Cationic ironporphyrins as catalyst in comparative oxidation of hydrocarbons: homogeneous and supported on inorganic matrices systems

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Abstract

Cationic ironporphyrins in solution and supported on imidazole propyl gel (IPG) and silica gel (SG) as catalyst in cyclohexane hydroxylation using iodosylarene as oxygen donor were studied. FeTM4PyP^{5+} **1** as homogeneous catalyst for cyclohexane hydroxylation, in acetonitrile (CH_3CN) and ultrasound stirring, gives cyclohexanol (C-ol) yields of 20%. The FeTM2PyP^{5+} **2** as catalyst for cyclohexene oxidation in CH_3CN and ultrasound stirring is a very efficient system, giving 93% of total yield, with an epoxide:alcohol:ketone selectivity of 77:12:11. The supported systems, 1–IPG and 1–SG are particularly efficient in dichloromethane (CH_2Cl_2), giving C-ol yields of 37% and 53%, respectively. These systems consist of polar hemin in isolated sites, which selectively catalyze cyclohexane oxidation in apolar solvent. They represent good cytochrome P-450 model systems. In the same way, the active site of P-450 consists of a polar protohemin in a hydrophobic pocket, promoting selective cyclohexane oxidation. These rigid cationic 1–IPG, 1–SG, 2–IPG, 2–SG, 3–IPG and 3–SG systems can catalyze with very small amounts of ironporphyrins, which correspond to about 30–80 times fewer numbers than the hemin in P-450 catalytic site.

Keywords: Cationic ironporphyrin; Epoxidation; Functionalized silica gel; Hydroxylation; Porphyrin; Supported catalyst

1. Introduction

Metalloporphyrins, specially iron and manganese complexes, are capable of oxygenating hydrocarbons in a catalytic way, yielding alcohol from alkane and epoxide from olefin under mild conditions [1]. Metalloporphyrins with bulky and electronegative substituents have been prepared in order to prevent the μ-oxo dimer formation and to increase the catalytic efficiency [2–5]. The combination of electron-withdrawing substituents in the metalloporphyrins with immobilization on inorganic supports results in very efficient, selective and easy to recover catalysts [5,6]. The site-isolation on a solid support prevents porphyrin oxidative degradation by bimolecular interaction [7]. These systems are potentially useful for selective oxidation in organic chemistry [1] and for the prediction of the oxidative metabolism of drugs or xenobiotics [8]

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Ironporphyrin

1 FeTM4PyP(ClO₄)₅   R = ⟨pyridyl⟩N⁺—CH₃

                                    CH₃
                                    |
2 FeTM2PyPCl₅   R = ⟨pyridyl⟩N⁺

3 FeTPPCl   R = ⟨phenyl⟩

                                    C₁₄H₂₉
                                    |
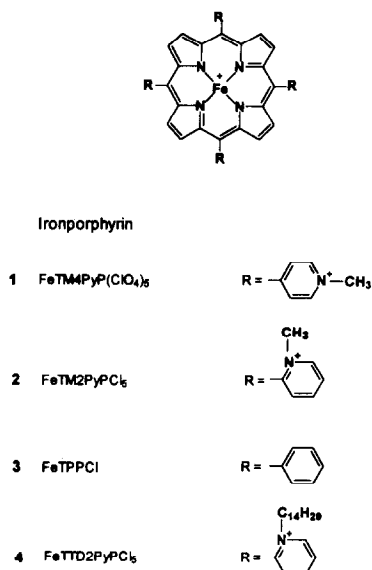4 FeTTD2PyPCl₅   R = ⟨pyridyl⟩N⁺

Fig. 1. Structures of the ironporphyrins.

Mansuy et al. [1,8] have reported charged manganese porphyrin adsorbed on silica as a specially efficient catalyst for alkane hydroxylation. Almost the same results were obtained when this catalyst was supported on montmorillonite clay [9]. It has also been shown that iron phthalocyanine encapsulated inside zeolites shows selectivity towards smaller substrates and regioselectivity for linear alkane hydroxylation [10].

The study of intermediates has arisen from the reaction between cationic methylpyridyl substituted iron porphyrins and iodosylbenzene, in methanol–dichloromethane systems, have been previously reported by us [11]. The results explained the low catalytic efficiency of cyclohexane hydroxylation in methanol containing systems, despite the fact that this solvent favors the ferryl radical, $Fe^{IV}(O)P^{+\cdot}$, species [12,13].

In this work we are reporting cationic ortho- and para-alkylpyridyl substituted iron porphyrins as catalysts for hydrocarbon oxidation (Fig. 1) in homogeneous systems or supported on IPG (FeP^{5+}–IPG) and silica gel (FeP^{5+}–SG) systems, using iodosylarene as oxygen donor. Methanol effects in hydroxylation and epoxidation reactions will be discussed. The electronic effect of ortho- and para-alkylpyridyl substituents are evident in the homogeneous oxidation reac-

tions studied. The strong interactions, catalyst–IPG and catalyst–SG, by coordination and/or adsorption promotes stable and particularly efficient supported systems in some particular solvent conditions, when compared to the corresponding homogeneous systems.

2. Experimental section

2.1. Materials

All the materials were of commercial reagent grade unless otherwise stated. Methanol, dichloromethane, acetonitrile and toluene were only distilled. N,N-Dimethylformamide (DMF) was stirred over KOH at room temperature overnight, decanted, then distilled at reduced pressure. All solvents were stored over activated 3 Å or 4 Å molecular sieves under argon atmosphere. Iodosylbenzene (PhIO) and iodosyltoluene (CH_3PhIO) were prepared by the hydrolysis of iodoarene diacetate with aqueous sodium hydroxide following Sharefkin and Saltzman's method [14]. Iodosylarene samples were stored in freezer and replaced every six months. The purity was controlled by iodometric assay.

2.1.1. Porphyrins and iron porphyrins

Meso-tetrakis(4-N-methylpyridyl)porphyrin iron(III) pentaperchlorate ($FeTM4PyP(ClO_4)_5$ 1 and meso-tetrakis(tetraphenyl)porphyrin iron(III) chloride FeTPPCl 3 were purchased from Midcentury. The corresponding ortho isomer $FeTM2PyP(ClO_4)_5$ 2 and the meso-tetrakis(tetradecyl-2-pyridyl)porphyrin iron(III) chloride ($FeTTD2PyP)Cl_5$ 4, an atropisomer mixture ($\alpha\alpha\beta\beta$, $\alpha\beta\alpha\beta$), were obtained according to procedure described previously [15].

2.1.2. Imidazolyl propyl gel

The support was prepared using the procedure presented in the literature [16,17]. 19 g of imidazole and 45 ml of 3-chloropropyl trimethoxysilane were refluxed at 100°C for 15 h in toluene. 170 g of silica gel (Merck 60 A, 0.063–0.2 mm

70–230 mesh) was added to this solution, which was refluxed for more 8 h. At the end of the reaction, the functionalized silica was washed with toluene, ethanol and dried in vacuum at 80–100°C. Elemental analysis: C = 5.34%; H = 1.20%; N = 0.65%.

2.1.3. Preparation of supported ironporphyrins

About 5×10^{-6} to 1.5×10^{-7} mol of FeP^{5+} were dissolved in 5 ml of methanol and added to 0.50 g of IPG or silica gel. The suspension was stirred for 30 min at room temperature. The supported solid was separated by filtration from the solvent and washed three times with about 3 ml of methanol. The amount of supported FeP^{5+} was determined by spectrophotometry, through the absorption intensity of the Soret band in the remaining methanol filtrate and washings solution. The supported solid was dried under vacuum at room temperature. The catalysts were characterized by UV–Vis spectra. FeP^{5+}–IPG (brownish), through the typical FeP–Im spectra with absorption at 552 nm [18], and FeP^{5+}–SG (greenish) through the absorption at 580 nm in FeP–OH species [19].

2.2. Oxidation reactions

The reactions were carried out in a 2 ml vial with an open top screw cap containing a silicone Teflon faced septum.

2.2.1. Solution catalysis

To the vial containing the ironporphyrin $(3.0 \times 10^{-7}$ mol) and CH_3PhIO or PhIO $(3.0 \times 10^{-6}$ mol) under argon atmosphere and in an adapted dark chamber, 100 μl of substrate (cyclohexane or cyclohexene) and 200 μl of the desired solvent were added. The reaction mixture was stirred at 0°C with ultrasound (ultrasound laboratory cleaner Minison–Thornton, 40 W, 50–60 Hz). After the desired time, sodium bisulfite-saturated methanol or acetonitrile solution (20 μl) was added to the reaction mixture in order to quench further oxidation, and the vial was then removed from the ultrasound bath.

2.2.2. Supported catalysis

To the vial containing 9.0×10^{-7} to 1.2×10^{-6} mol of PhIO and 0,1000 g of the solid catalyst under argon atmosphere, 300 μl of dichloromethane and 200 μl of cyclohexane were added. The mixture was stirred at room temperature for the specified time, in the absence of light. The product was extracted with 200 μl aliquots of solvent, followed by 5 min stirring, until 2 ml of extract was obtained.

For the recycling experiments, the catalyst was washed 10 times with solvent. This procedure was done to ensure that the remaining iodosylbenzene was totally removed from the catalyst. This catalyst was then dried for 3 h at 60°C, before the next recycling.

2.2.3. Product analysis

Gas chromatographic analysis were performed on a CG 500 gas chromatograph coupled to a CG-300 integrator. Nitrogen was used as the carrier gas with an hydrogen flame ionization detector. The Inox column (length 1.8 m, internal diameter 3 mm) was packed with 10% Carbowax 20M on chromosorb WHP. The products formed were analysed by comparison of their retention times with authentic samples. Yields were determined from a standard curve and using n-octanol as internal standard.

3. Results and discussion

3.1. Homogeneous catalysis

3.1.1. Cyclohexane as substrate

The catalytic activity is obviously limited by the ironporphyrin solubility in the selected solvent. Yields of cyclohexanol are higher in the solvents where FeP^{5+} or FeP^+ are soluble (Table 1): FeTPPCl **3** in dichloromethane, FeTM4PyP$(ClO_4)_5$ **1** in acetonitrile and (FeTTD2PyP)Cl$_5$ **4**, with amphiphilic character, in dichloromethane and acetonitrile [15]. Despite the high solubility of FeTM4PyP$(ClO_4)_5$ **1** in methanol and the favorable conditions for the for-

Table 1
Yields of cyclohexanol in the hydroxylation of cyclohexane with PhIO in different solvents, using ironporphyrins as catalyst in homogeneous systems

Ironporphyrin	Solvent	Yield [a], %	
		Cyclohexanol	Cyclohexanone
1 FeTM4PyP(ClO$_4$)$_5$	CH$_3$CN	20	–
	CH$_3$CN [b]	11	4
	CH$_2$Cl$_2$	3	–
	CH$_3$OH	1	–
	CH$_3$OH/ CH$_2$Cl$_2$	5	–
	CH$_3$OH/ CH$_2$Cl$_2$ [b]	4	2
2 FeTM2PyP(ClO$_4$)$_5$	CH$_3$CN	6	–
3 FeTPPCl	CH$_3$CN	5	–
	CH$_2$Cl$_2$	13	–
	CH$_3$OH	2	–
4 FeTTD2PyPCl$_5$	CH$_3$CN	15 [c]	–
	CH$_2$Cl$_2$	22 [c]	–

Conditions: [FeP] $\approx 10^{-4}$ mol·l^{-1}; [PhIO] $\approx 10^{-3}$ mol·l^{-1}; 0°C; stirring for 30 min by ultra sound, under argon atmosphere.
[a] Error average of 2%, based on the starting PhIO.
[b] Magnetic stirring.
[c] From [15].

mation of Fe^{IV}(O)P$^{+·}$ π-cation radical, the catalytic activity of 1 in this solvent is low [12,13]. There are two competitive reactions which contribute to deactivation: (i) conversion of Fe^{IV}(O)P$^{+·}$ to the Fe$^{·}$O$^{·}$N species [11,12]; (ii) Fe^{IV}(O)P$^{+·}$ is readily reduced to the PFe^{IV}POH by one electron by hydrogen abstraction from methanol and the latter is oxidized to formaldehyde [11,20,21].

In acetonitrile FeTM2PyPCl$_5$ 2 presents low activity, despite its good solubility. The *ortho*-methyl groups present some steric protection and the positive charges on the *ortho*-methylpyridyl nitrogens act by withdrawing electrons from the porphyrin ring, making the stabilization of the active ferryl-cationic species difficult if compared to the corresponding *para*-substituent 1 [15,22]. The best catalytic activity was attained with 4 (Table 1), an atropisomer mixture ($\alpha\alpha\beta\beta$, $\alpha\beta\alpha\beta$) with *ortho*-tetradecyl long chain groups and amphiphilic character in homogeneous dich-

loromethane system, despite the presence of positive charges on the *ortho*-substituents. The long alkyl chains can be oriented towards the solvent and the faces are symmetrically protected, however there is an easy access for PhIO and substrate [15].

Ultrasound effect: Our group has optimized homogeneous catalysis using FeP$^+$ and FeP^{5+}, attaining good results with ultrasound stirring [15,23,24]. The yields and selectivities towards cyclohexanol were better with ultrasound stirring for 1, when compared to magnetic stirring (Table 1), indicating that the hydrogen abstraction process is favored. Ultrasound promotes more effective mixture and homogenization of the reactants, favoring the reaction.

3.1.2. Cyclohexene as substrate

Solvent effect. It was discussed in the hydroxylation reactions section that, while on the one hand methanol can act favoring active species formation, on the other hand, competitive reactions lead to deactivation and low yields. However, the cyclohexene epoxidation in catalytic systems containing methanol are very efficient (Table 2). It was reported by Traylor et al. [25,26] that the epoxidation mechanism occurs via a carbocation

Table 2
Oxidation of cyclohexene with CH$_3$PhIO in different solvents, using ironporphyrins as the catalyst in homogeneous systems

Ironporphyrin	Solvent	Yield [a], %			
		Epoxide	Alcohol	Ketone	Total
1 FeTM4PyP(ClO$_4$)$_5$	CH$_3$CN	48	10	14	72
	CH$_3$OH/ CH$_2$Cl$_2$	68	9	20	97
2 FeTM2PyP(ClO4)$_5$	CH$_3$CN	72	11	10	93
3 FeTPPCl	CH$_3$CN	54	17	24	95
	CH$_3$OH/ CH$_2$Cl$_2$	50	7	16	73
	CH$_2$Cl$_2$	47	24	26	97
	CH$_2$Cl$_2$ [b]	55	15	0	70

Conditions: [FeP] $\approx 10^{-4}$ mol·l^{-1}; [CH$_3$PhIO] $\approx 10^{-3}$ mol·l^{-1}; 0°C; stirring for 30 min by ultrasound, under argon atmosphere.
[a] Error average of 2%, based on the starting CH$_3$PhIO.
[b] From [29].
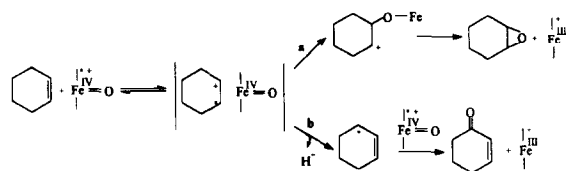
Scheme 1.

formed from electron transfer, followed by hydrocarbon birdcage collapse (Scheme 1a). The polar solvent increases electron transfer rates. This is explained by the better solvation of the alkene radical cation than of the porphyrin radical cation. In methanol containing cyclohexene reactions (Table 2), cyclohexenol yields were relatively lower, probably due to competitive reactions as we have seen before for hydroxylation reactions.

Distribution of products. Traylor and Miksztal [27] proposed two possible competitive mechanisms in order to determine the distribution of the products:

(i) Electron-transfer epoxidation (Scheme 1a), which is favored with electronegative iron(III)porphyrin. The results for cationic polar ironporphyrin show selectivity towards epoxidation like the more electronegative FeP$^+$. This tendency is more pronounced for *ortho*-methylpyridyl substituted FeP^{5+} 2, having acetonitrile as solvent (Table 2). Gunter and Turner [28] explain selectivity towards epoxides when there are meso-*ortho*-substituents in the FeP through a transient valence isomerization of the intermediates: O=Fe^{IV}P$^+$· (Type 2) → O=Fe^{V}P (Type 1). Type 1 would enhance epoxide formation.

(ii) Direct hydrogen atom abstraction, leading to cyclohexenyl radical resulting in allylic alcohol formation (Scheme 2). Our results using FeP^{5+} and FeP$^+$ as catalysts in cyclohexene oxidation always show additional yields of cyclohexenol (Table 2) if compared to the literature results [27,29]. The allylic hydroxylation process probably is favored by ultrasound, as we have discussed for hydroxylation.

The catalytic results presented in this work are more efficient particularly for FeTPPCl. However, they are less selective if compared with those

obtained by Groves [26] (Table 2) in cyclohexene oxidation. Besides allylic alcohol formation, there is additional cyclohexenone formation. With polar FeP^{5+} cyclohexenone yield was also increased (Table 2). The ultrasound effect probably favors this loss of selectivity through a radical formation process. The cyclohexenyl radical, formed rapidly via a single electron-transfer mechanism and proton loss [27], (Scheme 1b) can be oxidized by the Fe^{IV}(O)P$^+$·, affording cyclohexenone. Fontecave and Mansuy [30] suggested that cyclohexyl radical reacts with Mn(V)=O for MnP in the cyclohexane oxidation to cyclohexanone. Cyclohexenone as product in cyclohexene oxidation was almost absent for FeP$^+$ [27,29], the yield becoming higher for more electropositive catalysts, FeP$^+$ < MnP$^+$ < CrP$^+$ [27]. In this way, ultrasound is promoting ketone formation almost like the electropositive metalloporphyrins.

3.2. Supported catalysis

Supported ironporphyrins as catalysts in the cyclohexane hydroxylation present the same selectivity towards cyclohexanol and are more efficient than homogeneous systems (Table 1 and Table 3). Besides the efficiency, selectivity and resistance of the FeP$^+$ to oxidative degradation mentioned before for supported systems, there are additional advantages for polar FeP^{5+}. The optimum reaction conditions with the best yields for cationic FeP^{5+}–IPG and FeP^{5+}–SG systems are shown in Table 3. They are the result of an efficient system because a very low amount of FeP^{5+} (1.0×10^{-7} mol per gram of solid support) is used, and it is about ten times less than that used for the FeP$^+$ systems (1.0×10^{-6} mol per gram of solid support) [6].

The steric hindrance of methyl-2-pyridyl and tetradecyl-2-pyridyl *meso*-substituent in the porphyrin ring in 2 and 4 respectively leads to a
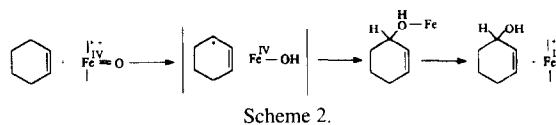
Scheme 2.

Table 3
Yields of cyclohexanol [a] in the hydroxylation of cyclohexane with PhIO using supported ironporphyrins in CH_2Cl_2

	Cyclohexanol yield [a], %	
	IPG [b]	Silica gel
1 FeTM4PyP^{5+}	37 [c]	53
2 FeTM2PyP^{5+}	11	21
4 FeTTD2PyP^{5+}	13	21
3 FeTPP^{+}	22 [d]	5 [d]

Conditions: 3.0×10^{-7} mol of FeP^{5+} per gram of solid support; PhIO: catalyst molar ratio of 30–40:1; magnetic stirring for 1 h, under argon atmosphere.
[a] Error average of 2%, based on the starting PhIO.
[b] 2.2×10^{-3} mol of imidazole per gram of IPG.
[c] 1.0×10^{-7} mol of FeP^{5+} per gram of solid support.
[d] From [6].

decrease in the efficiency when supported on IPG or SG compared to the **1**–IPG or **1**–SG systems.

3.2.1. FeP–IPG systems

The catalytic activity of these polar FeP^{5+} in homogeneous system are limited by solubility, so FeTM4PyP^{5+} **1** is inefficient in dichloromethane, yielding 1% (Table 1). However, with **1**–IPG, the yield is increased to 37% in the same solvent, higher than 22% for (FeTPP)$^{+}$–IPG (Table 3).

3.2.2. FeP–SG systems

Surprisingly, **1**–SG showed the best efficiency, 53% for cyclohexane hydroxylation, in contrast to that presented by (FeTPP)$^{+}$–SG (Table 3), which was only 5%. We have recently reported lower cyclohexanol yield, for (FeTDCPP)$^{+}$–SG and (FeTFPP)$^{+}$–SG 15 and 18% respectively [6]. The cationic FeTM4PyP^{5+} is rigidly supported through the adsorption of peripheral positively charged 4-methyl pyridynium groups on silica gel OH groups and coordination of central iron(III) site to the same kind of silica gel OH group. In this way, in the cationic FeP^{5+}–SG, the porphyrin ring is more planar and the active site is more regularly exposed than in FeP^{+}SG.

3.2.3. Recycling studies

The advantage of the immobilized systems is their easy recovery and usage, which allows recycling. The recycling of **1**–SG was made up to 3

Table 4
Catalytic activity of FeTM4PyP^{5+} **1** on solid support and recycling experiments for cyclohexane hydroxylation

	Cyclohexanol yield [a], %	
	1–IPG [b]	**1**–SG
unused catalyst	37	53
first recycle	29	40
second recycle	8	40
third recycle	4	40

Conditions: 1.0×10^{-7} mol of **1** per gram of IPG; 3.0×10^{-7} mol of **1** per gram of silica gel; PhIO:catalyst molar ratio of 40:1; magnetic stirring for 1 h, under argon atmosphere.
[a] Error average of 2%, based on the starting PhIO.
[b] 2.2×10^{-3} mol of imidazole per gram of IPG.

times, without leaching of FeP^{5+} from silica gel. There is a decrease in its activity from the unused catalyst to the first recycling and then it remains the same until the third recycling. For **1**–IPG, there is a considerable decrease after the first recycling, and in this case leaching occurs and there is bleaching of the brownish colour (Table 4).

4. Conclusions

We observed that in homogeneous system using cationic FeTM4PyP^{5+} **1** as catalyst in the cyclohexane hydroxylation, reaction conditions such as acetonitrile as solvent and ultrasound stirring method increase the efficiency and selectivity towards cyclohexanol. Factors such as methanol, which deactivate the species Fe^{IV}(O)P$^{+\cdot}$ cation radical [11,20] or the ortho-methylpyridyl substituent in the FeP^{5+}, which makes it difficult to stabilize this active species [22], affect the catalysis decreasing the yield of cyclohexanol. However these factors do not affect the very fast epoxidation of cyclohexene. In this way, **1** in the methanol containing system shows high total yields of 97%, with an epoxide:alcohol:ketone selectivity of 70:9:21. FeTM2PyP^{5+} **2** in acetonitrile is a particularly good catalyst, with 93% of total yield, with an epoxide:alcohol:ketone selectivity of 77:12:11. Ultrasound stirring increases the efficiency of cyclohexene oxidation, however

it decreases the selectivity towards epoxidation.

In homogeneous systems, these FeP^{5+} do not catalyze cyclohexane hydroxylation in dichloromethane, except for **4**, which is amphiphilic and inherently is a good P-450 model system [15]. When supported, the polar FeP^{5+}–IPG and FeP^{5+}–SG are particularly efficient in dichloromethane (Table 3). These systems consist of polar hemin in isolated sites, which selectively catalyze cyclohexane oxidation in apolar solvent. In the same way, the active site of P-450 is a polar protohemin in a hydrophobic pocket, which promotes selective cyclohexane oxidation. It represents a good cytochrome P-450 model system [31].

The FeP^+ in homogeneous biomimetic systems requires high concentrations $\approx 10^{-3}$ mol·l^{-1} to promote good catalysis conditions [32]. In this work, with cationic FeP^{5+}, the more diluted $\approx 10^{-4}$ mol·l^{-1} was the best concentration range. These rigid cationic **1–IPG**, **1–SG**, **2–IPG** and **2–SG** systems catalyze oxidations with very low amounts of ironporphyrins (1–3×10^{-7} mol of FeP^{5+} per gram of solid support), which correspond to 30–80 times fewer numbers of heme catalytic sites in P-450, consider, for example, the hemoprotein P450BM-3, a holoenzyme containing one heme per unit (molecular weight of 119,000) [33].

Acknowledgements

References

[1] (a) D. Mansuy, Coord. Chem. Rev., 125 (1993) 129; (b) D. Mansuy, Pure and Appl. Chem., 62 (1990)741.

[2] T.G. Traylor, Pure and Appl. Chem., 63 (1991) 265.

[3] P.S. Traylor, D. Dolphin and T.G. Traylor, J. Chem. Soc., Chem. Commun., (1984) 279.

[4] T.G. Traylor and S. Tsuchiya, Inorg. Chem., 26 (1987) 1338.

[5] B. Meunier, Chem. Rev., 92 (1992) 1411.

[6] Y. Iamamoto, K.J. Ciuffi, H.C. Sacco, C.M.C. Prado, M. Moraes and O.R. Nascimento, J. Mol. Catal., 88 (1994) 167.

[7] P.R. Cooke and J.R. Lindsay-Smith, Tetrahedron Lett., 33 (1992) 2737.

[8] (a) M.N. Carrier, P. Battioni and D. Mansuy, Bull. Soc. Chim. Fr., 130 (1993) 405; (b) P. Battioni, J.P. Lallier, L. Barloy and D. Mansuy, J. Chem. Soc., Chem. Commun., (1989) 1149.

[9] L. Barloy, P. Battioni and D. Mansuy, J. Chem. Soc., Chem. Commun., (1990) 1365.

[10] N. Herron, G.D. Stucky and C.A. Tolman, J. Chem. Soc., Chem. Commun., (1986) 1521.

[11] S. Nakagaki, Y. Iamamoto, O. Baffa and O.R. Nascimento, Inorg. Chim. Acta, 186 (1991) 39.

[12] Y. Iamamoto, M.D. Assis, O. Baffa, S. Nakagaki and O.R. Nascimento, J. Inorg. Biochem., 52 (1993) 191.

[13] D. Mandon, R. Weiss, K. Jayaraj, A. Gold, J. Terner, E. Bill and A.X. Trautwein, Inorg. Chem., 31 (1992) 4404.

[14] J.G. Sharefkin and H. Saltzman, Org. Synth., 43 (1963) 62.

[15] Y. Iamamoto, O.A. Serra and Y.M. Idemori, J. Inorg. Biochem., 54 (1994) 55.

[16] O. Leal, D.L. Anderson, R.G. Bowman, F. Basolo and R.L. Burwell, Jr, J. Am. Chem. Soc., 97 (1975) 5125.

[17] Y. Gushikem and J.C. Moreira, J. Colloid Interface Sci., 107 (1985) 70.

[18] K. Hatano, M.K. Safo, F.A. Walker and W.R. Scheidt, Inorg. Chem., 30 (1991) 1643.

[19] R.J. Cheng, L. Latos-Grazynski and A.L. Balch, Inorg. Chem. 21 (1982) 2412.

[20] A. Gold, K. Jayaraj, P. Doppelt, R. Weiss, G. Chottard, E. Bill, X.-Q. Ding and A.X. Trautwein, J. Am. Chem. Soc., 110 (1988) 5756.

[21] D.R. Leanord, J.R. Lindsay-Smith, J. Chem. Soc. Perkin Trans. II, (1991) 25.

[22] S.E.J. Bell, P.R. Cooke, P. Inchley, D.R. Leanord, J.R. Lindsay Smith and A. Robbins, J. Chem. Soc. Perkin Trans., 2 (1991) 459.

[23] M.D. Assis, Ph.D. Thesis, Universidade de São Paulo, Brazil (1988).

[24] S. Nakagaki, Ph.D. Thesis, Instituto de Quimica, UNESP, Brazil (1993).

[25] T.G. Traylor, Y. Iamamoto and T. Nakano, J. Am. Chem. Soc., 108 (1986) 3529.

[26] T.G. Traylor, T. Nakano, B.E. Dunlap, P.S. Traylor and D. Dolphin, J. Am. Chem. Soc., 108 (1986) 2782.

[27] T.G. Traylor and A.R. Miksztal, J. Am. Chem. Soc., 111 (1989) 7443.

[28] M.J. Gunter and P. Turner, J. Mol. Catal., 66 (1991) 121

[29] (a) J.T. Groves, T.E. Nemo and R.S. Myers, J. Am. Chem. Soc., 101 (1979) 1032; (b) J.T. Groves and W.J. Kruper, Jr., J. Am. Chem. Soc., 101 (1979) 7613.

[30] M. Fontecave and D. Mansuy, Tetrahedron, 40 (1984) 4297.

[31] J.H. Dawson, Science, 240 (1988) 433.

[32] M.J. Nappa and C.A. Tolman, Inorg. Chem., 24 (1985) 4711.

[33] K.G. Ravichandran, S.S. Boddupalli, C.A. Hasemann, J.A. Peterson, J. Deisenhofer, Science, 261 (1993) 731.