Journal of Organometallic Chemistry, 474 (1994) C24–C26

Preliminary Communication

Heteropolynuclear complexes containing multiple redox sites: cyanometal ligand derivatives of the triazenido-bridged dirhodium fragment

Manuel Bardaji, Nathan C. Brown,
Aristides Christofides and Neil G. Connelly

School of Chemistry, University of Bristol, Bristol BS8 1TS (UK)

(Received January 13, 1994)

Abstract

The reactions of $[Rh_2(CO)_4(\mu\text{-RNNNR})_2]$ (R=*p*-tolyl) with cyanometal ligands such as *trans*-$[Mn(CN)(CO)_2\{P(OEt)_3\}(dppm)]$, $[Mn(CN)(NO)(PPh_3)(\eta\text{-}C_5H_4Me)]$, and $[Re(CN)(CO)_3(4,4'\text{-dimethyl-2,2'-bipyridyl})]$ give heteropolynuclear complexes containing multiple redox sites.

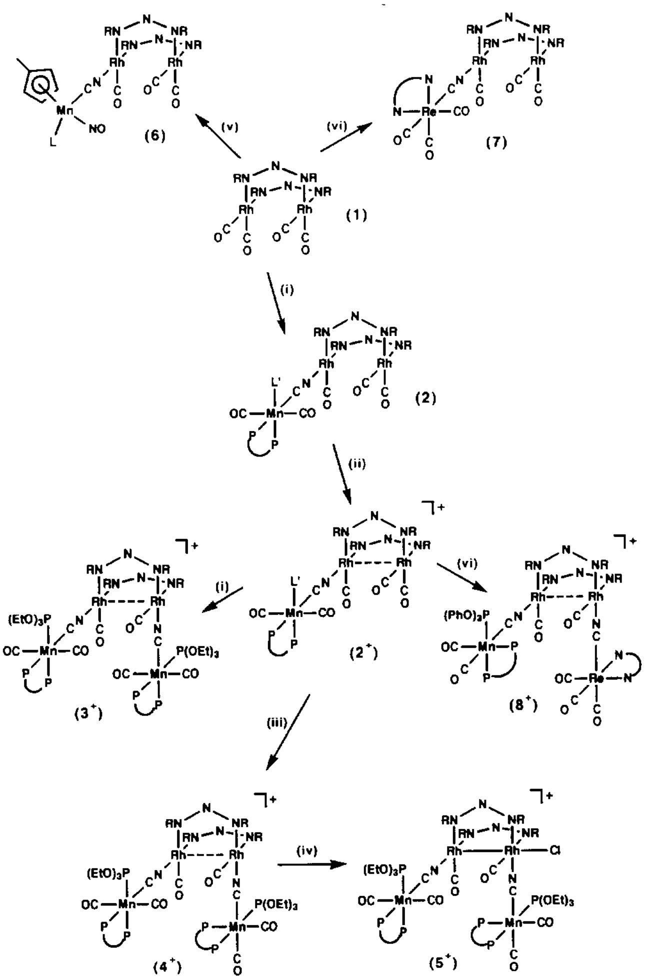
Key words: Manganese; Rhodium; Cyanide; Triazenide; Electrochemistry; Photochemistry

1. Introduction

In recent years we have carried out extensive studies of the electron-transfer chemistry of (i) derivatives of the triazenido-bridged complex $[Rh_2(CO)_4(\mu\text{-RNNNR})_2]$ (R = *p*-tolyl), which can be selectively stabilised [1–3] with core oxidation levels of $[Rh_2]^{z+}$ ($z = 2$–4), and (ii) cyanometal complexes such as *cis*- and *trans*-$[Mn(CN)(CO)_2L(P\text{-}P)]$ (L = phosphine or phosphite, P–P = dppm or dppe) [4,5], $[Mn(CN)(NO)LCp']$ ($Cp' = \eta\text{-}C_5H_4Me$) [6], and $[Re(CN)(CO)_3(N\text{-}N)]$ (N–N = bipy, *etc.*) [7], which can act as redox-active ligands [8]. We now describe preliminary synthetic studies in which the two types of complex are brought together in the designed construction of low-valent heteropolynuclear complexes with multiple redox sites.

2. Results and discussion

At room temperature the reaction of $[Rh_2(CO)_4(\mu\text{-RNNNR})_2]$ (1) (Scheme 1) in CH_2Cl_2 with *trans*-$[Mn(CN)(CO)_2\{P(OEt)_3\}(dppm)]$ in the presence of



Scheme 1. R = *p*-tolyl, P–P = dppm ($Ph_2PCH_2PPh_2$), L = PPh_3 or $P(OPh)_3$, L′ = $P(OEt)_3$ or $P(OPh)_3$, N–N = 4,4′-dimethyl-2,2′-bipyridyl. (i) *trans*-$[Mn(CN)(CO)_2\{P(OEt)_3\}(dppm)]$, (ii) $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$, (iii) *cis*-$[Mn(CN)(CO)_2\{P(OEt)_3\}(dppm)]$, (iv) $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ and Cl^-, (v) $[Mn(CN)(NO)L(\eta\text{-}C_5H_4Me)]$, (vi) $[Re(CN)(CO)_3(N\text{-}N)]$.

$ONMe_3$ results in *mono*substitution at the rhodium site {*c.f.* the reactions of (1) with PPh_3 [1] and 2,2′-bipyridyl [2] which lead to dicarbonyl complexes} and the isolation of high yields of red [*trans*-$\{(dppm)(EtO)_3P\}(CO)_2Mn(\mu\text{-CN})\}Rh_2(CO)_3(\mu\text{-RNNNR})_2]$ (2) readily characterised by elemental analysis and IR spectroscopy (Table 1). The cyclic voltammogram of 2 shows two reversible oxidation waves ($E^\circ = 0.15$ and 0.84 V) which, by comparison with data [1,2,4] for species containing the individual Rh_2 and Mn(CN) units, can be

---

Correspondence to: Dr. N.G. Connelly.

0022-328X/94/$7.00
SSDI 0022-328X(94)24543-R

TABLE 1. Electrochemical [a] and IR spectroscopic data for $[\{L_xM(\mu\text{-CN})\}_nRh_2X(CO)_{4-n}(\mu\text{-RNNNR})_2]^z$

L_x	*n*	Z [d]	X	Yield (%)	Potential [b] (V)		IR [c] cm^{-1}			
					E(Mn)	*E*(other)	*ν*(CN)	*ν*(CO)(Rh)	*ν*(CO) [e]	*ν*(NO)
(**2**) *trans*-$Mn(CO)_2\{P(OEt)_3\}(dppm)$	1	0	-	75	0.84	0.15 [f], 1.28 [g] (I_{ox})	2108(w)	2052, 1987, 1971 (m, sh)	1919	-
(**2**$^+$) *trans*-$Mn(CO)_2\{P(OEt)_3\}(dppm)$	1	1	-	72	0.84	0.15 [f], 1.27 [g] (I_{ox})	2087(w)	2113(ms), 2073(ms), 2052(mw)	1927	-
(**3**$^+$) *trans*-$Mn(CO)_2\{P(OEt)_3\}(dppm)$	2	1	-	73	0.73 [h]	−0.63 [f], 0.95 [g,h], 1.75 (I_{ox})	2099(w)	2053(mw), 2028(mw)	1924	-
(**4**$^+$) *trans*-$Mn(CO)_2\{P(OEt)_3\}(dppm)$ and *cis*-$Mn(CO)_2\{P(OEt)_3\}(dppm)$ (1:1)	2	1	-	68	[i], 1.39 (I_{ox})	−0.60 [f] (I_{red}), [i], 1.76 (I_{ox})	2110(w), 2097(m)	2052(m), 2028(m)	1963, 1923, 1917(s, sh)	-
(**5**$^+$) *trans*-$Mn(CO)_2\{P(OEt)_3\}(dppm)$ and *cis*-$Mn(CO)_2\{P(OEt)_3\}(dppm)$ (1:1)	2	1	Cl	71	0.78, 1.31 (I_{ox})	−0.69 [g] (I_{red}), 1.60 (I_{ox})	2120(w)	2099(m), 2069(mw)	1964, 1922, 1910	-
(**6**) $Mn(NO)(PPh_3)Cp'$	1	0	-	61	1.28	0.19 [f], 1.18 [g]	2138(w)	2053, 1991, 1979 (sh)	-	1741(m)
(**6**) $Mn(NO)\{P(OPh)_3\}Cp'$	1	0	-	47	1.52	0.22 [f], 1.21 [g]	2144(w)	2053, 1991, 1978 (m, sh)	-	1765(m)
(**7**) *fac*-$Re(CO)_3$(dimethylbipy)	1	0	-	58	−1.64 (I_{red})	0.16 [f], 1.16 [g]	[j]	2055(m), 1991(m), 1977 (w, sh)	2025, 1931(m), 1922(m) [k]	-
(**8**$^+$) *cis*-$Mn(CO)_2\{P(OPh)_3\}(dppm)$ and *fac*-$Re(CO)_3$(dimethylbipy) (1:1)	2	1	-	57	-	-	2154(w), 2115(w)	2056(w) [l]	1976(m), 1938(m, sh) Mn; 2028, 1923(brd) [k]	-

[a] Cyclic voltammetry in CH_2Cl_2 at a platinum disc electrode unless stated otherwise. [b] $E°$ for reversible wave unless stated otherwise. The oxidation or reduction peak potential, $(E_p)_{ox}$ or $(E_p)_{red}$, at a scan rate of 200 mV s^{-1} is given for an incompletely reversible oxidation (I_{ox}) or reduction (I_{red}) wave. Under the conditions used the potentials for the couples $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$ and $[Fe(\eta\text{-}C_5Me_5)_2]^+$–$[Fe(\eta\text{-}C_5Me_5)_2]$ are 0.47 and −0.09 V respectively. [c] In CH_2Cl_2. Strong (s) absorptions unless stated otherwise; m = medium, w = weak, sh = shoulder. [d] Cationic complexes isolated as $[PF_6]^-$ salts. [e] $Mn(CO)_2$ bands unless stated otherwise. [f] $[Rh_2]^{2+}$–$[Rh_2]^{3+}$ couple. [g] $[Rh_2]^{3+}$–$[Rh_2]^{4+}$ couple. [h] Overlapping waves in cyclic voltammogram, resolved by differential pulse voltammetry. [i] Waves due to oxidation of *trans*-Mn(I) and $[Rh_2]^{3+}$ centres overlap at *ca.* 0.8–1.0 V. [j] Not observed. [k] $Re(CO)_3$ bands. [l] Second band obscured by $Re(CO)_3$ absorption at 2028 cm^{-1}.

assigned to $[Rh_2]^{2+}$–$[Rh_2]^{3+}$ and Mn(I)–Mn(II) couples respectively; a third, incompletely reversible wave, $(E_p)_{ox} = 1.28$ V, scan rate $= 200$ mV s^{-1}, is associated with the formation and further reaction of the $[Rh_2]^{4+}$ core.

Treatment of **2** with one equivalent of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ in CH_2Cl_2 gave a good yield of the green monocation (**2**$^+$). In agreement with the conclusions drawn from the CV study of **2**, the IR spectrum of **2**$^+$ shows large shifts (*ca.* 60–85 cm^{-1}) to higher energy in the carbonyl bands associated with the $Rh_2(CO)_3$ fragment and a small shift (8 cm^{-1}) in the band due to the *trans*-$Mn(CO)_2$ group (Table 1); the ESR spectrum is also consistent with the formation of an $[Rh_2]^{3+}$ core (*c.f.* $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-RNNNR})_2]^+$ [1,3]).

Unlike **2**, complex **2**$^+$ is substitutionally labile, and treatment with a second cyanomanganese ligand, namely *trans*- or *cis*-$[Mn(CN)(CO)_2\{P(OEt)_3\}(dppm)]$, gives the green, symmetrical and unsymmetrical dicarbonyls **3**$^+$ and **4**$^+$ respectively (Scheme 1). The isolation of complex **4**$^+$ and related species will allow an investigation to be made of long-range interactions between non-equivalent manganese redox sites through a $[Rh_2]^{3+}$ core.

The extent of such interactions is expected to increase on further oxidation of the dirhodium centre in that the HOMO of **1** is an Rh–Rh σ^* orbital [1,3]. Although complex **4**$^+$ is oxidised only at 0.86 V, making chemical access to **4**$^{2+}$ relatively difficult, the higher oxidation level ($[Rh_2]^{4+}$) is stabilised by axial coordination at rhodium [2]. Thus, treatment of **4**$^+$ with Cl^- in the presence of $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ gave a high yield of the green, diamagnetic $[Rh_2]^{4+}$-containing cation (**5**$^+$).

Other redox-active ligands may also be coordinated to the $Rh_2(\mu\text{-RNNNR})_2$ fragment, including tetrahedral $[Mn(CN)(NO)LCp']$ [6] and $[Re(CN)(CO)_3(N\text{–}N)]$ [7], providing the basis for studies of (i) the dependence of long-range electron transfer on structure (octahedral *vs.* tetrahedral manganese centres) or (ii) of photoinduced redox reactions [9]. Thus, treatment of **1** with $[Mn(CN)(NO)LCp']$ [$L = PPh_3$ or $P(OPh)_3$] or $[Re(CN)(CO)_3$(4,4′-dimethyl-2,2′-bipyridyl)] in the presence of $ONMe_3$ in CH_2Cl_2 gave red (**6**) and red–brown (**7**), respectively (Table 1). The reaction of $[\{\textit{trans}\text{-}(dppm)\{PhO)_3P\}(CO)_2Mn(\mu\text{-CN})\}Rh_2(CO)_3(\mu\text{-RNNNR})_2]^+$ {**2**$^+$, $L' = P(OPh)_3$, Scheme 1} with $[Re(CN)(CO)_3$(4,4′-dimethyl-2,2′-bipyridyl)] gave brown (**8**$^+$), photolysis of the Re(N–N) chromophore of which may induce *cis–trans* isomerisation [4] at the manganese centre following charge separation [to $N\text{–}N^-$ and Re(II)] and intramolecular oxidation to Mn(II) (*c.f.* the photolysis of $[(bipy)_2(CN)Ru(\mu\text{-CN})Re(CO)_3(phen)]^+$ [10]). This and other aspects of the electro- and photo-chemical behaviour of the new complexes described herein are under investigation.

Acknowledgment

We thank the SERC for a studentship (to NCB) and Caja de Ahorros de la Immaculade for a grant (to MB).

References

1 N.G. Connelly, G. Garcia, M. Gilbert and J.S. Stirling, *J. Chem. Soc., Dalton Trans.* (1987) 1403.

2 T. Brauns, C. Carriedo, J.S. Cockayne, N.G. Connelly, G. Garcia Herbosa and A.G. Orpen, *J. Chem. Soc., Dalton Trans.* (1989) 2049.

3 D.C. Boyd, N.G. Connelly, G. Garcia Herbosa, M.G. Hill, K.R. Mann, C. Mealli, A.G. Orpen, K.E. Richardson and P.H. Rieger, *Inorg. Chem., 33* (1994) 960.

4 N.G. Connelly, K.A. Hassard, B.J. Dunne, A.G. Orpen, S.J. Raven, G.A. Carriedo and V. Riera, *J. Chem. Soc., Dalton Trans.* (1988) 1623.

5 G.A. Carriedo, N.G. Connelly, E. Perez-Carreno, A.G. Orpen, A.L. Rieger, P.H. Rieger, V. Riera and G.M. Rosair, *J. Chem. Soc., Dalton Trans.* (1993) 3103.

6 D.L. Reger, D.J. Fauth and M.D. Dukes, *J. Organomet. Chem., 170* (1979) 217.

7 R.M. Leasure, L.A. Sacksteder, D. Nesselrodt, G.A. Reitz, J.N. Demas and B.A. DeGraff, *Inorg. Chem., 30* (1991) 3722.

8 G.A. Carriedo, N.G. Connelly, M.C. Crespo, I.C. Quarmby, V. Riera and G.H. Worth, *J. Chem. Soc., Dalton Trans.* (1991) 315; A. Christofides, N.G. Connelly, H.J. Lawson, A.C. Loyns, A.G. Orpen, M.O. Simmonds and G.H. Worth, *J. Chem. Soc., Dalton Trans.* (1991) 1595; G.A. Carriedo, N.G. Connelly, S. Alvarez, E. Perez-Carreno and S. Garcia-Granda, *Inorg. Chem., 32* (1993) 272; F.L. Atkinson, A. Christofides, N.G. Connelly, H.J. Lawson, A.C. Loyns, A.G. Orpen, G.M. Rosair and G.H. Worth, *J. Chem. Soc., Dalton Trans.* (1993) 1441; M. Bardaji, N.C. Brown, N.G. Connelly, R. Davies, A.G. Orpen, G.M. Rosair and N.R. Seear, *J. Organomet. Chem., 474* (1994) C21.

9 L. Wallace and D.P. Rillema, *Inorg. Chem., 32* (1993) 3836; and refs. therein.

10 J.R. Schoonover, K.C. Gordon, R. Argazzi, W.H. Woodruff, K.A. Peterson, C.A. Bignozzi, R.B. Dyer and T.J. Meyer, *J. Am. Chem. Soc., 115* (1993) 10996.