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Reactivity studies of biomimetic catalytic epoxidation of alkenes with tetrabutylammonium periodate in the presence of various manganese porphyrins and nitrogen donors: significant axial ligand π-bonding effects

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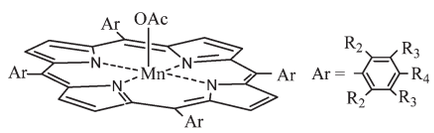
Highly selective epoxidation (> 95%) of unfunctionalized alkenes was performed by tetrabutylammonium periodate in the presence of six different phenyl substituted manganese(III) *meso*-tetraphenylporphyrins [Mn(Por)] and imidazole in CH_2Cl_2. Electron-withdrawing and bulky substituents on the phenyl groups lowered the catalytic activities of the corresponding Mn(Por). Less bulky alkenes with electron -rich double bonds showed greater reactivity in the epoxidation. Co-catalytic activities of four different classes of axial nitrogen donors are compared in the presence of various Mn(Por). In general no direct correlation was found between co-catalytic activities and the pK_a values of the nitrogen donors. Strong σ-donor amines (pK_a = 10.6 to 11.123) and weak π-donor pyridines (pK_a = 5.25 to 6.65) showed comparable co-catalytic activities. Strong π-donor aminopyridines (pK_a = 7 to 9.71) and imidazoles (pK_a = 6.95 to 7.86) are generally much better co-catalysts than pure σ-donors, suggesting the importance of π-bonding interactions of the nitrogenous donors. N–H imidazoles with the possibility for N–H···B hydrogen bonding are much more effective co-catalysts than 1-methylimidazole. Methylpyridines and aminopyridines with substituents at the 2 or 2,6 positions showed particularly high co-catalytic activities toward manganese(III) *meso*-tetrakis(pentafluorophenylporphyrin) acetate. This "unusual" observation suggests the occurrence of some attractive hydrogen bonding interactions between *ortho*-fluorines of the manganese porphyrin and the substituents of these donors. A simple qualitative molecular orbital diagram is presented to describe the possible π-interactions of (d_{xz}, d_{yz}) metal orbitals with axially coordinated ImH and periodate in six-coordinate Mn(Por)(ImH)(IO_4), as the active oxidizing species. A catalytic cycle is postulated in which the intermediate involves complexation of an alkene to the coordinated periodate, and attempts have been made to visualize the orbital interactions for this intermediate species.

Introduction

Synthetic manganese and iron porphyrins have long been of great interest because of their potential as functional models of cytochrome P-450 and peroxidases.[1] It has been shown that the steric and electronic properties of metalloporphyrins and alkenes substantially affect the product distribution, selectivity and the rate of the oxygenation.[2] The employment of nitrogenous donors in metalloporphyrin systems for mimicking the oxygenation function of P-450 has led to marked improvements in selectivities and turnover rates in the epoxidation of alkenes.[3]

In this work epoxidation of different alkenes by tetrabutylammonium periodate (*n*-Bu_4NIO_4) in the presence of phenyl substituted manganese(III) *meso*-tetraphenylporphyrin catalysts (Fig. 1) was studied. Particular focus was placed on exploring the co-catalytic effects of various classes of nitrogen donors. The key role played by the steric effects of all the species involved in the epoxidation is described. It is also demonstrated that Mn(Por) catalysts with high electron density on their phenyl groups, electron-rich alkenes and π-donor ligands, especially imidazoles (ImH) with hydrogen bonding ability, dramatically increase the overall rate of epoxidation. The "unusual" co-catalytic activities of 2,6-dimethylpyridine and 2,6-diaminopyridine observed only in the presence of Mn(TPFPP)OAc, for the first time, is suggestive of intermolecular hydrogen bonding between *ortho*-C–F groups of Mn(Por) and the 2,6-substituents of the pyridines. A simple molecular orbital scheme is presented as an attempt to clarify features of the possible π-interactions that may be operative along the unique molecular axis containing the axial ligands in six-coordinate Mn(Por)(ImH)(IO_4). Based on our experimental results a mechanism is proposed for the epoxidation.



	R_2	R_3	R_4
Mn(TPP)OAc	H	H	H
Mn(TMP)OAc	CH_3	H	CH_3
Mn(TDCPP)OAc	Cl	H	H
Mn(TPFPP)OAc	F	F	F
Mn[T(4-OCH_3P)P]OAc	H	H	OCH_3
Mn[T(4-NO_2P)P]OAc	H	H	NO_2

Fig. 1 Manganese(III) *meso*-tetraphenylporphyrin catalysts used in this work.

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Results and discussion

Catalytic alkene epoxidation by Mn(Por)/ImH/*n*-Bu_4NIO_4 systems

Epoxidation of various alkenes by *n*-Bu_4NIO_4 in the presence of different Mn(Por) and ImH proceeded quantitatively in CH_2Cl_2. The only exception was oxidation of α-methylstyrene with Mn(TMP)OAc and Mn(TPFPP)OAc catalysts, where ~5% acetophenone by-product was obtained (Table 1). The electron-rich dialkylsubstituted *cis*-2-hexene displayed a much greater reactivity than 1-octene with all the catalysts. Also, it was observed that α-methylstyrene was more reactive than the less electron-rich styrene in the presence of Mn(TPP)OAc, and Mn(TPFPP)OAc. However, when the bulky Mn(TMP)-OAc was used the steric factors clearly became dominant and styrene displayed a greater reactivity than the hindered α-methylstyrene. It appears that the steric and electronic factors are balanced for Mn(TDCPP)OAc with which styrene and α-methylstyrene show similar reactivities. The greater reactivity of cyclohexene than the electron-rich and sterically hindered 1-methycyclohexene, with all the Mn(Por), again demonstrates the importance of steric effects in the alkenes. The higher reactivity of cyclooctene relative to cyclohexene might be due to the greater flexibility of the former. In the epoxidation of *cis*- and *trans*-stilbenes the steric effects are particularly quite distinct. The sterically demanding *trans*-stilbene is much less reactive than the *cis* isomer and its oxidation gives only *trans*-stilbene oxide with all the catalysts. Similarly, oxidation of *cis*-stilbene in the presence of bulky Mn(TMP)OAc and Mn(TDCPP)OAc is 100% stereoselective and leads to formation of the *cis* isomer as the sole product. In contrast the oxygenation of *cis*-stilbene with less hindered catalysts [*i.e.*, Mn(TPP)OAc and Mn(TPFPP)OAc] results in a mixture of *cis* and *trans* isomers. Apparently, formation of the thermodynamically more stable *trans*-stilbene oxide requires a free rotation about the alkene C–C bond at some intermediate step;[4] such a rotation is expected to be more feasible using catalysts with less steric strain, as observed.

Electronic effects of Mn(Por)

The much longer reaction times required for the Mn(TDCPP)OAc and Mn(TPFPP)OAc catalysts compared to Mn(TPP)OAc and Mn(TMP)OAc (24 h *vs.* 4 h for the former) definitely reflect the negative effects of electron-withdrawing substituents on the phenyl groups upon their catalytic activities (Table 1). Comparison of the catalytic properties of three different *para*-substituted Mn(Por) in the epoxidation of styrene and α-methylstyrene, provides additional evidence for this viewpoint (Table 2). Presuming that these Mn(Por) have very similar steric environments at their Mn centers, it may be concluded that the lower activity of Mn[T(4-NO_2P)-P]OAc is due to the presence of the electron-withdrawing NO_2 substituent. On the other hand, the higher catalytic activity of Mn[T(4-OCH_3P)P]OAc compared to Mn(TPP)OAc is presumably caused by the π-resonance effects of its *p*-OCH_3 groups.

Co-catalytic effects of nitrogen donors

To better understand the role of nitrogenous bases in activating Mn(Por) catalysts, we investigated the co-catalytic effects of four classes of nitrogen donors with different stereoelectronic properties. The influence of such ligands in improving Mn(Por)-mediated epoxidation is especially high.[3d,5] A drawback to the study of nitrogenous axial ligand effects is their oxidation. Pyridine can be oxidized by Mn(Por) catalytic systems containing iodosylbenzene (PhIO),[6] potassium monopersulfate ($KHSO_5$)[7] and (ClO^-).[8] In the present Mn(Por)/*n*-Bu_4NIO_4 epoxidation systems pyridines and imidazole are essentially robust. It is assumed that the epoxidation yields (%) or the turnover numbers (TON) for the oxygenation of cyclooctene are directly related to the co-catalytic activities of the nitrogen donors, since in the absence of such donors virtually no epoxidation occurred (Table 3).

Amines. Pure σ-donor amines, with very large pK_a values, are relatively poor co-catalysts in the epoxidation of cyclooctene (Table 3). Within this group, it appears that steric properties rather than pK_a values are the dominant factor in determining their co-catalytic activities. However, the least steric σ-donor, piperidine, with the highest pK_a value, shows the greatest co-catalytic activity with all the Mn(Por) catalysts. Quinuclidine, which is less sterically hindered and a weaker base than Et_2NH and Et_3N, is in the second place in the series. However, the importance of the size of these σ-donors becomes more pronounced when their relative activities are examined in the presence of the sterically demanding Mn(TMP)OAc and Mn(TDCPP)OAc catalysts. Et_3N shows very little or no ability to promote the catalytic activities of the bulky Mn(Por).[9]

Pyridines. Pyridine and methyl-substituted pyridines with weak π-donating ability[10] and pK_a values much smaller than

Table 1 Epoxidation of alkenes with Mn(Por)/ImH/*n*-Bu_4NIO_4 catalytic systems[a]

	% Conversion[b] (TON[c])			
Substrate	Mn(TPP)OAc (4 h)	Mn(TMP)OAc (4 h)	Mn(TDCPP)OAc (24 h)	Mn(TPFPP)OAc (24 h)
cis-2-Hexene	58 (48.3)	16 (13.3)	37 (30.8)	26 (21.6)
1-Octene	14 (11.7)	8 (6.7)	21 (17.5)	18 (15.0)
α-Methylstyrene	80 (66.6)	51[d] (42.5)	59 (49.1)	51[d] (42.5)
Styrene	66 (55)	58 (48.3)	57 (47.5)	45 (37.5)
Cyclohexene	78 (65.0)	40 (33.3)	46 (38.3)	29 (24.1)
1-Methylcyclohexene	62 (51.6)	22 (18.3)	25 (20.8)	21 (17.5)
Cyclooctene	92 (77.0)	48 (40.0)	60 (50.0)	47 (39.1)
cis-Stilbene	50 (41.7) *cis* 11 (9.2) *trans*	47 (39.1) *cis*	67 (55.8) *cis*	39 (32.5) *cis* 8 (6.7) *trans*
trans-Stilbene	16 (13.3) *trans*	<5 (4.1) *trans*	10 (8.3) *trans*	18 (15.0) *trans*

[a] The molar ratios for Mn(Por):imidazole:substrate:oxidant are 1:10:83:167. The imidazole ratio for Mn(TDCPP)OAc is 1.5 rather than 10, since under the latter conditions, Mn(TDCPP)OAc loses almost all its activity. The reactions were performed in CH_2Cl_2 with [Mn(Por)] = 3×10^{-3} M under air at 25 ± 2 °C with 100% selectivity. [b] The GLC conversion (%) or epoxide yield (%) are measured relative to the starting alkenes. [c] Turnover number (TON) is the ratio of the number of moles of produced epoxide to the number of moles of catalyst. [d] Selectivities for the epoxidations are 100% except for α-methylstyrene, which gives 5% acetophenone by-product.

Table 2 Effect of *para*-substituents on the catalytic activity of Mn(Por) in the epoxidation of styrene and α-methylstyrene (α-Mesty)[a]

	% Conversion (TON)[b]		
Substrate	Mn(TPP)OAc	Mn[T(4-OCH_3P)P]OAc	Mn[T(4-NO_2P)P]OAc
Styrene	70 (58.3)	76 (63.3)	51 (42.5)
α-Mesty	91 (75.8)	95 (79.1)	72 (60.0)

[a] The molar ratios and general reaction conditions are the same as in Table 1, with 5 h reaction time. [b] The turnover number is defined in Table 1.

those of σ-donor amines generally show co-catalytic activities similar to those of amines (Table 3). These results may suggest the importance of π- rather than σ-interactions of the nitrogenous donors with Mn(Por). The observed order of co-catalytic activities of 4-MePy > Py ≫ 4-CNPy seems to be directly related to both the σ- and π-donor abilities of these nitrogen donors. The weak base 4-CNPy ($pK_a = 1.86$), with an electron-withdrawing CN substituent, essentially displays no co-catalytic activity. The higher co-catalytic activity of 4-MePy than Py is apparently due to its better σ- and π- donation, caused by hyperconjugation of the methyl group.[11] The steric properties of alkylpyridines play an important part in determining the extent of their interactions with various Mn(Por).[12] The lower activity of 4-*t*-BuPy than Py apparently indicates the effect of steric bulk of the 4-substituent. 2-MePy with one methyl group near to the nitrogen donor atom, and particularly 2,6-Me_2Py with two such groups, hindering their coordination to the Mn(Por), are poor co-catalysts. They actually show no co-catalytic activity in the presence of Mn(TMP)OAc. The remarkable co-catalytic activity of 2,6-Me_2Py, and to a lesser extent that of 2-MePy, toward Mn(TPFPP)OAc is of considerable interest. This observation, with no precedence in the literature as far as we know, suggests the occurrence of some attractive interactions between 2,6-Me_2Py or 2-MePy and Mn(TPFPP)OAc, which is not present for the other manganese porphyrin catalysts. We propose that formation of C–H···F–C hydrogen bonds[13] between the methyl groups of 2,6-Me_2Py or 2-MePy and the *ortho*-fluorines of the coordinated Mn(TPFPP)OAc might be responsible for this behavior. The lower co-catalytic activity of 2-MePy than 2,6-Me_2Py may reflect the fewer number of C–H···F–C hydrogen bonds in the former, leading to its less efficient coordination as a nitrogen donor to the Mn center.

Aminopyridines. These nitrogenous bases are in general much better co-catalysts than pyridines and amines, unless some steric effects are involved. Comparison of pK_a values of aminopyridines with those of pure σ-donor amines confirms the fact that no direct correlation exists between their co-catalytic activities and simple σ-donor strength. Apparently, the π-resonance effect of the lone pair(s) on the amino substituent(s) makes the nitrogen donor site of the aminopyridines both good σ- and π-donors. While both 4-NH_2Py and the sterically demanding 4-NMe_2Py show similar co-catalytic activities toward Mn(TPP)OAc (25 *vs.* 23), they act differently in the presence of the bulky Mn(TMP)OAc (22 *vs.* 12) and Mn(TDCPP)OAc (30 *vs.* 22). Varied co-catalytic activities of 3,4-, 2,3- and 2,6-$(NH_2)_2$Py clearly illustrate the importance of their steric properties (Table 3). As the amino substituents are placed closer to the nitrogen donor site, hindering its coordination, the corresponding aminopyridine demonstrates a lower co-catalytic activity. Thus, 2,6-$(NH_2)_2$Py is the least

Table 3 Epoxidation yields (co-catalytic activities) for nitrogenous donors in the epoxidation of cyclooctene by Mn(Por) catalysts[a]

		% Epoxidation			
Nitrogenous bases[b]	pK_a (BH^+)[c]	Mn(TPP)OAc (4 h)	Mn(TMP)OAc (8 h)	Mn(TDCPP)OAc (24 h)	Mn(TPFPP)OAc (24 h)
None	–	2	1	<2	2
Piperidine	11.123	9	10	12	12
Quinuclidine	10.6	7	8	6	9
Et_2NH	11.02	7	7	5	9
Et_3N	10.75	5	3	2	6
Py	5.25	7	8	10	10
4-CNPy	1.86[d]	2	2	2	3
4-MePy	6.02	10	11	15	15
4-*t*-BuPy	5.99[d]	4	5	6	12
2-MePy	5.97	6	2	6	12
2,6-Me_2Py	6.65	5	1	4	15
4-NH_2Py	9.114	25	22	30	26
4-NMe_2Py	9.71[d]	23	12	22	19
3,4-$(NH_2)_2$Py	9.08[d]	23	15	9	22
2,3-$(NH_2)_2$Py	7[e]	14	9	6	16
2,6-$(NH_2)_2$Py	–	7	5	4	20
ImH	6.953	50	42	38	30
4(5)-MeImH	7.52[f]	47	40	35	32
2-MeImH	7.86[f]	18	7	16	16
2-EtImH	7.86[g]	17	6	13	17
BzImH	5.532	19	12	19	20
1-MeIm	6.95	13	5	14	12
DMF	−2[h]	6	4	3	3

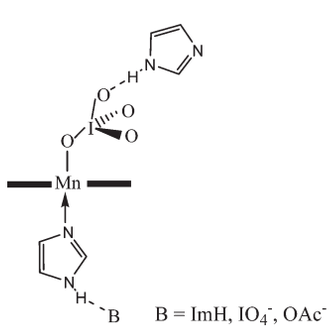
[a] Mn(Por):nitrogenous base:cyclooctene:oxidant molar ratios are: 1:10:90:100 [Mn(TPP)OAc], 1:10:83:83 [Mn(TMP)OAc and Mn(TPFPP)OAc], 1:1.5:83:83 [Mn(TDCPP)OAc] with [Mn(Por)] = 3×10^{-3} M in CH_2Cl_2 at 25 ± 2 °C. [b] Abbreviations: Et_2NH, diethylamine; Et_3N, triethylamine; Py, pyridine; 4-CNPy, 4-cyanopyridine; 4-MePy, 4-methylpyridine; 4-*t*-BuPy, 4-*tert*-butylpyridine; 2-MePy, 2-methylpyridine; 2,6-Me_2Py, 2,6-dimethylpyridine; 4-NH_2Py, 4-aminopyridine; 4-NMe_2Py, 4-(dimethylamino)pyridine; 3,4-$(NH_2)_2$Py, 3,4-diaminopyridine; 2,3-$(NH_2)_2$Py, 2,3-diaminopyridine; 2,6-$(NH_2)_2$Py, 2,6-diaminopyridine; ImH, imidazole; 4(5)-MeImH, 4- or 5-methylimidazole (tautomeric); 2-MeImH, 2-methylimidazole; 2-EtImH, 2-ethylimidazole; BzImH, benzimidazole; 1-MeIm, 1-methylimidazole; DMF, N,N-dimethylformamide. [c] pK_a values obtained from: ref. 33. [d] ref. 34. [e] ref. 35. [f] ref. 36. [g] Very little change in base strength accompanying the change of a methyl substituent to ethyl was observed (see ref. 11). [h] See ref. 17.

active one in association with all Mn(Por) except for Mn(TPFPP)OAc. In line with the arguments presented above for 2,6-Me_2Py, this is presumably related to the formation of N–H···F–C hydrogen bonds[13b] between N–H groups of an axially coordinated 2,6-$(NH_2)_2$Py and the *ortho*-fluorines of two nearby *meso*-pentafluorophenyl groups of the bonded Mn(TPFPP)OAc. Such hydrogen bonding is expected to lead to:(i) a closer approach of the nitrogen donor site of 2,6-$(NH_2)_2$Py to the Mn center and (ii) a shift of some electron density to the hydrogen-bonded N–H group, leading to an increase in the donor ability of the nitrogen donor atom.

Imidazoles. Strong π-donors ImH[10,14] and 4(5)-MeImH are generally far better co-catalysts than all the nitrogen donors presented in Table 3. The much lower co-catalytic activities of 2-MeImH and 2-EtImH than ImH and 4(5)-MeImH are presumably due to the steric properties of the 2-substituents,[2c] which is more clearly shown in the presence of bulky Mn(TMP)OAc. Rather bulky and flat BzImH displays similar or even greater co-catalytic activity than 2-MeImH and 2-EtImH, whereas they have greater pK_a values (Table 3). This may primarily reflect the effects of the more extended π-system of BzImH, its better π-donor ability and also a comfortable coordination to the Mn center. 1-MeIm with a pK_a value very close to that of ImH and a size approaching that of 4(5)-MeImH is the weakest co-catalyst in this class. 1-MeIm is the only one in this class that lacks an N–H bond and, consequently, it cannot form N–H···B hydrogen bonds when it is coordinated to the Mn(Por)[15] (Scheme 1).

Formation of such hydrogen bonds leads to a shift of electron density from B to the N–H group, making its nitrogen donor site a stronger donor. To examine the importance of this hydrogen bonding in enhancing the donor ability of ImH, we added different amounts of an essentially non-coordinating 2,6-Me_2Py into the Mn(TMP)OAc/ImH/*n*-Bu_4NIO_4 catalytic system and monitored the epoxidation of cyclooctene (Table 4). With no 2,6-Me_2Py in the system, and at an ImH/Mn(TMP)OAc ratio of 0.8, the epoxidation yield was 25% (Run 2). Under similar conditions but with a 2,6-Me_2Py/Mn(TMP)OAc ratio of 2 (Run 3), the epoxidation yield reached 29%. When the ratio of 2,6-Me_2Py was further increased to 10 (Run 4) an epoxidation yield of 32% was achieved. Similar experiments using 1-MeIm instead of ImH showed that the presence or absence of 2,6-Me_2Py in the system has no effect on the epoxidation yield. These results strongly suggest that ImH can form hydrogen bonds with 2,6-Me_2Py through its N–H group, thus increasing its donor ability, whereas 1-MeIm is structurally incapable of such bonding. Possible distal hydrogen bonding between the coordinated periodate and one or more ImH should also be considered[16] (Scheme 1). Such interactions are expected to contribute to a facile dissociation of IO_3^- prior to the oxygen transfer step.

The co-catalytic effect of DMF, as a very weak base, is notable (Table 3). The comparable activation achieved for Mn(TPP)OAc with DMF and strong σ-donor amines provides evidence for the importance of π-donation by DMF.[17]



Scheme 1

Table 4 Effect of 2,6-Me_2Py on cyclooctene epoxidation by the Mn(TMP)OAc/ImH/*n*-Bu_4NIO_4 system

Run	ImH/Mn(TMP) OAc ratio	2,6-Me_2Py/ Mn(TMP) OAc ratio	% Epoxidation,[a]
1	0	10	1
2	0.8	0	25
3	0.8	2	29
4	0.8	10	32

[a] Epoxide yields after 6 h are based on the starting cyclooctene in CH_2Cl_2 with a fixed Mn(TMP)OAc:cyclooctene:*n*-Bu_4NIO_4 ratio of 1:83:83 under air at 25 ± 3 °C with [Mn(Por)] = 3×10^{-3} M.

Fig. 2 shows the yield of cyclooctene epoxidation for Mn(TPP)OAc in the presence of various donors. The four classes of nitrogen donors are generally grouped in separate regions, with less steric strong π-donors manifesting the best co-catalytic activities. Similar diagrams for Mn(TMP)OAc and Mn(TDCPP)OAc (not shown) are more scattered, reflecting greater steric effects within each class of donors with these catalysts.

Active oxidant

The nature of the active oxidant in the Mn(Por)/ImH/*n*-Bu_4NIO_4 system is of interest. Interaction of the Mn(TPP)OAc catalyst with an excess of *n*-Bu_4NIO_4 and exchange of OAc^- with IO_4^-, leading to the formation of six-coordinate Mn(TPP)(IO_4)(ImH), under catalytic conditions, essentially caused no changes in the position of its Soret band.[18] While the positions of the Soret bands for Mn(TPP)X (X = OAc^-, IO_4^-) are very close to each other (~478 nm) that of Mn(TPP)F (456 nm) is quite different.[19] Employment of the latter as the starting manganese porphyrin catalyst clearly indicated the formation of Mn(TPP)(IO_4)(ImH) as the active oxidant, with a drastic red shift in the Soret position [Fig. 3(A)].

It is notable that addition of H_2O (2 ml) into this one-phase catalytic system immediately led to the formation of a high-valent Mn-oxo porphyrin species (Soret λ_{max} = 406 nm), which had been observed in the two-phase $NaIO_4$/Mn(TPP)OAc system[2a] [Fig. 3(B)]. Parallel results were obtained with Mn(TMP)OAc in terms of formation of Mn(TMP)(IO_4)(ImH) (Soret λ_{max} = 479 nm) as the active oxidant, or formation of the corresponding high-valent Mn-oxo porphyrin species (Soret λ_{max} = 408 nm), by adding H_2O.

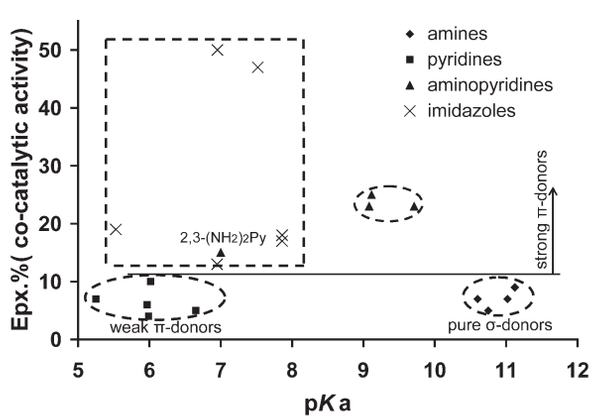


Fig. 2 Scatter diagram showing co-catalytic activities *versus* pK_a values of four classes of nitrogen donors for Mn(TPP)OAc.

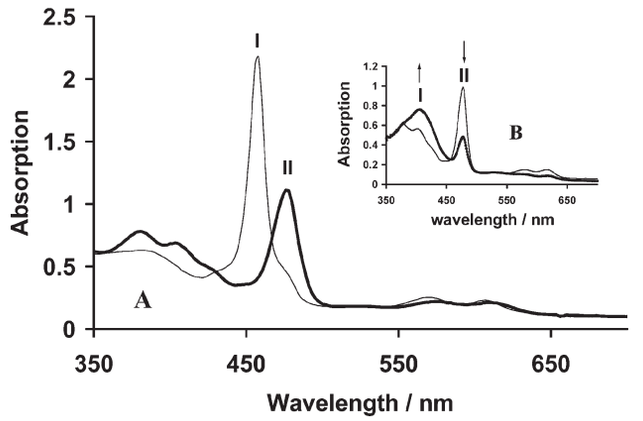


Fig. 3 (A) The spectra represent complete conversion of Mn(TPP)F (peak I) into Mn(TPP)(IO_4)(ImH) (peak II) in the presence of *n*-Bu_4NIO_4 and ImH in CH_2Cl_2 under catalytic molar ratios. The inset B demonstrates formation of a high-valent Mn-oxo species (peak I) (Soret $\lambda_{max} = 406$ nm) by adding some H_2O into a CH_2Cl_2 solution of Mn(TPP)(IO_4)(ImH) (peak II).

To confirm that the active oxidizing species in the one-phase system is indeed the six-coordinate Mn(Por)(IO_4)(ImH) and not a transiently formed high-valent Mn-oxo porphyrin species, we performed three different competitive epoxidation reactions of *cis*- and *trans*-stilbene with *n*-Bu_4NIO_4, $NaIO_4$ (two-phase) and PhIO oxidants in the presence of Mn(TMP)OAc, using similar molar ratios of the reagents (Table 5). With this bulky catalyst and periodate as the starting oxidant, each isomer only yields its corresponding epoxide, with no formation of isomerized products. While oxidation of *trans*-stilbene with PhIO gave only the *trans*-stilbene oxide, oxidation of *cis*-stilbene produced >98% *cis*-stilbene oxide and <2% of *trans*-stilbene oxide. Thus, simply from the *cis*- to *trans*-stilbene oxide ratios direct information may be obtained about the relative reactivities of the related alkenes in these catalytic systems.

The higher ratio of *cis*- to *trans*-stilbene oxide products obtained for the one-phase (~8) as compared to the two-phase (3.26) system clearly suggests that a larger steric hindrance is operative at the active site of the intermediate oxidant in the one-phase system than in the two-phase one, hence favoring better oxidation of the less hindered *cis*-stilbene. The formation of a high-valent O=Mn(TMP)(ImH) (Soret $\lambda_{max} = 407$ nm)[2a] species and the relatively bulky Mn(TMP)(IO_4)(ImH) as the reactive oxidants in the two-phase and one-phase systems, respectively, seem to be quite consistent with the results of these competition reactions. It appears that the presence of H_2O in the two-phase catalytic system plays a key role in generating the high-valent O=Mn(Por)(ImH) species. The strong hydrogen bonding ability of H_2O as the solvent with the coordinated periodate and the effective solvation and stabilization of the dissociated IO_3^- anion seems to provide a strong driving force for the formation of an O=Mn(TMP)(ImH) species. In contrast, CH_2Cl_2 lacks these capabilities and consequently the coordinated periodate apparently remains almost intact prior to the epoxidation step in the one-phase system.

Interestingly, the competitive epoxidation of *cis*- and *trans*-stilbenes with the one-phase Mn(TMP)OAc/ImH/PhIO system in CH_2Cl_2 resulted in a *cis* : *trans* ratio of 3.7 (3.65, alkenes/PhIO = 50) for the products, which is very different from that of the one-phase Mn(TMP)OAc/ImH/n-Bu_4NIO_4 system. Knowing that the former catalytic system would also give a O=Mn(Por) species as the active intermediate complex,[20] and based on the arguments presented above, this finding is again suggestive of a bulky Mn(TMP)(IO_4)(ImH) as the functioning oxidant in the one-phase periodate system.

Axial π-bonding

The key role of π-bonding interactions of nitrogenous axial ligands in activating periodate is clearly shown by our experimental data. To explain this effect a simple qualitative d orbital splitting scheme for the possible π-interactions along the *z* molecular axis of Mn(Por)(IO_4)(ImH), is presented in Fig. 4. In the middle (A) no π-interactions between (d_{xz}, d_{yz}) orbitals and axial ligands are assumed, whereas Por → metal π-bonds are considered to be present.[21] For a perfect matching of the π orbitals of the axial ligands with the metal π(d_{xz}, d_{yz}) orbitals, and on the basis of the relative orientations of the ImH and Mn–O–I planes, two idealized forms (B and C) may be envisioned. Actually, these are the preferred orientations of ImH since metal p_x and p_y orbitals, which are fixed by the strong σ-bond with the porphyrin nitrogens, can also make an important contribution to the π-bonding interactions with axial ligands.[22] In the B configuration the ImH and Mn–O–I planes are co-planar and only the d_{xz} orbital of Mn(III) overlaps with both the π-donor orbital of ImH and the empty π_x^* orbital of O–IO_3^-. In the C form ImH and Mn–O–I planes are perpendicular and d_{yz} accepts π-electron density from ImH and d_{xz} donates electron density into the π_x^* orbital of the bound O–IO_3^-. Clearly such unsymmetrical π-bonding between Mn(III) dπ orbitals and the axial ligand π-systems will remove the degeneracy of the d_{xz}, d_{yz} orbitals. Shift of electron density from the dπ orbital into π_x^* will facilitate eventual cleavage of the metal bound O–I and the transfer of a single oxygen to alkene. Strong π-donor nitrogenous ligands such as ImH and 4-NH_2Py are expected to be more effective in elevating the energy of the dπ-donor orbital at the Mn(III) center. The π-acceptor 4-CNPy would lower the energy of the interacting dπ orbital and hence reducing the electron transfer into the π_x^* orbital. In the absence of a description for the spin state of Mn(Por)(ImH)(IO_4), particularly when it is involved in the oxygenation of alkenes, possible occurrence of a low-spin ↔ high-spin dynamic equilibrium is of concern. In accordance with Fig. 4, it might be anticipated that a high-spin Mn(Por)(IO_4)(ImH) with the B configuration, $(d_{xy})^1 < (d_{yz})^1 < (\pi_{xz}^*)^1 < (d_z^2)^1$, would be more favorable than the C form, $(d_{xy})^1 < (d_{xz})^1 < (\pi_{yz}^*)^1 < (d_z^2)^1$, for electron

Table 5 Competitive catalytic epoxidation of *cis*- and *trans*-stilbenes with Mn(TMP)OAc/ImH/*n*-Bu_4NIO_4, Mn(TMP)OAc/ImH/$NaIO_4$ and Mn(TMP)OAc/ImH/PhIO systems[a]

% Epoxidation								
Mn(TMP)OAc/ImH/*n*-Bu_4NIO_4 (4 h)			Mn(TMP)OAc/ImH/$NaIO_4$ (4 h)			Mn(TMP)OAc/ImH/PhIO (5 min)		
cis	*trans*	*cis*/*trans* ratio	*cis*	*trans*	*cis*/*trans* ratio	*cis*	*trans*	*cis*/*trans* ratio
8.3	1.04	~8	9.01	2.76	3.26	12 (4.5)[b]	3.24 (1.23)[b]	3.7 (3.65)[b]

[a] The molar ratios for Mn(TMP)OAc:ImH:(*cis*- and *trans*- stilbene):*n*-Bu_4NIO_4 are 1:10:(501 and 501):167 in CH_2Cl_2, for Mn(TMP)OAc:ImH:(*cis*- and *trans*- stilbenes):$NaIO_4$:*n*-Bu_4NBr (phase transfer catalyst) are 1:10:(501 and 501):167:8 in CH_2Cl_2/H_2O (1:5 v/v) and for Mn(TMP)OAc:ImH:(*cis*- and *trans*- stilbenes):PhIO are 1:10:(501 and 501):167. [b] 1:10:(2075 and 2075):83 in CH_2Cl_2 under air at 25 ± 2 °C.

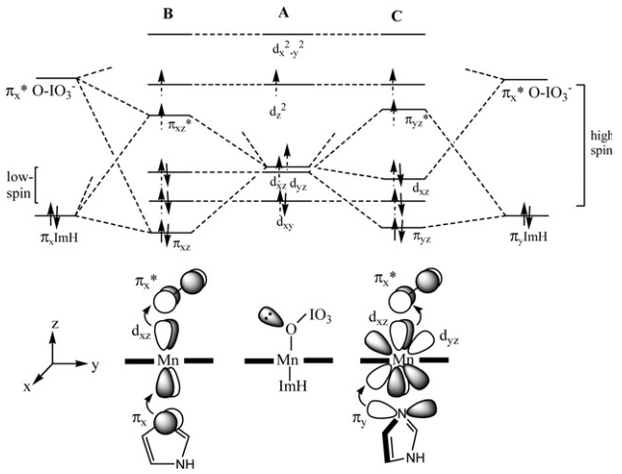


Fig. 4 A simple idealized molecular orbital diagram illustrating the maximum possible π-interactions of axial ImH and IO_4^- ligands with (d_{xz}, d_{yz}) metal orbitals in low- and high-spin [Mn(Por)(ImH)(IO_4)]: (A) no π-bonding along the *z* axis, (B) π-bonding with a single d_{xz} orbital; (C) π-bonding with both d_{xz} and d_{yz} orbitals.

donation to π_x* because the π-donor orbital (π_{xz}*) in the former is apparently higher in energy than the π-donor (d_{xz}) in the latter. In contrast, for the low-spin case the filled d_{xz} in the C form is closer to π_x* than π_{xz} is in the B form, hence the C configuration is preferred.

An effective π-interaction between porphyrin π-orbitals and (d_{xz}, d_{yz}) is also expected to occur in Mn(Por)(ImH)(IO_4). Comparison of the results of styrene epoxidation by various *para*-substituted Mn(Por) showed the importance of Por → Mn π-donation[21] in activating periodate (*vide supra*). Axial σ-donation by nitrogenous ligands, which raises the metal d_z^2 energy, is expected to be of less importance to the energies of the dπ orbitals of the complexes than are the π-bonds of the ligand donor atom. However, the observed co-catalytic activities of σ-donor axial ligands may be explained in terms of their ability to bring Mn(III) closer toward the center of the porphyrin core plane, making π-donation from porphyrin into (d_{xz}, d_{yz}) more feasible.

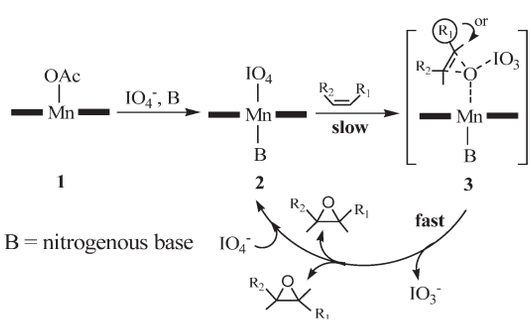
When Fe(TPP)OAc and Cr(TPP)Cl were utilized instead of Mn(TPP)OAc, very little (5% epoxide yield) or no catalytic activity, respectively, was observed under similar conditions. While formation of a six-coordinate $[Fe(TPP)(ImH)_2]^{+}$[3c,23] seems to be the primary reason for the inactivity of the iron complex, the absence of activity for Cr(TPP)Cl may be related to π-bonding effects. Assuming the simple diagram to be appropriate for chromium, then six-coordinate low-spin Cr(TPP)(ImH)(IO_4), $(d_{xy})^2 < (d_{xz}, d_{yz})^1$, having a single electron available for π-interactions is expected to be less active than the corresponding low-spin Mn(Por) with two such electrons. This suggests that the number of electrons in (d_{xz}, d_{yz}) orbitals is critically important in activating the periodate. However, it should be noted that if both Cr(TPP)(ImH)(IO_4) and Mn(TPP)(ImH)(IO_4) were high-spin with similar $(d\pi)^1$ electron populations, the simple diagram seems to provide no clue for their different catalytic behavior. Thus, from all considerations above, it may be concluded that if a low-spin ↔ high-spin equilibrium existed at all for Mn(Por)(ImH)(IO_4), then the low-spin C form would probably be the most effective catalytic center for epoxidation.

While for all axial ligands, σ-interaction with the Mn center is independent of ligand orientation, significant variation in bonding parameters is found for the metal-imidazole π-interaction as a function of rotation.[22] Possible orientations of various nitrogenous axial ligands are a result of competition between their π-bonding propensity and their steric interactions with the porphyrin core. For the idealized orientations in which the planes of the coordinated axial ligands eclipse the equatorial Mn–N_{por} bonds, maximum steric repulsions are expected to occur with the porphyrin core.[24] Pyridine derivatives with lower π-donor abilities than imidazoles and presumably with larger non-bonding interactions with the porphyrin core are expected to deviate more from the ideal geometries.[22] It seems reasonable to suppose that the observed differences in co-catalytic activities of axial nitrogen donors are partly a consequence of their orientation caused by a combination of steric and electronic factors.

Postulated mechanism

Based on the available data in this study concerning the nature of the active oxidant, the higher reactivities of electron-rich alkenes and electron-rich Mn(Por), and also the high co-catalytic activities of strong π-donor nitrogenous axial ligands, as well as the excellent selectivities of the epoxidations, a concerted mechanism is proposed. Scheme 2 represents a possible catalytic cycle for alkene epoxidation, in which formation of the proposed intermediate **3** involves interaction of the alkene with the bound oxygen atom of the active oxidant **2**, resembling the active intermediate in alkene epoxidation by Mn(Por)X/$KHSO_5$/4-*t*-BuPy.[7b] A similar epoxidizing intermediate in iron porphyrin complex catalyzed epoxidation reactions has also been proposed.[25] Possible orbital interactions for the idealized stereochemistry in the intermediate **3**, with alkene C–C bond located in the *yz* plane, are given in Fig. 5. These consist of a nucleophilic attack of the alkene π-orbital on the σ* of O–IO_3^- [Fig. 5(a)] and a back-bonding of the metal-bound oxygen sp^2 lone pair to the alkene π* ([Fig. 5(b)]. Both of these interactions can reduce the alkene's C–C bond order, facilitating free rotation around this bond, leading to the *cis* → *trans* isomerization. It is reasonable to presume that the free rotation occurs prior to the formation of intermediate **3**. The epoxide ring closure, in the course of formation of intermediate **3**, requires some major structural changes in the alkene and also involves strong steric interactions with the porphyrin ligand. Thus, it is expected to have a high energy barrier and is presumably the rate-limiting step. This view is apparently in agreement with our experimental results, the proposed π-bonding model and the orbital interactions assumed for ring closure. The observed higher epoxidation rate of electron-rich alkenes, relative to electron-poor ones, may be explained in terms of their better π-donation toward σ* of the metal-bound O–I. The influence of strong π-donor nitrogenous ligands and Mn(Por) with π-donor substituents (Table 3) upon the rate-limiting step is probably due to their ability to populate the d_{yz} donor orbital. Interaction of d_{yz} as a π-donor with the sp^2 lone pair would destabilize this orbital and make it a stronger donor toward alkene π*, hence enhancing the rate of ring closure.

The alternative approach of alkene through the *xz* plane toward coordinated periodate, and its interaction with the



Scheme 2 Proposed catalytic cycle for epoxidation of alkenes by the *n*-Bu_4NIO_4/Mn(Por)X/ImH system.

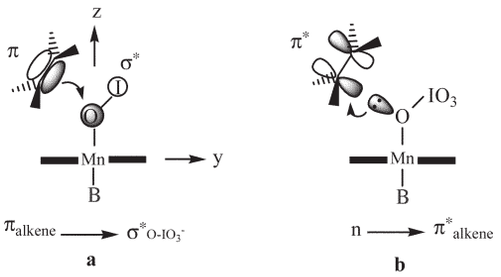


Fig. 5 Possible orbital interactions for the idealized stereochemistry in the intermediate **3**: (a) nucleophilic attack of the alkene π-orbital on the σ* orbital of the O–IO_3^- bond, (b) back-bonding of the metal-bound oxygen sp^2 lone pair to the alkene π* orbital.

π_x* orbital of O–IO_3^-, may also be considered. However, this side attack might seriously be hampered by steric effects due to the close proximity of alkene and the coordinated periodate, and also from mutual interactions of both alkene and the bound IO_4^- with the single phenyl group located in between them. Also, the electron density in π_x* from the $d\pi \rightarrow \pi_x$* bonding interaction (Fig. 4) may inhibit the alkene's nucleophilic attack.

It is notable that *cis* → *trans* isomerization in the epoxidation of *cis*-stilbene has been taken as evidence for a radical intermediate.[2b,4a,20a] However, in accord with our proposed mechanism and the possible orbital interactions in the formation of intermediate **3** (Fig. 5), it appears that *cis* → *trans* isomerization does not necessarily require formation of a radical species. This seems to be consistent with the very high selectivities of epoxidation reactions observed with the Mn(Por)/ImH/*n*-Bu_4NIO_4 catalytic system.

Conclusions

While the steric properties of Mn(Por), alkenes and axial nitrogenous bases used in this study are of paramount importance in determining the overall catalytic reaction times and epoxidation yields, clear evidence is provided for: (i) Mn(Por) with electron-withdrawing substituents on their phenyl groups are much less effective catalysts than those with electron-donor substituents; (ii) electron-rich alkenes display higher reactivity than electron-poor ones; (iii) nitrogen donor axial ligands with π-donor capability are much more effective co-catalysts than pure σ-donor amines and no definite general correlation exists between co-catalytic activities and pK_a values of nitrogenous bases; (iv) pyridines with methyl or amino groups in their 2 or 2,6 positions demonstrate exceptionally high co-catalytic activities in the presence of Mn(TPFPP)OAc, suggesting the presence of C–F···H–C and C–F···H–N hydrogen bonding in these systems.

Experimental

Materials

The free base porphyrins: $TPPH_2$,[26] T(4-OMeP)PH_2,[26] T(4-NO_2P)PH_2,[27] $TDCPPH_2$,[28] $TMPH_2$[28] and $TPFPPH_2$[29] were prepared and purified by methods reported previously. Mn(TPP)OAc, Mn[T(4-OMeP)P]OAc, Mn[T(4-NO_2P)P]OAc, Mn(TDCPP)OAc, Mn(TMP)OAc, Fe(TPP)OAc and Cr(TPP)Cl were obtained using the corresponding $Mn(OAc)_2{\cdot}4H_2O$, $Fe(OAc)_2$ or $CrCl_2$ according to the procedure of Adler *et al.*.[30] Mn(TPFPP)OAc was synthesized in a manner similar to that described by Kadish and coworkers.[31] Nitrogenous bases were purchased from Merck or Fluka. BzImH, 4-NH_2Py, 2,3-$(NH_2)_2$Py, 3,4-$(NH_2)_2$Py and 2,6-$(NH_2)_2$Py were recrystallized before use.[32] Pyridine was distilled on NaOH and kept over molecular sieves. Tetrabutylammonium periodate (*n*-Bu_4NIO_4; Merck) was dried under vacuum and P_2O_5. All the alkenes were purchased from commercial vendors and passed through a short column of neutral alumina immediately prior to use. Dichloromethane (Merck) was further purified by repeated washing with concentrated H_2SO_4 until the aqueous layer was colorless, followed by washing with water and 5% Na_2CO_3 solution. Then, it was dried by $CaCl_2$ and distilled over CaH_2.

General oxidation procedure

Stock solutions of Mn(Por) catalysts (0.003 M) and nitrogenous bases (0.5 M) in CH_2Cl_2 were prepared. In a 10 mL round-bottom flask were added in order: alkene (0.25 mmol), Mn(Por) (0.003 mmol, 1.0 mL), nitrogenous base (0.03 mmol, 60 μL) and tetrabutylammonium periodate (required amount) to achieve the desired ratio (see footnotes in Table 1 and 3). In the case of Mn(TDCPP)OAc, 0.0045 mmol (9.0 μL), of nitrogenous base was used. The mixture was stirred thoroughly for the required time at ambient temperature in air. The resulting solution was directly analyzed by GLC. Similar results were obtained under Ar. Epoxidations of *cis*- and *trans*-stilbenes were determined by ^{1}H NMR (Bruker Avance DPX 250 MHz spectrometer). All the reactions were run at least in duplicate. The electronic absorption spectra were recorded in CH_2Cl_2 solutions utilizing a MultiSpect-150-Shimadzu spectrophotometer.

Competition reactions

Competitive catalytic epoxidations of *cis*- and *trans*-stilbenes were performed at ambient temperature. In the one-phase system, *cis*- and *trans*-stilbenes (1.5 mmol each) were reacted with *n*-Bu_4NIO_4 (0.5 mmol) in the presence of Mn(TMP)OAc (0.003 mmol) and imidazole (0.03 mmol) in CH_2Cl_2 (1.0 mL). The solution was stirred for 4 h and the *cis*/*trans* epoxide ratio was measured by ^{1}H NMR. Similarly, in the two-phase system equal amounts of *cis*- and *trans*-stilbenes (1.5 mmol each) were mixed with Mn(TMP)OAc (0.003 mmol), imidazole (0.03 mmol) and the phase-transfer catalyst *n*-Bu_4NBr (0.024 mmol) in CH_2Cl_2 (1.0 mL), and reacted with 0.5 mmol of $NaIO_4$ (in 5 mL H_2O). The solvent mixture was stirred for 4 h and the *cis*/*trans* epoxide ratio was analyzed by ^{1}H NMR.

For the PhIO system *cis*- and *trans*-stilbenes (1.5 mmol each) were reacted with PhIO (0.5 mmol) in the presence of Mn(TMP)OAc (0.003 mmol) and imidazole (0.03 mmol) in CH_2Cl_2 (1.0 mL). The reaction mixture was stirred for 5 min at ambient temperature and then quenched by addition of an aqueous solution of sodium metabisulfite (10%) with stirring. The analysis was performed by ^{1}H NMR. The reaction was repeated using a large excess (12.45 mmol) of *cis*- and *trans*-stilbenes (6.225 mmol each) with 0.25 mmol of PhIO without changing the amounts of the other components.

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References

1 (*a*) D. Mansuy and P. Battioni, in *The Porphyrin Handbook*, eds. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, 2000, vol. 4, ch. 26, p. 1; (*b*) J. T. Groves, K. Shalyaev and J. Lee, in *The Porphyrin Handbook*, eds. K. M. Kadish,

K. M. Smith and R. Guilard, Academic Press, San Diego, 1999, ch. 27, p. 17; (*c*) D. Dolphin, T. G. Traylor and L. Y. Xie, *Acc. Chem. Res.*, 1997, **30**, 251; (*d*) P. Bhyrappa, J. K. Young, J. S. Moore and K. S. Suslick, *J. Mol. Catal. A: Chem.*, 1996, **113**, 109; (*e*) A. Maldotti, A. Molinari, P. Bergamini, R. Amadelli and D. Mansuy, *J. Mol. Catal. A: Chem.*, 1996, **113**, 147; (*f*) D. Mansuy, *Coord. Chem. Rev.*, 1993, **125**, 129; (*g*) B. Meunier, *Chem. Rev.*, 1992, **92**, 1411; (*h*) I. Tabushi, *Coord. Chem. Rev.*, 1988, **86**, 1; (*i*) T. J. McMurry and J. T. Groves, *Cytochrome P-450: Mechanism and Biochemistry*, ed. P. R. Ortiz de Montellano, Plenum Press, New York and London, 1986, ch. 1.

2 (*a*) D. Mohajer, R. Tayebee and H. Goudarziafshar, *J. Chem. Res.*, 1999, (S) 168; (*b*) R. D. Arasasingham, G. X. He and T. C. Bruice, *J. Am. Chem. Soc.*, 1993, **115**, 7985; (*c*) P. Battioni, J. P. Renaud, J. F. Bartoli, M. Reins-Artiles, M. Fort and D. Mansuy, *J. Am. Chem. Soc.*, 1988, **110**, 8462; (*d*) J. P. Collman, J. I. Brauman, B. Meunier, T. Hayashi, T. Kodadek and S. A. Raybuck, *J. Am. Chem. Soc.*, 1985, **107**, 2000; (*e*) B. de Poorter and B. Meunier, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1735; (*f*) J. R. Lindsay-Smith and P. R. Sleath, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1009; (*g*) J. T. Groves, T. E. Nemo and R. S. Myers, *J. Am. Chem. Soc.*, 1979, **101**, 1032.

3 (*a*) D. Mohajer and A. Rezaeifard, *Tetrahedron Lett.*, 2002, **43**, 1881; (*b*) J. P. Collman, J. I. Brauman, J. P. Fitzgerald, P. D. Hampton, Y. Naruta and T. Michida, *Bull. Chem. Soc. Jpn.*, 1998, **61**, 47; (*c*) Z. Gross and S. Ini, *J. Org. Chem.*, 1997, **62**, 5514; (*d*) D. Mohajer and S. Tangestaninejad, *Tetrahedron Lett.*, 1994, **35**, 945; (*e*) Y. Naruta and K. Maruyama, *Tetrahedron Lett.*, 1987, **28**, 4553.

4 (*a*) D. Ostavic and T. C. Bruice, *Acc. Chem. Res.*, 1992, **25**, 314; (*b*) D. Ostavic and T. C. Bruice, *J. Am. Chem. Soc.*, 1989, **111**, 6511; (*c*) J. T. Groves and T. E. Nemo, *J. Am. Chem. Soc.*, 1983, **105**, 5786.

5 (*a*) J. Y. Liu, X. F. Li, Y. Z. Li, W. B. Chang and A. J. Huang, *J. Mol. Catal. A: Chem.*, 2002, **187**, 163; (*b*) E. Baciocchi, T. Boschi, C. Galli, A. Lapi and P. Tagliatesta, *Tetrahedron*, 1997, **53**, 4497; (*c*) K. Konishi, K. Oda, K. Nishida, T. Aida and S. Inoue, *J. Am. Chem. Soc.*, 1992, **114**, 1313; (*d*) R. L. Halterman and S. T. Jan, *J. Org. Chem.*, 1991, **56**, 5253; (*e*) J. P. Battioni, D. Dupre and D. Mansuy, *J. Organomet. Chem.*, 1987, **328**, 173; (*f*) D. Mansuy, *Pure Appl. Chem.*, 1987, **59**, 759; (*g*) E. Guilmet and B. Meunier, *Tetrahedron Lett.*, 1982, **23**, 2449; (*h*) E. Guilmet and B. Meunier, *Nouv. J. Chim.*, 1982, **6**, 511.

6 J. P. Collman, A. S. Chien, T. A. Eberspacher, M. Zhong and J. I. Brauman, *Inorg. Chem.*, 2000, **39**, 4625.

7 (*a*) B. M. Trost and R. Braslau, *J. Org. Chem.*, 1988, **53**, 532; (*b*) A. Robert and B. Meunier, *New. J. Chem.*, 1988, **12**, 885; (*c*) R. J. Kennedy and A. M. Stock, *J. Org. Chem.*, 1960, **25**, 1901.

8 S. Banfi, F. Montanari and S. Quici, *J. Org. Chem.*, 1989, **54**, 1850.

9 E. M. Davoras and A. G. Coutsolelos, *J. Inorg. Biochem.*, 2003, **94**, 161.

10 (*a*) M. K. Safo, F. A. Walker, A. M. Raitsimring, W. P. Walters, D. P. Dolata, P. G. Debrunner and W. R. Scheidt, *J. Am. Chem. Soc.*, 1994, **116**, 7760; (*b*) M. K. Safo, G. P. Gupta, C. T. Watson, U. Simonis, F. A. Walker and W. R. Scheidt, *J. Am. Chem. Soc.*, 1992, **114**, 7066; (*c*) M. K. Safo, G. P. Gupta, F. A. Walker and W. R. Scheidt, *J. Am. Chem. Soc.*, 1991, **113**, 5497.

11 H. C. Brown and X. R. Mihm, *J. Am. Chem. Soc.*, 1955, **77**, 1723.

12 B. Meunier, E. Guilmet, M.-E. De Carvalho and R. Poilblanc, *J. Am. Chem. Soc.*, 1984, **106**, 6668.

13 (*a*) G. C. Cole and A. C. Legon, *Chem. Phys. Lett.*, 2003, **369**, 31; (*b*) F. Grepioni, G. Cojazzi, S. M. Draper, N. Scully and D. Braga, *Organometallics*, 1998, **17**, 296.

14 C. K. Chang and T. G. Traylor, *J. Am. Chem. Soc.*, 1973, **95**, 8477.

15 (*a*) L. C. Yuan and T. C. Bruice, *J. Am. Chem. Soc.*, 1986, **108**, 1643; (*b*) P. Obrien and D. A. Sweigart, *Inorg. Chem.*, 1985, **24**, 1405; (*c*) F. A. Walker, M. W. Lo and M. T. Ree, *J. Am. Chem. Soc.*, 1976, **98**, 5552.

16 (*a*) G. B. Jameson and J. A. Ibers, in *Bioinorganic Chemistry*, eds. I. Bertini, H. B. Gray, S. Lippard and J. Valentine, University Science Books, 20 Edgehill Road, Mill Valley, CA 94941, 1994, ch. 4, p. 167; (*b*) G. A. Tondreau and D. A. Sweigart, *Inorg. Chem.*, 1984, **23**, 1060.

17 D. V. Stynes, H. C. Stynes, B. R. James and J. A. Ibers, *J. Am. Chem. Soc.*, 1973, **95**, 1796.

18 D. Mohajer and M. Bagherzadeh, *J. Chem. Res.*, 1998, (S) 556.

19 M. F. Powell, E. F. Pai and T. C. Bruice, *J. Am. Chem. Soc.*, 1984, **106**, 3277.

20 (*a*) J. T. Groves, W. J. Kruper, Jr. and R. C. Haushalter, *J. Am. Chem. Soc.*, 1980, **102**, 6375; (*b*) Y. Iamamoto, M. D. Assis, K. J. Ciuffi, C. M. C. Prado, B. Z. Prellwitz, M. Moraes, O. R. Nascimento and H. C. Sacco, *J. Mol. Catal. A: Chem.*, 1997, **116**, 365.

21 G. N. La Mar and F. A. Walker, *J. Am. Chem. Soc.*, 1975, **97**, 5103.

22 W. R. Scheidt and D. M. Chipman, *J. Am. Chem. Soc.*, 1986, **108**, 1163.

23 (*a*) Y. Iamamoto, M. D. Assis, K. J. Ciuffi, H. C. Sacco, L. Iwamoto, A. J. B. Melo, O. R. Nascimento and C. M. Prado, *J. Mol. Catal. A: Chem.*, 1996, **109**, 189; (*b*) M. J. Nappa and C. A. Tolman, *Inorg. Chem.*, 1985, **24**, 4711.

24 D. M. Collins, R. Countryman and J. L. Hoard, *J. Am. Chem. Soc.*, 1972, **94**, 2066.

25 W. Nam, S. W. Jin, M. H. Lim, J. Y. Ryu and C. Kim, *Inorg. Chem.*, 2002, **41**, 3647.

26 A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem.*, 1967, **32**, 476.

27 A. Bettelheim, B. A. White, S. A. Raybuck and R. W. Murray, *Inorg. Chem.*, 1987, **26**, 1009.

28 P. Hoffmann, A. Robert and B. Meunier, *Bull. Soc. Chim. Fr.*, 1992, **129**, 85.

29 J. S. Lindsey, I. C. Schreiman, H. C. Hsu, P. C. Kearney and A. M. Marguerettaz, *J. Org. Chem.*, 1987, **52**, 827.

30 A. D. Adler, F. R. Longo, F. Kampas and J. Kim, *J. Inorg. Nucl. Chem.*, 1970, **32**, 2443.

31 K. M. Kadish, C. Araullo-McAdams, B. C. Han and M. M. Franzen, *J. Am. Chem. Soc.*, 1990, **112**, 8364.

32 D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Elmsford, NY, 2nd edn., 1980.

33 R. L. David, *Handbook of Chemistry and Physics*, CRC Press, New York, 80th edn., 1999–2000, pp. 8, 46–56.

34 K. Schofield, *Hetero-Aromatic Nitrogen Compounds, Pyrroles and Pyridines*, Plenum Press, New York, 1967, p. 146.

35 A. Albert, in *Physical Methods in Heterocyclic Chemistry*, ed. A. R. Katritzky, Academic Press, New York, 1971, Vol III, p. 1–26.

36 K. Hoffmann, *Imidazole and its Derivatives*, Interscience Publishers Inc., New York, 1953, Part I, p. 15.