

Triazenide-bridged dirhodium complexes containing redox-active cyanomanganese ligands

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The complex $[\text{Rh}_2(\text{CO})_4(\mu\text{-RN}_3\text{R}_2)]$ **1** reacted with the cyanomanganese ligands *cis*- $[\text{Mn}(\text{CN})(\text{CO})_2(\text{L-L})]$ [$\text{L-L} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm), $\text{L} = \text{P}(\text{OEt})_3$ **2** or $\text{P}(\text{OPh})_3$ **3**; $\text{L-L} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe), $\text{L} = \text{PEt}_3$ **4**] in *n*-hexane under reflux, or with *trans*- $[\text{Mn}(\text{CN})(\text{CO})_2(\text{L-L})]$ [$\text{L-L} = \text{dppm}$, $\text{L} = \text{P}(\text{OEt})_3$ **8** or $\text{P}(\text{OPh})_3$ **9**] or $[\text{Mn}(\text{CN})(\text{NO})\text{L}(\text{cp}')]$ [$\text{L} = \text{P}(\text{OPh})_3$ **12** or PPh_3 **13**, $\text{cp}' = \eta\text{-C}_5\text{H}_4\text{Me}$], in CH_2Cl_2 in the presence of ONMe_3 , giving $[\text{Rh}_2\{(\mu\text{-NC})\text{MnL}_x\}(\text{CO})_3(\mu\text{-RN}_3\text{R}_2)]$ [$\text{L}_x = \text{cis}(\text{CO})_2[\text{P}(\text{OEt})_3](\text{dppm})$ **5**, *cis*- $(\text{CO})_2\text{-}[\text{P}(\text{OPh})_3](\text{dppm})$ **6**, *cis*- $(\text{CO})_2(\text{PEt}_3)(\text{dppe})$ **7**, *trans*- $(\text{CO})_2[\text{P}(\text{OEt})_3](\text{dppm})$ **10**, *trans*- $(\text{CO})_2[\text{P}(\text{OPh})_3](\text{dppm})$ **11**, $(\text{NO})[\text{P}(\text{OPh})_3](\text{cp}')$ **14** or $(\text{NO})(\text{PPh}_3)(\text{cp}')$ **15**]. The tricarbonyls underwent one-electron oxidation at a platinum-disc electrode and reacted with $[\text{Fe}(\text{cp})_2][\text{PF}_6]$ ($\text{cp} = \eta\text{-C}_5\text{H}_5$) in CH_2Cl_2 to give the corresponding paramagnetic complexes **5**⁺–**7**⁺, **10**⁺, **11**⁺, **14**⁺ and **15**⁺ which contain $[\text{Rh}_2]^{3+}$ cores. The addition of compounds **2** or **8** to **5**⁺ or **10**⁺, or of **3** or **9** to **6**⁺ or **11**⁺, resulted in further carbonyl substitution to give the dicarbonyl complexes $[\text{Rh}_2\{(\mu\text{-NC})\text{MnL}_x\}_2(\text{CO})_2(\mu\text{-RN}_3\text{R}_2)]^+$ **16**⁺–**21**⁺ which reacted with $[\text{Fe}(\text{cp})_2][\text{PF}_6]$ in the presence of chloride ion to give the diamagnetic $[\text{Rh}_2]^{4+}$ -containing cations $[\text{Rh}_2\text{Cl}\{(\mu\text{-NC})\text{MnL}_x\}_2(\text{CO})_2(\mu\text{-RN}_3\text{R}_2)]^+$ **22**⁺–**24**⁺. The ESR spectra of the paramagnetic $[\text{Rh}_2]^{3+}$ -containing cations, and the effects of varying the cyanomanganese ligand on the order in which the redox-active sites (Rh_2 and Mn) of the tri- and tetra-metallic complexes are oxidised, are discussed.

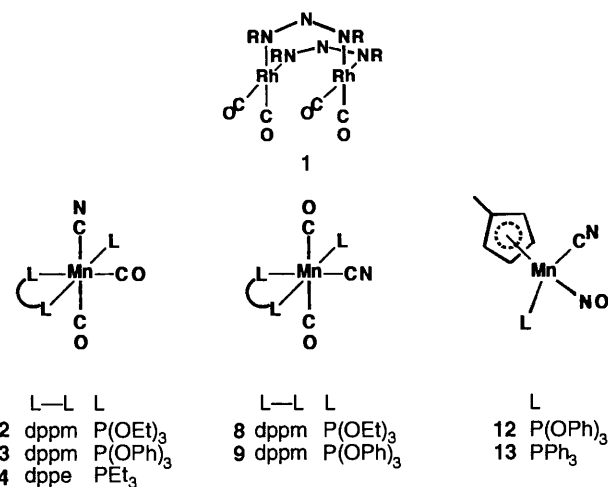
In recent years we have carried out extensive studies of two series of redox-active complexes. First, the triazenide-bridged dimer $[\text{Rh}_2(\text{CO})_4(\mu\text{-RN}_3\text{R}_2)]$ **1** (Scheme 1) is the precursor to a wide range of binuclear complexes in which the dirhodium cores $[\text{Rh}_2]^{z+}$ ($z = 2\text{--}4$) may be systematically and selectively stabilised.^{1–5} Secondly, the octahedral cyanide complexes *cis*- $[\text{Mn}(\text{CN})(\text{CO})_2(\text{L-L})]$ [$\text{L-L} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm), $\text{L} = \text{P}(\text{OEt})_3$ **2** or $\text{P}(\text{OPh})_3$ **3**; $\text{L-L} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe), $\text{L} = \text{PEt}_3$ **4**] and *trans*- $[\text{Mn}(\text{CN})(\text{CO})_2(\text{L-L})]$ [$\text{L-L} = \text{dppm}$, $\text{L} = \text{P}(\text{OEt})_3$ **8** or $\text{P}(\text{OPh})_3$ **9**] can be used in the construction of a wide variety of hetero-bi- and tri-metallic species in which the extent of intramolecular electron transfer can be varied by changing the ligands and their geometry at manganese.^{6–15} This paper gives details¹⁶ of the systematic synthesis, from **1** and the cyanomanganese ligands **2–4**, **8**, **9** and $[\text{Mn}(\text{CN})(\text{NO})\text{L}(\text{cp}')]$ [$\text{L} = \text{P}(\text{OPh})_3$ **12** or PPh_3 **13**, $\text{cp}' = \eta\text{-C}_5\text{H}_4\text{Me}$], of tri- and tetra-metallic complexes where the order in which the redox-active sites (Rh_2 and Mn) is oxidised can be controlled by the selective variation of the ancillary ligands at manganese.

Results and Discussion

$[\text{Rh}_2]^{2+}$ complexes with a $\text{Rh}_2(\text{CO})_3$ core

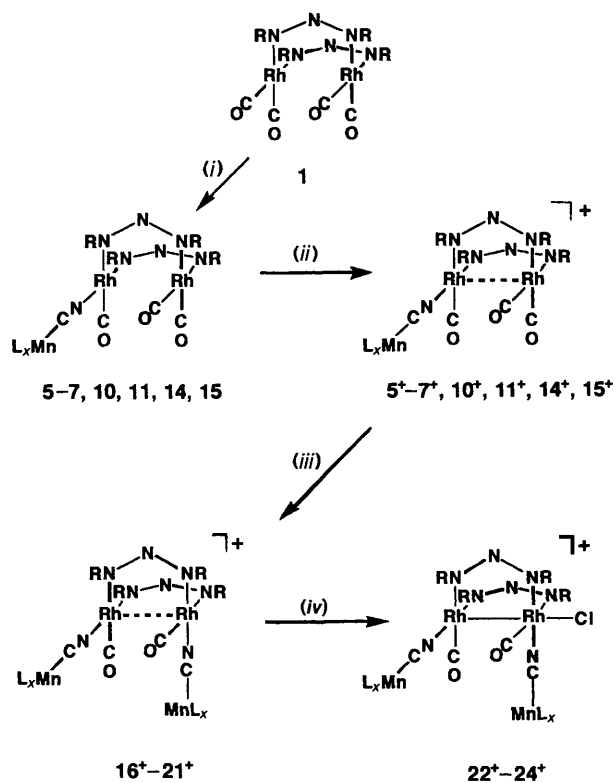
On heating a 1:1 mixture of **1** and **2**, **3** or **4** under reflux in *n*-hexane for 2 h, deep red solutions are formed from which $[\text{Rh}_2\{(\mu\text{-NC})\text{MnL}_x\}(\text{CO})_3(\mu\text{-RN}_3\text{R}_2)]$ [$\text{L}_x = \text{cis}(\text{CO})_2\text{-}[\text{P}(\text{OEt})_3](\text{dppm})$ **5**, *cis*- $(\text{CO})_2[\text{P}(\text{OPh})_3](\text{dppm})$ **6** and *cis*- $(\text{CO})_2(\text{PEt}_3)(\text{dppe})$ **7**] (Scheme 1) are isolated in good yield as red powders after recrystallisation from *n*-hexane. In contrast to the reactions between **1** and PPh_3 ¹ or 2,2'-bipyridyl (bipy),² which result in the formation of dicarbonyl complexes, only monosubstitution at the dirhodium core is observed with **2–4**.

This preparative route cannot be used to give complexes having the *trans*-dicarbonyl structure at manganese in that compounds **8** and **9** isomerise to the thermodynamically more stable *cis*-manganese dicarbonyls, **2** and **3**, on heating.⁷ However, complexes $[\text{Rh}_2\{(\mu\text{-NC})\text{MnL}_x\}(\text{CO})_3(\mu\text{-RN}_3\text{R}_2)]$ [$\text{L}_x = \text{trans}(\text{CO})_2[\text{P}(\text{OEt})_3](\text{dppm})$ **10** or *trans*- $(\text{CO})_2\text{-}$



$[\text{P}(\text{OPh})_3](\text{dppm})$ **11**] can be prepared at room temperature by treating 1 equivalent of **1** in CH_2Cl_2 with **8** or **9** in the presence of the decarbonylating agent ONMe_3 ; this method also affords complexes containing the tetrahedral cyanomanganese ligands $[\text{Mn}(\text{CN})(\text{NO})\text{L}(\text{cp}')]$ [$\text{L} = \text{P}(\text{OPh})_3$ **12** or PPh_3 **13**, $\text{cp}' = \eta\text{-C}_5\text{H}_4\text{Me}$], namely $[\text{Rh}_2\{(\mu\text{-NC})\text{MnL}_x\}(\text{CO})_3(\mu\text{-RN}_3\text{R}_2)]$ [$\text{L}_x = (\text{NO})\text{L}(\text{cp}')$, $\text{L} = \text{P}(\text{OPh})_3$ **14** or PPh_3 **15**]. Unfortunately, no synthetic route could be devised to dirhodium triazenido derivatives containing the most electron-rich cyanomanganese ligand we have previously used, namely *trans*- $[\text{Mn}(\text{CN})(\text{CO})(\text{dppm})_2]$.

Complexes **5–7**, **10**, **11**, **14** and **15** were characterised by elemental analysis and IR spectroscopy (Table 1). Each complex shows four or five bands in the IR carbonyl region, three associated with the $\text{Rh}_2(\text{CO})_3$ unit and one or two for the dicarbonylmanganese fragment (having *trans* or *cis* geometry respectively). Varying the ancillary ligands at manganese has little effect on $\nu(\text{CO})_{\text{Rh}}$. However, a comparison with the data for $[\text{Rh}_2(\text{CO})_3(\text{CNBu}')(\mu\text{-RN}_3\text{R}_2)]$ [$\nu(\text{CO})$ 2062, 2010 and



Scheme 1 R = *p*-tolyl. (i) $[\text{Mn}(\text{CN})\text{L}_x]$ (and ONMe₃ for **10**, **11**, **14** and **15**); (ii) $[\text{Fe}(\text{cp})_2][\text{PF}_6]$; (iii) $[\text{Mn}(\text{CN})\text{L}_x]$; (iv) $[\text{Fe}(\text{cp})_2][\text{PF}_6]$ and Cl⁻

1998 cm⁻¹]¹ shows the cyanomanganese ligands to be net better donors than the isocyanide.

The effect on $\nu(\text{CO})_{\text{Mn}}$ of co-ordinating the $\text{Rh}_2(\text{CO})_3(\mu\text{-RN}_3\text{R})_2$ group to the N atom of the cyanomanganese ligand is minor, the increase in energy (*ca.* 7 cm⁻¹) being much less than that observed (*ca.* 20 cm⁻¹) on N-co-ordination of $\text{Fe}(\text{NO})_2(\text{PPh}_3)^+$ or $\text{Fe}(\text{NO})_2$.¹⁴ The small increase in $\nu(\text{CO})_{\text{Mn}}$ indicates the relatively poor electron-withdrawing capacity of the $\text{Rh}_2(\text{CO})_3(\mu\text{-RN}_3\text{R})_2$ group, as also suggested by the large increase in $\nu(\text{CN})$ on cyanide bridge formation. As noted previously,¹⁴ the increase expected¹⁷ in $\nu(\text{CN})$ on N-co-ordination (because of the mechanical restraint imposed by bridge formation) is opposed if the N-bound group acts to increase the population of the C–N π^* orbitals (by enhancing π -back donation from Mn to the cyanide bridge). With good N-bound π acceptors there may be a net *decrease* in $\nu(\text{CN})$, as observed for $[\text{Fe}\{\{\mu\text{-CN}\}\text{MnL}_x\}(\text{NO})_2(\text{PPh}_3)]^+$ [$\Delta\nu(\text{CN}) = -20$ to -25 cm⁻¹].¹⁴

The new dirhodium triazenido complexes described in this paper undergo multiple oxidation and/or reduction steps in the potential range -0.70 to 1.8 V. However, the cyclic voltammograms were often ill-defined even though all of the electrochemical experiments were performed on analytically (C, H and N) and spectroscopically pure samples. The quality of the electrochemical data was not improved by changing the solvent [from CH_2Cl_2 to tetrahydrofuran (thf) or MeCN] or electrode material (from platinum to glassy carbon). Discussion is therefore largely confined to complexes showing relatively well resolved cyclic voltammograms.

The cyclic voltammogram of complex **10** shows three oxidation waves, at 0.15, 0.84 and 1.28 V [Fig. 1(a)]. The first two are reversible ($i_{\text{red}}/i_{\text{ox}} = 1.0$ for scan rates 50 to 200 mV s⁻¹) but the third is incompletely so [$i_{\text{red}}/i_{\text{ox}} < 1.0$ for all scan rates used and the return (reduction) wave is broadened; ($E_{\text{p,ox}}$ is given at a scan rate of 200 mV s⁻¹]. The waves may be assigned to specific couples by noting the changes in the voltammogram when the ligands at manganese are varied. For example, the

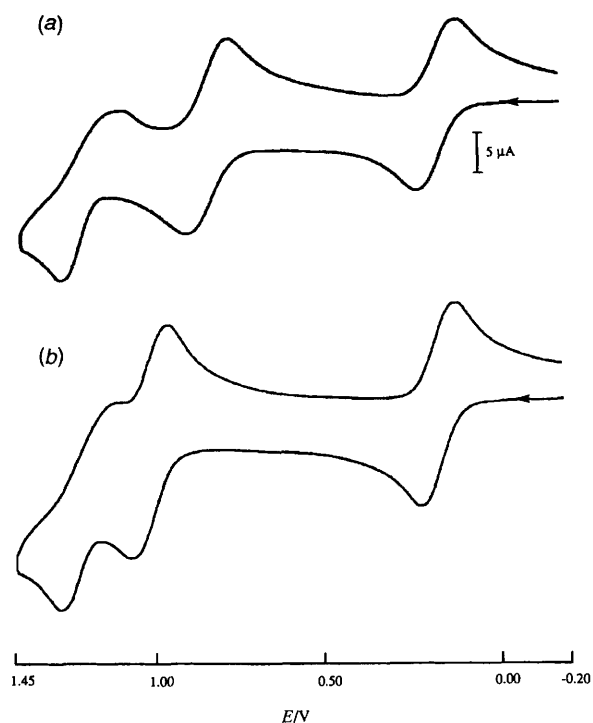


Fig. 1 The cyclic voltammograms, from -0.20 to 1.45 V at a scan rate of 200 mV s⁻¹, of complexes (a) **10** and (b) **11** in CH_2Cl_2 at a platinum disc electrode

cyclic voltammogram of **11** [containing $\text{P}(\text{OPh})_3$ in place of $\text{P}(\text{OEt})_3$] shows oxidation waves at 0.16, 1.05 and 1.33 V [Fig. 1(b)]; the potentials of the first and third waves are essentially unchanged from those of **10** and can therefore be assigned to the oxidation of the dirhodium core (to the $[\text{Rh}_2]^{3+}$ and $[\text{Rh}_2]^{4+}$ states respectively). The second wave is shifted to a more positive potential for **11** and is therefore due to the $\text{Mn}^{\text{I}}\text{-Mn}^{\text{II}}$ couple.

The cyclic voltammogram of complex **5** shows two oxidation waves, at 0.17 and 1.26 V, again corresponding to the oxidation of the dirhodium core. In this case, the third oxidation wave (irreversible, at 1.38 V) is observed at a potential *more positive* than that for the $[\text{Rh}_2]^{3+}\text{-}[\text{Rh}_2]^{4+}$ couple. Moreover, this wave is coupled to a reversible product wave centred at 0.78 V, (*i.e.* at a potential very similar to that of the $\text{Mn}^{\text{I}}\text{-Mn}^{\text{II}}$ couple in **10**). Here, then, a change in geometry at manganese (*trans* in **10** to *cis* in **5**) leads to a change in the order in which the redox sites of the trimetallic complexes are oxidised. In addition, oxidative isomerisation at the *cis*- $\text{Mn}(\text{CO})_2$ site (shown by the coupling of the irreversible oxidation wave to the reversible product wave, and as found in the free cyanomanganese ligand⁷) also leads to a change in this order. Thus oxidation of **5** follows the order $[\text{Rh}_2]^{2+}$, $[\text{Rh}_2]^{3+}$, Mn^{I} but the resulting trication is reduced in the order $[\text{Rh}_2]^{4+}$, Mn^{II} , $[\text{Rh}_2]^{3+}$.

The behaviour of complex **6** is very similar to that of **5**. However, the cyclic voltammogram of **7** (Fig. 2) shows that the oxidation of the *cis*- $\text{Mn}(\text{CO})_2$ fragment occurs at a more negative potential than the oxidation of the $[\text{Rh}_2]^{3+}$ core, brought about by replacing the phosphite ligands at manganese by the more electron-donating PET_3 . These results show, therefore, that varying the arrangement and donor ability of the ancillary ligands at manganese allows control over the order in which the dirhodium core and the cyanomanganese ligand are oxidised.

The cyclic voltammograms of complexes **14** and **15**, which contain the relatively electron-poor, pseudo-tetrahedral manganese cyanide ligands $[\text{Mn}(\text{CN})(\text{NO})\text{L}(\text{cp}')]$ [$\text{L} = \text{P}(\text{OPh})_3$ **12** or PPh_3 **13**], also show three one-electron oxidation waves. The first two (at *ca.* 0.20 and 1.20 V) are at very similar potentials to those of the rhodium oxidations in **5-7**, **10** and **11**; the assignment to rhodium-based oxidation processes is confirmed

Table 1 Analytical and IR spectroscopic data for $[\text{Rh}_2\text{X}_2\{(\mu\text{-NC})\text{MnL}_x\}_n(\text{CO})_{4-n}(\mu\text{-RNNNR})_2]^{2+}$ ($\text{R} = p\text{-tolyl}$)

L_x^a	X	n	z ^b	Colour	Yield (%)	Analysis (%) ^c				IR ^d /cm ⁻¹		$\nu(\text{CO})_{\text{Rh}}$	$\nu(\text{CO})_{\text{Mn}}$
						C	H	N		$\nu(\text{CN})$			
5 <i>cis</i> -(CO) ₂ [P(OEt) ₃] ₂ (dppm)	—	1	0	Red	52	55.1 (54.8)	4.9 (4.6)	6.7 (6.8)		2115w	2052, 1988, 1971m (sh)	1960, 1903m	
5⁺ <i>cis</i> -(CO) ₂ [P(OEt) ₃] ₂ (dppm)	—	1	1	Green	56	50.0 (49.7)	4.2 (4.2)	5.9 (6.2)		^e	2113, 2073, 2053m	1967, 1913	
6 <i>cis</i> -(CO) ₂ [P(OPh) ₃] ₂ (dppm)	—	1	0	Dark red	85	58.4 (58.9)	4.4 (4.2)	6.2 (6.2)		2121w	2053, 1989, 1974 ^f	1974 ^f , 1918m	
6⁺ <i>cis</i> -(CO) ₂ [P(OPh) ₃] ₂ (dppm)	—	1	1	Dark green	67	54.1 (53.9)	4.1 (3.8)	5.3 (5.7)		^e	2115, 2074, 2057m	1978, 1927	
7 <i>cis</i> -(CO) ₂ (PEt ₃)(dppe)	—	1	0	Red	41	56.5 (56.9)	5.2 (4.9)	6.7 (7.1)		2113w	2053, 1988, 1973m (sh)	1943, 1885	
7⁺ <i>cis</i> -(CO) ₂ (PEt ₃)(dppe)	—	1	1	Green	48	51.2 (51.6)	4.7 (4.4)	5.9 (6.4)		2098m	2113, 2073, 2050m	1950, 1896	
10 <i>trans</i> -(CO) ₂ [P(OEt) ₃] ₂ (dppm)	—	1	0	Red	75	55.0 (54.8)	5.0 (4.6)	6.5 (6.8)		2108w	2052, 1987, 1971m (sh)	1920	
10⁺ <i>trans</i> -(CO) ₂ [P(OEt) ₃] ₂ (dppm)	—	1	1	Dark green	72	50.0 (49.7)	4.7 (4.2)	5.9 (6.2)		2087m	2114, 2073, 2053m	1927	
11 <i>trans</i> -(CO) ₂ [P(OPh) ₃] ₂ (dppm)	—	1	0	Red	67	58.4 (58.9)	4.2 (4.2)	6.2 (6.2)		2113w	2053, 1989, 1974m (sh)	1937	
11⁺ <i>trans</i> -(CO) ₂ [P(OPh) ₃] ₂ (dppm)	—	1	1	Dark green	85	53.8 (53.9)	4.0 (3.8)	5.6 (5.7)		2098m	2115, 2074, 2053m	1940	
14 (NO)[P(OPh) ₃] ₂ (cp) ^g	—	1	0	Dark red	47	54.3 (54.3)	4.3 (4.1)	8.6 (9.1)		2144w	2053, 1990, 1978 (sh)	1765m ^g	
14⁺ (NO)[P(OPh) ₃] ₂ (cp) ^g	—	1	1	Dark green	52	48.1 (48.6)	4.2 (3.7)	8.0 (8.1)		2131m	2114, 2074, 2057m	1771 ^g	
14⁺ (NO)[P(OPh) ₃] ₂ (cp) ^h	—	1	1	Green	64	45.7 (45.6)	3.4 (3.4)	7.4 (7.6)		2132m	2114, 2074, 2058m	1773 ^g	
15 (NO)(PPh ₃)(cp) ⁱ	—	1	0	Dark red	61	56.8 (56.5)	4.5 (4.3)	9.4 (9.4)		2138w	2053, 1990, 1976 (sh)	1741m ^g	
15⁺ (NO)(PPh ₃)(cp) ⁱ	—	1	1	Green	60	50.9 (50.4)	4.0 (3.8)	8.0 (8.4)		2123m (sh)	2113, 2073, 2057m	1750 ^g	
16⁺ <i>cis</i> -(CO) ₂ [P(OEt) ₃] ₂ (dppm)	—	2	1	Green-brown	57	52.3 (52.8)	5.0 (4.6)	4.6 (5.0)		2109m	2053m, 2031m	1965vs, 1910vs	
18⁺ <i>cis</i> -(CO) ₂ [P(OEt) ₃] ₂ (dppm)	—	2	1	Dark green	68	52.6 (52.8)	4.9 (4.6)	4.5 (5.0)		2110 (sh), 2097m	2052m, 2028m	1963vs, 1923vs, 1917 (sh)	
18⁺ <i>trans</i> -(CO) ₂ [P(OEt) ₃] ₂ (dppm)	—	2	1	Green	73	53.0 (52.8)	4.9 (4.6)	4.9 (5.0)		2099m	2053m, 2029m	1925vs	
19⁺ <i>cis</i> -(CO) ₂ [P(OPh) ₃] ₂ (dppm)	—	2	1	Green-brown	69	58.2 (58.2)	4.1 (4.1)	4.3 (4.5)		2115m	2057m, 2033m	1976vs, 1922vs	
20⁺ <i>cis</i> -(CO) ₂ [P(OPh) ₃] ₂ (dppm)	—	2	1	Green	71	58.0 (58.2)	4.4 (4.1)	4.2 (4.5)		2106 (br)	2058m, 2031m	1976, 1937vs, 1925 (sh)	
21⁺ <i>trans</i> -(CO) ₂ [P(OPh) ₃] ₂ (dppm)	—	2	1	Green	75	58.3 (58.2)	4.4 (4.1)	4.3 (4.5)		2105m	2057m, 2035m	1936vs	
22⁺ <i>cis</i> -(CO) ₂ [P(OEt) ₃] ₂ (dppm)	Cl	2	1	Dark green	71	51.9 (52.0)	4.7 (4.5)	4.9 (5.0)		2110m (sh)	2100ms, 2069m	1965, 1922vs, 1910 (sh)	
23⁺ <i>trans</i> -(CO) ₂ [P(OEt) ₃] ₂ (dppm)	Cl	2	1	Dark green	77	51.7 (52.0)	4.8 (4.5)	4.7 (5.0)		2098m	2088 (sh), 2068m	1925vs	
24⁺ <i>cis</i> -(CO) ₂ [P(OPh) ₃] ₂ (dppm)	Cl	2	1	Dark green	70	57.4 (57.4)	4.3 (4.0)	4.3 (4.4)		2104ms (br)	2072m ⁱ	1977, 1936vs, 1929 (sh)	

^a Prefixes in italics refer to the arrangement of the carbonyl ligands bonded to manganese. Where two such prefixes are given, the complex contains two cyanomanganese ligands in a 1:1 ratio. ^b Cations isolated as $[\text{PF}_6]^-$ salts unless otherwise stated. ^c Calculated values in parentheses. ^d In CH_2Cl_2 ; strong (s) absorptions unless otherwise stated, w = weak, m = medium, vs = very strong, sh = shoulder. ^e Obscured by $\nu(\text{CO})_{\text{Rh}}$. ^f Overlapping bands. ^g $\nu(\text{NO})$. ^h Isolated as a $[\text{SbF}_6]^-$ salt. ⁱ Second carbonyl band obscured by $\nu(\text{CN})$.

Table 2 Cyclic voltammetric data^a for the dirhodium complexes

Complex	Potential/V ^b		
	[Rh ₂] ²⁺ -[Rh ₂] ³⁺	[Rh ₂] ³⁺ -[Rh ₂] ⁴⁺ ^c	Mn
5	0.17	1.26 ^d	1.38 ^{d,e} (0.78)
5 ⁺	0.16	1.25 ^d	1.34 ^{d,e} (0.78)
6	0.17	1.29	1.58 ^e (0.98)
6 ⁺	0.16	1.29	1.58 ^e (0.98)
7	0.22	1.35	1.09 ^e (0.71)
7 ⁺	0.23	1.27	1.06 ^e (0.70)
10	0.15	1.28	0.84
10 ⁺	0.15	1.27	0.84
11	0.16	1.33	1.05
11 ⁺	0.15	1.32	1.06
14	0.22	1.22	1.58
14 ⁺	0.21	1.22	1.58
14 ⁺	0.20	1.23	1.59
15	0.19	1.18	1.33
15 ⁺	0.19	1.20 ^{d,f}	1.32 ^{d,f}
16 ⁺	-0.57 ^g	0.95	1.34 ^e (0.72)
17 ⁺	-0.60 ^g	0.92	0.78, 1.34 ^e (0.73)
18 ⁺	-0.65 ^g	0.93 ^h	0.73 ^h
19 ⁺	-0.60 ^g	0.95	1.56 ^e (1.00)
20 ⁺	-0.66 ^g	0.94	1.07, 1.56 ^e (0.99)
21 ⁺	-0.67 ^g	0.96	1.07
22 ⁺	—	-0.69 ⁱ	0.78, 1.31 ^e (0.74)
23 ⁺	—	-0.72 ⁱ	0.81
24 ⁺	—	-0.71 ⁱ	0.98, 1.59 ^e (0.91)

^a In CH₂Cl₂ at a platinum disc electrode. Under the conditions used the potentials for the couples [Fe(cp)₂]⁺-[Fe(cp)₂] and [Fe(η-C₅Me₅)₂]⁺-[Fe(η-C₅Me₅)₂] are 0.47 and -0.09 V respectively. ^b E⁰ for reversible wave unless otherwise stated. For an irreversible wave the peak potential [(E_p)_{ox} or (E_p)_{red}] is given at a scan rate of 200 mV s⁻¹. ^c Incompletely reversible oxidation wave; the return (reduction) wave is broadened. ^d Potentials estimated for two closely spaced waves. ^e Irreversible oxidation wave; (E_p)_{red} for the associated product wave is given in parentheses. ^f Peaks (at 1.11 and 1.22 V) resolved by differential pulse voltammetry. ^g Reduction wave, not fully reversible; (i_p)_{ox}/(i_p)_{red} ca. 0.9 at 200 mV s⁻¹ and return (oxidation) wave broadened. ^h Overlapping waves resolved by differential pulse voltammetry. ⁱ (E_p)_{red} for an irreversible reduction wave.

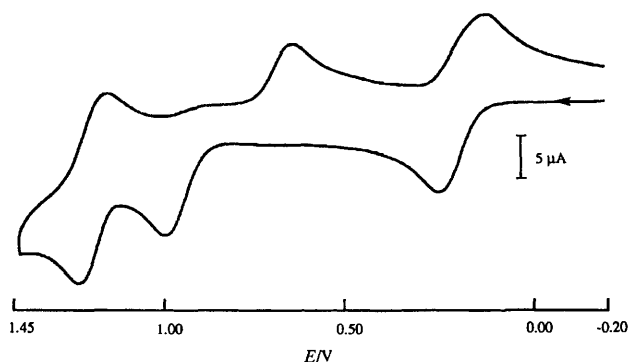


Fig. 2 The cyclic voltammogram, from -0.20 to 1.45 V at a scan rate of 200 mV s⁻¹, of complex 7 in CH₂Cl₂ at a platinum-disc electrode

by the change in potential of the third oxidation wave (by 250 mV to more negative potential) when PPh₃ is replaced by P(OPh)₃ at manganese.

The cyclic voltammogram of complex 1 shows three oxidation waves, at 0.83, 1.42 and 1.70 V, corresponding to the formation of [Rh₂]³⁺, [Rh₂]⁴⁺ and [Rh₂]⁵⁺ cores respectively, and [Rh₂(CO)₃(CNBu^t)(μ-RN₃R)₂] is oxidised at 0.45 V ([Rh₂]²⁺-[Rh₂]³⁺) and 1.28 V ([Rh₂]³⁺-[Rh₂]⁴⁺).¹ Comparing these data with those for 5-7, 10, 11, 14 and 15 (Table 2) shows that the potential of the [Rh₂]²⁺-[Rh₂]³⁺ couple for [Rh₂(CO)₃L(μ-RN₃R)₂] increases in the order L = Mn(CN) < CNBu^t < CO, mirroring the IR spectroscopic data which show that carbonyl substitution causes an increase in electron density at the dirhodium core.

Cationic [Rh₂]³⁺ complexes with a Rh₂(CO)₃ core

The reversibility and potential (ca. 0.20 V) of the first oxidation waves of complexes 5-7, 10, 11, 14 and 15 suggested that the monocations would be chemically accessible. Accordingly, 1

equivalent of [Fe(cp)₂][PF₆]⁻ or AgX (X = [PF₆]⁻ or [SbF₆]⁻) was added to the neutral tricarbonyls in CH₂Cl₂ to give green solutions from which [Rh₂{(μ-NC)MnL_x}(CO)₃(μ-RN₃R)₂]⁺X⁻ {L_x = *cis*-(CO)₂[P(OEt)₃](dppm) 5⁺, *cis*-(CO)₂-[P(OPh)₃](dppm) 6⁺, *cis*-(CO)₂(PEt₃)(dppe) 7⁺, *trans*-(CO)₂-[P(OEt)₃](dppm) 10⁺, *trans*-(CO)₂[P(OPh)₃](dppm) 11⁺ or (NO)L(cp') where L = P(OPh)₃ 14⁺ or PPh₃ 15⁺} were isolated in good yield as green powders. The salts were readily characterised by elemental analysis (Table 1) and by their cyclic voltammograms (Table 2) which are very similar to those of the neutral complexes except that the first reversible wave corresponds to the reduction (confirmed by voltammetry at a rotating platinum electrode) of the [Rh₂]³⁺ core.

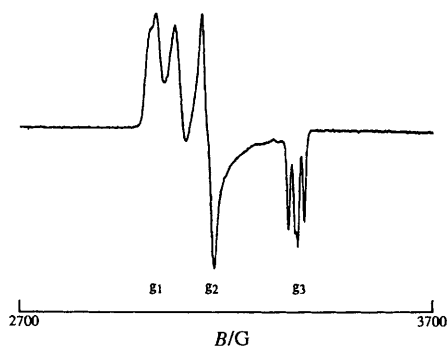
The IR spectra of the cations confirm the suggestion that the neutral complexes are oxidised at the [Rh₂]²⁺ centre. First, the ν(CO)_{Rh} bands are ca. 60-80 cm⁻¹ higher in energy than those of the neutral complexes. Secondly, the energy of ν(CO)_{Mn} increases only very slightly, the two bands of the monocations 5⁺-7⁺ showing retention of geometry at the *cis*-manganese dicarbonyl centre on oxidation; manganese-based oxidation is expected to result in *cis-trans* isomerisation.⁷ Thirdly, the energy of the bridging cyanide group *decreases* (by ca. 15 cm⁻¹), as previously found when the N-bound end of an M-CN-M' unit is oxidised, e.g. in [Ru{(μ-NC)MnL_x}(CO)₂(PPh₃)(*o*-O₂-C₆Cl₄)] {Δν(CN) = -15 cm⁻¹, L_x = *trans*-(CO)₂[P(OPh)₃](dppm)},⁹ [Fe{(μ-NC)MnL_x}(dppe)(cp)]⁺ {Δν(CN) = -89 cm⁻¹, L_x = *trans*-(CO)₂[P(OPh)₃](dppm)}¹⁸ and [Fe{(μ-NC)-Cr(CO)₅}(dppe)(cp)] [Δν(CN) = -104 cm⁻¹].¹⁹

The room temperature ESR spectra of 5⁺-7⁺, 10⁺, 11⁺ and 15⁺ appear as broad singlets (e.g. 5⁺, g = 2.132), similar to that of [Rh₂(CO)₂(PPh₃)₂(μ-RN₃R)₂]⁺ (g = 2.135)¹ and suggesting a [Rh₂]³⁺-based singly occupied molecular orbital (SOMO) for the monocations.⁴ The well resolved frozen solution spectra, in CH₂Cl₂-thf (1:2) glasses at 77 K, each show three features, the first and third of which show hyperfine coupling to ¹⁰³Rh (I = ½) (Table 3). The g_{av} and A(¹⁰³Rh)

Table 3 The ESR spectroscopic data^a for paramagnetic dirhodium complexes

Complex	g_1	g_2	g_3	g_{av}	$A_1(^{103}\text{Rh})^b/\text{G}$	$A_3(^{103}\text{Rh})^c/\text{G}$
5⁺	2.2139	2.1411	2.0039	2.120	43, 11	17, 6
6⁺	2.2181	2.1458	2.0099	2.125	43	17, 6
7⁺	2.2145	2.1389	2.0047	2.119	44	17, 7
10⁺	2.2134	2.1376	2.0026	2.118	46	17, 5
11⁺	2.2189	2.1381	2.0024	2.120	43, 13	17, 6
15⁺	2.2128	2.1419	2.0026	2.119	42	16, 5
16⁺	2.1966	2.1879	2.0027	2.129	—	18 ^d
17⁺	2.1968	2.1865	2.0019	2.128	—	18 ^d
18⁺	2.1982	2.1874	2.0031	2.129	—	18 ^d
19⁺e	2.1968	2.1822	2.0079	2.128	—	18 ^d
20⁺	2.2049	2.1826	2.0031	2.130	—	18 ^d

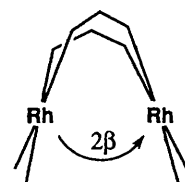
^a In CH_2Cl_2 -thf (1:2) at 77 K. ^b Broad doublet of doublet coupling; second coupling not resolved unless stated otherwise. ^c Doublet of doublet coupling at g_3 unless stated otherwise. ^d 1:2:1 Triplet coupling at g_3 . ^e At 140 K.

**Fig. 3** The ESR spectrum of complex **5⁺** at 77 K, in CH_2Cl_2 -thf (1:2)

values of **5⁺**-**7⁺**, **10⁺**, **11⁺** and **15⁺** are very similar and show that the ligand set at manganese has little effect on the dirhodium-based SOMO. The spectrum of **5⁺** is shown in Fig. 3.

The high field feature, g_3 , appears as a well resolved doublet of doublets, the hyperfine coupling to two inequivalent ^{103}Rh nuclei reflecting the asymmetry of the cations. This contrasts with the frozen solution ESR spectrum of $[\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2(\mu\text{-RN}_3\text{R}_2)]^+$ which shows coupling to two equivalent rhodium nuclei,⁴ but is more similar, in this respect, to the spectrum of the asymmetric complex $[\text{Rh}_2(\text{CO})_2(\text{bipy})(\mu\text{-RN}_3\text{R}_2)]^+$.² The central feature, g_2 , shows little or no hyperfine coupling to ^{103}Rh but g_1 is observed as a broad doublet for **5⁺**-**7⁺**, **10⁺**, **11⁺** and **15⁺**. (There is some indication, in Fig. 3, that the signal for **5⁺** is actually a doublet of doublets; in the other cases, therefore, the signal is probably broadened by unresolved coupling.) The main hyperfine splitting on g_1 is surprisingly large (ca. 45 G). No coupling is observed on g_1 for $[\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2(\mu\text{-RN}_3\text{R}_2)]^+$; where coupling to g_1 is observed for other complexes containing the $[\text{Rh}_2]^{3+}$ core it is of the order of 12–17 G.⁴ The reason for the magnitude of this coupling is unknown but appears in the ESR spectra of all six tricarbonyl cations [all of which were spectroscopically (IR) and analytically (C, H and N analysis) pure] and therefore seems genuine. The alternative, that part of the feature at g_1 is attributable to a paramagnetic impurity, seems less likely. Oxygen forms a paramagnetic complex with $[\text{Rh}_2(\text{CO})(\text{PPh}_3)(\text{bipy})(\mu\text{-RN}_3\text{R}_2)]^+$ {but not with $[\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2(\mu\text{-RN}_3\text{R}_2)]^+$ } but none of the features of the anisotropic ESR spectrum of $[\text{Rh}_2(\text{O}_2)(\text{CO})(\text{PPh}_3)(\text{bipy})(\mu\text{-RN}_3\text{R}_2)]^+$ ($g_1 = 2.079$, $g_2 = 2.009$, $g_3 = 1.988$), which is typical of a superoxide derivative,²⁰ corresponds to those found in the spectra of **5⁺**-**7⁺**, **10⁺**, **11⁺** and **15⁺**.

X-Ray structural and ESR spectroscopic studies on ligand bridged $[\text{Rh}_2]^{3+}$ complexes have shown⁴ that anisotropic g values can be related to the inter-co-ordination plane angle, 2β (Fig. 4); the plot of $\Delta g_3/\Delta g_{av}$ ($\Delta g_i = g_i - g_e$; $g_e =$ the electron

**Fig. 4** The angle, 2β , between the mean planes defined by the rhodium atom and the four equatorial ligands

g factor = 2.002 32) against β for complexes whose structures have been determined provides a means by which β can be estimated for related complexes.⁴ For complexes **5⁺**-**7⁺**, **10⁺** and **11⁺**, $\Delta g_3/\Delta g_{av}$ is in the range 0.0 to 0.06, implying that $0 < 2\beta < 14^\circ$. The structurally determined interplanar angle of $[\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2(\mu\text{-RN}_3\text{R}_2)][\text{PF}_6]$ (31.3°) is much larger than that calculated for **5⁺**-**7⁺**, **10⁺** and **11⁺** and probably results from the greater steric effects of two phosphine ligands [cf. the one bulky (cyanomanganese) ligand in each of **5⁺**-**7⁺**, **10⁺** and **11⁺**].

Tetrametallic $[\text{Rh}_2]^{3+}$ complexes with a $\text{Rh}_2(\text{CO})_2$ core

Complexes **5–7**, **10**, **11**, **14** and **15** are inert to carbonyl substitution (cf. the reaction of **1** with PPh_3 which gives only the disubstituted product²¹) and hence tetrametallic species with a $[\text{Rh}_2]^{2+}$ core and two cyanomanganese ligands are not directly accessible from **1**. However, the neutral tricarbonyls are activated by one-electron oxidation and the addition of **2** or **8** to **5⁺** or **10⁺** or of **3** or **9** to **6⁺** or **11⁺** in CH_2Cl_2 gave dark green solutions from which $[\text{Rh}_2\{(\mu\text{-NC})\text{MnL}_x\}_2(\text{CO})_2(\mu\text{-RN}_3\text{R}_2)]^+$ **16⁺**-**21⁺** were isolated in 60–75% yield as green powders (Table 1).

Each of the tetrametallic cations shows two IR carbonyl bands due to the $\text{Rh}_2(\text{CO})_2$ fragment. The separation of the two bands [$\Delta\nu(\text{CO}) = \text{ca. } 25 \text{ cm}^{-1}$] is more similar to that of $[\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2(\mu\text{-RN}_3\text{R}_2)]^+$ [$\Delta\nu(\text{CO}) = 20 \text{ cm}^{-1}$],¹ in which one carbonyl ligand is bound to each rhodium atom, than to that of $[\text{Rh}_2(\text{CO})_2(\text{bipy})(\mu\text{-RN}_3\text{R}_2)]^+$ [$\Delta\nu(\text{CO}) = 45 \text{ cm}^{-1}$] which contains² a single *cis*- $\text{Rh}(\text{CO})_2$ group. Accordingly, the structure shown in Scheme 1 is assigned to **16⁺**-**21⁺**. The $\nu(\text{CO})_{\text{Rh}}$ bands are more similar in energy to those of $[\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2(\mu\text{-RN}_3\text{R}_2)][\text{PF}_6]$ [$\nu(\text{CO})$ 2047 and 2027 cm^{-1}] than to those of $[\text{Rh}_2(\text{CO})_2(\text{CNBu}')_2(\mu\text{-RN}_3\text{R}_2)][\text{PF}_6]$ [$\nu(\text{CO})$ 2070 and 2058 cm^{-1}],¹ again suggesting that the manganese cyanide ligands behave more like the weak π acceptor PPh_3 than CNBu' .

The IR spectra also show bands associated with the two cyanomanganese carbonyl ligands. For example, **17⁺**, formed from *trans*- $[\text{Mn}(\text{CN})(\text{CO})_2\{\text{P}(\text{OEt})_3\}(\text{dppm})]$ **8** and $[\text{Rh}_2\{(\mu\text{-NC})\text{MnL}_x\}(\text{CO})_3(\mu\text{-RN}_3\text{R}_2)]^+$ [$L_x = \text{cis}(\text{CO})_2\{\text{P}(\text{OEt})_3\}(\text{dppm})$ **5⁺**], shows three $\nu(\text{CO})_{\text{Mn}}$ absorptions, two for the *cis*- $\text{Mn}(\text{CO})_2$ group and one for *trans*- $\text{Mn}(\text{CO})_2$. The cyanide

bands of the dicarbonyl cations are observed at slightly higher energy (*ca.* 10 cm⁻¹; compare **10**⁺ with **18**⁺, for example) than those of the tricarbonyls, in accord with the lower electron-withdrawing capacity of Rh₂[(μ-NC)MnL_x](CO)₂ relative to Rh₂(CO)₃. In complex **17**⁺, where two ligands having different geometry at manganese are present, two cyanide bands are observed, one for the *cis* ligand and one for the *trans*. For complex **20**⁺, the two peaks are unresolved and only one broad band is observed.

The cations **16**⁺–**21**⁺ contain three redox-active centres and their cyclic voltammograms are therefore complex. Moreover, they are poorly defined. In CH₂Cl₂, each voltammogram shows two waves attributable to oxidation or reduction at the Rh₂ centre as well as waves associated with the oxidation of the two cyanomanganese ligands. Each complex shows an incompletely reversible reduction wave at *ca.* -0.60 V [(*i*_p)_{ox}/*(i*_p)_{red} is *ca.* 0.9 at a scan rate of 200 mV s⁻¹, and the return (oxidation) wave is broadened] and an oxidation wave at *ca.* 0.95 V. Both waves are essentially independent of the nature of the Mn ligand and are therefore assigned to the reduction of [Rh₂]³⁺ to [Rh₂]²⁺, and the oxidation of [Rh₂]³⁺ to [Rh₂]⁴⁺ (Table 2). (A third wave at *ca.* 1.75 V, close to the base electrolyte oxidation wave, might be assigned to the oxidation of [Rh₂]⁴⁺ to [Rh₂]⁵⁺.) The shift to more negative potential of these couples when compared with those of the tricarbonyls is consistent with carbonyl replacement by the donor cyanomanganese ligand.

The incomplete reversibility of the [Rh₂]²⁺–[Rh₂]³⁺ couple for **16**⁺–**21**⁺ contrasts with the reversibility of the corresponding wave for the tricarbonyls (where both neutral and monocationic species are isolable). The instability of the neutral complexes **16**–**21** is further underlined by the observation that treatment of **16**⁺–**21**⁺ with the one-electron reductant [Co(cp)₂] leads only to decomposition.

The oxidative behaviour of the co-ordinated cyanomanganese ligands again varies with the geometry and ligand set. For example, the cyclic voltammogram of **17**⁺ [which contains P(OEt)₃ ligands] shows oxidation waves at 0.78 and 1.34 V (Table 2) which are shifted to 1.07 and 1.56 V respectively in the voltammogram of **20**⁺ [which contains the more electron withdrawing P(OPh)₃ ligands]. These two waves can therefore be assigned to the oxidation of the *trans*- and *cis*-Mn centres respectively. The cyclic voltammogram of **16**⁺ is similar to that of **17**⁺ except that the two *cis*-Mn centres are irreversibly oxidised at the same potential (1.34 V).

The frozen-solution ESR spectra of **16**⁺–**21**⁺ in CH₂Cl₂-thf (1:2) show three *g* values with *g*₁ ≈ *g*₂ > *g*₃ (Table 3); that of **18**⁺ is shown in Fig. 5. The spectra are typical of a complex with a symmetric [Rh₂]³⁺ core in that the high field component, *g*₃, is a 1:2:1 triplet (coupling of the unpaired electron to two equivalent ¹⁰³Rh nuclei) as found for [Rh₂(CO)₂(PPh₃)₂(μ-RN₃R)₂][PF₆].⁴ By contrast to the tricarbonyl cations **5**⁺–**7**⁺, **10**⁺, **11**⁺ and **15**⁺, the dicarbonyls show no hyperfine coupling on *g*₁. However, the values of *g*_{av} and *A*₃(¹⁰³Rh) for the two series of complexes are very similar (Table 3) suggesting that the Rh₂-based SOMO is little affected by changing the number of cyanomanganese ligands co-ordinated to the dirhodium core.

As for the tricarbonyls **5**⁺–**7**⁺, **10**⁺, **11**⁺ and **15**⁺, the angle, β, between the rhodium co-ordination planes of the dicarbonyl cations can be estimated from the anisotropic *g* values. Thus, Δ*g*₃/Δ*g*_{av} are *ca.* 0.005, implying that the interplanar angle 2β (Fig. 4) for **16**⁺–**21**⁺ is close to zero.⁴ Surprisingly, this angle appears to be smaller, on average, in the dicarbonyl complexes but in the absence of X-ray structural studies (none of the complexes could be successfully crystallised) this cannot be verified.

Tetrametallic [Rh₂]⁴⁺ complexes with a Rh₂Cl(CO)₂ core

The potential of the [Rh₂]³⁺–[Rh₂]⁴⁺ couple of **16**⁺–**21**⁺ (*ca.* 0.9 V) suggests that chemical oxidation of the monocations

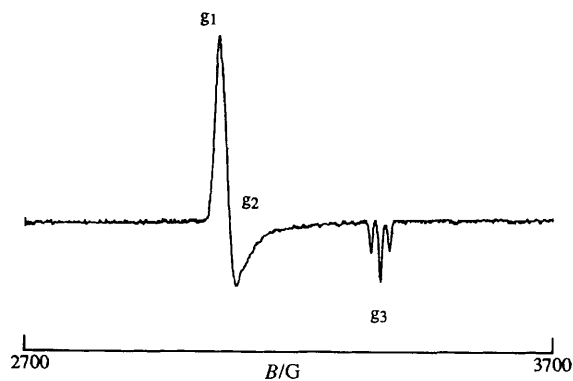


Fig. 5 The ESR spectrum of complex **18**⁺ at 77 K, in CH₂Cl₂-thf (1:2)

would require the use of a strong oxidant, such as [N(C₆H₄Br)₃][PF₆]. However, attempts to synthesise dicationic species containing a [Rh₂]⁴⁺ core, such as **16**²⁺, proved unsuccessful with decomposition following oxidation.

Extended-Hückel molecular-orbital studies have shown that axial co-ordination of a nucleophilic ligand to a [Rh₂]³⁺ core destabilises the SOMO (by interaction of the ligand lone pair with a Rh d_{z²} orbital) and hence facilitates oxidation to [Rh₂]⁴⁺.² Thus, the oxidation of [Rh₂(CO)L(bipy)(μ-RN₃R)₂]⁺ [L = PPh₃ or P(OPh)₃] by [Fe(cp)₂][PF₆] in the presence of chloride ion provides a route to [Rh₂Cl(CO)L(bipy)(μ-RN₃R)₂][PF₆].² The reduction potential of the ferrocenium ion (0.47 V) is *ca.* 400 mV less positive than the potential required to oxidise **16**⁺–**21**⁺ and, indeed, [Fe(cp)₂]⁺ does not react with the monocations. However, in the presence of [NEt₃Ph]Cl it does react with **17**⁺, **18**⁺ or **21**⁺ in CH₂Cl₂, giving dark green solutions from which diamagnetic [Rh₂Cl(μ-NC)MnL_x]₂(CO)₂(μ-RN₃R)₂]⁺ **22**⁺–**24**⁺ can be isolated in good yield as dark green powders (Table 1). Again, axial co-ordination of chloride ion promotes the formation of a [Rh₂]⁴⁺ core.

The decrease in electron density at the dirhodium core is reflected in the IR spectra of **22**⁺–**24**⁺. Thus, the ν(CO)_{Rh} bands, somewhat obscured by the cyanide stretching vibrations, increase in energy by *ca.* 35 cm⁻¹ as a result of the decrease in π-back bonding from Rh to π*(CO). Oxidation of the tricarbonyls **5**–**7**, **10**, **11**, **14** and **15** causes ν(CN) to decrease by *ca.* 20 cm⁻¹. By contrast, the formation of **22**⁺–**24**⁺ from **16**⁺–**21**⁺ results in little change in ν(CN) despite a similar increase in the Rh₂ core oxidation level. The effect of increasing the dirhodium oxidation state seems to be offset by the effect of axial co-ordination of chloride. The energies of ν(CO)_{Mn} are also largely unaffected.

The cyclic voltammogram of **22**⁺ shows an irreversible reduction wave at -0.69 V corresponding to the reduction of the [Rh₂]⁴⁺ core; the reduction of [Rh₂Cl(CO)L(bipy)(μ-RN₃R)₂][PF₆] is similarly irreversible, due to the rapid loss of Cl⁻ from the neutral [Rh₂]³⁺ complex [Rh₂Cl(CO)L(bipy)(μ-RN₃R)₂].² The substantial shift to more negative potential (by *ca.* 1.5 V) of the [Rh₂]³⁺–[Rh₂]⁴⁺ couple in complexes **22**⁺–**24**⁺ (*cf.* the same couple in **16**⁺–**21**⁺) underlines the stabilising influence of axial co-ordination of the chloride ion to the [Rh₂]⁴⁺ core.

Complex **22**⁺ also shows oxidation waves at 0.78 and 1.31 V. The first is reversible and corresponds to oxidation of the *trans*-Mn centre; the second is irreversible and due to oxidation of the *cis*-Mn site and the [Rh₂]⁴⁺ core respectively. (A third wave at *ca.* 1.60 V might be assigned to the oxidation of [Rh₂]⁴⁺ to [Rh₂]⁵⁺.) The cyclic voltammogram of **23**⁺ is ill-defined but shows an oxidation wave at 0.81 V which is approximately twice the height of the other wave. The two *trans*-Mn(CO)₂ centres

appear to be oxidised at almost identical potentials despite coordination to rhodium centres with different ligand sets [*i.e.* Rh(CO) and Rh(CO)Cl].

Conclusion

Cyanomanganese ligands react with dirhodium triazenide fragments to form novel tri- and tetra-metallic complexes, such as $[\text{Rh}_2\{(\mu\text{-NC})\text{MnL}_x\}(\text{CO})_3(\mu\text{-RN}_3\text{R})_2]$ **10**, $[\text{Rh}_2\{(\mu\text{-NC})\text{MnL}_x\}_2(\text{CO})_2(\mu\text{-RN}_3\text{R})_2]^+$ **18**⁺ and $[\text{Rh}_2\text{Cl}\{(\mu\text{-NC})\text{MnL}_x\}_2(\text{CO})_2(\mu\text{-RN}_3\text{R})_2]^+$ **23**⁺ $\{\text{L}_x = \text{trans}(\text{-CO})_2\text{-}[\text{P}(\text{OEt})_3](\text{dppm})\}$, which have two or three redox-active sites. The oxidation state of the dirhodium core can be systematically varied, from $[\text{Rh}_2]^{2+}$ to $[\text{Rh}_2]^{4+}$ (*e.g.* in **10**, **18**⁺ and **23**⁺ respectively), and the order in which the various sites are oxidised can be controlled by varying the ancillary ligands and their arrangement at the Mn centres.

Experimental

The preparation, purification and reactions of the complexes described were carried out under an atmosphere of dry nitrogen using dried, distilled and deoxygenated solvents; reactions were monitored by IR spectroscopy where necessary. Unless stated otherwise, complexes (*i*) are stable in the solid state under nitrogen and (*ii*) dissolve in polar solvents such as CH_2Cl_2 , thf and MeCN to give moderately air-sensitive solutions. The compounds $[\text{Fe}(\text{cp})_2][\text{PF}_6]^{2,2}$ *cis*- and *trans*- $[\text{Mn}(\text{CN})(\text{CO})_2\text{L}(\text{dppm})]$ $[\text{L} = \text{P}(\text{OEt})_3^8$ or $\text{P}(\text{OPh})_3^{2,3}]$, *cis*- $[\text{Mn}(\text{CN})(\text{CO})_2(\text{PEt}_3)(\text{dppe})]$,⁸ $[\text{Mn}(\text{CN})(\text{NO})\text{L}(\text{cp}')]$ $[\text{L} = \text{P}(\text{OPh})_3$ or $\text{PPh}_3]$,^{2,4} and $[\text{Rh}_2(\text{CO})_4(\mu\text{-RN}_3\text{R})_2]$ ($\text{R} = p\text{-tolyl}$)¹ were prepared by published methods. Trimethylamine *N*-oxide was purchased from Aldrich and $[\text{NEt}_3\text{Ph}]\text{Cl}$ from Fluka. Infrared spectra were recorded on a Nicolet 5ZDX FT spectrometer. X-Band ESR spectra were recorded on a Bruker 300ESP spectrometer equipped with a Bruker variable-temperature accessory and a Hewlett-Packard 5350B microwave frequency counter. The field calibration was checked by measuring the resonance of the diphenylpicrylhydrazyl (dpph) radical. Electrochemical studies were carried out using an EG&G model 273 potentiostat in conjunction with a three-electrode cell. For cyclic voltammetry the auxiliary electrode was a platinum wire and the working electrode was a platinum disc. The reference was an aqueous saturated calomel electrode (SCE) separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl. Voltammetry used a platinum disc electrode rotated at 600 revolutions min^{-1} . Differential-pulse voltammetry was carried out using the PAR model 270 Electrochemical Analysis software. Dichloromethane solutions were 0.1×10^{-3} mol dm^{-3} or 0.5×10^{-4} mol dm^{-3} in the test compound and 0.1 mol dm^{-3} in $[\text{NBu}_4][\text{PF}_6]$ as the supporting electrolyte and were shielded from light by aluminium foil and from air by nitrogen. At the end of each experiment $[\text{Fe}(\text{cp})_2]$ or $[\text{Fe}(\eta\text{-C}_5\text{Me}_5)_2]$ was added to the solution as an internal standard for potential measurements. Under these conditions, E° for the couples $[\text{Fe}(\text{cp})_2]^+ - [\text{Fe}(\text{cp})_2]$ and $[\text{Fe}(\eta\text{-C}_5\text{Me}_5)_2]^+ - [\text{Fe}(\eta\text{-C}_5\text{Me}_5)_2]$ are 0.47 and -0.09 V respectively. Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Syntheses

$[\text{Rh}_2\{(\mu\text{-NC})\text{MnL}_x\}(\text{CO})_3(\mu\text{-RN}_3\text{R})_2]$ **5** $\{\text{L}_x = \text{cis}(\text{-CO})_2\text{-}[\text{P}(\text{OEt})_3](\text{dppm})\}$. A mixture of $[\text{Rh}_2(\text{CO})_4(\mu\text{-RN}_3\text{R})_2]$ **1** (0.20 g, 0.26 mmol) and *trans*- $[\text{Mn}(\text{CN})(\text{CO})_2\text{P}(\text{OEt})_3](\text{dppm})$ (0.178 g, 0.26 mmol) in *n*-hexane (50 cm^3) was heated under reflux for 4 h. On cooling to -10 °C, a red solid was deposited which was recrystallised from *n*-hexane to give the product, yield 0.193 g (52%). The complex was soluble in toluene and in hot *n*-hexane.

$[\text{Rh}_2\{(\mu\text{-NC})\text{MnL}_x\}(\text{CO})_3(\mu\text{-RN}_3\text{R})_2]$ **11** $\{\text{L}_x = \text{trans}(\text{-CO})_2\text{-}[\text{P}(\text{OPh})_3](\text{dppm})\}$. To a stirred solution of $[\text{Rh}_2(\text{CO})_4(\mu\text{-RN}_3\text{R})_2]$ **1** (0.154 g, 0.202 mmol) in CH_2Cl_2 (40 cm^3) was added *trans*- $[\text{Mn}(\text{CN})(\text{CO})_2\text{P}(\text{OPh})_3](\text{dppm})$ (0.163 g, 0.202 mmol) and then ONMe_3 (0.030 g, 0.040 mmol). After 5 min the solvent was removed *in vacuo* and the red residue was extracted into diethyl ether (100 cm^3). The extract was filtered through Celite and precipitation was induced by reducing the volume of solvent *in vacuo* to *ca.* 50 cm^3 and adding *n*-pentane (30 cm^3). The precipitate was then dissolved in diethyl ether and the resulting solution filtered and treated with pentane to give the pure product as a red powder, yield 0.21 g (67%).

The complexes $[\text{Rh}_2\{(\mu\text{-NC})\text{MnL}_x\}(\text{CO})_3(\mu\text{-RN}_3\text{R})_2]$ $\{\text{L}_x = \text{cis}(\text{-CO})_2[\text{P}(\text{OEt})_3](\text{dppm})$ **5**, *cis*- $(\text{-CO})_2[\text{P}(\text{OPh})_3](\text{dppm})$ **6**, *cis*- $(\text{-CO})_2(\text{PEt}_3)(\text{dppe})$ **7**, *trans*- $(\text{-CO})_2[\text{P}(\text{OEt})_3](\text{dppm})$ **10** and $(\text{NO})\text{L}(\text{cp}')$, $\text{L} = \text{P}(\text{OPh})_3$ **14** or PPh_3 **15}\} were prepared similarly.**

$[\text{Rh}_2\{(\mu\text{-NC})\text{MnL}_x\}(\text{CO})_3(\mu\text{-RN}_3\text{R})_2][\text{PF}_6]$ **11**⁺ $\{\text{L}_x = \text{trans}(\text{-CO})_2[\text{P}(\text{OPh})_3](\text{dppm})\}$. To a stirred solution of $[\text{Rh}_2\{(\mu\text{-NC})\text{MnL}_x\}(\text{CO})_3(\mu\text{-RN}_3\text{R})_2]$ **11** (0.190 g, 0.012 mmol) in CH_2Cl_2 (25 cm^3) was added $[\text{Fe}(\text{cp})_2][\text{PF}_6]$ (0.039 g, 0.012 mmol). The mixture was stirred for 5 min and the resulting dark green solution was filtered through Celite. *n*-Hexane was added and the volume of the mixture was reduced *in vacuo* to induce precipitation of a green powder, yield 0.175 g (85%).

The complexes $[\text{Rh}_2\{(\mu\text{-NC})\text{MnL}_x\}(\text{CO})_3(\mu\text{-RN}_3\text{R})_2][\text{PF}_6]$ $\{\text{L}_x = \text{cis}(\text{-CO})_2[\text{P}(\text{OEt})_3](\text{dppm})$ **5**⁺, *cis*- $(\text{-CO})_2[\text{P}(\text{OPh})_3](\text{dppm})$ **6**⁺, *cis*- $(\text{-CO})_2(\text{PEt}_3)(\text{dppe})$ **7**⁺, *trans*- $(\text{-CO})_2[\text{P}(\text{OEt})_3](\text{dppm})$ **10**⁺, $(\text{NO})[\text{P}(\text{OPh})_3](\text{cp}')$ **14**⁺ and $(\text{NO})(\text{PPh}_3)(\text{cp}')$ **15**⁺ $\}$ were prepared similarly.

$[\text{Rh}_2\{(\mu\text{-NC})\text{MnL}_x\}_2(\text{CO})_2(\mu\text{-RN}_3\text{R})_2][\text{PF}_6]$ **20**⁺ $\{\text{L}_x = \text{cis}(\text{-CO})_2[\text{P}(\text{OPh})_3](\text{dppm})/\text{trans}(\text{-CO})_2[\text{P}(\text{OPh})_3](\text{dppm})\}$. To a stirred solution of $[\text{Rh}_2\{(\mu\text{-NC})\text{MnL}_x\}(\text{CO})_3(\mu\text{-RN}_3\text{R})_2][\text{PF}_6]$ $\{\text{L}_x = \text{cis}(\text{-CO})_2[\text{P}(\text{OPh})_3](\text{dppm})$ **6**⁺ $\}$ (0.100 g, 0.058 mmol) in CH_2Cl_2 (25 cm^3) was added *trans*- $[\text{Mn}(\text{CN})(\text{CO})_2\text{P}(\text{OPh})_3](\text{dppm})$ (0.048 g, 0.058 mmol). After 2 h the green solution was filtered through Celite, *n*-hexane was added and the volume of the mixture reduced *in vacuo* to induce precipitation of a green oil. Trituration of the oil with diethyl ether gave a green solid, yield 0.104 g (71%).

The complexes $[\text{Rh}_2\{(\mu\text{-NC})\text{MnL}_x\}_2(\text{CO})_2(\mu\text{-RN}_3\text{R})_2][\text{PF}_6]$ $\{\text{L}_x = \text{cis}(\text{-CO})_2[\text{P}(\text{OEt})_3](\text{dppm})$ **16**⁺, *trans*- $(\text{-CO})_2\text{-}[\text{P}(\text{OEt})_3](\text{dppm})$ **18**⁺, *cis*- $(\text{-CO})_2[\text{P}(\text{OPh})_3](\text{dppm})$ **19**⁺ and *trans*- $(\text{-CO})_2[\text{P}(\text{OPh})_3](\text{dppm})$ **21**⁺; $(\text{L}_x)_2 = \text{cis}(\text{-CO})_2\text{-}[\text{P}(\text{OEt})_3](\text{dppm})/\text{trans}(\text{-CO})_2\text{-}[\text{P}(\text{OEt})_3](\text{dppm})$ **17**⁺ (from **5**⁺ and **8**) $\}$ were prepared similarly.

$[\text{Rh}_2\text{Cl}\{(\mu\text{-NC})\text{MnL}_x\}_2(\text{CO})_2(\mu\text{-RN}_3\text{R})_2][\text{PF}_6]$ **24**⁺ $\{\text{L}_x = \text{cis}(\text{-CO})_2[\text{P}(\text{OPh})_3](\text{dppm})/\text{trans}(\text{-CO})_2[\text{P}(\text{OPh})_3](\text{dppm})\}$. To a stirred solution of $[\text{Rh}_2\{(\mu\text{-NC})\text{MnL}_x\}_2(\text{CO})_2(\mu\text{-RN}_3\text{R})_2][\text{PF}_6]$ **20**⁺ (0.250 g, 0.010 mmol) in CH_2Cl_2 (30 cm^3) was added $[\text{Fe}(\text{cp})_2][\text{PF}_6]$ (0.033 g, 0.010 mmol) and $[\text{NEt}_3\text{-Ph}]\text{Cl}$ (0.023 g, 0.010 mmol). After 45 min the dark green solution was filtered through Celite and *n*-hexane was added. Reduction of the volume of the mixture *in vacuo* gave a precipitate of $[\text{NEt}_3\text{Ph}][\text{PF}_6]$, which was discarded, and then the product as a dark green powder, yield 0.180 g (70%).

The complexes $[\text{Rh}_2\text{Cl}\{(\mu\text{-NC})\text{MnL}_x\}_2(\text{CO})_2(\mu\text{-RN}_3\text{R})_2][\text{PF}_6]$ $\{\text{L}_x = \text{cis}(\text{-CO})_2[\text{P}(\text{OEt})_3](\text{dppm})/\text{trans}(\text{-CO})_2\text{-}[\text{P}(\text{OEt})_3](\text{dppm})$ **22**⁺ or $\text{L}_x = \text{trans}(\text{-CO})_2[\text{P}(\text{OEt})_3](\text{dppm})$ **23**⁺ $\}$ were prepared similarly.

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