## Metal-metal charge transfer and solvatochromism in cyanomanganese carbonyl complexes of ruthenium and osmium<sup>†</sup>

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The complexes  $[(H_3N)_5Ru^{II}(\mu-NC)Mn^{I}L_x]^{2^+}$ , prepared from  $[Ru(OH_2)(NH_3)_5]^{2^+}$  and  $[Mn(CN)L_x] \{L_x = trans-(CO)_2\{P(OPh)_3\}(dppm); cis-(CO)_2(PR_3)(dppm), R = OEt or OPh; (PR_3)(NO)(\eta-C_5H_4Me), R = Ph or OPh\}$ , undergo two sequential one-electron oxidations, the first at the ruthenium centre to give  $[(H_3N)_5Ru^{III}(\mu-NC)Mn^{I}L_x]^{3^+}$ ; the osmium(III) analogues  $[(H_3N)_5Os^{III}(\mu-NC)Mn^{I}L_x]^{3^+}$  were prepared directly from  $[Os(NH_3)_5(O_3SCF_3)]^{2^+}$  and  $[Mn(CN)L_x]$ . Cyclic voltammetry and electronic spectroscopy show that the strong solvatochromism of the trications depends on the hydrogen-bond accepting properties of the solvent. Extensive hydrogen bonding is also observed in the crystal structures of  $[(H_3N)_5Ru^{III}(\mu-NC)Mn^{I}(PPh_3)(NO)(\eta-C_5H_4Me)][PF_6]_3 \cdot 2Me_2CO \cdot 1.5Et_2O, [(H_3N)_5Ru^{III}(\mu-NC)Mn^{I}(PPh_3)(NO)(\eta-C_5H_4Me)][PF_6]_3 \cdot 2Me_2CO \cdot 1.5Et_2O, [(H_3N)_5Ru^{III}(\mu-NC)Mn^{I}(PPh_3)(DO)(\eta-C_5H_4Me)][PF_6]_3 \cdot 2Me_2CO \cdot 1.5Et_2O \cdot 1.5Et$ 

#### Introduction

Our investigations of polynuclear compounds in which a cyanomanganese(I) carbonyl or nitrosyl group is N-bound to another metal centre<sup>1-12</sup> are part of a wider effort<sup>13</sup> to understand the structural, magnetic, electronic and optical properties of cyanidebridged metal species. In the course of our studies we noted<sup>14</sup> that certain compounds were solvatochromic, e.g.  $[X_3Fe(\mu-NC)MnL_x]$ {X = Cl or Br;  $L_x = trans$ - or cis-(CO)<sub>2</sub>(PR<sub>3</sub>)(dppm), R = OEt or OPh}. The present paper describes a detailed study of the synthesis, structure, electrochemistry (including spectroelectrochemical identification of redox products) and solvatochromic behaviour of a second series of such compounds, namely  $[(H_3N)_5M^{III}(\mu$ -NC)Mn<sup>1</sup>L<sub>x</sub>]<sup>3+</sup> {M = Ru or Os; L<sub>x</sub> = *trans*-(CO)<sub>2</sub>{P(OPh)<sub>3</sub>}(dppm); cis-(CO)<sub>2</sub>(PR<sub>3</sub>)(dppm), R = OEt or OPh; (PR<sub>3</sub>)(NO)(\eta-C<sub>5</sub>H<sub>4</sub>Me), R = Ph or OPh. Our work is complementary to important studies by Laidlaw et al.<sup>15-17</sup> of  $[(\eta-C_5R_5)(Ph_3P)_2M'^{II}(\mu-CN)M^{III}(NH_3)_5]^{3+1}$  $(M, M' = Ru \text{ or } Os; R_5 = H_5, H_4Me \text{ or } Me_5) \text{ and } [\{(CO)_5Cr^0(\mu - M_5)\}]$ CN) $_{n}$ {Ru<sup>III</sup>(NH<sub>3</sub>)<sub>6-n</sub>}]<sup>3-n</sup> (n = 0 - 3)<sup>18</sup> in providing further insight into the electronic properties of mixed-valence complexes by means of X-ray crystal structure determinations and the use of carbonyl-containing fragments to enable IR spectroscopic identification of the site of first oxidation in the heterobimetallic precursors  $[(H_3N)_5M^{II}(\mu-NC)Mn^IL_x]^{2+}$ .

#### **Results and discussion**

## Synthesis and characterisation of cyanomanganese(I) pentaammineruthenium(II) complexes

The reaction of  $[Ru(NH_3)_5(OH_2)][PF_6]_2$  with one equivalent of *trans*- $[Mn(CN)(CO)_2{P(OPh)_3}(dppm)]$  (*trans*-1), *cis*- $[Mn(CN)-(CO)_2(PR_3)(dppm)]$  (R = OPh, *cis*-1 or OEt, *cis*-2) or  $[Mn(CN)-(PR_3)(NO)(\eta-C_5H_4Me)]$  (R = Ph, 3 or OPh, 4) (Scheme 1) in acetone gave orange or red solutions from which  $[(H_3N)_5Ru^{II}(\mu-NC)Mn^1L_x][PF_6]_2$  { $L_x = trans$ - $(CO)_2{P(OPh)_3}-(dppm) 5^{2+}[PF_6]_2$ ;  $L_x = cis$ - $(CO)_2(PR_3)(dppm)$ , R = OEt  $6^{2+}[PF_6]_2$  or OPh  $7^{2+}[PF_6]_2$ ;  $L_x = (PR_3)(NO)(\eta-C_5H_4Me)$ , R = Ph  $8^{2+}[PF_6]_2$  or OPh  $9^{2+}[PF_6]_2$  (Scheme 2) were isolated as air-sensitive yellow or orange powders which dissolve in polar solvents such as CH<sub>2</sub>Cl<sub>2</sub>, thf, MeCN and acetone to give air-sensitive solutions.



 $\label{eq:scheme 1} \begin{array}{ll} P-P=Ph_2PCH_2PPh_2=dppm. \end{array}$ 

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<sup>&</sup>lt;sup>†</sup> Dedicated to Professor Victor Riera, good friend and colleague, on his 70th birthday.



Scheme 2 Complexes  $[(H_3N)_5M(\mu-NC)MnL_x]^{z+}$ .

Attempts to prepare  $[(H_3N)_5Ru(\mu-NC)Mn(CO)_2\{P(OEt)_3\}-(dppm)-trans][PF_6]_2$  by a similar method were unsuccessful, IR spectroscopy of the isolated yellow powder showing the presence of significant quantities of the *cis* isomer  $6^{2+}[PF_6]_2$ , presumably formed by *trans–cis* isomerisation at the Mn(1) centre.<sup>19-20</sup> The monocarbonyl complex  $[(H_3N)_5Ru(\mu-NC)Mn(CO)(dppm)_2-trans][PF_6]_2$   $10^{2+}[PF_6]_2$  (solutions of which are more air-stable than those of  $5^{2+}[PF_6]_2-9^{2+}[PF_6]_2$ ) was prepared as an orange powder by reacting *trans*-[Mn(CN)(CO)(dppm)\_2] with [Ru(NH\_3)\_5(OH\_2)][PF\_6]\_2.

The complexes  $5^{2+}[PF_6]_2-10^{2+}[PF_6]_2$  were characterised by elemental analysis, IR spectroscopy (Table 1) and cyclic voltammetry (Table 2). In all cases, v(CO) or v(NO) is shifted only minimally (*ca.* 5 cm<sup>-1</sup>) to higher wavenumber when the cyanide complexes 1–4 or *trans*-[Mn(CN)(CO)(dppm)\_2] are *N*-bound to the Ru<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub> fragment. In each bimetallic complex v(CN) is almost unchanged from that of the corresponding mononuclear manganese cyanide

complex suggesting that the increase in  $\nu$ (CN) expected on *N*-bonding to the second metal (the kinematic effect<sup>21</sup>) is offset by a decrease due to the relatively strong  $\pi$ -donating ability of the Ru<sup>II</sup>(NH<sub>3</sub>)<sub>5</sub> group {*cf.* the 13 cm<sup>-1</sup> reduction in  $\nu$ (CN) when this group is attached to [Re(CN)(CO)<sub>3</sub>(phen)] in [(H<sub>3</sub>N)<sub>5</sub>Ru( $\mu$ -NC)Re(CO)<sub>3</sub>(phen)]<sup>2+</sup> (phen = 1,10-phenanthroline)<sup>22</sup>}.

The cyclic voltammograms (CVs) of the dications  $5^{2+}-9^{2+}$  show two oxidation waves in CH<sub>2</sub>Cl<sub>2</sub>. The first is always reversible  $[(i_p)_{red}/(i_p)_{ox} = 1.0]$  and diffusion-controlled  $[(i_p)_{ox}/\nu^{1/2}$  is constant at scan rates,  $\nu$ , between 50 and 500 mV s<sup>-1</sup>] with the potential only slightly dependent on the ligand set at manganese (Table 2). By contrast, the potential (and reversibility) of the second wave is highly dependent on that ligand set. The first wave is therefore assigned to the oxidation of Ru(II) to Ru(III) and the second to the oxidation of Mn(I) to Mn(II).

For  $5^{2+}$ , both oxidation waves are reversible suggesting that the trication  $5^{3+}$  and the tetracation  $5^{4+}$  are stable on the cyclic voltammetric time scale. The CVs of  $8^{2+}$  and  $9^{2+}$  are similar to that of  $5^{2+}$  except that the second oxidation wave of the former appears to be incompletely reversible, indicating that the tetracation  $8^{4+}$ is unstable on the CV time scale. The second oxidation wave for  $9^{2+}$  is at a more positive potential than that of  $8^{2+}$ , consistent with replacement of PPh<sub>3</sub> by P(OPh)<sub>3</sub>, a better  $\pi$ -acceptor. The second wave for  $9^{2+}$  shows a sharp 'spike' on the return sweep of the CV suggesting that  $9^{4+}$  deposits as an insoluble conducting layer on the electrode surface, redissolving on reduction back to  $9^{3+}$ .

The salt  $10^{2+}$ [PF<sub>6</sub>]<sub>2</sub> is insoluble in CH<sub>2</sub>Cl<sub>2</sub> and thf but its CV in MeCN, at a glassy carbon electrode, shows two reversible oxidation waves. The much lower oxidation potential for the second wave (*cf.*  $5^{2+}-9^{2+}$ ) is due to the more electron-rich Mn(CO)(dppm)<sub>2</sub> group. However, this wave is at a much more positive potential (by over 0.4 V) than that for the uncoordinated cyanomanganese complex *trans*-[Mn(CN)(CO)(dppm)<sub>2</sub>].

The electrochemistry of the species containing cis-Mn(CO)<sub>2</sub> fragments,  $6^{2+}$  and  $7^{2+}$ , is complicated by redox-induced cis-trans isomerisation at manganese, as observed<sup>19-20</sup> for uncoordinated cis-1 and cis-2 and for all cyanide-bridged complexes containing

Table 1 Analytical and IR spectroscopic data for [(H<sub>3</sub>N)<sub>5</sub>M(µ-NC)MnL<sub>x</sub>]<sup>z+</sup>

			Analysis <sup>b</sup> (%)			$IR^{c}/cm^{-1}$		
Compound <sup>a</sup>	Colour	Yield (%)	C	Н	N	v(CN)	$v(CO)^d$	v(NO)
<b>5</b> <sup>2+</sup>	Yellow	48	41.8 (42.3)	4.0 (4.0)	5.9 (6.4)	2086 vw	1930, (2012)	_
<b>6</b> <sup>2+</sup>	Yellow	46	$32.4(32.4)^{e}$	4.5 (4.2)	6.1 (6.3)	ſ	1959, 1901	
<b>7</b> <sup>2+</sup>	Yellow	63	42.4 (42.3)	3.9 (4.0)	6.1 (6.4)	2093 vw	1972, 1915	
<b>8</b> <sup>2+</sup>	Orange	79	32.3 (32.3)	3.9 (4.0)	10.3 (10.6)	2099 w		1736
<b>9</b> <sup>2+</sup>	Orange	57	30.9 (30.8)	3.8 (3.8)	9.7 (10.0)	ſ		1760
<b>10</b> <sup>2+</sup>	Orange	78	46.3 (46.1)	4.4 (4.3)	6.6 (6.2)	ſ	1865 <sup>g</sup>	
<b>5</b> <sup>3+</sup>	Green	77	38.2 (38.0)	3.6 (3.6)	6.0 (5.8)	2046 w	1998 m, 1950	
<b>6</b> <sup>3+</sup>	Blue-green	75	30.9 (31.2)	4.1 (4.0)	6.6 (6.4)	2045 w	1958, 1928	
<b>7</b> <sup>3+</sup>	Blue	85	37.4 (38.0)	3.6 (3.6)	5.9 (5.8)	2048 w	1971 ms, 1941	
<b>8</b> <sup>3+</sup>	Purple	63	27.6 (28.0)	3.3 (3.5)	8.8 (9.1)	2060 mw	_ `	1756
<b>9</b> <sup>3+</sup>	Brown	83	27.1 (26.8)	3.2 (3.3)	8.4 (8.7)	2071 mw		1777
<b>10</b> <sup>3+</sup>	Red-brown	73	41.4 (41.7)	4.4 (4.0)	5.6 (5.6)	2000 m <sup>g</sup>	1939 ms, 1890 <sup>g</sup>	
<b>11</b> <sup>3+</sup>	Blue-green	64	34.6 (34.8) <sup>h</sup>	4.5 (4.7)	5.7 (5.7)	2035 w	1990 m, 1948	
12 <sup>3+</sup>	Purple	67	$29.6(29.7)^{e}$	3.4 (3.6)	5.3 (5.3)	2074 w	1966, 1919	
<b>13</b> <sup>3+</sup>	Green	51	40.9 (41.3)	3.6 (3.7)	5.3 (5.3)	2025 m	1886	

<sup>*a*</sup> Isolated as  $[PF_6]^-$  (M = Ru) or  $[CF_3SO_3]^-$  (M = Os) salts. <sup>*b*</sup> Calculated values in parentheses. <sup>*c*</sup> Strong (s) absorptions in CH<sub>2</sub>Cl<sub>2</sub> unless stated otherwise, vw = very weak, m = medium. <sup>*d*</sup> Very weak A-mode given in parentheses. <sup>*c*</sup> Analysed as a 1 : 2 CH<sub>2</sub>Cl<sub>2</sub> solvate. <sup>*f*</sup> Not observed. <sup>*g*</sup> In MeCN. <sup>*h*</sup> Analysed as a 1 : 3 acetone solvate.

		$E^{\circ,b}/V$		
Compound	Solvent	M(II)/M(III)	Mn(I)/Mn(II)	$\Delta E^c/V$
<b>5</b> <sup>3+</sup>	CH <sub>2</sub> Cl <sub>2</sub>	0.34	1.12	0.78
	MeCN	0.17	1.04	0.87
		$0.16^{d}$	1.03 <sup>d</sup>	0.87
	thf	0.26	1.11	0.85
<b>6</b> <sup>3+</sup>	CH <sub>2</sub> Cl <sub>2</sub>	0.37	1.34(I) (0.93)	0.91 <sup>e</sup>
	MeCN	0.24	1.27(I) (0.85)	$0.97^{e}$
	thf	0.26	f	
<b>7</b> <sup>3+</sup>	CH <sub>2</sub> Cl <sub>2</sub>	$0.42^{d}$	$1.52(I) (1.13)^d$	$1.07^{e}$
	MeCN	$0.28^{d}$	$1.47(I)(1.04)^{d}$	1.15 <sup>e</sup>
	thf	0.33	f	
<b>8</b> <sup>3+</sup>	CH <sub>2</sub> Cl <sub>2</sub>	$0.39 (0.18)^{h,i}$	$1.16^{g,i}$	$0.84^{e}$
	MeCN	0.19	1.12(I) (0.44)	0.93
	thf	0.22	f	
<b>9</b> <sup>3+</sup>	$CH_2Cl_2$	0.37	$1.37^{i}$	1.00
	MeCN	0.22	1.42(I) (0.92)	1.16 <sup>e</sup>
	thf	0.25	ſ	
10 <sup>3+</sup>	MeCN	0.20	0.50	0.30
	thf	0.28	0.57	0.29
	dmf	-0.04	0.40	0.44
11 <sup>3+</sup>	$CH_2Cl_2$	0.30	0.94	0.64
	thf	0.18	0.90	0.72
	dmf	-0.14	0.81	0.95
12 <sup>3+</sup>	$CH_2Cl_2$	-0.42	1.26(I) (0.83)	1.65 <sup>e</sup>
	MeCN	-0.52	1.21(I) (0.75)	1.70 <sup>e</sup>
	thf	-0.49	f	
	dmf	-0.73	ſ	
<b>13</b> <sup>3+</sup>	$CH_2Cl_2$	$-0.45^{d,j}$	$0.52^{d}$	0.98
	MeCN	-0.50	0.43	0.92
	thf	-0.45	0.51	0.96
	dmf	-0.71	0.41	1.11

<sup>*a*</sup> Data reported from measurements on the tricationic complexes but potentials identical (to within 10 mV) for measurements also carried out on dicationic analogues (see text). <sup>*b*</sup> E<sup>o</sup>, for a reversible wave at a platinum disc electrode at a scan rate of 200 mV s<sup>-1</sup>, unless stated otherwise. For an irreversible (I) oxidation wave, the peak potential,  $(E_p)_{ox}$ , is accompanied by  $E^{\circ}$  (in parentheses) for the reversible product wave. <sup>*c*</sup>  $\Delta E$  is the difference between the potentials for the Mn(I)/Mn(II) and M(II)/M(III) couples. <sup>*d*</sup> At a glassy carbon electrode. <sup>*e*</sup>  $\Delta E$  values calculated as described in text. <sup>*f*</sup> Not observed; wave obscured by base electrolyte curve. <sup>*s*</sup> At a gold electrode. <sup>*k*</sup> For the trication, the reduction wave is broad;  $(E_p)_{red}$  is accompanied by  $(E_p)_{\alpha x}$  in parentheses. <sup>*i*</sup> Spike' observed on reverse scan, with  $(i_p)_{red}/(i_p)_{\alpha x} \gg 1$ ; unable to measure reversibility. <sup>*j*</sup> Presence of internal potential reference compound  $[Fe(\eta-C_5Me_5)_2]$  necessary for observation of reversible and reproducible behaviour.

such units. Thus, the CV of  $7^{2+}$  in CH<sub>2</sub>Cl<sub>2</sub> shows a reversible oxidation wave at 0.42 V (at a scan rate of 200 mV s<sup>-1</sup>) and a partially reversible oxidation wave at 1.52 V { $E^{\circ'}$  is estimated as 1.46 V based on the average of the peak potentials, ( $E_p$ )<sub>ox</sub> and ( $E_p$ )<sub>red</sub>}. The second wave becomes less reversible with decreasing scan rates and at 50 mV s<sup>-1</sup> the oxidation process is fully irreversible [( $E_p$ )<sub>ox</sub> = 1.51 V]. It is coupled to a product wave which, when the CV of  $7^{2+}$  is scanned from -0.2 to 1.7 to 0.9 and finally to 1.4 V, is reversible and centred at 1.13 V, *i.e.* the potential of the Mn(I)/Mn(II) couple of  $5^{2+}$ . Thus, oxidative isomerisation to  $5^{4+}$ occurs only after formation of  $7^{4+}$ .

#### Synthesis and characterisation of cyanomanganese(I) pentaammineruthenium(III) and pentaammineosmium(III) complexes

On the basis of the potentials noted above, the chemical oxidation of the dication  $10^{2+}$  should require only a mild one-electron

oxidant to produce  $[(H_3N)_5Ru^{III}(\mu-NC)Mn^I(CO)(dppm)_2-trans]^{3+}$ **10**<sup>3+</sup>. Accordingly, the addition of  $[Fe(\eta-C_5H_5)_2][PF_6]$  to a solution of  $[(H_3N)_5Ru^{II}(\mu-NC)Mn^I(CO)(dppm)_2-trans][PF_6]_2$  **10**<sup>2+</sup> $[PF_6]_2$  in acetone gave an immediate colour change from orange to darker orange-brown; filtration of the reaction mixture, reduction of the volume of the filtrate *in vacuo* and then layering it with diethyl ether gave red-brown crystals of  $[(H_3N)_5Ru^{III}(\mu-NC)Mn^I(CO)(dppm)_2$  $trans][PF_6]_3 \cdot 5Me_2CO$ , **10**<sup>3+</sup> $[PF_6]_3 \cdot 5Me_2CO$ , at -10 °C. When these crystals were carefully washed with diethyl ether, loss of solvent from the lattice resulted in an air-sensitive red-brown powder the elemental analysis of which was consistent with unsolvated **10**<sup>3+</sup> $[PF_6]_3$  (Table 1).

The trications  $5^{3+}-9^{3+}$  were isolated as their  $[PF_6]^-$  salts after oxidation of the corresponding dications prepared *in situ*. Thus, treatment of stirred solutions of  $[Ru(NH_3)_5(OH_2)][PF_6]_2$  in acetone with one equivalent of *trans*-1, *cis*-1, *cis*-2, 3 or 4, also in acetone, gave orange or red solutions of  $[(H_3N)_5Ru^{II}(\mu-NC)Mn^1L_x][PF_6]_2$ , as above. After ten minutes, one equivalent of the oxidising agent  $[N_2C_6H_4F-p][PF_6]$  was added to the mixture, resulting in colour changes to deep blue-green for the reactions starting from *trans*-1, *cis*-1 and *cis*-2, and deep purple-brown and deep green for those involving 3 and 4 respectively. The complexes  $[(H_3N)_5Ru^{III}(\mu-NC)Mn^1L_x][PF_6]_3 \{L_x = trans-(CO)_2(PR_3)(dppm),$  $R = OPh 5^{3+}[PF_6]_3; L_x = cis-(CO)_2(PR_3)(dppm), R = OEt 6^{3+}[PF_6]_3$ or OPh 7<sup>3+</sup>[PF\_6]\_3; L\_x = (PR\_3)(NO)(\eta-C\_3H\_4Me), R = Ph 8^{3+}[PF\_6]\_3 or OPh 9<sup>3+</sup>[PF\_6]\_3 were then isolated as air-stable solids.

 $[(H_3N)_5Ru^{III}(\mu-NC)Mn^{I}(CO)_2-$ Attempts to prepare  $\{P(OEt)_3\}(dppm)$ -trans  $[PF_6]_3$  in the same way gave a bluegreen powder which IR spectroscopy showed to contain a large proportion of the isomer with the cis-Mn<sup>I</sup>(CO)<sub>2</sub> fragment, *i.e.*  $6^{3+}$ . However, after layering the concentrated acetone reaction mixture with diethyl ether, blue-green crystals of  $[(H_3N)_5Ru(\mu-$ NC)Mn(CO)<sub>2</sub>{P(OEt)<sub>3</sub>}(dppm)-trans][PF<sub>6</sub>]<sub>3</sub>, which analysed (C, H and N) as the acetone solvate  $11^{3+}$  [PF<sub>6</sub>]<sub>3</sub>·3Me<sub>2</sub>CO, were isolated after four weeks at -10 °C; the IR spectrum of the crystals showed no sign of the cis isomer. These crystals are air-stable and do not undergo trans-to-cis isomerisation on storage at -10 °C. However, when crushed and placed in vacuo for 24 hours at room temperature the IR spectrum of the resulting blue-green powder showed the presence of a significant quantity of the *cis* isomer  $6^{3+}$ .

Heating a mixture of  $[Os(NH_3)_5(O_3SCF_3)][CF_3SO_3]_2$  with *cis*-2 or *trans*- $[Mn(CN)(CO)(dppm)_2]$  under reflux in thf yielded the air-stable solids  $[(H_3N)_5Os(\mu-NC)Mn(CO)_2\{P(OEt)_3\}(dppm)$ *cis* $][CF_3SO_3]_3$ **12** $<sup>3+</sup>[CF_3SO_3]_3 and <math>[(H_3N)_5Os(\mu-NC)Mn(CO) (dppm)_2-$ *trans* $][CF_3SO_3]_3$ **13** $<sup>3+</sup>[CF_3SO_3]_3; the latter is mildly light$ sensitive in the solid state and was therefore stored in the dark. $Attempts to form <math>[(H_3N)_5Os(\mu-NC)Mn(CO)_2\{P(OEt)_3\}(dppm)$ *trans* $][CF_3SO_3]_3 from <math>[Os(NH_3)_5(O_3SCF_3)][CF_3SO_3]_2$  and *trans*-**2** were only partly successful; substitution of the coordinated triflate anion required the use of high temperatures for an extended period, conditions which led to *trans*-to-*cis* isomerisation at manganese. The product obtained from this reaction was therefore an isomeric mixture.

The salts  $5^{3+}[PF_6]_3-9^{3+}[PF_6]_3$ ,  $11^{3+}[PF_6]_3$  and  $12^{3+}[CF_3SO_3]_3$  are readily soluble in polar solvents such as  $CH_2Cl_2$ ,  $CHCl_3$ , thf, MeCN, acetone and dmf to give mildly air-sensitive solutions. The monocarbonyl analogues  $10^{3+}[PF_6]_3$  and  $13^{3+}[CF_3SO_3]_3$  are rather less soluble, and in solution the former decomposes rapidly in air. The salts of the trications have been characterised by elemental analysis, IR spectroscopy (Table 1), cyclic voltammetry (Table 2) and, in the cases of  $8^{3+}$ [PF<sub>6</sub>]<sub>3</sub>,  $10^{3+}$ [PF<sub>6</sub>]<sub>3</sub> and  $11^{3+}$ [PF<sub>6</sub>]<sub>3</sub>, by X-ray crystallography (see below).

In contrast to the IR spectra of  $5^{2+}-9^{2+}$ , the numbers and relative intensities of the carbonyl and cyanide bands in the spectra of the ruthenium complexes  $5^{3+}-11^{3+}$  are unusual (Table 1) and surprisingly solvent dependent. For example, Fig. 1 shows the spectra of [(H<sub>3</sub>N)<sub>5</sub>Ru<sup>II</sup>(µ-NC)Mn<sup>1</sup>(CO)<sub>2</sub>{P(OPh)<sub>3</sub>}(dppm)-*trans*]<sup>2+</sup>,  $5^{2+}$ , in CH<sub>2</sub>Cl<sub>2</sub> (2086vw, 2012vw, 1930s cm<sup>-1</sup>) and of [(H<sub>3</sub>N)<sub>5</sub>Ru<sup>II</sup>(µ-NC)Mn<sup>1</sup>(CO)<sub>2</sub>{P(OPh)<sub>3</sub>}(dppm)-*trans*]<sup>3+</sup>,  $5^{3+}$ , in CH<sub>2</sub>Cl<sub>2</sub> (2046w, 1998m, 1950s cm<sup>-1</sup>) and MeCN (2045w, 1989w, 1946s cm<sup>-1</sup>).



Fig. 1 IR spectra of (a)  $\mathbf{5}^{2*}$  in  $CH_2Cl_2,$  (b)  $\mathbf{5}^{3*}$  in  $CH_2Cl_2,$  and (c)  $\mathbf{5}^{3*}$  in MeCN.

Of the three bands observed for  $5^{3+}$ , that at highest energy is assigned to the cyanide stretch; v(CN) is invariably higher than v(CO) in complexes of cyanomanganese carbonyls. As is expected when oxidation of a cyanide-bridged complex occurs at the *N*-bound metal site, v(CN) for  $5^{3+}$  is observed at lower wavenumber than for  $5^{2+}$ . Moreover, v(CN) in  $5^{3+}$  is much lower in energy (by *ca.* 40 cm<sup>-1</sup>) than in the mononuclear precursor *trans*-[Mn(CN)(CO)<sub>2</sub>{P(OPh)<sub>3</sub>}(dppm)], suggesting that the *N*-bound pentaammineruthenium(III) centre is strongly electron withdrawing {*cf.* the *N*-bound Ru(II) centre in  $5^{2+}$ }, as also deduced for species such as  $[(\eta-C_3H_5)(Ph_3P)_2Ru^{II}(\mu-CN)Ru^{III}(NH_3)_5]^{3+}$  where a similar large shift in v(CN) to lower wavenumber, relative to that of [Ru(CN)(PPh\_3)<sub>2</sub>( $\eta-C_5H_5$ )], was observed.<sup>15</sup> The two lower energy absorptions in the CH<sub>2</sub>Cl<sub>2</sub> spectrum of  $5^{3+}$  (at 1998 and 1950 cm<sup>-1</sup>) are both assigned to carbonyl bands. However, their relative intensities (medium and strong respectively) contrast markedly with those of  $5^{2+}$  (and for the free ligand *trans*-[Mn(CN)(CO)<sub>2</sub>{P(OPh)<sub>3</sub>}(dppm)] and most of its *N*-bound complexes) where the strong band for the *trans*-Mn(CO)<sub>2</sub> group is accompanied by a very weak absorption for the IR-inactive A-mode.

It is noteworthy that the only other cyanomanganese carbonyl complexes to show similarly unusual IR spectra are [X<sub>3</sub>Fe<sup>III</sup>(µ-NC)Mn<sup>I</sup>L<sub>x</sub>] [X = Cl or Br;  $L_x = trans$ - or cis-(CO)<sub>2</sub>(PR<sub>3</sub>)(dppm), R = OEt or OPh<sup>14</sup> in which the  $Fe^{III}X_3$  fragments are also strongly electron withdrawing. Thus, it is likely that N-bonding of a strongly withdrawing group lowers v(CN) to bring it much closer in energy to those of the carbonyl bands. Coupling between the cyanide and carbonyl stretching vibrations then results in the observed increased intensity for the absorption from the IR-inactive A-mode of the *trans*-dicarbonyl group. {One might visualise the Mn(CN)(CO)<sub>2</sub> unit as being equivalent to a mertricarbonyl fragment for which three bands of similar intensity would be expected.} The osmium-containing trication  $12^{3+}$ , with the Os<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub> fragment a weaker acceptor than Ru<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>, displays carbonyl bands with the more usual relative intensities (Table 1) {and with v(CN), at 2074 cm<sup>-1</sup>, shifted less to lower wavenumber than in the ruthenium analogue  $6^{3+}$  (2045 cm<sup>-1</sup>)}, consistent with this explanation.

## The X-ray structures of $8^{3+}$ [PF<sub>6</sub>]<sub>3</sub>·2Me<sub>2</sub>CO·1.5Et<sub>2</sub>O, $10^{3+}$ [PF<sub>6</sub>]<sub>3</sub>·5Me<sub>2</sub>CO and $11^{3+}$ [PF<sub>6</sub>]<sub>3</sub>·4Me<sub>2</sub>CO

Crystals of the solvated salts  $8^{3+}$ [PF<sub>6</sub>]<sub>3</sub>·2Me<sub>2</sub>CO·1.5Et<sub>2</sub>O,  $10^{3+}$ [PF<sub>6</sub>]<sub>3</sub>·5Me<sub>2</sub>CO and  $11^{3+}$ [PF<sub>6</sub>]<sub>3</sub>·4Me<sub>2</sub>CO were grown by allowing diethyl ether to diffuse into concentrated acetone solutions of the complexes at -10 °C. The molecular structures of the trications  $8^{3+}$ ,  $10^{3+}$  and  $11^{3+}$  are shown in Fig. 2–4 respectively and selected bond lengths and angles are given in Tables 3–5. In addition, the crystal structure of  $10^{3+}$ [PF<sub>6</sub>]<sub>3</sub>·5Me<sub>2</sub>CO is shown in Fig. 5.



Fig. 2 Structure of the trication  $[(H_3N)_5Ru^{III}(\mu$ -NC)Mn<sup>1</sup>(PPh<sub>3</sub>)(NO)-(\eta-C\_5H\_4Me)]^{3+} **8**<sup>3+</sup>. Hydrogen atoms and some disorder in the C<sub>5</sub>H<sub>4</sub>Me ligand are omitted for clarity.

Table 3 Selected bond lengths (Å) and angles (°) for  $8^{3+} [PF_6]_3 \cdot 2Me_2CO \cdot 1.5Et_2O$ 

$M_{n}(1) C(1)$	1.913(6)	N(7) = O(1)	1 192(()
$ \begin{array}{l} \text{Mn}(1) = C(1) \\ C(1) = N(1) \\ \text{Ru}(1) = N(1) \\ \text{Mn}(1) = N(7) \end{array} $	1.162(7) 2.003(4) 1.646(5)	$ \frac{Mn(1) - P(1)}{Ru(1) - N(4)} \\ Ru(1) - N_{cis}(ave) $	2.293(2) 2.103(4) 2.111(4)
Mn(1)-C(1)-N(1) C(1)-N(1)-Ru(1) Mn(1)-N(7)-O(1) N(7)-Mn(1)-C(1) N(7)-Mn(1)-P(1) C(1)-Mn(1)-P(1)	177.2(5) 177.0(4) 173.6(4) 99.6(2) 96.4(2) 87.6(2)	N(1)-Ru(1)-N(2) N(1)-Ru(1)-N(3) N(1)-Ru(1)-N(4) N(1)-Ru(1)-N(5) N(1)-Ru(1)-N(6)	88.5(2) 92.1(2) 178.2(2) 90.3(2) 89.1(2)



All of the trications are octahedral at ruthenium with deviations from the ideal value of 90° limited to  $\pm 3^{\circ}$ . The Ru–N bond lengths are in the range 2.08 to 2.11 Å and the bridging cyanide units are nearly linear, with Mn–C–N and C–N–Ru angles between 175.7° and 179.4°. As in previous structures containing the *N*-bound units (NC)Mn(CO)(dppm)<sub>2</sub><sup>4,7-10,14,23-24</sup> and (NC)Mn(CO)<sub>2</sub>{P(OEt)<sub>3</sub>}(dppm),<sup>6-7,23</sup> the geometry around manganese is essentially octahedral in both **10**<sup>3+</sup> and **11**<sup>3+</sup>; the largest angular distortions from regular geometry are due to the small bite of the dppm chelate which leads to P<sub>dppm</sub>–Mn–P<sub>dppm</sub>

Table 4 Selected bond lengths (Å) and angles (°) for  $10^{3+} [PF_6]_3 \cdot 5 Me_2 CO$ 

$\begin{array}{l} Mn(1)-C(1)\\ Mn(1)-C(2)\\ C(1)-N(1)\\ Ru(1)-N(1)\\ Ru(1)-N(3)\\ Ru(1)-N_{cis}(ave) \end{array}$	1.937(7) 1.790(7) 1.182(7) 1.998(6) 2.106(5) 2.111(5)	C(2)-O(1) Mn(1)-P(1) Mn(1)-P(2) Mn(1)-P(3) Mn(1)-P(4)	1.156(7) 2.302(3) 2.285(3) 2.300(3) 2.295(3)
$\begin{array}{l} Mn(1)-C(1)-N(1)\\ Ru(1)-N(1)-C(1)\\ C(1)-Mn(1)-C(2)\\ Mn(1)-C(2)-O(1)\\ P(1)-Mn(1)-P(2)\\ P(1)-Mn(1)-P(3)\\ P(2)-Mn(1)-P(4) \end{array}$	176.6(6) 175.4(5) 174.9(3) 178.0(7) 73.6(1) 106.3(1) 107.2(1)	P(3)-Mn(1)-P(4) N(1)-Ru(1)-N(2) N(1)-Ru(1)-N(3) N(1)-Ru(1)-N(4) N(1)-Ru(1)-N(5) N(1)-Ru(1)-N(6)	72.9(1) 90.7(2) 179.1(2) 88.2(2) 88.9(2) 92.8(2)



Fig. 4 Structure of the trication  $[(H_3N)_5Ru^{III}(\mu$ -NC)Mn<sup>I</sup>(CO)<sub>2</sub>-{P(OEt)<sub>3</sub>}(dppm)-*trans*]<sup>3+</sup> 11<sup>3+</sup>. Hydrogen atoms are omitted for clarity.

Table 5 Selected bond lengths (Å) and angles (°) for  $11^{3+}$  [PF<sub>6</sub>]<sub>3</sub>·4Me<sub>2</sub>CO

$\begin{array}{c} Mn(1)-C(1) \\ Mn(1)-C(2) \\ Mn(1)-C(3) \\ C(1)-N(1) \\ Ru(1)-N(1) \\ Ru(1)-N(6) \end{array}$	1.914(10) 1.797(13) 1.805(12) 1.198(10) 1.978(8) 2.104(7)	$\begin{array}{c} Ru(1)-N_{cis} (ave) \\ Mn(1)-P(1) \\ Mn(1)-P(2) \\ Mn(1)-P(3) \\ C(2)-O(1) \\ C(3)-O(2) \end{array}$	2.076(9) 2.211(3) 2.308(3) 2.285(3) 1.184(12) 1.184(11)
$\begin{array}{l} Mn(1)-C(1)-N(1)\\ Ru(1)-N(1)-C(1)\\ N(1)-Ru(1)-N(2)\\ N(1)-Ru(1)-N(3)\\ N(1)-Ru(1)-N(3)\\ N(1)-Ru(1)-N(4)\\ N(1)-Ru(1)-N(5)\\ N(1)-Ru(1)-N(6)\\ C(1)-Mn(1)-P(1) \end{array}$	179.0(9) 179.7(8) 89.6(3) 92.3(3) 88.7(3) 89.6(3) 179.0(3) 93.0(3)	$\begin{array}{c} C(1)-Mn(1)-P(2)\\ C(1)-Mn(1)-P(3)\\ C(1)-Mn(1)-C(2)\\ C(1)-Mn(1)-C(3)\\ C(2)-Mn(1)-C(3)\\ P(1)-Mn(1)-P(2)\\ P(1)-Mn(1)-P(3)\\ P(2)-Mn(1)-P(3)\\ \end{array}$	169.3(3) 96.4(3) 88.2(4) 88.9(4) 177.1(4) 97.7(1) 170.5(1) 72.9(1)

angles of less than  $74^{\circ}$ . In  $10^{3+}$  the carbonyl is *trans* to the cyanide bridge and the four phosphorus atoms of the two dppm ligands occupy the equatorial positions; in  $11^{3+}$  the CO ligands are mutually *trans*, with the cyanide bridge *trans* to a phosphorus atom of the bidentate dppm ligand.

Previous work has established that Mn–P bond lengths are diagnostic of the oxidation state of manganese in both mononuclear and polynuclear octahedral cyanomanganese compounds; Mn(II)–P bond lengths are substantially longer than Mn(I)–P bond lengths.<sup>10,23–25</sup> A comparison of the structures of  $10^{3+}$  and  $11^{3+}$  with literature data established that both contain Mn(I).

The manganese centre in  $\mathbf{8}^{3+}$  is significantly distorted from *pseudo*-tetrahedral geometry, with angles between the monodentate ligands closer to 90° than 109.5°. Comparison of the structure of  $\mathbf{8}^{3+}$  with that of [Mn(CNBPh<sub>3</sub>){P(OPh)<sub>3</sub>}(NO)(\eta-C\_5H\_4Me)]<sup>26</sup> again suggests a Mn(I) oxidation state. Thus, the assignment of manganese(I) centres to  $\mathbf{8}^{3+}$ ,  $\mathbf{10}^{3+}$  and  $\mathbf{11}^{3+}$  indicates Ru(III)Mn(I) core oxidation states for each complex, as deduced from the CV studies on the corresponding dications (*i.e.* ruthenium-based oxidation is the first step).

One of the main features common to the crystal structures of  $8^{\scriptscriptstyle 3+},\,10^{\scriptscriptstyle 3+}$  and  $11^{\scriptscriptstyle 3+}$  is the extensive hydrogen bonding involving



Fig. 5 Crystal structure of  $10^{3+}$  [PF<sub>6</sub>]<sub>3</sub>·5Me<sub>2</sub>CO. Hydrogen atoms are omitted for clarity. Dotted lines indicate the interactions between the NH<sub>3</sub> groups and acetone molecules or [PF<sub>6</sub>]<sup>-</sup> counterions.

the ammine groups (the H-bond donors) at the Ru(III) site and the oxygen atoms of solvent molecules (acetone or diethyl ether) in the crystal lattice, or the fluorine atoms of the  $[PF_6]^-$  counterions (the H-bond acceptors). Some of the H ··· O and H ··· F distances are less than 2 Å, corresponding to strong hydrogen bonds (*cf.* the sum of the van der Waals radii of hydrogen and oxygen, or hydrogen and fluorine, both of which can be approximated as 2.75 Å).

In the case of  $10^{3+}$  the hydrogen bonding network orders the structure such that distinct channels contain the acetone solvent molecules and the [PF<sub>6</sub>]<sup>-</sup> anions (Fig. 5). The hydrophilic pentaammineruthenium(III) centres are orientated towards the channels while the hydrophobic manganese carbonyl fragments are disposed away from the channels. Thus, a network of hydrophilic channels is interspersed with an equal number of hydrophobic channels. Because of this ordering, the structure has a degree of anisotropy which may account for the red-green dichroic nature of the crystals.

#### The electrochemistry of the trications 5<sup>3+</sup>-13<sup>3+</sup>

As expected from the electrochemistry of the dicationic complexes, each of the CVs of the trications  $5^{3+}-13^{3+}$  shows one reduction wave, associated with the Ru(II)/Ru(III) or Os(II)/Os(III) couple, and one oxidation wave associated with the Mn(I)/Mn(II) couple (Table 2). Treatment of the ruthenium trications  $5^{3+}-10^{3+}$  with the mild reducing agent [Fe( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] regenerates the Ru(II)Mn(I) dications  $5^{2+}-10^{2+}$  but similar reactions with the Os(III) complexes  $12^{3+}$  and  $13^{3+}$  did not result in reduction, consistent with the much more negative potentials (by *ca.* 0.6–0.8 V) for the Os(II)/Os(III) couple.

The reversibility of the oxidation waves for the *trans*-dicarbonyl trications  $5^{3+}$  and  $11^{3+}$  and for the monocarbonyl  $10^{3+}$  suggested that the tetracations  $5^{4+}$ ,  $10^{4+}$  and  $11^{4+}$  might also be synthetically accessible using a moderately strong oxidant. Attempts to prepare  $5^{4+}$  and  $11^{4+}$  were unsuccessful but treatment of an

orange suspension of  $10^{2+}$ [PF<sub>6</sub>]<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> with 2.5 equivalents of [NO][PF<sub>6</sub>] under argon, and with light excluded, gave a purple solution from which a purple solid was isolated. The IR spectrum of the solid showed a cyanide band at 2092 cm<sup>-1</sup> and one carbonyl band at 1956 cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>; the increase in energy of the carbonyl band (of *ca.* 90 cm<sup>-1</sup>) with respect to that of the dication  $10^{2+}$  (1865 cm<sup>-1</sup> in MeCN) is consistent with a carbonyl ligand bound to Mn(II), *i.e.* as in [(H<sub>3</sub>N)<sub>5</sub>Ru<sup>III</sup>( $\mu$ -NC)Mn<sup>II</sup>(CO)(dppm)<sub>2</sub>*trans*][PF<sub>6</sub>]<sub>4</sub> 10<sup>4+</sup>[PF<sub>6</sub>]<sub>4</sub>. However, the purple solid (for which an acceptable elemental analysis could not be obtained) was extremely air-sensitive and slowly decomposed even when stored under argon at -10 °C.

Further evidence for the formation of  $10^{4+}$  was obtained by an IR spectroelectrochemical study of the monocarbonyl dication  $10^{2+}$ , in MeCN at -40 °C. After electrochemical generation of the trication  $10^{3+}$ , which reaches completion at 0.4 V, further oxidation at a potential more positive than that of the Mn(1)/Mn(II) couple yielded new bands at 1958 and 2084 cm<sup>-1</sup>, in good agreement with the IR spectrum observed on chemical oxidation of  $10^{3+}$  in CH<sub>2</sub>Cl<sub>2</sub>. Lowering the potential led to the reformation of  $10^{3+}$  and then  $10^{2+}$ , showing the trication and tetracation to be stable at -40 °C.

A similar IR spectroelectrochemical study of the reduction of  $11^{3+}$  at -0.2 V, in CH<sub>2</sub>Cl<sub>2</sub> or thf at -40 °C, resulted in the collapse of the three bands observed for the trication to give a very weak cyanide band and a single carbonyl band [ $\nu$ (CO) = 1916 cm<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>] consistent with the formation of  $11^{2+}$  (which could not be made directly from [Ru(NH<sub>3</sub>)<sub>5</sub>(OH<sub>2</sub>)][PF<sub>6</sub>]<sub>2</sub> and *trans*-2 or by the chemical reduction of  $11^{3+}$  – see above); reoxidation at 0.4 V regenerated  $11^{3+}$ .

Applying a potential more positive than that of the Mn(I)/Mn(II) couple of  $11^{3+}$  in  $CH_2Cl_2$  (but not in thf in which the tetracation decomposes) resulted in a single carbonyl band at 2010 cm<sup>-1</sup> (*cf.* 1993 cm<sup>-1</sup> for free *trans*-1<sup>+</sup>), and returning the potential to 0.4 V led to the reformation of the three absorptions characteristic of  $11^{3+}$ , again implying the formation of  $11^{4+}$ . (These

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results also confirm that IR spectra with unusual relative intensities for the carbonyl and cyanide bands are confined to those of the mixed-valence trication  $11^{3+}$ .)

In CH<sub>2</sub>Cl<sub>2</sub>, **13**<sup>3+</sup> showed only a poorly resolved reduction wave for the Os(II)/Os(III) couple at either a Pt or glassy carbon working electrode. However, in the presence of a small amount of [Fe( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>], added as an internal calibrant, fully reversible and reproducible CVs were obtained, possibly because of mediation of the heterogeneous electron transfer to the Pt electrode.

The electrochemical studies reported above serve to identify the redox processes undergone and the potentials of the various couples present {*i.e.* Mn(I)/Mn(II), Ru(II)/Ru(III) and Os(II)/Os(III)}. However, voltammetric studies of the trications in a wider range of solvents provided insight into the extent of MMCT (metal-to-metal charge transfer), complementary to the results from the UV/visible spectra described below.

The CVs of  $11^{3+}$  in CH<sub>2</sub>Cl<sub>2</sub>, thf and dmf (Fig. 6, Table 2) show that the potentials for both the oxidation and the reduction waves are solvent dependent (referenced against [Fe( $\eta$ -C<sub>3</sub>H<sub>3</sub>)( $\eta$ -C<sub>3</sub>H<sub>4</sub>COMe)] as an internal potential standard). Both the Mn(I)/Mn(II) and Ru(II)/Ru(III) couples are shifted to more negative potentials as the solvent Gutmann donor number (DN) increases.<sup>27</sup> However, the effect of the solvent on the Ru(II)/Ru(III) couple is much greater, shifting to a more negative potential by *ca.* 400 mV from CH<sub>2</sub>Cl<sub>2</sub> to dmf, *cf.* a shift of only 90 mV for the Mn(I)/Mn(II) couple. Thus,  $\Delta E$  (Table 2), the difference between the Mn(I)/Mn(II) and Ru(II)/Ru(III) couples, for  $11^{3+}$  is greater in dmf than in CH<sub>2</sub>Cl<sub>2</sub>.



Fig. 6 Cyclic voltammograms of  $11^{3+}$  in (a) CH<sub>2</sub>Cl<sub>2</sub>, (b) thf, and (c) dmf.

A similar dependence on solvent of the Ru(II)/Ru(III) redox potential is observed for  $\mathbf{5}^{3+}$  though the oxidation wave for the Mn(I)/Mn(II) couple could not always be observed (for example, the solvent window in thf is limited to *ca*. 1 V) and  $\Delta E$  could not be calculated. For the *cis*-dicarbonyl trications  $\mathbf{6}^{3+}$ ,  $\mathbf{7}^{3+}$  and **12**<sup>3+</sup>, where the oxidation wave for the Mn(I)/Mn(II) couple was irreversible because of redox-induced *cis–trans* isomerisation, and the cases of **8**<sup>3+</sup> in CH<sub>2</sub>Cl<sub>2</sub> and **9**<sup>3+</sup> in MeCN, where the oxidation waves were incompletely defined, values of  $\Delta E$  were estimated.

The variation in  $\Delta E$  implies that the energy barrier to electron transfer from manganese(I) to ruthenium(III) or osmium(III),  $E_{\rm MMCT}$ , in the trications is higher in dmf than CH<sub>2</sub>Cl<sub>2</sub>, for example. Moreover,  $\Delta E$  in CH<sub>2</sub>Cl<sub>2</sub> for the Mn(I)/Mn(II) and Os(II)/Os(III) couples of **12**<sup>3+</sup> (1.65 V) and **13**<sup>3+</sup> (0.98 V) is greater than for the Mn(I)/Mn(II) and Ru(II)/Ru(III) couples of the analogues **6**<sup>3+</sup> (0.91 V) and **10**<sup>3+</sup> (*ca.* 0.30 V) because of the significantly more negative potentials for the Os(II)/Os(III) couples. Hence MMCT occurs at a higher energy for osmium than ruthenium complexes.

Overall, plots of  $\Delta E$  vs.  $E_{\text{MMCT}}$  are linear (e.g. for both CH<sub>2</sub>Cl<sub>2</sub> and MeCN,  $R^2 = 0.91$ ). However, attempts to quantify the extent of electronic interaction between the two metal sites should be treated with caution given the substantial medium effects (e.g. solvent and base electrolyte salt) on  $\Delta E$ .<sup>28-29</sup> A more quantitative approach has therefore been taken which is based on an extensive study of electronic spectra in a wide range of solvents.

#### Optical properties of cyanomanganese(I) pentaammineruthenium(III) and pentaammineosmium(III) complexes

The bimetallic M(III)Mn(I) (M = Ru or Os) species  $5^{3+}-13^{3+}$  are strongly solvatochromic, a characteristic of Robin–Day Class II mixed-valence compounds and stemming from a metal-tometal charge transfer (MMCT) band in the UV-visible region (Table 6).

Qualitatively, the band shapes and *relative* energies of the absorption spectra of the trications are similar regardless of the solvent. In CH<sub>2</sub>Cl<sub>2</sub>, the spectra of the *cis*-dicarbonyl trications  $6^{3+}$ ,  $7^{3+}$ and  $12^{3+}$  are the simplest, showing a single broad band at 843 nm  $(\varepsilon = 2370 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}), 780 \text{ nm} (\varepsilon = 2130 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$ and 531 nm ( $\varepsilon = 1980 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) respectively. The transdicarbonyl trications  $5^{3+}$  and  $11^{3+}$  show lower energy absorptions at 1134 nm ( $\varepsilon = 4730$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) and 1338 nm ( $\varepsilon =$ 7760 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>), which are significantly stronger than those of the cis-dicarbonyl analogues, and have shoulders towards lower wavelength. Fig. 7(a) shows the superimposed spectra of the cisand *trans*-dicarbonyl complexes  $5^{3+}$  and  $7^{3+}$ , indicating that the shoulders on the absorptions for the trans-dicarbonyl complexes are at a similar energy to the single absorption bands found for their cis-dicarbonyl analogues. (However, other characterisation methods described above, namely cyclic voltammetry and IR spectroscopy, imply these trans complexes are not contaminated by their *cis* isomers.)

In CH<sub>2</sub>Cl<sub>2</sub>, **8**<sup>3+</sup> and **9**<sup>3+</sup> show two distinct absorptions [Fig. 7(b)]. In each case, a band in the visible region is accompanied by a stronger band at lower energy, in the near-IR region. For example, **8**<sup>3+</sup> shows absorptions at 501 nm ( $\varepsilon = 930$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) and 1098 nm ( $\varepsilon = 3640$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>). In MeCN, the monocarbonyl **10**<sup>3+</sup> shows a single broad asymmetric absorption at 1453 nm ( $\varepsilon = 1360$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>), Fig. 7(c). For the analogous osmium species **13**<sup>3+</sup> this asymmetric peak is resolved into an absorption band at 746 nm ( $\varepsilon = 1940$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) in CH<sub>2</sub>Cl<sub>2</sub>, with a shoulder at higher energy.



Fig. 7 UV-visible-NIR spectra of (a)  $5^{3+}$  and  $7^{3+}$  in  $CH_2Cl_2$ , (b)  $8^{3+}$  and  $9^{3+}$  in  $CH_2Cl_2$ , and (c)  $10^{3+}$  in MeCN.

In order to determine which solvent properties most strongly influence solvatochromic behaviour, a more detailed investigation was made of the UV-visible spectra of  $6^{3+}$ ,  $12^{3+}$  and  $13^{3+}$  (Table 7).

Previous studies of solvatochromism<sup>30</sup> have shown that the effects of different solvent–solute interactions on  $E_{\rm MMCT}$  are additive, *i.e.* solvent properties such as polarity and propensity for hydrogen bonding can be added in a linear relationship to predict the energy of the UV-visible absorption band. The Kamlet–Taft expression<sup>31</sup> (eqn (1)) is one such relationship:

$$E_{\rm MMCT} = c_1 \pi^* + c_2 a + c_3 \beta + c_4 \delta + c_5 \tag{1}$$

where  $\pi^*$  provides a measure of the ability of the solvent to stabilize a solute dipole, and is nearly proportional to solvent dipole moment, *a* is a measure of solvent hydrogen bond donor ability, and  $\beta$  is a measure of solvent hydrogen bond acceptor ability. The  $\delta$ term is a correction factor sometimes required in order adequately to describe solvent polarisability, and the magnitude of  $c_4$  is related to  $c_1$ . (Indeed,  $c_4$  is more properly  $c_1d$ , where *d* is either zero or a small and usually negative number, depending on the nature of the solvatochromic process being described.<sup>32</sup>)

The magnitudes of the coefficients  $c_1-c_4$  reflect the relative importance of their respective parameters in solvatochromism, which in turn sheds light on which solvent properties stabilise or destabilise the ground state relative to the MMCT excited state.

Values of  $c_1-c_5$  were obtained for  $6^{3+}$ ,  $12^{3+}$  and  $13^{3+}$  by measuring their UV-visible spectra in a wide variety of solvents (solvent parameters were taken from ref. 31 and 32), and using multilinear regression analysis to fit the results to the Kamlet–Taft expression (eqn (1)). Variables which were not statistically valid were omitted stepwise from the analysis.

Not all solvents proved suitable because of problems of compound solubility or reactivity, the air-sensitivity of solutions or, in the case of some protic solvents, self-association. The final set of solvents used in the analysis of each of the three compounds studied was decided upon by studying correlation plots of  $E_{\rm MMCT}$ for pairs of the three compounds, by the observation of sample solution reactivity or air-sensitivity, and in some instances by the removal of outliers. In general, alcohols proved largely unsuitable, but more particular details are given below for each complex.

The final form of the Kamlet–Taft expression obtained for  $6^{3+}$  is shown in eqn (2), where data for all non-halogenated alcohols (reactive) and aniline (reactive, with poor correlation plots) were excluded from the regression analysis. Equations displaying statistically stronger correlations could be obtained by excluding different solvents, but it was unclear whether such exclusions were judicious or arbitrary. At any rate, parameter  $\beta$  was the only statistically significant variable influencing  $E_{\text{MMCT}}$ ; using slightly different solvent sets in the analysis did not change this, nor did it produce large changes in the value of  $c_3$ .

$$E_{\text{MMCT}} (\times 10^{-3} \text{ cm}^{-1}) = 6.19\beta + 11.24$$
  
(R<sup>2</sup> = 0.90, F = 144.8) (2)

$$E_{\text{MMCT}} (\times 10^{-3} \text{ cm}^{-1}) = 3.29\beta - 0.73a + 18.56$$
  
( $R^2 = 0.83, F = 39.8$ ) (3)

$$E_{\text{MMCT}} (\times 10^{-3} \text{ cm}^{-1}) = 3.80\beta + 12.61$$
  
(R<sup>2</sup> = 0.81, F = 53.7) (4)

The Kamlet–Taft expressions for  $12^{3+}$  and  $13^{3+}$  are shown in eqn (3) and (4) respectively. Eqn (3) (in which the statistical significance of *a* appears marginal, but see below) is also based on the exclusion of non-halogenated alcohols and aniline from the solvent set on the basis of their reactivity; diethylamine was omitted from the analysis because of low compound solubility. Eqn (4) is based on the exclusion of non-halogenated alcohols, glacial acetic acid, thf and aniline, all of which were either reactive or formed air-sensitive solutions. As for  $6^{3+}$ ,  $\beta$  was the only significant solvent parameter for  $12^{3+}$  and  $13^{3+}$ , regardless of the solvent set used.

On the basis of the UV/visible spectroscopic studies on  $6^{3+}$ ,  $12^{3+}$  and  $13^{3+}$ , the nature of the solvatochromism in the trications, with M(III)Mn(I) (M = Ru or Os) cores, can be explained. In all three cases the positive values of  $c_3$  show that the greater the hydrogen bond accepting ability of the solvent, the higher the energy of MMCT. The M<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub> fragment in the ground state is relatively

Compound	Solvent	$\lambda_{\rm max}/{\rm nm}$	$E/\mathrm{cm}^{-1}$	$\varepsilon/dm^3 \text{ mol}^{-1} \text{ cm}^{-1}$	$v_{1/2}/cm^{-1}$	$J/\mathrm{cm}^{-1}$	a <sup>2</sup> (%)
<b>5</b> <sup>3+a</sup>	$CH_2Cl_2$	1134	8820	4730	3980	1640	3.48
	MeCN	963	10390	2350	5360	1460	1.98
	thf	946	10580	2510	4400 <sup>b</sup>	1380 <sup>b</sup>	1.71 <sup>b</sup>
	dmf	574	17430	920	_	_	_
		740	13510	1130	5630 <sup>b</sup>	1180 <sup>b</sup>	0.77 <sup>b</sup>
<b>6</b> <sup>3+a</sup>	$CH_2Cl_2$	843	11870	2370	4580	1450	1.50
	MeCN	746	13400	1790	4750	1360	1.03
	thf	725	13790	1810	4800	1400	1.03
	dmf	629	15900	1310	4910	1290	0.66
$7^{3+a}$	$CH_2Cl_2$	780	12830	2130	4630	1430	1.25
	MeCN	685	14590	1510	4860	1320	0.82
	thf	689	14525	1730	4750	1390	0.92
	dmf	562	17810	1080	5650	1330	0.56
<b>8</b> <sup>3+ c</sup>	$CH_2Cl_2$	501	19945	930	_	_	
		1098	9110	3640	3060	1290	2.01
	MeCN	472	21210	890	_	_	_
		940	10640	2250	3380	1150	1.17
	thf	476	21010	920	_	_	_
		944	10600	2650	3210	1210	1.32
	dmf	$784^{d}$	12755 <sup>d</sup>	1350	3710	1020	0.64
<b>9</b> <sup>3+c</sup>	$CH_2Cl_2$	476	21005	880	_		_
		883	11330	2570	3630	1310	1.35
	MeCN	430	23255	890	_		_
		760	13155	1480	3820	1100	0.71
	thf	431	23180	860	_		_
		751	13310	1700	3780	1180	0.79
	dmf	634 <sup>d</sup>	15770 <sup>d</sup>	860	5870 <sup>b</sup>	1140 <sup>b</sup>	0.52 <sup>b</sup>
10 <sup>3+e</sup>	MeCN	1453	6885	1360	2490	610	0.79
	thf	578 <sup>f</sup>	17300		_	_	
		1364	7330	g	g	g	g
	dmf	1012	9890	810	5600	880	0.79
$12^{3+h}$	$CH_2Cl_2$	531	18820	1980	5130	1760	0.88
	MeCN	524	19100	2030	5030	1780	0.87
	thf	499	20020	1780	6280	1900	0.91
	dmf	477	20950	1680	5440	1760	0.71
13 <sup>3+h</sup>	$CH_2Cl_2$	746	13410	1940	2770	1080	0.65
	MeCN	742	13480	1720	3210	1100	0.67
	thf	712	14050	840	2990	760	0.29
	dmf	647	15450	1470	3660	1160	0.57

**Table 6** UV-visible spectroscopic data, and calculated values of J and  $a^2$ , for  $[(H_3N)_5M(\mu-NC)MnL_x]^{3+1}$ 

<sup>*a*</sup> Metal-metal separation, *r*, defined as 5.093 Å in calculations of *J* and  $a^2$ . <sup>*b*</sup> Bandwidth at half height estimated as in text. <sup>*c*</sup> Metal-metal separation, *r*, defined as 5.078 Å in calculations of *J* and  $a^2$ . <sup>*d*</sup> Higher energy band observed as shoulder at edge of solvent window;  $\lambda_{max}$  not obtained. <sup>*e*</sup> Metal-metal separation, *r*, defined as 5.118 Å in calculations of *J* and  $a^2$ . <sup>*f*</sup> Absorption for decomposition product. <sup>*g*</sup> Values not obtained because of decomposition. <sup>*h*</sup> Metal-metal separation, *r*, defined as 5.11 Å.

electron-poor when compared with the  $M^{II}(NH_3)_5$  fragment of the photoexcited state [*i.e.* after electron transfer from Mn(I) to M(III)], leading to stronger electrostatic interactions in the ground state between the N–H bonds and hydrogen bond accepting groups in the solvent. Thus, the greater the interaction with a hydrogen bond acceptor (larger  $\beta$ ), the greater the stabilization of the ground state relative to the excited state by solvent interactions, leading in turn to higher  $E_{MMCT}$ .

Previous studies<sup>15</sup> of solvatochromic pentaammine metal complexes such as  $[(\eta-C_5R_5)(Ph_3P)_2M'^{II}(\mu-CN)M^{III}(NH_3)_5]^{3+}$  (M, M' = Ru or Os;  $R_5 = H_5$ ,  $H_4$ Me or Me<sub>5</sub>) have shown a similar dependence of  $E_{MMCT}$  on hydrogen bond accepting ability, with linear plots against the Gutmann donor number.<sup>27</sup> Similar plots for  $6^{3+}$ ,  $12^{3+}$ and  $13^{3+}$  (Fig. 8) also show positive correlations ( $R^2 = 0.92$ , 0.78 and 0.89 respectively), consistent with the results of the Kamlet– Taft analysis. Moreover, as described above, extensive hydrogenbonding involving the ammine ligands is observed in the solid state structures of  $8^{3+}$ [PF<sub>6</sub>]<sub>3</sub>·2Me<sub>2</sub>CO·1.5Et<sub>2</sub>O,  $10^{3+}$ [PF<sub>6</sub>]<sub>3</sub>·5Me<sub>2</sub>CO and  $11^{3+}$ [PF<sub>6</sub>]<sub>3</sub>·4Me<sub>2</sub>CO.



Fig. 8 Plots of  $E_{\text{MMCT}}$  vs. Gutmann donor number for  $6^{3+}$ ,  $12^{3+}$  and  $13^{3+}$ .

Table 7Solvent parameters and UV-visible spectroscopic data for  $6^{3+}$ ,  $12^{3+}$  and  $13^{3+}$ 

						$\lambda_{\rm max}/{\rm nm}$		
	a	β	$\pi^*$	δ	DN <sup>a</sup>	<b>6</b> <sup>3+</sup>	<b>12</b> <sup>3+</sup>	<b>13</b> <sup>3+</sup>
Acetone	0.08	0.43	0.71	0.0	17.0	711.6	505.0	707.0
Water	1.17	0.47	1.09	0.0	18.0	683.9	501.4	
Nitromethane	0.22	0.06	0.85	0.0	2.7	843.7	542.8	781.2
Methanol	0.98	0.66	0.60	0.0	30.0	715.8	511.8	742.6
Chloroform	0.20	0.10	0.58	0.5	4.0	826.4	523.6	732.2
Ethyl acetate	0.00	0.45	0.55	0.0	17.1	710.1	497.0	689.0
dmf	0.00	0.69	0.88	0.0	26.6	628.8	477.3	647.1
Toluene	0.00	0.11	0.54	1.0	0.1	796.4	509.2	780.0
thf	0.00	0.55	0.58	0.0	20.0	725.4	499.4	711.6
Propan-2-ol	0.76	0.84	0.48	0.0	36.0	730.4	513.9	732.8
Acetonitrile	0.19	0.40	0.75	0.0	14.1	746.2	523.6	741.8
Methyl formate	0.00	0.37	0.62	0.0		723.6	502.6	699.7
$CH_2Cl_2$	0.13	0.10	0.82	0.5	1.0	842.5	531.4	745.8
dmso	0.00	0.76	1.00	0.0	29.8	613.0	469.4	624.6
dma	0.00	0.76	0.88	0.0	27.8	629.4	478.4	654.6
Nitrobenzene	0.00	0.30	1.01	1.0	4.4	845.3	535.0	770.6
Benzonitrile	0.00	0.37	0.90	1.0	11.9	763.5	522.2	737.6
Bromoform	0.05	0.05	0.62	0.5		803.2	516.8	738.9
Diethylamine	0.03	0.70	0.24	0.0	50.0		430.0	
Aniline	0.26	0.50	0.73	1.0	35.0	568.5	515.5	754.4
Glacial acetic acid	1.12	0.45	0.64	0.0	20.0	708.6	504.3	
Propan-1-ol	0.84	0.90	0.52	0.0		728.0	516.4	737.0
2,2,2-Trifluoroethanol	1.51	0.00	0.73	0.5		915.0	577.1	834.6
1,1,1,3,3,3-Hexafluoropropan-2-ol	1.96	0.00	0.65	0.5		946.0	606.0	
Diethyl ether	0.00	0.47	0.27	0.0	19.2			

If the small negative value (-0.73) of the *a* coefficient  $(c_2)$  in eqn (3) is real, it may result from the influence of solvents displaying both hydrogen bond donor and acceptor properties. For such solvents, self-association might act partially to diminish the interactions between the solvent and the N–H groups of the solute.

The UV-visible spectroscopic data can also be used to calculate values for the parameters J (eqn (5)) and  $a^2$  (eqn (6), unrelated to the solvent parameter a discussed above) which measure the degree of electronic communication between the metal centres in the dinuclear mixed valence complexes.

$$J = 2.05 \times 10^{-2} [\varepsilon \times v_{1/2} \times E]^{1/2} \times r^{-1} (\text{cm}^{-1})$$
 (5)

$$a^{2} = 4.24 \times 10^{-4} [(\varepsilon \times v_{1/2})/(E \times r^{2})] \,(\%) \tag{6}$$

Here,  $\varepsilon$  is the extinction coefficient for the MMCT band in dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>,  $v_{1/2}$  is the width of the band at half-height in cm<sup>-1</sup>, E is the energy of the band maximum in cm<sup>-1</sup> and r is the metalmetal separation in Å. [For the Ru(III)Mn(I) complexes  $\mathbf{8}^{3+}$ ,  $\mathbf{10}^{3+}$  and  $\mathbf{11}^{3+}$ , r was taken from the X-ray structures; in the absence of suitable crystals of analogous osmium complexes the Os–Mn distance was taken as 5.1 Å, *i.e.* the average of the Ru ··· Mn distance for  $\mathbf{8}^{3+}$ ,  $\mathbf{10}^{3+}$  and  $\mathbf{11}^{3+}$  (given that the ionic radii of second and third row transition metals are similar).]

The values of J and  $a^2$  for  $5^{3+}-9^{3+}$  (Table 6) fall in the ranges expected for Robin–Day Class II compounds (typically between several hundred and a few thousand cm<sup>-1</sup>, and 0.5-5% respectively), *i.e.* there is appreciable electronic communication between metal centres, but not to the degree where there is complete delocalisation of charge.

#### Conclusions

The complexes  $[Mn(CN)L_x] \{L_x = trans-(CO)_2 \{P(OPh)_3\}(dppm); cis-(CO)_2(PR_3)(dppm), R = OEt or OPh; (PR_3)(NO)(\eta-C_5H_4Me), R = Ph or OPh react with <math>[Ru(OH_2)(NH_3)_5]^{2+}$  to give  $[(H_3N)_5Ru^{II}(\mu-NC)Mn^{I}L_x]^{2+}$  which undergo two sequential oneelectron oxidations, the first at the ruthenium centre to give  $[(H_3N)_5Ru^{II}(\mu-NC)Mn^{I}L_x]^{3+}$ . These trications, and their osmium(III) analogues  $[(H_3N)_5Os^{III}(\mu-NC)Mn^{I}L_x]^{3+}$ , are strongly solvatochromic, the energy of the metal-to-metal charge transfer band,  $E_{MMCT}$ , varying with the ligand set,  $L_x$ , at manganese and the identity of the second metal (M = Ru or Os).

Multilinear regression analysis of the electronic spectra of  $[(H_3N)_5Ru^{III}(\mu-NC)Mn^I(CO)_2\{P(OEt)_3\}(dppm)][PF_6]_3$ ,  $[(H_3N)_5-Os(\mu-NC)Mn(CO)_2\{P(OEt)_3\}(dppm)-cis][CF_3SO_3]_3$  and  $[(H_3N)_5-Os(\mu-NC)Mn(CO)(dppm)_2-trans][CF_3SO_3]_3$  in a wide range of solvents showed  $E_{MMCT}$  to depend almost exclusively on the hydrogen-bond accepting properties of the solvent. This is consistent with the extensive hydrogen bonding observed between the ammine groups (the H-bond donors) at the Ru(III) site and the oxygen atoms of solvent molecules or the fluorine atoms of the  $[PF_6]^-$  counterions (the H-bond acceptors) in the crystal structures of  $[(H_3N)_5Ru^{III}(\mu-NC)Mn^I(PPh_3)(NO)(\eta-C_5H_4Me)]$ - $[PF_6]_3\cdot 2Me_2CO\cdot 1.5Et_2O, [(H_3N)_5Ru^{III}(\mu-NC)Mn^I(CO)(dppm)_2-trans][PF_6]_3\cdot 5Me_2CO$  and  $[(H_3N)_5Ru^{III}(\mu-NC)Mn^I(CO)_2\{P-(OEt)_3\}(dppm)-trans][PF_6]_3\cdot 4Me_2CO.$ 

#### Experimental

The preparation and purification of the complexes described was carried out under an atmosphere of dry nitrogen unless

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otherwise stated, using dried and deoxygenated solvents purified either by distillation or by using Anhydrous Engineering double alumina or alumina/copper catalyst drying columns. Reactions were monitored by IR spectroscopy where necessary. Reactions involving [Ru(NH<sub>3</sub>)<sub>5</sub>(OH<sub>2</sub>)][PF<sub>6</sub>]<sub>2</sub> were carried out under argon; the heterodinuclear products are light-sensitive in solution, so that light was excluded during their synthesis. The compounds *trans*- and *cis*-[Mn(CN)(CO)<sub>2</sub>(PR<sub>3</sub>)(dppm)] (R = OEt<sup>1</sup> and OPh<sup>33</sup>), *trans*-[Mn(CN)(CO)(dppm)<sub>2</sub>],<sup>2</sup> [Mn(CN)(PR<sub>3</sub>)(NO)( $\eta$ -C<sub>3</sub>H<sub>4</sub>Me)] (R = Ph<sup>26,34</sup> and OPh<sup>26</sup>), [Ru(NH<sub>3</sub>)<sub>5</sub>(OH<sub>2</sub>)][PF<sub>6</sub>]<sub>2</sub>,<sup>35</sup> [Os(NH<sub>3</sub>)<sub>5</sub>(O<sub>3</sub>SCF<sub>3</sub>)][CF<sub>3</sub>SO<sub>3</sub>]<sub>2</sub>,<sup>36</sup> [N<sub>2</sub>C<sub>6</sub>H<sub>4</sub>F-*p*][PF<sub>6</sub>],<sup>37-38</sup> [Fe( $\eta$ -C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>][PF<sub>6</sub>] and [Fe( $\eta$ -C<sub>3</sub>H<sub>3</sub>)( $\eta$ -C<sub>5</sub>H<sub>4</sub>COMe)][BF<sub>4</sub>]<sup>38</sup> were prepared by published methods or variations thereof. The salts [NO][PF<sub>6</sub>] and Tl[PF<sub>6</sub>] were purchased from Fluorochem and Strem Chemicals respectively.

IR spectra were recorded on a Nicolet 5ZDX FT spectrometer and UV-visible spectra on a Perkin Elmer Lambda 19 UV/VIS spectrometer. Electrochemical studies were carried out using an EG & G model 273A potentiostat linked to a computer using EG & G Model 270 Research Electrochemistry software in conjunction with a three-electrode cell. The auxiliary electrode was a platinum wire and the working electrode a platinum disc (1.6 or 2.0 mm diameter) or glassy carbon disc (3.0 mm diameter). The reference was an aqueous saturated calomel electrode separated from the test solution by a fine porosity frit and an agar bridge saturated with KCl. Solutions were 5  $\times$  10<sup>-4</sup> or 1  $\times$  10<sup>-3</sup> mol dm<sup>-3</sup> in the test compound and 0.1 mol dm<sup>-3</sup> in [NBu<sup>n</sup><sub>4</sub>][PF<sub>6</sub>] as the supporting electrolyte. Under the conditions used,  $E^{\circ}$  for the one-electron oxidation of  $[Fe(\eta-C_5H_4COMe)_2]$ ,  $[Fe(\eta-C_5H_5)($  $C_5H_4COMe$ ], [Fe( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] and [Fe( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>], and for the oneelectron reduction  $[Co(\eta-C_5H_5)_2]^+$ , added to the test solutions as internal calibrants, are 0.97, 0.74, 0.47, 0.08 and -0.87 V respectively in CH<sub>2</sub>Cl<sub>2</sub>; the  $E^{\circ_{\prime}}$  values for  $[Fe(\eta - C_5H_5)_2]$  in thf and MeCN are 0.54 and 0.39 V respectively; the  $E^{\circ}$  values for  $[Fe(\eta-C_5H_5)(\eta-C_5H_4COMe)]$  in thf and MeCN are 0.77 and 0.64 V respectively. IR spectroelectrochemical measurements were made using an EG & G model 273A potentiostat in conjunction with a three-electrode system linked to the Bruker IFS25 spectrometer. Microanalyses were carried out by the staff of the Microanalysis Service of the School of Chemistry, University of Bristol.

#### Syntheses

**[(H<sub>3</sub>N)<sub>5</sub>Ru(µ-NC)Mn(CO)<sub>2</sub>{P(OPh)<sub>3</sub>}(dppm)-***cis***][PF<sub>6</sub>]<sub>2</sub> 7<sup>2+</sup>[PF<sub>6</sub>]<sub>2</sub>. Addition of** *cis***-[Mn(CN)(CO)<sub>2</sub>{P(OPh)<sub>3</sub>}(dppm)] (200 mg, 0.241 mmol) in acetone (30 cm<sup>3</sup>) to [Ru(NH<sub>3</sub>)<sub>5</sub>(OH<sub>2</sub>)][PF<sub>6</sub>]<sub>2</sub> (119 mg, 0.241 mmol) in acetone (10 cm<sup>3</sup>), under argon and in the absence of light, gave an orange solution which was stirred for 20 min and then evaporated to dryness** *in vacuo***. The residue was extracted into CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) and filtered through Celite and the filtrate was evaporated to dryness** *in vacuo***. The orange residue was redissolved in the minimum volume of acetone (***ca***. 5 cm<sup>3</sup>) and added dropwise to stirred diethyl ether (125 cm<sup>3</sup>) to precipitate the product as a pale yellow solid. The air-sensitive solid was collected, washed with diethyl ether (3 × 20 cm<sup>3</sup>) and dried** *in vacuo* **for 24 h, yield 198 mg (63%).** 

The air-sensitive complexes  $[(H_3N)_5Ru(\mu-NC)MnL_x][PF_6]_2$ { $L_x = trans-(CO)_2$ {P(OPh)<sub>3</sub>}(dppm)  $5^{2+}[PF_6]_2$ ,  $cis-(CO)_2$ -{P(OEt)<sub>3</sub>}(dppm)  $6^{2+}[PF_6]_2$ , (PR<sub>3</sub>)(NO)( $\eta$ -C<sub>5</sub>H<sub>4</sub>Me), R = Ph

DEt1andextraction step required a larger volume of  $CH_2Cl_2$  (40 cm³) and<br/>the product was further purified by dissolution in  $CH_2Cl_2$  and<br/>dropwise addition to stirred diethyl ether. In the preparation of<br/> $\mathbf{8}^{2+}[PF_6]_2$ , the extraction step required MeCN (30 cm³) instead of<br/> $CH_2Cl_2$ . $\mathbf{8}^{2+}[PF_6]_2$  the extraction step required MeCN (30 cm³) instead of<br/> $CH_2Cl_2$ . $\mathbf{8}^{2+}[PF_6]_2$  the extraction step required MeCN (30 cm³) instead of<br/> $CH_2Cl_2$ . $\mathbf{8}^{2+}[PF_6]_2$  the extraction step required MeCN (30 cm³) instead of<br/> $CH_2Cl_2$ . $\mathbf{8}^{2+}[PF_6]_2$  the extraction step required MeCN (30 cm³) instead of<br/> $CH_2Cl_2$ . $\mathbf{8}^{2+}[PF_6]_2$  the extraction step required MeCN (30 cm³) instead of<br/> $CH_2Cl_2$ . $\mathbf{10}^{2+}[PF_6]_2$  the extraction step required MeCN (30 cm³) instead of<br/> $CH_2Cl_2$ . $\mathbf{10}^{2+}[PF_6]_2$  the extraction step required MeCN (30 cm³) instead of<br/> $CH_2Cl_2$ . $\mathbf{10}^{2+}[PF_6]_2$  the extraction step required MeCN (30 cm³) instead of<br/> $CH_2Cl_2$ . $\mathbf{10}^{2+}[PF_6]_2$  the extraction step required MeCN (30 cm³) instead of<br/> $CH_2Cl_2$ . $\mathbf{10}^{2+}[PF_6]_2$  the extraction step required MeCN (20)(dppm)\_2 trans[PF\_6]\_2 10^{2+}[PF\_6]\_2. $\mathbf{10}^{2+}[PF_6]_2$  (25 cm³) to [Ru(NH\_3)\_5(OH\_2)][PF\_6]\_2 (225 mg, 0.456 mmol)<br/>in acetone (100 cm³) gave an orange solution which was stirred for<br/>using an<br/>15 min before the solvent was removed *in vacuo*. The residue was

15 min before the solvent was removed *in vacuo*. The residue was extracted into MeCN (40 cm<sup>3</sup>) and filtered through Celite. The volume of the filtrate was reduced to *ca*. 5 cm<sup>3</sup> before diethyl ether (60 cm<sup>3</sup>) was added to give an orange solid. The air-stable solid was collected, washed with diethyl ether ( $3 \times 20$  cm<sup>3</sup>) and then dried *in vacuo* for 24 h, yield 483 mg (78%).

 $8^{2+}[PF_6]_2$  or OPh  $9^{2+}[PF_6]_2$  were prepared similarly. The salt

 $5^{2+}[PF_6]_2$  was further purified by dissolution in the minimum

volume of acetone and dropwise addition to stirred diethyl ether

as described above. The salt  $6^{2+}[PF_6]_2$  was purified by dissolution

in CH<sub>2</sub>Cl<sub>2</sub> and filtration through Celite before reduction of the

solvent volume to ca. 5 cm<sup>3</sup> in vacuo and dropwise addition of

the solution to stirred diethyl ether (100 cm<sup>3</sup>). For  $9^{2+}[PF_6]_2$  the

 $[(H_3N)_5Ru(\mu-NC)Mn(CO)_2{P(OPh)_3}(dppm)-cis][PF_6]_3 7^{3+}[PF_6]_3.$ Addition of cis-[Mn(CN)(CO)<sub>2</sub>{P(OPh)<sub>3</sub>}(dppm)] (300 mg, 0.361 mmol) in acetone (30 cm<sup>3</sup>) to a stirred solution of  $[Ru(NH_3)_5(OH_2)][PF_6]_2$  (178 mg, 0.361 mmol) in acetone (30 cm<sup>3</sup>) gave an orange solution. After 10 min  $[N_2C_6H_4F-p][PF_6]$  (97 mg, 0.361 mmol) was added to the mixture to give an immediate colour change to deep blue. The reaction mixture was stirred for a further 1 h before it was evaporated to dryness in vacuo. The residue was extracted into CH<sub>2</sub>Cl<sub>2</sub> (40 cm<sup>3</sup>) and filtered through Celite. The filtrate was reduced in volume to ca. 10 cm<sup>3</sup> and diethyl ether was added to give a blue powder which was washed with diethyl ether  $(3 \times 30 \text{ cm}^3)$ . The powder was redissolved in the minimum volume of acetone (less than 10 cm<sup>3</sup>) and the solution was added dropwise to stirred diethyl ether (125 cm<sup>3</sup>) to precipitate the product. The air-stable blue solid was washed with diethyl ether  $(3 \times 30 \text{ cm}^3)$ and dried in vacuo for 24 h, yield 447 mg (85%).

The complexes  $[(H_3N)_5Ru(\mu-NC)MnL_x][PF_6]_3 \{L_x = trans-(CO)_2\{P(OPh)_3\}(dppm) \mathbf{5}^{3+}[PF_6]_3, cis-(CO)_2\{P(OEt)_3\}(dppm) \mathbf{6}^{3+}[PF_6]_3; L_x = (PR_3)(NO)(\eta-C_3H_4Me), R = Ph \mathbf{8}^{3+}[PF_6]_3 \text{ or } OPh \mathbf{9}^{3+}[PF_6]_3 \}$  were prepared similarly. In the case of  $\mathbf{5}^{3+}[PF_6]_3$  and  $\mathbf{6}^{3+}[PF_6]_3$  the extraction step was effected with CHCl\_3. For  $\mathbf{9}^{3+}[PF_6]_3$  the slightly oily product was vigorously stirred with diethyl ether (40 cm<sup>3</sup>) for 2 h to give a dark brown powder.

[(H<sub>3</sub>N)<sub>5</sub>Ru( $\mu$ -NC)Mn(CO)(dppm)<sub>2</sub>-trans][PF<sub>6</sub>]<sub>3</sub> 10<sup>3+</sup>[PF<sub>6</sub>]<sub>3</sub>. To a stirred solution of [(H<sub>3</sub>N)<sub>5</sub>Ru( $\mu$ -NC)Mn(CO)(dppm)<sub>2</sub>trans][PF<sub>6</sub>]<sub>2</sub> (300 mg, 0.200 mmol) in acetone (30 cm<sup>3</sup>) was added [Fe( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>][PF<sub>6</sub>] (66 mg, 0.200 mmol) to give an immediate colour change from orange to orange-brown. The reaction mixture was stirred for 10 min before the solvent volume was reduced to *ca*. 10 cm<sup>3</sup> and the mixture filtered. The concentrated acetone solution was layered with diethyl ether and stored at -10 °C for 3 days. The resulting dark red-brown crystals were washed with diethyl ether (3 × 20 cm<sup>3</sup>) to give an air-sensitive red-brown powder, yield 219 mg (73%).

Compound	$8^{3+}[\mathrm{PF}_6]_3 \cdot 2\mathrm{Me}_2\mathrm{CO} \cdot 1.5\mathrm{Et}_2\mathrm{O}$	$10^{3+}$ [PF <sub>6</sub> ] <sub>3</sub> ·5Me <sub>2</sub> CO	$11^{3+}[PF_6]_3 \cdot 4Me_2CO$
Formula	$C_{37}H_{63}F_{18}MnN_7O_{4.5}P_4Ru$	$C_{67}H_{89}F_{18}MnN_6O_6P_7Ru$	$C_{46}H_{76}F_{18}MnN_6O_9P_6Ru$
M	1299.83	1789.24	1540.96
Crystal system	Triclinic	Triclinic	Monoclinic
Space group (no.)	<i>P</i> 1̄ (no. 2)	<i>P</i> 1̄ (no. 2)	$P2_1/n$ (no. 14)
a/Å	9.972(2)	11.596(8)	14.091(4)
b/Å	13.579(2)	14.943(8)	31.216(5)
c/Å	20.985(5)	25.237(15)	16.167(4)
$a/^{\circ}$	81.27(1)	104.96(2)	90
β/°	81.48(2)	100.72(4)	93.48(3)
y/°	76.76(1)	98.59(3)	90
T/K	173(2)	173(2)	293(2)
$U/Å^3$	2715.0(11)	4060(4)	7098(3)
Ζ	2	2	4
$\mu/\mathrm{mm}^{-1}$	0.735	0.571	0.622
Reflections collected	27761	21254	36451
Independent reflections $(R_{int})$	12195 (0.0602)	13903 (0.0807)	12454 (0.1689)
Final <i>R</i> indices $[I > 2\sigma(I)]$ : <i>R</i> 1, <i>wR</i> 2	0.0656, 0.1488	0.0710, 0.0997	0.0883, 0.1893

 $\label{eq:table_trans_constraint} \begin{array}{l} \textbf{Table 8} \quad Crystal \ and \ refinement \ data \ for \ [(H_3N)_5Ru(\mu-NC)Mn(PPh_3)(NO)(\eta-C_5H_4Me)][PF_6]_3\cdot 2Me_2CO\cdot 1.5Et_2O \ 8^{3+}[PF_6]_3\cdot 2Me_2CO\cdot 1.5Et_2O, \ [(H_3N)_5Ru(\mu-NC)Mn(CO)(dppm)_2-trans][PF_6]_3\cdot 5Me_2CO \ 10^{3+}[PF_6]_3\cdot 5Me_2CO \ and \ [(H_3N)_5Ru(\mu-NC)Mn(CO)_2\{P(OEt)_3\}(dppm)-trans][PF_6]_3\cdot 4Me_2CO \ 11^{3+}[PF_6]_3\cdot 4Me_2CO \ 11^{3+}$ 

 $[(H_3N)_5Ru(\mu-NC)Mn(CO)_2\{P(OEt)_3\}(dppm)-trans|[PF_6]_3$ .  $3Me_2CO, 11^{3+}[PF_6]_3\cdot 3Me_2CO$ . Addition of  $[Ru(NH_3)_5(OH_2)]$ -  $[PF_6]_2$  (216 mg, 0.436 mmol) in acetone (25 cm<sup>3</sup>) to a stirred solution of trans- $[Mn(CN)(CO)_2\{P(OEt)_3\}(dppm)]$  (300 mg, 0.436 mmol) in acetone (25 cm<sup>3</sup>) gave an orange solution. After 10 min  $[N_2C_6H_4F-p][PF_6]$  (117 mg, 0.436 mmol) was added to give an immediate colour change to blue. The reaction mixture was stirred for a further 45 min before the solvent volume was reduced to *ca*. 10 cm<sup>3</sup> and the reaction mixture filtered. The filtrate was layered with diethyl ether and stored at -10 °C for 4 weeks. The mother liquors were removed from the resulting dark blue-green crystals which were washed with diethyl ether (2 × 10 cm<sup>3</sup>) and then separated from a small amount of white powder, yield 412 mg (64%).

[(H<sub>3</sub>N)<sub>5</sub>Os( $\mu$ -NC)Mn(CO)<sub>2</sub>{P(OEt)<sub>3</sub>}(dppm)-*cis*][CF<sub>3</sub>SO<sub>3</sub>]<sub>3</sub>· 2CH<sub>2</sub>Cl<sub>2</sub> 12<sup>3+</sup>[CF<sub>3</sub>SO<sub>3</sub>]<sub>3</sub>·2CH<sub>2</sub>Cl<sub>2</sub>. A solution of [Os(NH<sub>3</sub>)<sub>5</sub>-(O<sub>3</sub>SCF<sub>3</sub>)][CF<sub>3</sub>SO<sub>3</sub>]<sub>2</sub> (88 mg, 0.122 mmol) and *cis*-[Mn-(CN)(CO)<sub>2</sub>{P(OEt)<sub>3</sub>}(dppm)] (84 mg, 0.122 mmol) in thf (20 cm<sup>3</sup>) was heated under reflux for 48 h and then stirred for a further 48 h. The solution was filtered through Celite, and the solution volume reduced *in vacuo* to *ca*. 5 cm<sup>3</sup>. Diethyl ether (40 cm<sup>3</sup>) was slowly added to the stirred solution to precipitate a purple powder which was washed with diethyl ether (2 × 20 cm<sup>3</sup>) and then dried *in vacuo*. Further purification, by slow evaporation under vacuum of a solution of the complex in CH<sub>2</sub>Cl<sub>2</sub> (30 cm<sup>3</sup>) and *n*-hexane (30 cm<sup>3</sup>), gave a purple powder which was washed with diethyl ether (2 × 20 cm<sup>3</sup>) and dried *in vacuo*, yield 129 mg (67%).

**[(H<sub>3</sub>N)<sub>5</sub>Os(\mu-NC)Mn(CO)(dppm)<sub>2</sub>-trans][CF<sub>3</sub>SO<sub>3</sub>]<sub>3</sub>13<sup>3+</sup>[CF<sub>3</sub>SO<sub>3</sub>]<sub>3</sub>. A mixture of [Os(NH<sub>3</sub>)<sub>5</sub>(O<sub>3</sub>SCF<sub>3</sub>)][CF<sub>3</sub>SO<sub>3</sub>]<sub>2</sub> (73 mg, 0.100 mmol) and** *trans***-[Mn(CN)(CO)(dppm)<sub>2</sub>] (89 mg, 0.101 mmol) in thf (20 cm<sup>3</sup>) was heated under reflux for 24 h and then stirred for another 24 h. The solution was then evaporated to dryness** *in vacuo***, and the residue extracted into CH<sub>2</sub>Cl<sub>2</sub> (1 × 10 cm<sup>3</sup> then 2 × 5 cm<sup>3</sup>). The extract was filtered,** *n***-hexane was added (25 cm<sup>3</sup>), and the product was precipitated by slow evaporation** *in vacuo***. The green powder was washed with hexane (2 × 10 cm<sup>3</sup>), before drying under vacuum in the absence of light. Allowing diethyl ether to** 

diffuse slowly into an acetone solution of the powder gave the product as light-sensitive green microcrystals after 14 d at 4  $^{\circ}$ C, yield 82 mg (51%).

# Structure determinations of $[(H_3N)_5Ru(\mu-NC)Mn(PPh_3)(NO)(\eta-C_5H_4Me)][PF_6]_3 \cdot 2Me_2CO \cdot 1.5Et_2O 8^{3+}[PF_6]_3 \cdot 2Me_2CO \cdot 1.5Et_2O, [(H_3N)_5Ru(\mu-NC)Mn(CO)(dppm)_2-trans][PF_6]_3 \cdot 5Me_2CO 10^{3+}[PF_6]_3 \cdot 5Me_2CO and [(H_3N)_5Ru(\mu-NC)Mn(CO)_2- {P(OEt)_3}(dppm)-trans][PF_6]_3 \cdot 4Me_2CO 11^{3+}[PF_6]_3 \cdot 4Me_2CO$

Dark purple crystals of  $[(H_3N)_5Ru(\mu-NC)Mn(PPh_3)(NO)(\eta-C_5H_4Me)][PF_6]_3\cdot 2Me_2CO\cdot 1.5Et_2O$  **8**<sup>3+</sup>[PF\_6]\_3·2Me\_2CO· 1.5Et\_2O, red-green dichroic crystals of  $[(H_3N)_5Ru(\mu-NC)Mn(CO)(dppm)_2$ -*trans*][PF\_6]\_3·5Me\_2CO **10**<sup>3+</sup>[PF\_6]\_3·5Me\_2CO and dark blue crystals of  $[(H_3N)_5Ru(\mu-NC)Mn(CO)_2{P(OEt)_3}(dppm)$ -*trans*]-[PF\_6]\_3·4Me\_2CO **11**<sup>3+</sup>[PF\_6]\_3·4Me\_2CO were grown by allowing diethyl ether to diffuse into a concentrated acetone solution of the complex at -10 °C. The crystals of **11**<sup>3+</sup>[PF\_6]\_3·4Me\_2CO were very poorly diffracting, leading to a high value of  $R_{int}$  (0.17) and ultimately to a relatively poor value of  $R_1$  (0.0883).

Many of the details of the structure analyses are listed in Table 8. CCDC reference numbers 603279–603281.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b602334g

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