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Ligand-localised oxidation of a 4,4′-bipyridyl-bridged diruthenium(II) carbonyl catecholate complex

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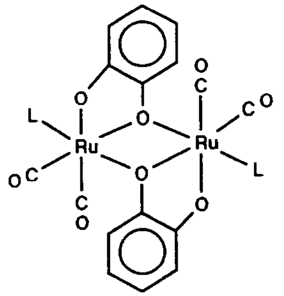
Abstract

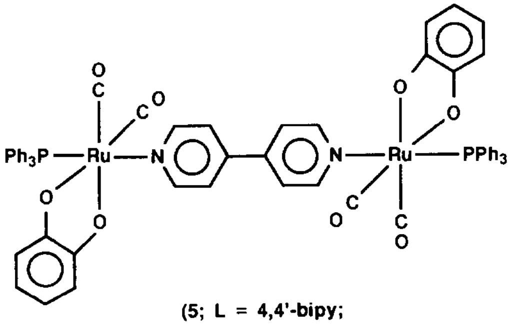
The reaction of $[\{Ru(CO)_2(PPh_3)(\mu\text{-}o\text{-}O_2C_6Cl_4)\}_2]$ (6) with 4,4′-bipyridyl (4,4′-bipy) gives $[\{Ru(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4\}_2(\mu\text{-}L)]$ (5, L = 4,4′-bipy) cyclic voltammetry and coulometry on which show a single two-electron oxidation process at a platinum electrode in CH_2Cl_2. The reaction of 5 (L = 4,4′-bipy) with $[NO][PF_6]$ yields the bis(*o*-benzosemiquinone) complex (5^{2+}, L = 4,4′-bipy) via localised, catecholate ligand-based oxidation at the two independent sites. The pyrazine-bridged analogue (5^{2+}, L = pyz) is prepared directly from 6, pyz, and $[NO][PF_6]$. The intermediate monocations 5^+, the expected conproportionation products of the reactions between 5 and 5^{2+}, have not been detected by spectroscopic (ESR, UV-VIS, IR) or cyclic voltammetric methods and have, by implication, localised electronic structures.

Introduction

Aromatic *N*-heterocycles have featured widely [1] in studies of the effects of bridging ligands on the extent of delocalisation in mixed-valence diruthenium complexes (with formal oxidation states $Ru^{II}Ru^{III}$). Qualitatively, pyrazine-bridged complexes are generally more delocalised than 4,4′-bipyridyl (4,4′-bipy) analogues as reflected in ΔE, the separation between the potentials of the $Ru^{II}Ru^{II}/Ru^{II}Ru^{III}$ and $Ru^{II}Ru^{III}/Ru^{III}Ru^{III}$ redox couples. Compare for example, the oxidation of $[(H_3N)_5Ru(\mu\text{-}L)Ru(NH_3)_5]^{4+}$ (1, L = pyz, $\Delta E = 390$ mV [2]; 2, L = 4,4′-bipy, ΔE = ca. 35–75 mV [3]) and $[Cl(2,2'\text{-bipy})_2Ru(\mu\text{-}L)Ru(2,2'\text{-bipy})_2Cl]^{2+}$ (3, L = pyz, $\Delta E = 120$ mV [4]; 4, L = 4,4′-bipy, ΔE = ca. 0.0 mV [5]). In all of these cases the mixed-valence $Ru^{II}Ru^{III}$ species have been characterised (at least spectroscopically in solution) most usually by intervalence transfer absorption bands in the near IR region. We now report on the pyrazine- and 4,4′-bipy-bridged carbonylruthenium(II) complexes $[\{Ru(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)\}_2(\mu\text{-}L)]$ (5) which undergo catecholate ligand-based oxidation to the dications $[\{Ru(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)\}_2(\mu\text{-}L)]^{2+}$ (5^{2+}). These dications contain two essentially non-interacting *o*-benzosemiquinoneruthenium(II) centres; the intermediate monocations 5^+ have not been detected.



(6; Cl atoms omitted)



(5; L = 4,4'-bipy; Cl atoms omitted)

Results and discussion

The reaction of 4,4′-bipy with $[\{Ru(CO)_2(PPh_3)(\mu\text{-}o\text{-}O_2C_6Cl_4\}_2]$ (**6**) in CH_2Cl_2 results in ruthenium-catecholate bridge cleavage and the isolation of a high yield of $[\{Ru(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)\}_2(\mu\text{-}L)]$ (**5**, L = 4,4′-bipy). The air-stable, orange crystalline product was characterised by elemental analysis and by the IR carbonyl and UV-VIS spectra which are very similar to those of the closely related [6] mononuclear species $[Ru(CO)_2(PPh_3)(pyr)(o\text{-}O_2C_6Cl_4)]$ (**7**, pyr = pyridine) (Table 1). The cyclic voltammogram (CV) of **5** (L = 4,4′-bipy) shows two oxidation waves at potentials almost identical those for the formation of $\mathbf{7}^+$ and $\mathbf{7}^{2+}$ from **7**. The

Table 1

Cyclic voltammetric and spectroscopic data for *o*-catecholate and *o*-benzosemiquinone complexes

Complex	*E*/Volts		$\tilde{\nu}$(CO)/ cm^{-1} [c]	λ_{max}/nm [c]		g_{ave} [c]
	E_1 [a]	E_2 [b]				
$[\{Ru(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)\}_2(\mu\text{-}4,4'\text{-bipy})]$	0.74	1.69	2048, 1985	322(28.0)	395(9.0)	–
$[Ru(CO)_2(PPh_3)(pyr)(o\text{-}O_2C_6Cl_4)]$	0.73	1.70	2047, 1982	322(14.6)	397(4.2)	–
$[\{Ru(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)\}_2(\mu\text{-}4,4'\text{-bipy})]^{2+}$	0.74	1.67	2081, 2027	328(30.0)	495(16.0)	2.004
$[Ru(CO)_2(PPh_3)(pyr)(o\text{-}O_2C_6Cl_4)]^+$	0.72	1.70	2079, 2025	327(15.6)	494(9.4)	2.004

[a] Reversible process. [b] Irreversible process; E_2 is the oxidation peak potential at a scan rate of 200 mV s^{-1}. [c] In CH_2Cl_2.

second oxidation wave of **5** (L = 4,4′-bipy) appears to be chemically irreversible ($(i_p)_{red}/(i_p)_{ox} = 1.0$) but occurs at a potential close to that for the oxidation of the base electrolyte and is therefore difficult to quantify. However, the first wave is diffusion controlled ($(i_p)_{ox}/\nu^{1/2}$ = constant) with the ratio of peak currents ($(i_p)_{red}/(i_p)_{ox}$) unity for scan rates, ν, between 50 and 500 mV s^{-1}. Exhaustive electrolysis of **5** (L = 4,4′-bipy) at a platinum basket electrode (1.0 V, 16 min, $n = 1.99$) showed that his first oxidation process results in the loss of two electrons per molecule and therefore contrast in this respect with the first oxidation wave for **7**. The CV and rotating platinum electrode voltammogram (RPEV) of the red-purple product solution were identical to those of **5** (L = 4,4′-bipy) (except that the wave at 0.74 V corresponded to a reduction process). Thus, electrolytic oxidation results in the direct, and quantitative, formation of $\mathbf{5}^{2+}$. The chemical oxidation of **5** (L = 4,4′-bipy) with $[NO][PF_6]$ exactly parallels the electrolytic process but in this case the salt $[\{Ru(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)\}_2(\mu\text{-}4,4'\text{-bipy})][PF_6]_2$ ($\mathbf{5}^{2+}$, L = 4,4′-bipy) was readily isolated after filtration of the reaction mixture and precipitation with n-hexane; the CV and RPEV of the isolated salt were identical to those of the electrolysed solution of **5** (L = 4,4′-bipy).

IR carbonyl spectroscopy shows that the neutral pyrazine-bridged complex **5** (L = pyz) is formed in solution from **6** and pyrazine. However, it clearly undergoes dissociation to the reactants on attempted isolation. The dication $\mathbf{5}^{2+}$ (L = pyz) can be prepared directly from **6**, pyr, and $[NO][PF_6]$ and has similar properties to the 4,4′-bipy analogue. The lability of the pyrazine–ruthenium bond of **5** (L = pyz) also extends to the dication in that the two IR carbonyl bands of $\mathbf{5}^{2+}$ (L = pyz), at 2039 and 2091 cm^{-1}, are accompanied by two others, at 2029 and 2081 cm^{-1}, in dilute solutions. The latter bands are also observed in the presence of an excess of pyrazine implying that they are due to the mononuclear species $[Ru(CO)_2(PPh_3)(pyz)(o\text{-}O_2C_6Cl_4)][PF_6]$. Nevertheless, $\mathbf{5}^{2+}$ (L = pyz) is the only complex isolable even in the presence of an excess of pyrazine.

The close similarity between the spectroscopic properties of $\mathbf{5}^{2+}$ (L = 4,4′-bipy) and those of $\mathbf{7}^{+}$ imply that the dication contains two equivalent, non-interacting, *o*-benzosemiquinone ligands (rather than two Ru^{III} centres). As in $\mathbf{7}^{+}$, the dication $\mathbf{5}^{2+}$ (L = 4,4′-bipy) shows two absorptions in the IR carbonyl spectrum, shifted to higher wavenumber by only ca. 40 cm^{-1}; a shift of 80–100 cm^{-1} is more common for metal-based oxidations of metal carbonyls [7]. In addition, the UV-VIS spectra of $\mathbf{5}^{2+}$ (L = 4,4′-bipy) and $\mathbf{7}^{+}$ are virtually indistinguishable save for the doubled extinction coefficients of the former. The room temperature ESR spectrum of $\mathbf{5}^{2+}$ (L = 4,4′-bipy) is also consistent with catecholate oxidation; the narrow line, with barely resolved ^{31}P hyperfine coupling (ca. 5 G), is centred ($g = 2.004$) close to the spin-only value. At 77 K only a broad line is observed at $g = 2.00$. No evidence for an additional feature at ca. $g = 4.00$ could be found suggesting there to be little or no interaction between the two paramagnetic centres of $\mathbf{5}^{2+}$.

The peak-to-peak separation ($(E_p)_{red} - (E_p)_{ox}$) for the first oxidation of **5** (L = 4,4′-bipy) (at 0.74 V), and for the reduction of $\mathbf{5}^{2+}$ (L = pyz) at 0.81 V (there is also an irreversible oxidation wave at ca. 1.7 V), varies from 70–90 mV over the scan range 50–500 mV s^{-1}. However similar separations are observed for the oxidation of ferrocene under the same experimental conditions (where the values in excess of the expected 59 mV are due to uncompensated resistance in CH_2Cl_2). The behaviour of **5** differs from that of complexes **1**–**4** where E° values for both of the two sequential one-electron transfer steps can be measured directly from the CVs of the pyrazine complexes **1** and **3** (or estimated for the 4,4′-bipy analogues **2** and **4**). It is clear, therefore, that $\mathbf{5}^+$ is likely to be less delocalised than any of the mixed-valence complexes formed from **1** to **4**. Qualitatively, at least, this may be rationalised in terms of the localisation of the unpaired electron on an *o*-benzosemiquinone ligand rather than a ruthenium-based orbital. In addition, delocalisation will be less favourable with the π-accepting ligand set of $\mathbf{5}^+$ compared with the more donating sets $(NH_3)_5$ and $(bipy)_2Cl$ of **1**–**4**.

Although the couples $\mathbf{5}/\mathbf{5}^+$ and $\mathbf{5}^+/\mathbf{5}^{2+}$ are not resolved by CV it is clear that $\mathbf{5}^+$ should be formed as the product of conproportionation of **5** and $\mathbf{5}^{2+}$. The spectra (IR, ESR and UV-VIS) of solutions containing equimolar quantities of **5** (L = 4,4′-bipy) and $\mathbf{5}^{2+}$ (L = 4,4′-bipy) show no new features and are merely the superimposition of the spectra of the individual components. Though negative, these results also support a localised electronic structure for $\mathbf{5}^+$ in that the spectra of the monocation would be essentially those of the unperturbed mononuclear units (and as noted above, **5** (L = 4,4′-bipy) and $\mathbf{5}^{2+}$ (L = 4,4′-bipy) are equivalent to **7** and $\mathbf{7}^+$).

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen; where necessary the progress of a reaction was monitored by IR spectroscopy. The complex $[\{Ru(CO)_2(PPh_3)(\mu\text{-}o\text{-}O_2C_6Cl_4\}_2]$ was prepared by the published method [6]. The salt $[NO][PF_6]$ was purchased from Fluorochem Ltd., Glossop, and 4,4′-bipyridyl and pyrazine were purchased from Aldrich Chemical Co. Ltd.

Electrochemical studies were carried out as previously described [8]. IR spectra were recorded on a Nicolet 5ZDX FT spectrometer and UV-VIS spectra on a Perkin-Elmer PE 555 instrument. X-Band ESR spectra were recorded on a Varian Associates 4502/15 spectrometer and were 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.

Tetracarbonyl-bis(tetrachloro-o-catecholato)-bis(triphenylphosphine)(μ-4,4′-bipyridyl)-diruthenium, $[\{Ru(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)\}_2(\mu\text{-}4,4'\text{-}bipy)]$

To a stirred solution of $[\{Ru(CO)_2(PPh_3)(\mu\text{-}o\text{-}O_2C_6Cl_4\}_2]$ (0.30 g, 0.23 mmol) in CH_2Cl_2 (30 cm³) was added 4,4′-bipyridyl (36 mg, 0.23 mmol). An orange solid began to form and after 15 min n-hexane was added to the mixture. Reduction of the volume of solvent in vacuo gave an orange precipitate which was washed with n-hexane and dried in vacuo to give the orange product, yield 0.32 g (95%) (Found: C, 49.8; H, 2.6; N, 1.7. $C_{62}H_{38}Cl_8N_2O_8P_2Ru_2$ calc.: C, 50.1; H, 2.6; N, 1.8%).

The air-stable solid is slightly soluble in CH_2Cl_2 and readily soluble in thf to give an orange solution which decomposes only slowly in air.

Tetracarbonyl-bis(tetrachloro-o-benzosemiquinone)-bis(triphenylphosphine)(μ-4,4′-bipyridyl)diruthenium bis(hexafluorophosphate) dichloromethane (1 : 1), $[\{Ru(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)\}_2(\mu\text{-}4,4'\text{-}bipy)][PF_6]_2 \cdot CH_2Cl_2$

To a suspension of $[\{Ru(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)\}_2(\mu\text{-}4,4'\text{-}bipy)]$ (70 mg, 0.047 mmol) in CH_2Cl_2 (35 cm³) was added solid $[NO][PF_6]$ (25 mg, 0.143 mmol). After

15 min the deep red solution was filtered and n-hexane (90 cm^3) was added to give a purple precipitate. Purification by dissolution in CH_2Cl_2, filtration, addition of n-hexane, and partial removal of the solvent in vacuo gave the red-purple solid product, yield 47 mg (54%). (Found: C, 40.6; H, 2.1; N, 1.4. $C_{63}H_{40}Cl_{10}F_{12}N_2O_8P_4Ru_2$ calc.: C, 40.6; H, 2.2; N, 1.5%).

The complex is moderately stable in the solid state and dissolves in polar solvents such as CH_2Cl_2, acetone, or THF to give purple solutions which slowly decompose in air.

*Tetracarbonyl-bis(tetrachloro-*o*-benzosemiquinone)-bis(triphenylphosphine)(μ-pyrazine) diruthenium bis(hexafluorophosphate),* $[\{Ru(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)\}_2(\mu\text{-}pyz)][PF_6]_2$

To a stirred solution of $[\{Ru(CO)_2(PPh_3)(\mu\text{-}o\text{-}O_2C_6Cl_4\}_2]$ (0.12 g, 0.09 mmol) in CH_2Cl_2 (15 cm^3) was added pyrazine (7 mg, 0.09 mmol) and $[NO][PF_6]$ (20 mg, 0.11 mmol). After 15 min the red-purple solution was filtered and n-hexane (80 cm^3) was added to give a purple precipitate. The complex was purified as described above, yield 0.14 g (96%). (Found: C, 39.3; H, 2.1; N, 1.7. $C_{56}H_{34}Cl_8F_{12}N_2O_8P_4Ru_2$ calc.: C, 39.5; H, 2.0; N, 1.7%).

Acknowledgements

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