Hydrocarbon oxidation with iodosylbenzene catalysed by the sterically hindered iron(III) 5-(pentafluorophenyl)-10,15,20-tris(2,6-dichlorophenyl)porphyrin in homogeneous solution and covalently bound to silica

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Iron(III) 5-(pentafluorophenyl)-10,15,20-tris(2,6-dichlorophenyl)porphyrin has been synthesised and used to catalyse hydrocarbon oxidation by iodosylbenzene. In homogeneous solution it is shown to be a stable and effective catalyst for alkene epoxidation and alkane hydroxylation with a selectivity and reactivity closer to iron(III) tetrakis(pentafluorophenyl)porphyrin than to iron(III) tetrakis(2,6-dichlorophenyl)porphyrin. The new sterically hindered iron porphyrin has also been covalently bound, by nucleophilic aromatic substitution to aminopropylated silica. The resulting heterogenised catalyst is also stable towards oxidation but is less reactive than its homogeneous analogue.

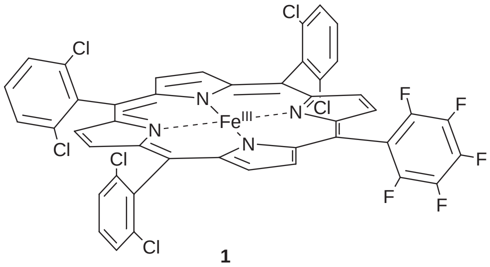
Introduction

It is well known that the oxidative stability of metallotetraarylporphyrins can be dramatically enhanced by bulky substituents on the *ortho*-positions of the aryl groups.[1] In particular, the tetrakis(2,6-dichloro- and 2,6-dibromo-phenyl)porphyrins have been shown to be effective and robust catalysts for hydrocarbon oxidation.[1,2] It is generally accepted that this increased stability towards oxidative self-destruction arises from a combination of the electron-withdrawing polar effects and steric hindrance of the substituents.

Polar effects are also important in stabilising unhindered porphyrins and, in this respect, the tetrakis(pentafluorophenyl)porphyrin ligand has been widely used in metalloporphyrin-catalysed oxidations. Halogenation or nitration of the β-pyrrole positions can lead to further improvements in catalyst stability.[3]

In previous studies we have explored the catalytic potential of iron and manganese porphyrins anchored to solid supports.[4] These materials have largely involved coordination of the metal centre of the catalyst to nitrogen ligands (*e.g.* imidazole and pyridine) covalently bound to the support surface. Although these heterogenised metalloporphyrin materials, in particular the supported sterically hindered FeTDCPP,† are effective catalysts for alkene epoxidation, the weakness of the coordinative bond makes them prone to catalyst leaching. To overcome this difficulty we are exploring the use of covalent links to bind sterically hindered iron porphyrins covalently to silica.

In this paper we report the synthesis and catalytic activity, in hydrocarbon oxidation, of the new sterically hindered iron porphyrin catalyst, iron(III) 5-(pentafluorophenyl)-10,15,20-tris(2,6-dichlorophenyl)porphyrin (FePFTDCPP) (**1**). This tetraarylporphyrin was selected to combine the beneficial steric hindrance of FeTDCPP with the ease of nucleophilic aromatic substitution of the *para*-fluorine in the pentafluorophenyl groups of FeTPFPP. The latter reaction provides a simple route to graft the catalyst to the support [reaction (1)].[5]



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Results

Synthesis of iron(III) 5-(pentafluorophenyl)-10,15,20-tris(2,6-dichlorophenyl)porphyrin

The required porphyrin ligand, PFTDCPP, was prepared using an acid-catalysed mixed aldehyde synthesis following the general procedure developed by Lindsey and his co-workers.[6] The relative proportions of the two aldehydes, pentafluoro- and 2,6-dichloro-benzaldehyde, employed were adjusted in small scale reactions to optimise the yield of PFTDCPP. The porphyrin product distributions were readily monitored by TLC once the identity of the products had been determined by FABMS. With pyrrole : 2,6-dichlorobenzaldehyde : pentafluorobenzaldehyde ratios 4 : 3 : 1 and 4 : 3.5 : 0.5 the six porphyrins TDCPP, PFTDCPP, DPFDDCPP (two isomers), TPFDCPP and TPFPP were observed with DPFDDCPP being the major product. By using a 4 : 3.9 : 0.1 ratio of reagents DPFDDCPP and TPFDCPP were not detected, however, the yield of PFTDCPP was very low. The reagent proportions selected for the preparation were 4 : 3.8 : 0.2 which gave 3.5% of PFTDCPP in an overall yield of TDCPP and the mono- and di-pentafluorophenyl analogues of 37%. The purified PFTDCPP was metallated using standard procedures to give the desired iron(III) porphyrin, FePFTDCPP.

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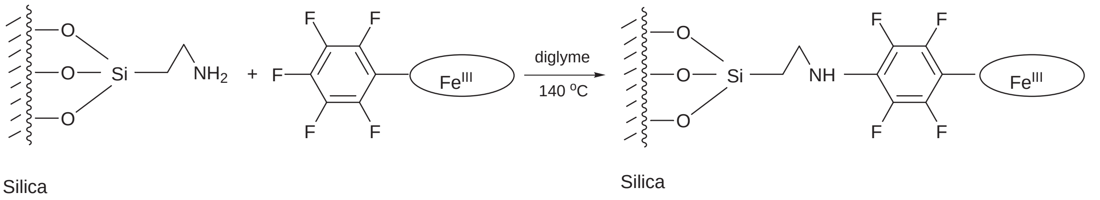
† **Abbreviations**: porphyrin ligands; TPP, 5,10,15,20-tetraphenylporphyrin; TTP, 5,10,15,20-tetra(2-tolyl)porphyrin; TMP, 5,10,15,20-tetramesitylporphyrin; TPFPP, 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin; TDCPP, 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin; TPCPP, 5,10,15,20-tetrakis(pentachlorophenyl)porphyrin; PFTDCPP, 5-(pentafluorophenyl)-10,15,20-tris(2,6-dichlorophenyl)porphyrin; DPFDDCPP, di(pentafluorophenyl)di(2,6-dichlorophenyl)porphyrin; TPFDCPP, 5,10,15-tris(pentafluorophenyl)-20-(2,6-dichlorophenyl)porphyrin. FeP for iron porphyrin in general. Prefix Si indicates the porphyrin has been covalently grafted to aminopropylated silica.



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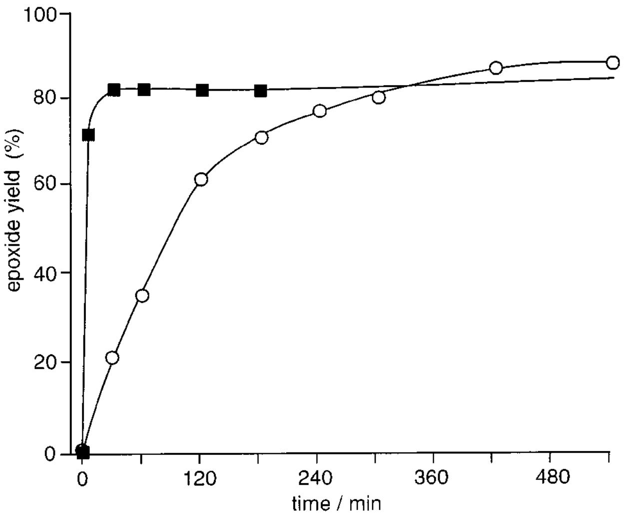


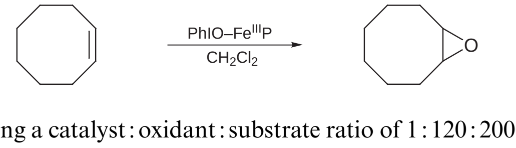
Fig. 1 A comparison of the rates of epoxidation of cyclooctene by PhIO in CH_2Cl_2 catalysed by FePFTCDPP (■) and Si-FePFTDCPP (○).

The synthesis of the supported iron porphyrin Si-FePFTDCPP

The iron porphyrin was grafted on to aminopropylated silica by nucleophilic aromatic substitution of the *para*-fluorine in the pentafluorophenyl group[5] [reaction (1)], to give a catalyst loading of 17.6 μmol g^{-1} of support. UV–VIS analysis showed the freshly prepared supported metalloporphyrin had a single Soret absorbance at 432 nm; when this material was left to stand for several weeks the spectrum changed with the appearance of a second Soret peak at 422 nm. An EPR investigation of the supported iron porphyrin at 3 K gave three signals with *g* values of 6.0, 4.3 and 2.0.

Alkene epoxidation by iodosylbenzene catalysed by FePFTDCPP in solution and supported on silica

The efficiency and the stability of the iron porphyrin as a catalyst for alkene epoxidation in free solution and supported on silica were examined using cyclooctene as the substrate [reaction (2)]. The epoxidations were carried out in dichloromethane



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using a catalyst : oxidant : substrate ratio of 1 : 120 : 2000. Table 1 records the epoxide yields from reactions in the presence and absence of air and for comparison some results using the related catalysts, FeTPFPP, Si-FeTPFPP and Si-FeTPCPP. Monitoring the production of the epoxide using FePFTDCPP showed that the homogeneous reaction is much faster than its heterogeneous analogue (Fig. 1).

UV–VIS analysis of the homogeneous reaction mixtures showed no evidence of porphyrin bleaching during the oxidations. UV–VIS analysis also showed that the iron porphyrin was not leached from the support since an equivalent analysis of the filtered reaction mixture from the heterogeneous oxidation did not show the porphyrin Soret peak (416 nm).

The oxidation of cyclohexene gave epoxycyclohexane, however, unlike that of cyclooctene it also gave significant yields of two allylic oxidation products, cyclohex-2-en-1-ol and cyclohex-2-en-1-one (Table 2) [reaction (3)]. A further difference

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

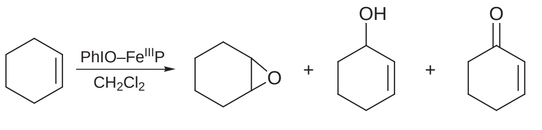
Catalyst	Epoxide yield (%)[b]	PhI yield (%)[b]
FePFTDCPP	82	88
FePFTDCPP (under N_2)	91	99
FeTDCPP	83	99
FeTPFPP	93	98
Si-FePFTDCPP	88	100
Si-FeTPFPP[c]	98	—
Si-FeTPCPP[c]	88	—

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

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

	Yield (%)		
Catalyst	Epoxide[b]	Cyclohex-2-en-1-one[b]	Cyclohex-2-en-1-ol[b]
FePFTDCPP	93	28	18
Si-FePFTDCPP	88	12	9

[a] FePFTDCPP, 2.5×10^{-7} mol; PhIO, 3×10^{-5} mol; CH_2Cl_2, 1.5 cm^3. [b] % Yield based on PhIO.



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between the two substrates is that the product yields from cyclohexene were consistently greater than 100%. Carrying out the reactions under nitrogen reduced the yield of the allylic products and in particular that of the ketone. Control reactions showed that stirring cyclohexene in air (24 h) in the presence of PhIO [no iron(III) porphyrin] resulted in significant autoxidation with the major products being allylic ketone and alcohol. Interestingly in the latter reactions the PhIO was converted to PhI indicating the participation of the PhIO in these reactions.

The two stereoisomers of 4-methylpent-2-ene were oxidised stereospecifically by PhIO using the homogeneous and supported catalysts (Table 3). The yields from the former oxidations were excellent (effectively quantitative) and comparable to those obtained using FeTPFPP, whereas the heterogeneous systems were less effective and like FeTDCPP showed a clear preference for the *Z*-alkene.

Stability of the FePFTDCPP and Si-FePFTDCPP catalysts in repeat oxidations

The Si-FePTFDCPP catalysed epoxidation of cyclooctene was monitored for four additions of PhIO (each with catalyst : oxidant, 1 : 320) added at 24 h intervals (Table 4). Analogous experiments were carried out with FePFTDCPP in solution in CH_2Cl_2 for seven additions of PhIO added at 2 h intervals (Table 5). The results with the supported catalyst reveal that the

Table 3 Epoxide yields from the oxidation of (*Z*)- and (*E*)-4-methylpent-2-ene with PhIO catalysed by homogeneous and supported iron porphyrins[a]

Catalyst	Substrate	Yield (%)	
		cis-Epoxide[b]	*trans*-Epoxide[b]
FePFTDCPP	(*Z*)-alkene	100	—
FePFTDCPP	(*E*)-alkene	—	100
FeTPFPP	(*Z*)-alkene	100	—
FeTPFPP	(*E*)-alkene	—	100
FeTDCPP	(*Z*)-alkene	96	—
FeTDCPP	(*E*)-alkene	—	54
Si-FePFTDCPP	(*Z*)-alkene	60	—
Si-FePFTDCPP	(*E*)-alkene	—	33

[a] FeP, 2.5×10^{-7} mol; PhIO, 3×10^{-5} mol; CH_2Cl_2, 1.5 cm^3. [b] % Yield based on PhIO.

Table 4 Epoxidation of cyclooctene by repeated additions of PhIO catalysed by Si-FePFTDCPP in dichloromethane[a]

Addition of PhIO	Epoxide yield (%)[b]	PhI yield (%)[b]
1	89	102
2	76	95
3	71	94
4[c]	88	98

[a] FeP, 2.5×10^{-7} mol; PhIO, 7.75×10^{-5} mol per addition; cyclooctene, 5.0×10^{-4} mol; CH_2Cl_2, 1.5 cm^3. [b] Per addition % yield based on PhIO added. [c] The Si-FePFTDCPP was filtered, washed and dried before being used in a half-scale reaction.

Table 5 Epoxidation of cyclooctene by repeated additions of PhIO catalysed by FePFTDCPP in dichloromethane[a]

Addition of PhIO	Epoxide yield (%)[b]	PhI yield (%)[b]
1	87	95
2	83	92
3	77	100
4	74	93
5	60	85
6	76	97
7	68	97
8[c]	68	102

[a] FeP, 2.5×10^{-7} mol; PhIO, 7.75×10^{-5} mol per addition; cyclooctene, 5.0×10^{-4} mol; CH_2Cl_2, 1.5 cm^3. [b] Per addition % yield based on PhIO added. [c] PhIO, 5.43×10^{-4} mol.

epoxide yield decreases slightly for the second and third additions. Before the fourth addition of PhIO, the supported iron porphyrin was recovered by filtration, washed with methanol and dried; this treatment restored the activity of the catalyst (Table 4).

The reactions following each of the seven consecutive additions of PhIO to the homogeneous system gave good epoxide yields, with an overall conversion of substrate to epoxide of 84.5% (equivalent to ~1700 catalyst turnovers). UV–VIS examination of the iron porphyrin after the seven sequential reactions showed that catalyst destruction was negligible, <5%.

When the supported catalyst was used with a large excess of oxidant (Si-FePFTDCPP : PhIO, 1 : 4630) the epoxide yield was 69% (3010 turnovers). UV–VIS analysis indicated that in this case the filtered reaction mixture, following this oxidation, contained approximately 1% of an iron porphyrin. Attempts to identify this by FABMS were unsuccessful and provided no clear evidence for its structure.

Table 6 Yields of adamantanols from the oxidation of adamantane with PhIO catalysed by homogeneous and supported iron porphyrins in dichloromethane[a]

Catalyst	Yield (%)		
	Adamantan-1-ol[b]	Adamantan-2-ol[b]	*tert* to *sec* relative reactivity[c]
FePFTDCPP	69	15	14
FeTDCPP	56	28	6
FeTPFPP	81	19	13
Si-FePFTDCPP	52	19	9
FeTPP[d]	13	<1	48
FeTTP[d,e]	39	5	20
FeTMP[d]	7.5	2	11

[a] FeP, 2.5×10^{-7} mol; PhIO, 7.75×10^{-5} mol per addition; cyclooctene, 5.0×10^{-4} mol; CH_2Cl_2, 1.5 cm^3. [b] Based on PhIO. [c] Statistically corrected reactivity of tertiary relative to secondary C–H bonds. [d] Data from reference 7. [e] 1% Adamantanone also formed.

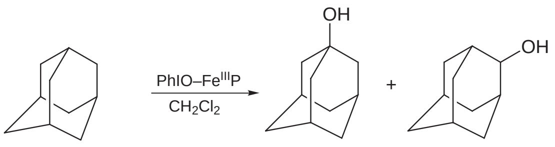
Table 7 Yields of cyclohexanol and cyclohexanone from the oxidation of cyclohexane with PhIO catalysed by homogeneous and supported iron porphyrins in CH_2Cl_2[a]

Catalyst	Yield (%)		
	Cyclohexanol[b]	Cyclohexanone[b]	Ratio of alcohol to ketone
FePFTDCPP	42	3	14
FeTDCPP	32	7	5
FeTPFPP	48	—	—
Si-FePFTDCPP	10	1	10
Si-FeTPFPP[c]	56	6	10
Si-FeTPCPP[c]	37	1.5	24

[a] FeP, 2.5×10^{-7} mol; PhIO, 7.75×10^{-5} mol per addition; cyclooctene, 5.0×10^{-4} mol; CH_2Cl_2, 1.5 cm^3. [b] Based on PhIO. [c] From reference 5, FeP : PhIO : cyclohexane ratio 1 : 20 : 400.

Hydroxylation of adamantane and cyclohexane by PhIO catalysed by FePFTDCPP and Si-FePFTCDPP

The catalytic activity of FePFTDCPP in homogeneous and supported systems for hydroxylation of adamantane was investigated to determine the relative reactivity of the tertiary and secondary C–H bonds [reaction (4)]. Both the homogeneous and supported catalysts gave very good yields of adamantanols, with a preference for the tertiary centre. The statistically corrected 1 : 2 isomer distributions for FePFTDCPP and Si-FePFTDCPP were 14 : 1 and 9 : 1, respectively (Table 6). Formation of adamantanone was not observed in either of the systems.



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The catalytic activities of FePFTDCPP and Si-FePFTDCPP, and for comparison FeTPFPP, were also examined using cyclohexane as the substrate. In homogeneous solution, FePFTDCPP gave moderate oxidation yields, similar to those of FeTFPP (Table 7), with high selectivity for cyclohexanol. However, Si-FePFTDCPP was a relatively poor catalyst for the hydroxylation of cyclohexane. In all these oxidations the yields of PhI from PhIO (typically 80 to 90%) were significantly greater than those of the alcohol and ketone.

Discussion

The sterically hindered iron porphyrin FeTDCPP is a robust and efficient catalyst for hydrocarbon oxidations mediated by PhIO and other oxidants.[1,2a] To explore its full potential we have investigated ways to graft this metalloporphyrin to solid supports. In this respect, coordinative binding of the iron porphyrin to ligands attached to the support surface provides a simple route to heterogenised FeTDCPP although the inherent weakness of the ligand–iron bond can lead to catalyst leaching.[4b] An alternative approach is to use a covalent linkage: this has been achieved previously through sulfonation of the porphyrin followed by amidation to surface amine groups,[8] however, in this study we chose to prepare a monopentafluorophenyl analogue of FeTDCPP. We argued that replacing one of the dichlorophenyls in FeTDCPP with a pentafluorophenyl group should not greatly affect the oxidative stability of the catalyst since both FeTDCPP and FeTPFPP are relatively inert towards degradation by oxidation. However, it would enable the resultant hybrid porphyrin to be covalently grafted on to a solid support by nucleophilic aromatic substitution.[5] It is noteworthy that in the resulting catalyst each iron complex is attached to the support by a single linker unit and differs in this respect from most other covalently bound metalloporphyrins where the heterogenisation process results in multiple bonding between support and iron porphyrin.[9]

A standard mixed aldehyde porphyrin synthesis was optimised to give acceptable yields of the desired compound. Using a stoichiometric 3 : 1 ratio of 2,6-dichloro- and pentafluorobenzaldehyde gave all six of the expected porphyrins (detectable by TLC) and the reaction had to be heavily biased towards the less reactive 2,6-dichlorobenzaldehyde, using a ratio of 2,6-dichlorobenzaldehyde to pentafluorobenzaldehyde of 19 : 1, to minimise the formation of unwanted di- and tri-(pentafluorophenyl)porphyrins. Using this ratio of reagents gave a mixture of porphyrins which was made up mainly of TDCPP but included an overall 3.5% yield of PFTDCPP. Chromatographic purification and insertion of iron gave the desired iron porphyrin.

The ^{1}H NMR chemical shifts of H_2PFTDCPP and FePFTDCPP are very similar to those of H_2TDCPP and FeTDCPP respectively[10] and likewise the ^{19}F NMR spectra closely resemble those of H_2TPFPP and FeTPFPP respectively.[11] These results indicate that the replacement of a dichlorophenyl by a pentafluorophenyl group does not have a major effect on the proton and fluorine environments in these porphyrins.

The iron(III) porphyrin was readily covalently bound to aminopropylated silica and the UV–VIS spectrum of the resulting material had a Soret band at 432 nm which is 16 nm red-shifted from the corresponding λ_{max} of the iron(III) porphyrin in solution. It is well known that iron(III) porphyrins, particularly those with electron-withdrawing substituents, can be reduced by amines to low-spin bis-ligated iron(II) porphyrins resulting in a red shift of the Soret peak.[12] We believe, as we and others have noted previously for coordinatively supported iron porphyrins,[13] that the covalently bound FePFTDCPP is reduced by the excess free NH_2 groups on the surface of the silica, leading to a supported iron(II) porphyrin. An identical spectral change has been observed with FeTPFPP covalently bound by aminoalkyl linkers to silica and to polystyrene suggesting that this is a general phenomenon with electron deficient iron porphyrins.[13b] Interestingly if the Si-FePFTDCPP is left to stand in air for several weeks the UV–VIS spectrum shows a double Soret band at 422 and 432 nm, indicating the presence of some iron(III) porphyrin arising from a slow aerobic oxidation. The EPR spectrum of this material confirmed the presence of high-spin iron(III) porphyrin and interestingly showed that this was present both as an axially symmetric species ($g_\perp = 6.0$ and $g_\| = 2.0$) and one with rhombic distortion ($g = 4.3$).[14]

The iron(III) mono(pentafluorophenyl)tris(dichlorophenyl)-porphyrin in homogeneous solution is a very efficient and robust catalyst for alkene epoxidation using PhIO. It promotes high conversions of cyclooctene to its epoxide in high turnover reactions with negligible catalyst destruction (Tables 1 and 5). In these respects it compares well with the related FeTDCPP. The reactions of both (*Z*)- and (*E*)-4-methylpent-2-ene are effectively quantitative and, as is general for iron porphyrin–PhIO systems, the monooxygenation of the alkene is stereospecific. Identical results were obtained with the symmetrical FeTPFPP catalyst; interestingly, however, FeTDCPP shows a marked preference for epoxidising the (*Z*)-alkene compared with the (*E*)-isomer. The stereoselective preference for epoxidising *cis*-dialkylalkenes is well documented and is attributed to the greater steric interaction of the *trans*-alkene and porphyrin in the side-on approach of the alkene to the oxoiron(IV) porphyrin π radical cation active oxidant.[15] In the present study this effect is not shown with FeTPFPP but is apparent with the more sterically hindered FeTDCPP. Surprisingly FePFTDCPP behaves like FeTPFPP rather than FeTDCPP suggesting that the replacement of one dichlorophenyl group by a pentafluorophenyl has a dramatic effect on the steric interactions in the epoxidation transition state. Very recently Collman *et al.*[16] reported that replacing one of the aryl groups in a very sterically crowded chiral porphyrin with a pentafluorophenyl group leads to the expected increase in alkene epoxidation yield since the modification allows easier access of the substrate to the oxometal centre of the active oxidant. Interestingly, however, and contrary to the present study the less hindered chiral catalyst showed a greater selectivity in its reactions.

The reaction of cyclohexene also gives excellent conversions to the epoxide. However, it is complicated by the well documented ready autoxidation of the substrate leading to the simultaneous formation of allylic alcohol and ketone with apparent total yields >100%.[4b,17] It seems likely that the iodosylbenzene is also involved in the radical autoxidation since in control reactions in the absence of iron porphyrin it is converted to iodobenzene. Baciocchi *et al.*[18] came to a similar conclusion in their study of cumene oxidation with FeTPP–PhIO where they reported that PhIO can trap and oxidise cumyl radicals to cumyloxyl radicals. An alternative explanation for the consumption of PhIO in the control reactions is that trace metal impurities may be responsible for catalysing the PhIO oxidations.[19]

The homogeneous FePFTDCPP–PhIO system is also very effective at hydroxylating aliphatic C–H bonds giving very comparable results to oxidations catalysed by FeTPFPP and FeTDCPP and significantly better than the non-halogenated catalysts FeTPP, FeTTP and FeTMP. With adamantane the alcohol yields were >84%, with no adamantanone and with cyclohexane the oxidation yield was 45% with an alcohol : ketone ratio of 14 : 1.

The statistically corrected selectivity for oxidation at the 1-relative to the 2-position (C_{tert}/C_{sec}) of adamantane provides a measure of the reactivity of the active site and the steric constraints around the oxo-iron group. The values in Table 6 reveal that, as expected, electron-withdrawing halogens on the porphyrin ligand, by increasing the reactivity of the active oxidant, decrease the selectivity of the oxidation (*cf.* the reactions of FeTPFPP and FeTPP and of FeTDCPP and FeTMP) and likewise increased steric hindrance at the active site results in a decrease in selectivity for the 1-position (*cf.* the reactions of FeTPP, FeTTP and FeTMP and of FeTPP and FeTDCPP). Interestingly, as noted above for the epoxidation of (*Z*)- and (*E*)-4-methylpent-2-ene, the C_{tert}/C_{sec} selectivity of FePFTCDPP resembles that of FeTPFPP rather than FeTDCPP. This supports the suggestion that replacing one of the 2,6-dichlorophenyls in FeTDCPP with a pentafluorophenyl group significantly reduces the steric constraints around the oxo-iron ion at the active site.

Supporting FePFTDCPP, by covalently binding it to aminopropylated silica, results in a less active catalyst with rates of cyclooctene epoxidation decreasing by ~10-fold (for example Fig. 1), however, the overall epoxide yields are very comparable for the two systems. This difference in reactivity is a common feature for these heterogenised iron porphyrins and has been attributed to slow diffusion of oxidant and substrate to and from the catalyst on the support surface.[4,9]

With adamantane hydroxylation, the supported iron porphyrin gives slightly lower yields and C_{tert}/C_{sec} selectivity than those from the homogeneous analogue. The latter can be attributed to increased steric constraints at the active site brought about by interactions between the porphyrin and the support: similar small differences between reactions catalysed by homogeneous and supported metalloporphyrins have been noted previously.[4c,20]

With cyclohexane, which is a less reactive alkane than adamantane, heterogenisation of the catalyst results in significantly lower yields of oxidation products. Interestingly, Mansuy *et al.*[5] report good yields for cyclohexane hydroxylation with PhIO catalysed by FeTPFPP covalently bound to aminopropylated silica. The origin of the difference in reactivity of these two structurally similar supported porphyrins is unclear but might arise from the difference in linkage of FePFTDCPP and FeTPFPP to the support surface. As noted above, the former is attached by one linker unit whereas with the latter di-, tri- and even tetra-linkage is possible. The polylinked FeTPFPP will be more closely associated with the support than FePFTDCPP which will affect the local environment of the catalyst and could in turn lead to enhanced catalyst activity.

The stability of the supported porphyrin is comparable with that of the homogeneous analogue. However, the former can become deactivated possibly by precipitation of iodoxylbenzene, from the iron porphyrin-catalysed disproportionation of iodosylbenzene [reaction (5)], on the catalyst surface. As is

$$\mathrm{PhIO} + \mathrm{Fe^{III}P} \longrightarrow \mathrm{PhI} + \mathrm{O{=}Fe^{IV}P^{+\cdot}} \xrightarrow{\mathrm{PhIO}} \mathrm{PhIO_2} + \mathrm{Fe^{III}P} \quad (5)$$

illustrated with cyclooctene epoxidation (Table 4) the catalyst's activity can be restored by washing the supported porphyrin with methanol. An overall 81% yield of epoxide based on PhIO and 864 catalyst turnovers from four sequential additions of PhIO was obtained. In a larger scale oxidation using a ratio of Si-FePFTDCPP : PhIO of 1 : 4630 the epoxide yield was somewhat lower, 69% (3200 turnovers) and there was evidence for a small amount of catalyst in solution (*ca.* 1% of the catalyst) at the end of the reaction. It is conceivable that this arises from oxidative cleavage of the linker, however, we were unable to detect any porphyrin derivatives by mass spectrometry. An alternative explanation is that the material detected by UV–VIS spectroscopy is microparticulate Si-FePFTDCPP formed by grinding of the solid catalyst between the magnetic stirrer bead and the surface of the reaction flask during the oxidation. In agreement with this suggestion, examination of the catalyst at the end of the reaction showed that there was significant physical degradation of the catalyst to form smaller particles. This microparticulate FePFTDCPP would be detectable by UV–VIS spectroscopy but not by MS.

Experimental

Materials

All compounds used in this study were commercially available and of analytical grade purity unless otherwise stated. Chloroform was distilled from calcium hydride immediately before use in the synthesis of the porphyrin. Iodosylbenzene was prepared from iodosylbenzene diacetate following the method of Saltzmann and Sharefkin[21] and the active oxygen content was shown to be 99% by iodometric titration.[22] Aminopropyl modified silica was prepared according to a literature procedure[23] using Kieselgel 60 (surface area 500 m^2 g^{-1}, pore size 60 Å and particle size 40–63 µm) and had a loading of 49% based on the nitrogen content (CHN analysis) assuming an average of two bonds between silane and silica and five silanol groups nm^{-2}.[24]

The alkenes were purified by passing them through a short activated alumina (UG1 100S; Phase Separations) column immediately before using them in an oxidation.

Silica used for column chromatography was Kieselgel 60 (230–400 mesh) (Camlab). TLC used aluminium backed silica gel 60 F_{254} plates (Merck).

Synthesis of the 5-(pentafluorophenyl)-10,15,20-tris(2,6-dichlorophenyl)porphyrin, PFTDCPP

This was achieved by Leanord's[25] modification of the method of Lindsey.[6] The optimum conditions for preparing the desired monopentafluorophenylporphyrin were found by reacting pyrrole (0.26 cm^3, 3.75 mmol) with 2,6-dichlorobenzaldehyde (0.495–0.640 g, 2.8–3.66 mmol) and pentafluorobenzaldehyde (0.184–0.0184 g, 0.94–0.094 mmol) in chloroform (250 cm^3) under nitrogen at room temperature, shielded from ambient light. The solution was stirred and boron trifluoride–diethyl ether (0.2 cm^3) was added. The water scavenger triethyl orthoacetate (0.2 cm^3) and a fresh charge of boron trifluoride–diethyl ether (0.2 cm^3) were added after 15 min. The condensation gave a mixture of porphyrinogens which were oxidised after 1 h by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1 g) to give a mixture of porphyrins. TLC analysis (silica gel; $CHCl_3$: hexane, 2 : 1) and column chromatography followed by MS analysis was used to identify the porphyrin products. The best procedure, using a pyrrole : 2,6-dichlorobenzaldehyde : pentafluorobenzaldehyde ratio of 4 : 3.8 : 0.2, was repeated on a larger scale with 15 mmol of pyrrole. Work-up involved the addition of triethylamine (0.9 cm^3) at the end of the reaction, to neutralise the acid catalyst, and removal of the solvent under vacuum to give the crude porphyrin mixture. This was purified by column chromatography on silica with chloroform as eluent and the main porphyrin containing fraction was then rechromatographed with chloroform : hexane (2 : 1) as eluent. The three main porphyrin products were eluted in the order TDCPP, PFTDCPP and DPFDDCPP. Solvent removal gave the desired porphyrin 0.118 g (3.5% yield based on pyrrole) which had $\lambda_{max}(CH_2Cl_2)$/nm (ε/m^2 mol^{-1}) 416 (3.6×10^4), 510 (2.1×10^3), 540, 586 (6.3×10^2), 654; $\delta_H(CDCl_3)$ 8.75 (4H, m, H-pyrrole), 8.69 (4H, br s, H-pyrrole), 7.80–7.71 (9H, m, *meta*- and *para*-phenyl), −2.63 (2H, s); $\delta_F(CDCl_3)$ −137.76 (dd, *ortho*-F), −153.85 (t, *para*-F), −163.56 (dt, *meta*-F); *m*/*z* (FAB$^+$) 907.9659, calc. for $C_{44}H_{19}N_4Cl_6F_5$ (using ^{35}Cl), 907.9661.

Iron porphyrin FePFTDCPP

This compound was prepared by refluxing the free base PFTDCPP (0.054 g, 0.06 mmol) with iron(II) chloride tetrahydrate (0.121 g) in acetonitrile (60 cm^3) for 6 h under nitrogen following the method described by Kadish *et al.*[26] The iron(III) porphyrin was purified by chromatography on silica with dichloromethane, to remove a small amount of the free base porphyrin, followed by dichloromethane with 5% of methanol. After solvent removal the FePFTDCPP was dissolved in dichloromethane and shaken with a few drops of HCl (6 mol dm^{-3}) to ensure that chloride was the axial ligand. This procedure gave 0.056 g of the required (FePFTDCPP)Cl (95% yield), $\lambda_{max}(CH_2Cl_2)$/nm (ε/m^2 mol^{-1}) 356 (3.6×10^3), 416 (1.03×10^4), 506 (1.2×10^2), 642 (4.5×10^2); $\delta_H(CDCl_3)$ ~81 (8H, br s, H-pyrrole), 13.8 (3H, br s, *meta*-phenyl), 12.5 (3H, br s, *meta*-phenyl), 8.25 (3H, br s, *para*-phenyl); $\delta_F(CDCl_3)$ −95.9 (*ortho*-F), −100.3 (*ortho*-F), −146.3 (*para*-F), −150.3 (*meta*-F), −152.7 (*meta*-F); *m*/*z* (FAB$^+$) 961.8850, calc. for $C_{44}H_{17}N_4Cl_6F_5Fe$ (using ^{35}Cl and ^{56}Fe) 961.8854.

Synthesis of FePFTDCPP supported on amino-modified silica

This was achieved by heating FePFTDCPP (10 µmol) with the aminopropylated-silica (0.5 g) in diglyme at 140 °C under argon for 3 h, following the method of Mansuy *et al.*[5] for covalently binding FeTPFPP to aminopropylated-silica. The resulting solid was treated with dichloromethane (24 h) and then methanol (24 h) using a Soxhlet apparatus. The porphyrin loading was obtained using UV–VIS spectroscopy to measure the amount of iron porphyrin in the combined washings.

Methods

Instrumentation

UV–VIS spectra were obtained with a Hewlett-Packard 8452A diode array spectrometer.

GC analyses were performed on Pye-Unicam GCD and Varian Star 3400 CX chromatographs with flame ionisation detectors using a column (1.5 m × 2 mm) packed with 20% w/w, Carbowax 20M on celite and a DB-wax (1 µm thickness) megabore column (30 m × 0.538 mm) respectively. The results were analysed on a PC using JCL 6000 software (Jones Chromatography) or on a Varian workstation.

Mass spectra were recorded on a V. G. Analytical Autospec instrument. For FAB^+ spectra, 4-nitrobenzyl alcohol was used as the matrix and fragments were generated by caesium ion bombardment.

^1H NMR spectra were recorded on a Bruker MSL 300 spectrometer (300 MHz) using $CDCl_3$ as solvent and tetramethylsilane as the reference.

EPR spectra of the supported iron porphyrin at 3 K were obtained with a Varian E-109 spectrometer, operating in the X-band frequency (9 GHz) with a gain of 1000 µV and 20 000 mW power.

Alkene and alkane oxidations

In a typical oxidation, the supported (14 mg, 0.25 µmol) or unsupported iron(III) porphyrin (0.25 µmol) was stirred with the alkene (500 µmol) in dichloromethane (1.5 cm^3) and the reaction was initiated by the addition of iodosylbenzene (30 µmol). The reactions were monitored at regular intervals by removing 1.5 µl samples for GC analysis.

Reactions in the absence of dioxygen were carried out in a flask sealed with a Subaseal. The solid metalloporphyrin and iodosylbenzene were thoroughly flushed with nitrogen or argon prior to addition of substrate and dichloromethane which had previously been thoroughly flushed with nitrogen. The reaction was monitored as described above.

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