$	MeOH	12	60
$MnTF_4TMAPP$–$SiSO_3^-$	CH_2Cl_2	62	85
$MnTF_4TMAPP$–$SiSO_3^-$	MeCN	92	100

[a] MnP, 5.0×10^{-7} mol or equivalent of supported catalyst; alkene, 0.15 cm^3; PhIO, 15 mg; acetonitrile, 3.0 cm^3. [b] Yields based on PhIO added. [c] Counter ion Na^+. [d] Counter ion NBu_4^+. [e] Counter ion PF_6^-. [f] CH_3CN–MeOH, 80:20, v/v.

Table 2 Product yields from cyclooctene epoxidation catalysed by homogeneous and supported manganese porphyrins[a]

Catalyst	Epoxide (%)[b]	PhI (%)[b]	$PhIO_2$ (%)[b]	[O] (%)[c]	[PhI] (%)[d]
MnTDCPPCl	87	100	0	87	100
MnTDCSPPCl[e]	96	100			
MnTDCSPP–$SiNMe_3^+$	91	103	0	91	103
MnTDCSPP–Amberlyst	97	98	0	97	98
$MnTF_5PPCl$	100	100	0	100	100
$MnTF_4TMAPP$[f]	97	100			
$MnTF_4TMAPP$–$SiSO_3^-$	92	100	0	92	100
$MnTF_4TMAPP$–Dowex	92	92	2	96	94

[a,b] See Table 1. [c] Oxidant mass balance, % yield of epoxide + $PhIO_2$. [d] Iodobenzene balance, % yield of PhIO + $PhIO_2$. [e] Counter ion NBu_4^+. [f] Counter ion PF_6^-.

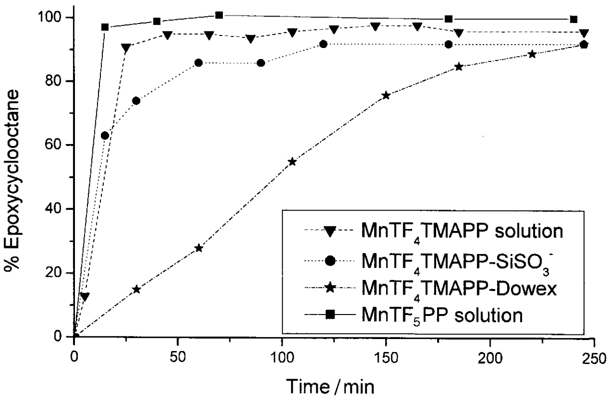


Fig. 5 The growth of epoxycyclooctane with time in the reaction of cyclooctene with PhIO catalysed by homogeneous and supported $MnTF_4TMAPP$ and $MnTF_5PP$ in acetonitrile (5.0×10^{-7} mol MnP; MnP : PhIO : cyclooctene, 1 : 136 : 2300).

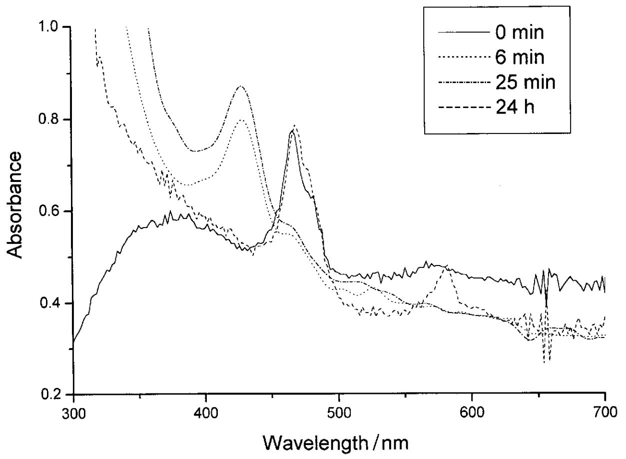


Fig. 6 UV–Vis spectra of reaction mixtures recorded during the oxidation of cyclooctene by PhIO catalysed by MnTDCSPP–$SiNMe_3^+$ in acetonitrile.

$SiSO_3^-$ were carried out in three solvents, namely, methanol, acetonitrile and CH_2Cl_2 (Table 1). Since the tetrasodium salt of MnTDCSPP is not soluble in relatively non-polar solvents, it was converted into the organic soluble tetrabutylammonium derivative for these studies. Based on the yields of epoxycyclooctane, the best solvent proved to be acetonitrile.

The results from oxidations in acetonitrile show that the homogeneous reactions are significantly faster than their heterogeneous analogues and that $MnTF_5PP$ and $MnTF_4TMAPP$ are more active catalysts than MnTDCPP and MnTDCSPP (Table 2). The rates of all the epoxidations catalysed by manganese(III) porphyrins (MnPs) on silica based supports are similar and faster than the reactions catalysed by MnPs on ion-exchange resins. The final yields and selectivities of all the epoxidations are excellent (Table 2). The oxidant mass balance was also checked by measuring the yields of PhI (GC analysis) and $PhIO_2$ (iodometric titration).[5a,12] These allowed calculations of oxygen and iodobenzene mass balances [O] and [PhI], respectively. Table 2 shows that most of these values are close to 100%.

The stability of the supported catalysts towards leaching was investigated by examining the UV–Vis spectrum of the filtered reaction mixtures and by testing the filtrates in further oxidations by the addition of fresh PhIO. Both tests showed that the ionic porphyrins on counterionic supports are not leached during these reactions.

The course of the oxidation catalysed by MnTDCSPP and $MnTF_4TMAPP$ in homogeneous solution and by the heterogeneous MnTDCSPP–$SiNMe_3^+$ was also monitored by UV–Vis spectroscopy. This showed that in each of the reactions the Soret peak (λ_{max} 460–480 nm) decreased as the absorbance of an oxomanganese(IV) porphyrin (λ_{max} 418–430 nm) increased. However, after several hours this change was reversed and the Soret peak of the manganese(III) porphyrin was fully restored (see for example Fig. 6). Interestingly these changes are only observed with $MnTF_4TMAPP$–$SiSO_3^-$ in the absence of the substrate. With the substrate present the UV–Vis spectrum remained effectively unchanged during the course of the reaction.

Cyclooctene epoxidation; multiple additions of iodosylbenzene

The stability of the supported MnTDCSPP and $MnTF_4TMAPP$ catalysts was monitored using multiple, sequential oxidations with PhIO. For each of the repeat oxidations the catalyst was recovered, washed exhaustively with methanol to remove $PhIO_2$ and dried before being reused with fresh substrate and oxidant. The iodoxybenzene by-product was measured by iodometric titration.

The two major limitations of this repeat use procedure are the physical stability of the support to prolonged stirring and the chemical stability of the support/MnP towards oxidative degradation. The catalysts were examined under three experimental regimes using catalyst : oxidant : substrate in the following molar ratios for each repeat oxidation: (*a*) 1 : 136 : 2300, (*b*) 1 : 816 : 4600 and (*c*) 1 : 8200 : 46000.

For repeat oxidations using the standard conditions, regime (*a*), both the catalysts on the modified silica and on ion-exchange resins, gave excellent repeatability for six to ten sequential oxidations and further recycling experiments were limited by the physical stability of the support rather than catalyst destruction (see for example, Table 3 and Fig. 7). The overall yields from these catalyst-reuse reactions for all four supported catalysts are shown in Table 4.

In regime (*b*), the oxidant to catalyst ratio was increased six-fold and the reaction profiles of each system showed that the catalyst's activity remained unchanged for five recycling experiments after which it became less effective. These oxidations were clearly limited by the stability of the catalyst rather than that of the support (see for example, Table 5 and Fig. 8). The overall yields and turnovers of these reactions are shown in Table 6.

The oxidations with regime (*c*) were investigated using the modified silica supports only. The catalyst : oxidant : substrate ratios were obtained in two ways, both of which maintained the same mass of support as in regimes (*a*) and (*b*). One used a lower loaded catalyst (1 mg g^{-1}) and the other a mixture of the standard catalyst (10 mg g^{-1}) diluted in a 1 : 9 ratio with unloaded support. The low loaded catalysts were significantly more effective than the 'diluted' ones (Tables 7 and 8). However, both were much more active than the homogeneous analogues. As with regime (*b*), catalyst rather than support stability was the limiting factor in the recycling experiments.

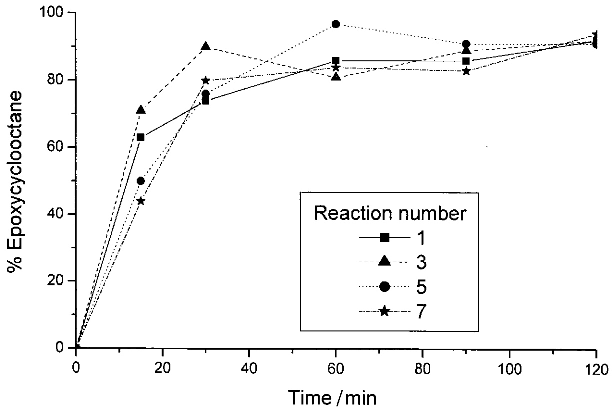


Fig. 7 The growth of epoxycyclooctane with time in repeat reactions of cyclooctene with PhIO catalysed by $MnTF_4TMAPP–SiSO_3^-$ in acetonitrile (5.0×10^{-7} mol MnP; MnP : PhIO : cyclooctene, 1 : 136 : 2300 per oxidation).

Table 3 Product yields from epoxidation of cyclooctene with recycled MnTDCSPP–Amberlyst catalyst[a]

Oxidation number	Epoxide (%)	Turnovers[e]	PhI (%)[b]	$PhIO_2$ (%)[b]	[O] (%)[c]	[PhI] (%)[d]
1	97	132	98	0	97	98
2	91	124	97	1	93	98
3	93	126	94	0	93	94
4	91	124	100	0	91	100
5	100	136	100	0	100	100
6	89	121	91	2	93	93
7	96	131	96	3	102	99
8	92	125	93	2	96	95
9	85	116	91	1	87	92
10	91	124	94	1	93	95

[a–d] See Table 2. [e] Turnover, mol of product/mol of catalyst used.

It is noteworthy that as the oxidant to catalyst ratio was increased [on going from regime (*a*) to (*c*)], the overall selectivity for epoxidation decreased and in general more iodoxybenzene was obtained.

Epoxidation of (*E*)- and (*Z*)-4-methylpent-2-ene: single substrate reactions

The conditions used to epoxidise the 4-methylpent-2-enes were identical to the standard procedure described above for cyclooctene and the product yields obtained are recorded in Table 9. From the epoxide yields, it is clear that, apart from the reaction of $MnTF_4TMAPP$, the (*Z*)-alkene reacts more readily than the (*E*)-alkene in both the homogeneous and heterogeneous systems. For the (*Z*)-isomer many of the reactions gave quantitative epoxide yields. The reactions of each isomer were highly stereoretentive.

Epoxidation of (*E*)- and (*Z*)-4-methylpent-2-ene: competitive reactions

Competitive epoxidations of the two isomers, as expected, showed the greater reactivity of the (*Z*)-alkene (Table 10). The differences in reactivity which are dependent on the catalyst and

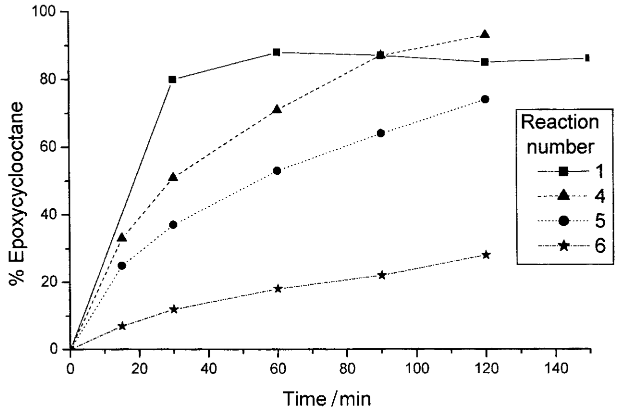


Fig. 8 The growth of epoxycyclooctane with time in repeat reactions of cyclooctene with PhIO catalysed by $MnTF_4TMAPP–SiSO_3^-$ in acetonitrile (2.5×10^{-7} mol MnP; MnP : PhIO : cyclooctene, 1 : 816 : 4600 per oxidation).

Table 5 Product yields from epoxidation of cyclooctene with recycled $MnTF_4TMAPP$–Dowex catalyst[a]

Oxidation number	Epoxide (%)[b]	Turnovers[e]	PhI (%)[b]	$PhIO_2$ (%)[b]	[O] (%)[c]	[PhI] (%)[d]
1	80	654	89	1	82	90
2	80	654	91	1	82	92
3	83	679	92	1	85	93
4	81	662	95	1	83	96
5	72	589	89	1	74	90

[a] Each oxidation cycle used supported catalyst equivalent to 2.5×10^{-7} mol of MnP; alkene, 0.15 cm^3; PhIO, 45 mg; acetonitrile, 3.0 cm^3. [b–d] See Table 2. [e] Turnovers, mol of product/mol catalyst used.

Table 4 Total yields, turnovers and oxidant and iodobenzene accountability for cyclooctene epoxidation by PhIO catalysed by supported $MnTF_4TMAPP$ and MnTDCSPP in catalyst-reuse experiments[a]

Catalyst	Catalyst cycles	Epoxide (%)[b]	Turnovers[e]	PhI (%)[b]	$PhIO_2$ (%)[b]	[O] (%)[c]	[PhI] (%)[d]
$MnTDCSPP–SiNMe_3^+$	6	88	718	102	0	88	102
MnTDCSPP–Amberlyst	10	93	1259	95	1	95	95
$MnTF_4TMAPP–SiSO_3^-$	8	91	995	102	2	95	104
$MnTF_4TMAPP$–Dowex	9	90	1097	91	2	94	93

[a] Each oxidation cycle used the conditions and amounts of reagents given in footnote (*a*) in Table 1; the catalyst was recovered, washed and dried as described in the text. [b–d] See Table 2. [e] Turnovers, mol of product/mol of catalyst used.

Table 6 Total yields, turnovers and oxidant and iodobenzene accountability for cyclooctene epoxidation by PhIO catalysed by supported $MnTF_4TMAPP$ and MnTDCSPP in catalyst reuse experiments: catalyst : PhIO : alkene, 1 : 816 : 4600 per cycle[a]

Catalyst	Catalyst cycles	Epoxide (%)[b]	Turnovers[e]	PhI (%)[b]	$PhIO_2$ (%)[b]	[O] (%)[c]	[PhI] (%)[d]
MnTDCSPP–$SiNMe_3^+$	5	64	2626	84			
MnTDCSPP–Amberlyst	5	79	3238	91	1	81	92
$MnTF_4TMAPP$–SiO_3^-	5	82	3362	99	4	90	101
$MnTF_4TMAPP$–Dowex	6	65	3182	85	1	67	86

[a] Conditions for each oxidation cycle given in footnote (*a*) in Table 5. [b–d] See Table 2. [e] Turnovers, mol of product/mol of catalyst used.

Table 7 Yields and turnovers for cyclooctene epoxidation by PhIO catalysed by $MnTF_4TMAPP$ in homogeneous solution and on modified silica supports: catalyst : PhIO : alkene, 1 : 8200 : 46000[a]

Catalyst	Oxidation number	Epoxide (%)[b]	Turn-overs[c]	PhI (%)[b]	$PhIO_2$ (%)[b]
(Solution)		21	1722	47	
On $SiSO_3^-$ (diluted)	1	76	6232	94	4
On $SiSO_3^-$ (diluted)	2	17	1394	56	22
On $SiSO_3^-$ (diluted)	3	9	738	32	37
On $SiSO_3^-$ (low loading)	1	100	8200	100	2
On $SiSO_3^-$ (low loading)	2	55	4510	85	9
On $SiSO_3^-$ (low loading)	3	24	1968	45	22

[a] Each oxidation cycle used 2.5×10^{-8} mol of catalyst or supported catalyst; alkene, 0.15 cm^3; PhIO, 45 mg; acetonitrile, 3.0 cm^3. [b] Yield based on PhIO. [c] Turnovers, mol of product/mol of catalyst used.

Table 8 Yields and turnovers for cyclooctene epoxidation by PhIO catalysed by MnTDCSPP in homogeneous solution and on $SiNMe_3^+$ 'diluted' and low loaded: catalyst : PhIO : alkene, 1 : 8200 : 46000[a]

Catalyst	Oxidation number	Epoxide (%)[b]	Turn-overs[c]	PhI (%)[b]	$PhIO_2$ (%)[b]
(Solution)		20	1640	55	
On $SiNMe_3^+$ (diluted)	1	61	5002	109	2
On $SiNMe_3^+$ (diluted)	2	37	3034	57	6
On $SiNMe_3^+$ (low loading)	1	62	5084	100	0
On $SiNMe_3^+$ (low loading)	2	55	4510	85	4
On $SiNMe_3^+$ (low loading)	3	38	3116	77	6

[a] Conditions for each oxidation cycle given in footnote (*a*) in Table 7. [b] Yield based on PhIO. [c] Turnovers, mol of product/mol of catalyst used.

Table 9 Product yields from the single substrate epoxidation of (*Z*)- and (*E*)-4-methylpent-2-ene with iodosylbenzene catalysed by homogeneous and supported manganese porphyrins[a]

Catalyst	Alkene isomer	Epoxide (%) *Z*[b]	Epoxide (%) *E*[b]	Total epoxide (%)[b]	PhI (%)[b]
MnTDCPP	*Z*	100	0	100	97
MnTDCPP	*E*	0	63	63	100
MnTDCSPP[c]	*Z*	100	1	101	94
MnTDCSPP[c]	*E*	1	39	40	99
MnTDCSPP–$SiNMe_3^+$	*Z*	88	1	89	87
MnTDCSPP–$SiNMe_3^+$	*E*	0	67	67	98
MnTDCSPP–Amberlyst	*Z*	78	4	82	90
MnTDCSPP–Amberlyst	*E*	3	36	39	96
$MnTF_5PP$	*Z*	100	0	100	100
$MnTF_5PP$	*E*	0	80	80	90
$MnTF_4TMAPP$[d]	*Z*	100	2	102	90
$MnTF_4TMAPP$[d]	*E*	1	99	100	92
$MnTF_4TMAPP$–$SiSO_3^-$	*Z*	99	4	193	89
$MnTF_4TMAPP$–$SiSO_3^-$	*E*	0	65	65	100
$MnTF_4TMAPP$–Dowex	*Z*	81	2	83	72
$MnTF_4TMAPP$–Dowex	*E*	0	36	36	95

[a,b] See Table 1. [c] Counter ion, NBu_4^+. [d] Counter ion, PF_6^-.

the support, are in the range 0.9–6.2 The comparison between the relative reactivities obtained using the supported and homogeneous catalysts provides information about the access of the substrates to the active oxidant.

Discussion

Previous work has described the immobilisation of metalloporphyrins by coordinative binding to ligands attached to a solid support.[3,4a,b,5] However, metalloporphyrins on these materials have been found to be prone to leaching and for this reason more robust anchoring methods, such as covalent[4h,13] or ionic binding,[14] have been developed. The aim of this research was to examine the performance of ionic MnPs bound to supports by electrostatic interactions. Two types of support were chosen for this study: surface-modified silica and

Table 10 Competitive epoxidations of (*E*)- and (*Z*)-4-methylpent-2-ene with iodosylbenzene catalysed by homogeneous and supported manganese porphyrins[a]

Catalyst	Epoxide (%) (*Z*)[b]	Epoxide (%) (*E*)[b]	Ratio *Z*/*E* epoxide	Total yield (%)[b]	PhI (%)[b]
MnTDCPP	73	27	2.7	100	99
MnTDCSPP[c]	81	13	6.2	94	92
MnTDCSPP–$SiNMe_3^+$	90	17	5.3	107	100
MnTDCSPP–Amberlyst	37	21	1.8	58	99
$MnTF_5PP$	52	11	4.7	63	100
$MnTF_4TMAPP$[d]	74	33	2.2	107	94
$MnTF_4TMAPP$–$SiSO_3^-$	52	33	1.6	85	95
$MnTF_4TMAPP$–Dowex	25	29	0.9	54	95

[a] Conditions as in Table 1 with 0.075 cm^3 of each alkene isomer. [b–d] See Table 9.

ion-exchange resins, with SO_3^- functional groups to bind the cationic manganese porphyrin ($MnTF_4TMAPP$) and equivalent materials with NMe_3^+ substituents to interact with the anionic manganese porphyrin (MnTDCSPP). The surface modification of the silica gel was readily brought about using the appropriate silylating agent (Fig. 1).

Ion-exchange resins have been used previously by us to support the iron(III) complexes of 5,10,15,20-tetrakis(*N*-methyl-4-pyridyl)-, 5,10,15,20-tetrakis(4-sulfonatophenyl)- and 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)-porphyrins and it was noted that rigid, heavily cross-linked resins produce the best organic supports for oxidation catalysts.[14a] Based on our earlier studies we selected the cation-exchange resin Dowex MSC1 (20% cross-linked) and the anion-exchanger Amberlyst A-27 (20% cross-linked) for this investigation.

The results confirm, as expected, that immobilising metalloporphyrins by ionic binding is easy to achieve and leads to strongly bound catalysts. The cationic manganese porphyrin used in this study can also be bound directly to unmodified silica, as has been noted before for metallo-tetrakis(*N*-methylpyridyl)porphyrins.[15] However, this binding is weaker than that to $SiSO_3^-$ and the catalysts obtained are less efficient.[16] The results from these systems are not included in this paper.

Coordinated MnPs can be relatively easily leached with solvents such as acetonitrile or methanol, presumably by competitive coordination displacing the MnP from the support. This restricts their use as catalysts to oxidations in non-polar, non-coordinating solvents, such as dichloromethane and dichloroethane. The ionic manganese porphyrins bound to counter-charged supports, however, can be used without leaching in these solvents as well as in acetonitrile and methanol. They are, however, leached from the supports in water and cannot be used in aqueous reaction systems.[17]

Optimisation of the epoxidation of cyclooctene

The epoxidising systems were compared and optimised using cyclooctene as the standard substrate. This alkene was selected as it is reactive towards metalloporphyrin-based epoxidising agents, is not prone to allylic oxidation[18] and has been widely used in previous epoxidation studies with both homogeneous and heterogeneous catalysts.

The choice of solvent is critical since it should be oxidatively stable, it should dissolve the substrate and catalyst (in homogeneous reactions) and at least partially dissolve the relatively insoluble oxidant PhIO. For comparison of the supported catalysts with metalloporphyrins in homogeneous solution, it is also important that the same solvent is employed for both systems. Three solvents were selected, namely, dichloromethane, acetonitrile and methanol, and, to ensure complete solubility of the homogeneous catalyst in each of these, the counter ion used for MnTDCSPP was Bu_4N^+ and for $MnTF_4TMAPP$ it was PF_6^-.

In the catalysed oxidations, it is also very informative to measure the overall accountability of the oxidant. In this study this was achieved in two ways, by measuring the oxidant ([O]) and the PhI accountability ([PhI]) of each reaction. The former involved measuring the total % yield of oxidised products detected as epoxide (analysed by GC) and as $PhIO_2$ (analysed iodometrically) and the latter required the total % yield of PhI (analysed by GC) and $PhIO_2$ based on the amount of PhIO used. These PhIO accountabilities provide information on the fate of the oxidant where the epoxide yield is not quantitative: the missing oxidising equivalents forming undetected products from competitive oxidations of solvent and/or support.

The results obtained from the present study allow several comparisons, including solvent effects, anionic *versus* cationic manganese porphyrin catalysts in homogeneous and heterogeneous systems, inorganic *versus* organic supports and homogeneous *versus* heterogeneous catalysts.

All three solvents have been used previously for alkene epoxidation with PhIO catalysed by metalloporphyrins. In this study acetonitrile was clearly the best solvent (Table 1). Methanol, unlike dichloromethane and acetonitrile, dissolves PhIO,[19] however, the epoxidation yields in methanol were disappointingly low and the yields of the unwanted $PhIO_2$ were high. It seems likely that the increased concentration of PhIO in methanol solution results in the formation of $PhIO_2$ at the expense of epoxycyclooctane from the competition between PhIO and cyclooctene for the active oxidant. Using methanol–acetonitrile mixtures, as expected, led to more epoxide but the yield of $PhIO_2$ was still relatively high. All subsequent reactions were carried out in acetonitrile.

Under the standard reaction conditions (catalyst : oxidant : substrate molar ratios 1 : 136 : 2300), the epoxide yield from the charged porphyrins was almost quantitative with both homogeneous and heterogeneous systems (Table 2). It is clear that under these conditions, oxidations of the solvent, PhIO and support do not compete effectively with that of the substrate. For the two homogeneous oxidations with the charged MnPs, the [O] and [PhI] accountabilities could not be measured because the metalloporphyrin in solution masked the iodometric titration end-points; however, the epoxide and PhI yields show these reactions are also very selective. Allowing for this, the overall accountability of the PhIO as [O] and [PhI] was quantitative.

The efficiencies of the different catalyst systems can be compared by monitoring the growth of epoxide with time (Figs. 4 and 5). This reveals that for each MnP, the homogeneous epoxidation is approximately three times faster than that using a modified silica support and ten times faster than that with an ion-exchange resin. One factor that contributed to the slower oxidations using the resin-supported catalysts compared with those on modified silica was the rate of stirring of the reaction mixtures. Since the ion-exchange resins are more fragile than the modified silicas, it was necessary to use slower rates of stirring with the former systems to minimise the grinding of the support during the reactions. In agreement with this conclusion, when the slower rate of stirring was used with the silica-supported catalysts the rate of reaction was also lowered. Previous studies on FeP-catalysed epoxidation of cyclooctene with PhIO showed that homogeneous systems were approximately 10 times more reactive than their silica-supported analogues.[4b] This difference in the rates of homogeneous and heterogeneous reactions was ascribed to diffusional problems with the latter which retard the approach of PhIO and cyclooctene to the catalyst on the highly polar supports and the diffusion of product epoxide back into the reaction medium. Presumably these effects are also important in the present study and would account for the somewhat slower rates of epoxidation with the supported catalysts.

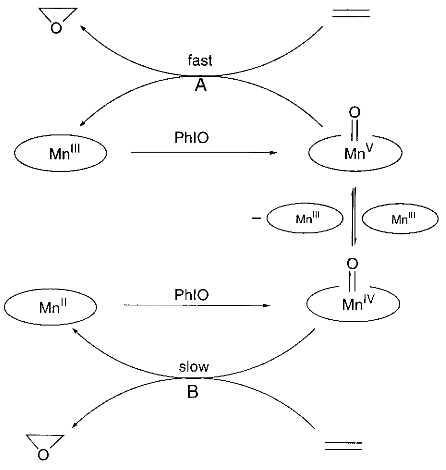
Since all the catalysts gave excellent yields of epoxycyclooctane under the standard conditions, they were tested much more extensively in repeat oxidations. Initially each of these used a 136-fold excess of oxidant over catalyst; however, in later experiments this was increased to 816- and 8220-fold. It is important to note that for these studies, in each repeat oxidation, the catalyst was used in a fresh reaction mixture, after it had been recovered, washed and dried. This procedure was used rather than simply adding repeated aliquots of PhIO to a single reaction mixture (the latter method was employed by us in previous studies[4b,h,5b,14]). Although it is more time consuming, it prevents the problematic build-up of PhIO$_2$ in the reaction mixture. Using the standard set of conditions, the modified silica-supported catalysts maintained their activity for 6–8 cycles; however, the stirring fragmented the support and further repeat oxidations were limited by loss of catalyst as fines in the recovery process. Other methods of agitating the reaction mixtures, such as shaking, rotation or ultra-sonication or using the supported catalyst in a catalytic filter in a flow system, might be more appropriate; however, these were not investigated in this study. Interestingly, the more fragile catalysts on ion-exchange resins, using slower stirring, survived better, showing little evidence of degradation even after 9 cycles (MnTF$_4$TMAPP–Dowex) and 10 cycles (MnTDCSPP–Amberlyst) and gave 1097 and 1259 turnovers corresponding to 90 and 93% yields of epoxycyclooctane, respectively (Tables 3 and 4). Clearly under the standard conditions these systems are not restricted by degradation of the MnP but rather by the physical strength of the support.

In repeat oxidations, using a catalyst to oxidant ratio of 1:816 per oxidation cycle, the activity of each system was significantly reduced after 5–6 cycles with overall epoxycyclooctane yields of 64–83%. Under these conditions manganese porphyrin destruction is the critical factor that determines the overall yield. To explore this further, an even larger catalyst to oxidant ratio (1:8200) was used with the modified silica-supported catalysts. This was achieved by reducing the amount of catalyst employed ten-fold, in two ways: first by using a low loading of catalyst (1 mg g^{-1}) and secondly by 'diluting' the 10 mg g^{-1} supported catalyst with modified silica without catalyst, in the ratio of 1:9. Both experiments effectively maintained a constant mass of support and manganese porphyrin. The first batch of PhIO with all the catalysts gave moderate to excellent yields of epoxycyclooctane (62–100%); however, repeat oxidations gave lower yields (Tables 7 and 8). The 'low loaded' MnPs produced better catalysts than the materials 'diluted' with modified silica. Thus the 'low loaded' MnTF$_4$TMAPP–SiSO$_3^-$ and MnTDCSPP–SiNMe$_3^+$ catalysts gave approximately 15000 and 13000 turnovers, respectively, from three sequential oxidations (Tables 7 and 8 respectively). Interestingly, as the catalyst became degraded the selectivity of the oxidation shifted from cyclooctene towards PhIO so that the decrease in epoxidation yield was largely offset by an increase in the yield of PhIO$_2$. Presumably this change in reaction selectivity arises from the oxidation of the catalyst which produces a modified active oxidant with an increased preference for reaction with PhIO.

It is noteworthy that homogeneous oxidations using acetonitrile solutions of MnTDCSPP and MnTF$_4$TMAPP with the addition of a single 8200-fold excess of PhIO led to the complete deactivation of the catalyst and very low yields of epoxide (~ 20%, ~ 1700 turnovers). The results show that for these large turnover reactions manganese porphyrin immobilisation leads to a dramatic improvement in catalyst stability and consequently to increased epoxide yields. We assume that this arises from site-isolation and immobilisation of the manganese porphyrin species on the surface of the modified silica which restricts porphyrin–porphyrin interactions and intermolecular oxidative destruction of the catalyst molecules. The superior performance of the 'low loaded' as opposed to 'diluted' catalyst supports this conclusion since the more effective separation of the MnPs on the surface of the low loaded catalyst reduces still further catalyst–catalyst interactions which in turn leads to better catalysts. It is, however, probable that, even if all catalyst–catalyst interactions are effectively eliminated, some catalyst destruction will occur by intramolecular self-reaction of the oxomanganese(V) species.

(*Z*)- and (*E*)-methylpent-2-ene epoxidation

The stereochemistry of the epoxidations by the homogeneous and heterogeneous MnP systems was studied using (*E*)- and (*Z*)-4-methylpent-2-ene in both single substrate and competitive reactions. Interestingly, the epoxidations of both substrates show very high stereoretention with very small amounts of the diastereoisomeric epoxide being formed. Based on the earlier studies of Groves and Bruice and their co-workers,[20,21] which showed that the epoxidations of (*Z*)-β-methylstyrene and (*Z*)-stilbene with oxomanganese(V) porphyrins occur with stereoretention whereas those with oxomanganese(IV) porphyrins lead to significant loss of stereochemistry, it is clear that the main active oxidant in the present study is the oxomanganese(V) porphyrin. Thus, although the oxomanganese(IV) porphyrin was detected by UV–Vis spectroscopy as a major species in the reaction mixtures, it is less reactive than the oxomanganese(V) porphyrin and only accounts for a minimal amount of the epoxide formed. Bruice and co-workers[21] came to a similar conclusion when carrying out computer simulations of their kinetic studies on the manganese(III) porphyrin-catalysed epoxidation of alkenes by hypochlorite. Although oxomanganese(IV) porphyrin was a major species in their reactions, the inclusion of its epoxidation of alkenes in the kinetic model was unnecessary to obtain a good simulation of the kinetics. Thus the majority of the oxidation takes place *via* an Mn(III)–OMn(V) cycle (Scheme 1, route A) rather than the Mn(II)–Mn(IV) cycle (Scheme 1, route B).



Scheme 1

The single substrate reactions show that for each catalyst the (*Z*)-alkene gives higher epoxide yields (80–100%) than the (*E*)-isomer (40–80%), with the exception of the reactions with $MnTF_4TMAPP$ which catalysed the quantitative epoxidation of both alkenes. The preferential reaction of the (*Z*)-alkene was explored further by examining the intermolecular stereoselectivity of the epoxidations of the two substrates in competitive reactions. These also show that with both the homogeneous and heterogeneous catalysts, the (*Z*)-alkene reacts more readily than its (*E*)-isomer, with the exception of $MnTF_4TMAPP$–Dowex where both substrates have very similar reactivities.

Since, (*a*) the reactions used equimolar quantities of each alkene, (*b*) both substrates show very high stereoretention in their reactions and (*c*) the overall conversions of the substrates were low, the ratios of the epoxide yields (Table 10) are effectively equivalent to the ratios of the rate constants for epoxidation of the two alkenes [$k_{(Z)\text{-alkene}}/k_{(E)\text{-alkene}}$]. The greater reactivity of (*Z*)- than (*E*)-disubstituted alkenes is expected based on previous studies.[4b,22,23] Bruice and co-workers[22b] have carried out extensive studies on the difference in reactivities of (*Z*)- and (*E*)-alkenes towards high valent oxometal porphyrin oxidants, including energy minimisation calculations of the approach of the alkene. They concluded that the preferred trajectory of the alkene is parallel to the plane of the porphyrin ring but at a smaller angle to the oxo–metal bond rather than side-on as originally suggested by Groves and Nemo.[22a] Such a direction of approach would result in smaller steric effects between alkene and porphyrin than in the side-on model. Interestingly the intermolecular selectivities for these alkenes are smaller [$k_{(Z)\text{-alkene}}/k_{(E)\text{-alkene}}$, 0.9–6.2] than those observed using iron and supported iron porphyrins [$k_{(Z)\text{-alkene}}/k_{(E)\text{-alkene}}$, ~ 13].[4b,h,24] This could arise from a greater separation of the alkene and the oxomanganese(V) in the rate determining step (formation of the charge-transfer complex between alkene and oxomanganese(V) porphyrin[21,24]) than that for the equivalent oxoiron(IV) porphyrin π radical cation complex. Alternatively, the angle of approach of the alkene on the oxomanganese(V) could be smaller than that on the oxoiron analogue. Both these explanations could also explain why supported MnTDCSPP is an effective catalyst for the epoxidation of (*E*)-4-methylpent-2-ene, whereas FeTDCPP supported on pyridine-modified silica was inactive.[4b] The total lack of catalytic activity of the supported FeTDCPP was attributed to the steric hindrance from both the support and 2,6-dichlorophenyl substituents on the porphyrin ring. If the steric interactions between alkene and oxomanganese porphyrin are smaller than those of the iron porphyrin system, the rate of epoxidation of the (*E*)-isomer would increase relative to and might even become equivalent to that of the (*Z*)-isomer. In this respect, it is noteworthy that in the epoxidation of alkenes by peracids, where the rates are controlled more by electronic rather than steric effects, the differences in the rates of epoxidation of (*Z*)- and (*E*)-alkene isomers are small.[25]

The lower intermolecular substrate selectivities of the epoxidations catalysed by the $MnTF_5PP$ and $MnTF_4TMAPP$ systems than the comparable oxidations with the MNTDCPP and MnTDCSPP systems can be accounted for by a combination of the greater reactivity and smaller steric interactions of the oxomanganese(V) active oxidant with the fluorophenyl substituents than with dichlorophenyl groups. Furthermore, for the fluorophenylporphyrin the support might well lead to a flattening of the tetraarylporphyrin by reducing the dihedral angle between the aromatic substituents and the plane of the porphyrin ring. Such a change would result in a further reduction in the substrate selectivity. In this respect, it is noteworthy that the $MnTF_4TMAPP$–Dowex catalyst shows no selectivity between the (*E*)- and the (*Z*)-4-methylpent-2-enes.

For the dichlorophenyl-substituted porphyrin, the bulky *ortho*-chlorines should make the flattening of the tetraarylporphyrin more difficult. Interestingly, however, the MnTDCSPP–Amberlyst catalyst also shows a very low substrate selectivity. The origin of this support effect on stereoselectivity remains to be resolved.

Conclusions

1. The homogeneous and supported polyionic manganese porphyrins used in this study are effective catalysts for alkene epoxidation by PhIO.
2. In large turnover reactions the supported catalysts are superior to their homogeneous analogues.
3. With (*E*)- and (*Z*)-4-methylpent-2-ene the epoxidations with all the catalysts show very high retention of stereochemistry.
4. Although UV–Vis studies during reactions show the formation of oxomanganese(IV) porphyrins, the main active oxidant in these systems is the oxomanganese(V) species.

Experimental

Instrumentation

UV-Vis spectra were recorded on a Hewlett Packard 8452A diode array spectrometer. ^1H NMR spectra were obtained using Bruker MSL 300 and Jeol JNM-EX270 spectrometers using TMS as the internal standard. EI and FAB mass spectra were recorded on a VG Analytical Autospec mass spectrometer and ESI mass spectra were run by the EPSRC Mass Spectrometry Service Centre (University of Wales, Swansea). Gas chromatography was carried out with a Pye-Unicam 204 chromatograph with a flame ionisation detector using a carbowax capillary column [30 m, id 0.25 mm, phase thickness 0.25 μm (Alltech)]. The data were recorded and processed on a Viglen 486 PC running JCL 6000 software (Jones Chromatography Ltd). CHN analyses were measured by Butterworths Laboratories Ltd and by the Chemical Analytical Services Unit, University of Newcastle.

Materials

All materials were commercial reagent grade unless otherwise stated. Cyclooctene was purified by elution through a dry packed silica column immediately before use. Iodosylbenzene and iodoxybenzene were prepared following the methods of Sharefkin and Saltzman[26] and were shown to be >99% pure by iodometric titration.[12]

cis- and *trans*-2,3-Epoxy-4-methylpentanes were obtained from the alkenes using 3-chloroperoxybenzoic acid, as described previously.[4b] The epoxides were purified by distillation to >98% purity by GC.

Manganese(III) 5,10,15,20-tetrakis(2,6-dichlorophenyl)-porphyrin (MnTDCPP). The free base porphyrin was prepared following Lindsey *et al.*[27] and the manganese complex was obtained using the method of Adler and Longo[9] and had λ_{max} (CH_2Cl_2) 370, 392, 478 (1.2×10^4 m^2 mol^{-1}, lit.[27] 1.26×10^4 m^2 mol^{-1}), 574 nm. FAB$^+$-MS (NOBA matrix) molecular ion at *m*/*z* 943.5.

5,10,15,20-Tetrakis(2,6,-dichlorophenyl-3-sulfonatophenyl)-porphyrin ($H_2TDCSPP$). This was prepared from H_2TDCPP following Gonçalvez *et al.*[10] The tetrasodium salt of $H_2TDCSPP$ had λ_{max} (CH_3OH) 412 (12.9×10^4 m^2 mol^{-1}), 516, 546, 590 nm and λ_{max} (H_2O) 412, 514, 580, 634 nm. To obtain FAB$^+$ mass spectra the counter ion of $H_2TDCSPP$ was exchanged from sodium to tetrabutylammonium by dissolving the tetrasodium salt in water and adding tetrabutylammonium (TBA) chloride and extracting the $H_2TDCSPP$ as its Bu_4N^+ salt into dichloromethane. FAB$^+$-MS *m*/*z* (molecular mass) 2419 ($M + TBA^+$, calc. av. mass 2419), 2176 (M^+, calc. av. mass 2176), 1934 ($M - TBA^+$, calc. av. mass 1934).

Manganese(III) 5,10,15,20-tetrakis(2,6-dichloro-3-sulfonatophenyl)porphyrin (MnTDCSPP). Manganese insertion into the tetrasodium salt of H_2TDCSPP was achieved using manganese powder by the method of Herrmann *et al.*[11] H_2TDCSPP (250 mg) and manganese powder (3.5 g) were refluxed in deionized water (350 cm^3). After 3 h the mixture was cooled, filtered and the manganese porphyrin was purified by converting it into the tetrabutylammonium salt and extracting it into dichloromethane as described above. The counter ion was exchanged back to Na^+ by ion-exchange chromatography using an Amberlite CG-120 column (Na^+ form) and elution with deionised water. The MnTDCSPP was recrystallised from chloroform–methanol to give 70 mg (28% yield) of the desired product, λ_{max} (CH_3OH) 374, 396, 464 (1.2×10^4 m^2 mol^{-1}), 560 nm. Negative ion ESI-MS *m*/*z* 1262 ($M - H^-$), 630 ($M - 2H^{2-}$), 421 ($M - 3H^{3-}$). MnTDCSPP and TBA counter ion had λ_{max} (CH_2Cl_2), 386, 411, 478, 574 nm and FAB$^+$-MS (NOBA matrix) *m*/*z* 2470 ($M + TBA^+$, calc. av. *m*/*z* 2470), 2229 (M^+, calc. av. *m*/*z* 2229), 1987 ($M - TBA^+$, calc. av. *m*/*z* 1987), 1745 ($M - 2TBA^+$, calc. av. *m*/*z* 1745). Found: C, 34.91; H, 3.13; N, 3.49. Calc. for $C_{44}H_{20}N_4Cl_9MnO_{12}S_4 \cdot 12H_2O$: C, 34.89; H, 2.90; H, 3.70%.

Manganese(III) 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin ($MnTF_5PP$). This was prepared by metallation of the free base H_2TF_5PP with $MnCl_2$ by the method of Adler and Longo,[9] λ_{max} (CH_2Cl_2) 366, 474 (8.5×10^3 m^2 mol^{-1}, lit.[28] 8.7×10^3 m^2 mol^{-1}), 576 nm; FAB$^+$-MS (NOBA matrix) molecular ion at *m*/*z* 1027.5.

Manganese(III) 5,10,15,20-tetrakis[2,3,5,6-tetrafluoro-4-(trimethylammonio)phenyl]porphyrin ($MnTF_4TMAPP$). This was obtained from $MnTF_4DMAPP$ by a modification of the method of Miskelly and co-workers.[8] $MnTF_4DMAPP$ (204.0 mg, 1.8×10^{-4} mol) and methyl trifluoromethanesulfonate (0.42 cm^3, 3.7×10^{-3} mol) were stirred in trimethyl phosphate (11 cm^3) (dried over molecular sieve 4 Å) at 60 °C under N_2 overnight; then methanol (0.15 cm^3) was added to destroy unreacted methyl trifluoromethanesulfonate. The porphyrin was precipitated by adding diethyl ether (65 cm^3) to the mixture. The $CF_3SO_3^-$ counter-ion was exchanged for PF_6^- by dissolving $MnTF_4TMAPP$ in water, adding KPF_6 in a 1 : 1, v/v acetonitrile–dichloromethane mixture. The $MnTF_4TMAPP$, as its tetra(PF_6^-) salt, was extracted into the organic phase and purified by ion-pair chromatography on silica using 3 : 1, v/v acetonitrile–dichloromethane containing KPF_6 (10%, w/v) as the eluent. The solvent was removed under vacuum and the MnP(PF_6) was then dissolved in 1 : 3, v/v acetonitrile–dichloromethane and the excess of KPF_6 was extracted into water. The organic solution of the porphyrin was dried ($MgSO_4$) and the $MnTF_4TMAPP$ was recrystallised from dichloromethane–acetonitrile to give 356.2 mg (54% yield), one spot by TLC on silica gel (3 : 1, v/v acetonitrile–dichloromethane containing 10%, w/v KPF_6), λ_{max} (CH_3OH) 366, 414, 456 (1.02×10^4 m^2 mol^{-1}), 558 nm and FAB$^+$-MS *m*/*z* 1622.5 ($M - PF_6^+$), 1462.5 $[M - (PF_6 + CH_3PF_6)^+]$, 1302 $[M - (PF_6 + 2CH_3PF_6)^+]$. ESI-MS of $MnTF_4TMAPP(CF_3SO_3^-)_4$ *m*/*z* 817.1 $[(M - CF_3SO_3^-)^{2+}]$, 735.0 $[M - (CF_3SO_3^- + CF_3SO_3Me)^{2+}]$, 660.6 $[M - (2CF_3SO_3^- + CF_3SO_3Me)^{2+}]$, 653.0 $[M - (CF_3SO_3^- + 2CF_3SO_3Me)^{2+}]$, 578.6 $[M - (2CF_3SO_3^- + 2CF_3SO_3Me)^{2+}]$, 495.1 $[(M - 2CF_3SO_3^-)^{3+}]$, 440.5 $[M - (2CF_3SO_3^- + CF_3SO_3Me)^{3+}]$. Found: C, 34.02; H, 2.38; N, 5.55. Calc. for $C_{56}H_{44}N_8P_5F_{46}Mn \cdot 4H_2O$: C, 33.87; H, 2.32; N, 5.86%.

Preparation of modified silica supports. These were prepared by refluxing the silica (Kieselgel 60, surface area 500 m^2, pore size 60 Å and particle size 40–63 μm) in toluene in the presence of the appropriate trichloro- or trimethoxysilane derivative following the method of Leal *et al.*[7] $SiNMe_3^+$ was obtained using *N*-3-(trimethoxysilyl)propyl-*N*,*N*,*N*-trimethylammonium chloride (Fluorochem) and based on the nitrogen content (CHN analysis: C 7.86, H 2.3, N 1.40%), assuming an average of two bonds between the silane and the silica and five silanols groups nm^{-2},[7] had a loading of 48%. 2-(4-Chlorosulfonylphenyl)ethyltrichlorosilane (Fluorochem) was used to make chlorosulfonated phenylethylated silica and this was hydrolysed to the sulfonated phenylethylated silica by refluxing in water overnight to give $SiSO_3^-$. The resulting material was filtered, washed sequentially with toluene, acetone, water, 10% (w/v) aqueous sodium bicarbonate, water and methanol and dried under vacuum at 100 °C for 12 h. Based on the elemental analysis (CH analysis: C 5.41, H 0.94%) and the assumptions above, the $SiSO_3^-$ had a 27% loading.

Ion-exchange resins Dowex MSC-1 and Amberlyst A-27 were first washed with a ten-fold (v/v) excess of 10% (w/v) aqueous sodium carbonate and then sequentially with water, methanol and acetone before drying under vacuum at 100 °C for 12 h.

Preparation of supported catalysts

A typical loading procedure used the support (1 g) in methanol, acetonitrile or dichloromethane (4 cm^3) to which was added a solution of the manganese porphyrin (10 mg). The mixture was stirred until the supernatant liquid became colourless. The supported catalyst was collected by filtration and was washed overnight first with methanol and then with acetonitrile in a Soxhlet extractor. The supernatant and washings were combined and used to determine the unloaded manganese porphyrin by UV–Vis spectroscopy.

Alkene epoxidations

In a typical single substrate oxidation, the MnP or supported MnP (5.0×10^{-7} mol) was mixed with the substrate (~ 10^3 mol) in the solvent (3 cm^3) and the oxidation was initiated by the addition of iodosylbenzene (15 mg). The mixture was stirred and aliquots were removed at appropriate time intervals for GC analysis. The iodoxybenzene formed was determined iodometrically at the end of the reaction.

Competitive substrate oxidations were carried out as for the single substrates using equimolar quantities of each alkene substrate to give the same total amount of alkene as used for the single substrate experiments.

Repeat use oxidations were carried out as for single substrate oxidations above. After each oxidation the catalyst was separated by centrifugation and washed with methanol (10×3 cm^3). The catalyst was dried and then fresh substrate and iodosylbenzene were added. The combined washings were used for the iodometric determination of iodoxybenzene.

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References

1 (*a*) B. Meunier, *Chem. Rev.*, 1992, **92**, 1411; (*b*) D. Mansuy, *Coord. Chem. Rev.*, 1993, **125**, 129; (*c*) D. Dolphin, T. G. Traylor and L. Y. Xie, *Acc. Chem. Res.*, 1997, **30**, 251.
2 (*a*) P. S. Traylor, D. Dolphin and T. G. Traylor, *J. Chem. Soc., Chem. Commun.*, 1984, 279; (*b*) D. Ostovic and T. C. Bruice, *J. Am. Chem. Soc.*, 1989, **111**, 6511.
3 J. R. Lindsay Smith, in *Metalloporphyrins in Catalytic Oxidations*, ed. R. A. Sheldon, Marcel Dekker, New York, 1994, ch. 11.
4 (*a*) Y. Iamamoto, K. J. Ciuffi, H. C. Sacco, C. M. C. Prado, M. Moraes and O. R. Nascimento, *J. Mol. Catal.*, 1994, **88**, 167; (*b*) C. Gilmartin and J. R. Lindsay Smith, *J. Chem. Soc., Perkin Trans. 2*, 1995, 243; (*c*) P. Battioni, E. Cardin, M. Louloudi, G. Schollhorn, G. A. Spyroullias, D. Mansuy and T. G. Traylor, *Chem. Commun.*, 1996, 2037; (*d*) P. Battioni, R. Iwanejko,

D. Mansuy, T. Mlodnicka, J. Poltowicz and F. Sanchez, *J. Mol. Catal. A*: *Chem.*, 1996, **109**, 91; (*e*) H. S. Hilal, W. Jondi, S. Khalaf, A. Keilani, M. Suleiman and A. F. Schreiner, *J. Mol. Catal. A: Chem.*, 1996, **113**, 35; (*f*) M. A. Martinez-Lorente, P. Battioni, W. Kleemiss, J. F. Bartoli and D. Mansuy, *J. Mol. Catal. A*: *Chem.*, 1996, **113**, 343; (*g*) B.-Z. Zhan and X.-Y. Li, *Chem. Commun.*, 1998, 349; (*h*) M. D. Assis and J. R. Lindsay Smith, *J. Chem. Soc.*, *Perkin Trans. 2*, 1998, 2221; (*i*) C.-J. Liu, W.-Y. Yu, S.-G. Li and C.-M. Che, *J. Org. Chem.*, 1998, **63**, 7364; (*j*) B. T. Holland, C. Walkup and A. Stein, *J Phys. Chem.*, 1998, **102**, 4301; (*k*) P. E. F. Neys, I. F. J. Vankelecom, M. L'abbè, P. F. Parton, E. Cenlemans, W. Dehaen, G. L'abbè and P. A. Jacobs, *J. Mol. Catal. A: Chem.*, 1998, **134**, 209; (*l*) K. J. Ciuffi, H. C. Sacco, J. B. Valim, C. M. C. P. Manso, O. A. Serra, O. R. Nascimento, E. A. Vidoto and Y. Iamamoto, *J. Non-cryst. Solids*, 1999, **247**, 146.

5 (*a*) S. Campestrini and B. Meunier, *Inorg. Chem.*, 1992, **31**, 1999; (*b*) P. R. Cooke and J. R. Lindsay Smith, *J. Chem. Soc.*, *Perkin Trans. 1*, 1994, 1914.

6 R. A. Sheldon, M. Wallau, I. W. C. E. Arends and U. Schuchardt, *Acc. Chem. Res.*, 1998, **31**, 485.

7 O. Leal, D. L. Anderson, R. C. Bowman, F. Basolo and R. L. Burwell, *J. Am. Chem. Soc.*, 1975, **97**, 5125.

8 T. La, R. Richards and G. M. Miskelly, *Inorg. Chem.*, 1994, **33**, 3159.

9 A. D. Adler, F. R. Longo, F. Kampas and J. Kim, *J. Inorg. Nucl. Chem.*, 1970, **32**, 443.

10 A. M. A. Rocha Gonçalvez, R. A. W. Johnstone, M. M. Pereira, A. M. P. SantAna, A. C. Serra, A. J. F. N. Sobral and P. A. Stockes, *Heterocycles*, 1996, **4**, 43.

11 O. Herrmann, S. H. Mehdi and A. Corsini, *Can. J. Chem.*, 1978, **56**, 1084.

12 H. Lucas and E. R. Kennedy, *J. Org. Chem.*, 1955, **3**, 484.

13 P. Battioni, J. F. Bartoli, D. Mansuy, Y. S. Byun and T. G. Traylor, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1051.

14 (*a*) D. R. Leanord and J. R. Lindsay Smith, *J. Chem. Soc.*, *Perkin Trans. 2*, 1990, 1917; (*b*) D. R. Leanord and J. R. Lindsay Smith, *J. Chem. Soc.*, *Perkin Trans. 2*, 1991, 25.

15 P. Battioni, J.-P. Lallier, L. Barloy and D. Mansuy, *J. Chem. Soc.*, *Chem. Commun.*, 1989, 1149.

16 J. R. Lindsay Smith and H. C. Sacco, unpublished results.

17 J. R. Lindsay Smith and C. M. Mallabon, unpublished results.

18 A. J. Appleton, S. Evans and J. R. Lindsay Smith, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 281.

19 P. Inchley and J. R. Lindsay Smith, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 1579.

20 J. T. Groves and M. K. Stern, *J. Am. Chem. Soc.*, 1988, **110**, 8628; R. D. Arasasingham, G.-X. He and T. C. Bruice, *J. Am. Chem. Soc.*, 1993, **115**, 7985.

21 R. W. Lee, P. C. Nakagaki and T. C. Bruice, *J. Am. Chem. Soc.*, 1989, **111**, 1368.

22 (*a*) J. T. Groves and T. E. Nemo, *J. Am. Chem. Soc.*, 1981, **103**, 5786; (*b*) G.-X. He, H.-Y. Mei and T. C. Bruice, *J. Am. Chem. Soc.*, 1991, **113**, 5644.

23 J. R. Lindsay Smith and P. R. Sleath, *J. Chem. Soc.*, *Perkin Trans. 2*, 1982, 1009.

24 D. Ostovic and T. C. Bruice, *Acc. Chem. Res.*, 1992, **25**, 314; D. Ostovic, G.-X. He and T. C. Bruice, in *Metalloporphyrins in Catalytic Oxidations*, ed. R. A. Sheldon, Marcel Dekker, New York, 1994, ch. 2.

25 R. G. Carlson, N. S. Behn and C. Cowles, *J. Org. Chem.*, 1971, **36**, 3832.

26 (*a*) J. G. Sharefkin and H. Saltzman, *Org. Synth.*, 1963, **43**, 60; (*b*) J. G. Sharefkin and H. Saltzman, *Org. Synth.*, 1963, **43**, 65.

27 (*a*) J. S. Lindsey and R. W. Wagner, *J. Org. Chem.*, 1989, **54**, 828; (*b*) J. S. Lindsey, S. Prathapan, T. E. Johnson and R. W. Wagner, *Tetrahedron*, 1995, **50**, 8941.

28 S. Banfi, F. Montanari, M. Paenso, V. Sosnovskikh and P. Vigano, *Gazz. Chim. Ital.*, 1987, **117**, 3137.