

Fig. 1 Yields of nitro aromatic compounds from catalytic oxidation of aromatic amines **5–12** by Fe(tpp)Cl and Bu^tOOH in the presence of varying amounts of 1-methylimidazole: (◇) **5a**; (▲) **6a**; (●) **7a**; (□) **8a**; (■) **9a**; (△) **10a**; (×) **11a**; (○) **12a**. **1**, 10⁻³ mmol; amine, 0.1 mmol; Bu^tOOH, 0.3 mmol; solvent, CH₂Cl₂ (5 ml). Yields are for isolated nitro derivatives **5a–12a**.

At room temperature, in CH₂Cl₂ (5 ml) and in the presence of an appropriate amount of 1-methylimidazole, the conversion of **5–12** is total after 15 min, while the yields of **5a–12a** range between 93 and 15% (see Fig. 1). The products, detected by gas chromatography–mass spectrometry and gas chromatography and quantified after separation by flash chromatography were not appreciably different under aerobic or anaerobic conditions. Among the oxidation products, only the nitro aromatic compounds **5a–12a** were clearly identified.

Only in the oxidation of **12**, at -40 °C, were the corresponding azo and azoxy derivatives (arising from the intermediate formation of the hydroxylamine and the nitroso derivative) detected. This evidence and the molar ratio of amine to oxidant (1 : 3) suggest that the oxidation could follow the usual steps: amine → hydroxylamine → nitroso → nitro. However, none of these intermediate compounds was detected using higher molar ratios of amine to oxidant.

Blank experiments carried out on the amines **5** and **7–11** showed that, in the absence of catalyst or Bu^tOOH or axial ligand L, no oxidation to the nitro compounds occurs, although complete conversion of the substrates to unidentified products may occur. In contrast, **6** and **12**, even in the absence of L, gave the expected products but with longer reaction times (1.5 h). Under these conditions, the yields of *p*-nitrotoluene **6a** and *p*-nitroanisole **12a** were 64 and 17.5% respectively.

The effect of various ligands (imidazole, 1-methylimidazole, 2-methylimidazole, 4-*tert*-butylpyridine) on the yields of nitro derivatives was studied (Fig. 2). No significant differences were observed within the imidazole series, while the more weakly coordinating 4-*tert*-butylpyridine⁴ gave lower yields. The amount of added ligand for optimum yields of the nitro derivatives **5a–12a**, obtained with Fe(tpp)Cl as catalyst (Fig. 1) depends on the amine, but the best results were obtained, as a rule, with molar ratios of ligand to amine in the range 0.3–0.5 : 1, which corresponds to an initial molar ratio of ligand to metallo-porphyrin of 30–50 : 1.

These results clearly indicate that an electron-donating axial substituent coordinated to the metal is essential to force the reaction pathway towards the desired products. Indeed, the best results were obtained by using the most strongly coordinating ligand, 1-methylimidazole, whose effect is analogous to that reported on olefin epoxidation by Fe³⁺ or Mn³⁺ porphyrins in the presence of hydrogen peroxide or hypochlorite.⁵ The higher coordinative capability of the ligand L compared to the amines is evidenced by the spectral changes of the Fe(tpp)Cl Soret band at 416 nm, in the presence of 1-methylimidazole (0–40 mol. equiv.) or in the presence of

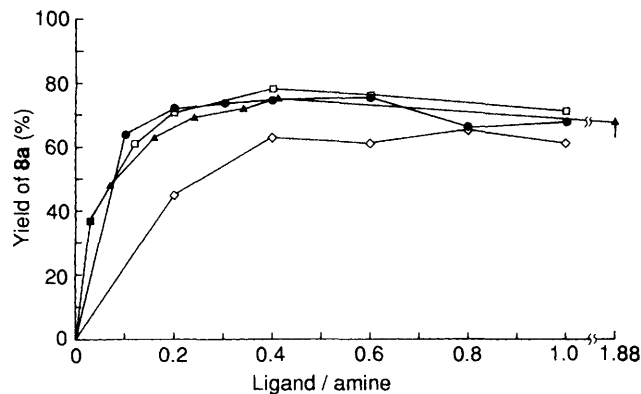


Fig. 2 Yields of *p*-ClC₆H₄NO₂ **8a** from catalytic oxidation of **8** by Fe(tpp)Cl and Bu^tOOH in the presence of varying amounts of axial ligands: (▲) imidazole; (●) 2-methylimidazole; (□) 1-methylimidazole; (◇) 4-*tert*-butylpyridine. **1**, 10⁻³ mmol; **8**, 0.1 mmol; Bu^tOOH, 0.3 mmol; solvent, CH₂Cl₂ (5 ml). Yields are for isolated **8a**.

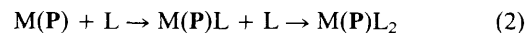
Table 1 Yields of *p*-ClC₆H₄NO₂ **8a** from catalytic oxidation of **8** in the presence of varying amounts of Fe(tpp)Cl^a

<i>t</i> /h	Cat. : 8 : Bu ^t OOH : L	Conversion (%)	Yield of 8a (%)	Turnover/h ⁻¹
0.25	1 : 10 : 30 : 4	99	73	27.6
0.25	1 : 100 : 300 : 40	100	78	312
0.25	1 : 1000 : 3000 : 400	100	64	2560
0.33	1 : 10000 : 30000 : 4000	100	63	18920
0.25	1 : 1000 : 3000 : 40	20	14	

^a **8**, 0.1 mmol; Bu^tOOH, 0.3 mmol; 1-methylimidazole (L), 0.4 mmol; Fe(tpp)Cl, 10⁻², 10⁻³, 10⁻⁴ and 10⁻⁵ mmol; solvent, CH₂Cl₂ (5 ml). Yields are for isolated **8a**. Turnover = mol of nitro compound/mol of catalyst.

toluidine (0–100 mol. equiv.), the presence of the former showing a tenfold greater effect.

The catalytic system still proved to be efficient when 10⁴ mol equiv. of amine with respect to the catalyst were used (Table 1). Very high turnovers/hour (18 900) were observed. On increasing the molar ratio of amine to catalyst, longer reaction times are needed in order to obtain the highest yield of nitro compound (entry 4, Table 1). In this case, the ratio of axial ligand to substrate must be about 0.4 : 1, *i.e.* 4000 times the amount of metallo-porphyrin. It is interesting that a very large quantity of ligand has the opposite effect in olefin epoxidation promoted by hypochlorite, hydrogen peroxide and other oxidants, which may be explained by the formation of the poorly reactive bis-ligated M(P)L₂ species⁶ [eqn. (2)].



The difference in the two systems could be due to the fact that the amine coordinates, albeit weakly, to the M(P) species whereas the olefin does not and therefore the imidazole must compete for the coordination with the amine [eqn. (3)]. Thus



the equilibrium (3) is shifted far to the right only in the presence of a large excess of L.

The reactions of the manganese(III) porphyrins **2** and **4** with the amines **6**, **8** and **12** were carried out under the same conditions as for the iron(III) complexes. Good yields of the nitro derivatives **6a** and **8a** were obtained, but longer reaction times were needed for the highest conversions (2 and 5 h, respectively). Both the manganese(III) complexes **2** and **4** are

less efficient in the oxidation of the aromatic amines to the nitro derivatives than the iron(III) complexes.

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