Metalloporphyrinosilicas: a new class of hybrid organic–inorganic materials acting as selective biomimetic oxidation catalysts

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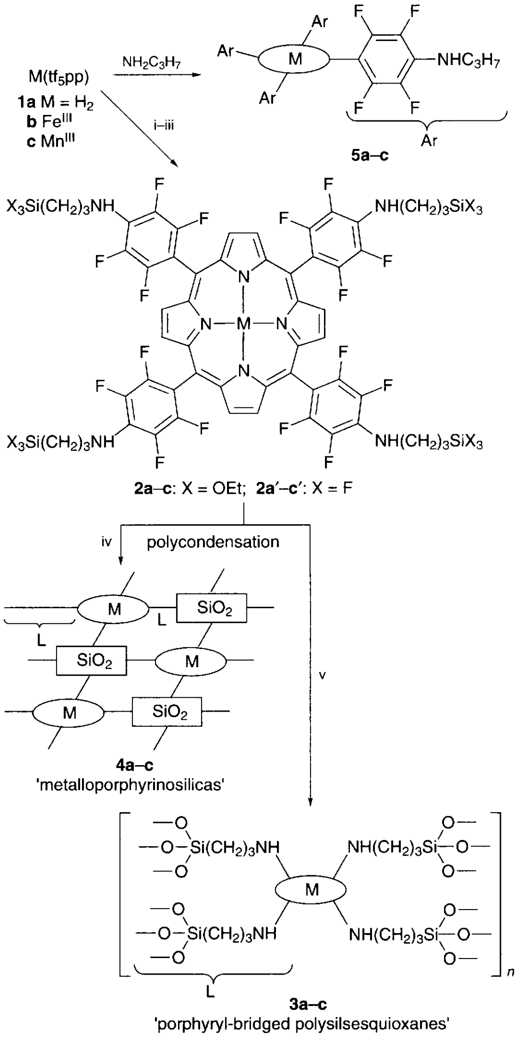
New hybrid organic–inorganic materials are prepared by hydrolysis and polycondensation, or cocondensation with tetraethoxysilane, of iron porphyrins bearing a trifluorosilyl function; despite their insolubility, these 'metalloporphyrinosilicas' are efficient catalysts for alkene epoxidation by PhIO or Bu^{t}OOH and alkane hydroxylation by PhIO, the iron porphyrinosilicas with low specific surface areas ($\approx$ 60 m^2 g^{-1}) catalysing a shape-selective hydroxylation of alkane mixtures.

During the last decade, several generations of homogeneous metalloporphyrin catalysts that mimic cytochrome P450 have been prepared.[1] High yields, rates and recycling numbers for hydrocarbon oxidation have been obtained, especially with polyhalogenated metalloporphyrins.[1] Supported catalysts based on such metalloporphyrins adsorbed or covalently bound to polymers have also been described.[1,2] High enantiomeric excesses were observed for alkene epoxidation using metalloporphyrins bearing chiral superstructures.[3] In all these studies the selectivities of P450 models were achieved by modifying the porphyrin macrocycle rather than by using specific local surroundings of the catalytic site as is the case in enzymes. A different strategy towards selective catalysis could be to build hybrid organic–inorganic materials in which the metalloporphyrin is part of the matrix, since it is now possible to engineer some microstructural properties, such as porosity and specific surface area, of hybrid materials.[4] Here, we describe our first results in that direction, concerning the synthesis and catalytic properties of a new class of materials that we have termed 'metalloporphyrinosilicas'. They are prepared by polycondensation, or cocondensation with tetraalkoxysilanes, *via* a sol–gel process, of iron porphyrinotrifluorosilane monomers. These insoluble polymers catalyse hydrocarbon oxidation by PhIO and Bu^{t}OOH; those with low specific surface areas lead to a shape-selective hydroxylation of alkanes.

The porphyrin precursors of bridged porphyrylpolysilsesquioxanes and porphyrinosilicas were synthesized as outlined in Scheme 1. Porphyrinosilane monomer **2a** was prepared by reaction of *meso*-tetrakispentafluorophenylporphyrin **1a** (H_2tf_5pp) with excess 3-aminopropyltriethoxysilane (aptes) for 3 h under argon, in the presence of triethylamine in dmf at 140 °C.[5] Monomer **2a** could not be directly purified from the reaction mixture, numerous attempts to do so by distillation or crystallization having led to partial polymerization. Thus a two-step purification process was devised. It involved the hydrolysis and polycondensation of the crude mixture, followed by treatment of the resulting polysiloxanes by HF[6] to produce a porphyrinotrifluorosilane monomer **2a′** in CH_2Cl_2 solution. The excess aptes was simultaneously converted to aminopropyltrifluorosilane, which was extracted with aqueous acid. In order to better control the further sol–gel process, it was necessary to remove HF from solutions of **2a′**. This was done either by carefully washing the solution of **2a′** with water or by reversion to **2a** by treatment with anhydrous ethanol. Monomer **2a′** exhibited UV–VIS and ^{1}H NMR spectra [λ/nm (CH_2Cl_2): 421, 511, 546, 587; NMR (CD_2Cl_2, D_2O, HF) δ 9.01 (8H, s), 3.74 (8H, t), 2.10 (8H, m)‡] very similar to those of *meso*-tetrakis(4-propylamino-2,3,5,6-tetrafluorophenyl)porphyrin **5a** prepared by reaction of H_2tfpp **1a** with propylamine[5] [λ/nm (CD_3COCD_3): 420, 509, 545, 586; NMR ($CDCl_3$), δ 8.93 (8H, s), 4.23 (4H, m), 3.68 (8H, t), 1.85 (8H, h), 1.22 (12H, t) −2.85(2H, s)]. Iron porphyrinosilanes **2b,b′** were prepared from **1b** and purified by the same methods.

Bridged porphyrylpolysilsesquioxanes **3a,b** were prepared by hydrolysis and polycondensation of **2a,b** in a biphasic CH_2Cl_2–H_2O system, at room temp. for 48 h, in the presence of a catalyst [either HF or 1-methylimidazole (mim)]. 'Iron porphyrinosilicas' **4b** were prepared according to the well known sol–gel procedure,[7] by hydrolysis and cocondensation of **2b** with $Si(OEt)_4$ in EtOH in the presence of water and



Scheme 1 *Reagents and conditions:* i, $H_2N(CH_2)_3Si(OEt)_3$; ii, H_2O, filtration; iii, purification , HF treatment; iv, $Si(OEt)_4$, H_2O; v, H_2O

Table 1 Properties of iron porphyrinosilicas: porphyrin loading, specific surface area and efficiency in oxidation catalysis

			Oxidation reactions				
			PhIO,[a] cyclohexane	PhIO,[b] heptane	PhIO,[c] adamantane + cyclohexane	PhIO,[d] cyclododecane + cyclohexane	Bu^{t}OOH,[e] cyclooctene
Catalyst	Loading of porphyrin % (m/m)	Surface area (m^2 g^{-1})	Cyclohexanol + cyclohexanone yield (%)[f,g]	Heptanols[h] + heptanones yield (%)[i]	Adamantanols : cyclohexanol ratio (total yield/PhIO)	Cyclododecanol : cyclohexanol ratio (total yield/PhIO)	Cyclooctene oxide yield (%)
3a	84	30[j]		—	—		—
3c	27	25[k]	56	38	5.2 (50)	1.1 (30)	—
3b$_1$	59	60[j]	48	41	5.6 (54)	1.1 (52)	64
3b$_2$	61	105[k]	47	49	9.9 (64)	—	45
4b$_1$	15	690[k]	41	45	12 (50)	1.7 (38)	54
4b$_2$	16	770[j]	44	47	17 (57)	2.0 (45)	50

[a] *Conditions*: molar ratio of catalyst : PhIO : hydrocarbon = 1 : 20 : 800; 'equivalent concentration' of supported catalyst 1 mmol l^{-1} in 1 ml of CH_2Cl_2 at 20 °C for 2 h. Yields based on PhIO were found unchanged after 24 h; further additions of PhIO (at least 10) to the medium led to identical yields; Yields were determined by GC using internal standard methods. [b] Molar ratio of catalyst : PhIO : hydrocarbon = 1 : 20 : 2100 in 1 ml of CH_2Cl_2–MeCN (1 : 1). [c] Molar ratio of catalyst : PhIO : adamantane : cyclohexane = 1 : 20 : 200 : 200, in 1 ml of CH_2Cl_2. [d] Molar ratio of catalyst: PhIO : cyclododecane : cyclohexane = 1 : 20 : 400 : 400, in 1 ml of CH_2Cl_2. [e] Molar ratio of catalyst: Bu^{t}OOH : hydrocarbon = 1 : 200 : 600 in 1 ml of CH_2Cl_2 : MeOH (1 : 3), yields based on starting Bu^{t}OOH. [f] For total yields it was assumed that 2 mol of PhIO were necessary for ketone formation. [g] Alcohol to ketone ratio > 10. [h] Relative ratios of heptan-2-, 3- and 4-ol, = 40 : 20 : 20. [i] Only traces of heptanones (< 1%) were observed. [j] Sol–gel catalyst: HF. [k] Sol–gel catalyst: mim.

concentrated HCl (or mim) as catalysts, while stirring at room temp. for several days. The resulting materials **3a,b** and **4b** were filtered, washed with various solvents [H_2O, MeOH, Me_2CO, MeCN, Et_2O, CH_2Cl_2–1%HCl (g)], extracted in a Soxhlet apparatus with CH_2Cl_2 overnight and dried at 80 °C for 24 h. **3a,b** and **4b** exhibited UV–VIS spectra similar to those of the parent porphyrins **5a,b**, indicating that the porphyrin rings were not modified during the preparation. For example, **4b** showed bands at 350, 418, 511, 548, 590 and 654 nm, at positions close to those exhibited by the iron porphyrin **5b**. Moreover the EPR spectra of **3b** showed *g* values at 5.8 and 2, as expected for supported high-spin iron(III) porphyrins. Porphyrin loadings were obtained by measuring the amount of iron and fluorine in the resulting materials. For porphyrylpolysilsesquioxanes **3a,b**, the porphyrin content was high and reached 84% (m/m). Porphyrin loading in 'porphyrinosilicas' **4b** varied between 0.5 and 50%. Although we have not yet made a thorough study of the control of surface areas in these resulting polymers, it is noteworthy that homopolymers **3a,b** exhibit lower specific surface areas (30– 105 m^2 g^{-1}) than copolymers **4b** (> 690 m^2 g^{-1}) (Table 1).

All the iron(III) porphyrinosilicas catalyse the epoxidation of cyclooctene in high yields (> 90%) as well as the hydroxylation of cyclohexane and heptane with PhIO with yields of *ca.* 50%, almost identical to those observed with similar polyhalogenated iron porphyrins covalently bound to a silica surface.[6b] They also catalyse the epoxidation of cyclooctene by Bu^{t}OOH, with yields between 45 and 64% (Table 1); they are more stable during this reaction than the homogeneous catalyst **1b**, as catalyst **3b**$_2$ remains intact after about 1000 turnovers under conditions (catalyst : cyclooctene : Bu^{t}OOH = 1 : 1000 : 1500) under which **1b** is deactivated. A possible role of the inorganic matrix in such catalysts could be to select between various substrates because of varying access to the iron centres. Preliminary indicative results (Table 1) were observed in oxidations of an adamantane–cyclohexane mixture (1:1) with PhIO in the presence of catalysts **3b** and **4b** exhibiting different specific surface areas. Interestingly, the adamantane : cyclohexane oxidation product ratio is much higher for iron porphyrinosilicas with high specific surface areas (up to 17 for a surface area of 770 m^2 g^{-1}) than for catalysts **3b** with low surface areas (5.6 for surface area of 60 m^2 g^{-1}). Hydroxylation of cyclohexane, which is less reactive and less bulky, is thus favoured in the case of the latter catalysts that could have a more difficult access to the metal centres. Similar data were obtained for the oxidation of a cyclododecane–cyclohexane mixture (1 : 1). Supported catalysts with high specific surface areas led to cyclododecanol: cyclohexanol ratios of *ca.* 2, as expected from the number of CH_2 groups per substrate molecule, whereas supported catalysts with a low surface area gave a markedly lower ratio (≈ 1) (Table 1). Analogous results were obtained with manganese(III) porphyrylpolysilsesquioxanes **3c** prepared in a manner identical to their parent iron(III) materials.

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Footnotes

† Deceased, June 1993.

‡ CH_2Si and NH signals were not observed because of the presence of H_2O and D_2O.

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