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Co-catalytic effects of nitrogen donors on the epoxidation of cyclooctene with tetra-*n*-butylammonium hydrogen monopersulfate in the presence of manganese(III) tetraarylporphyrins: A comparative study

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Abstract

The epoxidation of cyclooctene by tetra-*n*-butylammonium hydrogen monopersulfate was performed in the presence of four different manganese(III)tetraarylporphyrins as catalysts and a number of nitrogen donors as co-catalysts under a fixed co-catalyst/catalyst ratio (100:1). It was observed that the σ-bonding abilities of the nitrogen donors, as related to their pK_a (BH^+) values, were not a reliable factor for determining their co-catalytic activities, unless there were no π-interactions and/or no significant involvement of steric hindrance. On the other hand, the π-donating ability of the nitrogen donors was found to be of importance in defining their role as co-catalysts. The strong π-donor N–H imidazoles displayed co-catalytic activities greater than strong σ-donor amines and weak π-donor pyridines in the presence of manganese(III)tetraphenylporphyrin acetate (MnTPP(OAc)). In the case of hindered manganese(III)tetramesitylporphyrin acetate and manganese(III)tetrakis(2,6-dichlorophenyl)porphyrin acetate steric hindrance of the nitrogen donors played a dominant role, and the least hindered imidazole (ImH) was the best co-catalyst. When manganese(III)tetrakis(pentafluorophenyl)porphyrin acetate(MnTPFPP(OAc)) was employed as catalyst then pyridines, in general, demonstrated a higher co-catalytic activities than imidazoles. The same trend was also observed under various co-catalyst/catalyst ratios (1–200), and pyridines were always more effective co-catalysts than imidazoles with MnTPFPP(OAc), whereas for MnTPP(OAc) the order for co-catalytic activities of these nitrogen donors was inverted. Also, in the presence of electron deficient manganese(III)tetrakis(4-nitrophenyl)porphyrin acetate imidazoles acted generally as more effective co-catalysts than pyridines, at co-catalyst/catalyst ratios < 100. It is proposed that the varied attractive C–H···F–C interactions between the *ortho*-C–F σ* orbitals of the pentafluorophenyl groups in MnTPFPP(OAc) complex and C–H σ bonds adjacent to the nitrogen donor sites of pyridines or imidazoles could be responsible for the observed differences. The UV–vis spectra of the catalytic systems containing pyridine and ImH in association with MnTPP(OAc) and MnTPFPP(OAc) were examined for the active oxygen intermediates.

Keywords: Manganese porphyrins; Nitrogen donors; Co-catalyst; Epoxidation; Tetra-*n*-butylammonium hydrogen monopersulfate

1. Introduction

Nitrogen donors have long been used as axial ligands to mimic the function of axial cysteine thiolate or histidine imidazole in natural metalloproteins [1–8]. Much improvements have been achieved in catalytic properties of synthetic metalloporphyrins for alkene epoxidation from the employment of pyridines and imidazoles as co-catalyst [9–21]. To understand the role of the axial nitrogen donors in oxygenation reactions, mediated by metalloporphyrins, a detailed analysis of the influences of the stereoelectronic properties of the nitrogen donors and the metalloprorphyrins is required.

In this work co-catalytic activities of a selected series of nitrogen donors, in the presence of five different manganese porphyrins (MnPor) (Fig. 1) as catalysts, in the epoxidation of cyclooctene with *n*-Bu_4NHSO_5 were studied. The effects of various co-catalyst/catalyst ratio upon co-catalytic properties of nitrogen donors were also investigated. Particular attention has been given to inverted order of co-catalytic activities of pyridines versus imidazoles in the presence of MnTPP(OAc) as compared

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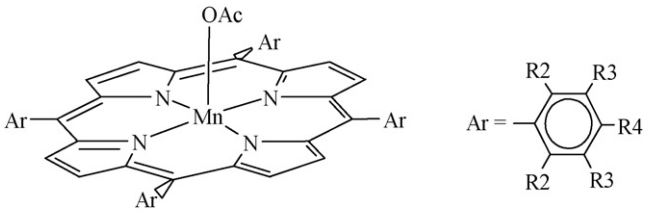

	R_2	R_3	R_4
MnTPP(OAc)	H	H	H
MnTMP(OAc)	CH_3	H	CH_3
MnTDCPP(OAc)	Cl	H	H
MnTPFPP(OAc)	F	F	F
MnT(4-NO_2P)P(OAc)	H	H	NO_2

Fig. 1. Manganese(III)tetraarylporphyrins employed in this study.

to MnTPFPP(OAc). Attempts were made to explain the varied co-catalytic activities of nitrogen donors in terms of their stereoelectronic properties and those of the MnPor complexes.

2. Experimental

2.1. Material

The free base porphyrins $TPPH_2$ [22], T(4-NO_2P)PH_2 [23], $TDCPPH_2$ [24], $TMPH_2$ [24] and $TPFPPH_2$ [25] were prepared and purified as reported previously. MnTPP(OAc), MnT(4-NO_2P)P(OAc), MnTDCPP(OAc), MnTMP(OAc) were obtained using $Mn(OAc)_2{\cdot}4H_2O$ according to the procedure of Adler et al. [26] MnTPFPP(OAc) was synthesized in a manner similar to that described by Kadish et al. [27]. Nitrogenous bases were purchased from Merck or Fluka. BzImH was recrystallized before use [28]. Pyridine, 2-MePy and 2,6-Me_2Py were distilled on KOH and kept over molecular sieves.

n-Bu_4NHSO_5 was prepared by adding potassium monopersulfate (2.0 g, 6.5 mmol) to a solution of tetra-*n*-butylammonium hydrogen sulfate (2.0 g, 5.9 mmol) in water (20 mL) [9,29,30]. The solution was extracted with CH_2Cl_2 (40 mL) and the organic phase was dried over sodium sulfate and filtered. After evaporation of the solvent, the remaining paste was washed with hexane (10 mL) and dried under vacuum. The freshly prepared *n*-Bu_4NHSO_5 was a much stronger oxidant than commercially available samples. Since the oxidizing ability of *n*-Bu_4NHSO_5 samples would reduce with time, in order to obtain reproducible results, the *freshly* prepared oxidant was refrigerated and used within 3 days. *Caution*: *n*-Bu_4NHSO_5 should be considered as a potential explosive.

2.2. General oxidation procedure

Stock solutions of MnPor catalysts (0.003 M) and nitrogen donors (0.5 M) (except BzImH (0.0625 M)) were prepared in CH_2Cl_2. In a 10 mL round-bottom flask the following were added in the order: MnPor (0.001 mmol, 0.3 mL), nitrogen donor (*x* mmol, as required), cyclooctene (0.1 mmol) and 1.5 mL CH_2Cl_2. Tetra-*n*-butylammonium hydrogen monopersulfate (0.19 mmol) was then added to the reaction solutions, at 25 °C. The reaction solutions were analyzed immediately by GLC after stirring for 2 min.

The electronic absorption spectra were recorded in CH_2Cl_2 solutions utilizing a MultiSpec-1501 Shimadzu spectrophotometer.

3. Results and discussion

3.1. Co-catalytic effects of nitrogen donors

The results of epoxidation of cyclooctene by *n*-Bu_4NHSO_5 in the presence of four differing MnPor as catalysts, in association with a number of nitrogen donors as co-catalysts, under similar conditions, are given in Table 1. The nitrogen donors may be grouped into three classes, the strong pure σ-donor amines (pK_a, 10.75–11.123), the strong π-donor imidazoles (pK_a, 5.532–7.86), and the weak π-donor pyridines (pK_a, 1.86–6.65). The yields of the epoxidation of cyclooctene presumably reflect the co-catalytic activities of the nitrogenous bases, in the presence of the MnPor catalysts. The co-catalytic activities of the nitrogenous bases depend upon not only their stereoelectronic properties, but also they relate to the nature of the MnPor catalysts [31]. The general order of the co-catalytic activities of the various classes of the nitrogen donors for MnTPP(OAc), MnTMP(OAc), and MnTDCPP(OAc) (imidazoles > amines > pyridines) suggests that the imidazoles are the most effective co-catalysts, whereas in the case of MnTPFPP(OAc), the general order of the co-catalytic activities of the nitrogen donors (pyridines > amines > imidazoles) indicates that pyridines are the best co-catalysts.

3.1.1. Amines

The order of the co-catalytic activities of the amines in the presence of the MnPor catalysts is piperidine > Et_2NH > Et_3N, except for MnTPFPP(OAc) (Table 1). This order is in complete accord with the order of increasing basicities and decreasing steric hindrances of the amines. The least hindered piperidine, which is also the strongest base (pK_a = 11.123), is the best co-catalyst. Indeed, piperidine is two times stronger than Et_2NH, and four times stronger than Et_3N, as co-catalyst, in the presence of MnTPP(OAc). The order of the co-catalytic effects of the amines, in combination with MnTMP(OAc), is the same as that of MnTPP(OAc). In the case of MnTDCPP(OAc), Et_2NH and Et_3N show similar activities. On the other hand, for MnTPFPP(OAc) the co-catalytic activities of piperidine and Et_2NH are similar and much greater than that of Et_3N.

3.1.2. Imidazoles

The imidazoles are generally more efficient co-catalysts than the amines and the pyridines in the presence of MnTPP(OAc), MnTMP(OAc), and MnTDCPP(OAc) (Table 1). The order of the co-catalytic activities of the imidazoles in association with MnTPP(OAc), ImH > 2-MeImH > BzImH > 2-EtImH ≫ 1-MeIm, and in combination with MnTMP(OAc) and MnTDCPP(OAc), ImH ≫ 2-MeImH > 2-EtImH ≫ BzImH ≫ 1-MeIm, are rather closely related, except for the relative order

Table 1
Epoxidation yield (%) (co-catalytic activity) for nitrogen donors in the epoxidation of cyclooctene with MnPor catalysts[a,b,c]

Nitrogen donor	pK_a (BH^+)[d]	Epoxidation (%)			
		MnTPP(OAc)	MnTMP(OAc)	MnTDCPP(OAc)	MnTPFPP(OAc)
Piperidine	11.123	40 ± 4	42 ± 3	45 ± 4	74 ± 2
Et_2NH	11.02	24 ± 2	20 ± 1	4 ± 1	77 ± 3
Et_3N	10.75	10 ± 1	6 ± 1	3 ± 1	48 ± 3
ImH	6.953	87 ± 4	70 ± 2	55 ± 2	42 ± 2
2-MeImH	7.86[e]	81 ± 3	30 ± 3	42 ± 4	52 ± 2
2-EtImH	7.86[f]	69 ± 2	20 ± 2	36 ± 2	35 ± 4
BzImH	5.532	75 ± 4	6 ± 1	9 ± 1	65 ± 2
1-MeIm	6.95	8 ± 1	1 ± 0.3	5 ± 1	11 ± 1
Py	5.25	35 ± 3	4 ± 1	9 ± 1	90 ± 3
4-MePy	6.02	47 ± 2	10 ± 1	17 ± 2	91 ± 3
4-*t*-BuPy	5.99[g]	10 ± 1	<1	2 ± 0.5	22 ± 1
2-MePy	5.97	7 ± 1	2 ± 0.5	4 ± 1	93 ± 4
2,6-Me_2Py	6.65	9 ± 1	2 ± 0.3	5 ± 0.8	100 ± 0
4-CNPy	1.86[g]	2 ± 0.4	1 ± 0.3	2 ± 0.7	6 ± 1
None	–	<1	Trace	2	3

Et_2NH, diethylamine; Et_3N, triethylamine; ImH, imidazole; 2-MeImH, 2-methylimidazole; 2-EtImH, 2-ethylimidazole; BzImH, benzimidazole; 1-MeIm, 1-methylimidazole; Py, pyridine; 4-MePy, 4-methylpyridine; 4-*t*-BuPy, 4-*tert*-butylpyridine; 2-MePy, 2-methylpyridine; 2,6-Me_2Py, 2,6-dimethylpyridine; 4-CNPy, 4-cyanopyridine.

[a] MnPor/nitrogen donor/cyclooctene/oxidant molar ratio is 1/100/100/190 with [MnPor] = 5×10^{-4} M, in CH_2Cl_2 at 25 ± 1 °C.

[b] The reactions proceeded with 100% selectivity.

[c] The epoxidation yield (%) were measured relative to the starting cyclooctene. All the reactions were run at least in triplicate, and the data represent an average of these reactions.

[d] pK_a values obtained from Ref. [40].

[e] Ref. [41].

[f] Very little change in base strength accompanying the change of a methyl substituent to ethyl was observed (see Ref. [42]).

[g] See Ref. [43].

of the BzImH and 2-EtImH. The least hindered ImH is the best co-catalyst in the presence of all the MnPor catalysts, with the exception of MnTPFPP(OAc). In fact, the order of the co-catalytic activities of the imidazoles primarily reflect the steric hindrances of both the nitrogen donors and the MnPor catalysts. In the case of MnTMP(OAc) and MnTDCPP(OAc) the steric effects are quite pronounced, and the bulky BzImH is the least effective co-catalyst among the N–H imidazoles. For the most bulky MnTMP(OAc) catalyst, the co-catalytic effects of the N–H imidazoles were widely separated (70 ± 2 to 6 ± 1), whereas for MnTPP(OAc) the co-catalytic activities of N–H imidazoles were much closer to each other (87 ± 4 to 69 ± 2).

The good π-donating capability of the N–H imidazoles seems to play an important role in determining their greater co-catalytic activities than the strong σ-donor amines [31]. A particularly interesting case is the higher co-catalytic activity of BzImH than the stronger base amines and pyridines, in the presence of MnTPP(OAc). This is presumably due to the more extended π-system of BzImH, and its greater π-donating ability toward the Mn center of the catalyst.

The much lower co-catalytic activity of 1-MeIm than the N–H imidazoles in the presence of all the MnPor catalysts clearly demonstrates the significance of the occurrence of N–H···B (B = nitrogen donor or anionic species) hydrogen bondings in the case of the N–H imidazoles. Such interactions in the reaction solution are believed to increase substantially the donor abilities of the N–H imidazoles toward the MnPor catalysts [32–34].

The order of the co-catalytic activities of the imidazoles in the presence of MnTPFPP(OAc), BzImH > 2-MeImH > ImH > 2-EtImH ≫ 1-MeIm is sharply different from those observed for the other MnPor catalysts. This "unusual" order seems not to correspond to the simple stereoelectronic properties of the imidazole and/or MnTPFPP(OAc) complex. It is noteworthy that both BzImH and 2-MeImH are more effective co-catalysts than the less hindered ImH.

3.1.3. Pyridines

The co-catalytic behavior of the pyridines, generally, correlates well with their intrinsic basicities, and steric properties, in association with all the MnPor, except MnTPFPP(OAc). 4-MePy (pK_a = 6.02) is the best co-catalyst followed by the weaker base Py (pK_a = 5.25) in the presence of all the MnPor catalysts, except MnTPFPP(OAc). The bulky 4-*t*-Bu substituent of 4-*t*-BuPy (pK_a = 5.99) dramatically decreased its co-catalytic activity, as compared to Py and 4-MePy, in the presence of all the MnPor, including MnTPFPP(OAc). Also, in the case of 2-MePy and 2,6-Me_2Py the steric hindrance(s) of the methyl group(s), adjacent to the nitrogen donor sites, significantly decreased their co-catalytic activities, in comparison with Py, in the presence of MnTPP(OAc), MnTMP(OAc), and MnTDCPP(OAc). In contrast, when MnTPFPP(OAc) was used, 2-MePy and 2,6-Me_2Py acted as excellent co-catalysts. The 4-CNPy, with the lowest basicity, containing electron withdrawing CN group, was the weakest co-catalyst.

Pyridines with pK_a values similar to or less than those of imidazoles, and with ring sizes larger than imidazoles, are generally much weaker co-catalysts than imidazoles, in the presence of the MnPor catalysts, except for MnTPFPP(OAc) (Table 1). In par-

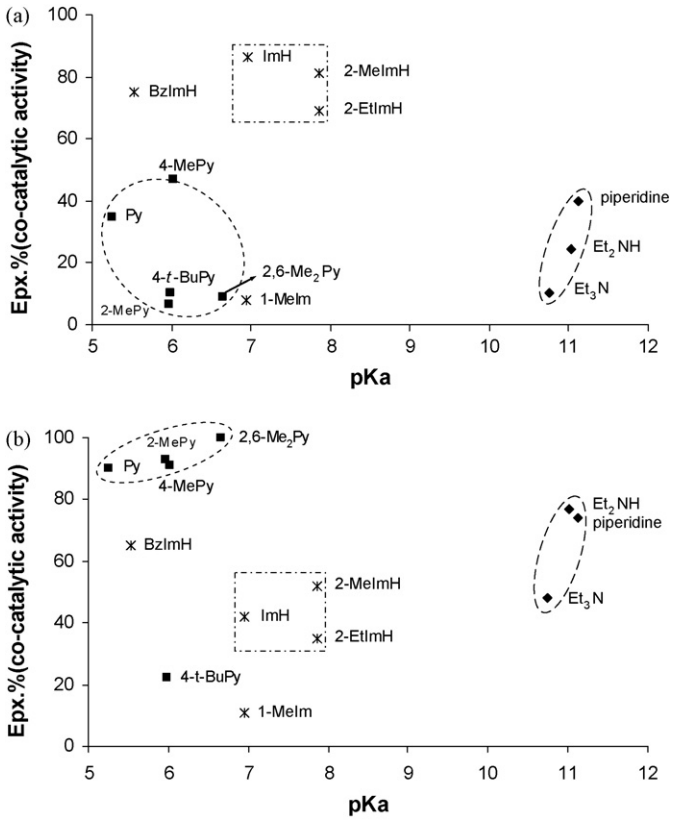

Fig. 2. Scatter diagrams for the co-catalytic activities of the nitrogen donors in the presence of (a) MnTPP(OAc) and (b) MnTPFPP(OAc).

ticular, the lower co-catalytic activities of the pyridines than the imidazoles are more pronounced when the bulky MnTMP(OAc) and MnTDCPP(OAc) are used.

Fig. 2a and b represents the scatter diagrams for the co-catalytic properties of the different classes of the nitrogen donors in the presence of MnTPP(OAc) and MnTPFPP(OAc). They clearly illustrate that the relative order of the co-catalytic activities of the pyridines and the imidazoles are reversed in the presence of these two MnPor catalysts. The scatter diagrams for MnTMP(OAc) and MnTDCPP(OAc) (not shown) resemble that of MnTPP(OAc). The inverted order of the co-catalytic activities of imidazoles versus pyridines observed in the presence of MnTPFPP(OAc) as compared to those of the other MnPor catalysts raises some serious questions concerning their causes. Here we examine how the co-catalyst/catalyst ratio can possibly affect the relative order of a number of nitrogen donors as co-catalysts, in the presence of MnTPP(OAc) and MnTPFPP(OAc) complexes.

3.2. The effect of co-catalyst/catalyst ratio

The interaction of MnPor catalysts with nitrogen donors (D) can very rapidly lead to the formation of both catalytically active 1:1 DMnPor and catalytically inactive 2:1 D_2MnPor species, with the formation constants K_1 and K_2, respectively [16]. Both K_1 and K_2 are related to the nature of MnPor and D [16]. Large steric hindrance of the species involved would lead to small K_1 and K_2, whereas high electrophilicity of MnPor and also high electron donating ability of D result in large K_1 and K_2, as expected. The concentration of the 1:1 DMnPor complex, defining the co-catalytic activity of the nitrogen donors, is presumably related to the nitrogen donor/MnPor ratio. The co-catalytic activities of six different nitrogen donors in the presence of MnTPP(OAc) and MnTPFPP(OAc), at various co-catalyst/catalyst ratios, are presented in Table 2. The general order of the co-catalytic activities of the nitrogen donors are the same, for each of the two MnPor catalysts, at all the co-catalyst/catalyst ratios (10–200) (Fig. 3). The exceptions correspond to 2-MeImH in combination with MnTPP(OAc) and 2,6-Me_2Py with MnTPFPP(OAc). The order of the co-catalytic activities of some of the nitrogen donors are very close and not distinguishable at co-catalyst/catalyst ratios ≤ 5 (Fig. 3b).

3.2.1. MnTPP(OAc)

Imidazoles were better co-catalysts than pyridines, in association with MnTPP(OAc) at all co-catalyst/catalyst ratios (10–200) (Fig. 3a). This is primarily due to the greater π-donating ability of the former than the latter ones toward the Mn center. ImH demonstrates the highest co-catalytic activities among all the nitrogen donors, at all the co-catalyst/catalyst ratios. However, its co-catalytic activity decreased at co-

Table 2
Cyclooctene epoxidation yield (%) (co-catalytic activity) for nitrogen donors in association with MnTPP(OAc) and MnTPFPP(OAc) catalysts under different co-catalyst/catalyst ratios[a,b]

Nitrogen donor	Co-catalyst/catalyst ratio						
	1	5	10	25	50	100	200
ImH	(8)[c]	(12)	36 (22)	62 (46)	85 (70)	88 (43)	77 (29)
2-MeImH	(8)	(16)	32 (30)	56 (61)	82 (74)	81 (51)	58 (35)
BzImH	(14)	(27)	20 (41)	39 (68)	67 (77)	75 (65)	71 (47)
Py	(12)	(44)	6 (75)	16 (94)	28 (98)	38 (91)	47 (76)
2-MePy	(20)	(88)	0.7 (96)	1.3 (98)	4 (98)	7 (93)	8 (85)
2,6-Me_2MePy	(10)	(28)	0.8 (70)	3 (86)	6 (94)	10 (100)	14 (100)

[a] The molar ratios for MnPor/nitrogen donor/cyclooctene/oxidant were 1/x/100/190 with x = 10, 25, 50, 100, 200 for MnTPP(OAc) and x = 1, 5, 10, 25, 50, 100, 200 for MnTPFPP(OAc) and [MnPor] = 5×10^{-4} M, in CH_2Cl_2 at 25 ± 1 °C.

[b] The epoxidation yield (%) were measured relative to the starting cyclooctene. All the reactions were run at least in triplicate, and the data represent an average of these reactions, with ±10–20%. The largest uncertainty (±20%) corresponds to some of the lower epoxidation yield (%), *i.e.*, <10.

[c] Data inside the parentheses are for MnTPFPP(OAc).

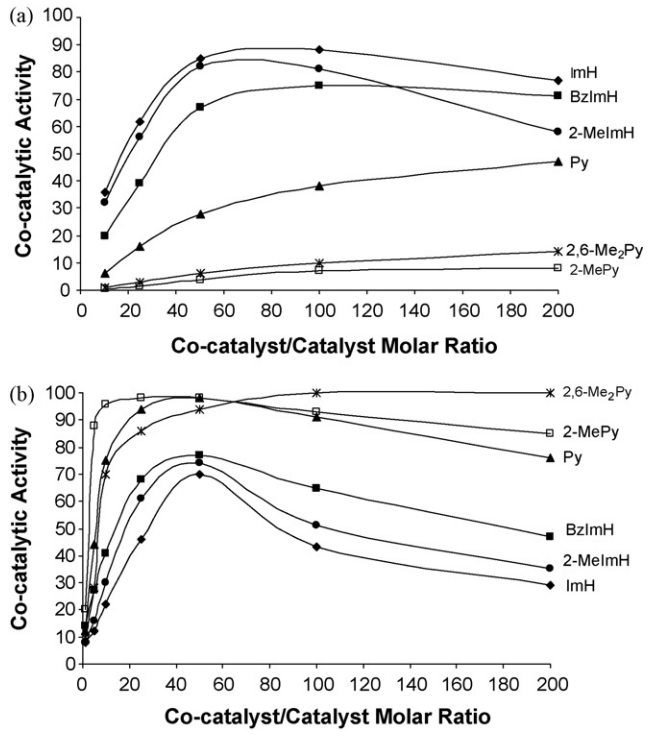

Fig. 3. Co-catalytic activities of nitrogen donors in the presence of (a) MnTPP(OAc) and (b) MnTPFPP(OAc), as a function of different co-catalyst/catalyst ratio.

catalyst/catalyst ratios > ~100. The co-catalytic activity of 2-MeImH, which is slightly less than that of ImH at co-catalyst/catalyst ratios < ~50, decreased more rapidly than ImH, at the ratios > 50. This may indicate that 2-MeImH is either more effective than ImH in forming the catalytically inactive 2:1 D_2MnTPP(OAc) complex, and/or it acts better than ImH, as a substrate, in a competitive oxidation with cyclooctene [35], at high concentrations. The co-catalytic activity of BzImH reached to its maximum value at co-catalyst/catalyst ratio of ~100, and then remained practically unchanged at the higher ratios (Fig. 3a). This suggests that the concentration of the catalytically active 1:1 DMnTPP(OAc) complex is virtually unchanged under these conditions, and BzImH is incapable of effectively forming the catalytically inactive 2:1 D_2MnTPP(OAc) species.

Among the pyridines, Py is a better co-catalyst than hindered 2,6-Me_2Py and 2-MePy, at almost all the co-catalyst/catalyst ratios, perhaps reflecting the influence of the steric effects of the latter ones. However, 2,6-Me_2Py is a slightly better co-catalyst than 2-MePy. In this case, probably the greater basicity of 2,6-Me_2Py has taken precedence over its steric hindrance. The co-catalytic activities of the pyridines increased continuously as the co-catalyst/catalyst ratios increased, indicating that the concentration of the catalytically active 1:1 DMnTPP(OAc) species was always increasing.

3.2.2. *MnTPFPP(OAc)*

Fig. 3b illustrates how the co-catalytic properties of the nitrogen donors can change by enhancing the co-catalyst/catalyst ratio, in the presence of MnTPFPP(OAc). Pyridines clearly displayed co-catalytic activities greater than imidazoles, at all co-catalyst/catalyst ratios (10–200), contrasting their behavior in the presence of MnTPP(OAc). Even at the low ratio of 5, where formation of [D_2MnTPFPP]OAc complex is of little significance, pyridines seemed to be generally better co-catalysts than imidazoles (Table 2).

Hindered 2,6-Me_2Py showed a greater co-catalytic activity than the less hindered 2-MePy, and Py at co-catalyst/catalyst ratios > ~100. The fixed co-catalytic activity of 2,6-Me_2Py at co-catalyst/catalyst ratios > ~100 may indicate the inability of 2,6-Me_2Py to produce the inactive D_2MnPor species. At co-catalyst/catalyst ratios < ~60 the co-catalytic activity of 2,6-Me_2Py was either close to or less than those of Py and 2-MePy. On the other hand, Py displayed co-catalytic activities similar to or less than that of 2-MePy at different co-catalyst/catalyst ratios (1–200), and its co-catalytic effect never exceeded that of 2-MePy. In addition, pyridines demonstrated a much sharper increase in their co-catalytic activities than imidazoles at co-catalyst/catalyst ratios < ~20. This suggests that pyridines are more efficient than imidazoles in forming the catalytically active DMnTPFPP(OAc), and/or less effective in producing D_2MnTPFPP(OAc).

The order of co-catalytic activities of imidazoles in combination with MnTPFPP(OAc) showed no changes over the entire range of the co-catalyst/catalyst ratio. BzImH was the best co-catalyst followed by hindered 2-MeImH, and the least hindered ImH acted as the weakest co-catalyst.

The larger size and greater electronegativity of F than H, should lead to more hindrance and electrophilicity at the Mn center in MnTPFPP(OAc) than MnTPP(OAc). These effects should cause the less hindered and relatively stronger nitrogen donor ImH to act more efficiently than 2,6-Me_2Py as co-catalyst, in the presence of MnTPFPP(OAc). However, this was not the case at any co-catalysts/catalyst ratio.

3.2.3. *MnT(4-NO_2P)P(OAc)*

To examine how the electrophilicity at the Mn center of MnPor catalysts can possibly affect the order of the co-catalytic activities of the nitrogen donors, we used MnT(4-NO_2P)P(OAc) as catalyst in the epoxidation of cyclooctene (Table 3). The steric hindrance at the Mn center for both MnTPP(OAc) and MnT(4-NO_2P)P(OAc) are very similar. However, the strong π-acceptor 4-NO_2 groups in MnT(4-NO_2P)P(OAc) can induce a large electrophilicity at its Mn center. It was observed that, similar to MnTPP(OAc) catalyst, imidazoles were better co-catalysts than pyridines in the presence of MnT(4-NO_2P)P(OAc), particularly, at low co-catalyst/catalyst ratios (<50) (Fig. 4). Thus, one may suspect that the higher electrophilicity of the Mn center in MnTPFPP(OAc) than MnTPP(OAc) may not be the cause of the inverted order of the co-catalytic activities of the imidazoles as compared to the pyridines.

The excellent co-catalytic activity of hindered 2,6-Me_2Py and 2-MePy in the presence of MnTPFPP(OAc) versus their very poor behavior as co-catalysts in the presence of less hindered MnTPP(OAc) and MnT(4-NO_2P)P(OAc) suggests that some attractive interactions may be operative between the C–H bonds of their methyl substituents and the *ortho*-C–F groups

Table 3
Epoxidation yield (%) (co-catalytic activity) for nitrogen donors in the epoxidation of cyclooctene with MnT(4-NO_2P)P(OAc) catalyst under various co-catalyst/catalyst ratios[a,b]

Nitrogen donor	Co-catalyst/catalyst ratio				
	10	25	50	100	200
ImH	28	54	59	45	31
2-MeImH	21	48	55	40	27
BzImH	50	81	85	75	59
Py	19	31	52	67	80
2-MePy	5	9	16	25	31
2,6-Me_2Py	13	19	28	34	40

[a] The molar ratios for MnT(4-NO_2P)P(OAc)/nitrogen donor/cyclooctene/oxidant were 1/*x*/100/190 with $x = 10$, 25, 50, 100, 200 and [MnPor] = 5×10^{-4} M, in CH_2Cl_2 at 25 ± 1 °C.

[b] The epoxidation yield (%) was measured relative to the starting cyclooctene. All the reactions were run at least in triplicate, and the data represent an average of these reactions, with ±10–20%. The largest uncertainty (±20%) corresponds to some of the lower epoxidation yield (%), *i.e.*, <10.

of MnTPFPP(OAc) [31,36]. This interaction is expected to lead to effective coordination of 2,6-Me_2Py or 2-MePy to MnTPFPP(OAc), causing their very large co-catalytic activities. It has been demonstrated that electron delocalization from C–H σ bonds into C–F σ* orbitals may account for some unrelated phenomena [37]. Accordingly, it may be that the low-lying *ortho*-C–F σ* orbitals of the pentafluoro phenyl groups in MnTPFPP(OAc) may indeed act as electron acceptors toward the C–H σ bonds of the methyl substituents of 2,6-Me_2Py. The proposed C–H···F–C interactions may actually occur between any C–H σ bonds of the nitrogen donors adjacent to their donor sites and the *ortho*-C–F σ* orbitals of MnTPFPP(OAc). However, it seems that C–H (sp^3) σ bonds of methyl substituents in the case of 2,6-Me_2Py, 2-MePy and 2-MeImH can have better contacts and stronger donor ability than C–H (sp^2) σ bonds of Py and ImH rings, toward the empty *ortho*-C–F σ* orbitals of MnTPFPP(OAc). Thus, the former may coordinate more effectively than the latter ones to MnTPFPP(OAc) and act more efficiently as co-catalysts, as it is observed. Absence of such interactions in the case of MnTPP(OAc) and MnT(4-NO_2P)P(OAc) would make the hindered 2,6-Me_2Py an extremely weak co-catalyst.

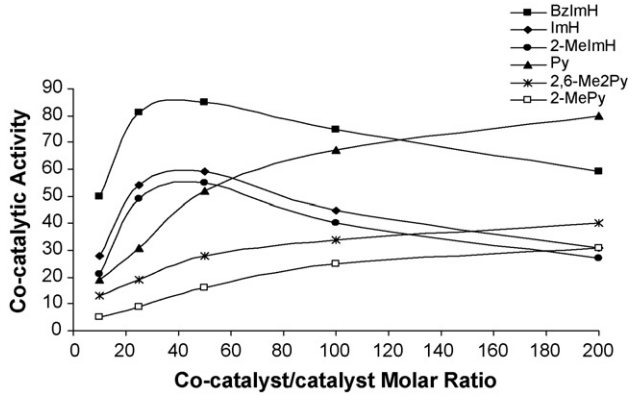

Fig. 4. Co-catalytic activities of nitrogen donors in the presence of MnT(4-NO_2P)P(OAc) under different co-catalyst/catalyst ratio.

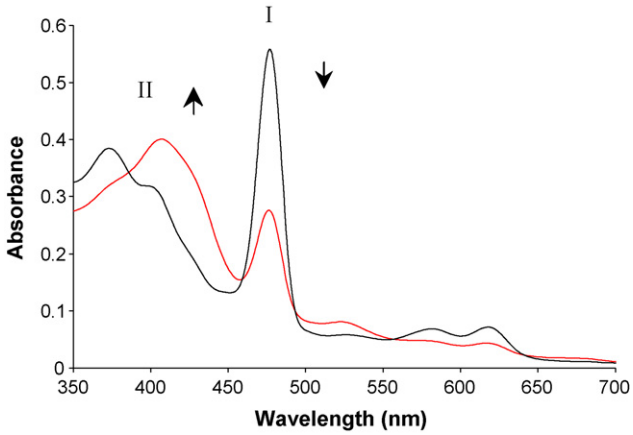

Fig. 5. The UV–vis spectra represent the conversion of (I) Mn(TPP)OAc, Soret, $\lambda_{max} = 478$ nm to an Mn-oxo species (II) (Soret, $\lambda_{max} = 406$ nm) immediately after adding both ImH (100 equiv.) and then (n-Bu_4N)HSO_5 (190 equiv.) to Mn(TPP)OAc solution (~10^{-6} M) in CH_2Cl_2, at 25 ± 1 °C.

3.3. Active oxidant

UV–vis spectra show that addition of n-Bu_4NHSO_5 (190 equiv.) to a solution of MnTPP(OAc) (~10^{-6} M) (Soret, $\lambda_{max} = 478$ nm), in CH_2Cl_2 (2 mL), containing ImH (100 equiv.), in the absence or presence of 100 equiv. cyclooctene, yield an intense Soret band, $\lambda_{max} = 406$ nm, presumably due to the formation of MnTPP(ImH)(O) species [31,38], at room temperature (Fig. 5). On the other hand, when electron deficient MnTPFPP(OAc) was employed as catalyst, a very unstable Mn-oxo (Soret, $\lambda_{max} = 428$ nm) [39] was formed transiently and then disappeared rapidly (<15 s), giving a spectrum similar to that of MnTPFPP(OAc) (Fig. 6). This suggests that, in the case of MnTPP(OAc), the active oxidizing species may involve an Mn-oxo compound, whereas for MnTPFPP(OAc), the active oxidant is perhaps predominately, the six coordinate (ImH)MnTPFPP(HSO_5) complex [29]. The employment of weak π-donor Py as co-catalyst, under similar conditions

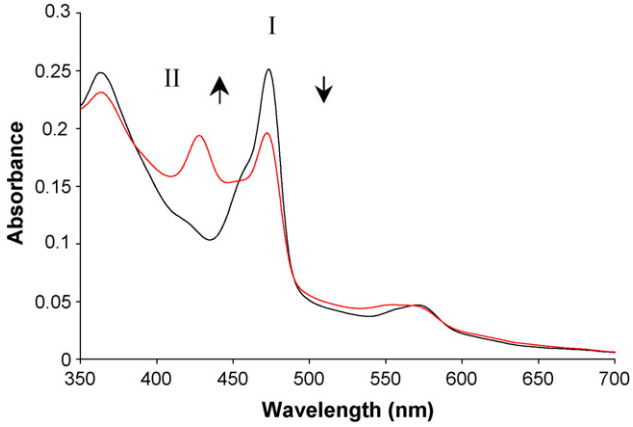

Fig. 6. The UV–vis spectra display the formation of an Mn-oxo species (II) (Soret, $\lambda_{max} = 428$ nm), with very short life time (<15 s) immediately after adding both ImH (100 equiv.) and then (n-Bu_4N)HSO_5 (190 equiv.) to Mn(TPFPP)OAc solution (~10^{-6} M) in CH_2Cl_2, Soret, $\lambda_{max} = 474$ nm, at 25 ± 1 °C.

as those for ImH, yielded no Mn-oxo species, and the spectrum of both MnTPP(OAc) and MnTPFPP(OAc) displayed no changes, indicating that the active oxygen intermediate is probably PyMnPor(HSO_5) complex. It seems that formation of an Mn-oxo species requires both a strong π-donor axial ligand, and also a non-electron deficient MnPor.

4. Conclusions

It was observed that the orders of the co-catalytic effects of the nitrogen donors were critically dependent upon the steric hindrances and electronic structures of both the nitrogen donors and MnPor catalysts. No direct general correspondence was found between the co-catalytic effects of the nitrogen donors and their pK_a (BH^+) values. While the strong π-donating N–H imidazoles displayed higher co-catalytic activities than the weak π-donor pyridines, in the presence of MnTPP(OAc), an inverted order was observed for MnTPFPP(OAc) complex. This behavior might be related to the differences in C–H···F–C contacts and interactions between the *ortho*-C–F bonds of MnTPFPP(OAc) and the C–H σ bonds adjacent to the nitrogen donors sites in pyridines as compared to imidazoles. Accordingly, it seems that one has to be very cautions about interpreting the experimental results concerning the interaction of MnTPFPP(OAc) with any nitrogen donor containing potential C–H σ bond donors. Finally, it is noteworthy that the order of the co-catalytic activities of nitrogen donors could also be greatly influenced by their relative capabilities for the formation of various DMnPor (K_1) and D_2MnPor (K_2) species.

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