Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 19.[1] Carbonylruthenium Catecholate and Semiquinone Complexes

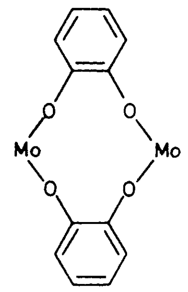
Neil G. Connelly,* Ian Manners, John R. C. Protheroe, and Mark W. Whiteley
Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS

Tetrachlorobenzene-*o*-quinone (*o*-chloranil) and $[Ru(CO)_2(PPh_3)L']$ (L' = η^4-2,3-dimethylbuta-1,3-diene) give the catecholate-bridged dimer $[\{Ru(CO)_2(PPh_3)(\mu\text{-}o\text{-}O_2C_6Cl_4)\}_2]$ (1) which undergoes bridge-cleavage reactions with Group 5 donors, L, and halide ions, X^-, yielding the complexes $[Ru(CO)_2(PPh_3)L(o\text{-}O_2C_6Cl_4)]$ [2; L = PPh_3, $AsPh_3$, $P(OPh)_3$, or pyridine] and $[RuX(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)]^-$ (3; X = Cl, Br, or I), respectively. Cyclic voltammetry at a platinum electrode shows that compounds (2) and (3) undergo two one-electron oxidations; chemical oxidation of (2), with $AgPF_6$ or $[NO][PF_6]$, and of (3), with $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$, yields $[Ru(CO)_2(PPh_3)L(o\text{-}O_2C_6Cl_4)][PF_6]$ [4; L = PPh_3, $AsPh_3$, $P(OPh)_3$, or pyridine] and $[RuX(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)]$ (5; X = Cl, Br, or I), respectively. Complex (5; X = Br or I) may also be prepared directly from (1) and bromine or iodine. E.s.r. spectroscopy suggests that (4) and (5) are semiquinone complexes of ruthenium(II) and, therefore, that the oxidation of (2) and (3) is largely associated with the chelating ligand. However, the hyperfine coupling observed shows the unpaired electron density to be partially delocalised over the metal and axial ligands.

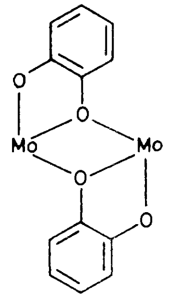
In the preceding paper [1] we described the stabilisation of the radical cation $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ [2] by *o*-quinone substitution. We have tried similarly to stabilise the highly reactive species $[M(CO)_{3-n}L_n(\eta^4\text{-polyene})]^+$ [M = Fe or Ru, n = 0—3, L = P-donor ligand, polyene = butadiene, cycloheptatriene, cyclo-octatetraene (cot), *etc.*],[3,4] but have found, for example, that the reaction between $[Ru(CO)_2(PPh_3)L']$ (L' = η^4-2,3-dimethylbuta-1,3-diene) and tetrachlorobenzene-*o*-quinone (*o*-chloranil) results in diene displacement rather than carbonyl substitution. Nevertheless, the product of this reaction, $[\{Ru(CO)_2(PPh_3)(\mu\text{-}o\text{-}O_2C_6Cl_4)\}_2]$, is the precursor to mononuclear catecholate complexes, $[RuX(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)]^-$ (X = halide) and $[Ru(CO)_2(PPh_3)L(o\text{-}O_2C_6Cl_4)]$ (L = Group 5-donor ligand), which undergo one-electron oxidation to stable, paramagnetic semiquinone complexes of ruthenium(II).

Results and Discussion

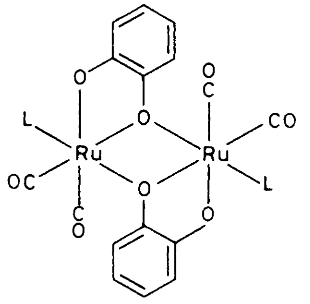
On adding tetrachlorobenzene-*o*-quinone (*o*-chloranil) to $[Ru(CO)_2(PPh_3)L']$ (L' = η^4-2,3-dimethylbuta-1,3-diene) in CH_2Cl_2 an orange solution is rapidly formed from which near-quantitative yields of $[\{Ru(CO)_2(PPh_3)(\mu\text{-}o\text{-}O_2C_6Cl_4)\}_2]$ (1) are readily isolable. Although the detailed structure of compound (1) is not known, the observation of four terminal carbonyl absorptions in the i.r. spectrum [$\tilde{\nu}$(CO)(CH_2Cl_2) = 2 065 (sh), 2 057s, 2 007s, and 1 989m cm^{-1}] verifies the dimeric nature of the complex, and implies the presence of bridging O-donor ligands. Although *X*-ray crystallography has shown that both $[Mo_2(o\text{-}O_2C_6Cl_4)_4(\mu\text{-}o\text{-}O_2C_6Cl_4)_2]$ [5] and $[Mo_2O_2(o\text{-}O_2C_6H_2Bu^t_2)_2(\mu\text{-}o\text{-}O_2C_6H_2Bu^t_2)_2]$ [6] contain bridging catecholate ligands, the $Mo_2(\mu\text{-}O^\frown O)$ cores, shown in (A) and (B) respectively, are rather different. Because complex (1) readily undergoes bridge-cleavage reactions, giving mononuclear catecholate derivatives (see below), the bridging system shown in (B) seems more likely than that in (A), and the structure shown in (C) is assigned to (1).



(A)



(B)



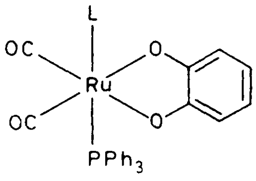
(C) L = PPh_3; Cl atoms omitted

With donor ligands, L, complex (1) rapidly gives high yields of the yellow or orange, six-co-ordinate, monomers $[Ru(CO)_2(PPh_3)L(o\text{-}O_2C_6Cl_4)]$ [2; L = PPh_3, $AsPh_3$, $P(OPh)_3$, or pyridine (py)] (Table 1). The bis(triphenylphosphine) complex (2; L = PPh_3) has been prepared [7] previously from $[Ru(CO)_3(PPh_3)_2]$ and *o*-chloranil or from $[RuCl_2(CO)_2(PPh_3)_2]$ and the tetrachloro-*o*-catecholate dianion, $[o\text{-}O_2C_6Cl_4]^{2-}$. On the basis of the two carbonyl absorptions in the i.r. spectrum, and the e.s.r. spectrum of the monocation $[Ru(CO)_2(PPh_3)_2(o\text{-}O_2C_6Cl_4)]^+$ (see below), which showed two equivalent phosphorus atoms, a *cis,trans*-dicarbonylbis(phosphine) structure was assigned [7] to (2; L = PPh_3). The ^{31}P n.m.r. spectrum, which shows one singlet resonance (δ = 17.46 p.p.m.), directly confirms this assignment, and the structure of compound (2) is, therefore, as shown in (D).

Table 1. I.r. and analytical data for $[Ru(CO)_2(PPh_3)L(o\text{-}O_2C_6Cl_4)]^Z$

L	Z	Colour	Yield (%)	Analysis [a] (%) C	H	N	$\tilde{\nu}(CO)$ [b]/cm^{-1}
PPh_3	0	Orange	91	57.1 (57.0)	3.3 (3.2)		2 045, 1 983
PPh_3	1	Dark brown	82	48.8 (49.3)	3.0 (2.8)		2 073, 2 021
$AsPh_3$	0	Orange	79	54.6 (54.4)	3.0 (3.1)		2 044, 1 982
$AsPh_3$	1	Dark brown	86	47.4 (47.3)	2.8 (2.7)		2 074, 2 022
$P(OPh)_3$	0	Yellow	86	54.0 (54.1)	3.1 (3.1)		2 060, 2 001
$P(OPh)_3$	1	Purple	88	47.9 (47.1)	2.9 (2.7)		2 089, 2 040
py	0	Yellow	86	49.9 (50.0)	2.8 (2.7)	1.6 (2.0)	2 047, 1 982
py	1	Purple	86	40.8 (41.8)	2.5 (2.3)	1.2 (1.6)	2 079, 2 025
Cl	−1 [c]	Yellow	85	52.1 (52.4)	4.2 (4.2)	1.4 (1.6)	2 045, 1 977
Cl	0	Green	49	44.7 (44.5)	1.9 (2.1)		2 073, 2 016
Br	−1 [d]	Orange	83	51.8 (51.1)	5.5 (5.2)	1.2 (1.4)	2 042, 1 976
Br	0	Green	71	42.0 (41.9)	2.2 (2.0)		2 071, 2 016
I	−1 [e]	Orange	75	50.4 (50.5)	3.1 (3.1)		2 037, 1 973
I	0	Dark brown	92	39.4 (39.4)	1.9 (1.9)		2 067, 2 013

[a] Calculated values in parentheses. [b] In CH_2Cl_2. [c] $[N(CH_2Ph)Et_3]^+$ salt. [d] $[NBu^n{}_4]^+$ salt. [e] $[PMePh_3]^+$ salt.



(D) Cl atoms omitted

Complex (1) also undergoes bridge-splitting reactions with halides, giving yellow to orange anions, $[RuX(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)]^-$ (3; X = Cl, Br, or I), which are readily isolated as crystalline, quaternary ammonium or phosphonium salts (Table 1). Their physical and chemical properties are very similar to those of (2) and they, also, are likely to adopt the structure shown in (D) (L = halide).

Balch and his co-workers [7] previously showed that compound (2; L = PPh_3) is oxidised in two, one-electron steps [$E_{\frac{1}{2}}$ = 0.65 and 1.76 V, *vs.* saturated calomel electrode (s.c.e.)] to $[Ru(CO)_2(PPh_3)_2(o\text{-}O_2C_6Cl_4)]^Z$ (Z = 1 or 2). Although the monocation was successfully generated by silver(I) salt oxidation of (2; L = PPh_3), and characterised in solution by i.r. and e.s.r. spectroscopy, no attempt was made to isolate the solid complex. Our cyclic voltammetric studies (Table 2) have more fully defined the redox behaviour of (2) and (3), and we have successfully isolated the products of the first electron-transfer process.

At a platinum-wire electrode, in CH_2Cl_2, complexes (2) and (3) undergo two one-electron oxidations the first of which is diffusion controlled ($i_{ox}/\sqrt{v}$ = constant for scan rates, v, from 50 to 1 000 mV s^{-1}) and fully reversible (i_{ox}/i_{red} = 1.0) for v = 200 mV s^{-1}. The second oxidation occurs at a potential close to that at which the supporting electrolyte decomposes and is, therefore, less well defined; it appears to be diffusion controlled in all cases, but reversible only for (2; L = PPh_3 or $AsPh_3$).

The electron-transfer reactions of *o*-quinone complexes [8] usually involve the interconversion of *o*-quinone, semiquinone, and catecholate ligands, and the small variations of $E^\ominus$ within the series comprising (2) and (3) suggest, once again, that oxidation occurs at the ligand rather than at the metal. Whereas the $E^\ominus$ values for the oxidation of the neutral complexes (2) are only 0.2—0.3 V more positive than those of the anions (3), and the dependence on L or X is small, much larger changes are found for metal-based oxidations. Compare, for example, $[CrBr(CO)_5]^-$ ($E^\ominus$ = 0.40 V) and $[CrL(CO)_5]$ [L = PPh_3, $E^\ominus$ = 0.80 V; L = $P(OPh)_3$, $E^\ominus$ = 1.25 V; L = py, $E^\ominus$ = 1.20 V, *vs.* Ag–AgCl in CH_2Cl_2].[9]

Table 2. Electrochemical data for $[Ru(CO)_2(PPh_3)L(o\text{-}O_2C_6Cl_4)]^Z$

L	Z	Process	$E^\ominus$/V	Process	$E^\ominus$/V
PPh_3	0	$0 \rightleftharpoons 1$	0.55	$1 \rightleftharpoons 2$	1.58
PPh_3	1	$1 \rightleftharpoons 0$	0.54	$1 \rightleftharpoons 2$	1.58
$AsPh_3$	0	$0 \rightleftharpoons 1$	0.58	$1 \rightleftharpoons 2$	1.62
$AsPh_3$	1	$1 \rightleftharpoons 0$	0.58	$1 \rightleftharpoons 2$	1.60
$P(OPh)_3$	0	$0 \rightleftharpoons 1$	0.64	$1 \rightleftharpoons 2$	1.71 *
$P(OPh)_3$	1	$1 \rightleftharpoons 0$	0.65	$1 \rightleftharpoons 2$	1.71 *
py	0	$0 \rightleftharpoons 1$	0.68	$1 \rightleftharpoons 2$	1.66 *
py	1	$1 \rightleftharpoons 0$	0.69	$1 \rightleftharpoons 2$	1.66 *
Cl	−1	$-1 \rightleftharpoons 0$	0.39	$0 \rightleftharpoons 1$	1.41 *
Cl	0	$0 \rightleftharpoons -1$	0.39	$0 \rightleftharpoons 1$	1.45 *
Br	−1	$-1 \rightleftharpoons 0$	0.38	$0 \rightleftharpoons 1$	1.44 *
Br	0	$0 \rightleftharpoons -1$	0.37	$0 \rightleftharpoons 1$	1.45 *
I	−1	$-1 \rightleftharpoons 0$	0.34	$0 \rightleftharpoons 1$	1.35 *
I	0	$0 \rightleftharpoons -1$	0.35	$0 \rightleftharpoons 1$	1.36 *

* Irreversible wave. The oxidation peak potential at 200 mV s^{-1} is given.

The magnitudes of $E^\ominus$ for (2) and (3), and the reversibility of the electron-transfer process, suggested that the products of the first oxidation reaction should be chemically isolable. In CH_2Cl_2, or in methanol–toluene (1 : 5), $[NO][PF_6]$ and (2) readily afford brown to purple solutions from which the air-stable, crystalline salts $[Ru(CO)_2(PPh_3)L(o\text{-}O_2C_6Cl_4)][PF_6]$ [4; L = PPh_3, $AsPh_3$, $P(OPh)_3$, or py] are readily isolated (Table 1). Similarly, ferrocenium ion oxidation of (3) in CH_2Cl_2 affords neutral $[RuX(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)]$ (5; X = Cl, Br, or I) as green or brown crystals. Complexes (5; Br or I), but not the chloride, can also be prepared from (1) and the appropriate halogen. This more direct route is unusual in that a bridge-splitting reaction of a diamagnetic dimer directly affords a paramagnetic monomeric product.

Complexes (4) and (5) are readily characterised by elemental analysis, i.r. (Table 1), and e.s.r. spectroscopy (Table 3), and by their cyclic voltammograms (Table 2), which show reduction waves at potentials virtually identical to those of the oxidation waves of (2) and (3).

The presence of two carbonyl absorptions in the i.r. spectrum of compounds (4) and (5), and of a 1 : 2 : 1 triplet [$A(^{31}P)$ = 25.1 G] in the e.s.r. spectrum of (4; L = PPh_3), clearly defines the *cis,trans*-dicarbonylbis(triphenylphosphine) structure of (4; L = PPh_3). That there is no geometric isomerisation during electron transfer contrasts with the behaviour of,

Table 3. E.s.r. spectral data for $[Ru(CO)_2(PPh_3)L(o\text{-}O_2C_6Cl_4)]^Z$

L	Z	$g_{av.}$	$A(^{31}P)^a$/G	A(other)/G	Multiplicity [b]
PPh_3 [c]	1	2.002	25.1	—	t (1 : 2 : 1)
$AsPh_3$	1	2.003	20.6	30.8 (^{75}As)	qd
$P(OPh)_3$	1	2.003	18.2	35.4 (^{31}P)	dd
py	1	2.004	*ca.* 6.0	—	d
Cl	0	2.002	10.3	<1.8 (^{35}Cl, ^{37}Cl)	d
Br	0	2.004	10.4	10.2 (^{79}Br, ^{81}Br)	qnt (1 : 2 : 2 : 2 : 1)
I [d]	0	2.006	12.4	*ca.* 15.2 (^{127}I)	d

[a] 1 G = 10^{-4} T. [b] Lines of equal intensity unless otherwise stated; d = doublet, t = triplet, q = quartet, and qnt = quintet. [c] A (^{99}Ru, ^{101}Ru) = 3.7 G. [d] See Figure 1.

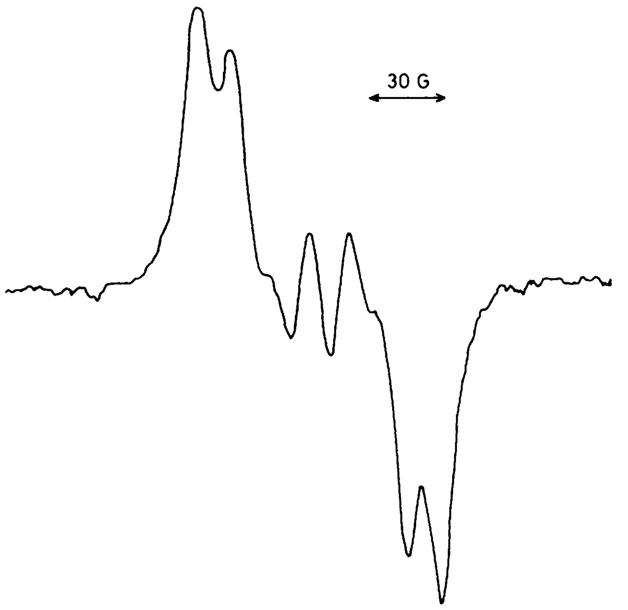


Figure 1. The e.s.r. spectrum of $[RuI(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)]$ in CH_2Cl_2

for example, *cis*-$[M(CO)_2(L\text{-}L)_2]$ (M = Cr, Mo, or W; L-L = $Ph_2PCH_2CH_2PPh_2$)[10] and *fac*-$[MnX(CO)_3L_2]$ (X = halide, L = P donor, *etc.*)[11] for which one-electron oxidation yields *trans* and *mer* monocations, respectively.

Although major structural changes do not appear to occur when compounds (2) and (3) are oxidised, a comparison of the relative intensities of the two carbonyl bands of (2) or (3) with those of (4) or (5) suggests that the angle subtended by the two ligands at the metal decreases by *ca.* 5° on oxidation. *X*-Ray crystallographic studies currently in progress on $[Ru(CO)_2(PPh_3)_2(o\text{-}O_2C_6Cl_4)]^Z$ do indeed show the following intercarbonyl angles: $Z = 0$, 93.3(2)°; $Z = 1$, 90.5(2)°.[12]

The cyclic voltammetric studies on compounds (2) and (3) (see above) suggest that oxidation involves removal of an electron from an orbital based primarily on the chelating ligand. The relatively small increases in $\tilde{\nu}$(CO) when (2) and (3) are oxidised to (4) and (5) (*ca.* 30—40 cm^{-1}) also support ligand-based electron transfer. By comparison, the one-electron oxidations of $[Fe(CO)\{P(OMe)_3\}_2(\eta^4\text{-}C_4Ph_4)]$ (C_4Ph_4 = tetraphenylcyclobutadiene)[3] and $[Mn(CO)(dppe)(\eta^5\text{-}C_6H_6Ph)]$ (C_6H_6Ph = 6-phenylcyclohexa-2,4-dienyl)[13] are accompanied by much larger increases in $\tilde{\nu}$(CO), of 80 and 102 cm^{-1}, respectively; for these complexes, *X*-ray crystallography has revealed metal-based oxidation.[12]

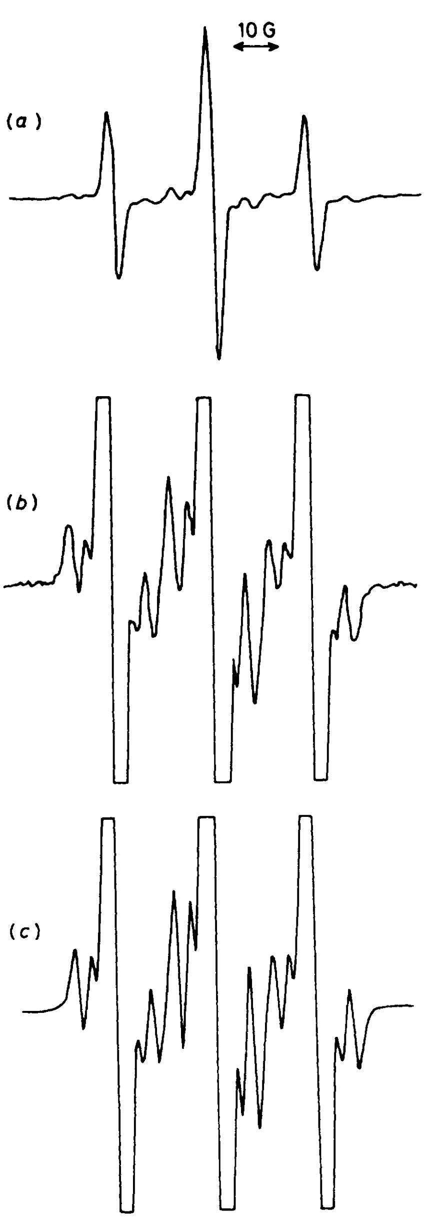


Figure 2. The e.s.r. spectrum, in CH_2Cl_2, of $[Ru(CO)_2(PPh_3)_2(o\text{-}O_2C_6Cl_4)]^+$, (*a*) showing coupling to ^{31}P ($I = \frac{1}{2}$), (*b*) showing coupling to ^{99}Ru and ^{101}Ru ($I = \frac{5}{2}$), and (*c*) computer simulated

The suggestion that (2) and (3) are catecholate complexes which are oxidised to semiquinone derivatives, (4) and (5), is largely borne out by the isotropic e.s.r. spectra (Table 3) of the paramagnetic complexes; the $g_{av.}$ values of (4) and (5) are close to that of the uncomplexed semiquinone anion radical $[o\text{-}O_2C_6Cl_4]^-$ ($g_{av.}$ = 2.0053).[14] All of the complexes (4) and (5), however, show hyperfine coupling to the phosphorus atom of the PPh_3 group, and most also show coupling to the second axial ligand, implying small but significant delocalisation. For the pyridine complex, no ^{14}N hyperfine interaction is apparent, and for the chloride compound (5; X = Cl) the doublet spectrum shows only barely defined shoulders which could, however, be computer-simulated if the coupling to ^{35}Cl and ^{37}Cl was *ca.* 1.8 G. The e.s.r. spectrum of compound (5; X = I), shown in Figure 1, could not be satisfactorily simulated, but clearly shows coupling to both ^{31}P ($I = \frac{1}{2}$) and ^{127}I ($I = \frac{5}{2}$).

The most intense peaks in the e.s.r. spectra of (4) and (5) are due to complexes having ruthenium nuclei with spin $I = 0$. However, most of the spectra also show satellites due to the complexes of ^{99}Ru and ^{101}Ru, both nuclei having $I = \frac{5}{2}$. The metal hyperfine coupling, again confirming delocalisation away from the chelate ligand, is small (*ca.* 4 G) and best seen in the spectrum of (4; L = PPh_3) which is shown, together with a computer simulation, in Figure 2.

Conclusions

Synthetic and spectroscopic studies show that the one-electron oxidation of the *o*-catecholate complexes $[Ru(CO)_2L(PPh_3)(o\text{-}O_2C_6Cl_4)]^Z$ (L = P donor, $Z = 0$; L = halide, $Z = -1$) involves the formation of species best formulated as ruthenium(II) complexes of semiquinone ligands. However, some delocalisation of unpaired electron density, onto the metal and axial ligands, also occurs.

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 i.r. spectroscopy. Unless stated otherwise, the purification of a complex involved dissolution in CH_2Cl_2, filtration, addition of n-hexane, and partial evaporation of the solvent mixture *in vacuo* to induce precipitation. The solid products are air-stable, dissolving in polar solvents such as acetone and CH_2Cl_2 to give moderately air-sensitive solutions.

The complex $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ was prepared by a published method.[15] The salt $[NO][PF_6]$ was purchased from Fluorochem Ltd., Glossop, and *o*-chloranil from Aldrich Chemical Co. Ltd.

Cyclic voltammetry was performed as previously described.[1] Infrared spectra were recorded on Perkin-Elmer 257 or Nicolet FT 7199 instruments. *X*-Band e.s.r. spectra were recorded on a Varian Associates 4502/15 spectrometer and were calibrated against a 10^{-4} mol dm^{-3} aqueous solution of $K_2[NO(SO_3)_2]$ (5×10^{-2} mol dm^{-3} in K_2CO_3 as buffer). The e.s.r. spectra were simulated on an Apple Microcomputer using a PASCAL program written [16] by Dr. J. P. Maher and Mr. A. P. Grigg of the Department of Inorganic Chemistry, University of Bristol. Phosphorus-31 n.m.r. spectra were recorded at 36 MHz on a JEOL FX 90Q instrument and calibrated against H_3PO_4 as external standard.

Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Dicarbonyl(η-2,3-*dimethylbuta*-1,3-*diene*)(*triphenylphosphine*)*ruthenium*, $[Ru(CO)_2(PPh_3)(\eta^4\text{-}C_4H_4Me_2)]$.—A mixture of $[Ru_3(CO)_{12}]$ (2.0 g, 3.13 mmol) and 2,3-dimethylbuta-1,3-diene (5 cm^3) in n-heptane (100 cm^3) was heated under reflux for 20 h. After adding PPh_3 (2.0 g, 7.63 mmol) the solution was heated for a further 3 d. The solvent was then removed *in vacuo*, and the residue dissolved in CH_2Cl_2 (5 cm^3) and transferred to a large (55 × 3 cm) alumina column containing n-hexane. Elution with n-hexane gave small quantities of $[Ru(CO)_3(\eta^4\text{-}C_4H_4Me_2)]$, and with n-hexane–diethyl ether (20 : 1) gave a colourless solution of $[Ru(CO)_2(PPh_3)(\eta^4\text{-}C_4H_4Me_2)]$. Removal of the solvent and purification of the residue from CH_2Cl_2–n-hexane gave the product as a white solid, yield 2.15 g (46%) (Found: C, 63.1; H, 5.0. $C_{26}H_{25}O_2PRu$ requires C, 62.3; H, 5.0%), $\tilde{\nu}(CO)$ (n-hexane) = 1 999 and 1 941 cm^{-1}. The air-stable complex is barely soluble in n-hexane but soluble in all other common organic solvents to give colourless solutions which slowly decompose in air.

Tetracarbonyl-bis(μ-*tetrachloro*-o-*catecholato*)-*bis*(*triphenylphosphine*)*diruthenium*, $[\{Ru(CO)_2(PPh_3)(\mu\text{-}o\text{-}O_2C_6Cl_4)\}_2]$.—To a stirred, colourless solution of $[Ru(CO)_2(PPh_3)(\eta^4\text{-}C_4H_4Me_2)]$ (2.4 g, 4.8 mmol) in CH_2Cl_2 (25 cm^3) was added *o*-chloranil (1.7 g, 6.9 mmol). After 15 min the orange-brown solution was filtered and n-hexane (100 cm^3) was added to give an orange precipitate which was washed with n-hexane (2 × 25 cm^3) and purified from CH_2Cl_2–n-hexane, yield 2.8 g (88%) (Found: C, 47.1; H, 2.2. $C_{50}H_{30}Cl_8O_6P_2Ru_2$ requires C, 46.9; H, 2.3%).

Dicarbonyl(*tetrachloro*-o-*catecholato*)*bis*(*triphenylphosphine*)*ruthenium*, $[Ru(CO)_2(PPh_3)_2(o\text{-}O_2C_6Cl_4)]$.—To a stirred solution of $[\{Ru(CO)_2(PPh_3)(\mu\text{-}o\text{-}O_2C_6Cl_4)\}_2]$ (2.17 g, 1.63 mmol) in CH_2Cl_2 (40 cm^3) was added PPh_3 (0.85 g, 3.24 mmol). An orange solid began to form, and after 10 min n-hexane (80 cm^3) was added and the volume of solvent reduced *in vacuo* to complete precipitation. The product was recrystallised twice from CH_2Cl_2–n-hexane to give a bright orange powder, yield 2.75 g (91%). The complexes $[Ru(CO)_2(PPh_3)L(o\text{-}O_2C_6Cl_4)]$ [L = $AsPh_3$, $P(OPh)_3$, or py] were prepared similarly.

Dicarbonyl(*tetrachloro*-o-*benzosemiquinone*)(*triphenylphosphine*)(*triphenyl phosphite*)*ruthenium Hexafluorophosphate*, $[Ru(CO)_2(PPh_3)\{P(OPh)_3\}(o\text{-}O_2C_6Cl_4)][PF_6]$.—To a stirred solution of $[Ru(CO)_2(PPh_3)\{P(OPh)_3\}(o\text{-}O_2C_6Cl_4)]$ (0.22 g, 0.23 mmol) in CH_2Cl_2 was added $[NO][PF_6]$ (0.04 g, 0.23 mmol). After 30 min the deep purple solution was filtered and n-hexane (100 cm^3) was added to give a purple precipitate. The compound was purified from CH_2Cl_2–diethyl ether, yield 0.22 g (88%). The salts $[Ru(CO)_2(PPh_3)L(o\text{-}O_2C_6Cl_4)][PF_6]$ (L = PPh_3, $AsPh_3$, or py) were prepared similarly.

Benzyltriethylammonium Dicarbonylchloro(*tetrachloro*-o-*catecholato*)(*triphenylphosphine*)*ruthenium*, $[N(CH_2Ph)Et_3][RuCl(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)]$.—To a stirred solution of $[\{Ru(CO)_2(PPh_3)(\mu\text{-}o\text{-}O_2C_6Cl_4)\}_2]$ (0.25 g, 0.19 mmol) in CH_2Cl_2 (35 cm^3) was added $[N(CH_2Ph)Et_3]Cl$ (0.09 g, 0.39 mmol). After 10 min the bright yellow solution was filtered and n-hexane (100 cm^3) was added to give a yellow precipitate. Recrystallisation from CH_2Cl_2–n-hexane gave the product as a yellow solid, yield 0.29 g (85%). The complexes $[NBu^t_4][RuBr(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)]$ and $[PMePh_3][RuI(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)]$ were prepared similarly, using the appropriate halide salt.

Bromodicarbonyl(*tetrachloro*-o-*benzosemiquinone*)(*triphenylphosphine*)*ruthenium*, $[RuBr(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)]$.—To a stirred solution of $[\{Ru(CO)_2(PPh_3)(\mu\text{-}o\text{-}O_2C_6Cl_4)\}_2]$ (0.20 g, 0.15 mmol) in CH_2Cl_2 (20 cm^3) was added dropwise a dilute solution of bromine in CH_2Cl_2. After the reaction was complete, n-hexane (60 cm^3) was added to the dark green solution and partial removal of the solvent *in vacuo* gave a green precipitate. Recrystallisation twice from CH_2Cl_2–n-hexane gave the product as green crystals, yield 0.16 g (71%). The complex $[RuI(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)]$ was prepared similarly.

Dicarbonylchloro(*tetrachloro*-o-*benzosemiquinone*)(*triphenylphosphine*)*ruthenium*, $[RuCl(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)]$.—To a stirred solution of $[N(CH_2Ph)Et_3][RuCl(CO)_2(PPh_3)(o\text{-}O_2C_6Cl_4)]$ (0.13 g, 0.15 mmol) in CH_2Cl_2 (35 cm^3) was added $[Fe(\eta\text{-}C_5H_5)_2][PF_6]$ (0.05 g, 0.15 mmol). After stirring for 1.5 h the green-black solution was evaporated to dryness and the residue washed with n-hexane (2 × 25 cm^3). Extraction with toluene (25 cm^3), filtration, and addition of n-hexane to the resulting solution gave the product as a green solid, 0.05 g (49%).

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References

1 Part 18, N. G. Connelly, M. J. Freeman, I. Manners, and A. G. Orpen, preceding paper.
2 N. G. Connelly, A. R. Lucy, J. D. Payne, A. M. R. Galas, and W. E. Geiger, *J. Chem. Soc., Dalton Trans.*, 1983, 1879.
3 N. G. Connelly, R. L. Kelly, and M. W. Whiteley, *J. Chem. Soc., Dalton Trans.*, 1981, 34.
4 N. G. Connelly, R. L. Kelly, M. D. Kitchen, R. M. Mills, R. F. D. Stansfield, M. W. Whiteley, S. M. Whiting, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 1317.
5 C. G. Pierpont and H. H. Downs, *J. Am. Chem. Soc.*, 1975, **97**, 2123.
6 R. M. Buchanan and C. G. Pierpont, *Inorg. Chem.*, 1979, **18**, 1616.
7 A. Y. Girgis, Y. S. Sohn, and A. L. Balch, *Inorg. Chem.*, 1975, **14**, 2327.
8 C. G. Pierpont and R. M. Buchanan, *Coord. Chem. Rev.*, 1981, **38**, 45.
9 A. M. Bond, S. W. Carr, R. Colton, and D. P. Kelly, *Inorg. Chem.*, 1983, **22**, 989.
10 A. M. Bond, B. S. Grabaric, and J. J. Jackowski, *Inorg. Chem.*, 1978, **17**, 2153 and refs. therein.
11 A. M. Bond, R. Colton, and M. E. McDonald, *Inorg. Chem.*, 1978, **17**, 2842 and refs. therein.
12 M. J. Freeman and A. G. Orpen, unpublished work.
13 N. G. Connelly, A. R. Sheehan, and J. B. Sheridan, unpublished work.
14 L. Pasimeni, M. Brustolon, and C. Corvaja, *J. Magn. Reson.*, 1976, **21**, 259.
15 J. C. Smart and B. L. Pinsky, *J. Am. Chem. Soc.*, 1980, **102**, 1009.
16 J. P. Maher and A. P. Grigg, unpublished work.

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