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Catalytic olefin epoxidations with $KHSO_5$: the first report on manganese hemiporphyrazines as catalysts in oxygenation reactions

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Abstract

The oxidation of cyclooctene to cyclooctene epoxide by Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) as probe for evaluating the catalytic activity of a few manganese hemiporphyrazines has been studied. The oxidations have been carried out in an anhydrous two-phase system (solid Oxone®/solid catalyst/1,2-dichloroethane solution). In the absence of manganese hemiporphyrazine and/or of an aromatic nitrogen base only the slow stoichiometric epoxidation by $KHSO_5$ is observed. On the contrary, in the presence of pyridine and catalytic amount of manganese hemiporphyrazine (0.13–1% with respect to the organic substrate) either suspended in the reaction medium or adsorbed on a suitable polymer (silica gel or poly(vinylpyridine)) enhanced reaction rates are observed. The presence of an axial ligand in the coordination sphere of the catalyst appears to be essential for promoting the catalytic activity of the manganese complex. Moreover, the manganese hemiporphyrazine was subject to a colour change upon addition of the oxidant, thus suggesting the formation of a high valency oxo intermediate that oxidizes the olefin in a successive step. Under the experimental conditions adopted, epoxide yields up to 86% are obtained.

Keywords: Oxidation; Peroxomonosulfate; Manganese; Hemiporphyrazine

1. Introduction

Iron and manganese complexes of porphyrin macrocycles are widely used as chemical models of the active site of cytochrome P-450 enzymes [1–6]. In fact, these complexes, in association with an appropriate oxygen donor, may mimic several oxidative transformations carried out by the enzymes of the cytochrome P-450 family, such as hydroxylation [7–9] and epoxidation [9–14]. The porphyrin ring plays a relevant role in the formation of an oxo ipervalent iron or manganese derivative that is the intermediate responsible for the electrophilic oxygen transfer to the substrate. There is a number of other macrocycles derived from porphyrin ring, which could exhibit features similar to those of porphyrins (Fig. 1). In particular, a few macrocycles that can be considered as being derived from porphyrin by the following modifications: (i) substitution of the pyrrole rings by pyridine;

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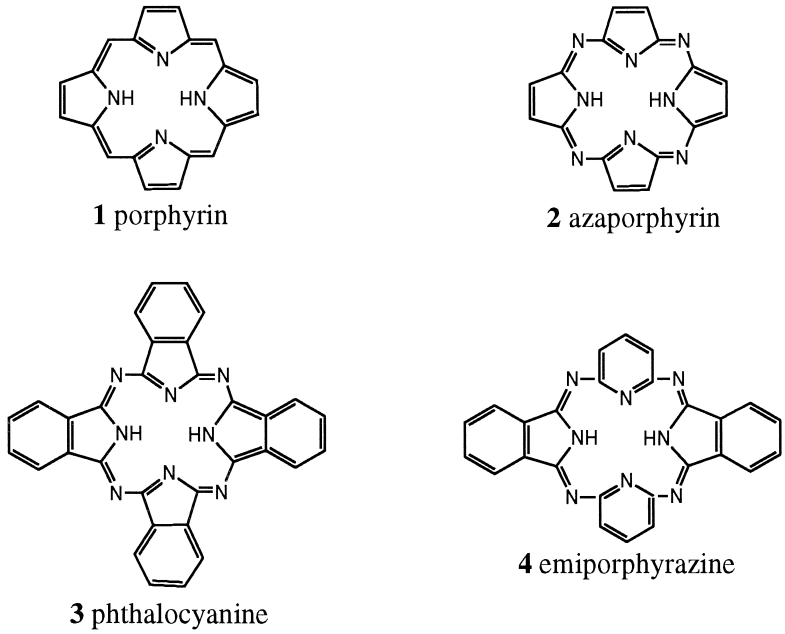


Fig. 1. Porphyrin and some related macrocycles.

(ii) substitution of the meso methine groups by nitrogen atoms; (iii) substitution of the pyrrole rings by isoindole. These modifications produce a family of eight macrocycles whose best known members are, besides porphyrin (**1**), azaporphyrin (**2**), phthalocyanine (**3**), and hemiporphyrazine (**4**).

The porphyrin macrocycle is the only member of this family found in biological systems promoting relevant biochemical processes [15]. However, this peculiarity could be the result of some special requirements of biomolecular evolution and does not exclude that other members of the extended family were even better qualified for catalyzing the same reactions. Very recently indeed, the efficiency of iron and cobalt tetraazaporphyrins and phthalocyanines in catalyzing alkane oxidation by cumene hydroperoxide has been established [16,17]. Moreover, manganese azaporphyrins were shown to catalyze the stereoselective epoxidation of olefins by peracetic acid [18]. Hemiporphyrazine (hpH_2), synthesized for the first time by Linstead more than 40 years ago [19], is a highly conjugated tetraazamacrocyclic ligand with a number of features in common with the much popular porphyrin (pH_2) and phthalocyanine (pcH_2). Likewise porphyrin, hemiporphyrazine easily forms derivatives with metals of the first row, such as Mn, Fe, Co, Ni, Cu, and Zn [20–23]. Furthermore, these metal complexes easily coordinate axial ligands [22–25] and, in the case of protic molecules, the adducts are strongly stabilized by proton ligand interactions with partial dissociation of the coordinated molecules. The ability to fill the axial positions of the coordinated metal appears to be greater with respect to porphyrins, and it depends on a minor extent on the metal nature. A further remarkable analogy with iron porphyrins is the possibility to oxidize the metal center forming a metal 'oxo' functionality [26,27]. This feature is particularly important because the formation of a labile metal–oxygen bond is often an essential requisite in transition metal mediated oxidations. The first μ-oxo compound of a hemiporphyrazine iron complex isolated $[hpOFe]_n$, was prepared by treating hemiporphyrazine with iron (II) acetate in boiling nitrobenzene [26]. The compound shows a polymeric structure in which

the iron is designated as Fe(IV), $S = 1$. Under these conditions nitrobenzene was reported to behave as an oxidizing agent since $[hpOFe]_n$ was also obtained when the reaction was carried out in an inert atmosphere. Subsequently, the same species was also obtained by oxidizing Fe(II) hemiporphyrazine with gaseous O_2 in γ-picoline solution at room temperature [27]. In particular, anhydrous conditions led to the polymeric μ-oxo compound whereas, in the presence of water traces, a dimeric μ-oxo derivative was obtained in which the iron is a high-spin Fe(III). Interestingly, both μ-oxo derivatives were reduced to the native Fe(II) structure by reaction with Ph_3P suggesting that an oxygen transfer occurred, even though Ph_3PO could not be detected. Unlike hpFe, hpMn is O_2 stable both in solid state and in solution. Besides these features, which formally resemble the behaviour of porphyrins, hemiporphyrazines exhibit also remarkable differences. As an example, the aromatic character of hemiporphyrazine ring is much lower than that of porphyrins or even phthalocyanines because of a delocalization pathway of 20 electrons (against 18 of porphyrins) and of the strong inequivalence of the two pairs of inner nitrogens [28,29]. Furthermore, in striking contrast to the behaviour of the related porphyrins and phthalocyanines, typical high-spin magnetic moments were found for hpCo and hpMn [30–32].

Recently, hemiporphyrazines have received renewed attention as building blocks of supramolecular architectures. Oligomers with ladder-type structures derived from nickel hemiporphyrazine and pentaene [33,34], and adducts with [6O]fullerene have been synthesized [35]. Germanium hemiporphyrazines [36] and complexes of triazolhemiporphyrazines with nickel, cobalt, and copper [37,38] have been used as monomers for the synthesis of rod-like macromolecules, which may be exploited in the preparation of monomolecular layer films by the Langmuir–Blodgett technique.

To our knowledge, there are no data available concerning oxygenations promoted by metal hemiporphyrazines. In this paper, we present the results of a study that reveals the ability of manganese emiporphyrazines to act as catalysts in oxygenation reactions. The activity as catalyst of such manganese complexes comes out entirely only when a nitrogen aromatic base is present, thus connoting a further analogy with the behaviour of manganese porphyrins [39–42].

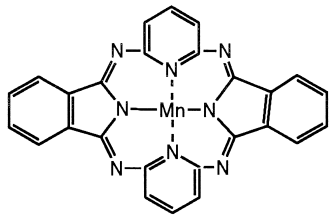
2. Results and discussion

The oxidation of cyclooctene with potassium monopersulfate (used as triple salt, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) in the presence of manganese hemiporphyrazines **5–7** shown in Fig. 2, in 1,2-dichloroethane (DCE) at 25°C has been studied.

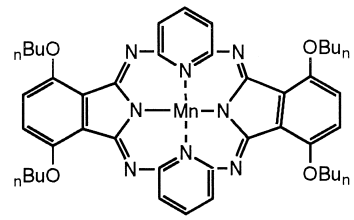
The amount of catalyst normally employed in our experiments (~4 mg in 5 ml DCE) is present mainly as suspended particles. Only compound **6** exhibits a sparingly solubility in DCE as revealed by the pale green-brownish colour assumed by the solutions. Therefore, this oxidizing system has a definite heterogeneous nature being both oxidant and catalyst insoluble in the reaction medium. The course of the reaction was monitored by measuring the epoxide concentration against time by GLC analysis. Table 1 collects a series of data indicating the relative ability of manganese complexes **5**–**7** in catalyzing cyclooctene oxidation.

Control experiment (run 1) shows that a slow, non catalytic reaction leading to cyclooctene oxide is occurring between cyclooctene and $KHSO_5$. Epoxide concentration increases linearly with time thus indicating a zero kinetic order in oxidant (see Fig. 3, ▲).

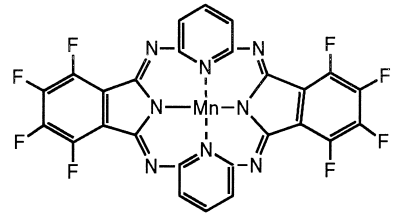
This outcome likely relates with the heterogeneous nature of the system in which the area of the oxidant in contact with the solution may be considered roughly constant. Experiments 2, 4, and 6 of Table 1 indicate that the three manganese hemiporphyrazines examined do not exhibit any catalytic activity in the absence of a nitrogen base. In fact, although the profile of



5 hpMn



6 $(OBu_n)_4$hpMn



7 F_8hpMn

Fig. 2. Manganese hemiporphyrazines utilized in this study.

product appearance differs from that of the control experiment (see Fig. 3, ■), the epoxide yields become comparable at prolonged reaction times. The kinetic profile of the reaction changes when pyridine is added to the reaction mixtures. In fact, in the presence of the nitrogen base, likely acting as axial ligand of the manganese hemiporphyrazines, a burst in the cyclooctene oxide formation is observed (see Fig. 3, ●). In these reactions, the same amount of oxidant employed in the control experiment (0.8 mmol) yields to 25–30% epoxide in 10–30 h. Moreover, the addition of further oxidant aliquots leads again to the formation of epoxide although at lower rates (see Fig. 3, ●). When pyridine is present in a 10-fold excess with respect to cyclooctene, the system stands the addition of three oxidant aliquots leading to total epoxide yields ranging from 68% to 86% (runs 3, 5, and 7). It is noteworthy that, by adding the oxidant

Table 1
Oxidation of cyclooctene (0.8 mmol) by adding various aliquots of $KHSO_5$ (0.8 mmol each), in the presence of various manganese hemiporphyrazines (8.0 μmol), pyridine, in 5 ml DCE, at 25°C

Run	Catalyst	Pyridine (mmol)	$KHSO_5$ total (mmol)	Cyclooctene oxide yield[b] (%)	Reaction time (h)
1	–	–	0.8	78	413
2	$(OBu)_4$ hpMn	–	0.8	66	413
3	$(OBu)_4$ hpMn	8.0	3.2[a]	86	211[c]
4	hpMn	–	0.8	70	406
5	hpMn	8.0	3.2[a]	70	90[c]
6	F_8hpMn	–	0.8	72	410
7	F_8hpMn	8.0	3.2[a]	68	63[c]

[a] The oxidant was added in three separate aliquots of 0.8 mmol each.
[b] Cyclooctene oxide yields are calculated on the initial amount of cyclooctene.
[c] Reaction time does not include the plateau intervals where reaction stops because of oxidant exhaustion.

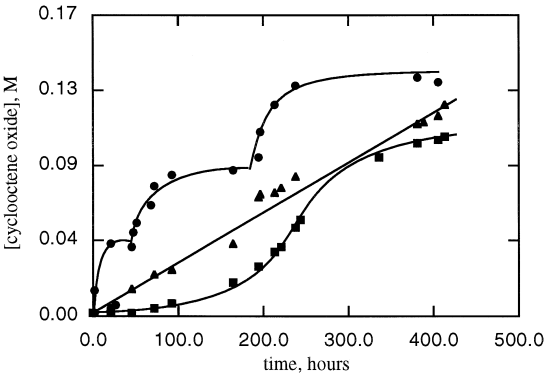


Fig. 3. Dependence of cyclooctene oxide concentration vs. time in experiments 1 (▲), 2 (■), and 3 (●) of Table 1.

to the mixture of catalyst and pyridine, the manganese complexes are subjected to a colour change from green-brownish to orange, thus suggesting a variation in the oxidation state of the metal. This observation may be taken as an indication that pyridine coordination to manganese makes the metal prone to oxidation by monopersulfate and promotes the formation of an 'oxo' manganese hemiporphyrazine intermediate. This species then oxidizes the olefin more efficiently than monopersulfate itself does. Data of Table 1 also provide useful hints on the role played by the macrocycle ligand on the reactivity of such 'oxo' manganese emiporphyrazine derivative. The catalytic activity order observed is F_8hpMn > hpMn > $(OBu)_4$hpMn, thus indicating that the presence of electron withdrawing substituents on the macrocycle periphery makes the 'oxo' functionality a better oxidant. The effect of the reagent ratio on the yields of the product has also been briefly investigated. The pertinent results are listed in Table 2.

In these experiments the amount of oxidant exploited was added at the beginning of the reaction in a single aliquot. Note that under these conditions the reaction times are remarkably shorter than those of experiments reported in Table 1. When cyclooctene and pyridine are present in equal amount with an excess of oxidant (run 8), a 31% epoxide yield in only 5 h is obtained. This reaction probably stops because of free pyridine exhaustion and of the consequent catalyst activity drop-out. Accordingly, when a 10-fold excess of pyridine respect with cyclooctene is used (run 9), epoxide yield increases as consequence of the prolonged time of catalyst activity. In this case the reaction stops because of oxidant exhaustion. The amount of epoxide formed rises also by increasing the substrate/pyridine ratio maintaining the catalyst and oxidant concentrations constant (runs 9–11). However, under these conditions, the epoxide yields calculated on the initial amount of cyclooctene decrease since oxidant becomes the defecting reagent. Epoxide production does not increase further even by increasing the amount of the catalyst (runs 12 and 13) presumably because all the processes involved are accelerated, including side reactions as pyridine oxidation and monopersulfate decomposition. The outcome of these experiments is that pyridine, although essential, does represent a limiting factor of the oxidizing system because its competi-

Table 2
Oxidation of cyclooctene by $KHSO_5$ (3.2 mmol) catalyzed by hpMn in the presence of pyridine, in 5 ml DCE at 25°C

Run	Cyclooctene (mmol)	Pyridine (mmol)	hpMn (μmol)	Cyclooctene oxide (mmol)	Yield[a] (%)	Reaction time (h)
8	0.8	0.8	8.0	0.25	31	5
9	0.8	8.0	8.0	0.33	42	9
10	1.6	8.0	8.0	0.69	46	14
11	3.2	8.0	8.0	0.95	31	14
12	1.6	8.0	16.0	0.52	33	12
13	1.6	16.0	16.0	0.43	28	9

[a]Cyclooctene oxide yields are calculated on the initial amount of cyclooctene.

tive oxidation is always occurring and subtracts oxidant to the epoxidation process. Thus, given the crucial role played by the nitrogen ligand, the study of the effect of other bases than pyridine on the system efficiency has been performed. The results obtained are collected in Table 3.

In spite of the fact that preliminary results reported in Tables 1 and 2 showed that pyridine oxidation led to loss of catalyst activity, we decided to examine the effect of pyridine *N*-oxide on the cyclooctene catalyzed epoxidation. The reason of this attempt was originated by the possibility that pyridine-*N*-oxide resistance to oxidation could counterbalance its moderate ability in activating the manganese complex. Unfortunately, the basicity of this oxygenated ligand revealed to be insufficient to activate the catalyst (run 14). Similar unsatisfactory results were obtained with *N*-methylimidazole and trioctylamine whose higher basicity respect with *N*-oxides suggested a potential strong coordinative effect on the catalyst (runs 15 and 16). Apparently, the fast degradation of these nitrogen ligands accounts for the lack of catalyst activity. On the contrary, pyridine and alkyl substituted pyridines revealed to be an acceptable arrangement between manganese coordinating ability and resistance to oxidative conditions (runs 17–19). In fact, these nitrogen ligands survive long enough to allow that the activity of manganese emiporphyrazine in catalyzing cyclooctene epoxidation emerges. Moreover, the electronic effects of alkyl substituents on nitrogen basicity and consequently on ligand coordinating ability appear to prevail against the steric effects (runs 17–19).

Since cyclooctene shows a peculiar high reactivity toward oxidizing systems based on manganese porphyrin catalyst, we checked if this was the case also for manganese hemiporphyrazine [43]. The results obtained in the oxidation of three common alkenes are shown in Table 4.

Experiments 20, 22, and 24 confirm once more that in the absence of an aromatic nitrogen base no catalysis by manganese hemiporphyrazine is taking place. In the presence of the base acting as axial ligand, an enhanced epoxide production for all substrates is observed (runs 21, 23, and 25). Furthermore, styrene and cyclohexene were much more reactive than cyclooctene. The observation that cyclohexene and styrene epoxides are not stable under the conditions adopted and decompose with reaction time accounts for the discrepancy between substrate conversions and epoxide yields.

In the attempt to increase the catalyst performances we prepared two supported manganese hemiporphyrazine catalysts. From a general point of view the following advantages can be listed in favour of the use of supported catalysts: (i) an easy catalyst recovery; (ii) a physical separation of active sites by dispersion on

Table 3
Oxidation of cyclooctene (1.6 mmol) by $KHSO_5$ (3.2 mmol) catalyzed by hpMn (8.0 μmol) in the presence of various bases (8.0 mmol), in 5 ml DCE at 25°C

Run	Base	Cyclooctene oxide yield[a] (%)	Reaction time (h)
14	pyridine-*N*-oxide	17	50
15	*N*-methylimidazole	4	24
16	trioctylamine	7	48
17	pyridine	46	14
18	4-*tert*-butylpyridine	51	8
19	2,4,6-trimethylpyridine	60	16

[a]Cyclooctene oxide yields are calculated on the initial amount of cyclooctene.

Table 4
Oxidation of various alkenes (1.6 mmol) by $KHSO_5$ (3.2 mmol) catalyzed by hpMn (8.0 μmol) in the presence of 4-*tert*-butylpyridine (8.0 mmol), in 5 ml DCE at 25°C

Run	Substrate	Substrate conversion (%)	Epoxide yield[a] (%)	Reaction time (h)
20	cyclooctene	–	1.6	8.0
21	cyclooctene	–	51.0	8.0
22	cyclohexene	38	7.0	4.5
23	cyclohexene	93	51.0	0.75
24	styrene	13	7.0	30
25	styrene	100	61.0	0.50

[a]Cyclooctene oxide yields are calculated on the initial amount of olefin.

the support; and (iii) the possibility to modulate the selectivity of the oxygenation reaction by acting on the support nature. The main drawback of supported catalysts insoluble in the reaction media, i.e., a reduced activity respect with the soluble form because of mass transfer limitations, in our case should not be critical. In fact, we are comparing in both circumstances two heterogeneous catalysts; the former is represented by a suspension of the manganese complex itself and the latter by a suspension of the manganese complex adsorbed on the support. We examined two different supports, namely silica gel and a poly(vinylpyridine) polymer (PVP). The results obtained in the cyclooctene epoxidation promoted by these catalysts are summarized in Table 5.

The experiments of entries 26–28, graphically shown in Fig. 4, attest that the support itself induces a catalytic activity in manganese hemiporphyrazine even in the absence of a nitrogen base.

In fact, after an induction period of ca. 20 h, the reactions performed in the presence of both supported catalysts become significantly faster than the control experiment (see Fig. 4, ●, ■, □). A plausible rationale of this behaviour is that some kind of coordination to manganese complex is provided by the support. In particular, one may conceive that silanolic groups in silica and pyridine residues on the external surface of PVP offer the necessary axial ligands to the metal complex. In these reactions high epoxide yields are obtained ($> 80\%$), because of the lack of any competitive reactions other than a potential catalytic decomposition of the oxidant.

Again, the addition of pyridine to the reaction mixtures induces a ca. 100-fold acceleration in cyclooctene oxidation (entries 29 and 30; see Fig. 4, ▲, △). On the other hand, in these

Table 5
Oxidation of cyclooctene (0.8 mmol) by $KHSO_5$ (3.2 mmol) catalyzed by hpMn (8.0 μmol) adsorbed on silica gel or poly(vinylpyridine) (PVP) in the presence of pyridine, in 5 ml DCE at 25°C

Run	Catalyst	Pyridine (mmol)	Cyclooctene oxide yield[a] (%)	Reaction time (h)
26	–	–	26	165
27	hpMn/silica	–	84	145
28	hpMn/PVP	–	83	145
29	hpMn/silica	8.0	35	2.0
30	hpMn/PVP	8.0	56	2.0

[a]Cyclooctene oxide yields are calculated on the initial amount of cyclooctene.

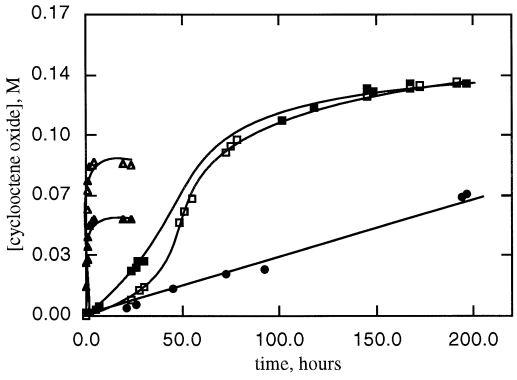


Fig. 4. Dependence of cyclooctene oxide concentration vs. time in experiments 26 (●), 27 (■), 28 (□), 29 (▲), and 30 (△) of Table 5.

reactions epoxide yields decrease to 35–50% because of the competitive pyridine oxidation. We checked the stability of these supported catalysts by reloading the reaction mixtures with cyclooctene, pyridine and monopersulfate: epoxide production resumed with the same rate thus indicating no loss of catalyst activity. However, only a limited number of oxidant charges can be accomplished because of the formation of slurry mixtures that are difficult to analyze.

Finally, it may be underlined that these manganese emiporphyrazine catalysts show efficiencies in epoxidation comparable with those of some of the most efficient supported metalloporphyrin catalysts [44].

3. Conclusions

We have established for the first time the effectiveness of manganese hemiporphyrazine complexes as catalyst in olefin epoxidation by monopersulfate. The catalytic activity of such compounds emerges completely when an aromatic nitrogen base is acting as axial ligand of the manganese complex. On the other hand, adsorption of the manganese hemiporphyrazine on a suitable support leads to a catalyst that exhibits a detectable activity also in the absence of nitrogen bases. Although reaction rates with supported catalysts were rather low, higher epoxide yields were obtained as a consequence of the minor number of side reactions involving the oxidant. On the basis of these preliminary results, a catalyst based on manganese emiporphyrazine complex exhibiting both high activity and product yields, appears accessible. The development of new supports with higher pyridine residue/gram resin ratios and the improvement of complex deposition technique may facilitate the achievement of this goal. To this aim, further work is now in progress in our laboratory.

4. Experimental section

4.1. Solvents and reagents

1,2-Dichloroethane (DCE) was purified by treatment with 3–4 aliquots of 96% sulfuric acid (100 ml each for 1 l DCE) in order to eliminate oxidizable contaminants, and following distillation over P_2O_5. A.C.S. Spectrophotometric grade *N*,*N*′-dimethylformamide (DMF, 99.8%) from Aldrich was used without further purification as solvent for hemiporphyrazine metallation.

The free hemiporphyrazine ligands (hpH_2, F_8hpH_2, $(n\text{BuO})_4hpH_2$) were synthesized following a slightly modified Campbell method starting from 2,6-diaminopyridine and the appropriate substituted phthalonitrile [45,28].

The manganese complexes of hemiporphyrazines were prepared by treating the free ligands (1.82 mmol) with an excess of manganese(II) diacetate tetrahydrate (18.0 mmol) in 50 ml of DMF. The reaction mixtures were refluxed for 1 h. The products were collected as a dark green solid by filtration, washed with water and acetone, and vacuum dried (yields ranging from 55 to 80%). Anal. Calculated for $MnHp(H_2O)$, $C_{26}H_{16}N_8OMn$: C, 61.07; H, 3.15; N, 21.91. Found: C, 59.79; H, 2.93; N, 21.71.

Oxone®, pyridine, 4-*tert*-butylpyridine, 1,2-dibromobenzene and *n*-tridecane (GLC internal standards), cyclooctene, cyclohexene, styrene,

cyclooctene oxide, cyclohexene oxide, styrene oxide, were all commercially available, high purity products (Aldrich) and used as received. 4-Vinylpyridinium-toluene-4-sulfonate cross-linked with 2% of divinylbenzene was purchased from Fluka.

4.2. Preparation of manganese hemiporphyrazine complex supported on silica gel and poly(vinylpyridine) (PVP)

First, free poly(vinylpyridine) was obtained by treating 3.0 g of poly(4-vinylpyridinium-toluene-4-sulfonate) cross-linked with 2% of divinylbenzene (Fluka, 3.5 mmol of toluene-4-sulfonate/g of resin) with 50 ml of a 0.5 M NaOH solution for 30 min. After filtration, the polymer was washed with water until neutral pH and then with acetone and finally dried under vacuum. A total of 1.2 g of PVP was recovered.

A 200-mg sample of free PVP or silica gel (70–230 mesh ASTM, 0.063–0.2 mm) was added to a suspension of 20 mg of hpMn in 20 ml of methanol. After 24 h of gentle magnetic stirring, the solvent was eliminated by evaporation and the solid residue was washed with 100 ml of acetone and dried under vacuum. Aliquots of 40 mg of these supported catalysts, each containing 4 mg of manganese hemiporphyrazine (8.0 μmol), were used in catalytic oxidations.

4.3. Oxidation procedures and product analysis

Typically, the reactions were initiated by suspending under magnetic stirring 0.96 g of Oxone® (3.2 mmol of $KHSO_5$) in a DCE solution containing the olefin (1.6 mmol), the nitrogen base acting as axial ligand of the catalyst (8.0 mmol), an appropriate GLC internal standard (0.8 mmol), and a suspension of manganese hemiporphyrazine (8.0 μmol) in a jacketed reactor thermostated at 25°C. At various time intervals, the stirring was suspended and 100 μl of the supernatant solution were withdrawn, quenched with an equivalent volume of a 1.0 M solution of PPh_3 in DCE and analyzed by GL-chromatography on a 10% Carbowax 20 M stationary phase adsorbed on Chromosorb WAW-DMCS (1.8 m packed column). The concentration of the oxygenation products was measured on the basis of previously determined response factors.

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