Syntheses, Electrochemistry and Reactivities of Pyridine Amide Complexes of Chromium(III) and Manganese(III)

Wa-Hung Leung, Ji-Xiang Ma, Vivian Wing-Wah Yam, Chi-Ming Che* and Chung-Kwong Poon
Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

Reactions of anhydrous $CrCl_3$ with H_2bpb and H_2bpc [H_2bpb = 1,2-bis(pyridine-2-carboxamido)-benzene; H_2bpc = 4,5-dichloro-1,2-bis(pyridine-2-carboxamido)benzene] in dimethylformamide and manganese(III) acetate with H_2bpc in methanol, yielded the respective $[Cr^{III}(bpb)Cl]\cdot xH_2O$, $[Cr^{III}(bpc)Cl]\cdot H_2O$ and $[Mn^{III}(bpc)(O_2CMe)]$ complexes. The electrochemistry of the chromium(III) amide complexes has been studied by cyclic voltammetry. They exhibit reversible oxidation couples with E° values ranging from 0.28 to 0.80 V *vs.* ferrocenium–ferrocene. Except for $[Cr^{III}(bpb)(CN)_2]^-$ which has a quasireversible reduction couple at −1.97 V, the electrochemical reductions are irreversible. The complexes $[Cr^{III}(bpb)(H_2O)_2]ClO_4$, $[Cr^{III}(bpb)Cl(MeOH)]$ and $[Mn^{III}(bpc)(O_2CMe)]$ have been shown to catalyse olefin epoxidation by iodosobenzene. With $[Mn(bpc)(O_2CMe)]$, catalytic oxidation of alkanes by PhIO has also been observed. An oxygen-rebound mechanism involving a $Mn^V{=}O$ or a $Cr^V{=}O$ intermediate is proposed for the PhIO oxidation reactions.

The co-ordination chemistry of multianionic chelating ligands containing amide functional groups has received much attention recently.[1–3] These N-co-ordinated amide ligands, being anionic in nature, are capable of stabilizing metal complexes in high oxidation states.[2–4] Although polypeptides, dioxotetraazamacrocycles and 4,5-dichloro-1,2-bis(3,5-dichloro-2-hydroxybenzamido)benzene have been known to stabilize copper(III),[3b] nickel(III)[3a] and cobalt(IV) ions,[5] the chemistry of amide complexes of chromium,[2a] manganese and other metal systems is relatively unexplored. The numerous reports on the catalytic oxidation of organic substrates by porphyrin complexes of manganese[6–9] and chromium,[10] with terminal oxidants such as iodosoarenes, hypochlorites, hydroperoxides and amine *N*-oxides, have attracted our attention to the use of robust, anionic, non-porphyrinato complexes of manganese and chromium as catalysts for olefin epoxidation and alkane hydroxylation reactions.[11–13] The pyridine amide ligands, being inexpensive and easy to prepare, are ideal for such studies. Moreover, the chemical reactivity of this system can easily be tuned through modification of substituent groups at the pyridine ring or amide bridge. Herein are reported the syntheses and reactivities of manganese and chromium complexes of the ligands H_2bpc [4,5-dichloro-1,2-bis(pyridine-2-carboxamido)-benzene] and H_2bpb [1,2-bis(pyridine-2-carboxamido)-benzene]. The catalytic activity of the Mn–bpc and Mn–bpb complexes in alkene epoxidation has previously been communicated.[1]

Experimental

The ligand, 1,2-bis(pyridine-2-carboxamido)benzene (H_2bpb), was prepared by the literature method.[14] Dimethylformamide (dmf) was distilled over CaH_2 and stored over molecular sieve (4 Å). Acetonitrile was distilled over $KMnO_4$ and CaH_2 before use. Iodosylbenzene was prepared by hydrolysis of iodobenzene diacetate with sodium hydroxide solution as described previously.[15] Organic substrates for oxidation reactions were purified according to the literature procedure before use.[16] All other chemicals were of analytical grade and were used as received.

Syntheses.—*4,5-Dichloro-1,2-bis(pyridine-2-carboxamido)-benzene* (H_2bpc). Pyridine-2-carboxylic acid (12.5 g, 0.1 mol) and 4,5-dichloro-1,2-phenylenediamine (9.0 g, 0.05 mol) in pyridine were heated to 100 °C in an oil-bath. Triphenyl phosphite (31 g, 0.1 mol) was slowly added to the well stirred reaction mixture. After the addition process a white precipitate immediately appeared. The reaction mixture was stirred at 100 °C for 2 h and allowed to cool to room temperature. The white precipitate was collected by suction filtration, washed with ethanol and air dried. Yield 80% (Found: C, 55.7; H, 3.0; Cl, 18.1; N, 14.6. Calc. for $C_{18}H_{12}Cl_2N_4O_2$: C, 55.8; H, 3.1; Cl, 18.3; N, 14.5%). Mass spectrum: *m/z* 387.

Chromium complexes. $[Cr^{III}L(Cl)]\cdot xH_2O$ (H_2L = H_2bpb *or* H_2bpc). A mixture of anhydrous $CrCl_3$ (1.6 g, 0.01 mol) and H_2L (3.2 g, 0.01 mol) in dimethylformamide (80 cm^3) was refluxed for 4 h. The solution was then cooled to room temperature and filtered to remove traces of green residue. Water (120 cm^3) was slowly added to the filtrate to give a brown precipitate, which was collected by filtration, washed with water and propan-2-ol. Yield 3.8 g {Found: C, 43.8; H, 2.0; Cl, 21.5; N, 11.1. Calc. for $[Cr(bpc)Cl]\cdot H_2O$: C, 44.1; H, 2.1; Cl, 21.7; N, 11.4%}. The crude products, $[CrL(Cl)]\cdot xH_2O$, were used without purification for subsequent syntheses.

$[Cr^{III}L(L')_2]ClO_4$ [L′ = *pyridine* (py) *or* 4-tert-*butylpyridine* ($4Bu^t$-py)]. The complex $[CrL(Cl)]\cdot xH_2O$ (0.5 g), silver toluene-*p*-sulphonate (0.5 g) and L′ (10 cm^3) in methanol (30 cm^3) were refluxed for 1 h. The reaction mixture was then cooled to room temperature and filtered to remove the insoluble AgCl. Lithium perchlorate (3 g) was added to the filtrate, which on addition of diethyl ether gave a brownish red precipitate. Recrystallization was carried out by slow diffusion of diethyl ether into an acetonitrile solution of the crude product containing a few drops of L′. Yield 85% {Found: C, 53.6; H, 3.5; Cl, 5.9; N, 13.2. Calc. for $[Cr(bpb)(py)_2]ClO_4$: C, 53.7; H, 3.6; Cl, 5.7; N, 13.4. Found: C, 58.5; H, 4.8; Cl, 4.7; N, 11.1. Calc. for $[Cr(bpb)(4Bu^t\text{-}py)_2]ClO_4$: C, 58.6; H, 5.2; Cl, 4.8; N, 11.4%}. Λ_M (298 K, dmf)/S cm^2 mol^{-1}: $[Cr(bpb)(py)_2]ClO_4$, 91; $[Cr(bpb)(4Bu^t\text{-}py)_2]ClO_4$, 91. UV/VIS(dmf), λ_{max}/nm (log ε): $[Cr(bpb)(py)_2]ClO_4$, 270 (4.32), 336 (4.04) and 432(sh) (3.61); $[Cr(bpb)(4Bu^t\text{-}py)_2]ClO_4$, 268 (4.22), 341 (3.84) and 460(sh) (3.20).

$[Cr^{III}(bpb)Cl(MeOH)]$. A methanolic suspension of $[Cr(bpb)Cl]\cdot xH_2O$ (0.1 g in 20 cm^3) was refluxed in methanol for 20 min. Upon cooling a deep red solid was obtained. The crude product was recrystallized from methanol. Yield 90%. The structure of $[Cr(bpb)Cl(MeOH)]$ has been established by X-ray crystallography.[1d]

$[Cr^{III}L(H_2O)_2]ClO_4$ (L = bpb *or* bpc). The complex

$[CrL(Cl)]\cdot xH_2O$ (0.5 g) in 0.05 mol dm^{-3} NaOH solution (50 cm^3) was heated to boiling for 20 min. The resulting clear solution was allowed to cool to room temperature. Upon addition of perchloric acid (1 mol dm^{-3}, 100 cm^3) a brown solid was obtained. This was collected by suction filtration, washed with water and dissolved in water–acetone (1:3 v/v). Upon slow evaporation of acetone, brownish yellow crystals of $[CrL(H_2O)_2]ClO_4$ gradually deposited. Yield 70–80%. IR(Nujol mull, cm^{-1}): ν(O–H) 3400–2600(br) {Found: C, 41.6; H, 3.4; Cl, 6.7; N, 10.4. Calc. for $[Cr(bpb)(H_2O)_2]ClO_4\cdot H_2O$: C, 41.4; H, 3.5; Cl, 6.8; N, 10.7. Found: C, 37.7; H, 2.5; Cl, 18.4; N, 9.8. Calc. for $[Cr(bpc)(H_2O)_2]ClO_4$: C, 37.6; H, 2.5; Cl, 18.6; N, 9.8%}. Λ_M (298 K, dmf)/S cm^2 mol^{-1}: $[Cr(bpb)(H_2O)_2]ClO_4\cdot H_2O$, 86; $[Cr(bpc)(H_2O)_2]ClO_4$, 85. UV/VIS(dmf), λ_{max}/nm (log ε): $[Cr(bpb)(H_2O)_2]ClO_4\cdot H_2O$, 268 (4.23), 335 (3.88) and 430(sh) (3.48); $[Cr(bpc)(H_2O)_2]ClO_4$, 269 (4.44), 330 (4.06) and 420(sh) (3.64).

$[Cr^{III}(bpb)Cl(L')]$ [L′ = py *or 4-methylpyridine* (4Me-py)]. The complex $[Cr(bpb)Cl]\cdot xH_2O$ (0.1 g) in L′ (10 cm^3) was refluxed for 15 min. The solution was then cooled to room temperature. Addition of diethyl ether gave a reddish brown precipitate. Yield 90% {Found: C, 57.5; H, 3.3; Cl, 7.6; N, 14.4. Calc. for [Cr(bpb)(py)Cl]: C, 57.3; H, 3.6; Cl, 7.4; N, 14.5. Found: C, 57.7; H, 3.8; Cl, 7.1; N, 14.1. Calc. for [Cr(bpb)(4Me-py)Cl]: C, 58.0; H, 3.9; Cl, 7.1; N, 14.1%}. Λ_M (298 K, dmf)/S cm^2 mol^{-1}: [Cr(bpb)(py)Cl], 4; [Cr(bpb)(4Me-py)Cl], 2. UV/VIS(dmf), λ_{max}/nm (log ε): [Cr(bpb)(py)Cl], 268 (4.18), 341 (3.79) and 430(sh) (3.39); [Cr(bpb)(4Me-py)Cl], 269 (4.18), 340 (3.80) and 435(sh) (3.41).

$Na[Cr^{III}(bpb)(NCO)_2]\cdot H_2O$. A mixture of $[Cr(bpb)Cl]\cdot xH_2O$ (0.3 g) and NaNCO (0.5 g) in acetone (60 cm^3) was refluxed for 4 h. The reaction mixture was then filtered to remove the excess of NaNCO and rotary evaporated to dryness. The residue was dissolved in pyridine and, upon slow diffusion of diethyl ether, dark brown crystals of $Na[Cr(bpb)(NCO)_2]\cdot H_2O$ were obtained. Yield 60%. IR(Nujol mull, cm^{-1}): ν(C≡N) 2200 {Found: C, 48.5; H, 3.0; N, 16.8. Calc. for $Na[Cr(bpb)(NCO)_2]\cdot H_2O$: C, 48.7; H, 2.8; N, 17.0%}. Λ_M (298 K, MeOH)/S cm^2 mol^{-1}: 80. UV/VIS(dmf), λ_{max}/nm (log ε): 269 (4.29), 341 (3.93 and 415(sh) (3.62).

$K[Cr^{III}(bpb)(CN)_2]\cdot 3H_2O$. A mixture of $[Cr(bpb)(H_2O)_2]ClO_4$ (0.2 g) and KCN (0.2 g) in methanol (15 cm^3) was refluxed for 25 min. The solution was cooled to room temperature and filtered. Slow diffusion of diethyl ether into the filtrate gave red crystals of $K[Cr(bpb)(CN)_2]\cdot 3H_2O$. Yield 80%. IR(Nujol mull, cm^{-1}): ν(C≡N) 2225 and 2208w {Found: C, 46.6; H, 3.4; N, 16.1. Calc. for $K[Cr(bpb)(CN)_2]\cdot 3H_2O$: C, 46.9; H, 3.5; N, 16.4%}. Λ_M (298 K, MeOH)/S cm^2 mol^{-1}: 71, UV/VIS(dmf), λ_{max}/nm (log ε): 268 (4.26), 288(sh) (4.04), 347 (3.95) and 448(sh) (3.57).

$[Cr^{III}(bpb)(PBu_3)_2]ClO_4$. This was similarly prepared with similar yield as for $K[Cr(bpb)(CN)_2]\cdot 3H_2O$ except that tributylphosphine was used instead of NaCN {Found: C, 57.4; H, 7.3; Cl, 4.0; N, 6.3. Calc. for $[Cr(bpb)(PBu_3)_2]ClO_4$: C, 57.8; H, 7.6; Cl, 4.1; N, 6.4%}. Λ_M (298 K, dmf)/S cm^2 mol^{-1}: 80. UV/VIS(dmf), λ_{max}/nm (log ε): 268 (4.28), 335 (3.94) and 422(sh) (3.61).

Manganese complexes. $[Mn^{III}(bpc)(O_2CMe)]$. A methanolic suspension (30 cm^3) of H_2bpc (0.5 g), $[Mn(O_2CMe)_3]\cdot 2H_2O$ (0.8 g) and $Na(O_2CMe)$ (0.4 g) was heated for 10 min and filtered. Upon standing at room temperature, a yellow microcrystalline solid gradually deposited. This was collected by suction filtration, washed with water and methanol. Yield 70% {Found: C, 47.2; H, 2.95; N, 11.3. Calc. for $[Mn(bpc)(O_2CMe)]\cdot MeOH$: C, 47.4; H, 3.2; N, 10.5%}, μ_{eff} (Gouy method, solid sample) ≈ 5.1. UV/VIS(MeOH), λ_{max}(nm): 365. IR(Nujol mull, cm^{-1}): ν(C=O) 1630.

$[Mn^{III}(bpc)(N_3)]$. A methanolic suspension (30 cm^3) of H_2bpc (0.4 g), $[Mn(O_2CMe)_3]\cdot 2H_2O$ (0.8 g), and $Na(O_2CMe)$ (0.5 g) was refluxed for 10 min and filtered. To the filtrate was added $Na(N_3)$ (0.4 g) and the solution was heated for a further 15 min. The brown microcrystalline solid formed was filtered off and washed with water and methanol. Yield 80% (Found: C, 44.9; H, 2.1; N, 20.5. Calc. for $C_{18}H_{10}Cl_2MnN_7O_2$: C, 44.8; H, 2.1; N, 20.3%), μ_{eff} (Gouy method, solid sample) ≈ 4.53. UV/VIS(dmf), λ_{max}/nm (log ε): 360(br) (2.98). IR(Nujol mull, cm^{-1}): ν(C=O) 1630, ν(N_3) 2020.

$[Mn^{III}(bpc)Cl]$. A mixture of $MnCl_2$ (0.5 g), H_2bpc (0.5 g) and 2,4,6-trimethylpyridine (1 cm^3) in methanol (30 cm^3) was heated for 20 min. This was filtered and allowed to cool to room temperature. The yellow solid formed was filtered off and washed with methanol. Yield 10% (Found: C, 44.3; H, 2.1; Cl, 22.0; N, 11.9. Calc. for $[C_{18}H_{10}Cl_3MnN_4O_2$: C, 44.6; H, 2.3; Cl, 22.4; N, 11.6%). IR(Nujol mull, cm^{-1}): ν(C=O) 1630.

$[\{Mn^{IV}(bpc)(OH)\}_2O]$. To a methanolic suspension of $[Mn(bpc)(O_2CMe)]$ (0.2 g in 30 cm^3) was added an excess of PhIO (1 g). The mixture was stirred for 15 min, filtered and left to stand at room temperature for 1 d. The dark microcrystalline solid formed was filtered off and washed with methanol. Yield 10% (Found: C, 45.7; H, 2.2; N, 11.9. Calc. for $C_{36}H_{22}Cl_4Mn_2N_8O_7\cdot H_2O$: C, 45.6; H, 2.6; N, 11.8%), μ_{eff} (Gouy method, solid sample) ≈ 1.9. IR(Nujol mull, cm^{-1}): ν(C=O) 1630.

Physical Measurements.—The UV/VIS absorption spectra were recorded on a Shimadzu UV-240 spectrophotometer, IR spectra as Nujol mulls on a Perkin-Elmer 577 spectrophotometer. Magnetic susceptibility measurements were done by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. GLC was performed on a Varian model 940 gas chromatograph. Proton NMR spectra were recorded on a JEOL model FX 90Q spectrometer (90 MHz).

Cyclic voltammetric experiments were carried out using a Princeton Applied Research (PAR) model 175 universal programmer, model 173 potentiostat and model 179 digital coulometer. An Ag–$AgNO_3$ (0.1 mol dm^{-3} in MeCN) electrode was used as the reference electrode. The working electrode was either glassy carbon or pyrolytic graphite. The ferrocenium–ferrocene couple was used as the internal standard. Elemental analyses were performed by Butterworth Laboratories.

Catalytic Oxidation Reactions.—All catalytic oxidation reactions were carried out at room temperature and under argon using Schlenk techniques. In a typical run using manganese complexes as catalysts, a mixture of catalyst (10 μmol), PhIO (0.1 mmol) and organic substrate (0.2 cm^3, *ca.* 2 mmol) in solvent (MeCN or C_6H_6) (2 cm^3) was stirred at room temperature and under argon for 4 h. For the chromium complexes a typical run would involve $[Cr(bpb)(H_2O)_2]ClO_4$ or [Cr(bpb)Cl(MeOH)] (10 μmol), PhIO (0.2 mmol) and organic substrate (liquid, 0.5 cm^3; norbornene, 0.25 g; *trans*-stilbene, 0.5 g) in MeCN (2 cm^3), stirred at room temperature and under argon until all the suspended PhIO disappeared (3–4 h). The organic products were quantified by gas chromatography using the internal standard method. The yield for the PhIO oxidation was based on the amount of iodobenzene formed, with corrections for self-decompositions in the absence of catalysts in blank runs. Products for the catalytic oxidation of stilbenes were analysed by ^1H NMR spectroscopy using 1,1-diphenylethylene as internal standard.

Results and Discussion

Syntheses.—The ligands, H_2bpb and H_2bpc, were conveniently prepared by a one-pot synthesis.[14] Unlike the phenylene-bridged H_2bpb, H_2bpc is only sparsely soluble in most organic solvents. Because of the two chloro substituents, the two amido groups are found to be more acidic than that in H_2bpb and hence easily undergo deprotonation and co-ordinate to transition-metal ions.

Anhydrous $CrCl_3$ offers a good starting material for metal insertion reactions. It reacts with H_2L (L = bpb or bpc) to give $[CrL(Cl)]\cdot xH_2O$. Ligand-substitution reactions of $[CrL(Cl)]\cdot xH_2O$ with B (B = MeOH, py or 4Bu^t-py) and X^- (X = NCO

Table 1 Cyclic voltammetric data for chromium(III) amide complexes in acetonitrile[a]

Complex	$E_{\frac{1}{2}}{}^{b}$/V	$E_{p_c}{}^{b,c}$/V
H_2bpb	1.03[d]	−2.19
Na[Cr(bpb)(NCO)$_2$]	0.31	−2.02
K[Cr(bpb)(CN)$_2$]	0.30	−1.97[e]
[Cr(bpb)(py)$_2$]ClO$_4$	0.68	−1.33
[Cr(bpb)(4Bu^t-py)$_2$]ClO$_4$	0.65	−1.46
[Cr(bpb)(PBu$_3$)$_2$]ClO$_4$	0.58	−1.74
[Cr(bpb)(py)Cl]	0.46	−1.70
[Cr(bpb)(4Me-py)Cl]	0.48	−1.61
[Cr(bpc)(4Bu^t-py)$_2$]ClO$_4$	0.80	−1.34

[a] Working electrode, glassy carbon; supporting electrolyte, 0.1 mol dm^{-3} NEt_4BF_4; scan rate, 50 mV s^{-1}. [b] *vs.* Ferrocenium–ferrocene. [c] Irreversible reduction. [d] Irreversible oxidation; the potential is quoted for E_{p_a}. [e] A quasireversible reduction couple is observed for [Cr(bpb)(CN)$_2$]$^-$.

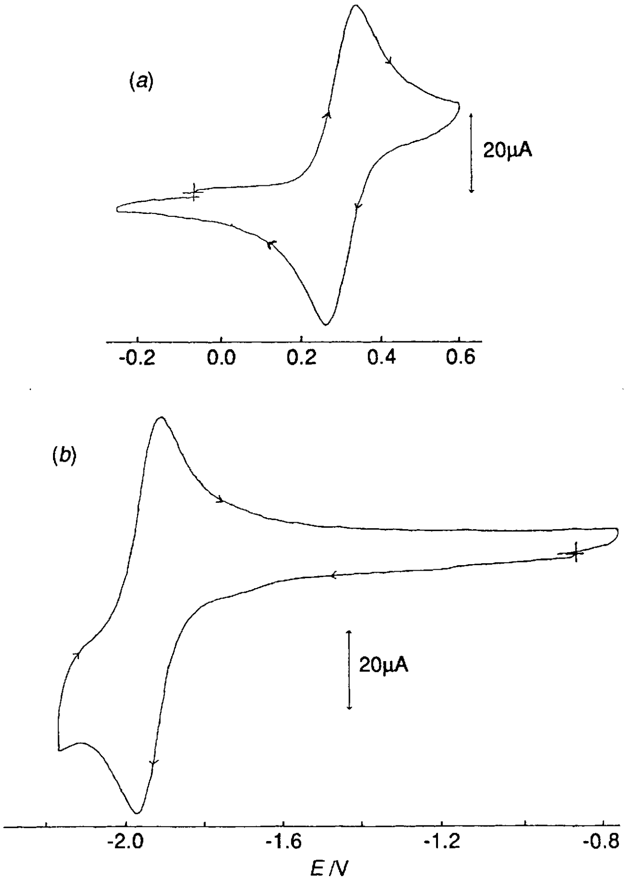

Fig. 1 Cyclic voltammograms of K[Cr(bpb)(CN)$_2$]·3H_2O in acetonitrile illustrating (*a*) reversible oxidation and (*b*) reduction reactions. Working electrode, glassy carbon; supporting electrolyte, 0.1 mol dm^{-3} NEt_4BF_4; scan rate, 50 mV s^{-1}. Potentials *vs.* ferrocenium–ferrocene

or CN) yielded the respective [CrL(B)Cl] and [CrL(X)$_2$]$^-$ complexes. The [CrL(B)$_2$]$^+$ complexes (B = py, 4Bu^t-py or PBu$_3$) could easily be prepared from [CrL(H_2O)$_2$]$^+$, obtained by the reaction of [CrL(Cl)]·$x$$H_2O$ with NaOH or Ag$^+$. All chromium(III) amide complexes are highly coloured and air-stable solids. The absence of the ν(N–H) stretches at *ca.* 3400–3150 cm^{-1} and the presence of intense bands at 1650–1550 cm^{-1} in the IR absorption spectra of the metal complexes established that the co-ordinated amide ligands are deprotonated. Magnetic susceptibility measurements showed that the chromium(III) complexes are high spin [$(t_{2g})^3$] with μ_{eff} values of 3.7–3.8. Their electronic absorption spectra exhibit intense charge-transfer (L→Cr) bands in the 300–500 nm region.

The Mn^{III}–bpc complexes are prepared in high yields from manganese(III) acetate and H_2bpc in methanol. Magnetic susceptibility measurements with μ_{eff} of 4.6 and 5.1 established the high-spin d^4 ground-state electronic configuration of the metal complexes. The complexes are likely to be five-co-ordinated. Their IR spectra in the regions 3400–3150 and 1650–1550 cm^{-1}, as in the case for the chromium system, also suggest that the co-ordinated amide ligands are deprotonated.

Electrochemistry.—The cyclic voltammogram of K[Cr(bpb)(CN)$_2$]·3H_2O in acetonitrile shows reversible oxidation and reduction couples ($\Delta E_p \approx$ 60–75 mV, scan rate 50–200 mV s^{-1}) at +0.30 and −1.97 V *vs.* ferrocenium–ferrocene respectively (Fig. 1). Both the current function ($i_{p_a}/\sqrt{v}$) and current ratio ($i_{p_a}/i_{p_c} \approx 1$) for these two couples are independent of scan rate (50–200 mV s^{-1}), indicating a simple one-electron transfer process for the electrode reactions. Other Cr^{III}–bpb complexes also exhibit reversible oxidation couples, but their reduction waves are irreversible (Table 1).

The electrochemical oxidation and reduction of Cr^{III}–bpb complexes show a strong dependence on the nature of the axial ligands (Table 1). The reduction of [Cr(bpb)(py)$_2$]$^+$ at −1.33 V is necessarily metal-centred since the free ligand, H_2bpb, is reduced at a potential as negative as −2.2 V. Moreover, upon changing the central metal ion to Rh^{III} in [Rh(bpb)(py)$_2$]ClO$_4$,[17] the reduction wave is found to shift to −1.70 V *vs.* ferrocenium–ferrocene. The sensitivity of E_{p_c} values to the nature of the metal ion suggests the reduction wave is metal-centred in nature. The small anodic shift of E_{p_c} from [Cr(bpb)(4Bu^t-py)$_2$]$^+$ to [Cr(bpc)(4Bu^t-py)$_2$]$^+$ is also in accordance with the formulation that the reduction is metal-centred ($Cr^{III} + e^- \longrightarrow Cr^{II}$) but not ligand-centred. The irreversible nature of the reduction wave in the Cr^{III}–bpb system has also been observed in the isoelectronic [Cr(tpp)X] system (H_2tpp = *meso*-5,10,15,20-tetraphenylporphyrin) in non-co-ordinating solvents.[18]

For the oxidation couples, the actual site of electron transfer is controversial. Although the free ligand, H_2bpb, is oxidized at 1.03 V *vs.* ferrocenium–ferrocene, oxidation of the π-unsaturated dianionic bpb ligand could occur at a much lower potential. From Table 1 it is obvious that the oxidation potentials increase with charge on the metal complexes. For complexes bearing the same charge the difference in $E°$ is small. This indicates the dominance of the potential-energy terms in charging the complexes over the effect of donor strength of the axial ligands. Similar $E°$ values have been observed for the oxidaton of other M^{III}–bpb complexes (M = Os, Co or Rh),[1,17,18] suggesting that the oxidation of Cr^{III}–bpb complexes is essentially ligand-centred. Controlled-potential electrolysis of [Cr(bpb)(CN)$_2$]$^-$ in acetonitrile at +0.5 V *vs.* ferrocenium–ferrocene revealed that the oxidation current did not decay after 1 C had been passed. At this stage the solution appeared green and its electronic absorption spectrum exhibited a broad band at 600–650 nm. Similar optical spectra have been obtained upon cerium(IV) and electrochemical oxidation of the bpb complexes of Co^{III} (ref. 18) and Rh^{III}.[17] Thus it is likely that the oxidation of Cr^{III}–bpb complexes is largely ligand-centred. For the Cr^{III}–bpc system the $E°$ values are *ca.* 150 mV more anodic than those for the corresponding bpb complexes. This is understandable since chloro substitution on the benzene ring would render it less susceptible to oxidation.

Attempts to study the electrochemical behaviour of the Mn^{III}–bpc complexes were unsuccessful owing to their limited solubilities in most common solvents.

Catalytic Epoxidation of Olefins by PhIO.—Table 2 summarizes the results of PhIO epoxidation reactions catalysed by [Cr(bpb)(H_2O)$_2$]ClO$_4$, [Cr(bpb)Cl(MeOH)] and [Mn(bpc)(O_2CMe)] in acetonitrile. In general, the manganese complexes are much more active catalysts as reflected by the shorter reaction time. For example, in the catalytic oxidation of

Table 2 Oxidation of olefins by PhIO catalysed by pyridine amide complexes of chromium(III) and manganese(III) in degassed acetonitrile

Complex	Substrate	Product	Yield (%)[a]
$[Cr(bpb)(H_2O)_2]ClO_4$	Norbornene	*exo*-2,3-Epoxynorbornane	70
	Styrene	Styrene oxide	47
	Cyclohexene	Cyclohexene oxide	23
		Cyclohex-2-en-1-one	2
		Cyclohex-2-en-1-ol	1
	Cyclooctene	Cyclooctene oxide	44
	trans-Stilbene	*trans*-Stilbene oxide	22
		cis-Stilbene oxide	7
	cis-Stilbene	*trans*-Stilbene oxide	18
		cis-Stilbene oxide	5
$[Cr(bpb)Cl(MeOH)]$	Norbornene	*exo*-2,3-Epoxynorbornane	55
	Styrene	Styrene oxide	44
	Cyclohexene	Cyclohexene oxide	14
		Cyclohex-2-en-1-one	6
		Cyclohex-2-en-1-ol	5
	Cyclooctene	Cyclooctene oxide	31
	trans-Stilbene	*trans*-Stilbene oxide	19
		cis-Stilbene oxide	6
	cis-Stilbene	*trans*-Stilbene oxide	17
		cis-Stilbene oxide	5
$[Mn(bpc)(O_2CMe)]$	Norbornene	*exo*-2,3-Epoxynorbornane	60
	Norbornene[b]	*exo*-2,3-Epoxynorbornane	60
	Norbornene[c]	*exo*-2,3-Epoxynorbornane	58
	Norbornene[d]	*exo*-2,3-Epoxynorbornane	15
	Styrene	Styrene oxide	85
	Styrene[c]	Styrene oxide	80
	Cyclohexene	Cyclohexene oxide	44
		Cyclohex-2-en-1-one	24
		Cyclohex-2-en-1-ol	11
	Hex-1-ene	1,2-Epoxyhexane	36
	trans-Stilbene	*trans*-Stilbene oxide	46
		cis-Stilbene oxide	Trace
	cis-Stilbene	*trans*-Stilbene oxide	49
		cis-Stilbene oxide	17

[a] Based on PhIO reacted; self-decomposition of PhIO has been taken into account. [b] In the presence of ionol. [c] MeCN as solvent and in the presence of air. [d] Degassed MeOH as solvent.

norbornene the reaction times for the complete consumption of PhIO were 40 min and 3 h, respectively, for the $[Mn(bpc)(O_2CMe)]$ and $[Cr(bpb)Cl(MeOH)]$ systems. Epoxides were detected in high yields in most cases. In the absence of the metal complexes or PhIO, no epoxide was found under similar reaction conditions. In the oxidation of styrene and norbornene, styrene oxide and *exo*-2,3-epoxynorbornane were formed, respectively, without oxidative cleavage of the C=C double bond. With cyclohexene the major product was cyclohexene oxide although minor products, cyclohex-2-en-1-one and cyclohex-2-en-1-ol, arising from oxidation of the allylic C–H bond, were also found. With terminal aliphatic olefins such as hex-1-ene, which are notoriously resistant to oxidation, only the manganese complexes are effective in bringing about oxidation and the epoxidized product was formed in moderate yield. The oxidation of stilbenes was found to be non-stereoretentive. In the catalytic oxidation of *trans*- and *cis*-stilbene a mixture of *cis*- and *trans*-stilbene oxides was obtained with the latter being the major product. Radical scavengers such as ionol (4-methyl-2,6-di-*tert*-butylphenol) and dioxygen were found to have no effect on the oxidation reactions. The PhIO oxidation chemistry of these chromium(III) and manganese(III) complexes is different from that of the $[Fe^{III}(tpp)Cl]$ system, where *trans*-stilbene was found to be relatively unreactive and the oxidation of *cis*-stilbene was stereoretentive.[19] Neither are they similar to the $[Cr^V(salen)O]^+$ system [salen = ethylenebis(salicylideneiminate)],[11] which reacts with *cis*-stilbene to give 44% *cis*- and 3% *trans*-stilbene oxides.

Previous work has shown that the reactions of PhIO with complexes of Cr^{III} and Mn^{III}, such as $[Cr(tpp)Cl]$,[10] $[Cr(salen)(H_2O)_2]^+$,[11] $[Mn(salen)]^+$,[12] and $[Mn(tpp)]^+$,[6,20] yielded the corresponding $Cr^V{=}O$ and $Mn^V{=}O$ species, which are responsible for olefin epoxidation reactions. Kochi and co-workers[11] recently reported the X-ray crystal structure of $[Cr^V(salen)O]^+$ which has been found to be reactive toward olefins. We believe that a similar high-valent manganese or chromium intermediate is involved in the catalytic oxidation.

The fact that other Cr^{III}–bpb complexes such as $[Cr(bpb)(py)_2]^+$ and $[Cr(bpb)(CN)_2]^-$ showed very low catalytic activities is understandable, since they do not have vacant co-ordination sites for reactions with PhIO. The lack of stereospecificity in the oxidation of stilbene suggested a radical or cation-radical mechanism for the reaction.[20] The observed ratio of *cis*-stilbene oxide:*trans*-stilbene oxide (*ca.* 1:3) (Table 2) is higher than that found in the manganese porphyrin system (1:1.9).[6b] The finding that the yields of epoxidation are insensitive to dioxygen and radical traps has also been observed in related studies using manganese(III) porphyrin as catalyst.[6c]

Fig. 2 shows the time course of the PhIO oxidation of norbornene by $[Mn^{III}(bpc)(O_2CMe)]$ in acetonitrile. Ten equivalents of PhIO were consumed in *ca.* 30 min and iodobenzene and *exo*-2,3-epoxynorbornane were formed quantitatively. No induction period was observed. Addition of a further portion of PhIO regenerated the catalytic cycle though with a lower yield. Similar observations have been made in the $[Cr^{III}L(H_2O)_2]^+$ (L = bpb or bpc) case. The longer reaction time and lower yield of oxidation in the second catalytic cycle indicated that the activities of the complexes diminish after every catalytic oxidation process, possibly as a result of some degradative side reactions. For the oxidation of styrene, similar product yields and reaction time are observed for both bpb and bpc complexes. Owing to the higher solubility of $[Mn(bpc)(O_2CMe)]$ in

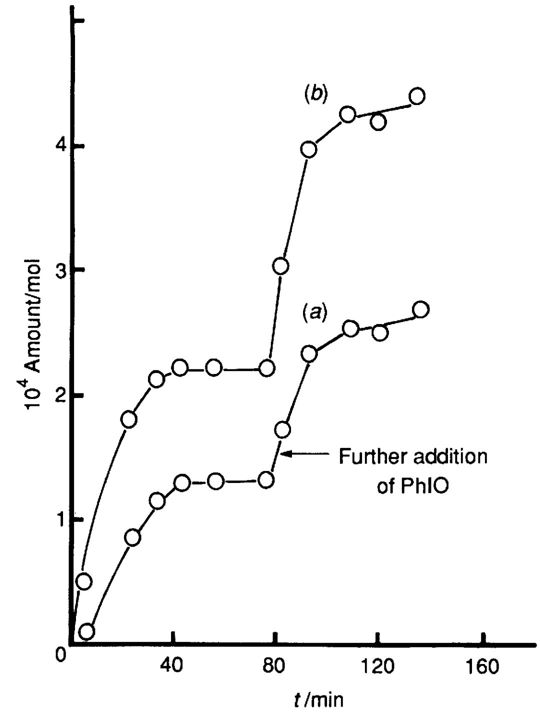

Fig. 2 Time course of the catalytic oxidation of norbornene by PhIO with $[\mathrm{Mn^{III}(bpc)(O_2CMe)}]$ in acetonitrile. Products: (*a*) norbornene oxide; (*b*) PhI

methanol than in acetonitrile, the catalytic oxidation of norbornene in methanol was found to be more rapid (*ca.* 10 *vs. ca.* 30 min in MeCN) but with a lower yield (15%) under the same conditions. Presumably methanol was also oxidized during the reaction.

Addition of PhIO to an acetonitrile solution of $[\mathrm{Cr(bpb)(H_2O)_2}]\mathrm{ClO_4}$ resulted in immediate darkening of the solution, which was restored to the original brown colour of the chromium(III) complex upon addition of norbornene. Attempts to isolate the reactive $\mathrm{Cr^V{=}O}$ intermediate have been unsuccessful. Similarly, addition of PhIO to a methanolic solution of $[\mathrm{Mn(bpc)(O_2CMe)}]$ caused an immediate darkening of the solution. The UV/VIS spectral change upon addition of PhIO is accompanied by an increase in absorbance in the 550 nm region. The same spectral change was also obtained with *m*-chloroperoxybenzoic acid as the oxidant. A similar spectral change was reported for the related $[\mathrm{Mn^{III}(salen)}]^+$ catalyst in which oxomanganese(V) was suggested to be the intermediate product in the PhIO oxidation.[12] Probably the manganese(III) complex reacted rapidly with PhIO to give an oxomanganese(V) intermediate. However, attempts to isolate this reactive intermediate were unsuccessful as it was found to degrade with time. The absorbance at *ca.* 550 nm decreased gradually with concomitant precipitation of an insoluble brown solid, the rate of which was accelerated by the addition of olefin to the solution. Elemental analyses of this insoluble material suggested its formulation as $[\{\mathrm{Mn(bpc)(OH)}\}_2\mathrm{O}]$. Furthermore, magnetic susceptibility measurement ($\mu_{\mathrm{eff}} = 1.9$) established that it is likely to be an antiferromagnetically coupled manganese(IV) species with ground state $S = \frac{1}{2}$. A similar μ_{eff} (1.88) is found for the low-spin $[\{\mathrm{Mn^{IV}(tpp)(N_3)}\}_2\mathrm{O}]$,[21] which was also prepared by PhIO oxidation. The $[\{\mathrm{Mn^{IV}(bpc)(OH)}\}_2\mathrm{O}]$ complex exhibits an IR absorption spectrum virtually identical to that of $[\mathrm{Mn^{III}(bpc)(O_2CMe)}]$ except with a band at 850 $\mathrm{cm^{-1}}$. Thus the bpc ligand remained intact during the oxidation. However, the poor solubility of $[\{\mathrm{Mn(bpc)(OH)}\}_2\mathrm{O}]$ in most common solvents prevents further characterization. Since neutral metal–bpc complexes are known to have low solubilities in common organic solvents, we believe that the initial clear brown solution resulting from the PhIO oxidation of $[\mathrm{Mn(bpc)(O_2CMe)}]$ is likely due to the formation of a more soluble cationic $[\mathrm{Mn^V(bpc)O}]^+$ complex, which gradually undergoes degradation and is precipitated as $[\{\mathrm{Mn^{IV}(bpc)(OH)}\}_2\mathrm{O}]$, equations (1) and (2).

Table 3 Oxidation of alkanes by PhIO catalysed by $[\mathrm{Mn(bpc)(O_2CMe)}]$ in degassed acetonitrile

Substrate	Product	Yield (%)[a]
Cyclohexane	Cyclohexanone	8
	Cyclohexanol	48
Cyclohexane[b]	Cyclohexanone	8
	Cyclohexanol	47
Cyclohexane[c]	Cyclohexyl chloride	Sole product
2,3-Dimethylbutane	2,3-Dimethylbutan-2-ol	11
Adamantane[b]	Adamantan-1-ol	23
	Adamantan-2-ol	<2
	Adamantan-2-one	Trace

[a] Based on PhIO reacted; self-decomposition of PhIO has been taken into account. [b] Degassed benzene as solvent. [c] Degassed MeCN as solvent and in the presence of $\mathrm{CCl_4}$.

$$[\mathrm{Mn^{III}(bpc)(O_2CMe)}] + \mathrm{PhIO} \longrightarrow [\mathrm{Mn^{V}(bpc)O}]^+ + \mathrm{PhI} \quad (1)$$

$$[\mathrm{Mn^{V}(bpc)O}]^+ + \mathrm{Mn^{III}} \longrightarrow [\{\mathrm{Mn^{IV}(bpc)(OH)}\}_2\mathrm{O}] \quad (2)$$

Catalytic Hydroxylation of Alkanes by PhIO.—Table 3 summarizes the results of alkane oxidation by the $[\mathrm{Mn(bpc)(O_2CMe)}]$–PhIO system. The chromium systems are ineffective in bringing about the alkane oxidation. Cyclohexane was oxidized to cyclohexanol and cyclohexanone with cyclohexanol as the major product in both degassed acetonitrile and benzene. When the reaction was carried out in MeCN–$\mathrm{CCl_4}$ (9:1 v/v), cyclohexyl chloride was detected quantitatively. This might suggest an hydrogen-atom abstraction mechanism for the reaction between the reactive manganese intermediate, possibly $\mathrm{Mn^V{=}O}$, and cyclohexane, which leads to the generation of a cyclohexyl radical intermediate. A similar observation has been reported by Smegal and Hill[22] and co-workers on the related manganese system.

In the oxidation of adamantane, both adamantan-1-ol and -2-ol were detected with a selectivity ratio $k[3^\circ(\mathrm{C{-}H})]/k[2^\circ(\mathrm{C{-}H})]$ of 22:1 taking the statistical factor into account, indicating that the tertiary C–H bond is preferentially oxidized over the secondary C–H bond.

Conclusion

The chromium(III) and manganese(III) complexes of pyridine amide ligands represent a new class of inexpensive catalysts for alkene epoxidation and alkane hydroxylation reactions. An oxygen-rebound mechanism involving the respective $\mathrm{Cr^V{=}O}$ and $\mathrm{Mn^V{=}O}$ intermediates is suggested for the PhIO oxidation reactions.

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