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Asymmetric, Redox-active Carbonyl Complexes with [Rh₂]²⁺, [Rh₂]³⁺, and [Rh₂]⁴⁺ Cores

Neil G. Connelly and Gabriel Garcia

Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, U.K.

The $[Rh_2]^{2+}$ complex $[Rh_2(CO)_2(bipy)(\mu-RNNR)_2]$ (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 $[Rh_2(CO)L(bipy)(\mu-RNNR)_2]^z$ (3+, $L = PPh_3$, z = 1; 4, L = I, z = 0) and $[Rh_2(CO)(S_2CNMe_2)(bipy)(\mu-RNNR)_2][PF_6]$ (5) respectively.

Our successful synthesis^{1,2} of delocalised mixed-valence complexes with the [Rh₂]³⁺ core, typified by [Rh₂(CO)₂(PPh₃)₂(μ -RNNR)₂][PF₆] (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 [Rh₂(CO)₂(bipy)(μ -RNNNR)₂] (2; bipy = 2,2'-bipyridyl) as the precursor to a range of redox-active species with [Rh₂]^{z+} (z = 2, 3, or 4) cores and with variable co-ordination geometry at each metal centre.

Air-sensitive, black crystals of $[Rh_2(CO)_2(bipy)(\mu-RNNR)_2]$ [(2), 82%, $\tilde{v}(CO)$ 2 027 and 1 962 cm^{-1†}], which deposited on heating $[Rh_2(CO)_4(\mu-RNNR)_2]$ and bipy in boiling heptane for 24 h, undergo two, reversible one-electron oxidations at a platinum bead electrode in CH₂Cl₂ (Table 1); the brown, paramagnetic monocation [(2+), 76%, $\tilde{v}(CO)$

2 095 and 2 050 cm⁻¹] is readily isolated after oxidation of (2) with $[Fe(\eta-C_5H_5)_2][PF_6]$ in CH₂Cl₂.

Unlike (1⁺), the asymmetric cation (2⁺) undergoes further carbonyl substitution with donor ligands. With PPh₃ in CH₂Cl₂, [Rh₂(CO)(PPh₃)(bipy)(μ -RNNNR)₂][PF₆] [(3⁺), 76%, \bar{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 [Rh₂]⁴⁺-containing dication [(3²⁺), \bar{v} (CO) 2054 cm⁻¹] can be generated from (3⁺) by Ag⁺ oxidation in CH₂Cl₂.

The cation $[Rh_2(CO)_2(bipy)(\mu-RNNNR)_2]^+$ reacts with X-(X = Cl, Br, or I) in CH₂Cl₂ to give the neutral compounds $[Rh_2X(CO)(bipy)(\mu-RNNNR)_2]$ [(4), e.g. X = I, brown, 70%, $\hat{v}(CO)$ 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 $[Rh_2X(CO)(bipy)(\mu-RNNNR)_2][PF_6]$ [(4⁺), e.g. X

 $[\]dagger$ All new compounds have satisfactory elemental analyses (C, H, and N); i.r. spectra were taken in CH₂Cl₂.

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

Complex ^a	[Rh ₂] ²⁺ /[Rh ₂] ^{3+ c}	Couple (E°/V°) [Rh ₂] ³⁺ /[Rh ₂] ⁴⁺	[Rh ₂] ⁴⁺ /[Rh ₂] ⁵⁺
$[Rh_2(CO)_2(bipy)(\mu-L)_2](2)$	-0.25	0.84	_
$[Rh_2(CO)_2(bipy)(\mu-L)_2][PF_6](2^+)$	-0.25	0.84	_
$[Rh_2(CO)(PPh_3)(bipy)(\mu-L)_2][PF_6](3^+)$	-0.53	0.78	1.47
$[Rh_2I(CO)(bipy)(\mu-L)_2](4)$	-1.07	0.21	1.25
$[Rh_2I(CO)(bipy)(\mu-L)_2][PF_6](4^+)$	-1.10	0.21	1.24
$[Rh_2(CO)(S_2CNMe_2)(bipy)(\mu-L)_2][PF_6](5)$	—	-0.84	1.13
$[Rh_2Cl(CO)(PPh_3)(bipy)(\mu-L)_2][PF_6](6)$		-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 [NBuⁿ₄][PF₆] as base electrolyte. Under these conditions, E° for the one-electron oxidation of ferrocene was 0.47 V. ^c [Rh₂]^{z+} refers to the overall charge on the dimetal core when all of the ligands are removed with their normal charge; L is uninegative.



Scheme 1. NNN = p-tolylNNNtolyl-p, N—N = 2,2'-bipyridyl, P = PPh₃, S—S = S₂CNMe₂.

= I, 87%, $\tilde{v}(CO)$ 2073 cm⁻¹] is readily accomplished using [Fe(η -C₅H₅)₂][PF₆].

The e.s.r. spectra of (2^+) , (3^+) , and (4) are of interest for two reasons. First, although their frozen solution spectra $[-120 \,^{\circ}\text{C}$, tetrahydrofuran (thf)–CH₂Cl₂ (2:1) or CH₂Cl₂– 1,2-dichloroethane (1:1)] show anisotropic g-values similar to those of $(1^+)^2$ and other geometrically symmetric $[\text{Rh}_2]^{3+}$ complexes³ the g_{\parallel} components at *ca*. 2.00 show, in each case, hyperfine coupling to two distinctly different rhodium atoms $[e.g. (3^+) A(^{103}\text{Rh}) = 28$ 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,



Figure 1. (a) The e.s.r. spectrum of $[Rh_2(CO)(PPh_3)(bipy)(\mu-RNNR)_2][PF_6](3^+)$ in $CH_2Cl_2-1,2$ -dichloroethane at $-110^{\circ}C$ 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).

 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 NaS₂CNMe₂·2H₂O in CH₂Cl₂ give moderate yields of $[Rh_2(CO)(S_2CNMe_2)(\mu$ -RNNNR)₂][PF₆] [(5), grey-green, 45%, $\tilde{v}(CO)$ 2 060 cm⁻¹], and $[Rh_2Cl(CO)(PPh_3)(bipy)(\mu$ -RNNNR)₂][PF₆] [(6), green, 45%, $\tilde{v}(CO)$ 2 043 cm⁻¹] results from the reaction of (3⁺) with chloride ion in the presence of $[Fe(\eta$ -C₅H₅)₂][PF₆]. 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 $[Rh_2XI(CO)(bipy)(\mu$ -RNNNR)₂] [(7), e.g. X = I, brown, 79%, $\tilde{v}(CO)$ 2 027 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 result⁴ in transannular oxidative addition (the resulting X-M-M-X backbone is created without ligand loss).

The sequence $(2) \rightarrow (2^+) \rightarrow (4) \rightarrow (4^+) \rightarrow (7)$, 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. We thank the S.E.R.C. for a post-doctoral research assistantship (to G. G.) and Johnson-Matthey p.l.c. for a generous loan of rhodium trichloride.

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