Chemistry of Bis(*o*-benzosemiquinonato)bis(triphenylphosphine)ruthenium(II) Complexes. Crystal and Molecular Structure of $[Ru(O_2C_6Cl_4)_2(PPh_3)_2]$[†]

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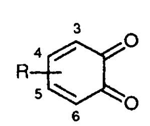
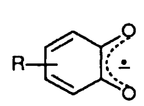
The green complexes $[Ru(L^s)_2(PPh_3)_2]\cdot 2H_2O$ (L^s = *o*-benzosemiquinonate) are obtained in excellent yields by the reaction of catechols H_2L^1–H_2L^4 with $[RuH(Hsa)(PPh_3)_3]$ {$H_2L^1 = C_6H_4(OH)_2$-1,2; H_2L^2 = 4-$Bu^tC_6H_3(OH)_2$-1,2; H_2L^3 = 3,5-$Bu^t{}_2C_6H_2(OH)_2$-1,2; $H_2L^4 = C_6Cl_4(OH)_2$-1,2; H_2sa = salicylic acid}. The crystals of the tetrachloro complex are triclinic, space group $P\bar{1}$ with a = 9.430(5), b = 11.689(4), c = 12.551(6) Å, α = 68.58(3), β = 72.07(4), γ = 79.92(4)° and Z = 1; the final R factor is 0.0406 for 4741 observed reflections. The complex is centrosymmetric with a *trans*-RuO_4P_2 co-ordination sphere; the average C–O distance is 1.310(5) Å. Significant d_π–p_{π^*} back-bonding occurs within the $Ru^{II}(L^s)_2$ fragment and metal-to-ligand charge-transfer (m.l.c.t.) transitions are observed in the near-IR region (900–1300 nm). In dichloromethane solution four successive one-electron cyclic voltammetric couples are observed. The product of the first one-electron reduction has been identified as $[Ru^{III}(L^c)_2]^-$ (L^c = catecholate) from ESR spectra. The probable nature of the other members of the redox series is discussed.

This work stems from our interest in the chemistry of ruthenium phenolates[1–3] and deals with complexes of 1,2-dihydroxy ligands which constitute the redox series[4] quinone–semiquinonate–catecholate symbolised L^q–L^s–L^c, **1**–**3** (when redox state specification is not desired the symbol L is used). Known ruthenium complexes of L span the types [RuL(D)],[5–12] $[RuL_2(D)]$[11,13–15] and $[RuL_3]$[16,17] [D = coligand (s)].



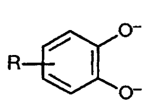
L^q

1



L^s

2



L^c

3

Virtually all reported $[RuL_2(D)]$ complexes have amines as coligands.[11,13–15] Herein we describe complexes $[RuL_2(PPh_3)_2]\cdot 2H_2O$ having PPh_3 as the coligand. The X-ray structure of one complex [$H_2L = C_6Cl_4(OH)_2$-1,2] has been determined revealing a *trans* geometry. A ruthenium(II)–semiquinonate formulation is consistent with all observations. Spectral and electrochemical properties are reported.

Results and Discussion

Synthesis and Properties.—We have found the yellow hydridic salicylate[18] $[RuH(Hsa)(PPh_3)_3]$ (H_2sa = salicylic acid) to be an excellent synthetic precursor for several types of complexes incorporating the $Ru^{II}(PPh_3)_2$ fragment. The green coloured diamagnetic $[RuL_2(PPh_3)_2]\cdot 2H_2O$ family reported here constitute a good example. These have been isolated in excellent yields by treating the catechols H_2L^1–H_2L^4 with $[RuH(Hsa)(PPh_3)_3]$ in acetone in the presence of NEt_3 {$H_2L^1 = C_6H_4(OH)_2$-1,2; H_2L^2 = 4-$Bu^tC_6H_3(OH)_2$-1,2; H_2L^3 = 3,5-$Bu^t{}_2C_6H_2(OH)_2$-1,2; $H_2L^4 = C_6Cl_4(OH)_2$-1,2}. The precursor complex was obtained in nearly quantitative yield from $[RuCl_2(PPh_3)_3]$, salicylic acid and base in ethanol.

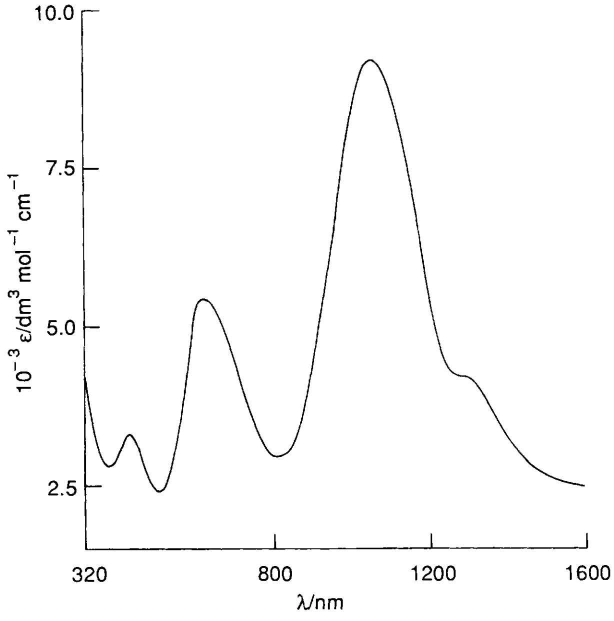


Fig. 1 Electronic spectra of $[Ru(L^{s4})_2(PPh_3)_2]\cdot 2H_2O$ in dichloromethane at 298 K

Solutions of complexes $[RuL_2(PPh_3)_2]$ absorb strongly in the visible and near-infrared regions in organic solvents. Spectral data are collected in Table 1 and a representative spectrum is shown in Fig. 1. The complexes display four one-electron cyclic voltammetric couples in dichloromethane solution. Formal potential data are listed in Table 1 and the voltammogram of the L^4 complex is shown in Fig. 2. The potentials which are referenced to the saturated calomel electrode (SCE) depend on the substituent R in the expected manner, electron-withdrawing R making the potentials more positive.

[†] Bis(tetrachloro-*o*-benzosemiquinonato-κ*O*,*O*′)bis(triphenylphosphine)ruthenium(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Electrochemical[a] and electronic spectral data of complexes $[Ru(L^s)_2(PPh_3)_2]\cdot 2H_2O$ in dichloromethane at 298 K

R	Compound	$E°_{298}/V$[b]	UV/VIS and NIR spectral data, λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
H	$[RuL^{s1})_2(PPh_3)_2]\cdot 2H_2O$	1.08, 0.38, −0.53, −1.13	1300(sh)(4000), 980(11 500), 615(7670), 400(4580)
4-Bu^t	$[RuL^{s2})_2(PPh_3)_2]\cdot 2H_2O$	0.84, 0.29, −0.61, −1.11	1300(sh)(5500), 980(13 330), 625(8830), 450(sh)(4250), 380(5080)
3,5-Bu$^t_2$	$[RuL^{s3})_2(PPh_3)_2]\cdot 2H_2O$	0.82, 0.21, −0.86, −1.34	1200(sh)(5450), 1000(11 270), 615(6270), 450(sh)(2890), 380(3840)
3,4,5,6-Cl$_4$	$[RuL^{s4})_2(PPh_3)_2]\cdot 2H_2O$	1.27, 0.80, 0.02, −0.63	1300(sh)(4130), 1050(9210), 625(5470), 430(3330)

[a] Conditions of cyclic voltammetry: supporting electrolyte, $[NEt_4][ClO_4]$ (0.1 mol dm^{-3}); working electrode, platinum; reference electrode aqueous saturated calomel electrode (SCE); solute concentration, 10^{-3} mol dm^{-3}; scan rate, 50 mV s^{-1}. [b] $E°_{298} = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials respectively, separation between E_{pa} and E_{pc} is in the range 120–200 mV.

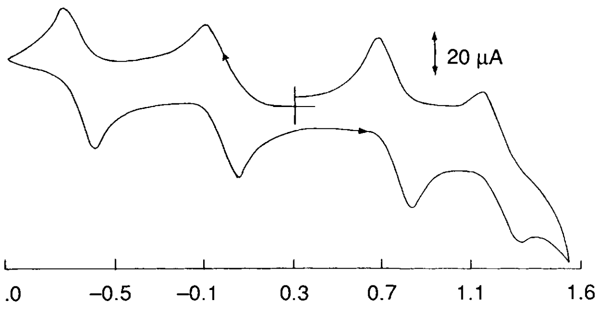


Fig. 2 Cyclic voltammogram (scan rate 50 mV s^{-1}) of a 10^{-3} mol dm^{-3} solution of $[Ru(L^{s4})_2(PPh_3)_2]\cdot 2H_2O$ in dichloromethane (0.1 mol dm^{-3} $[NEt_4][ClO_4]$) at a platinum electrode

Table 2 Selected bond lengths (Å) and angles (°) for $[Ru(L^4)_2(PPh_3)_2]\cdot 2H_2O$

Ru–P(1)	2.441(2)	Ru–O(2)	2.012(3)
Ru–O(1)	2.007(2)	O(1)–C(19)	1.312(5)
O(2)–C(20)	1.307(4)		
P(1)–Ru–O(2)	90.3(1)	P(1)–Ru–O(1)	86.3(1)
O(2)–Ru–O(1)	80.0(1)	Ru–O(2)–C(20)	112.5(2)
Ru–O(1)–C(19)	112.5(2)		

Structure of $[Ru(L^4)_2(PPh_3)_2]\cdot 2H_2O$.—The crystal lattice consists of discrete molecules in which the metal is centrosymmetrically located (0,0,0) in *trans*-RuO_4P_2 co-ordination. The two L^4 ligands are equivalent by symmetry as are the two PPh_3 ligands. A view of the molecule is shown in Fig. 3. Selected bond distances and angles are collected in Table 2.

The co-ordinated L^4 ligand is nearly exactly planar but the ruthenium atom lies slightly away from the plane such that the chelate ring has a 10.9° fold along the O • • • O line of L^4. The water molecules occupy general positions and are weakly hydrogen bonded to each other [$O_w \cdots O_w$ 2.953(4) Å]. The dimer occupies a channel between the complex molecules (Fig. 4).

The average C–O distance in the complex is 1.310(5) Å. This can be compared with the value 1.321(5) Å found in *trans*-$[Ru(L^3)_2(bupy)_2]$ (bupy = 4-*tert*-butylpyridine) which has a centrosymmetric RuO_4N_2 co-ordination sphere.[11] The complex $[Ru(L^1)_2(bipy)]$ (bipy = 2,2′-bipyridine) is necessarily *cis* but the average C–O distance is very similar, 1.321(6) Å.[14]

State of the Metal and Ligand.—The C–O distances in idealised L^s (semiquinonate) and L^c (catecholate) ligands are 1.29 Å and 1.34 Å respectively.[19] The observed distances in the above complexes including $[Ru(L^4)_2(PPh_3)_2]\cdot 2H_2O$ lie between these values. This could be rationalised by invoking resonance between the forms $Ru^{II}(L^s)(L^s)$ and $Ru^{III}(L^c)(L^s)$ with strong metal–L^s magnetic coupling (S = 0). However a careful

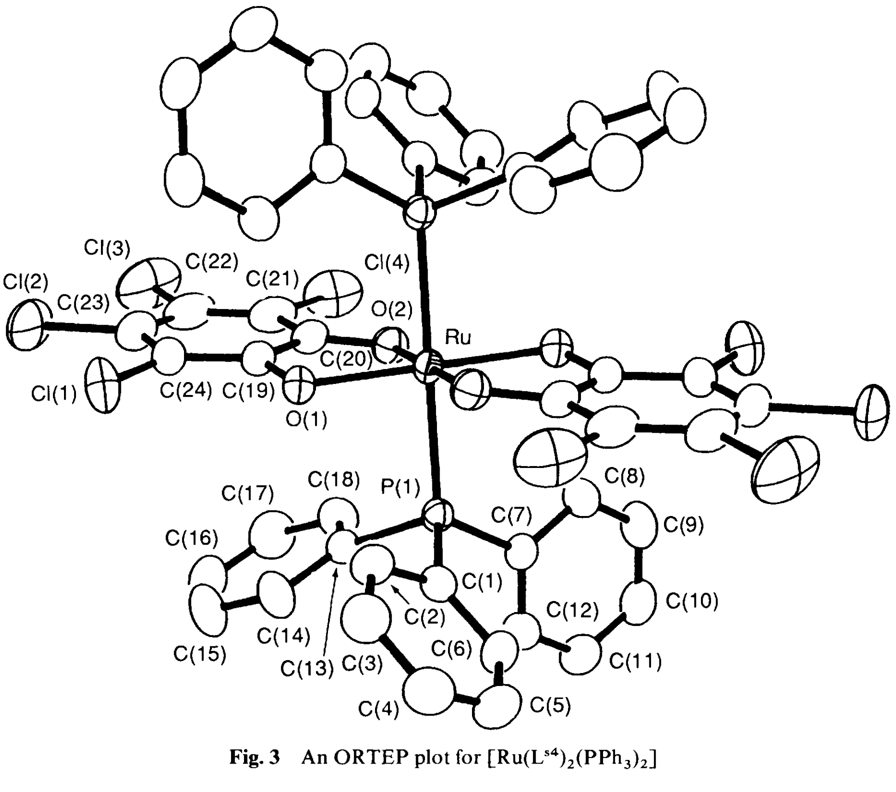


Fig. 3 An ORTEP plot for $[Ru(L^{s4})_2(PPh_3)_2]$

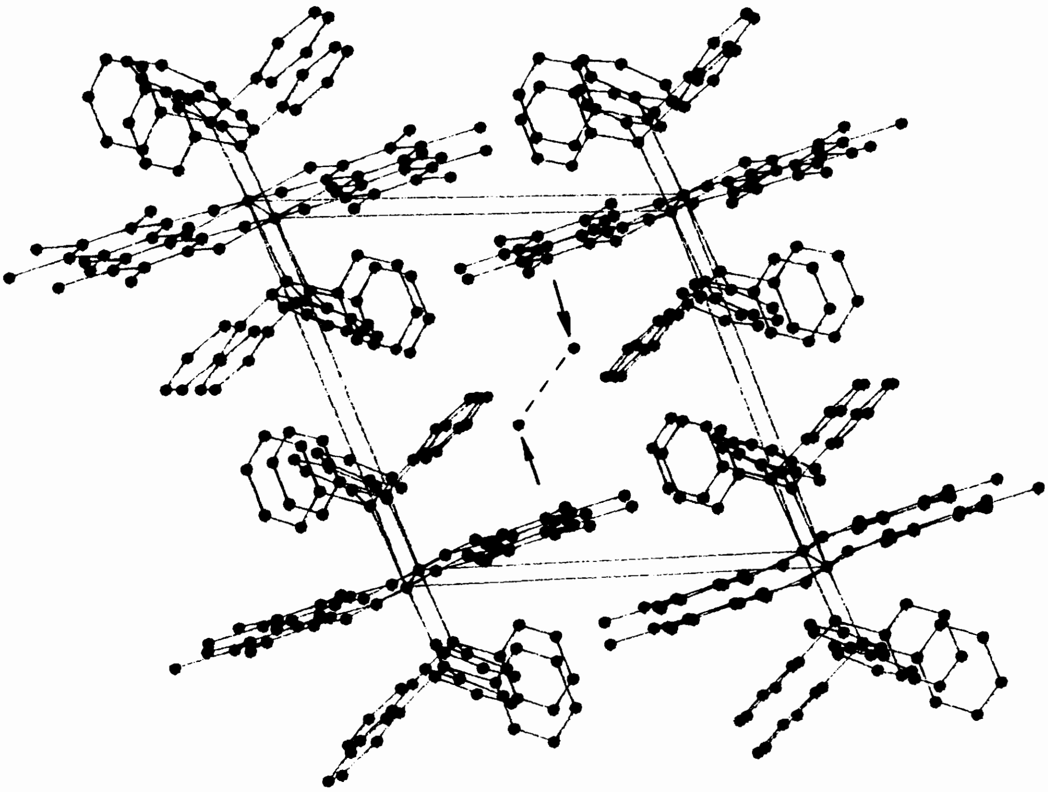


Fig. 4 Packing diagram (down *a* axis) for $[Ru(L^{s4})_2(PPh_3)_2]\cdot 2H_2O$. Water molecules are indicated by arrows

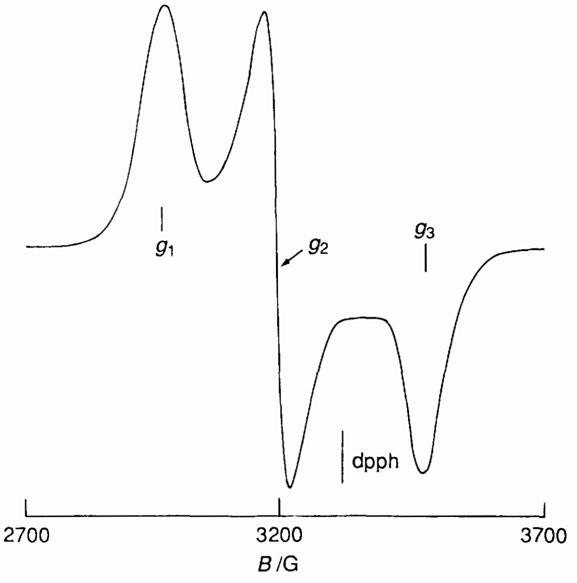


Fig. 5 X-Band ESR spectrum of electrogenerated $[Ru^{III}(L^{c4})_2(PPh_3)_2]$ in dichloromethane–toluene(1:1) glass (77 K)

analysis of numerous physical data has led to the conclusion that the bipy complex and by inference the bupy complex are best described as $[Ru^{II}(L^s)_2D]$ where L^s–L^s magnetic coupling is strong ($S = 0$).[15] The observed C–O distance is longer than 1.29 Å because of d_π–p_{π^*} back-bonding between metal-d_π and semiquinone-p_{π^*} orbitals. Bivalent ruthenium is well documented to be a strong π donor.

In this context, the phosphine complexes are also best formulated as $[Ru(L^s)_2(PPh_3)_2]$ and the spectral results discussed below are consistent with this. We also note that the C–O distance in the phosphine complex is slightly less than that in the amine complexes. This trend is expected since the phosphine ligand is a stronger π acceptor than amines and would therefore allow delocalisation of a smaller fraction of the metal d_π charge into the L^s p_{π^*} orbitals resulting in the observed effect on the C–O distance.

The relatively sharp and strong band system in the near-infrared region (900–1300 nm, Table 1) is characteristic[15] of the Ru^{II}–L^s chromophore and is assigned to the $Ru(d_\pi) \longrightarrow L(p_{\pi^*})$ excitation. The origin of the band near 600 nm is not clear. It can be explained if isomerisation occurs upon dissolution and the *cis* form is also present in solution since the $Ru^{II}(L^s)_2$ moiety is known to show an intense interligand $n \longrightarrow \pi^*$ transition in the *cis* but not in the *trans* isomer.[15] This point is under further scrutiny. We only note here that for the $Ru^{II}(PPh_3)_2$ moiety the *cis* form is electronically (back-bonding) more favoured over the *trans* form.[20]

Redox Series: Evidence for a Ruthenium(III) *Species* $[Ru^{III}(L^c)_2(PPh)_3)_2]^-$.—Of the four cyclic responses (Fig. 2, Table 1) the two at higher potentials correspond to successive oxidation of $[Ru(L^s)_2(PPh_3)_2]$ and the other two to reductions. This is proved by constant potential coulometry at −1.0 V (two-electron reduction) and +1.6 V (two-electron oxidation). Without specifying the site of redox, the series can be represented by equation (1) where the phosphine ligands are

$$[RuL_2]^{2+} \rightleftharpoons [RuL_2]^{+} \rightleftharpoons [Ru^{II}(L^s)_2] \rightleftharpoons [RuL_2]^{-} \rightleftharpoons [RuL_2]^{2-} \quad (1)$$

not shown. In the case of the tetrachloro substituted complex, the product of one-electron reduction can be generated in dichloromethane solution by constant potential electrolysis at −0.3 V. The species is ESR-active and in frozen solution (77 K) the spectrum is strongly anisotropic with *g* values of 2.2474, 2.0659 and 1.9061 (Fig. 5). Clearly in the reduced complex the metal is in the trivalent state which commonly displays this type of spectrum.[1,20,21] Thus $[RuL_2]^-$ is to be formulated as $[Ru^{III}(L^c)_2]^-$. Its formation from $[Ru^{II}(L^s)_2]$ corresponds to a one-electron oxidation at the metal in conjunction with reduction of both ligands to the catecholate (2 electrons). Since the ligand in $[\mathrm{Ru^{III}(L^c)_2}]^-$ is fully reduced, the next stage of reduction must occur at the metal and consequently $[\mathrm{RuL_2}]^{2-}$ is $[\mathrm{Ru^{II}(L^c)_2}]^{2-}$. We have, however, not succeeded in isolating either of the reduced complexes as pure salts.

The nature of the two oxidised complexes could not be experimentally ascertained due to their instability. Comparison with the behaviour of amine complexes,[15] however, suggests that $[\mathrm{RuL_2}]^+$ and $[\mathrm{RuL_2}]^{2+}$ may be $[\mathrm{Ru^{II}(L^s)(L^q)}]^+$ and $[\mathrm{Ru^{II}(L^q)_2}]^{2+}$ respectively. Here successive oxidations of the ligands beyond the semiquinonate stage occur while the metal remains bivalent. This is reasonable since *o*-benzoquinones are strong π acceptors and should stabilise the bivalent state of ruthenium better than higher oxidation states.

In summary the present work taken collectively with results available on $\mathrm{RuL_2}$ complexes with amines as coligands shows that catecholates bind both ruthenium-(II) and -(III) while semiquinonates and quinones bind only the bivalent metal (within the accessible voltage limit).

Experimental

Materials.—Commercial ruthenium trichloride was received from Arora Matthey, Calcutta, and purified by repeated evaporation to dryness with concentrated hydrochloric acid.[22] The compound $[\mathrm{Ru(PPh_3)_3Cl_2}]$ was prepared according to the reported procedure.[23] The catechols were purchased from Aldrich and used as received. The preparation of tetraethylammonium perchlorate and the purification of dichloromethane for electrochemical and spectroscopic work was done as before.[1] All other chemicals and solvents were of commercial grade and were used without further purification.

Physical Measurements.—UV/VIS/NIR spectra were recorded on a Hitachi 330 spectrophotometer. Electrochemical measurements were done on a PAR model 370-4 electrochemistry system. The three-electrode measurements were carried out with the use of a planar Beckman model 39273 platinum-inlay working electrode, a platinum-wire auxiliary electrode, and an aqueous saturated calomel reference electrode (SCE). A platinum wire-gauze working electrode was used in coulometric experiments. All experiments were done under a dinitrogen atmosphere, and the reported potentials are uncorrected for junction contributions. ESR measurements were made with a Varian model 109C E-line X-band spectrometer fitted with a quartz Dewar for measurements at 77 K (liquid dinitrogen). The spectrum was calibrated with the help of diphenylpicrylhydrazyl (dpph) (g = 2.0037). Microanalytical data (C, H, N) were obtained with the use of a Perkin-Elmer model 240 C elemental analyser. Infrared spectra were taken on a Perkin-Elmer 783 spectrophotometer. The magnetic susceptibility was measured on a PAR 155 vibrating-sample magnetometer.

Preparations. *Hydrido(salicylato-*κ^2*O,O′)tris(triphenylphosphine)ruthenium*, $[\mathrm{RuH(}o\text{-}\mathrm{HOC_6H_4CO_2)(PPh_3)_3}]$.—To a warm solution of $[\mathrm{Ru(PPh_3)_3Cl_2}]$ (250 mg, 0.26 mmol) in ethanol (30 cm^3) was added salicylic acid (100 mg, 0.72 mmol) along with a few drops of triethylamine. The mixture was refluxed for 2 h. Upon cooling a yellow microcrystalline solid separated which was collected by filtration, washed thoroughly with ethanol, and dried *in vacuo* over $\mathrm{P_4O_{10}}$, yield 95% (Found: C, 71.40; H, 4.90. Calc. for $\mathrm{C_{61}H_{51}O_3P_3Ru}$: C, 71.40; H, 5.00%); ν_{RuH} at 2010 cm^{-1} ($\mathrm{CH_2Cl_2}$). The previously used method of preparation[18] is more complex.

trans-*Bis(3,4,5,6-tetrachloro-*o*-benzosemiquinonato-*κ^2*O,O′)bis(triphenylphosphine)ruthenium dihydrate, trans-*$[\mathrm{Ru(L^{s4})_2(PPh_3)_2}]\cdot\mathrm{2H_2O}$.—Nitrogen gas was passed for 5 min through a yellow solution of $[\mathrm{RuH(}o\text{-}\mathrm{HOC_6H_4CO_2)(PPh_3)_3}]$ (100 mg, 0.1 mmol) in warm acetone (25 cm^3). To this was added 3,4,5,6-tetrachlorocatechol $\mathrm{H_2L^4}$ (60 mg, 0.24 mmol) and a few drops of triethylamine. The green mixture was warmed under magnetic stirring for 1 h under nitrogen. The solvent was then removed under reduced pressure, the residue dissolved in a small volume of dichloromethane and subjected to chromatography on a silica gel (60–120 mesh) column (20 × 1 cm). With benzene a deep green band was rapidly eluted and was collected. The complex was obtained from the eluent and recrystallised slowly from an undried dichloromethane–hexane mixture, yield 75% (Found: C, 50.15; H, 3.00. Calc. for $\mathrm{C_{48}H_{34}Cl_8O_6P_2Ru}$: C, 49.95; H, 2.95%).

Table 3 Atomic coordinates (× 10^4) for $[\mathrm{Ru(L^4)_2(PPh_3)_2}]\cdot\mathrm{2H_2O}$

Atom	x	y	z
Ru	0	0	0
P(1)	−474(1)	2074(1)	125(1)
Cl(1)	2643(1)	1616(1)	−4275(1)
Cl(2)	558(2)	1812(1)	−5885(1)
Cl(3)	−2795(2)	1231(1)	−4714(1)
Cl(4)	−4063(1)	402(1)	−1916(1)
O(1)	1053(2)	797(2)	−1715(2)
O(2)	−1710(2)	301(2)	−732(2)
C(1)	1161(3)	2535(2)	302(2)
C(2)	2536(3)	2318(3)	−460(3)
C(3)	3847(3)	2638(3)	−384(3)
C(4)	3805(4)	3165(3)	448(3)
C(5)	2438(4)	3372(3)	1221(3)
C(6)	1134(3)	3051(3)	1145(3)
C(7)	−2102(3)	2447(3)	1218(2)
C(8)	−3051(3)	1534(3)	2022(3)
C(9)	−4313(4)	1838(3)	2830(3)
C(10)	−4620(4)	3032(3)	2841(3)
C(11)	−3702(4)	3935(3)	2035(3)
C(12)	−2447(4)	3647(3)	1224(3)
C(13)	−757(3)	3197(2)	−1274(2)
C(14)	304(4)	3995(3)	−2101(3)
C(15)	15(5)	4774(4)	−3162(3)
C(16)	−1307(5)	4771(4)	−3406(3)
C(17)	−2382(5)	3983(4)	−2578(3)
C(18)	−2100(4)	3200(3)	−1520(3)
C(19)	248(4)	877(3)	−2429(2)
C(20)	−1267(3)	595(3)	−1887(3)
C(21)	−2217(4)	725(3)	−2605(3)
C(22)	−1647(6)	1101(3)	−3828(4)
C(23)	−148(6)	1371(3)	−4358(3)
C(24)	804(5)	1279(3)	−3671(3)
O(1W)	4325(4)	3963(3)	6038(3)

The complexes $[\mathrm{Ru(L^{s1})_2(PPh_3)_2}]\cdot\mathrm{2H_2O}$ (Found: C, 65.80; H, 4.80. Calc. for $\mathrm{C_{48}H_{42}O_6P_2Ru}$: C, 65.65; H, 4.80%), $[\mathrm{Ru(L^{s2})_2(PPh_3)_2}]\cdot\mathrm{2H_2O}$ (Found: C, 67.90; H, 5.90. Calc. for $\mathrm{C_{56}H_{58}O_6P_2Ru}$: C, 67.95; H, 5.85), and $[\mathrm{Ru(L^{s3})_2(PPh_3)_2}]\cdot\mathrm{2H_2O}$ (Found: C, 69.80; H, 6.80. Calc. for $\mathrm{C_{64}H_{74}O_6P_2Ru}$: C, 69.75; H, 6.70%) were prepared similarly. Yields varied in the range 70–75%.

X-Ray Structure Determination.—X-Ray quality hydrated single crystals of composition $[\mathrm{Ru(L^4)_2(PPh_3)_2}]\cdot\mathrm{2H_2O}$ were grown by slow diffusion of a dichloromethane solution into hexane.

Crystal data. $\mathrm{C_{48}H_{34}Cl_8O_6P_2Ru}$, M = 1153.4, triclinic, space group $P\bar{1}$, a = 9.430(5), b = 11.689(4), c = 12.551(6) Å, α = 68.58(3), β = 72.07(4), γ = 79.92(4)°, U = 1222(1) Å^3 (by least-squares refinement of 19 accurately measured reflections), Z = 1, D_c = 1.567 g cm^{-3}, dark brown parallelopiped (0.24 × 0.20 × 0.36 mm), μ(Mo-Kα) = 8.60 cm^{-1}, λ = 0.710 73 Å, $F(000)$ = 580.

Data collection and processing. Nicolet R3m/V diffractometer, θ–2θ scan method ($2 \leqslant 2\theta \leqslant 55$), graphite-monochromated Mo-Kα radiation; 5615 independent measured reflections, 4741 observed [$F > 6\sigma(F)$]; corrected for Lorentz and polarisation factors; semiempirical absorption correction (transmission 0.780–0.889). Two standard reflections monitored after every 98 reflections showed no significant variations.

Solution and refinement. The structure was solved using the heavy-atom method, the position of the ruthenium atom being determined from a Patterson map. The remaining non-hydrogen atoms were located from successive Fourier difference syntheses. The structure was subsequently refined by full-matrix least-squares procedures. All non-hydrogen atoms were made anisotropic. Most of the hydrogen atoms appeared in difference Fourier maps; the remainder were included in calculated positions. The isotropic thermal parameter (U) of hydrogen was fixed at 0.08 Å^2. The final R and R' values were 0.0406 and 0.0570 respectively. The function minimised was $\Sigma w(|F| - |F_c|)^2$ with weight $w = 1/[\sigma^2(F) + 0.0007(F)^2]$. The maximum and minimum residual electron densities in the final ΔF map were 0.22 and −0.32 e Å^{-3} respectively. Positional parameters of the non-hydrogen atoms are collected in Table 3. Computations were carried out on a MicroVAX II computer using the SHELXTL-PLUS program system.[24]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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