Asymmetric, Redox-active Carbonyl Complexes with $[Rh_2]^{2+}$, $[Rh_2]^{3+}$, and $[Rh_2]^{4+}$ Cores

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The $[Rh_2]^{2+}$ complex $[Rh_2(CO)_2(bipy)(\mu\text{-RNNNR})_2]$ (**2**, bipy = 2,2'-bipyridyl, R = *p*-tolyl) is the precursor to asymmetric, redox-active $[Rh_2]^{3+}$ and $[Rh_2]^{4+}$ derivatives such as $[Rh_2(CO)L(bipy)(\mu\text{-RNNNR})_2]^z$ (**3+**, L = PPh_3, z = 1; **4**, L = I, z = 0) and $[Rh_2(CO)(S_2CNMe_2)(bipy)(\mu\text{-RNNNR})_2][PF_6]$ (**5**) respectively.

Our successful synthesis[1,2] of delocalised mixed-valence complexes with the $[Rh_2]^{3+}$ core, typified by $[Rh_2(CO)_2(PPh_3)_2(\mu\text{-RNNNR})_2][PF_6]$ (**1+**, R = *p*-tolyl), has encouraged us to search for trapped-valence species capable of photo-induced intramolecular electron-transfer. We have therefore turned our attention to the electron-transfer reactions of geometrically asymmetric triazenido-bridged complexes related to (**1**), and we now report on $[Rh_2(CO)_2(bipy)(\mu\text{-RNNNR})_2]$ (**2**; bipy = 2,2'-bipyridyl) as the precursor to a range of redox-active species with $[Rh_2]^{z+}$ (z = 2, 3, or 4) cores and with variable co-ordination geometry at each metal centre.

Air-sensitive, black crystals of $[Rh_2(CO)_2(bipy)(\mu\text{-RNNNR})_2]$ [(**2**), 82%, $\tilde{v}(CO)$ 2027 and 1962 cm^{-1}†], which deposited on heating $[Rh_2(CO)_4(\mu\text{-RNNNR})_2]$ and bipy in boiling heptane for 24 h, undergo two, reversible one-electron oxidations at a platinum bead electrode in CH_2Cl_2 (Table 1); the brown, paramagnetic monocation [(**2+**), 76%, $\tilde{v}(CO)$

2095 and 2050 cm^{-1}] is readily isolated after oxidation of (**2**) with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ in CH_2Cl_2.

Unlike (**1+**), the asymmetric cation (**2+**) undergoes further carbonyl substitution with donor ligands. With PPh_3 in CH_2Cl_2, $[Rh_2(CO)(PPh_3)(bipy)(\mu\text{-RNNNR})_2][PF_6]$ [(**3+**), 76%, $\tilde{v}(CO)$ 2018 cm^{-1}] is readily isolable as brown crystals which undergo reversible one-electron reduction and two reversible one-electron oxidations. The potentials (Table 1) for these processes are shifted to more negative values than those of (**2+**) so that the $[Rh_2]^{4+}$-containing dication [(**3^2+**), $\tilde{v}(CO)$ 2054 cm^{-1}] can be generated from (**3+**) by Ag^+ oxidation in CH_2Cl_2.
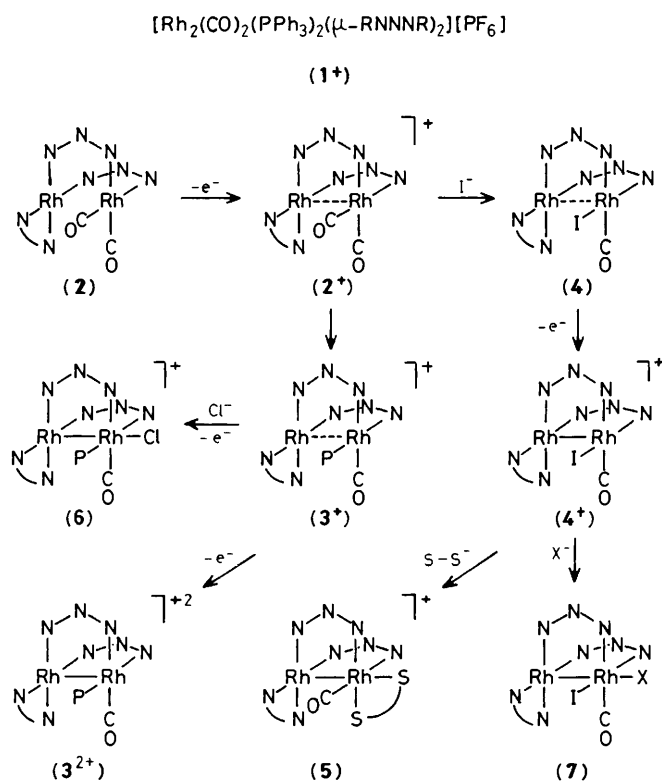
The cation $[Rh_2(CO)_2(bipy)(\mu\text{-RNNNR})_2]^+$ reacts with X$^-$ (X = Cl, Br, or I) in CH_2Cl_2 to give the neutral compounds $[Rh_2X(CO)(bipy)(\mu\text{-RNNNR})_2]$ [(**4**), *e.g.* X = I, brown, 70%, $\tilde{v}(CO)$ 1996 cm^{-1}]. The cyclic voltammogram of (**4**, X = I) is very similar to that of (**3+**) except that the three waves of the neutral iodide complex (Table 1) are observed at more negative potentials than those of the cationic phosphine derivative. Thus, oxidation of (**4**) to the air-stable, diamagnetic salt $[Rh_2X(CO)(bipy)(\mu\text{-RNNNR})_2][PF_6]$ [(**4+**), *e.g.* X

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† All new compounds have satisfactory elemental analyses (C, H, and N); i.r. spectra were taken in CH_2Cl_2.

Table 1. Electrochemical data for reversible one-electron transfer reactions.

Complex[a]	$[Rh_2]^{2+}/[Rh_2]^{3+}$ [c]	Couple (E°/V^b) $[Rh_2]^{3+}/[Rh_2]^{4+}$	$[Rh_2]^{4+}/[Rh_2]^{5+}$
$[Rh_2(CO)_2(bipy)(\mu\text{-}L)_2]$ (2)	−0.25	0.84	—
$[Rh_2(CO)_2(bipy)(\mu\text{-}L)_2][PF_6]$ (2+)	−0.25	0.84	—
$[Rh_2(CO)(PPh_3)(bipy)(\mu\text{-}L)_2][PF_6]$ (3+)	−0.53	0.78	1.47
$[Rh_2I(CO)(bipy)(\mu\text{-}L)_2]$ (4)	−1.07	0.21	1.25
$[Rh_2I(CO)(bipy)(\mu\text{-}L)_2][PF_6]$ (4+)	−1.10	0.21	1.24
$[Rh_2(CO)(S_2CNMe_2)(bipy)(\mu\text{-}L)_2][PF_6]$ (5)	—	−0.84	1.13
$[Rh_2Cl(CO)(PPh_3)(bipy)(\mu\text{-}L)_2][PF_6]$ (6)	—	−0.56	1.28

[a] L = RNNNR, R = p-tolyl. [b] Potentials are vs. an aqueous saturated calomel electrode (s.c.e.), at a platinum bead electrode, in CH_2Cl_2 containing 0.1 mol dm^{-3} [NBu$^n_4$][PF$_6$] as base electrolyte. Under these conditions, E° for the one-electron oxidation of ferrocene was 0.47 V. [c] $[Rh_2]^{z+}$ refers to the overall charge on the dimetal core when all of the ligands are removed with their normal charge; L is uninegative.

$[Rh_2(CO)_2(PPh_3)_2(\mu\text{-}RNNNR)_2][PF_6]$

(1+)

Scheme 1. NNN = p-tolylNNNtolyl-p, N—N = 2,2′-bipyridyl, P = PPh$_3$, S—S = S$_2$CNMe$_2$.

Figure 1. (a) The e.s.r. spectrum of $[Rh_2(CO)(PPh_3)(bipy)(\mu\text{-}RNNNR)_2][PF_6]$ (3+) in CH_2Cl_2–1,2-dichloroethane at −110 °C at 1.1 × 10⁻² mol dm^{-3}; (b) as (a) but at 1.5 × 10⁻⁴ mol dm^{-3} concentration; (c) the e.s.r. spectrum of $K_2[NO(SO_3)_2]$ (Fremy's salt) as standard (g 2.0057).

= I, 87%, $\tilde{v}(CO)$ 2073 cm⁻¹] is readily accomplished using [Fe(η-C$_5$H$_5$)$_2$][PF$_6$].

The e.s.r. spectra of (2+), (3+), and (4) are of interest for two reasons. First, although their frozen solution spectra [−120 °C, tetrahydrofuran (thf)–CH$_2$Cl$_2$ (2:1) or CH$_2$Cl$_2$–1,2-dichloroethane (1:1)] show anisotropic g-values similar to those of (1+)² and other geometrically symmetric [Rh$_2$]³⁺ complexes³ the $g_{\parallel}$ components at ca. 2.00 show, in each case, hyperfine coupling to two distinctly different rhodium atoms [e.g. (3+) A(¹⁰³Rh) = 28 and 11.5 G; 1 G = 10⁻⁴ T].

Second, the low temperature spectra are concentration dependent. Thus, for example, at concentrations >10⁻² mol dm⁻³ the spectrum of (3+) (Figure 1a, $g_\perp$ 2.240, $g_{\parallel}$ 2.007,
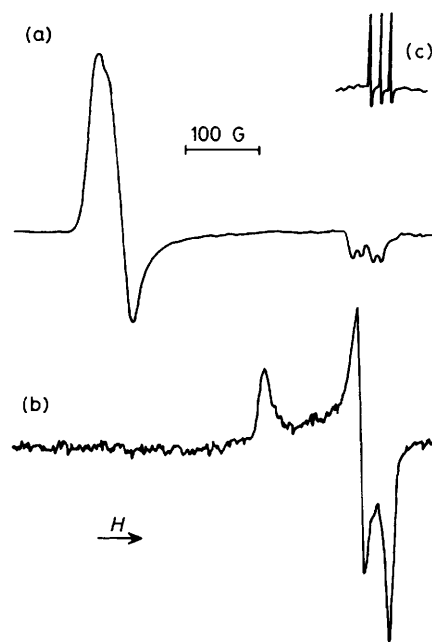
g_{av} 2.162) resembles those of the [Rh$_2$]³⁺ complexes³ referred to above. As the concentration is lowered, a second signal grows at the expense of the first so that below 10⁻⁴ mol dm⁻³ the spectrum is as shown in Figure 1b (g_1 2.084, g_2 2.013, g_3 1.989, g_{av} 2.025). The origin of this concentration dependence is, as yet, unknown; further studies are in progress.

The [Rh$_2$]³⁺ complexes described above effectively contain two square-planar metal centres (ignoring metal–metal interactions). They can, however, serve as precursors to more highly asymmetric species, each containing one square-planar and one square-pyramidal rhodium atom (Scheme 1). Thus, for example, (4+) and NaS$_2$CNMe$_2$·2H$_2$O in CH$_2$Cl$_2$ give moderate yields of $[Rh_2(CO)(S_2CNMe_2)(bipy)(\mu\text{-}RNNNR)_2][PF_6]$ [(5), grey-green, 45%, $\tilde{v}(CO)$ 2060 cm⁻¹], and $[Rh_2Cl(CO)(PPh_3)(bipy)(\mu\text{-}RNNNR)_2][PF_6]$ [(6), green, 45%, $\tilde{v}(CO)$ 2043 cm⁻¹] results from the reaction of (3+) with chloride ion in the presence of [Fe(η-C$_5$H$_5$)$_2$][PF$_6$].

The redox properties of the two, diamagnetic $[Rh_2]^{4+}$ complexes (5) and (6) are similar (Table 1), but very different from those of (3+) and (4+). Thus, the cyclic voltammograms of the former pair show reversible one-electron oxidation and reduction waves (corresponding to the formation of $[Rh_2]^{3+}$ and $[Rh_2]^{5+}$ species) separated by *ca.* 2.0 V [*cf.* 0.7—1.0 V for the analogous waves of (3+) and (4+)]. The possibility of localised electron addition to, or removal from, species such as (5) and (6) is under investigation.

Dihalide complexes related to (5) and (6), namely $[Rh_2XI(CO)(bipy)(\mu\text{-}RNNNR)_2]$ [(7), *e.g.* X = I, brown, 79%, $\tilde{\nu}(CO)$ 2027 cm^{-1}], can be prepared from (4+) and X$^-$ (X = Cl, Br, or I), or directly from (2) and iodine. The latter reaction, formally an oxidative elimination, differs from those of other binuclear rhodium (and iridium) complexes with halogens which almost invaribly result[4] in transannular oxidative addition (the resulting X–M–M–X backbone is created without ligand loss).

The sequence (2) → (2+) → (4) → (4+) → (7), which links five well-defined, isolable complexes, demonstrates that oxidative elimination at one metal centre mediated by a second can occur by an *ECEC* (*E* = electrochemical, *C* = chemical) mechanism.

References

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