Trinuclear Mixed-valence Complexes with the Linear $[Rh_3]^{4+}$ Core

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The complexes $[Rh_3(\mu_3\text{-}L)_2(CO)_4(PPh_3)_2][BF_4]$ [1^+; L = 1,8-naphthyridin-2-onate (napyo) or 5,7-dimethyl-1,8-naphthyridin-2-onate (dmnapyo)] and $[Rh_3(\mu_3\text{-}L)_2(CO)_2(\eta^4\text{-cod})_2][BF_4]$ (2^+; cod = cyclo-octa-1,5-diene) undergo two reversible one-electron oxidations at a platinum bead electrode in CH_2Cl_2. Chemical oxidation of (1^+) or (2^+) with $[N(C_6H_4Br\text{-}p)_3][BF_4]$ in CH_2Cl_2, or electrolytic oxidation at a platinum electrode, gave the mixed-valence dications $[Rh_3(\mu_3\text{-}L)_2(CO)_4(PPh_3)_2]^{2+}$ (1^{2+}; L = napyo or dmnapyo) and $[Rh_3(\mu_3\text{-}L)_2(CO)_2(\eta^4\text{-cod})_2]^{2+}$ (2^{2+}; L = napyo or dmnapyo), isolated as the violet bis(tetrafluoroborate) salts, and characterised by i.r., visible, and e.s.r. spectroscopy and by cyclic voltammetry.

Our recent studies[1] of the redox chemistry of face-to-face triazenido-bridged complexes derived from $[\{Rh(CO)_2(\mu\text{-}RNNNR)\}_2]$ (R = *p*-tolyl), taken with related work[2] on tetrabridged species such as $[Rh_2(\mu\text{-}L')_4]$ (L′ = carboxylate, benzamidinate, *N*-phenylacetamidate, formamidinate, *etc.*), show that the $[Rh_2]^{Z+}$ core can remain intact in at least five different redox states (*i.e.* $Z = 2$ to 6 inclusive). Linear polynuclear species might also be expected to act as precursors to extensive electron-transfer series, with the paramagnetic members of such series acting as short-chain models of one-dimensional conductors. We have therefore investigated the electron-transfer reactions of the $[Rh_3]^{3+}$-containing complexes[3] $[Rh_3(\mu\text{-}L)_2(CO)_4(PPh_3)_2]^+$ [1^+; L = 1,8-naphthyridin-2-onate (napyo) or 5,7-dimethyl-1,8-naphthyridin-2-onate (dmnapyo)] and $[Rh_3(\mu\text{-}L)_2(CO)_2(\eta^4\text{-cod})_2]^+$ (2^+; cod = cyclo-octa-1,5-diene) (Figure) which undergo two reversible one-electron oxidations to di- and tri-cations. The dications, containing the mixed-valence $[Rh_3]^{4+}$ core, have been isolated and fully characterised by spectroscopic and electrochemical methods.

Results and Discussion

The cyclic voltammograms of complexes (1^+) and (2^+), in CH_2Cl_2 at a platinum bead electrode, each show two oxidation waves which are fully reversible ($i_{red}/i_{ox} = 1.0$) and diffusion-controlled ($i_{ox}/v^{\frac{1}{2}}$ = constant) at scan rates, v, between 50 and 500 mV s^{-1} (Table 1). The loss of one electron during the first oxidation step was confirmed by coulometry. For example, controlled-potential electrolysis of (1^+; L = napyo) at 0.6 V (cylindrical platinum gauze electrode, in CH_2Cl_2, 20 min) resulted in the release of 0.9 F mol^{-1} (*i.e.* $n = 1$) and the formation of a deep purple solution. The cyclic and rotating platinum electrode voltammograms of this solution confirmed the quantitative formation of (1^{2+}; L = napyo), showing one reduction wave and one oxidation wave at potentials virtually identical to those for the oxidations of (1^+; L = napyo).

Further electrolysis of the purple solution, at 1.2 V [designed to generate (1^{3+})], resulted in an intense black-purple solution the cyclic voltammogram of which showed no waves assignable to identifiable products. The cyclic voltammetric wave heights for the two oxidation waves of (1^+) or (2^+) are similar so that the second process clearly also involves one-electron loss. The electrolytic experiments show, however, that the trications are stable at room temperature only on the time-scale of the cyclic voltammetric experiment.

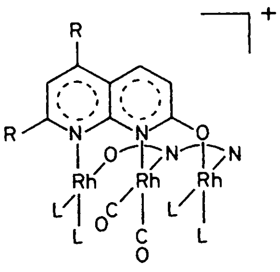

Figure. Structure of the complexes (1^+; R = H) and (2^+; R = Me); L_2 = (CO)(PPh$_3$) or η^4-cod

The complexes (1^+) and (2^+) also show reduction waves, at potentials given in Table 1. These waves are chemically irreversible, but have heights similar to those of the oxidation processes suggesting that one-electron reduction is followed by rapid reaction of the neutral species (**1**) and (**2**).

For each of the complexes (1^+) and (2^+) the two oxidation waves are well separated (by 0.6—0.8 V), as might be expected if di- and tri-cation formation involves electron loss from a h.o.m.o. (highest occupied molecular orbital) largely delocalised over the trimetal centre (*cf.* the binuclear ferrocenyl derivatives discussed in ref. 4). In terms of chemical synthesis, the large wave separation suggests that the $[Rh_3]^{4+}$ complexes (1^{2+}) and (2^{2+}) should be stable with respect to disproportionation to the corresponding mono- and tri-cations.

The potentials of the two waves of each compound are most dependent on the terminal ligands in that the PPh_3 complexes (1^+) are more easily oxidised than the η^4-cod analogues (2^+) (by *ca.* 0.3 V). However, there is also a dependence of potential on the bridging ligand such that the napyo derivatives are more difficult to oxidise than the dmnapyo analogues [by *ca.* 160 mV for (1^+) and 70 mV for (2^+)]. It is interesting that there is also a dependence of the energy of the visible absorption band observed[3] for (1^+) and (2^+) (and also of the dications, Table 2) on both the terminal and bridging ligands. Moreover, there is a linear correlation between E° for the couples (1^+)—(1^{2+}) or (2^+)—(2^{2+}) and $\lambda_{max.}$ for the monocations.

The potentials for the second oxidations of complexes (1^+) and (2^+) (1.01—1.34 V) were too positive to allow the chemical generation of the corresponding trications (and the electrolytic experiment described above suggested the trications to be unstable once generated). However, the dications, which are

Table 1. Cyclic voltammetric data[a] for trirhodium complexes

Complex	Process	$E^{\circ b}$/V	Process	$E^{\circ b}$/V	Process	$E_{pk}{}^{c}$/V
$[Rh_3(\mu_3\text{-napyo})_2(CO)_4(PPh_3)_2]^+$	$+1 \rightleftharpoons +2$	0.40	$+2 \rightleftharpoons +3$	1.03	$+1 \longrightarrow 0$	−1.32
$[Rh_3(\mu_3\text{-napyo})_2(CO)_4(PPh_3)_2]^{2+}$	$+2 \rightleftharpoons +1$	0.38	$+2 \rightleftharpoons +3$	1.06	*d*	
$[Rh_3(\mu_3\text{-napyo})_2(CO)_2(\eta^4\text{-cod})_2]^+$	$+1 \rightleftharpoons +2$	0.65	$+2 \rightleftharpoons +3$	1.30	$+1 \longrightarrow 0$	−1.43
$[Rh_3(\mu_3\text{-napyo})_2(CO)_2(\eta^4\text{-cod})_2]^{2+}$	$+2 \rightleftharpoons +1$	0.65	$+2 \rightleftharpoons +3$	1.32	*d*	
$[Rh_3(\mu_3\text{-dmnapyo})_2(CO)_4(PPh_3)_2]^+$	$+1 \rightleftharpoons +2$	0.22	$+2 \rightleftharpoons +3$	1.01	$+1 \longrightarrow 0$	−1.31
$[Rh_3(\mu_3\text{-dmnapyo})_2(CO)_4(PPh_3)_2]^{2+}$	$+2 \rightleftharpoons +1$	0.24	$+2 \rightleftharpoons +3$	1.03	*d*	
$[Rh_3(\mu_3\text{-dmnapyo})_2(CO)_2(\eta^4\text{-cod})_2]^+$	$+1 \rightleftharpoons +2$	0.59	$+2 \rightleftharpoons +3$	1.34	$+1 \longrightarrow 0$	−1.54
$[Rh_3(\mu_3\text{-dmnapyo})_2(CO)_2(\eta^4\text{-cod})_2]^{2+}$	$+2 \rightleftharpoons +1$	0.58	$+2 \rightleftharpoons +3$	1.33	*d*	

[a] Potentials are *versus* the saturated calomel electrode, measured at a platinum bead in CH_2Cl_2 with 0.1 mol dm^{-3} $[NBu^n{}_4][PF_6]$ as supporting electrolyte. Under these conditions, $E^{\ominus}$ values 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 −0.07 V respectively. [b] Reversible, diffusion-controlled process obeying the criteria $(i_p)_{red}/(i_p)_{ox} = 1$ and $(i_p)_{ox}/\nu^{\frac{1}{2}}$ = constant for scan rates, ν, from 50 to 500 mV s^{-1}. [c] Irreversible process, E_{pk} is the reduction peak potential at a scan rate of 200 mV s^{-1}. [d] Not measured.

Table 2. Analytical, i.r. and visible absorption spectroscopic data for trirhodium complexes

Complex	Colour	Yield/ %	Analysis[a]/% C	H	N	$\tilde{\nu}(CO)^b$/cm^{-1}	$\lambda_{max.}$/ nm
$[Rh_3(\mu_3\text{-napyo})_2(CO)_4(PPh_3)_2][BF_4]_2$	Violet	72	45.6 (45.7)	3.0 (2.8)	4.2 (3.7)[c]	2 108m, 2 070s, 2 020vs	540
$[Rh_3(\mu_3\text{-napyo})_2(CO)_4(PPh_3)_2][ClO_4]^d$						2 075s, 2 020s, 1 975vs	599
$[Rh_3(\mu_3\text{-dmnapyo})_2(CO)_4(PPh_3)_2][BF_4]_2$	Violet	69	47.3 (47.2)	3.4 (3.2)	4.2 (3.6)[c]	2 108m, 2 070s, 2 016vs	533
$[Rh_3(\mu_3\text{-dmnapyo})_2(CO)_4(PPh_3)_2][ClO_4]^d$						2 080s, 2 020s, 1 970vs	623
$[Rh_3(\mu_3\text{-napyo})_2(CO)_2(\eta^4\text{-cod})_2][BF_4]_2$	Violet	64	38.1 (39.0)	3.5 (3.3)	5.6 (5.4)	2 104vs, 2 068vs	554
$[Rh_3(\mu_3\text{-napyo})_2(CO)_2(\eta^4\text{-cod})_2][ClO_4]^d$						2 080vs, 2 020vs	555
$[Rh_3(\mu_3\text{-dmnapyo})_2(CO)_2(\eta^4\text{-cod})_2][BF_4]_2$	Violet	79				2 105vs, 2 068vs	549
$[Rh_3(\mu_3\text{-dmnapyo})_2(CO)_2(\eta^4\text{-cod})_2][ClO_4]^d$						2 075vs, 2 020s	576

[a] Calculated values in parentheses. [b] In CH_2Cl_2; m = medium, s = strong, and v = very. [c] Analysed as a 1:1 CH_2Cl_2 solvate. [d] Data from ref. 3.

Table 3. E.s.r. spectroscopic data for dicationic trirhodium complexes

Complex	Low temperature[a] g_1	g_2	g_3	$g_{av.}$	Room Temperature[b] $g_{av.}$
$[Rh_3(\mu_3\text{-napyo})_2(CO)_4(PPh_3)_2][BF_4]_2$	2.150	2.112	2.017	2.096	2.091
$[Rh_3(\mu_3\text{-dmnapyo})_2(CO)_4(PPh_3)_2][BF_4]_2$	2.135	2.099	2.015	2.083	2.085
$[Rh_3(\mu_3\text{-napyo})_2(CO)_2(\eta^4\text{-cod})_2][BF_4]_2$	2.150[c]		2.047	2.116	2.122
$[Rh_3(\mu_3\text{-dmnapyo})_2(CO)_2(\eta^4\text{-cod})_2][BF_4]_2$	2.157	2.134	2.046	2.112	2.119

[a] In CH_2Cl_2–thf (1:2) at −196 °C. [b] In CH_2Cl_2. [c] g_1 and g_2 unresolved.

formed at more accessible potentials (0.22—0.65 V), have been characterised.

The addition of solid $[NO][BF_4]$ or a solution of $[N(C_6H_4Br\text{-}p)_3][BF_4]$ {generated *in situ* by adding $[NO][BF_4]$ to $N(C_6H_4Br\text{-}p)_3$} to (**1**$^+$) or (**2**$^+$) in CH_2Cl_2 gives deep violet solutions from which good yields (60—80%) of the salts $[Rh_3(\mu_3\text{-}L)_2(CO)_4(PPh_3)_2][BF_4]_2$ (**1**$^{2+}$; L = napyo or dmnapyo) or $[Rh_3(\mu_3\text{-}L)_2(CO)_2(\eta^4\text{-cod})_2][BF_4]_2$ (**2**$^{2+}$; L = napyo or dmnapyo) were readily obtained.

The new complexes are air-sensitive solids which must be rapidly recrystallised for purification and are best stored at −20 °C under nitrogen. Nevertheless, all have been characterised by i.r., visible (Table 2), and e.s.r. spectroscopy (Table 3) and by electrochemical methods (Table 1). The complexes (**1**$^{2+}$) and (**2**$^{2+}$; L = napyo) have also been characterised by elemental analysis (Table 2).

The i.r. carbonyl spectra of the dications are similar to those of the corresponding monocations in terms of the numbers and relative intensities of the bands (Table 2). It is noteworthy that *all* of the bands of the dications are shifted to higher energy on oxidation, by similar amounts (30—50 cm^{-1}), again suggesting that oxidation results in electron removal from a delocalised h.o.m.o. of (**1**$^+$) and (**2**$^+$). Localised oxidation at one metal centre might be expected to lead to a larger shift of the bands associated with the carbonyl ligands attached to that centre, an effect which would have been particularly evident for the tetracarbonyls (**1**$^+$).

For the complex (**2**$^{2+}$; L = dmnapyo) the two intense bands at 2 105 and 2 068 cm^{-1} are accompanied by weak absorptions at 2 118 and 2 083 cm^{-1}. This second species, the presence of which may account for the poor microanalytical data, is not the trication (**2**$^{3+}$); addition of further oxidant does not result in an increase in intensity of the additional bands. Its identity is unknown, and it does not appear to be electroactive (see below).

Cyclic and rotating platinum electrode voltammetry provide conclusive proof of the identity of (**1**$^{2+}$; L = napyo or dmnapyo; **2**$^{2+}$; L = napyo) in that each of the dications shows one oxidation wave and one reduction wave at potentials identical to those for the oxidations of the monocations. The η^4-cod derivative (**2**$^{2+}$; L = dmnapyo) behaves similarly suggesting that even in the absence of acceptable analytical data the complex is substantially pure.

At room temperature, the dications (**1**$^{2+}$) and (**2**$^{2+}$) show single-line e.s.r. spectra with g values almost identical to $g_{\text{av.}}$ for the anisotropic spectra observed at −196 °C, in CH_2Cl_2–thf (1:2) glasses. These spectra confirm the paramagnetism of the dicationic complexes, but the lack of observable hyperfine coupling allows no comment to be made about the extent of delocalisation over the trimetallic $[Rh_3]^{4+}$ core. However, the large deviations of $g_{\text{av.}}$ from the free-electron value suggest considerable metal character in the singly occupied orbital.

Although no firm conclusions may be drawn concerning the electronic structure of the $[Rh^3]^{4+}$ cores of complexes (**1**$^{2+}$) and (**2**$^{2+}$), a delocalised mixed-valence state seems more likely than one in which the unpaired electron is associated with only one metal atom. In this context, the isolation of doubly oxidised species analogous to (**1**$^{3+}$) or (**2**$^{3+}$) would be of interest in that the $[Rh_3]^{5+}$ core may be either paramagnetic, with one unpaired electron on each of two of the metal atoms, or diamagnetic if spin pairing is preferred. Further synthetic studies are therefore in hand, designed to produce $[Rh_3]^{3+}$ complexes for which the second oxidation step will be more chemically accessible.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen, and i.r. carbonyl spectroscopy was used throughout to monitor the course of the reactions. The compounds $[Rh_3(\mu_3\text{-}L)_2(CO)_4(PPh_3)_2][BF_4]$, $[Rh_3(\mu_3\text{-}L)_2(CO)_2(\eta^4\text{-cod})_2][BF_4]$ (L = napyo or dmnapyo),[3] and $N(C_6H_4Br\text{-}p)_3$[5] were prepared by published methods, and $[NO][BF_4]$ was purchased from Fluorochem Ltd.

Infrared and visible absorption spectra were recorded on Perkin-Elmer 1710 IFTS and 552 instruments respectively. *X*-Band e.s.r. spectra were recorded on a Varian Associates 4502/15 spectrometer and were calibrated against a solid sample of the diphenylpicrylhydrazyl radical. Cyclic and rotating platinum-electrode voltammetry and controlled-potential electrolysis was carried out as described previously.[6] Under the conditions used, the E° values for the couples $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$ and $[Fe(\eta\text{-}C_5Me_5)_2]^+$–$[Fe(\eta\text{-}C_5Me_5)_2]$ were 0.47 and −0.07 V respectively. Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Tetracarbonyldi-μ-(5,7-dimethyl-1,8-naphthyridin-2-onato)-bis(triphenylphosphine)trirhodium Bis(tetrafluoroborate), $[Rh_3(\mu_3\text{-dmnapyo})_2(CO)_4(PPh_3)_2][BF_4]_2$.—To a stirred, dark blue solution of $[Rh_3(\mu_3\text{-dmnapyo})_2(CO)_4(PPh_3)_2][BF_4]$ (165 mg, 0.12 mmol) in CH_2Cl_2 (10 cm^3) was added a filtered solution of $[N(C_6H_4Br\text{-}p)_3][BF_4]$, generated *in situ* by treating $N(C_6H_4Br\text{-}p)_3$ (120 mg, 0.25 mmol) with solid $[NO][BF_4]$ (29 mg, 0.25 mmol) in CH_2Cl_2 (10 cm^3) for 12 min. After 10 min, the violet solution was filtered and concentrated *in vacuo* to *ca.* 5 cm^3. Slow addition of diethyl ether (30 cm^3) gave a violet solid which was purified by dissolution in CH_2Cl_2, filtration, and addition of diethyl ether to induce precipitation, yield 121 mg (69%).

The solid complex is air-sensitive but may be stored at −20 °C under nitrogen. It is soluble in polar solvents such as CH_2Cl_2, thf, and acetone to give violet solutions which rapidly decompose in air.

The complexes $[Rh_3(\mu_3\text{-napyo})_2(CO)_4(PPh_3)_2][BF_4]_2$ and $[Rh_3(\mu_3\text{-}L)_2(CO)_2(\eta^4\text{-cod})_2][BF_4]_2$ (L = napyo or dmnapyo) were prepared similarly and have similar physical properties.

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