

Alkene Epoxidation Catalysed by Iron(III) and Manganese(III) Tetraarylporphyrins Coordinatively Bound to Polymer and Silica Supports

Paul R. Cooke and John R. Lindsay Smith*
Department of Chemistry, University of York, York, UK YO1 5DD

Four tetraaryl metalloporphyrin catalysts [Fe^{III} , Ar = phenyl and pentafluorophenyl; Fe^{III} and Mn^{III} , Ar = 2,6-dichlorophenyl (Fe^{III} TDCPP and Mn^{III} TDCPP)] have been coordinatively bonded to poly(4-vinylpyridine), and imidazole modified polystyrene (PS-Im) and silica (Si-Im). Evidence is presented that suggests that the iron(III) porphyrins are predominantly bis-ligated to the polymer supports whereas with Mn^{III} TDCPP mono-ligation is preferred. On Si-Im all the complexes are mono-ligated. A fifth metalloporphyrin, the ionic manganese(III) 5,10,15,20-tetra(*N*-methyl-4-pyridyl)-porphyrin (Mn^{III} T4MPyP), which binds strongly to unmodified silica, does not ligate to Si-Im.

Leaching experiments show that Fe^{III} TDCPP is most strongly anchored to the supports. The resulting materials have been used as catalysts for the oxidation of cyclohexene and cyclooctene by iodosylbenzene. The oxidant accountabilities are good and product distributions from reactions under nitrogen are very comparable to those from analogous homogeneous oxidations. However, the rates of the former are markedly lower. Oxidations of cyclohexene, but not of cyclooctene, in air are biphasic. The first phase, where epoxidation predominates, is attributable to an Fe^{III} TDCPP-catalysed oxidation by PhIO and the second, which leads to allylic oxidation, to radical autoxidation.

The best catalysts for large turnover epoxidations are Fe^{III} TDCPP and Mn^{III} TDCPP on Si-Im. The causes of the lower yields with catalysts on the more flexible polymer supports are discussed.

A limited study with H_2O_2 as the oxidant reveals that Mn^{III} TDCPP on Si-Im, in contrast to the ionic Mn^{III} T4MPyP on silica, catalyses the epoxidation of cyclooctene.

Since the first report by Groves, Nemo and Myers¹ there have been great advances in the development of metalloporphyrin systems that mimic cytochrome P450 monooxygenases. Model systems are now available that will bring about all the major reactions of the enzymes and some show significant chemo-² and enantio-selectivity.³ However, almost all the research has been of a mechanistic nature and these systems have rarely been used in synthesis.

The main problem in developing these systems for synthesis has been the high cost of the catalysts. Although very stable metalloporphyrins are now available that will catalyse many thousands of oxidation turnovers,^{2a,4} further progress will probably require immobilising the catalysts on solid supports to aid their recovery and reuse.⁵ Supporting the catalysts might also have the added benefits of controlling the local environment of the oxidation and preventing deleterious intermolecular reactions between metalloporphyrins.

Five general methods have been used to anchor metalloporphyrins to solid surfaces, namely, covalent binding,⁶ coordinative binding,⁷ ionic interactions,⁸ intercalation^{8b,9} and entrapment.¹⁰ Each of these has potential advantages depending on factors such as, the strength of the attachment to the support, ease of preparation, general applicability to different metalloporphyrins, stability and selectivity.

Recently we have examined the potential of coordinatively bound supported metalloporphyrins as catalysts for alkene epoxidation and alkane hydroxylation. It was hoped that, provided the ligand-metal bond is sufficiently strong to prevent catalyst leaching, this approach could be used with a wide range

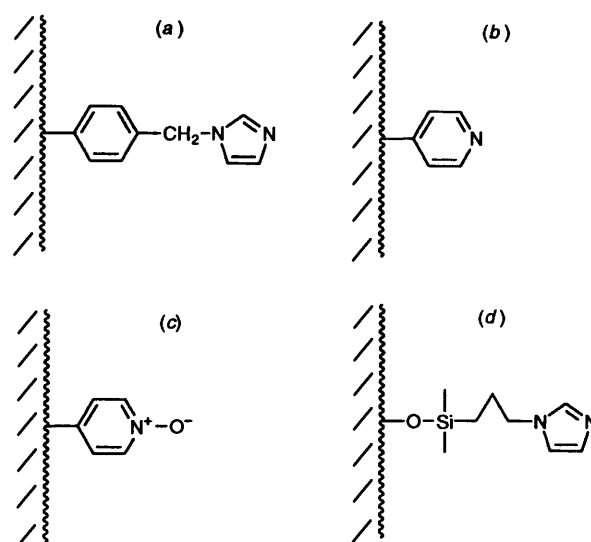


Fig. 1 Supports used for coordinative binding to metalloporphyrins: (a) imidazole modified polystyrene (PS-Im); (b) poly(4-vinylpyridine) (PVP); (c) poly(4-vinylpyridine *N*-oxide) (PVPO); (d) imidazole modified silica (Si-Im)

of metalloporphyrins and surface modified supports. In this paper we report on our studies using iron and manganese porphyrins coordinatively bound to nitrogen bases on the surface of organic and inorganic supports.

Results †

Preparation of Supported Metalloporphyrin Catalysts.—Preparation of supports. Imidazole was covalently bonded to silica using 3-chloropropyltrimethoxysilane as the coupling agent (Fig. 1).^{7b} Elemental analysis showed the loading of the imidazole to be 1.25 mmol g⁻¹ of silica. Assuming an average of

† The following abbreviations are used in this paper: PS-Im, imidazole modified polystyrene; Si-Im, imidazole modified silica; PVP, poly(4-vinylpyridine); PVPO, poly(4-vinylpyridine *N*-oxide); TPP, 5,10,15,20-tetraphenylporphyrin ligand; TDCPP, 5,10,15,20-tetra(2,6-dichlorophenyl)porphyrin ligand; TPFPP, 5,10,15,20-tetra(pentafluorophenyl)porphyrin ligand; T4MPyP, 5,10,15,20-tetra(*N*-methyl-4-pyridyl)porphyrin ligand.

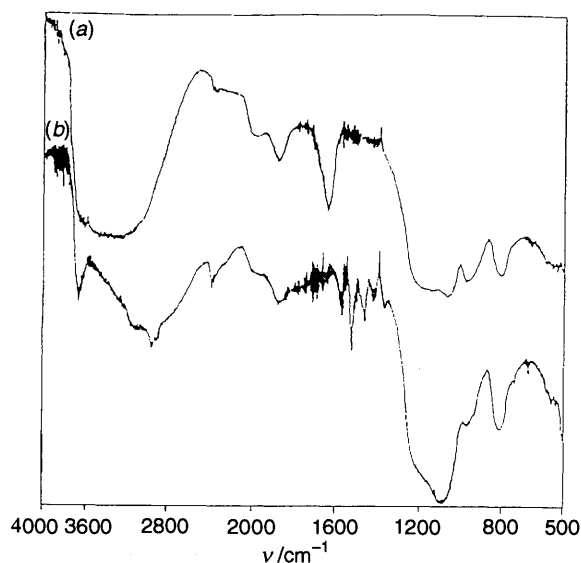


Fig. 2 IR spectra of silica (a) and imidazole-modified silica (b)

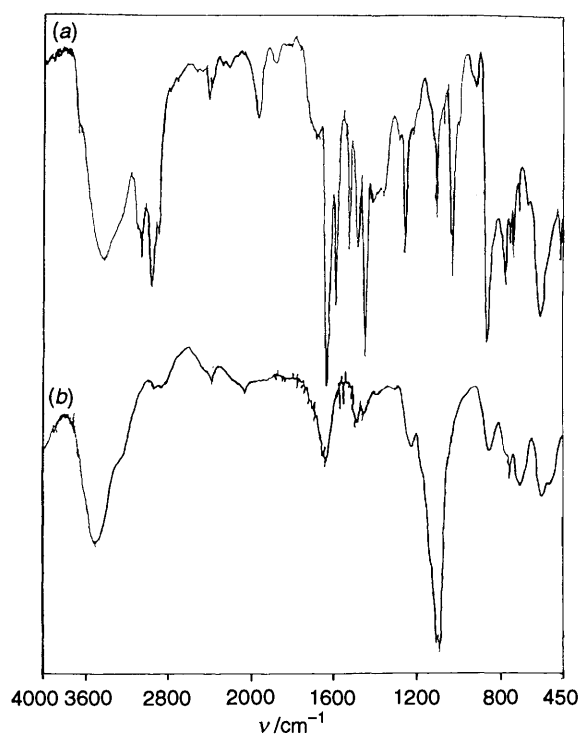


Fig. 3 IR spectra of PVP (a) and PVPO (b)

two bonds between the silane coupling agent and the silica and five silanol groups nm^{-2} ,^{7b,11} this is equivalent to approximately 60% coverage of the surface silanols by imidazoles. However, coverages of 26% and 11% were achieved by reducing the reaction time and ratio of imidazole and silane coupling agent to silica. IR Spectroscopy gave absorbances not present in the untreated silica, at 1566, 1515 and 1455 cm^{-1} (assigned to vibrations involving the imidazole ring) and 2960 cm^{-1} (the C-H stretch of the propyl coupling group) (Fig. 2).

Imidazole modified polystyrene (PS-Im) was prepared by the direct reaction of commercial 1% divinylbenzene crosslinked chloromethylated polystyrene with imidazole (Fig. 1). Elemental analysis showed this to have an imidazole loading of 4.09 mmol g^{-1} of polystyrene which corresponds to 97% conversion of the chloromethyl groups.

Poly(4-vinylpyridine *N*-oxide) was prepared by oxidation of

Table 1 Swelling characteristics of polystyrene, imidazole modified polystyrene and poly(4-vinylpyridine) in methanol and dichloromethane

Polymer	Volume ^a	
	MeOH	CH ₂ Cl ₂
Polystyrene	1.0	7.2
PS-Im	2.0	2.4
PVP	2.8	2.8

^a Relative to dry solid (1.0).

Table 2 Loadings of metalloporphyrins on organic and inorganic supports

Support	Metalloporphyrin	Washing solvent ^a	Loading ^b
PS	Fe ^{III} TDCPP	D	≈0
PS-Im	Fe ^{III} TDCPP	D, P, M	10 (or 49) ^c
PS-Im	Fe ^{III} TPP	D	<10
PS-Im	Fe ^{III} TPP	D, P, M	0
PS-Im	Fe ^{III} TPFPP	D, P, M	10
PS-Im	Mn ^{III} TDCPP	D, P, M	0
PVP	Fe ^{III} TDCPP	D, P, M	10
PVP	Fe ^{III} TPFPP	D, P, M	8
PVP	Mn ^{III} TDCPP	D, P, M	0
PVPO	Fe ^{III} TDCPP	D	0
PVPO	Mn ^{III} TDCPP	D	0
Si	Fe ^{III} TDCPP	D	0
Si	Mn ^{III} T4MPyP	D, A	10
Si-Im ^d	Fe ^{III} TDCPP	D	6
Si-Im ^d	Fe ^{III} TDCPP	D, P, M	4
Si-Im ^d	Fe ^{III} TPP	D	0
Si-Im ^d	Fe ^{III} TPFPP	D	6
Si-Im ^d	Mn ^{III} TDCPP	D	10 ^g
Si-Im ^d	Mn ^{III} T4MPyP	D, A	0.7
Si-Im ^e	Mn ^{III} T4MPyP	D, A	3
Si-Im ^f	Mn ^{III} T4MPyP	D, A	10

^a Washing solvents: D = dichloromethane; P = propanone; M = methanol and A = acetonitrile. ^b Loading in mg of metalloporphyrin per g of support. ^c Saturation loading. ^d 1.25 $\text{mmol imidazole g}^{-1}$. ^e 0.54 $\text{mmol imidazole g}^{-1}$ silica. ^f 0.23 $\text{mmol imidazole g}^{-1}$ silica. ^g Removed by washing in methanol.

6% divinylbenzene crosslinked poly(4-vinylpyridine). The resulting hygroscopic solid had a strong absorbance at 1088 cm^{-1} not present in the parent poly(4-vinylpyridine) (Fig. 3). The shift of this absorbance outside the typical range of N-O stretch (1150–1300 cm^{-1})¹² probably arises from the micro-environment of the polymer matrix.

The degree of swelling of the organic polymer supports in methanol and dichloromethane, the solvents chosen for metalloporphyrin loading and catalytic oxidations, are shown in Table 1. PS-Im and PVP both showed comparable swelling and little solvent dependence. By contrast the parent chloromethylated polystyrene is more swollen and more compatible with dichloromethane than the polar methanol.¹¹

Loading of metalloporphyrins onto the supports. The majority of the supported metalloporphyrin catalysts were prepared by stirring a suspension of the support in a solution of the metalloporphyrin in dichloromethane. These materials were subsequently washed with a range of organic solvents and the loadings were quantified by UV-VIS analysis of the metalloporphyrin in the combined filtrates and washings. The ionic porphyrin Mn^{III}T4MPyP was loaded from a solution in methanol. The loadings of the materials prepared in this study are recorded in Table 2. The data reveal that the final loading achieved depends on the metalloporphyrin, the support and the washing solvents used in the preparation. The two iron

Table 3 Product yields from reaction of (*Z*)-cyclooctene with iodosylbenzene catalysed by supported metalloporphyrins^a

Catalyst (loading) ^b	Solvent ^c	Yield ^d (%)				Turnover ^e	Leaching ^f
		Epoxide	HCHO	PhIO ₂	Total		
PS-Im-Fe ^{III} TDCPP (10)	M	78	14	3	95	104	No
PS-Im-Fe ^{III} TPFPP (10)	M	80	4	5	89	112	Yes
PVP-Fe ^{III} TDCPP (10)	M	40	n.d. ^g	n.d.	40	55	No
PVP-Fe ^{III} TDCPP (10) ^h	M	70	n.d.	n.d.	70	98	No
PVP-Fe ^{III} TPFPP (8)	M	80	7	4	91	135	Yes
Si-Mn ^{III} T4MPyP (10) ⁱ	D	95	—	1	96	640 ⁱ	No
Si-Mn ^{III} T4MPyP (10) ⁱ	A	97	—	0	97	655 ⁱ	No
Si-Im-Fe ^{III} TDCPP (4)	M	90	10	4	104	309	Yes
Si-Im-Fe ^{III} TDCPP (6)	D	99	—	2	101	1125 ⁱ	No
Si-Im-Mn ^{III} TDCPP (10) ⁱ	D	100	—	—	100	675 ⁱ	No
Si-Im-Mn ^{III} TDCPP (10) ⁱ	A	109	—	—	109	735 ⁱ	No
Si-Im-Mn ^{III} T4MPyP (10)	D-A	93	—	n.d.	93	126	No
Si-Im-Mn ^{III} T4MPyP (3)	D-A	77	—	n.d.	77	349	No
Si-Im-Mn ^{III} T4MPyP (0.7)	D-A	6	—	n.d.	6	116	No

^a Supported catalyst (100 mg), (*Z*)-cyclooctene (0.3 cm³), PhIO (30 mg), solvent (3 cm³). ^b Loading of metalloporphyrin on support/mg g⁻¹. ^c Solvents: methanol (M); dichloromethane (D); and acetonitrile (A). ^d Based on PhIO after 24 h. ^e Turnovers calculated on epoxide yield. ^f Monitored by UV-VIS spectroscopy of reaction solution. ^g Not determined. ^h Oxidation with a second addition of PhIO. ⁱ Total product yields from five additions of PhIO, interval between additions 24 h.

porphyrins with electron-withdrawing substituents are held more firmly than Fe^{III}TPP and the flexible polymer supports PS-Im and PVP coordinate these iron porphyrins better than Si-Im. These polymer supported materials have a pronounced orange-red colour similar to those observed with solutions of the bis-imidazole complexes of these iron(III) porphyrins. Saturation of the PS-Im with Fe^{III}TDCPP gave a maximum loading of 49 mg g⁻¹.

Mn^{III}TDCPP is more readily washed off the polymer supports than the iron(III) analogue. Acetone and methanol are more effective at leaching the metalloporphyrins from the support than dichloromethane. There was essentially no loading of Fe^{III}TDCPP on unmodified silica and neither iron(III) nor manganese(III) TDCPP bound to the poly(4-vinylpyridine *N*-oxide) (PVPO).

The ionic Mn^{III}T4MPyP, as reported by Mansuy and his co-workers,^{8b} is strongly bound to silica but the present studies show that coordinative binding to Si-Im is weak. Indeed there is a reverse correlation of Mn^{III}T4MPyP binding to Si-Im with the extent of imidazole modification of the silica.

Standard Conditions For Catalysed Epoxidations.—The epoxidations of (*Z*)-cyclooctene and cyclohexene were used as standard reactions to compare the efficiency and stability of the supported metalloporphyrin catalysts with each other and with analogous homogeneous systems. These substrates were selected as they have been used extensively in earlier metalloporphyrin catalysed oxidations.¹³ (*Z*)-Cyclooctene generally gives its epoxide as a single product, whereas with cyclohexene a mixture of epoxidation and allylic oxidation occurs. The solvents employed were methanol, dichloromethane, acetonitrile and an acetonitrile-dichloromethane mixture. The first solvent has the advantage that it dissolves PhIO, however, it is oxidised as a competitive substrate to formaldehyde and can act as a competitive ligand leading to leaching of the porphyrin from the support. Dichloromethane shows little reactivity towards the oxidant and is not a competitive ligand for the metalloporphyrin; however, it is not a good solvent for PhIO and it caused the less dense polymer supported metalloporphyrins to float, which resulted in less efficient mixing. Acetonitrile was used as the solvent or cosolvent with the oxidants Bu⁺O₂H and H₂O₂ to increase their solubilities and with the ionic Mn^{III}T4MPyP catalyst.

Of the five metalloporphyrins employed in this study all

except Fe^{III}TPP were used for cycloalkene epoxidation. Fe^{III}TPP was a very poor catalyst giving only a small number of catalytic turnovers before it was oxidatively bleached.

For the small scale oxidations typical reaction conditions involved treating 30 mg of PhIO with 0.3 cm³ of cycloalkene in 3 cm³ of solvent in the presence of 100 mg of supported catalyst.

Epoxidation of (*Z*)-Cyclooctene by PhIO Catalysed by Metalloporphyrins and Supported Metalloporphyrins.—The best yields of epoxycyclooctane from reactions with the heterogeneous catalysts were obtained with metalloporphyrins on the inorganic supports, largely because the solvents used in these reactions were not competitive substrates, whereas with the polymer-supported systems the solvent, methanol, consumed some of the oxidant to give formaldehyde (Table 3). Loss of oxidant by catalysed disproportionation to PhI and PhIO₂ was also lower in the former systems.

The oxidant balance in the oxidations was obtained by measuring the total percentage of the oxidant detected as epoxide (analysed by GC), PhIO/PhIO₂ (analysed iodometrically) and formaldehyde (where applicable, analysed colorimetrically).¹⁴ In all the reactions the oxidant accountability was good. For comparison, oxidations were also carried out under homogeneous conditions using 1 mg of metalloporphyrin (equivalent to the amount of metalloporphyrin in 100 mg of supported catalyst at a loading of 10 mg g⁻¹) (Table 4). These reactions gave very similar product yields and distributions to those catalysed by the corresponding supported metalloporphyrin, however, the homogeneous epoxidations were significantly faster (Figs. 4 and 5). In none of the oxidations were these rates or product yields affected by carrying out the reactions in an inert atmosphere (N₂).

In the reactions of some of the catalysts there was clear evidence of leaching of the metalloporphyrin from the support. Thus, with PS-Im-Fe^{III}TPFPP and PVP-Fe^{III}TPFPP there was an immediate loss of the metalloporphyrin into solution on addition of PhIO (UV-VIS analysis). Interestingly, on consumption of the oxidant, the metalloporphyrin reloaded onto the support. Control experiments showed that the leaching required the presence of PhIO but not the alkene and that it did not occur in CH₂Cl₂. The UV-VIS spectrum of the leached porphyrin showed it to be identical to that of a dilute solution of Fe^{III}TPFPP in methanol (λ_{\max} 404 and 580 nm).

The cause of the leaching of Fe^{III}TPFPP from the polymer

Table 4 Product yields from the reaction of (*Z*)-cyclooctene with iodosylbenzene catalysed by metalloporphyrins in homogeneous solution^a.

Catalyst	Solvent ^b	Yield ^c (%)				Turnover ^d
		Epoxide	HCHO	PhIO ₂	Total	
Fe ^{III} TDCPP	M-D	78	6	9	93	106
Fe ^{III} TPFPP	M-D	81	9	3	93	118
Fe ^{III} TTP ^e	M-D	41	12	40	93	39
Fe ^{III} TDCPP	D	90	—	5	95	121
Fe ^{III} TPFPP	D	85	—	8	93	124

^a Catalyst (1 mg), (*Z*)-cyclooctene (0.3 cm³), PhIO (30 mg), solvent (3 cm³). ^b Solvents: methanol (M) and dichloromethane (D). ^c Based on PhIO after 24 h. ^d Turnovers calculated on epoxide yield. ^e Catalyst bleached during reaction.

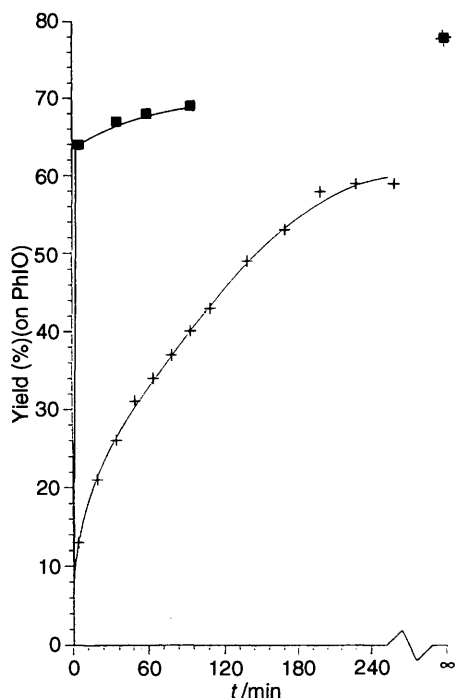


Fig. 4 Change of yield of epoxy cyclooctane with time in the epoxidation of (*Z*)-cyclooctene (0.3 cm³) by PhIO (30 mg) catalysed by Fe^{III}TDCPP (■, 1 mg) and PS-Im-Fe^{III}TDCPP (+, 100 mg) in methanol (3 cm³)

supports was investigated further. GC analysis of the reaction mixtures showed no evidence of any imidazole compounds. Oxidation of *N*-benzylimidazole (a model for PS-Im) with Fe^{III}TPFPP and PhIO in methanol or dichloromethane did not give benzaldehyde, benzyl alcohol or benzyl methyl ether, possible products from oxidative cleavage of the *N*-benzyl bond.

The use of Si-Im-Fe^{III}TDCPP in methanol also led to the slow leaching of the metalloporphyrin from the support. In this system, however, the metalloporphyrin did not reload after the reaction. This is consistent with the slow leaching of catalyst by competitive ligation to the solvent.

The catalytic behaviour of the supported metalloporphyrins was also assessed in repeat-use small and large turnover experiments (Table 5). The results reveal several interesting features of the reactions.

(i) Catalytic activity in large turnover experiments was maintained best with Si-Im supported materials, followed by PVP-Fe^{III}TDCPP and then PS-Im Fe^{III}TDCPP.

(ii) For a given catalyst and reaction conditions larger additions of PhIO led to smaller percentage yields of epoxide.

(iii) The loss of catalytic activity of the polymer-supported metalloporphyrins was not accompanied by any detectable catalyst bleaching.

(iv) With PVP-Fe^{III}TDCPP, the first addition of PhIO

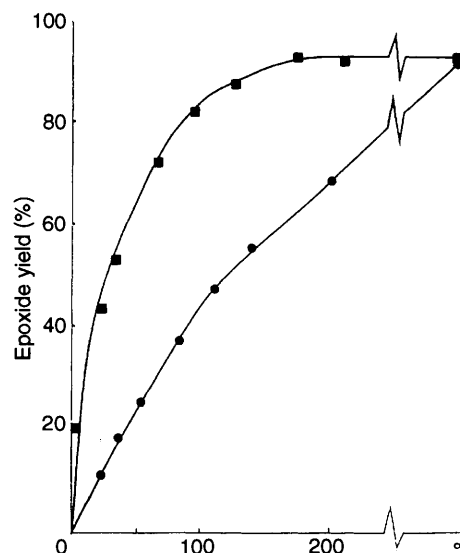


Fig. 5 Change of yield of epoxy cyclooctane with time in the epoxidation of (*Z*)-cyclooctene (0.3 cm³) by PhIO (30 mg) catalysed by Fe^{III}TDCPP (■, 1 mg) and Si-Im-Fe^{III}TDCPP (●, 100 mg) in dichloromethane (3 cm³)

invariably gave a low yield of epoxide. Subsequent additions resulted in higher and essentially constant yields.

(v) The activity of the Si-Im catalysts showed a small but significant increase in the rate of epoxidation with each addition of PhIO (Fig. 6). UV-VIS spectroscopy showed no evidence for catalyst leaching.

For Si-Im-Mn^{III}TDCPP a catalyst reuse experiment was carried out in which the catalyst was recovered after the first addition of PhIO, washed and the oxidation was repeated with fresh solvent, substrate and oxidant. Despite some minor loss of catalyst during this procedure, the second oxidation occurred at a slightly faster rate than the first (Fig. 7).

Oxidation of Cyclohexene by PhIO Catalysed by Fe^{III}TDCPP and PS-Im-Fe^{III}TDCPP.—PS-Im-Fe^{III}TDCPP and Fe^{III}TDCPP were used as the catalysts for the oxidation of cyclohexene in the presence and absence of air. As was observed for (*Z*)-cyclooctene, the reactions catalysed by the supported metalloporphyrin were significantly slower than those using the homogeneous catalyst. The results (Table 6) reveal that, unlike (*Z*)-cyclooctene, cyclohexene gives three products, the epoxide, cyclohex-2-en-1-ol and cyclohex-2-en-1-one and that the product distribution changes if the reaction is carried out in air in place of nitrogen. Under nitrogen, epoxy cyclohexane is the major product and the homogeneous and heterogeneous catalysts give very comparable results. Blank reactions show that, in the absence of either catalyst or oxidant, negligible oxidation occurs. In contrast, in air the predominant product after 24 h reaction is cyclohex-2-en-1-one with both homogeneous and heterogeneous catalysts and overall yields based

Table 5 Epoxidation yields from supported metalloporphyrin-catalysed oxidation of (*Z*)-cyclooctene with repeated additions of iodossylbenzene

Catalyst (loading) ^a	Solvent ^b	PhIO addition	% Yield ^c epoxide	Turnover	Total ^d turnover
PS-Im-Fe ^{III} TDCPP (10) ^e	M	first	78	104	104
		second	59	79	183
		third	55	74	257
PVP-Fe ^{III} TDCPP (10) ^e	M	first	40		55
		second	70		153
		third	77		258
		fourth	71		354
Si-Im-Fe ^{III} TDCPP (6) ^e	D	5 in total	99		1 125
Si-Im-Mn ^{III} TDCPP (10) ^e	D	5 in total	100		625
Si-Im-Mn ^{III} TDCPP (10) ^e	A	5 in total	109		735
Si-Mn ^{III} T4MPyP (10) ^e	D	5 in total	95		640
Si-Mn ^{III} T4MPyP (10) ^e	A	5 in total	97		655
PS-Im-Fe ^{III} TDCPP (10) ^f	M	4 in total	26		1 110
PVP-Fe ^{III} TDCPP (10) ^f	M	8 in total	64		5 100
Si-Im-Fe ^{III} TDCPP (6) ^g	D	2 in total	66		11 100
Si-Im-Fe ^{III} TDCPP (6) ^h	D	8 in total	93		7 900
Si-Im-Mn ^{III} TDCPP (10) ⁱ	D	28 in total	86		24 700

^a Loading of metalloporphyrin on support/mg g⁻¹. ^b Solvents: methanol (M); dichloromethane (D); and acetonitrile (A). ^c Based on PhIO after 24 h. ^d Calculated on epoxide yield. ^e Catalyst (100 mg), PhIO (30 mg) per addition, (*Z*)-cyclooctene (0.3 cm³), solvent (3 cm³). ^f Catalyst (50 mg), PhIO (110 mg) per addition, (*Z*)-cyclooctene (1.3 cm³), solvent (40 cm³). ^g Catalyst (50 mg), PhIO (0.5 g) per addition, (*Z*)-cyclooctene (0.65 cm³), solvent (50 cm³). ^h Catalyst (50 mg), PhIO (70 mg) per addition, (*Z*)-cyclooctene (1.3 cm³), solvent (50 cm³). ⁱ Catalyst (50 mg), PhIO (110 mg) per addition, (*Z*)-cyclooctene (2.2 cm³), solvent (50 cm³).

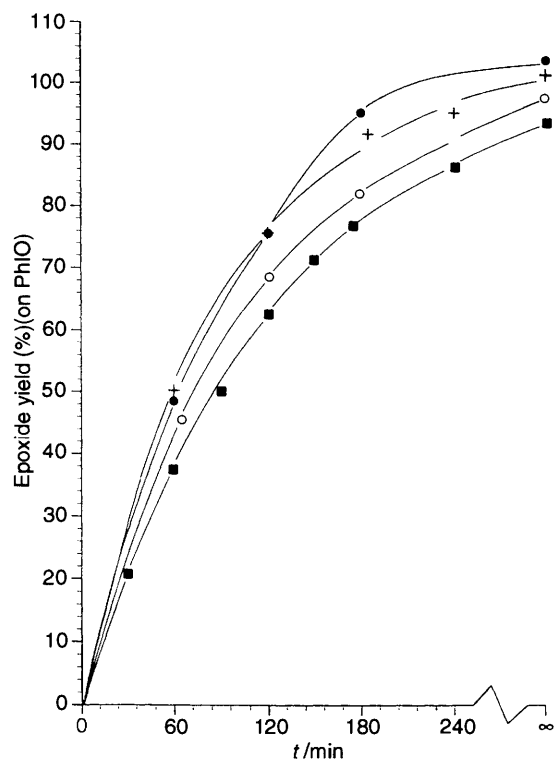


Fig. 6 Change of yield of epoxycyclooctane with time in the epoxidation of (*Z*)-cyclooctene (0.3 cm³) by repeat additions of PhIO (30 mg per addition) catalysed by Si-Im-Fe^{III}TDCPP (100 mg) in dichloromethane (3 cm³): first (■), second (○), third (+), fourth (●) addition

on PhIO are greater than 100%. Monitoring the product yields with time for the Fe^{III}TDCPP-catalysed oxidation in air reveals that the reaction is biphasic (Fig. 8). The epoxide is the major product in the first (0–2 h) and this is surpassed by the enone in the second phase. Control reactions show that in the absence of metalloporphyrin or PhIO, significant quantities of cyclohex-2-en-1-one are formed.

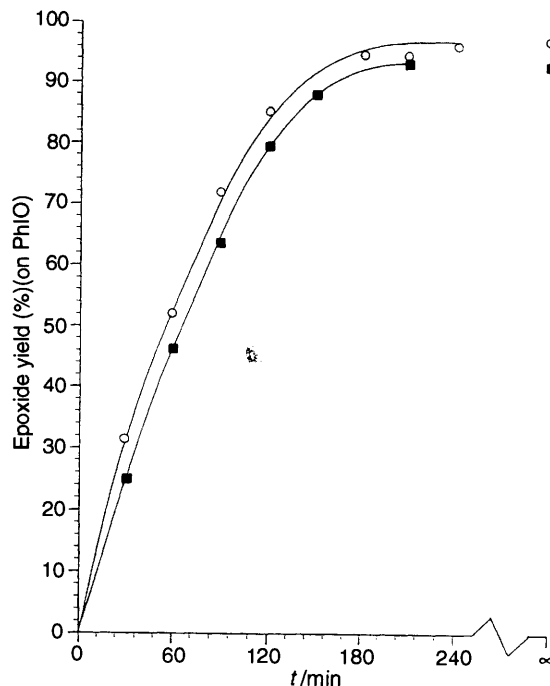


Fig. 7 Change of yield of epoxycyclooctane with time in the epoxidation of (*Z*)-cyclooctene (30 mg) by PhIO (0.3 cm³) catalysed by Si-Im-Mn^{III}TDCPP (■, 50 mg) and by washed and reclaimed Si-Im-Mn^{III}TDCPP (○, 43.4 mg) in dichloromethane (3 cm³)

Green Species Formed in Anaerobic Oxidations Catalysed by PS-Im-Fe^{III}TDCPP.—In PS-Im-Fe^{III}TDCPP-catalysed epoxidations of (*Z*)-cyclooctene by PhIO under nitrogen, the catalyst's colour changed from orange-red to green in the first 30 min of the reaction. However, there was no colour change in the analogous reactions in air, or in anaerobic reactions when cyclohexane was used as the substrate. The use of cyclohexene under nitrogen also resulted in a similar colour change, although it occurred approximately ten times more slowly. The metalloporphyrins, on other supports or in free solution, did not show this colour change.

Table 6 Yields of products from the oxidation of cyclohexene catalysed by supported and homogeneous Fe^{III}TDCPP in the presence and absence of air^a

Catalyst	N ₂ /Air	Solvent ^b	Yield ^c (%)					Total
			Epoxide	Enol	Enone	HCHO	PhIO ₂	
PS-Im-Fe ^{III} TDCPP	N ₂	M	70	4	4	4	6	88
Fe ^{III} TDCPP	N ₂	M-D	78	2	4	3	5	92
— ^d	N ₂	M	3	0	0	7	76	86
PS-Im-Fe ^{III} TDCPP	Air	M	6	18	122	9	2	156
Fe ^{III} TDCPP	Air	M-D	71	12	126	4	1	214
— ^d	Air	M	3	23	122	11	2	161
Fe ^{III} TDCPP ^e	Air	M-D	3	2	70	0	—	75

^a Supported Fe^{III}TDCPP (100 mg) or unsupported Fe^{III}TDCPP (1 mg), (*Z*)-cyclooctene (0.3 cm³), PhIO (30 mg), solvent (3 cm³). ^b Methanol (M), Dichloromethane (D). ^c Based on PhIO after 24 h. ^d No Fe^{III}TDCPP. ^e No PhIO, yields based on equivalent reaction containing 30 mg PhIO.

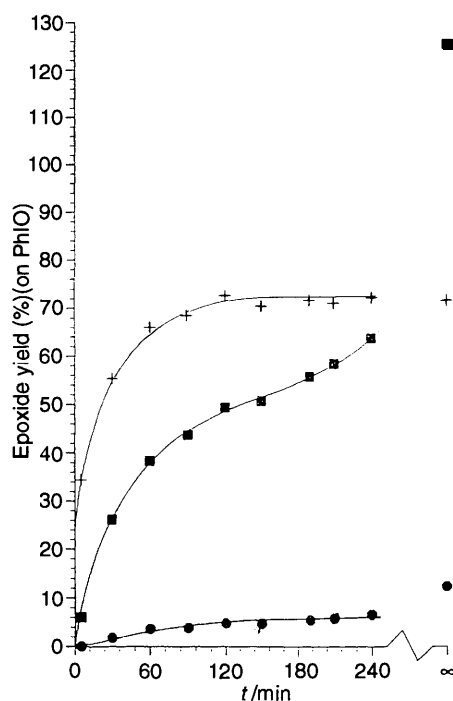


Fig. 8 Change of yield of products with time in the oxidation of cyclohexene (0.3 cm³) by PhIO (30 mg) catalysed by Fe^{III}TDCPP (1 mg) in dichloromethane-methanol (1:2, 3 cm³) in air; epoxy cyclohexane (+), cyclohex-2-en-1-ol (●) and cyclohex-2-en-1-one (■)

When PhIO was added to a methanolic suspension of PS-Im-Fe^{III}TDCPP under nitrogen, no colour change was detected. Addition of (*Z*)-cyclooctene, after 0.5 or 5 h, generated the green species in both reactions and *cis*-epoxycyclooctane in 77% and 38% yield respectively. The used catalyst was treated with a solution of imidazole in methanol in an attempt to remove the green species from the support. This treatment displaced Fe^{III}TDCPP from the support as its bis-imidazole complex and the residue became a brighter green. Repeated treatment in this way did not dislodge the green species. Attempts to remove it by demetallation with aqueous HCl were also unsuccessful and the solid remained a green colour.

Manganese(III) Porphyrin-catalysed Epoxidation of (*Z*)-Cyclooctene with H₂O₂ or Bu^oO₂H.—The Si-Im-Mn^{III}TDCPP-catalysed oxidation of (*Z*)-cyclooctene with H₂O₂ was significantly faster than the comparable reaction using PhIO (20–30 vs. 180–240 min). The epoxidations were carried out under two regimes. The first with a large excess of alkene over catalyst (4600:1) and the second with a smaller excess of alkene

(160:1) (Table 7). Homogeneous reactions with Mn^{III}TDCPP in the presence and absence of a 20-fold excess of imidazole over catalyst were carried out for comparison (Table 8). For reactions using supported and unsupported Mn^{III}TDCPP, significant catalyst bleaching and evolution of gas occurred. UV-VIS analysis of the reaction mixture from oxidations using Si-Im-Mn^{III}TDCPP had peaks at 418 nm (Soret band for H₂TDCPP) and 478 nm (Soret band for Mn^{III}TDCPP).

Attempted epoxidations, with the smaller excess of cyclooctene, using the three Si-Im-Mn^{III}T4MPyP catalysts and Si-Mn^{III}T4MPyP gave no epoxide after four additions of H₂O₂. Negligible yields of epoxycyclooctane were obtained using Si-Im-Mn^{III}TDCPP with Bu^oO₂H as the oxidant.

Discussion

The catalyst supports used in this study had surface-bound imidazole, pyridine and pyridine *N*-oxide groups. These materials were either available or readily prepared following literature procedures. Imidazoles and pyridines were chosen since they ligate strongly to the axial positions of metalloporphyrins in free solution,¹⁵ and furthermore, such nitrogen bases can give increased catalytic efficiency in epoxidations with alkyl hydroperoxides and H₂O₂.¹⁶ *N*-Oxides have also been reported to be effective ligands for manganese(III) porphyrins in epoxidations with H₂O₂.¹⁷ The selection of both flexible polymer amines (with low percentage crosslinking) and rigid modified silica allows the influence of the support's structure on catalytic activity to be examined.

With the polymer-supports the loading of the metalloporphyrin was generally maintained at 10 mg g⁻¹, although higher values were attainable. For Fe^{III}TDCPP on PS-Im a saturation loading of 49 mg g⁻¹ was achieved. Interestingly, this corresponds to approximately 1% of the available imidazole groups being involved in ligation, assuming a mono-imidazole complex. A probable explanation for this low figure is that the flexible nature of the polymer allows the thermodynamically favoured bis-imidazole complex to form.^{7a,18} Hence, binding the iron(III) porphyrin effectively crosslinks the polymer which leads to reduced flexibility and restricts access to the large majority of the imidazole groups. In agreement with this conclusion, Fe^{III}TDCPP and Fe^{III}TPFP give orange-red polymer bound materials similar in colour to solutions of bis-imidazole and bis-pyridine complexes of these iron(III) porphyrins, whilst in contrast, the Si-Im complex, where the support's rigidity prevents bis-ligation, are brown coloured. Furthermore, manganese(III) porphyrins tend to form stable mono-imidazole complexes which may account for why Mn^{III}TDCPP was more readily leached from these polymer amines than the iron(III) porphyrins.¹⁹

PS-Im binds all the iron(III) porphyrins used in this study,

Table 7 Yield of *cis*-epoxycyclooctane from the reaction of (*Z*)-cyclooctene with H₂O₂ catalysed by Si-Im-Mn^{III}TDCPP

Molar ratio Catalyst : alkene	H ₂ O ₂ addition ^a	Epoxide (%) yield based on:		
		H ₂ O ₂ ^b	Alkene ^c	Total turnover ^d
1 : 4600 ^e	1st	21	—	60
	2nd	23	—	124
	3rd	13	—	161
	4th	4	—	173
	5th	6	—	189
	6th	1	—	193
1 : 160 ^f	1st	16	16	27
	2nd	12	28	48
	3rd	12	40	68
	4th	11	51	87
	5th	6	56	96
	6th	4	61	104

^a H₂O₂ added every 30 min. ^b Yield per addition. ^c Total yield of epoxide based on initial (*Z*)-cyclooctene. ^d Turnovers based on epoxide yield. ^e Si-Im-Mn^{III}TDCPP (50 mg), (*Z*)-cyclooctene (0.3 cm³), 31% w/v aq. H₂O₂ (14 mm³) per addition, dichloromethane (1.5 cm³) acetonitrile (1.5 cm³). ^f As for (*d*) except (*Z*)-cyclooctene (10 mm³) and H₂O₂ (8 mm³) per addition.

Table 8 Yield of *cis*-epoxycyclooctane from the reaction of (*Z*)-cyclooctene with H₂O₂ catalysed by Mn^{III}TDCPP in the presence and absence of imidazole

Imidazole	H ₂ O ₂ addition ^a	Epoxide (%) yield based on:		
		H ₂ O ₂ ^b	Alkene ^c	Total turnovers ^d
+ ^{e,f}	1st	16	16	22
	2nd	26	42	58
	3rd	12	54	75
	4th	5	59	82
	5th	5	64	90
- ^e	1st	0	0	0
	2nd	2	2	3
	3rd	4	6	8
	4th	1	7	10

^a H₂O₂ added every 20 min. ^b Yield per addition of H₂O₂. ^c Total yield based on initial (*Z*)-cyclooctene. ^d Turnovers based on epoxide yield. ^e Mn^{III}TDCPP (0.5 mg), (*Z*)-cyclooctene (10 mm³), 31% w/v aq. H₂O₂ (7 mm³) per addition, dichloromethane (1.5 cm³), acetonitrile (1.5 cm³). ^f With imidazole (0.68 mg).

however, Fe^{III}TPP, unlike Fe^{III}TDCPP and Fe^{III}TPFPP, is readily leached from the polymer by methanol. This was unexpected since the reported equilibrium constants for bis-ligation of *N*-methylimidazole show that electron-donating rather than withdrawing substituents on the porphyrin favour the bis-complex formation.^{15a} These values, however, were obtained in non-coordinating solvents and we conclude that competitive ligation by the washing solvent (MeOH) is also a key factor in determining the stability of the bound metalloporphyrin. Indeed, loading of Fe^{III}TPFPP onto PS-Im in methanol occurs approximately 50 times slower than in CH₂Cl₂.

As described above, the iron porphyrins are restricted to mono-ligation by the rigid Si-Im support and consequently, because they are less tightly bound than to the polymer amines they can be removed by washing or Soxhlet extraction with MeOH. It is noteworthy that a loading of 10 mg g⁻¹ of metalloporphyrin on Si-Im equates to only one metalloporphyrin to approximately 500 bound imidazoles. It is likely that steric constraints and restricted access of the metalloporphyrin to the silica's internal surfaces will severely limit the number of imidazole groups that are available for ligation.

Interestingly, the ionic Mn^{III}T4MPyP, which is strongly bound by electrostatic interactions to silica,^{8b} is not coordinatively bound by Si-Im. Indeed, increased imidazole modification of silica leads to decreased binding of Mn^{III}T4MPyP. We conclude that derivatisation of silica with

silylpropylimidazole groups leads to a marked decrease in surface polarity, with a consequent decrease in the electrostatic affinity of the support for the ionic porphyrin, which is not compensated for by axial coordination of the imidazole groups to the metal atom.

Although PS-Im-Fe^{III}TPFPP and PVP-Fe^{III}TPFPP are stable to leaching by MeOH, the addition of PhIO leads to the immediate displacement of metalloporphyrin from the supports. No leaching occurs when the reaction is carried out in CH₂Cl₂. UV-VIS spectroscopy shows that the leached porphyrin is the same as a dilute solution of Fe^{III}TPFPP in methanol. Comparison with the reported spectrum of Fe^{III}TPP in ethanol suggests that the leached porphyrin has methanol and methoxide axial ligands [Fe^{III}TPFPP(MeOH)(MeO)].²⁰ Two alternative bond-cleavages that might lead to this iron(III) porphyrin, each of which is initiated by reaction of PhIO with the mono-ligated catalyst, are illustrated in Fig. 9. Path A was eliminated since neither imidazole nor *N*-substituted imidazoles were detected in the reaction of PhIO with PS-Im-Fe^{III}TPFPP in methanol. Furthermore, *N*-benzylimidazole and Fe^{III}TPFPP, a homogeneous model for the supported catalyst, with PhIO gave none of the likely products from the oxidative cleavage of the *N*-benzyl bond. It is probable that the leaching arises from the weakening of the axial bond to the support in one of the intermediates in the catalytic oxidation cycle (Path B). The absence of leaching in CH₂Cl₂ suggests a

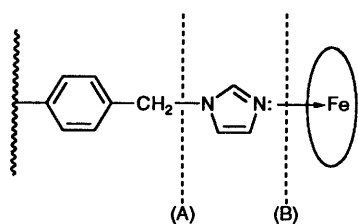


Fig. 9 Possible bond cleavages that could result in the leaching of Fe^{III} TPFP complexes into solution following addition of PhIO to PS-Im- Fe^{III} TPFP in methanol

competitive axial ligand (MeOH) is required to encourage cleavage by Path B. In agreement with this explanation for the leaching, the process reverses and the Fe^{III} TPFP rebinds to the support when all the oxidant has been consumed.

The difference in the behaviour of Fe^{III} TPFP and Fe^{III} TDCPP is interesting, since the latter is not removed from the polymer amines by PhIO. It is possible that this arises from differences in the electron distributions in the oxidised intermediates from Fe^{III} TPFP and Fe^{III} DCFP, leading to different affinities for the two iron porphyrins.

The present study shows there are significant limitations to the use of coordinative binding to anchor metalloporphyrin oxidation catalysts to supports. It is not a general method which can be routinely applied to all iron and manganese porphyrins. However, by careful selection of porphyrin, solvent and support, stable catalysts can be prepared. In our studies the best porphyrin has been H_2 TDCPP and the results using the iron(III) and manganese(III) complexes are discussed below.

Oxidations with PhIO Catalysed by Supported Fe^{III} TDCPP and Mn^{III} TDCPP.—The epoxidations of (*Z*)-cyclooctene and cyclohexene with PhIO catalysed by the supported metalloporphyrins are markedly slower than the comparable homogeneous reactions. With the polymer-supported catalyst several factors could contribute to this difference.

(i) Strong bis-ligation of the polymer amines could inhibit the formation of the active oxidant which would first require dissociation to a mono-ligated complex (Fig. 10).

(ii) As described above, bis-ligation of PS-Im and PVP to the iron porphyrin would effectively crosslink the polymers and trap catalyst molecules within the polymer matrix. The active catalyst molecules would then be on the surface, whilst the majority would be unavailable and inactive. In agreement with this hypothesis, used polymer-supported Fe^{III} TDCPP that had lost its catalytic activity retained its original orange-red colour, suggesting that only the active Fe^{III} TDCPP species on the surface had been destroyed with the remainder being intact but unreactive.

(iii) The slow diffusion of oxidant and alkene to and from the metalloporphyrin catalyst could also account for the difference in rates of the hetero- and homo-geneous oxidations. This explanation is supported by relatively slow oxidations catalysed by Si-Im based catalysts where bis-ligation and catalyst entrapment are unlikely. In the latter oxidations slow diffusion of reactants and products to and from catalyst molecules, especially those in the pores of the silica, seems the most likely cause of the slow rates of reaction.

The yields and product distributions from the small turnover oxidations catalysed by supported Fe^{III} TDCPP and Mn^{III} TDCPP are very comparable to those from the corresponding homogeneous reactions, with the exception of cyclohexene oxidations in air (see below). The oxidant accountability in both is good and shows that, although the former are slower, loss of oxidant arising from support oxidation is unimportant. Again there is an exception in the first

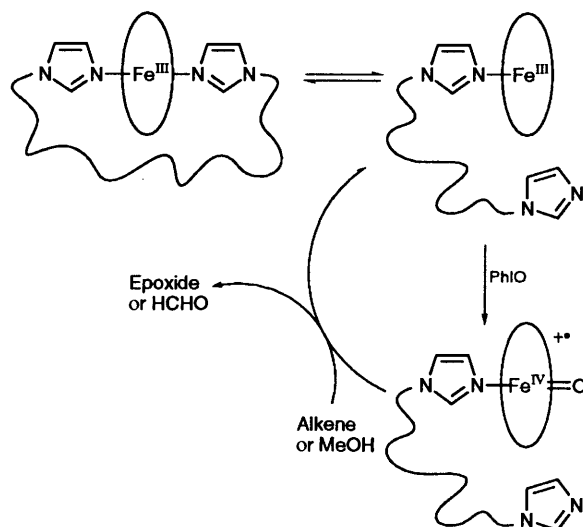


Fig. 10 Proposed mechanism for alkene epoxidation by PhIO catalysed by PS-Im- Fe^{III} TDCPP

use of PVP- Fe^{III} TDCPP, where overall yields are unusually low, however, this effect is not seen in catalyst reuse experiments. We attribute this catalyst conditioning to a small amount of competitive support oxidation, possibly *N*-oxidation of pyridine groups and/or oxidation of any unpolymerised vinyl groups near the active oxidant, which, once achieved, leads to increased substrate oxidation.

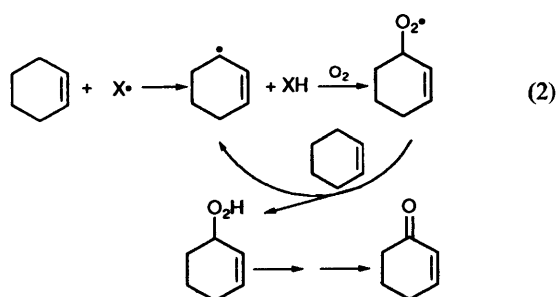
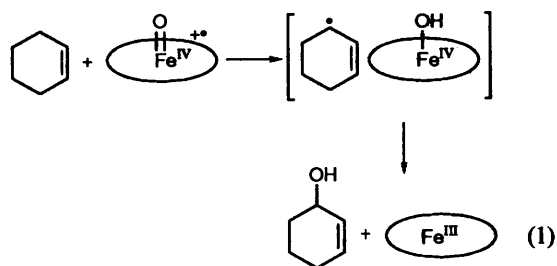
The best selectivity for (*Z*)-cyclooctene epoxidation is achieved by the Si-Im supported catalysts in CH_2Cl_2 with a relatively small excess of PhIO, since under these conditions a negligible amount of oxidant is wasted in solvent oxidation and disproportionation of PhIO to oxidatively inert PhI and PhIO_2 . With a large excess of PhIO the latter reaction is the major cause for reduced epoxidation yields whilst with MeOH as solvent competitive oxidation to give formaldehyde also diverts some of the active oxidant from epoxidation.

(*Z*)-Cyclooctene oxidations with PhIO, catalysed by either supported or homogeneous iron(III) porphyrins, were unaffected by the presence of dioxygen. This is a common feature of these catalysed oxidations of alkenes, even though iron porphyrins are known to be effective autoxidation catalysts.²¹ However, the oxidations of cyclohexene showed a marked dependence on dioxygen (Table 6). Under nitrogen the predominant product (after 24 h) was epoxide and oxidant accountabilities were 90–100%. Very comparable results have been reported previously for cyclohexene oxidation with other iron(III) porphyrin-PhIO systems.^{1,16c,22} In contrast, under air, total yields (after 24 h based on PhIO) were greater than 100% and cyclohex-2-en-1-one was the major product. We attribute this to radical autoxidation occurring simultaneously with, or subsequent to, the PhIO-iron porphyrin-catalysed oxidation. Fig. 8 reveals that, with the homogeneous system, epoxy-cyclohexane is the major product in the first part of the reaction, but once the oxidant has been consumed, radical autoxidation and enone formation take over. Under the conditions used in this study, autoxidation typically had an induction period of 3–4 h.

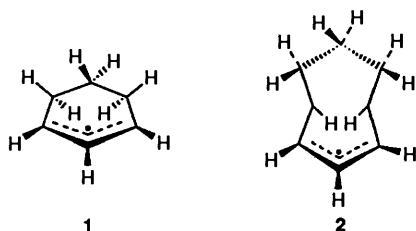
With PS-Im- Fe^{III} TDCPP, where the catalysed oxidation with PhIO is relatively slow, or in control reactions in the absence of PhIO or iron(III) porphyrin, autoxidation predominates to give the enone. Interestingly, the comparable product distributions from the PhIO oxidations of cyclohexene in air in the presence and absence of PS-Im- Fe^{III} TDCPP suggests that PhIO may be able to participate in radical oxidations. However, this aspect was not investigated further.

The marked difference in behaviour of cyclohexene and (*Z*)-

cyclooctene must arise from the relative ease of competitive oxidations at the C=C and allylic C-H bonds for the two substrates. With the latter, allylic oxidation is disfavoured. Since both iron(III) porphyrin-catalysed oxidations with PhIO and radical autoxidation of aliphatic C-H groups [reactions (1) and (2), illustrated with cyclohexene] occur by hydrogen atom



abstraction, we attribute the difference to a less reactive allylic C-H bond in (*Z*)-cyclooctene than in cyclohexene. This may be rationalised by considering the allylic radical from each cycloalkene **1** and **2**. The cyclooctenyl radical **2** will be



disfavoured by a transannular hydrogen interaction, whereas with the cyclohexenyl radical **1**, no such effect arises and substantial quantities of both epoxide and allylic oxidation products are formed.

Another feature observed specifically in PS-Im-Fe^{III}TDCPP-catalysed oxidations of the cycloalkenes in methanol was the change in colour of the catalyst from orange-red to green when the reactions were carried out under N₂. In contrast with reactions, (a) in air, with cyclohexane or without a substrate, (b) with PVP-Fe^{III}TDCPP or Si-Im-Fe^{III}TDCPP, or (c) in CH₂Cl₂, the colour of the catalyst was unaltered. Interestingly, the results show that premixing of catalyst and oxidant resulted in epoxidation and colour change only on addition of (*Z*)-cyclooctene, and even occurred when the alkene was added 5 h after premixing. The failure to extract the green pigment from PS-Im using imidazole as a competitive ligand or using aqueous acid to demetallate the catalyst, suggests that the green material is covalently bound to the support.

The change in the catalyst's appearance is not easy to rationalise, however, we suspect that it involves an *N*-alkylation of the porphyrin ring. *N*-Alkylporphyrins, which are known to be green, have been identified as products in the homogeneous iron(III) porphyrin-catalysed oxidation of alkenes.²³ The

requirement for an inert atmosphere suggests the reaction involves carbon radicals which in air are removed by their rapid reaction with dioxygen. The precise nature of this reaction is currently under investigation.

An effective supported metalloporphyrin catalyst must be capable of a large number of turnovers without the loss of catalytic activity. In this respect Fe^{III}TDCPP was better on PVP than on the more flexible PS-Im. The best catalysts were Fe^{III}TDCPP and Mn^{III}TDCPP on Si-Im. We suspect that the more flexible the organic support the more readily the ligated porphyrins can oxidise each other or the polymer backbone. Even if these are very minor side-reactions, with large turnover experiments they become significant. It is noteworthy that the partially deactivated PS-Im-Fe^{III}TDCPP from repeat use experiments retains its orange-red colour with no apparent bleaching. As is discussed above, this suggests that the loss of activity may only involve the accessible iron(III) porphyrin molecules, leaving the large majority of inaccessible or inactive Fe^{III}TDCPP unaffected.

Another feature of the silica based catalysts is the break-up of the particles with extensive stirring in the repeat use experiments. Scanning electron microscopy with Fe^{III}TDCPP on a pyridine modified silica clearly reveals the dramatic roughening and fragmentation of the particles that arises during oxidations.²⁴ This, however, has a beneficial effect since by exposing more of the metalloporphyrin molecules to the PhIO and improving the diffusion of reactants and products to and from the surface, the rate of epoxidation increases.

Oxidations with H₂O₂ and Bu'O₂H Catalysed by Supported and Homogeneous Manganese(III) Porphyrins.—Iodosylbenzene is a convenient source of oxygen for use in small scale epoxidations since it can give good oxidant conversions and does not normally react without catalysis. However, its expense, low oxygen content (7.3% w/w) and polymeric nature are significant disadvantages. For these reasons the relatively inexpensive oxidants H₂O₂ and Bu'O₂H, which contain 47% and 18% w/w active oxygen, respectively, are attractive alternatives.

With metalloporphyrin catalysts, epoxidation with H₂O₂ or Bu'O₂H requires the heterolytic cleavage of the peroxide bond and also the suppression of catalytic and radical reactions which lead to wasteful consumption of oxidant and to catalyst degradation respectively. With manganese porphyrins this can be achieved in the presence of nitrogenous bases such as imidazole. For H₂O₂, this is attributed to imidazole, in the mono-ligated imidazole complex, being a good donor ligand and also to its ability to take part in acid/base catalyses;^{16c} both effects encourage the two-electron heterolytic O-O bond cleavage (Fig. 11). Tatsumi and his coworkers^{7c} have reported the use of supported Mn^{III}TTP to catalyse the oxidation of cyclohexane by H₂O₂. They showed that the manganese(III) porphyrin coordinatively bound to imidazole modified silica was a significantly better catalyst than the same metalloporphyrin in solution or adsorbed on unmodified silica or silica that had been pretreated with *N*-methylimidazole. However, this study did not determine whether these oxidations were brought about by an oxomanganese(v) porphyrin from heterolysis or a hydroxyl radical from homolysis of the H₂O₂. For these reasons it was of interest to determine whether Si-Im-supported manganese(III) porphyrins, where axial ligation but not acid/base catalysis by surface imidazoles could occur, would bring about alkene epoxidation with H₂O₂ or Bu'O₂H. Only heterolysis leading to the oxomanganese(v) species would be expected to yield *cis*-epoxycyclooctane from (*Z*)-cyclooctene. The results show that Si-Im-Mn^{III}TDCPP and Mn^{III}TDCPP-imidazole have comparable catalytic activities for (*Z*)-cyclooctene epoxidation by H₂O₂ (Tables 7 and 8).

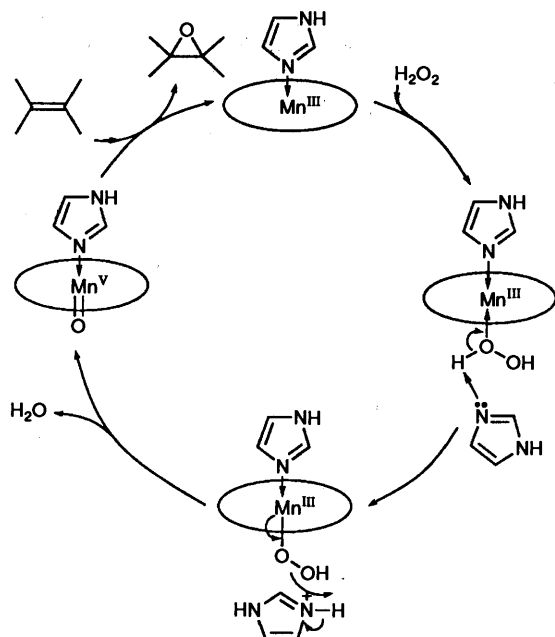
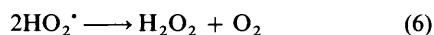
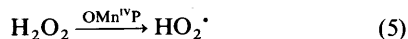
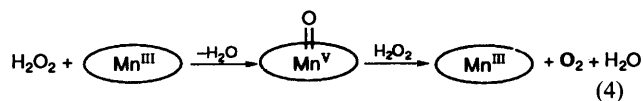
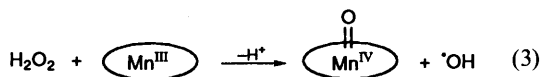


Fig. 11 The role of imidazole in promoting heterolytic cleavage of hydrogen peroxide by manganese(III) porphyrins^{16c}

However, both systems also lead to extensive porphyrin degradation, presumably by species such as the hydroxyl radical [reaction (3)], and the evolution of dioxygen from the catalysed dismutation of H_2O_2 [reaction (4), a model for catalase] and/or the self-reaction of HO_2^\bullet [reactions (5) and (6)].



The lack of epoxidation when using Si-Mn^{III}T4MPyP or Mn^{III}TDCPP shows that without imidazole the manganese porphyrins, as has been reported previously,^{16c} are ineffective catalysts for alkene epoxidation with H_2O_2 . This, in turn, implies that epoxidation by the Si-Im-Mn^{III}TDCPP- H_2O_2 system must arise from supported catalyst and not from any leached manganese porphyrin in solution. Furthermore, the lack of epoxidation with Si-Im-Mn^{III}T4MPyP catalysts and H_2O_2 is in agreement with the conclusion above that the ionic manganese(III) porphyrin, Mn^{III}T4MPyP, is bound to the Si-Im support by electrostatic interactions with unmodified surface silanols rather than by ligation to the imidazole groups.

Although manganese(III) porphyrins have been reported to catalyse alkene epoxidation by $\text{Bu}^t\text{O}_2\text{H}$ in the presence of imidazole,^{16a} in this study the supported catalyst Si-Im-Mn^{III}TDCPP led to very poor yields of epoxide. Further work is in hand to determine the precise cause of this ineffective catalysis.

Experimental

Materials.—Unless otherwise stated the reagents were commercially available. Iodosylbenzene was prepared from

iodosylbenzene diacetate following Saltzmann and Sharefkin²⁵ and the active oxygen content was shown to be >99% by iodometric titration.²⁶ 5,10,15,20-Tetra(2,6-dichlorophenyl)porphyrin free base was prepared from 2,6-dichlorobenzaldehyde and pyrrole by the method of Lindsey *et al.*²⁷ and metallated with iron(II) chloride and manganese(II) bromide following the method of Dolphin and Nakano.²⁸ The axial ligand on Mn^{III}TDCPP was converted from bromide to chloride by shaking a solution (CH_2Cl_2) of the former with a few drops of concentrated hydrochloric acid followed by water washing and precipitation with hexane.

Imidazole modified silica (Si-Im) was prepared by refluxing Kieselgel 60 (surface area $500 \text{ m}^2 \text{ g}^{-1}$, pore size 60 \AA and particle size $40\text{--}63 \text{ \mu m}$) (2 g), imidazole ($5.5 \times 10^{-3} \text{ mol}$) and 3-chloropropyltrimethoxysilane ($2.8 \times 10^{-3} \text{ mol}$) in 1,3-dimethylbenzene (100 cm^3) for 15 h following the method of Leal *et al.*^{7b} The percentage loading of the imidazole units on the Si-Im (60%) was calculated from the nitrogen content (3.50% by CHN analysis) assuming an average of two bonds between silane and silica and five silanol sites nm^{-2} . Lower loadings were obtained by refluxing for 1 h (26% loading) or by decreasing the ratio of silane and imidazole to Kieselgel 60 by a factor of 4 (11% loading).

Imidazole modified polystyrene (PS-Im) was prepared by refluxing Bio-Beads S-XI (Bio-Rad Laboratories Ltd.) (6.66 g) with imidazole ($6 \times 10^{-2} \text{ mol}$) in 1,3-dimethylbenzene (50 cm^3) for 17 h. The modified resin was washed sequentially with benzene, methanol, 5% aqueous sodium carbonate, water and acetone and dried at $100 \text{ }^\circ\text{C}/0.1 \text{ mmHg}$. The nitrogen content (8.88% from CHN analysis) gave an imidazole loading of 4.09 mmol g^{-1} . This is equivalent to 97% conversion of the chloromethyl groups by imidazole.

Poly(4-vinylpyridine *N*-oxide) (PVPO) was obtained by heating PVP (3 g) in glacial acetic acid (5 cm^3) and 100 volume H_2O_2 (7 cm^3) for 3 h. After cooling, the filtered solid was washed sequentially with water, 5% aqueous sodium carbonate and water and dried in a vacuum desiccator. The IR spectrum (Fig. 3) had a strong band at 1088 cm^{-1} assigned to the N-O stretch.

The uncharged metalloporphyrins (10 mg) were loaded onto the supports (1 g) by stirring in dichloromethane (50 cm^3) for 24 h. The material was recovered by filtration and washed with either dichloromethane alone or dichloromethane followed by acetone and methanol. The final loadings were obtained by quantifying (UV-VIS analysis) the non-loaded metalloporphyrin in the combined reaction solution and washings. Before use the supported metalloporphyrin was dried at $100 \text{ }^\circ\text{C}/0.1 \text{ mmHg}$ and stored in a desiccator.

The charged Mn^{III}T4MPyP (10 mg) was loaded onto Kieselgel 60 or Si-Im (1 g) by stirring in methanol for 24 h. The filtered solid was washed with dichloromethane and acetonitrile and dried at $100 \text{ }^\circ\text{C}/0.1 \text{ mmHg}$. The metalloporphyrin loading was obtained as described above.

Methods.—Instrumentation. UV-VIS spectra were obtained with a Hewlett-Packard 8452A diode array spectrometer. Fixed wavelength determinations (412 nm) for the Nash test for formaldehyde were recorded with a Pye-Unicam SP1750 spectrometer.¹⁴

IR spectra of the solid supports and supported catalysts (KCl discs) were obtained using a Perkin-Elmer 1720 FT-IR spectrometer.

GC analysis was performed on a Pye-Unicam GCD chromatograph with a flame ionisation detector. The results were recorded and processed on a Trivector Trilab 2000 data station.

Alkene oxidations. In a typical oxidation supported metalloporphyrin (100 mg) or unsupported metalloporphyrin (1 mg)

was stirred with alkene (0.3 cm³) and dichloromethane (3 cm³) and reaction initiated by the addition of the oxidant, e.g. PhIO (30 mg). For reactions in methanol the oxidant was added as a solution (10 mg in 2 cm³) to the substrate and catalyst in methanol (1 cm³). The reactions were monitored at regular intervals by removing samples for GC analysis. After 24 h the formaldehyde yield was estimated colorimetrically and iodoxybenzene determined iodometrically. Reactions under nitrogen were carried out in a flask sealed with a subseal. The reaction mixture was thoroughly flushed with nitrogen prior to addition of a solution of oxidant.

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