Manganese(III) Amide Complexes as a New Class of Catalyst for Efficient Alkene Epoxidation

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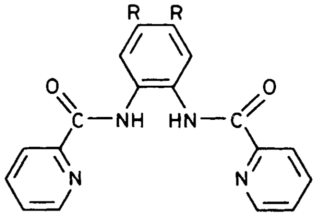
Complexation of 1,2-bis(pyridine-2-carboxamido)benzene (H_2bpb) and 1,2-bis(pyridine-2-carboxamido)-4,5-dichlorobenzene (H_2bpcb) with manganese(III) yielded [Mn^{III}(bpb)Cl], [Mn^{III}(bpb)(N_3)], and [Mn^{III}(bpcb)Cl]; the manganese(III) complexes have been found to catalyse the expoxidation of alkenes in the presence of PhIO.

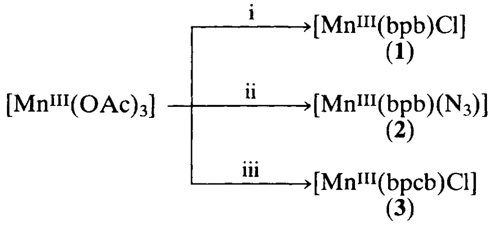
It has been suggested that the activation of dioxygen by cytochrome P-450 haemoprotein enzymes involves oxometalloporphyrin intermediates.[1] There is current interest in the design of synthetic models such as the porphyrin complexes of Fe^{III}, Mn^{III}, and Cr^{III}[2—4] as biomimics of the oxidative enzymatic reactions of cytochrome P-450. Although metalloporphyrins effect the selective oxidation of hydrocarbons, these complexes have not yet proved to be of general applicability in industry. Our recent interests concern the development of non-porphyrin type inorganic reagents that are potent synthetic oxidation catalysts. The oxidation-resistant dianionic ligand bpb[5] has been shown to be useful in the generation of highly oxidizing metal complexes; [Os^{III}(bpb)(PPh_3)Cl][6] catalysed the PhIO epoxidation of cyclohexene. We have thus explored the co-ordination chemistry of bpb with manganese, since this metal is inexpensive and well known to be crucial for oxygen evolution in the photosynthetic process,[7] and now report the synthesis and reactivity of [Mn^{III}(bpb)Cl] (**1**) and [Mn^{III}(bpb)(N_3)] (**2**), and of the complex [Mn^{III}(bpcb)Cl] (**3**) of the related dichloro substituted ligand H_2bpcb.

Refluxing [$Mn^{III}(OAc)_3$] with H_2bpb or H_2bpcb in methanolic LiX (X = Cl or N_3) for 5—10 min yielded complexes (**1**),



H_2bpb, R = H

H_2bpcb, R = Cl



Scheme 1. *Reagents:* i, H_2bpb, LiCl, MeOH, heat, ii, H_2bpb, NaN_3, MeOH, heat; iii, H_2bpcb, LiCl, MeOH, heat.

Table 1. Oxidation of organic substrates with PhIO in MeCN[a] catalysed by Mn^{III} complexes.[a]

Substrate	Product	Yield, %[b]/Turnover[c] (1)	(2)	(3)
Cyclohexene	Cyclohexene oxide	58/29	39/12	53/28
Styrene	Styrene oxide	69/64	58/49	65/60
Norbornene	*exo*-2,3-Epoxynorbornane	68/36	56/27	62/37
Toluene	Benzaldehyde	7/4	19/2	32/5

[a] Reaction for 6 h at 25 °C. [b] Based on the amount of iodobenzene (PhI) produced. [c] Turnover based on the amount of catalyst used.

(**2**), and (**3**) as brownish microcrystalline solids (Scheme 1).† They showed no ν(N–H) i.r. stretching band in the 3000—3500 cm^{-1} region, indicating deprotonation of the two amide protons.[5,6] Co-ordinated amide and pyridine stretches were found at 1610—1670 and 1580 cm^{-1} respectively. An intense i.r. band at 2050 cm^{-1} for (**2**) suggested the presence of co-ordinated azide. The measured $\mu_{eff.}$ values of 4.7—4.9 μ_B (crystalline samples, Guoy method) for (**1**), (**2**), and (**3**) are in accord with a high-spin d^4 electron configuration; the isoelectronic Mn^{III} Schiff base complexes were found to have similar magnetic moments.[8]

Catalytic oxidations were performed by stirring the Mn^{III} complex (8—12 μmol), organic substrate (1 ml), and PhIO (1 mmol) in MeCN (1 ml) at 25 °C for 6 h; results are in Table 1. The organic products were identified by g.c.–mass spectrometry and PhIO was found to be transformed into PhI after the reaction. In the absence of catalyst, only trace amounts of the epoxide and benzaldehyde (from toluene) were produced. Table 1 shows clearly that the Mn^{III} complexes offer a much better system than $[Os^{III}(bpb)(PPh_3)Cl]$ in the catalysed expoxidation of simple alkenes by PhIO. Under the same conditions, the yield of epoxide using (**1**)—(**3**) is much higher than that obtained using the Os^{III} complex (3.6% yield of cyclohexene oxide from cyclohexene).[6] The detection of cyclohexene oxide as the only product in the oxidation of cyclohexene reflects the high chemoselectivity of the manganese catalysts. Unactivated C–H bonds such as in toluene are also oxidized, although yields are moderate.

The 'Mn^{III}-bpb complexes + PhIO' system thus epoxidises alkenes under simple and mild conditions, and may provide a useful model for the design of inexpensive and efficient inorganic oxidizing materials. The exact mechanism is unknown, but it is likely that the catalytic cycle involves a high-valent oxo manganese intermediate, as in the analogous Mn–porphyrin system.[9]

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† H_2bpcb was obtained by chlorination of H_2bpb; *m/z* 389 (M^+). Satisfactory elemental analyses were obtained for (**1**)—(**3**).

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