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Cyanomanganese-(I) and -(II) Carbonyls as Redox-active Donor Ligands: the Synthesis of Novel Paramagnetic Heterobinuclear Complexes

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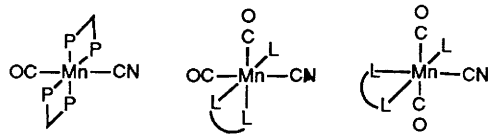
The cyanomanganese complexes *trans*-$[Mn(CN)(CO)(dppm)_2]^z$ (z = 0, 1+) (dppm = $Ph_2PCH_2PPh_2$), *cis*-$[Mn(CN)(CO)_2L(L–L)]$, and *trans*-$[Mn(CN)(CO)_2L(L–L)]^z$ (z = 0, 1+) have been used as ligands in the synthesis of redox-active heterobinuclear complexes such as $[L(L–L)(CO)_2Mn(\mu\text{-}CN)Ru(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)]^z$ (z = 0, 1+) and $[(dppm)_2(CO)Mn(\mu\text{-}CN)RhCl(CO)_2]^z$ (z = 0, 1+).

We have recently described the one-electron oxidation reactions of the octahedral manganese carbonyl complexes *trans*-$[Mn(CN)(CO)(dppm)_2]$ (**1**) (dppm = $Ph_2PCH_2PPh_2$),[1] *cis*-$[Mn(CN)(CO)_2L(L–L)]$ [**2**; L = $P(OPh)_3$, L–L = dppm][2] and, in particular, the isomerisation of the latter to *trans*-$[Mn(CN)(CO)_2L(L–L)]$ [**3**; L = $P(OPh)_3$, L–L = dppm] *via* the isolable low-spin manganese(II) salt $[Mn(CN)(CO)_2L(L–L)][PF_6]$ [$\mathbf{3}^+$; L = $P(OPh)_3$, L–L = dppm]. We now show that these complexes can be used as ligands in the synthesis of novel cyanide-bridged heterobinuclear complexes in which the interactions between two very different redox centres or between one redox centre and an otherwise inactive metal site may be studied by electrochemical and spectroscopic methods.

The reaction of [**2**; L = $P(OPh)_3$, L–L = dppm; L = PEt_3, L–L = dppe] (dppe = $Ph_2PCH_2CH_2PPh_2$) with $[\{Ru(CO)_2(PPh_3)(\mu\text{-}o\text{-}O_2C_6Cl_4)\}_2]$ (**4**) in CH_2Cl_2 results in bridge cleavage and the isolation of the orange, heterobinuclear complex (**5**) (Scheme 1)† whose cyclic voltammogram shows two sequential one-electron oxidation waves in the potential range 0.0 to 1.5 V (Table 1). The first wave is reversible with a potential (Table 1) essentially independent of the ligands bound to manganese but very similar to that for the oxidation of the mononuclear catecholate complex $[Ru(CO)_2(PPh_3)_2(o\text{-}O_2C_6Cl_4)]$ (E° 0.59 V)[3] to the *o*-benzosemiquinone-containing cation $[Ru(CO)_2(PPh_3)_2(o\text{-}O_2C_6Cl_4)]^+$. The second oxidation wave is irreversible and coupled to a reversible product wave at a more negative potential. This behaviour, where the potentials of both waves are dependent on L and L–L (Table 1), is diagnostic[2] of the redox-induced isomerisation of a *cis*- to a *trans*-$MnX(CO)_2L(L–L)$ unit.



(**1**) (**2**) (**3**)

† All new complexes have satisfactory elemental analyses.

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Table 1. IR spectroscopic and cyclic voltammetric data for heterobinuclear complexes.

Complex	Yield (%)	IR/cm^{-1} [a] $\tilde{\nu}$(CN)	$\tilde{\nu}$(CO)[c]	E°/V[d]
[**5**; L = $P(OPh)_3$, L–L = dppm]	56	2132	1972(sh), 1919,[e] 2051, 1983[f]	0.54, 1.53(I) (0.98[g])
[**5**; L = PEt_3, L–L = dppe]	84	2118	1943, 1883,[e] 2049, 1983[f]	0.57, 1.12(I) (0.72)
[**5**$^+$; L = $P(OPh)_3$, L–L = dppm]	90	2120	1977, 1927,[e] 2081, 2027[f]	0.53, 1.49(I), (1.00[g])
(**5**$^+$; L = PEt_3, L–L = dppe)	52	2106	1949, 1895,[e] 2080, 2026[f]	0.56, 1.08(I) (0.73[g])
[**6**$^+$; L = $P(OPh)_3$, L–L = dppm]	30	2105	1939,[e] 2080, 2025[f]	0.53, 1.05
(**7**)	40	2095	1871(m),[e] 2050, 1983[f]	0.19, 0.64
(**7**$^+$)	43	2126	1947(m),[e] 2050, 1983[f]	0.18, 0.64
(**8**)	47	2102	1874(m),[e] 2076, 2004[h]	0.23
(**8**$^+$)	56	2136	1948(m),[e] 2085, 2014[h]	0.23

[a] In CH_2Cl_2. [b] Weak. [c] Strong unless stated otherwise; sh = shoulder, m = medium. [d] At a platinum bead electrode, in CH_2Cl_2 with 0.1 mol dm^{-3} $[NBu^n_4][PF_6]$ as base electrolyte. Unless stated otherwise the electron-transfer is reversible. Potentials are *vs.* the saturated calomel electrode; I = irreversible. Under the conditions of the experiment the E° values for the couples $[Fe(\eta\text{-}C_5H_5)_2]^{+/0}$ and $[Fe(\eta\text{-}C_5Me_5)_2]^{+/0}$ are 0.47 and −0.07 V respectively. [e] Carbonyls on Mn. [f] Carbonyls on Ru. [g] Reduction peak potential of the reversible product wave (see text). [h] Carbonyls on Rh.

The electrochemical study indicates that (**5**) undergoes stepwise oxidation at two localised redox centres, the first at the *o*-$O_2C_6Cl_4$ ligand on ruthenium and the second at manganese. Spectroscopic studies on (**5**$^+$), isolated as red $[PF_6]^-$ salts after reacting (**5**) with $[NO][PF_6]$ (1 : 1) in CH_2Cl_2, support this suggestion. The IR carbonyl stretching frequencies associated with the *cis*-$Mn(CO)_2$ unit show little change in energy [*cf.* (**5**)] whereas those of the *cis*-$Ru(CO)_2$ group are shifted by 30—40 cm^{-1} to higher wavenumber {*cf.* $[Ru(CO)_2(PPh_3)_2(o\text{-}O_2C_6Cl_4)]^z$; z = 0, $\tilde{\nu}$(CO) 2045, 1983 cm^{-1}; z = 1, $\tilde{\nu}$(CO) 2073, 2021 cm^{-1}}. The room temperature ESR spectra of (**5**$^+$) in CH_2Cl_2 are also consistent with the formation of an *o*-benzosemiquinone ligand, showing narrow doublets [$A(^{31}P)$ 8.3 G (1 G = 10^{-4} T)] with *g*-values (2.004) close to the spin-only value.

Although these results imply little or no interaction between the two redox centres of (**5**$^+$), the cyanide bridge is not insulating. Thus, the reaction between the paramagnetic Mn^{II} ligand (**3**$^+$; L = PEt_3, L–L = dppe) with (**4**) rapidly gives (**5**$^+$), *via* N-co-ordination at ruthenium, intramolecular electron-transfer through the cyanide bridge, and isomerisation of the *trans*-Mn^{I} centre.‡ Interestingly [**3**$^+$; L = $P(OPh)_3$ L–L = dppm] and (**4**) give (**6**$^+$) (Scheme 1), an isomer of (**5**$^+$) in which the *trans*-$Mn(CO)_2$ geometry is retained after electron-transfer {note that the mononuclear complex [**3**; L = $P(OPh)_3$, L–L = dppm] is isolable and isomerises to [**2**; L = $P(OPh)_3$, L–L = dppm] very slowly; the isomerisation of (**3**; L = PEt_3, L–L = dppe) to (**2**; L = PEt_3, L–L = dppe) is too fast to allow isolation of the neutral *trans*-complex}.

The reaction of (**4**) with *trans*-$[Mn(CN)(CO)(dppm)_2]$ (**1**) gives $[(dppm)_2(CO)Mn(\mu\text{-}CN)Ru(CO)_2(PPh)_3(o\text{-}O_2C_6Cl_4)]$ (**7**) which also undergoes two one-electron oxidations; both are reversible (Table 1). In this case, however, the presence of the more electron-rich donor set $(CO)(dppm)_2$ [*cf.* $(CO)_2L(L\text{–}L)$ of (**2**) and (**3**)] results in localisation of the first oxidation step at manganese {the potential of the second step is again similar to that for the oxidation of $[Ru(CO)_2(PPh_3)_2(o\text{-}O_2C_6Cl_4)]$}. Thus, $[N_2C_6H_4F\text{-}p]$ and (**7**) in CH_2Cl_2 gives the orange–red $[PF_6]^-$ salt of (**7**$^+$) whose IR carbonyl spectrum shows a large shift in the band associated with the Mn(CO) unit but no change in those of the *cis*-$Ru(CO)_2$ group (Table 1). In addition, the ESR spectrum of (**7**$^+$) [−196 °C; tetrahydrofuran (THF): CH_2Cl_2 (2 : 1) glass] is virtually identical to that of (**1**$^+$) itself.[1]

It is interesting to note that the oxidation of (**5**) to (**5**$^+$) (*i.e.* at the N-bound redox centre) is accompanied by a decrease in $\tilde{\nu}$(CN) (Table 1) whereas that of (**7**) to (**7**$^+$) (*i.e.*, at the C-bound redox centre) results in an increase in $\tilde{\nu}$(CN). The implication of these observations for the bonding in, and possible bending of, the Mn–C–N–Ru backbone is under structural investigation.

The redox-active cyanomanganese ligands (**1**), (**1**$^+$), (**2**), and (**3**$^+$) may also be attached to sites which are otherwise redox-inactive. Thus, for example, (**1**) and $[\{RhCl(CO)_2\}_2]$ gives yellow–orange $[(dppm)_2(CO)Mn(\mu\text{-}CN)RhCl(CO)_2]$ (**8**) which shows one reversible oxidation wave (Table 1) associated with the manganese centre. Oxidation of (**8**) with $[N_2C_6H_4F\text{-}p][PF_6]$ gives red (**8**$^+$), which can also be prepared directly from (**1**$^+$) and $[\{RhCl(CO)_2\}_2]$. The frozen solution ESR spectrum of the cation again implies manganese-localised oxidation but there is a small increase in energy of the IR carbonyl bands of the *cis*-$Rh(CO)_2$ unit (Table 1) suggesting an induced change in the electron-density, and therefore reactivity, of the square planar rhodium centre. Studies of this

‡ Alternative mechanisms, involving intermolecular (outer-sphere) electron-transfer between (**3**$^+$) and (**4**), isomerisation of (**3**) to (**2**), and reaction between (**2**) and (**4**$^+$) [or (**4**$^{2+}$)], are much less likely; complex (**4**) is irreversibly oxidised (implying a short lifetime for the primary oxidation product) at a potential (*ca.* 1.0 V) which is rather more positive than that of the couple (**3**$^+$/**3**; L = PEt_3, L–L = dppe, $E^{\circ} \approx$ 0.64 V).

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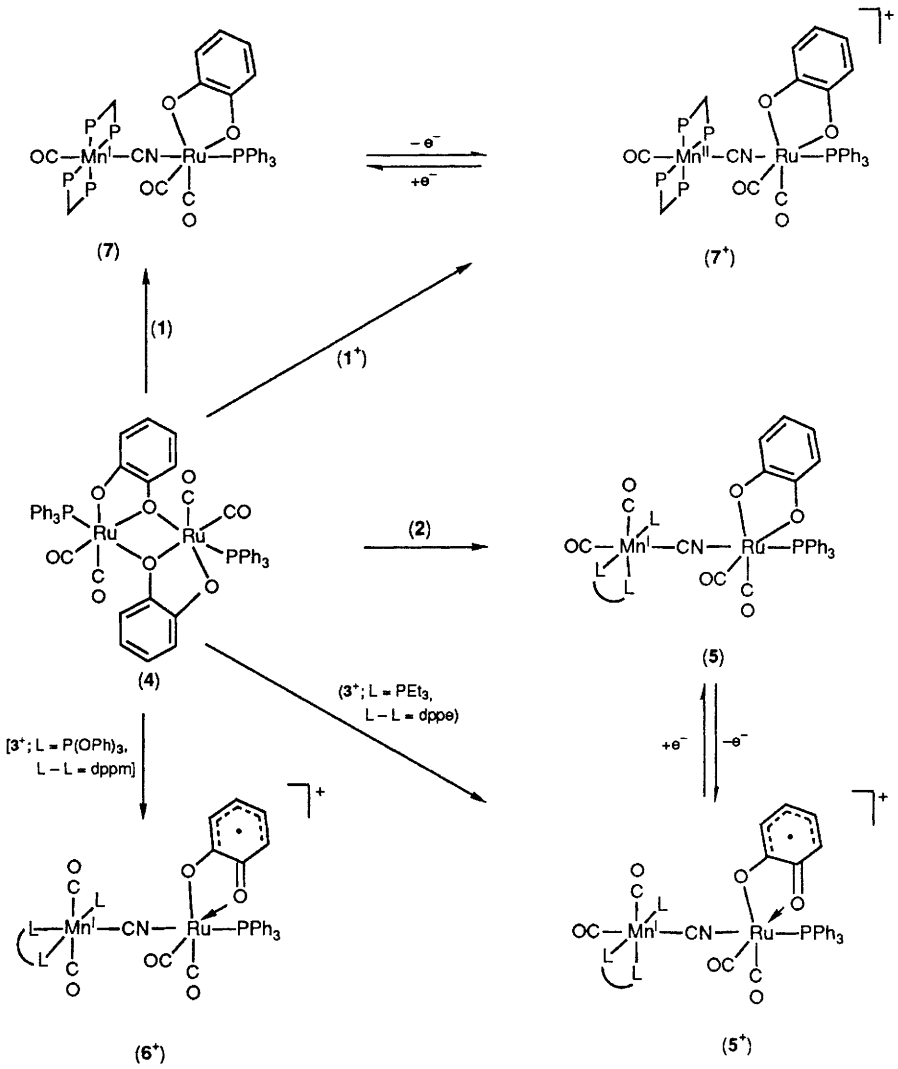

Scheme 1. Chlorine atoms omitted from *o*-$O_2C_6Cl_4$ ligands for clarity.

$[(dppm)_2(CO)Mn(\mu\text{-}CN)RhCl(CO)_2]$
(8)

induced reactivity, and of the synthesis of heteropolynuclear species by the methods outlined above, are in progress.

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