

Preliminary Communication

Low-valent metal complexes as redox-active ligands: new heteropolynuclear derivatives of manganese and rhenium cyanides and the crystal structure of [(*o*-phen)(OC)₃Re(μ-CN)-Ru(CO)₂(PPh₃)(*o*-O₂C₆Cl₄)]

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(Received January 13, 1994)

Abstract

New redox-active homo- and heteropolynuclear complexes, including the X-ray structurally characterised species [(*o*-phen)(OC)₃Re(μ-CN)Ru(CO)₂(PPh₃)(*o*-O₂C₆Cl₄)], have been constructed using the cyanometal ligands [Mn(CN)L(NO)Cp'] (Cp' = η-C₅H₄Me) and [Re(CN)(CO)₃(N–N)] (N–N = bipy, *o*-phen, etc.).

Key words: Manganese; Rhenium; Cyanide; Electrochemistry; Crystal structure

In previous studies we have shown that octahedral cyanomanganese(I) carbonyls such as *cis*- or *trans*-[Mn(CN)(CO)₂(P(OPh)₃)(dppm)] (dppm = Ph₂PCH₂-PPh₂) can act as redox-active ligands in both homo- [1] and heterobinuclear [2,3] systems. Not only does the oxidatively-induced isomerisation of a *cis*- to a *trans*-[Mn(CN)(CO)₂L(L–L)] unit provide a means by which intramolecular electron-transfer can be detected within the binuclear complexes [1] but the extent to which that electron-transfer occurs through the cyanide bridge can be controlled by varying both the nature and the arrangement of the ancillary ligands about the manganese centre [3,4]. We now describe preliminary studies of two additional types of cyanometal ligand, namely four-coordinate (pseudo-tetrahedral) [Mn(CN)L(NO)-Cp'] (Cp' = η-C₅H₄Me) [5], used to test further the effect of geometry on the extent of intramolecular electron transfer, and [Re(CN)(CO)₃(N–N)] (N–N =

bipy, etc.) [6], containing the photoactive Re(N–N) unit [7].

The complexes [Mn(CN)L(NO)Cp'] [1; L = PPh₃ or P(OPh)₃], prepared in 59% and 33% yield respectively from [Mn(CO)L(NO)Cp']⁺ and [NEt₄][CN] in CH₂Cl₂ under reflux and purified by column chromatography on alumina, undergo one-electron oxidation at a platinum electrode in CH₂Cl₂. The process is incompletely reversible {at a cyclic voltammetric scan rate of 200 mV s⁻¹, (i_p)_{red}/(i_p)_{ox} = 0.93 and 0.77 for L = PPh₃ and P(OPh)₃ respectively} but E⁰ can be estimated (0.85 and 1.11 V respectively) from the average of the oxidation and reduction peak potentials; small product waves (at 0.49 and 1.49 V for 1; L = P(OPh)₃), which appear to be reversible, are also observed.

The room temperature reaction of [1; L = PPh₃ or P(OPh)₃] with [Mn(CO)L'(NO)Cp']⁺ [2; L' = PPh₃ or P(OPh)₃] in the presence of ONMe₃ in CH₂Cl₂ gives moderate yields of the green homobinuclear species [Cp'L(NO)Mn(μ-CN)MnL'(NO)Cp']⁺ (3), each of which shows two reversible oxidation waves in the cyclic voltammogram (Table 1). Variation of L and L' in 1 and 2, results in the isolation, *inter alia*, of the linkage isomers [Cp'(Ph₃P)(NO)Mn(μ-CN)Mn{P(OPh)₃}(NO)Cp']⁺ and [Cp'((PhO)₃P)(NO)Mn(μ-CN)Mn(PPh₃)(NO)Cp']⁺, and leads to changes in E₁⁰ and E₂⁰ for 3 such that the N-bound manganese is identified as the first oxidised site. Similar site selectivity was found [1] in the homobinuclear complexes of octahedral Mn(CN) ligands, though the tetrahedral derivatives described in the present paper are oxidised at rather more positive potentials.

Heteropolynuclear complexes may also be prepared by treating 1 with [(Ru(CO)₂(PPh₃)(μ-*o*-O₂C₆Cl₄))₂] to give, for example, orange [Cp'(Ph₃P)(NO)Mn(μ-CN)Ru(CO)₂(PPh₃)(*o*-O₂C₆Cl₄)] (4) or, with [(Rh(μ-Cl)(CO)₂)] in the presence of TlPF₆, red-brown [(Cp'L(NO)Mn(μ-CN))₂Rh(CO)₂]⁺ (5). Complex 4 shows three oxidation waves, the first and third associated with catecholate/semiquinone and semiquinone/quinone couples bound to ruthenium and the second with the manganese centre. The trinuclear complex 5 shows only one, reversible, oxidation wave in the cyclic voltammogram, in contrast to [(*trans*-(dppm)-(EtO)₃P)(OC)₂Mn(μ-CN))₂Rh(CO)₂]⁺ (6), which shows two closely spaced waves [3]. These data suggest a greater interaction, through the *cis*-Rh(CO)₂ bridge,

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TABLE 1. Cyclic voltammetric ^a and IR spectroscopic data for [(M(μ-CN))_nM']^z

Complex		M'	n	Z ^d	Yield/ (%)	Potential ^b (V)		IR ^c (cm ⁻¹)		ν(NO)
M	M'					E(Mn)	E(other)	ν(CN)	ν(CO)	
3	Mn(NO)(PPh ₃) ₃ Cp'	Mn(NO)(PPh ₃) ₃ Cp'	1	1	42	0.83, 1.39	-	2125(w)	-	1746
3	Mn(NO)(P(OPh) ₃) ₃ Cp'	Mn(NO)(P(OPh) ₃) ₃ Cp'	1	1	37	0.88, 1.60	-	2133(w)	-	1768, 1738
4	Mn(NO)(PPh ₃) ₃ Cp'	Ru(CO) ₂ (PPh ₃) ₃ κ ^o -O ₂ C ₆ Cl ₄	1	0	78	1.19	0.58, 1.68(t)	2137(w)	2050, 1985	1742(m)
5	Mn(NO)(PPh ₃) ₃ Cp'	cis-Rh(CO) ₂	2	1	77	1.15	-	2127(w)	2094, 2031	1748(m)
7	fac-Re(CO) ₃ (bipy)	Ru(CO) ₂ (PPh ₃) ₃ κ ^o -O ₂ C ₆ Cl ₄	1	0	66	-	0.61, 1.60(t) Ru); -1.46(t) (Re)	2166(w)	2053, 1988 (Ru); 2028, 1936(m), 1924(m) (Re)	-
7 ⁺	fac-Re(CO) ₃ (bipy)	Ru(CO) ₂ (PPh ₃) ₃ κ ^o -O ₂ C ₆ Cl ₄	1	1	73	-	-	2158(w)	2084 ^e (Ru); 2032, 1947(m), 1929(m) (Re)	-

^a In CH₂Cl₂ at a platinum disc electrode. Under the conditions used the potentials for the couples [Fe(η-C₅H₅)₂]⁺-[Fe(η-C₅H₅)₂]⁺ and [Fe(η-C₅Me₅)₂]⁺-[Fe(η-C₅Me₅)₂]⁺ are 0.47 and -0.09 V respectively. ^b E⁰ for reversible wave unless stated otherwise. The oxidation or reduction peak potential, (E_p)_{red}, or (E_p)_{ox}, at a scan rate of 200 mV s⁻¹ is given for an irreversible oxidation (I_{ox}) or reduction (I_{red}) wave. ^c In CH₂Cl₂. Strong absorptions unless stated otherwise; m = medium, w = weak. ^d Cationic complexes isolated as [PF₆]⁻ salts. ^e Second carbonyl absorption of cis-Ru(CO)₂ group obscured by Re(CO)₃ band at 2032 cm⁻¹.

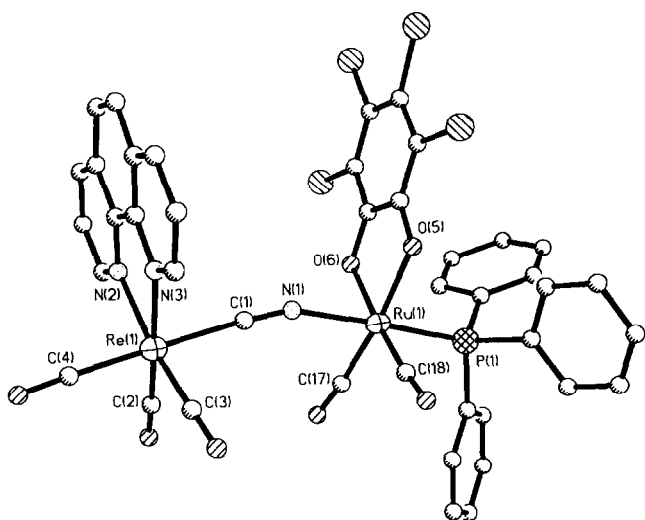


Fig. 1. Molecular geometry of **7**. Important molecular geometry parameters include: bond lengths (Å), Re(1)–C(3) 1.913(11), Re(1)–C(2) 1.929(11), Re(1)–C(4), 1.948(9), Re(1)–C(1), 2.132(9), Re(1)–N(3) 2.177(7), Re(1)–N(2) 2.202(7), Ru(1)–C(18) 1.878(9), Ru(1)–C(17) 1.885(8), Ru(1)–O(6) 2.063(6), Ru(1)–O(5) 2.086(5), Ru(1)–N(1) 2.147(7), Ru(1)–P(1) 2.335(2); bond angles (°) C(1)–N(1)–Ru(1) 160.2(6), N(1)–C(1)–Re(1) 174.7(7).

between the octahedral cyanometal ligands in **6** than between the tetrahedral cyanometal ligands in **5**.

A further dimension is added to the construction of low-valent complexes containing cyanide bridges by using the photoactive species *fac*-[Re(CN)(CO)₃(N–N)] (N–N = bipy, *o*-phen, etc.) [6]. For example, the reaction with $[\{\text{Ru}(\text{CO})_2(\text{PPh}_3)(\mu\text{-}o\text{-O}_2\text{C}_6\text{Cl}_4)\}_2]$ gave orange $[(\text{N}-\text{N})(\text{OC})_3\text{Re}(\mu\text{-CN})\text{Ru}(\text{CO})_2(\text{PPh}_3)(\mu\text{-}o\text{-O}_2\text{C}_6\text{Cl}_4)]$ (**7**). A single crystal structure analysis [8*] was carried out on (**7**; N–N = *o*-phen) as its bis(dichloromethane) solvate.

The molecular structure (Fig. 1) is of the form suggested on the basis of the spectroscopic evidence. The Re–CN–Ru backbone links *fac*-Re(CO)₃(*o*-phen) and *cis*-Ru(CO)₂(PPh₃)(*o*-O₂C₆Cl₄) fragments. The local coordination geometry at each metal is near octahedral, with the orientation of the ML₆ fragments such that the arene π systems are near eclipsed. The notable bending at the cyano nitrogen increases the separation between the *o*-phen and *o*-O₂C₆Cl₄ ligands. The cyano ligand is C-bonded *trans* to CO at Re and N-bonded *trans* to PPh₃ at Ru. The dimensions of the *o*-O₂C₆Cl₄ ligand {C–O distances 1.334(9), 1.325(9) Å and Ru–O distances 2.063(6), 2.086(5) Å} are consistent with it being in the catecholate form (*cf.* the structures of the mononuclear complex [Ru(CO)₂(PPh₃)₂(*o*-O₂C₆Cl₄)] which contains the ligand as the catecholate {C–O distances 1.334(5), 1.326(5) Å and

Ru–O distances 2.062(3), 2.065(3) Å} and of the cation [Ru(CO)₂(PPh₃)₂(*o*-O₂C₆Cl₄)]⁺ which contains the ligand as the semiquinone {C–O distances 1.291(5), 1.289(5) Å and Ru–O distances 2.098(3), 2.088(3) Å} [9].

Complex **7** is oxidised in two steps at the O–O chelate, as in **4**, and is irreversibly reduced at the Re(N–N) centre; chemical oxidation of (**7**, N–N = *o*-phen) with one equivalent of [N₂C₆H₄F-p][PF₆] in thf gave a dark red solid the isotropic ESR spectrum of which {doublet; *g* = 2.007; *A*(³¹P) = 8.9 G; further partially resolved couplings of *ca.* 0.7 G, possibly to the Cl atoms of the O₂C₆Cl₄ ligand} confirmed the formation of the semiquinone-containing cation [(*o*-phen)(OC)₃-Re(μ-CN)Ru(CO)₂(PPh₃)(*o*-O₂C₆Cl₄)]⁺ (**7**⁺). The photochemistry of these and other Re(N–N) complexes, and the extensive electrochemistry of all of the new species reported herein is under investigation.

Acknowledgment

We thank the SERC for studentships (to NCB and GMR) and the Caja de Ahorros de la Inmaculada for a grant (to MB).

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- Crystal data for **7** · 2CH₂Cl₂, N–N = *o*-phen: C₄₅H₂₆Cl₈N₃O₇PRu; *M* = 1322.53; triclinic, space group *P* $\bar{1}$ (No. 2); *a* = 10.383(3), *b* = 14.894(4), *c* = 16.703(6) Å; α = 77.86(2), β = 79.90(2), γ = 72.97(2)°; *V* = 2399(2) Å³; *Z* = 4; *D*_x = 1.83 g cm^{−3}; λ = 0.71073 Å; μ = 33.7 cm^{−1}; *F*(000) = 1286; *T* = 295K. Data were collected on a Nicolet P3m diffractometer for a unique portion of reciprocal space for 4 < 2θ < 50°. The structure was solved by heavy atom methods and refined by least-squares against all *F*² data to *R*1 = 0.051 and *wR*2 = 0.115 for 6283 unique, observed, absorption corrected [*I* > 2σ(*I*)] intensity data. The two molecules of dichloromethane are highly disordered. Atomic coordinates, bond lengths, bond angles and displacement parameters for **7** · 2CH₂Cl₂ have been deposited with the Cambridge Crystallographic Data Centre.
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* Reference number with an asterisk indicates a note in the list of references.