

Reduction–oxidation properties of organo-transition metal complexes

XXXIV *. Superoxide and semi-quinone derivatives of the triazenido-bridged $[\text{Rh}_2]^{4+}$ unit

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Abstract

The $[\text{Rh}_2]^{3+}$ -containing complex $[\text{Rh}_2(\text{CO})_2(\text{bipy})(\mu\text{-RNNNR})_2]^+$ (**1**; R = *p*-tolyl) undergoes carbonyl substitution with molecular oxygen to give $[\text{Rh}_2(\text{CO})(\text{O}_2)(\text{bipy})(\mu\text{-RNNNR})_2]^+$ (**4**), the ESR spectrum of which shows a superoxide ligand bound to an $[\text{Rh}_2]^{4+}$ core. By contrast, the complex $[\text{Rh}_2(\text{CO})(\text{PPh}_3)(\text{bipy})(\mu\text{-RNNNR})_2]^+$ (**2**) binds O_2 , again as a superoxide ligand, in the adduct $[\text{Rh}_2(\text{CO})(\text{PPh}_3)(\text{O}_2)(\text{bipy})(\mu\text{-RNNNR})_2]^+$ (**3**). In a similar reaction involving co-ordination of a redox-active ligand and intramolecular metal-ligand electron-transfer, **1** and the *o*-quinone $o\text{-O}_2\text{C}_6\text{Cl}_4$ (*o*-chloranil, tetrachloro-1,2-benzoquinone) give $[\text{Rh}_2(\text{CO})(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{bipy})(\mu\text{-RNNNR})_2]^+$ (**5**) in which the O₂-chelate, in the *o*-benzosemiquinone form, is bonded to an $[\text{Rh}_2]^{4+}$ centre. The cyclic voltammogram of **5** shows two oxidation and two reduction waves at a platinum electrode in CH_2Cl_2 , and electrochemical or chemical (with ferrocene) reduction yields the diamagnetic catecholate- $[\text{Rh}_2]^{4+}$ complex **6**.

Introduction

We have recently described [2] how the ESR spectra of the complexes $[\text{Rh}_2(\text{CO})\text{L}(\text{bipy})(\mu\text{-RNNNR})_2]^+$ (**1**, L = CO; **2**, L = PPh₃; R = *p*-tolyl) vary in the presence of oxygen, attributing the spectral changes observed to the formation of complexes containing a coordinated superoxide ligand. Here we describe attempts to characterise more fully these complexes by their direct isolation and by the characterisation of related *o*-benzosemiquinone complexes prepared from **1** and *o*-chloranil (tetrachloro-1,2-benzoquinone).

* For Part XXXIII see ref. 1

Results and discussion

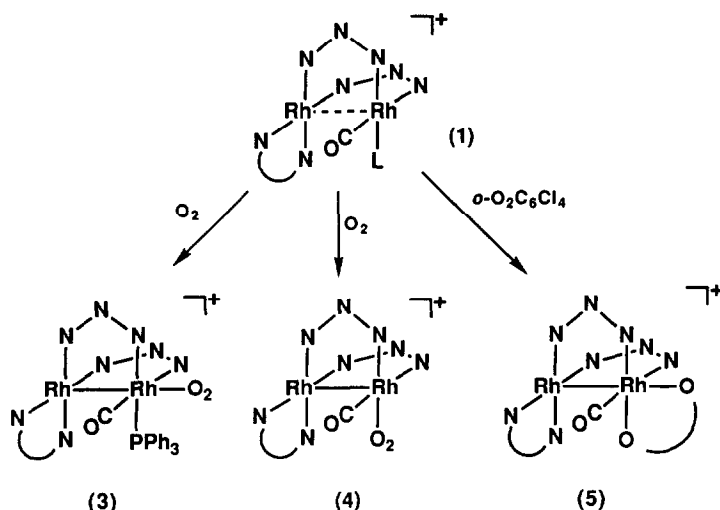
The reactions of $[\text{Rh}_2]^{3+}$ complexes with molecular oxygen

The reactions of $[\text{Rh}_2(\text{CO})\text{L}(\text{bipy})(\mu\text{-RNNNR})_2]^+$ (**1**, $\text{L} = \text{CO}$; **2**, $\text{L} = \text{PPh}_3$) and $[\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2(\mu\text{-RNNNR})_2]^+$ with oxygen were studied first by ESR spectroscopy, in the following way. The spectrum of each complex was recorded at 77 K, in the non-coordinating solvent CH_2Cl_2 . The sample was then warmed to room temperature, oxygen gas was passed through the solution, the IR spectrum was recorded in the carbonyl region, and the ESR spectrum were then re-recorded at 77 K. The solvent was then removed at room temperature and the residue dried *in vacuo*. This residue was then redissolved in CH_2Cl_2 and the IR and ESR spectra were re-recorded.

At 77 K the ESR spectrum of **1** shows two g -values, at 2.229 ($g_\perp$) and 2.009 ($g_\parallel$) ($g_{\text{ave}} = 2.156$). [The spectrum is the same as that previously obtained [2] in a $\text{THF}:\text{CH}_2\text{Cl}_2$ (2:1) glass but less well resolved]. After bubbling O_2 through the CH_2Cl_2 solution of **1** for a few minutes, or after exposing the solution to air for a more prolonged period, the IR spectrum showed a single carbonyl absorption at 2075 cm^{-1} . The ESR spectrum at 77 K then showed a rhombic signal with $g_1 = 2.078$, $g_2 = 2.011$, and $g_3 = 1.988$ ($g_{\text{ave}} = 2.026$). After solvent removal, overnight pumping of the residue *in vacuo*, redissolving the sample in CH_2Cl_2 , and cooling to 77 K no further change in the ESR spectrum was observed.

The behaviour of **2** is somewhat different from that of **1**. A concentrated ($1.0 \times 10^{-2}\text{ mol dm}^{-3}$) solution of **2** in CH_2Cl_2 shows an anisotropic signal at 77 K with $g_\perp = 2.244$ and $g_\parallel = 2.006$ ($g_{\text{ave}} = 2.164$). Passage of O_2 through the solution at 20°C resulted in no change in the IR carbonyl spectrum, and at 77 K the ESR spectrum was the same as that of the oxygen-free sample. However, dilution of the sample with CH_2Cl_2 (to ca. $1.0 \times 10^{-4}\text{ mol dm}^{-3}$) resulted in the observation of only a rhombic signal ($g_1 = 2.079$, $g_2 = 2.009$, and $g_3 = 1.988$; $g_{\text{ave}} = 2.028$) very similar to that for the oxygenated sample of **1**. After solvent removal and pumping *in vacuo* for several hours the ESR spectrum showed peaks due both to the oxygenated species and **2**. In this case, therefore, oxygen co-ordination is at least partially reversible and no carbonyl substitution is observed. For comparison, the complex $[\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2(\mu\text{-RNNNR})_2]^+$ was studied in the same way as the bipy complexes. In this case, however, no change in the ESR spectrum was observed on prolonged exposure of the sample to oxygen.

The ESR spectra of $[\text{Rh}_2(\text{CO})\text{L}(\text{bipy})(\mu\text{-RNNNR})_2]^+$ ($\text{L} = \text{CO}$ or PPh_3) and $[\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2(\mu\text{-RNNNR})_2]^+$ show [2,3] that the unpaired electron is delocalised over the two rhodium atoms, occupying the out-of-phase combination of the two rhodium $4d_{z^2}$ σ -orbitals. The reactions of **1** and **2** with oxygen most likely give superoxide complexes in that the new spectra are very similar to those of other species in which O_2^- is bound to mono- [4] and binuclear [5] rhodium centres. Of particular note is the complex $[\text{Rh}_2(\text{ap})_4(\text{O}_2)]^-$ which has an ESR spectrum almost identical to those of the oxygenated samples described above and which is formulated as an axial superoxide adduct of an $[\text{Rh}_2]^{4+}$ centre. (Note, also, that the low temperature ESR spectra [6] of the "second isomers" of paramagnetic $[\text{Rh}_2]^{3+}$ species such as $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CN}^t\text{Bu})_2(\mu\text{-pyrazolate})]^{2+}$ are very similar to those of the superoxide rhodium complexes). Thus, co-ordination of O_2 to the $[\text{Rh}_2]^{3+}$



Scheme 1. NNN = *p*-tolyl-NNN-tolyl-*p*, $\overline{\text{NN}}$ = 2,2'-bipyridyl, L = CO or PPh₃, $\widehat{\text{OO}}$ = tetrachloro-*o*-benzoquinone; Rh — — Rh and Rh — Rh represent [Rh₂]³⁺ and [Rh₂]⁴⁺ cores, respectively.

centres in **1** and **2** is accompanied (or followed) by intramolecular electron transfer to give [Rh₂]⁴⁺ centres bound to O₂[−].

The reaction between **2** and O₂ appears to be reversible and the product is formulated as the axial adduct [Rh₂(CO)(O₂)(PPh₃)(bipy)(μ-RNNNR)₂]⁺ (**3**) (Scheme 1), with the superoxide ligand bound to the rhodium atom carrying the CO ligand. By contrast, the irreversibility of the reaction of O₂ with **1**, and the changes in the IR carbonyl spectrum, suggest that carbonyl substitution after adduct formation gives [Rh₂(CO)(O₂)(bipy)(μ-RNNNR)₂]⁺ (**4**). An attempt was therefore made to isolate and characterise **4** in order to verify the proposed formula.

The passage of O₂ through a CH₂Cl₂ solution of **1** gave a brown solution showing only one carbonyl band, at 2075 cm^{−1} (as in the spectroscopic experiments described above). On addition of *n*-hexane and partial removal of the solvent *in vacuo* a brown solid was isolated having the correct elemental analysis for [Rh₂(CO)(O₂)(bipy)(μ-RNNNR)₂][PF₆]. The solid shows the same carbonyl band as before but further characterisation proved impossible. The Nujol mull IR spectrum failed to show the weak O—O stretch expected for the co-ordinated superoxide ion [7], the cyclic voltammogram in CH₂Cl₂ showed only ill-defined waves, and suitable crystals for an X-ray structural study could not be obtained. Thus, a search was made for other redox-active ligands whose co-ordination to **1** or **2** might also lead to intramolecular electron transfer and to the isolation of a more fully characterised [Rh₂]⁴⁺ derivative. One such ligand is tetrachloro-1,2-benzoquinone (*o*-chloranil) which indeed reacts with **1** to give a semiquinone complex of the [Rh₂]⁴⁺ core.

*The synthesis and redox chemistry of [Rh₂(CO)(*o*-O₂C₆Cl₄)(bipy)(μ-RNNNR)₂][PF₆]*

The addition of *o*-O₂C₆Cl₄ (*o*-chloranil) to **1** in CH₂Cl₂ gave a green solution from which [Rh₂(CO)(*o*-O₂C₆Cl₄)(bipy)(μ-RNNNR)₂][PF₆] **5** (Scheme 1) was readily isolated in high yield; the salt was characterised by elemental analysis and

shows a single IR carbonyl band (2087 cm^{-1}), similar in energy to that of **4**. The room temperature ESR spectrum of **5** shows a single line centred at $g = 2.004$, more typical of a ligand-based radical than an $[\text{Rh}_2]^{3+}$ complex such as **1** or **2**. The cyclic voltammogram of **5** also supports a formulation in which a semiquinone ligand is bound to an $[\text{Rh}_2]^{4+}$ centre.

In the potential range -1.2 to 1.65 V , four reversible one-electron waves are observed; other irreversible waves are observed at more negative potentials. The two waves at -0.96 and 0.53 V were identified as reduction waves by rotating platinum electrode voltammetry (RPEV) and those at 1.31 and 1.50 were similarly identified as oxidation waves. The site of electron transfer associated with these waves can be assigned by comparing the relevant potentials with those of related species. Thus, the waves at -0.96 and 1.31 V are very similar to those of $[\text{Rh}_2(\text{CO})(\text{S}_2\text{CNMe}_2)(\text{bipy})(\mu\text{-RNNNR})_2]^+$ (-0.84 and 1.13 V) and may be assigned to the $[\text{Rh}_2]^{3+}$ – $[\text{Rh}_2]^{4+}$ and $[\text{Rh}_2]^{4+}$ – $[\text{Rh}_2]^{5+}$ couples, respectively. The waves at 0.53 and 1.50 V occur at potentials typical of the two-step oxidation of co-ordinated *o*-tetrachlorocatecholate ligands {e.g. in $[\text{Ru}(\text{CO})_2(\text{PPh}_3)_2(o\text{-O}_2\text{C}_6\text{Cl}_4)]$ (0.65 and 1.76 V) [8]} and may be assigned to co-ordinated catecholate–semiquinone and semiquinone–quinone couples.

The relatively positive potential of the wave at 0.53 V , and its assignment to a ligand-based process, suggested that the one-electron reduction of $[\text{Rh}_2(\text{CO})(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]$ would require only a mild reductant and that the product would be the neutral catecholate complex $[\text{Rh}_2(\text{CO})(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{bipy})(\mu\text{-RNNNR})_2]$ (**6**). The addition of one equivalent of $[\text{Co}(\eta\text{-C}_5\text{H}_5)_2]$ to a suspension of the salt **5** in toluene gave a green-brown solid showing one carbonyl band at 2060 cm^{-1} . However, an analytically pure product could not be isolated, perhaps because cobaltocene ($E^\circ = -0.9\text{ V}$) is capable of further reduction of the expected neutral compound. A similar reaction was therefore carried out with ferrocene (0.47 V). In this case, pure $[\text{Rh}_2(\text{CO})(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{bipy})(\mu\text{-RNNNR})_2]$ (**6**) was readily isolated in moderate yield; the relatively small shift to lower energy of $\nu(\text{CO})$ (27 cm^{-1}) on reduction of **5** is consistent with the proposed ligand-centred reduction to the catecholate complex **6**. Similar ligand-centred electron-transfer has been observed [9] for $[\text{Rh}_2(\mu\text{-dppm})_2(\text{CO})(o\text{-O}_2\text{C}_6\text{Cl}_4)]$ [$\nu(\text{CO})$ 1960 cm^{-1} ; oxidation peak potential, 0.52 V] where Ag^+ oxidation gave a monocation [$\nu(\text{CO})$ 1997 cm^{-1}] whose ESR spectrum was consistent with the presence of a semiquinone ligand co-ordinated to $[\text{Rh}_2]^{4+}$.

Cyclic voltammetry confirmed that a simple reversible one electron-transfer process relates **5** to **6** in that the latter shows four waves at potentials identical to those of the cation (except that the wave at 0.53 V is an oxidation wave, confirmed by RPEV). The one-electron reduction of **5** was also carried out via controlled potential electrolysis at a platinum basket electrode (0.0 V , CH_2Cl_2 , 25 min , $n = 0.9$); the brown product solution showed identical voltammetric behaviour to the isolated complex **6**. Further electrolysis of this solution, at -1.2 V (negative of the second reduction wave of **5**), resulted in a darker brown solution which, however, showed no identifiable waves in the cyclic voltammogram. Thus, the expected $[\text{Rh}_2]^{3+}$ -containing anion $[\text{Rh}_2(\text{CO})(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{bipy})(\mu\text{-RNNNR})_2]^-$ is not stable in CH_2Cl_2 on the time-scale of the electrolytic experiment.

The reactions of **1** with other *o*-quinones were briefly investigated. The addition of *dl*-camphorquinone, 1,2-naphthoquinone, or phenanthrenequinone to **1** in CH_2Cl_2

slowly gave solutions showing single carbonyl bands at 2079, 2082, and 2080 cm^{-1} , respectively, and each solution also showed a single-line ESR spectrum ($g = 2.004$). No attempt was made to isolate the complexes but the spectroscopic results described suggest the formation of semiquinone derivatives of the $[\text{Rh}_2]^{4+}$ core. Intramolecular metal–ligand electron transfer in rhodium catecholate complexes is not without precedent. The ESR spectra of mononuclear complexes such as $[\text{Rh}\{o\text{-O}_2\text{C}_6\text{H}_4\text{Bu}_2(\text{OMe})\}(\eta^4\text{-cyclooctadiene})(\text{AsEt}_3)]$ suggest there is a solvent and temperature dependent equilibrium between Rh^{II} (catecholate) and Rh^{I} (semiquinone) isomers [10].

Conclusions

The synthesis and full characterisation of $[\text{Rh}_2(\text{CO})(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{bipy})(\mu\text{-RNNNR})_2]^+$ and $[\text{Rh}_2(\text{CO})(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{bipy})(\mu\text{-RNNNR})_2]$ has shown that the reaction of $[\text{Rh}_2(\text{CO})_2(\text{bipy})(\mu\text{-RNNNR})_2]^+$ with *o*-quinones results in intramolecular metal–ligand electron transfer after co-ordination, converting the $[\text{Rh}_2]^{3+}$ core to the $[\text{Rh}_2]^{4+}$ core. This chemistry provides further evidence for the formation of superoxide complexes from $[\text{Rh}_2(\text{CO})\text{L}(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]$ ($\text{L} = \text{CO}$ or PPh_3) via the axial co-ordination of molecular oxygen.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen, using dried, distilled, de-oxygenated solvents. Unless stated otherwise (i) the complexes were purified by dissolving in CH_2Cl_2 , filtering, adding *n*-hexane, and reducing the solvent volume *in vacuo* to induce precipitation, and (ii) the complexes are air-stable solids which dissolve in polar solvents such as CH_2Cl_2 or THF to give moderately air-sensitive solutions. Where necessary the progress of a reaction was monitored by IR spectroscopy.

The compounds $[\text{Rh}_2(\text{CO})\text{L}(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]$ ($\text{L} = \text{CO}$ or PPh_3) were prepared by published methods [2], and tetrachloro-*o*-benzoquinone (chloranil) was purchased from Aldrich. Electrochemical studies were carried out as previously described [11]. Under the conditions used, E° for the couples $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]^+ - [\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]$ and $[\text{Fe}(\eta\text{-C}_5\text{Me}_5)_2]^+ - [\text{Fe}(\eta\text{-C}_5\text{Me}_5)_2]$, used as internal standards, are 0.47 and -0.09 V, respectively. IR spectra were recorded on a Nicolet 5ZDX FT spectrometer, and X-band ESR spectra were recorded on a Varian Associates 4502/15 spectrometer and calibrated against a solid sample of the diphenylpicrylhydrazyl (dpph) radical. Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Carbonyl(superoxide)(bipyridyl)-di-μ-(di-p-tolyltriazenido- N^1N^3)dirhodium hexafluorophosphate, $[\text{Rh}_2(\text{CO})(\text{O}_2)(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]$

Oxygen gas was slowly passed through a CH_2Cl_2 solution (10 cm^3) of $[\text{Rh}_2(\text{CO})_2(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]$ (0.21 g, 0.21 mmol) for 10 min. The solution was then filtered, evaporated to low volume *in vacuo*, and treated with *n*-hexane (20 cm^3) to precipitate the product. Purification gave a brown solid, yield 0.145 g (69%).

(Anal. Found: C, 46.1; H, 3.8; N, 10.7. $C_{39}H_{36}F_6N_8O_3PRh_2$ calc.: C, 46.1; H, 3.6; N, 11.0%).

Carbonyl(tetrachloro-o-benzosemiquinone)(bipyridyl)-di-μ-(di-p-tolyltriazenido-N¹N³)-dirhodium hexafluorophosphate, $[Rh_2(CO)(o-O_2C_6Cl_4)(bipy)(μ-RNNNR)_2][PF_6]$

To a stirred solution of $[Rh_2(CO)_2(bipy)(μ-RNNNR)_2][PF_6]$ (0.101 g, 0.10 mmol) in CH_2Cl_2 (25 cm³) was added *o*-chloranil (0.030 g, 0.12 mmol). After 3 h the dark green solution was filtered, evaporated to low volume *in vacuo*, and treated with n-hexane (30 cm³) to give a green precipitate. Purification gave a green solid, yield 98 mg (82%). (Anal. Found: C, 43.9; H, 3.1; N, 8.9. $C_{45}H_{36}Cl_4F_6N_8O_3PRh_2$ calc.: C, 44.0; H, 3.0; N, 9.1%).

Carbonyl(tetrachloro-o-catecholato)(bipyridyl)-di-μ-(di-p-tolyltriazenido-N¹N³)-dirhodium, $[Rh_2(CO)(o-O_2C_6Cl_4)(bipy)(μ-RNNNR)_2]$

To a suspension of $[Rh_2(CO)(o-O_2C_6Cl_4)(bipy)(μ-RNNNR)_2][PF_6]$ (0.52 g, 0.42 mmol) in toluene (60 cm³) was added $[Fe(η-C_5H_5)_2]$ (0.40 g, 2.20 mmol). After 1 h the brown solution was filtered and concentrated to low volume *in vacuo* to ca 10 cm³. Slow addition of n-hexane (50 cm³) gave a green-brown solid which was washed with n-hexane, yield 0.14 g (31%). (Anal. Found: C, 49.8; H, 3.6; N, 9.7. $C_{45}H_{36}Cl_4N_8O_3Rh_2$ calc.: C, 49.8; H, 3.4; N, 10.3%).

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