Reduction–Oxidation Properties of Organotransition-metal Complexes. Part 18.[1] The Stabilisation of Paramagnetic Cyclopentadienylrhodium Compounds *via* *o*-Quinone Complexation: *X*-Ray Crystal Structure of $[\overline{\mathrm{Rh}(\mathrm{PPh_3})\{o\text{-}\mathrm{C(O)OC_6Cl_4O}}\}(\eta\text{-}\mathrm{C_5H_5})]\cdot0.25\mathrm{CH_2Cl_2}$ †

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o-Chloranil (3,4,5,6-tetrachloro-*o*-benzoquinone) and $[\mathrm{Rh(CO)L}(\eta\text{-}\mathrm{C_5R_5})]$ in n-hexane give yellow $[\overline{\mathrm{RhL}\{o\text{-}\mathrm{C(O)OC_6Cl_4O}}\}(\eta\text{-}\mathrm{C_5R_5})]$ (1; R = H or Me, L = CO or $\mathrm{PPh_3}$); an *X*-ray study of (1; R = H, L = $\mathrm{PPh_3}$) as its $\mathrm{CH_2Cl_2}$ solvate reveals that the linking of catecholate and carbonyl ligands has occurred. The Rh atom is therefore co-ordinated by an η-$\mathrm{C_5H_5}$ ligand and a $\mathrm{PPh_3}$ moiety, and in addition forms part of a six-membered $\overline{\mathrm{RhOCCOC}}\mathrm{(O)}$ metallacycle. Mean bond lengths are Rh–P 2.298(3), Rh–C (of metallacycle) 1.994(12), and Rh–O 2.079(6) Å. The metallacycle adopts a distorted boat conformation, partly because it is fused to the aryl $\mathrm{C_6Cl_4}$ moiety. Complex (1; R = H, L = $\mathrm{PPh_3}$) reacts with $\mathrm{HBF_4{\cdot}OEt_2}$ to give $[\mathrm{Rh}\{o\text{-}\mathrm{OC_6Cl_4(OH)}\}\mathrm{(CO)(PPh_3)}(\eta\text{-}\mathrm{C_5H_5})][\mathrm{BF_4}]$, *via* cleavage of the bond linking the CO and catecholate groups. When dissolved in $\mathrm{CH_2Cl_2}$, the carbonyls (1; L = CO) rapidly lose 2 equivalents of CO to give the deep blue or purple chelated catecholato-complexes $[\mathrm{Rh}(o\text{-}\mathrm{O_2C_6Cl_4})(\eta\text{-}\mathrm{C_5R_5})]$ (2; R = H or Me). By contrast, the phosphine derivatives (1; L = $\mathrm{PPh_3}$) slowly decarbonylate to $[\mathrm{RhL}(o\text{-}\mathrm{O_2C_6Cl_4})(\eta\text{-}\mathrm{C_5R_5})]$ (3; R = H or Me, L = $\mathrm{PPh_3}$); related complexes [3; R = H, L = $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$, $\mathrm{P(OPh)_3}$, or pyridine (py); R = Me, L = $\mathrm{PPh_3}$ or $\mathrm{AsPh_3}$] result from the reaction between (2) and L. Complexes (3) undergo reversible one-electron oxidation at a platinum electrode in $\mathrm{CH_2Cl_2}$, and reaction with $\mathrm{AgPF_6}$ yields the stable, paramagnetic salts $[\mathrm{RhL}(o\text{-}\mathrm{O_2C_6Cl_4})(\eta\text{-}\mathrm{C_5R_5})][\mathrm{PF_6}]$ [4; R = H, L = $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$, $\mathrm{P(OPh)_3}$, or py; R = Me, L = $\mathrm{PPh_3}$ or $\mathrm{AsPh_3}$]. The e.s.r. spectra of salts (4) suggest that the unpaired electron resides mainly on the semiquinone ligand, but hyperfine coupling to rhodium and to the donor atom (P or As) of L implies some delocalisation.

Whereas the one-electron oxidation of $[\mathrm{Co(CO)L}(\eta\text{-}\mathrm{C_5H_5})]$ [L = $\mathrm{P(C_6H_{11})_3}$ or $\mathrm{PPh_3}$] gives [2,3] isolable, metal-based radical cations such as $[\mathrm{Co(CO)}\{\mathrm{P(C_6H_{11})_3}\}(\eta\text{-}\mathrm{C_5H_5})][\mathrm{PF_6}]$, electron loss from the analogous rhodium compound, $[\mathrm{Rh(CO)(PPh_3)}(\eta\text{-}\mathrm{C_5H_5})]$, yields the fulvalene derivative $[\mathrm{Rh_2(CO)_2(PPh_3)_2}(\eta^5:\eta'^5\text{-}\mathrm{C_{10}H_8})]^{2+}$.[1,4] The mechanism of formation of this dication, from the highly reactive intermediate $[\mathrm{Rh(CO)(PPh_3)}(\eta\text{-}\mathrm{C_5H_5})]^+$, is unclear, possibly involving either initial metal–metal bond making or cyclopentadienyl ring coupling. We have, therefore, attempted to prepare stable analogues of $[\mathrm{Rh(CO)(PPh_3)}(\eta\text{-}\mathrm{C_5H_5})]^+$ in order to study the dimerisation process in more detail.

ortho-Quinone complexation has been successfully used previously to study both neutral [5] and cationic [1,6] organometallic radicals. We now describe the synthesis of the compounds $[\mathrm{RhL}(o\text{-}\mathrm{O_2C_6Cl_4})(\eta\text{-}\mathrm{C_5R_5})]$ [L = $\mathrm{PPh_3}$, $\mathrm{AsPh_3}$, $\mathrm{P(OPh)_3}$, or pyridine (py), R = H; L = $\mathrm{PPh_3}$ or $\mathrm{AsPh_3}$, R = Me] and their chemical and electrochemical one-electron oxidation to isolable, paramagnetic organorhodium complexes $[\mathrm{RhL}(o\text{-}\mathrm{O_2C_6Cl_4})(\eta\text{-}\mathrm{C_5R_5})][\mathrm{PF_6}]$. We also describe the preparation of $[\overline{\mathrm{RhL}\{o\text{-}\mathrm{C(O)OC_6Cl_4O}}\}(\eta\text{-}\mathrm{C_5R_5})]$ (R = H or Me, L = CO or $\mathrm{PPh_3}$), the *X*-ray crystal structure of one of which (L = $\mathrm{PPh_3}$, R = H) has revealed an unusual chelate comprising linked carbonyl and catecholato-ligands, and its protonation to give $[\mathrm{Rh}\{o\text{-}\mathrm{OC_6H_4(OH)}\}\mathrm{(CO)(PPh_3)}(\eta\text{-}\mathrm{C_5H_5})][\mathrm{BF_4}]$.

Results and Discussion

Synthesis of Complexes (1)—(3).—The addition of 3,4,5,6-tetrachloro-*o*-benzoquinone (*o*-chloranil) to $[\mathrm{Rh(CO)L}(\eta\text{-}\mathrm{C_5R_5})]$ (R = H or Me, L = CO or $\mathrm{PPh_3}$) in n-hexane gives a yellow precipitate which elemental analysis (C and H) (Table 1) suggests to be the simple substitution product $[\mathrm{RhL}(o\text{-}\mathrm{O_2C_6Cl_4})(\eta\text{-}\mathrm{C_5R_5})]$ (1; R = H or Me, L = CO or $\mathrm{PPh_3}$). Although the ^{1}H and ^{31}P n.m.r. spectra are in agreement with this formulation, other properties of compounds (1) suggest it to be incorrect. First, the pale colour contrasts with those of other metal complexes of *o*-quinones;[7] secondly, thermolysis of (1) gives intensely coloured products which are correctly formulated as $[\mathrm{RhL}(o\text{-}\mathrm{O_2C_6Cl_4})(\eta\text{-}\mathrm{C_5R_5})]$ (see below); thirdly, the i.r. spectra of (1) show absorptions associated with the presence of ketonic carbonyl groups (Table 1). In order to determine the structure of compounds (1) fully, a single-crystal *X*-ray diffraction study was carried out on (1; R = H, L = $\mathrm{PPh_3}$) as its $\mathrm{CH_2Cl_2}$ solvate.

The crystal structure of (1; R = H, L = $\mathrm{PPh_3}$)$\cdot0.25\mathrm{CH_2Cl_2}$ contains two crystallographically distinct molecules of $[\overline{\mathrm{Rh(PPh_3)}\{o\text{-}\mathrm{C(O)OC_6Cl_4O}}\}(\eta\text{-}\mathrm{C_5H_5})]$ as well as molecules of $\mathrm{CH_2Cl_2}$ disordered about crystallographic inversion centres. All molecules are separated by normal van der Waals distances; the geometries of the two independent molecules of (1; R = H, L = $\mathrm{PPh_3}$) are shown in Figure 1(*a*) and (*b*) respectively. Selected bond lengths and interbond angles for the structure are given in Table 2. The two independent molecules of (1; R = H, L = $\mathrm{PPh_3}$) are chemically identical,

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† (η-Cyclopentadienyl)(tetrachloro-2-oxidophenoxycarbonyl-C^2O^2)(triphenylphosphine)rhodium(III)–dichloromethane (4/1).

Supplementary data available (No. SUP 56044, 4 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. unit employed: G = 10^{-4} T.

Table 1. Analytical, i.r. carbonyl, and ^{1}H n.m.r. spectral data

Complex	Colour	Yield (%)	Analysis [a] (%)		$\tilde{\nu}$(CO) [b]/cm^{-1}	N.m.r. data [c] (δ/p.p.m.)	
			C	H		^{1}H	^{31}P
$[\overline{\mathrm{Rh(CO)\{\mathit{o}\text{-}C(O)OC_6Cl_4O}}\}(\eta\text{-}\mathrm{C_5H_5})]$	Orange-red	50	32.9 (32.6)	0.9 (1.1)	2 110s, 1 710m (br)	—	—
$[\overline{\mathrm{Rh(CO)\{\mathit{o}\text{-}C(O)OC_6Cl_4O}}\}(\eta\text{-}\mathrm{C_5Me_5})]$	Yellow-brown	79	39.5 (40.0)	2.7 (2.8)	2 095s, 1 711m	—	—
$[\overline{\mathrm{Rh(PPh_3)\{\mathit{o}\text{-}C(O)OC_6Cl_4O}}\}(\eta\text{-}\mathrm{C_5H_5})]$	Yellow	89	51.6 (51.2)	3.2 (2.9)	1 712m	5.24 [5 H, d, $J(^1\mathrm{H}^{31}\mathrm{P})$ 4, $\mathrm{C_5H_5}$], 7.50 (15 H, m, $\mathrm{PPh_3}$)	34.73 [d, $J(^{31}\mathrm{P}^{103}\mathrm{Rh})$ 148.9, $\mathrm{PPh_3}$]
$[\overline{\mathrm{Rh(PPh_3)\{\mathit{o}\text{-}C(O)OC_6Cl_4O}}\}(\eta\text{-}\mathrm{C_5Me_5})]$	Yellow	83	54.6 (54.3)	4.1 (3.9)	1 696m (br)	1.30 [15 H, d, $J(^1\mathrm{H}^{31}\mathrm{P})$ 4, $\mathrm{C_5Me_5}$], 7.40 (15 H, m, $\mathrm{PPh_3}$)	31.56 [d, $J(^{31}\mathrm{P}^{103}\mathrm{Rh})$ 148.9, $\mathrm{PPh_3}$]
$[\mathrm{Rh\{\mathit{o}\text{-}OC_6Cl_4(OH)\}(CO)(PPh_3)(\eta\text{-}C_5H_5)][BF_4]}$	Red-purple	76	45.1 (45.4)	2.6 (2.7)	2 110s	—	—
$[\mathrm{Rh(\mathit{o}\text{-}O_2C_6Cl_4)(\eta\text{-}C_5H_5)}]$	Blue-black	72	31.5 (31.9)	1.5 (1.2)	—	5.60 (5 H, s, $\mathrm{C_5H_5}$)	—
$[\mathrm{Rh(\mathit{o}\text{-}O_2C_6Cl_4)(\eta\text{-}C_5Me_5)}]$	Deep purple	79	40.0 (39.7)	3.4 (3.1)	—	1.87 (15 H, s, $\mathrm{C_5Me_5}$)	—
$[\mathrm{Rh(PPh_3)(\mathit{o}\text{-}O_2C_6Cl_4)(\eta\text{-}C_5H_5)}]$	Purple	85	51.3 (51.5)	3.1 (3.0)	—	5.40 [5 H, d, $J(^1\mathrm{H}^{31}\mathrm{P})$ 2, $\mathrm{C_5H_5}$], 7.30 (15 H, m, $\mathrm{PPh_3}$)	35.93 [d, $J(^{31}\mathrm{P}^{103}\mathrm{Rh})$ 153.8, $\mathrm{PPh_3}$] [d]
$[\mathrm{Rh(AsPh_3)(\mathit{o}\text{-}O_2C_6Cl_4)(\eta\text{-}C_5H_5)}]$	Brown-purple	69	48.2 (48.4)	3.1 (2.8)	—	5.45 (5 H, s, $\mathrm{C_5H_5}$), 7.33 (15 H, m, $\mathrm{AsPh_3}$)	—
$[\mathrm{Rh\{P(OPh)_3\}(\mathit{o}\text{-}O_2C_6Cl_4)(\eta\text{-}C_5H_5)}]$	Brown-purple	72	47.6 (48.1)	3.1 (2.8)	—	5.13 (5 H, s, $\mathrm{C_5H_5}$), 7.22 [15 H, m, $\mathrm{P(OPh)_3}$]	—
$[\mathrm{Rh(py)(\mathit{o}\text{-}O_2C_6Cl_4)(\eta\text{-}C_5H_5)}]$ [e]	Brown-purple	86	38.6 (39.0)	2.2 (2.0)	—	5.48 (5 H, s, $\mathrm{C_5H_5}$), 7.25 (3 H, m, $\mathrm{C_5H_5N}$), 8.60 (2 H, m, $\mathrm{C_5H_5N}$)	—
$[\mathrm{Rh(PPh_3)(\mathit{o}\text{-}O_2C_6Cl_4)(\eta\text{-}C_5Me_5)}]$	Purple	63	54.8 (54.7)	4.0 (4.1)	—	1.35 (15 H, s, $\mathrm{C_5Me_5}$), 7.30 (15 H, m, $\mathrm{PPh_3}$)	—
$[\mathrm{Rh(AsPh_3)(\mathit{o}\text{-}O_2C_6Cl_4)(\eta\text{-}C_5Me_5)}]$	Purple	74	51.0 (51.7)	3.8 (3.8)	—	1.48 (15 H, s, $\mathrm{C_5Me_5}$), 7.25 (15 H, m, $\mathrm{AsPh_3}$)	—
$[\mathrm{Rh(PPh_3)(\mathit{o}\text{-}O_2C_6Cl_4)(\eta\text{-}C_5H_5)][PF_6]}$	Purple	76	42.6 (42.4)	2.8 (2.5)	—	—	—
$[\mathrm{Rh(AsPh_3)(\mathit{o}\text{-}O_2C_6Cl_4)(\eta\text{-}C_5H_5)][PF_6]}$	Purple	63	39.8 (40.3)	2.5 (2.3)	—	—	—
$[\mathrm{Rh\{P(OPh)_3\}(\mathit{o}\text{-}O_2C_6Cl_4)(\eta\text{-}C_5H_5)][PF_6]}$	Purple	61	40.3 (40.1)	2.4 (2.3)	—	—	—
$[\mathrm{Rh(py)(\mathit{o}\text{-}O_2C_6Cl_4)(\eta\text{-}C_5H_5)][PF_6]}$ [f]	Purple	65	29.5 (30.1)	2.1 (1.6)	—	—	—
$[\mathrm{Rh(PPh_3)(\mathit{o}\text{-}O_2C_6Cl_4)(\eta\text{-}C_5Me_5)][PF_6]}$	Black-purple	68	45.0 (45.8)	3.4 (3.4)	—	—	—
$[\mathrm{Rh(AsPh_3)(\mathit{o}\text{-}O_2C_6Cl_4)(\eta\text{-}C_5Me_5)][PF_6]}$	Black	75	43.4 (43.7)	3.3 (3.2)	—	—	—
$[\mathrm{Rh(NCMe)(\mathit{o}\text{-}O_2C_6Cl_4)(\eta\text{-}C_5Me_5)][PF_6]}$ [g]	Purple	46	32.4 (32.2)	3.0 (2.7)	—	—	—

[a] Calculated values in parentheses. [b] In Nujol. [c] In $\mathrm{CDCl_3}$ unless stated otherwise, *J* values in Hz. [d] In $\mathrm{CH_2Cl_2{-}CD_2Cl_2}$. [e] N 2.0 (2.8)%. [f] N 1.4 (2.2)%. [g] N 1.9 (2.1)%.

differing only in the orientation of the phenyl rings of the $\mathrm{PPh_3}$ moiety. Molecular dimensions referred to in the discussion are therefore averaged over the two molecules.

The rhodium atom is not only co-ordinated to $\mathrm{PPh_3}$ and η^5-cyclopentadienyl ligands but also to a chelate formally produced by the joining of the carbon atom of CO with one oxygen atom of the dianion $[\mathrm{O_2C_6Cl_4}]^{2-}$; the chelate bonds to rhodium *via* the second oxygen atom of the catecholate moiety and the carbonyl carbon atom. The metal is, therefore, part of a six-membered metallacycle $\overline{\mathrm{Rh{-}O{-}C{-}C{-}O{-}C}}\mathrm{(O)}$, and its formal oxidation state is III if the o-C(O)–$\mathrm{OC_6Cl_4O}$

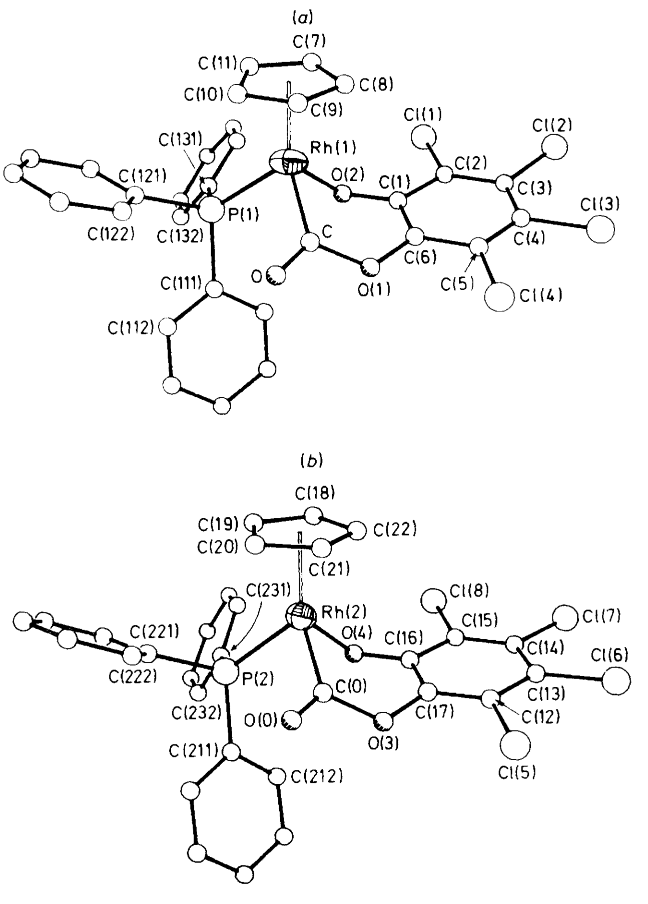
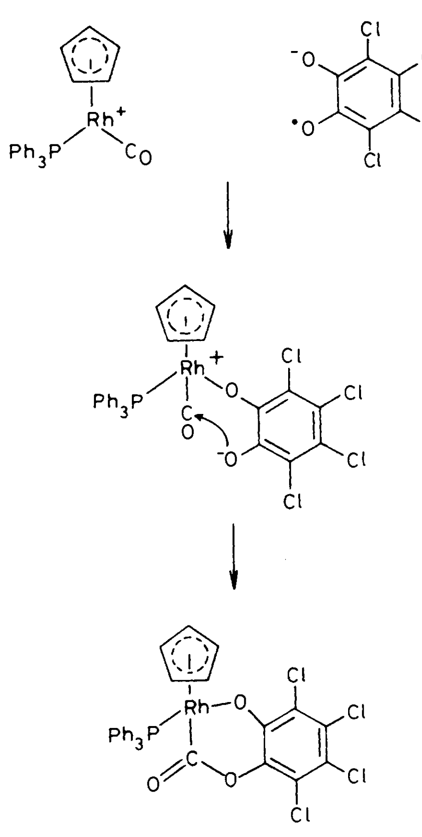


Figure 1. Molecular geometry of [Rh(PPh_3){*o*-C(O)OC_6Cl_4O}(η-C_5H_5)], molecules 1 (*a*) and 2 (*b*), showing atom labelling scheme



Scheme.

ligand is viewed as a dianion containing an aromatic C_6 ring.

The mean rhodium–phosphorus distance of 2.298(3) Å is within the range previously observed for other rhodium–triphenylphosphine complexes, for example [Rh(η-C_2H_4)(PPh_3)(η-C_5Me_5)] [2.223(2) Å],[8] [RhCl(PMe_3)$_2$(PPh_3)] [2.231(1) Å],[9] [Rh(CO)(PPh_3)(acac)] [2.244(2) Å] [10] (acac = acetylacetonate), [RhH(CO)(PPh_3)$_3$] [2.34(1) Å],[11] and [RhH(PPh_3)$_4$] [2.34(5) and 2.39(3) Å].[12] The average rhodium–oxygen distance of 2.079(6) Å is slightly longer than that observed in [Rh(*o*-$O_2C_6H_4$)(η-C_5Me_5)] [2.011(10) Å] [13] but shorter than in the dimeric dication [Rh_2(μ-acac)$_2$(η-C_5Me_5)$_2$]$^{2+}$ [2.102(2) Å].[14]

As in other complexes containing the catecholate moiety, the C_6 ring is aromatic and does not display the localised double bonds of the parent *o*-quinone {*cf.* the structures of [Cr(*o*-$O_2C_6Cl_4$)$_3$],[15] [Mo_2(μ-*o*-$O_2C_6Cl_4$)$_2$(*o*-$O_2C_6Cl_4$)$_4$],[16] [Pd(PPh_3)$_2$(*o*-$O_2C_6Cl_4$)],[17] and [Rh(*o*-$O_2C_6Cl_4$)(η-C_5Me_5)] [13] with that of *o*-$O_2C_6Cl_4$ [18]}. Thus, the (O)C–C(O) bond length in (1; R = H, L = PPh_3) is 1.40(1) Å [*cf.* 1.44(1), 1.39(1), 1.40(1), 1.40(2), and 1.532(5) Å respectively for the complexes listed above] and the other C_6-ring C–C distances vary unsystematically between 1.37(3) and 1.43(2) Å.

The bond lengths within the C(=O)–O unit appear to be localised, with C–O 1.199(16) and C–O(1) 1.412(9) Å close to the standard values for carbon-oxygen double and single bonds respectively [1.23(1) and 1.43(1) Å]. The other C–O distances within the metallacycle are less clear cut in terms of bond order and length [C(1)–O(2) 1.315(9), C(6)–O(1) 1.358(17) Å]. However, they indicate that there is some delocalisation of π-electron density into the aromatic system from the *ortho*-oxygen substituents, resulting in C–O bond orders somewhat greater than one (but <2).

The torsion angles around the metallacycle reflect the enforced coplanarity of the *ortho*-substituents on the aromatic ring, and the strained, highly non-planar, boat-like conformation of the ring [the averaged intra-ring torsion angles about Rh–C, C–O(1), O(1)–C(6), C(6)–C(1), C(1)–O(2), and O(2)–Rh bonds are 32.0, 10.3, −40.7, 2.2, 53.1, and −61.1° respectively]. The angular strains present are no doubt aggravated by the small O(2)–Rh(1)–C angle [86.5(3)°] which is close to the *ca.* 90° angle favoured for the three-legged piano-stool geometry about Rh. The Rh(1)–C length [1.994(12) Å] is similar to that observed for a methoxycarbonyl-rhodium linkage [Rh–C(=O)–OMe 1.96(2) Å] in [Rh_6{C(O)OMe}(CO)$_{15}$]$^-$.[19] Other dimensions of the molecule are unremarkable and typical of similar mononuclear rhodium species (*cf.* examples noted above).

The mechanism for the formation of the ligand [*o*-C(O)OC_6Cl_4O]$^{2-}$ is unclear but the Scheme shows one possibility. Initial electron transfer between *o*-chloranil and [Rh(CO)L(η-C_5R_5)] is followed by coupling of the [Rh(CO)L(η-C_5R_5)]$^+$ and semiquinone radicals to give the zwitterion [Rh$^+$(CO)L(*o*-OC_6Cl_4O$^-$)(η-C_5R_5)]; nucleophilic attack of the anionic oxygen at the carbonyl carbon atom then yields compound (1).

On the basis of the potentials for the irreversible one-electron oxidation of [Rh(CO)L(η-C_5R_5)] (R = H, L = PPh_3, E_p^{ox} = 0.43 V; R = Me, L = CO, E_p^{ox} = 0.49 V, L = PPh_3, E_p^{ox} = 0.07 V in CH_2Cl_2, at a scan rate of 200 mV s^{-1}) and the one-electron reduction of *o*-chloranil to [$O_2C_6Cl_4$]$^-$ (E° = 0.11 V) the initial redox reaction would, in most cases, seem unfavourable. However, the potentials are close enough for small quantities of [Rh(CO)L(η-C_5R_5)]$^+$ and [$O_2C_6Cl_4$]$^-$ to

Table 2. Selected bond lengths (Å) and interbond angles (°) for (1; R = H, L = $\mathrm{PPh_3}$)$\cdot 0.25\mathrm{CH_2Cl_2}$

Rh(1)–P(1)	2.302(3)	Rh(1)–O(2)	2.079(6)	C(7)–C(8)	1.390(22)	C(7)–C(11)	1.352(31)
Rh(1)–C(7)	2.263(27)	Rh(1)–C(8)	2.237(16)	C(8)–C(9)	1.396(29)	C(9)–C(10)	1.386(16)
Rh(1)–C(9)	2.203(10)	Rh(1)–C(10)	2.161(13)	C(10)–C(11)	1.433(32)	C–O	1.207(16)
Rh(1)–C(11)	2.250(16)	Rh(1)–C	1.986(11)	P(2)–C(211)	1.812(12)	P(2)–C(221)	1.824(7)
Rh(2)–P(2)	2.294(3)	Rh(2)–O(4)	2.078(4)	P(2)–C(231)	1.826(9)	C(12)–C(13)	1.401(16)
Rh(2)–C(18)	2.271(15)	Rh(2)–C(19)	2.251(12)	C(12)–C(17)	1.371(9)	C(12)–Cl(5)	1.734(11)
Rh(2)–C(20)	2.168(9)	Rh(2)–C(21)	2.200(13)	C(13)–C(14)	1.398(16)	C(13)–Cl(6)	1.717(7)
Rh(2)–C(22)	2.232(14)	Rh(2)–C(0)	2.001(12)	C(14)–C(15)	1.363(9)	C(14)–Cl(7)	1.718(11)
P(1)–C(111)	1.834(11)	P(1)–C(121)	1.834(11)	C(15)–C(16)	1.403(14)	C(15)–Cl(8)	1.737(11)
P(1)–C(131)	1.828(11)	C(1)–C(2)	1.427(26)	C(16)–C(17)	1.395(14)	C(16)–O(4)	1.309(7)
C(1)–C(6)	1.427(19)	C(1)–O(2)	1.322(9)	C(17)–O(3)	1.373(12)	O(3)–C(0)	1.423(7)
C(2)–C(3)	1.413(17)	C(2)–Cl(1)	1.720(19)	C(18)–C(19)	1.365(14)	C(18)–C(22)	1.425(14)
C(3)–C(4)	1.376(31)	C(3)–Cl(2)	1.736(26)	C(19)–C(20)	1.404(18)	C(20)–C(21)	1.399(13)
C(4)–C(5)	1.365(28)	C(4)–Cl(3)	1.720(11)	C(21)–C(22)	1.390(20)	C(0)–O(0)	1.192(13)
C(5)–C(6)	1 428(12)	C(5)–Cl(4)	1.654(16)	C(23)–Cl(9)	1.702(26)	C(23)–Cl(9a)	1.589(23)
C(6)–O(1)	1.341(17)	O(1)–C	1.401(9)				

P(1)–Rh(1)–O(2)	87.1(2)	P(1)–Rh(1)–C(7)	126.4(3)	C(111)–P(1)–C(121)	103.8(6)	Rh(1)–P(1)–C(131	112.3(4)
O(2)–Rh(1)–C(7)	99.1(6)	P(1)–Rh(1)–C(8)	159.2(3)	C(111)–P(1)–C(131)	102.1(4)	C(121)–P(1)–C(131)	107.4(4)
O(2)–Rh(1)–C(8)	104.8(4)	C(7)–Rh(1)–C(8)	36.0(6)	C(2)–C(1)–C(6)	116.3(9)	C(2)–C(1)–O(2)	121.2(12)
P(1)–Rh(1)–C(9)	134.6(5)	O(2)–Rh(1)–C(9)	138.2(5)	C(6)–C(1)–O(2)	122.4(13)	C(1)–C(2)–C(3)	120.0(18)
C(7)–Rh(1)–C(9)	59.9(7)	C(8)–Rh(1)–C(9)	36.6(7)	C(1)–C(2)–Cl(1)	115.9(8)	C(3)–C(2)–Cl(1)	124.1(18)
P(1)–Rh(1)–C(10)	101.8(4)	O(2)–Rh(1)–C(10)	159.1(7)	C(2)–C(3)–C(4)	120.0(20)	C(2)–C(3)–Cl(2)	116.5(18)
C(7)–Rh(1)–C(10)	60.3(8)	C(8)–Rh(1)–C(10)	61.6(6)	C(4)–C(3)–Cl(2)	123.4(11)	C(3)–C(4)–C(5)	124.3(12)
C(9)–Rh(1)–C(10)	37.0(4)	P(1)–Rh(1)–C(11)	98.7(4)	C(3)–C(4)–Cl(3)	117.0(15)	C(5)–C(4)–Cl(3)	118.7(14)
O(2)–Rh(1)–C(11)	122.6(6)	C(7)–Rh(1)–C(11)	34.9(8)	C(4)–C(5)–C(6)	115.8(13)	C(4)–C(5)–Cl(4)	123.8(8)
C(8)–Rh(1)–C(11)	60.6(6)	C(9)–Rh(1)–C(11)	61.5(5)	C(6)–C(5)–Cl(14)	120.3(13)	C(1)–C(6)–C(5)	123.6(14)
C(10)–Rh(1)–C(11)	37.8(8)	P(1)–Rh(1)–C	89.4(3)	C(1)–C(6)–O(1)	119.6(8)	C(5)–C(6)–O(1)	116.7(12)
O(2)–Rh(1)–C	85.2(3)	C(7)–Rh(1)–C	144.0(4)	C(6)–O(1)–C	123.4(9)	Rh(1)–O(2)–C(1)	108.7(5)
C(8)–Rh(1)–C	108.2(5)	C(9)–Rh(1)–C	93.2(5)	Rh(1)–C–O(1)	119.1(9)	Rh(1)–C–O	127.6(5)
C(10)–Rh(1)–C	113.4(6)	C(11)–Rh(1)–C	151.1(6)	O(1)–C–O	113.3(8)	Rh(2)–P(2)–C(211)	117.1(2)
P(2)–Rh(2)–O(4)	84.6(2)	P(2)–Rh(2)–C(18)	121.4(2)	Rh(2)–P(2)–C(221)	111.6(3)	C(211)–P(2)–C(221)	105.4(5)
O(4)–Rh(2)–C(18)	100.2(3)	P(2)–Rh(2)–C(19)	98.6(3)	Rh(2)–P(2)–C(231)	113.9(4)	C(211)–P(2)–C(231)	103.1(5)
O(4)–Rh(2)–C(19)	127.7(4)	C(18)–Rh(2)–C(19)	35.1(4)	C(221)–P(2)–C(231)	104.5(4)	C(13)–C(12)–C(17)	121.4(10)
P(2)–Rh(2)–C(20)	107.3(3)	O(4)–Rh(2)–C(20)	160.6(5)	C(13)–C(12)–Cl(5)	119.8(6)	C(17)–C(12)–Cl(5)	118.8(9)
C(18)–Rh(2)–C(20)	60.6(5)	C(19)–Rh(2)–C(20)	37.0(5)	C(12)–C(13)–C(14)	118.0(7)	C(12)–C(13)–Cl(6)	120.5(8)
P(2)–Rh(2)–C(21)	142.2(3)	O(4)–Rh(2)–C(21)	133.1(3)	C(14)–C(13)–Cl(6)	121.5(8)	C(13)–C(14)–C(15)	119.9(10)
C(18)–Rh(2)–C(21)	61.2(5)	C(19)–Rh(2)–C(21)	61.5(4)	C(13)–C(14)–Cl(7)	118.2(6)	C(15)–C(14)–Cl(7)	121.9(9)
C(20)–Rh(2)–C(21)	37.3(3)	P(2)–Rh(2)–C(22)	157.8(3)	C(14)–C(15)–C(16)	122.7(10)	C(14)–C(15)–Cl(8)	120.3(9)
O(4)–Rh(2)–C(22)	102.1(3)	C(18)–Rh(2)–C(22)	36.9(4)	C(16)–C(15)–Cl(8)	117.0(5)	C(15)–C(16)–C(17)	116.8(6)
C(19)–Rh(2)–C(22)	60.5(4)	C(20)–Rh(2)–C(22)	61.3(4)	C(15)–C(16)–O(4)	121.0(9)	C(17)–C(16)–O(4)	122.1(9)
C(21)–Rh(2)–C(22)	36.5(5)	P(2)–Rh(2)–C(0)	88.7(3)	C(12)–C(17)–C(16)	121.0(9)	C(12)–C(17)–O(3)	117.5(9)
O(4)–Rh(2)–C(0)	87.7(3)	C(18)–Rh(2)–C(0)	149.3(3)	C(16)–C(17)–O(3)	121.4(6)	C(17)–O(3)–C(0)	122.8(8)
C(19)–Rh(2)–C(0)	144.2(3)	C(20)–Rh(2)–C(0)	107.4(5)	Rh(2)–O(4)–C(16)	109.3(4)	O(3)–C(0)–O(0)	114.1(9)
C(21)–Rh(2)–C(0)	91.8(5)	C(22)–Rh(2)–C(0)	112.5(4)	Rh(2)–C(0)–O(0)	129.0(5)	Rh(2)–C(0)–O(3)	116.9(7)
Rh(1)–P(1)–C(111)	118.4(2)	Rh(1)–P(1)–C(121)	111.9(3)	Cl(9)–C(23)–Cl(9a) *	87.5(12)		

* Cl(9a) is related to Cl(9) by 2 − *x*, 2 − *y*, −*z*.

be generated. Once formed, the paramagnetic species can be irreversibly coupled, allowing the overall reaction to proceed.

The bond linking the carbonyl and catecholate units in compound (1) is cleaved on reaction with acid. Treatment of a suspension of (1; R = H, L = $\mathrm{PPh_3}$) in diethyl ether with $\mathrm{HBF_4{\cdot}OEt_2}$ gave a red-purple solid which is formulated as $[\mathrm{Rh}\{o\text{-}\mathrm{OC_6Cl_4(OH)}\}(\mathrm{CO})(\mathrm{PPh_3})(\eta\text{-}\mathrm{C_5H_5})][\mathrm{BF_4}]$ (Figure 2) on the basis of elemental analysis and i.r. spectroscopy (Table 1). Thus, absorptions at 3 400(br), 2 110s, and 1 110s(br), assigned to $\tilde{\nu}$(OH), $\tilde{\nu}$(CO), and $\tilde{\nu}$(BF) respectively, confirm the presence of a cationic carbonyl complex and the protonation of one of the oxygen atoms of the chelate ligand of compound (1). Further spectroscopic characterisation was precluded by the immediate decomposition of the complex in solvents in which it dissolves.

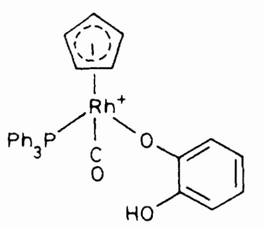


Figure 2. Proposed structure of $[\mathrm{Rh}\{o\text{-}\mathrm{OC_6Cl_4(OH)}\}(\mathrm{CO})(\mathrm{PPh_3})(\eta\text{-}\mathrm{C_5H_5})][\mathrm{BF_4}]$, chlorine atoms being omitted

On dissolving compounds (1) in $\mathrm{CH_2Cl_2}$, complete loss of CO from the co-ordinated $o\text{-}\mathrm{C(O)OC_6Cl_4O}$ ligand occurs, the final product depending on L. The carbonyls (1; R = H or Me, L = CO) rapidly lose the metal-bound carbon monoxide also, to give deep blue (R = H) or purple (R = Me) solutions from which high yields of the catecholate complexes $[\mathrm{Rh}(o\text{-}\mathrm{O_2C_6Cl_4})(\eta\text{-}\mathrm{C_5R_5})]$ (2; R = H or Me) are isolable. The cyclopentadienyl derivative (2; R = H) may also be prepared directly from $[\mathrm{Rh}(\eta^4\text{-cod})(\eta\text{-}\mathrm{C_5H_5})]$ (cod = cyclo-octa-1,5-diene) and *o*-chloranil, and related species $[\mathrm{Rh}(o\text{-}\mathrm{O_2C_6H_3R})(\eta\text{-}\mathrm{C_5Me_5})]$ (R = H, Cl, Me, or $\mathrm{Bu^t}$) have previously been

Table 3. Visible spectra [a] of $[RhL(o\text{-}O_2C_6Cl_4)(\eta\text{-}C_5H_5)]$

L	$\lambda_{max.}$/nm	$\varepsilon_{max.}$/dm^3 mol^{-1} cm^{-1}
—	609	10 700
PPh_3	536	930
$AsPh_3$ [b]	558	830
$P(OPh)_3$	508	724
py [b]	475	560

[a] In CH_2Cl_2. [b] In the presence of excess of ligand.

synthesised from $[Rh_2Cl_4(\eta\text{-}C_5Me_5)_2]$ and the disodium salt of the appropriate catechol.[13]

The phosphine complexes (1; L = PPh_3) undergo chelate-ligand decarbonylation in polar solvents, albeit more slowly than (1; L = CO), affording purple $[RhL(o\text{-}O_2C_6Cl_4)(\eta\text{-}C_5R_5)]$ (3; R = H or Me, L = PPh_3). These species, formally Lewis-base adducts of (2), may also be prepared by adding the ligand [L = PPh_3, $AsPh_3$, $P(OPh)_3$, or py; R = H or Me] to solutions of (2; R = H or Me) in CH_2Cl_2.

The adducts (3) are readily isolable as crystalline solids, and are fully characterised by elemental analysis (Table 1). However, u.v.-visible spectroscopy (and cyclic voltammetry, see below) revealed that they are substitution labile in solution [equation (i)]. Thus, CH_2Cl_2 solutions of [3; L = $AsPh_3$, py, or $P(OPh)_3$] show absorptions due not only to the adduct but

$$\underset{(3)}{[RhL(o\text{-}O_2C_6Cl_4)(\eta\text{-}C_5R_5)]} \rightleftharpoons \underset{(2)}{[Rh(o\text{-}O_2C_6Cl_4)(\eta\text{-}C_5R_5)]} + L \quad \text{(i)}$$

also to (2) (Table 3). Authentic electronic spectra of compounds (3) may be recorded on addition of an excess of the ligand L, and it should be noted that the ^1H n.m.r. spectra reported for (3), in Table 1, were also measured under these conditions.

Maitlis and co-workers [13] have previously noted the lability of $[Rh(PPh_3)(o\text{-}O_2C_6H_3X)(\eta\text{-}C_5Me_5)]$ (X = H, Me, or Cl), and also that the visible absorption bands of the adducts are less intense than those of $[Rh(o\text{-}O_2C_6H_3X)(\eta\text{-}C_5Me_5)]$ but occur at higher energy; similar trends are apparent for compounds (2) and (3). It should also be noted that both (2) and (3) show intense ($\varepsilon_{max.}$ *ca.* 10^4 dm^3 mol^{-1} cm^{-1}) absorptions at 235—240 nm, assigned to π–π^* transitions associated with the catecholate ligands.

The Cyclic Voltammetry of Complexes (1)—(3).—Cyclic voltammetry shows that complexes (1)—(3) undergo electron-transfer reactions at a platinum-wire electrode in CH_2Cl_2 (Table 4). The electrochemistry of (3; L = PPh_3) is the best defined, with each complex oxidised in two, one-electron steps. Although both processes are diffusion controlled ($i/\sqrt{v}$ is constant for scan rates, v, between 50 and 500 mV s^{-1}), only the first is fully reversible (i_{ox}/i_{red} close to unity for the scan rates given). The second oxidation wave, corresponding to the formation of $[Rh(PPh_3)(o\text{-}O_2C_6Cl_4)(\eta\text{-}C_5R_5)]^{2+}$ and occurring at a much more positive potential, is either totally irreversible (R = H), or partially reversible (R = Me) with i_{ox}/i_{red} reaching 1.0 with scan rates in excess of 200 mV s^{-1}.

The redox chemistry of [3; R = H, L = $AsPh_3$, $P(OPh)_3$, or py; R = Me, L = $AsPh_3$] is complicated by the equilibrium (i). Although these complexes are similar in behaviour to the PPh_3 derivatives discussed above, their cyclic voltammograms clearly show the presence of waves due to (2).

Table 4. Cyclic voltammetric [a] data for $[Rh(o\text{-}O_2C_6Cl_4)(\eta\text{-}C_5H_5)]$ (2) and $[RhL(o\text{-}O_2C_6Cl_4)(\eta\text{-}C_5R_5)]^Z$ (3; Z = 0) and (4; Z = 1)

Complex	L	R	Z	Process	E/V [b]
(2)	—	H	0	$0 \longrightarrow -1$	−0.58(R)
				$0 \longrightarrow +1$	1.06(I)
				$+1 \longrightarrow +2$	1.27(I)
(2)	—	Me	0	$0 \longrightarrow -1$	−1.08(R)
				$0 \longrightarrow +1$	0.80(R)
				$+1 \longrightarrow +2$	1.06(I)
(3)	PPh_3	H	0	$0 \longrightarrow +1$	0.54(R)
				$+1 \longrightarrow +2$	1.38(I)
(4)	PPh_3	H	1	$+1 \longrightarrow 0$	0.54(R)
				$+1 \longrightarrow +2$	1.37(I)
(3)	$AsPh_3$	H	0	$0 \longrightarrow +1$	0.55(R)
				$+1 \longrightarrow +2$	1.39(I)
(4)	$AsPh_3$	H	1	$+1 \longrightarrow 0$	0.55(R)
				$+1 \longrightarrow +2$	1.39(I)
(3)	$P(OPh)_3$	H	0	$0 \longrightarrow +1$	0.65(R)
				$+1 \longrightarrow +2$	1.47(I)
(4)	$P(OPh)_3$	H	1	$+1 \longrightarrow 0$	0.65(R)
				$+1 \longrightarrow +2$	1.47(I)
(3)	py	H	0	$0 \longrightarrow +1$	0.61(R)
				$+1 \longrightarrow +2$	1.32(I)
(4)	py	H	1	$+1 \longrightarrow 0$	0.61(R)
				$+1 \longrightarrow +2$	1.31(I)
(3)	PPh_3	Me	0	$0 \longrightarrow +1$	0.39(R)
				$+1 \longrightarrow +2$	1.28(R)
(4)	PPh_3	Me	1	$+1 \longrightarrow 0$	0.39(R)
				$+1 \longrightarrow +2$	1.25(R)
(3)	$AsPh_3$	Me	0	$0 \longrightarrow +1$	0.41(R)
				$+1 \longrightarrow +2$	1.26(R)
(4)	$AsPh_3$	Me	1	$+1 \longrightarrow 0$	0.43(R)
				$+1 \longrightarrow +2$	1.25(R)

[a] In CH_2Cl_2. [b] Potentials are relative to the saturated calomel electrode. Under the conditions used, $E^{\ominus}$ for the oxidation of ferrocene is 0.43 V. R = Reversible, I = irreversible at a scan rate, v, of 200 mV s^{-1}.

In Figure 3(*a*) the cyclic voltammogram of compound (3; R = Me, L = $AsPh_3$) not only shows the reversible (or nearly so) oxidation waves of the adduct (centred at 0.41 and 1.26 V) but also two smaller waves at 0.81 and 1.06 V due to (2; R = Me). Figure 3(*b*), the cyclic voltammogram of compound (2; R = Me), clearly identifies the smaller waves, and Figure 3(*c*) shows that the addition of $AsPh_3$ to the solution causes the equilibrium (i) to shift in favour of (3; R = Me, L = $AsPh_3$). Although the two oxidation waves of compound (2; R = H) are both irreversible, the first of (2; R = Me) is reversible and the second is partially so with i_{ox}/i_{red} increasing from 0.65 to 0.93 as v is increased from 50 to 200 mV s^{-1}. In addition, (2; R = H or Me) shows a partially reversible reduction wave implying some stability for the anion $[Rh(o\text{-}O_2C_6Cl_4)(\eta\text{-}C_5R_5)]^-$; sulphur-ligand analogues, namely $[M(S_2C_2R_2)(\eta\text{-}C_5H_5)]^-$ (R = CF_3, M = Co or Rh; [20] R = CN, M = Co [21]), have been generated in solution and, for the cobalt complexes, characterised by e.s.r. spectroscopy.

The electrochemistry of compounds (1) is also of interest in that oxidatively induced ligand decarbonylation is evident. Figure 4(*a*) shows two scans of the cyclic voltammogram of (1; R = Me, L = PPh_3), between 0.23 and 0.97 V, at 100 mV s^{-1}. On the first scan the irreversible oxidation wave at 0.78 V is accompanied by a product reduction wave at 0.35 V; on the second scan it is apparent that the wave at 0.35 V is part of a reversible system centred at 0.39 V. The new wave is clearly due to the formation of (3; R = Me, L = PPh_3) in that addition of this species to the solution of (1; R = Me, L = PPh_3) enhances the wave height, as shown in Figure 4(*b*).

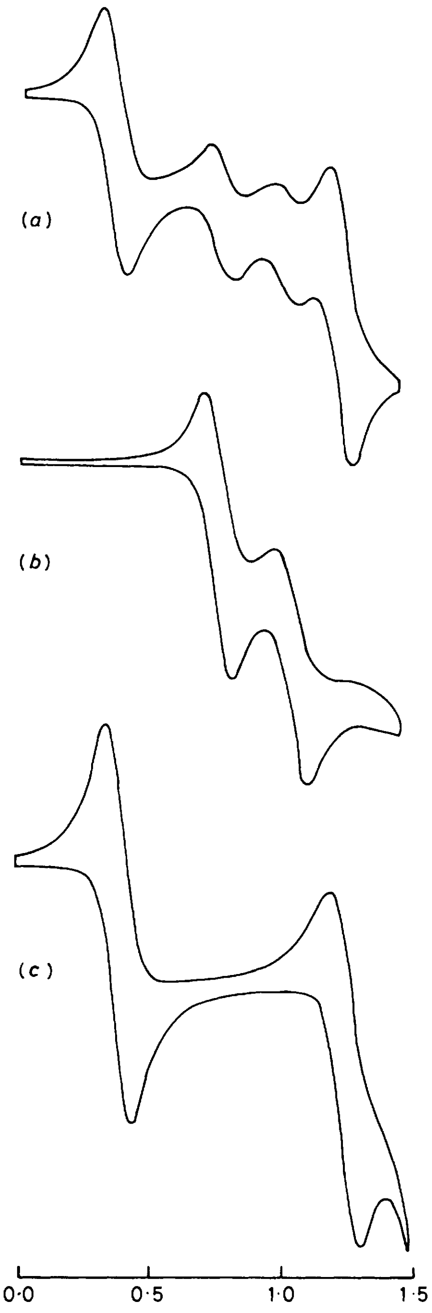


Figure 3. Cyclic voltammograms, from 0 to 1.5 V at a scan rate of 100 mV s^{-1}, in CH_2Cl_2, (*a*) of compound (3; R = Me, L = $AsPh_3$), (*b*) of (2; R = Me), and (*c*) of a 1 : 1 mixture of (3; R = Me, L = $AsPh_3$) and $AsPh_3$

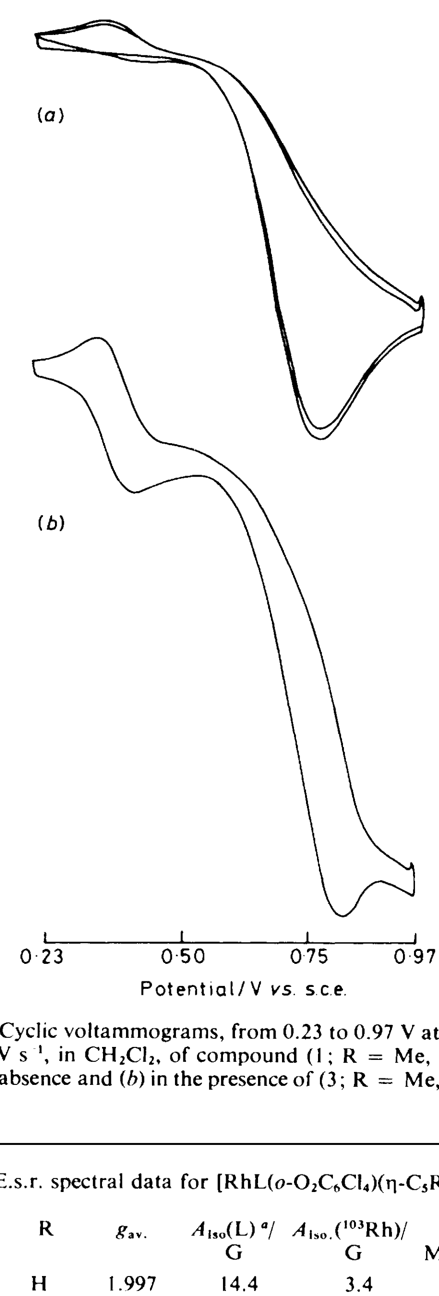


Figure 4. Cyclic voltammograms, from 0.23 to 0.97 V at a scan rate of 100 mV s^{-1}, in CH_2Cl_2, of compound (1; R = Me, L = PPh_3), (*a*) in the absence and (*b*) in the presence of (3; R = Me, L = PPh_3)

Table 5. E.s.r. spectral data for $[RhL(o\text{-}O_2C_6Cl_4)(\eta\text{-}C_5R_5)]^+$

L	R	$g_{av.}$	$A_{iso}(L)$ [a]/ G	$A_{iso.}(^{103}Rh)$/ G	Multiplicity [b]
PPh_3	H	1.997	14.4	3.4	dd
$AsPh_3$	H	1.997	20.8	3.1	qd
$P(OPh)_3$	H	2.000	20.8	2.4	dd
py	H	2.003	—	—	s
PPh_3	Me	1.999	16.7	3.3	dd
$AsPh_3$	Me	2.000	22.8	3.1	qd
MeCN	Me	2.005	—	—	s

[a] ^{31}P or ^{75}As coupling. [b] s = Singlet, d = doublet, and q = quartet.

The Chemical Oxidation of Complexes (1)—(3).—The cyclic voltammetric results outlined above suggest that chemical one-electron oxidation of (3) to cations analogous to $[Co\{P(C_6H_{11})_3\}(o\text{-}O\text{-}O)(\eta\text{-}C_5H_5)]^+$ (O–O = *o*-chloranil, phenanthrenequinone, naphthoquinone, *etc.*)[2] should be readily achieved. Although the $E^{\ominus}$ values (Table 4) are relatively high {*cf.* $[Fe(\eta\text{-}C_5H_5)_2]$ oxidation at 0.43 V}, the salts $[RhL(o\text{-}O_2C_6Cl_4)(\eta\text{-}C_5R_5)][PF_6]$ [4; L = PPh_3, $AsPh_3$, $P(OPh)_3$, or py, R = H; L = PPh_3 or $AsPh_3$, R = Me] can be prepared from equivalent quantities of (3) and $AgPF_6$ in CH_2Cl_2. Alternatively, and as suggested by cyclic voltammetry (see above), (4; R = H or Me, L = PPh_3) can be made directly from (1; R = H or Me, L = PPh_3) and silver(I) salts.

In contrast to $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$, the deep purple salts (4) are air-stable crystalline solids, readily characterised by elemental analysis (Table 1), by cyclic voltammetry, which showed reversible one-electron reduction waves with $E^{\ominus}$ values (Table 4) identical to those for the one-electron oxidation of (3), and by e.s.r. spectroscopy (Table 5).

The isotropic *g* values of compounds (4) are close to the free-electron value, and to that of the anion radical of *o*-

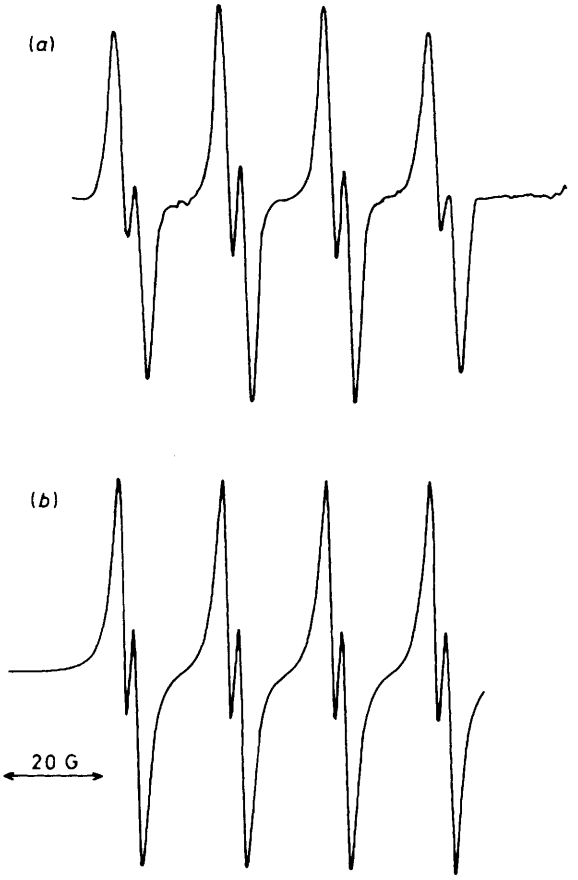


Figure 5. Observed (a) and simulated (b) CH_2Cl_2 solution e.s.r. spectra of $[Rh(AsPh_3)(o\text{-}O_2C_6Cl_4)(\eta\text{-}C_5H_5)][PF_6]$

chloranil itself ($g = 2.0053$).[22] The cations (4) are, therefore, probably best regarded as rhodium(III) complexes of a semiquinone ligand. However, some delocalisation of the unpaired electron density is evident in that hyperfine coupling to both the rhodium atom and to the donor atom (P or As) of the ligand L is readily observed. Thus, for example, the e.s.r. spectrum of compound (4; R = H, L = $AsPh_3$), shown together with the computer-simulated spectrum in Figure 5, consists of a quartet of doublets with $A_{iso}(^{103}Rh) = 3.1$ G and $A_{iso}(^{75}As) = 20.8$ G.

The cyclic voltammogram of (2; R = Me) implied the existence of a stable cation $[Rh(o\text{-}O_2C_6Cl_4)(\eta\text{-}C_5Me_5)]^+$, at least on the time-scale of the electrochemical experiment. However, chemical oxidation of (2; R = Me) with $[NO][PF_6]$ in MeCN, followed by recrystallisation of the product from CH_2Cl_2–n-hexane, gave only the paramagnetic adduct (4; R = Me, L = MeCN). Like (4; L = P or As donor), the e.s.r. spectrum of the nitrile complex implied unpaired electron density localised largely on the O-donor ligand; like (4; R = H, L = py), however, the spectrum showed no evidence for ^{14}N hyperfine coupling.

The synthesis of the stable, paramagnetic cations (4) was designed to aid a study of the mechanism of the dimerisation of $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$. While the latter is formally the parent of (4), the localisation of the unpaired electron on the semiquinone ligand renders the reactivity of the two species totally dissimilar. Thus, we have been unable to induce the dimerisation of (4) either by deprotonation or by thermal methods, and the reactions with halide or phosphine nucleophiles lead only to the reduction of (4) to (3). Our investigations of the formation of fulvalene derivatives *via* the oxidation of $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ have, therefore, now turned to analogues such as $[RhL(L')(\eta\text{-}C_5R_5)]$ (L = L′ = CO or P donor, R = Me or Ph).

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Unless otherwise stated, products were purified by dissolution in CH_2Cl_2, filtration, addition of n-hexane, and partial evaporation of the solvent mixture *in vacuo* to induce precipitation. Unless otherwise stated, the complexes are air-stable, dissolving in polar solvents such as acetone and CH_2Cl_2 to give solutions which slowly decompose in air.

The complexes $[Rh(CO)_2(\eta\text{-}C_5R_5)]$ (R = H [23] or Me [24]) $[Rh(CO)(PPh_3)(\eta\text{-}C_5R_5)]$,[25] and $[Rh(\eta^4\text{-}cod)(\eta\text{-}C_5H_5)]$ [26] (cod = cyclo-octa-1,5-diene), were prepared by published methods. *o*-Chloranil and $HBF_4{\cdot}OEt_2$ were purchased from the Aldrich Chemical Co. and BDH Chemicals Ltd. respectively.

Cyclic voltammetry was carried out using an AMEL Electrochemolab in conjunction with a three-electrode cell. The auxiliary and working electrodes were platinum wires and the reference was an aqueous saturated calomel electrode (s.c.e.) separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl. Solutions were 0.5×10^{-3} mol dm^{-3} in complex and 0.1 mol dm^{-3} in $[NBu^n_4][PF_6]$ as supporting electrolyte. Under these conditions, $E^\ominus$ for the couple $[Fe(\eta\text{-}C_5H_5)_2]^+$–$[Fe(\eta\text{-}C_5H_5)_2]$ is 0.43 V.

Infrared spectra were recorded on Perkin-Elmer PE257 or 297 spectrometers and calibrated against the absorption band of polystyrene at 1 601 cm^{-1}. U.v.–visible spectra were obtained on a Unicam SP1700 ultraviolet spectrophotometer. Proton n.m.r. spectra were recorded on a JEOL PMX60 instrument and calibrated against $SiMe_4$ as an internal reference, phosphorus-31 n.m.r. spectra on a JEOL FX90Q instrument calibrated against 85% H_3PO_4 as an external reference. *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} solution of $K_2[NO(SO_3)_2]$ (Fremy's salt) in water containing 10^{-2} mol dm^{-3} K_2CO_3 as a buffer. The spectra were simulated on an Apple Microcomputer using a PASCAL program written [27] by Dr. J. P. Maher and Mr. A. P. Grigg of the Department of Inorganic Chemistry, University of Bristol.

Mass spectra were recorded on an AEI MS902 spectrometer. Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Carbonyl(η-pentamethycyclopentadienyl)(triphenylphosphine)rhodium, $[Rh(CO)(PPh_3)(\eta\text{-}C_5Me_5)]$.—A mixture of $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$ (2.3 g, 7.8 mmol) and PPh_3 (2.0 g, 7.6 mmol) in n-heptane (125 cm^3) was heated under reflux for 3 d. Cooling to −78 °C gave an orange precipitate which was dissolved in hot hexane and filtered. The filtrate was cooled slowly to −20 °C to give orange-red crystals which were washed with methanol (2 × 10 cm^3) and dried, yield 2.2 g (54%) (Found: C, 65.4; H, 5.4. $C_{29}H_{30}OPRh$ requires C, 65.9; H, 5.7%), ν(CO) (CH_2Cl_2) = 1 924 cm^{-1}; ^{31}P n.m.r., δ 52.74 p.p.m. [d, $J(^{31}P^{103}Rh)$ 197.75 Hz].

Reactions of o-*Chloranil.—With* $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$: *synthesis of* $[Rh(CO)\{o\text{-}C(O)OC_6Cl_4O\}(\eta\text{-}C_5Me_5)]$ (1; R = Me, L = CO). To a stirred solution of $[Rh(CO)_2(\eta\text{-}C_5Me_5)]$

Table 6. Atomic co-ordinates ($\times 10^4$) for compound (1; R = H, L = PPh_3)$\cdot 0.25CH_2Cl_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh(1)	2 612(1)	5 658(1)	2 764(1)	P(2)	7 965(1)	3 393(2)	1 582(2)
Rh(2)	7 391(1)	4 870(1)	2 505(1)	C(211)	8 504(5)	3 162(6)	2 426(6)
P(1)	3 661(1)	7 184(2)	3 492(2)	C(212)	9 293(5)	3 843(7)	3 119(7)
C(111)	4 286(5)	7 245(6)	2 535(6)	C(213)	9 759(6)	3 709(8)	3 781(7)
C(112)	4 341(6)	8 039(7)	2 477(8)	C(214)	9 403(6)	2 873(7)	3 743(7)
C(113)	4 835(6)	8 063(8)	1 768(9)	C(215)	8 593(7)	2 197(7)	3 079(7)
C(114)	5 288(5)	7 295(7)	1 102(7)	C(216)	8 150(6)	2 338(7)	2 425(7)
C(115)	5 245(5)	6 492(7)	1 149(7)	C(221)	7 110(6)	2 186(6)	567(7)
C(116)	4 744(5)	6 459(7)	1 857(6)	C(222)	6 318(6)	2 004(7)	900(9)
C(121)	3 170(6)	8 340(7)	4 207(8)	C(223)	5 666(7)	1 100(10)	118(13)
C(122)	2 476(6)	8 302(7)	3 605(9)	C(224)	5 785(11)	394(10)	−969(13)
C(123)	2 101(7)	9 154(10)	4 095(11)	C(225)	6 556(11)	583(9)	−1 275(10)
C(124)	2 376(9)	10 022(11)	5 196(14)	C(226)	7 215(7)	1 462(7)	−530(7)
C(125)	3 045(11)	10 069(11)	5 801(11)	C(231)	8 815(5)	3 368(6)	767(6)
C(126)	3 449(7)	9 215(9)	5 312(8)	C(232)	9 436(6)	2 766(7)	471(7)
C(131)	4 553(6)	7 473(7)	4 496(6)	C(233)	10 012(7)	2 657(9)	−252(8)
C(132)	5 359(8)	8 187(10)	4 804(8)	C(234)	9 983(7)	3 187(10)	−631(9)
C(133)	6 047(8)	8 395(13)	5 555(9)	C(235)	9 389(8)	3 780(10)	−349(10)
C(134)	5 927(9)	7 877(13)	5 985(10)	C(236)	8 798(6)	3 884(8)	352(8)
C(135)	5 159(9)	7 192(11)	5 682(9)	C(12)	8 424(5)	7 598(7)	6 036(6)
C(136)	4 455(8)	6 956(10)	4 905(8)	C(13)	8 883(6)	8 552(7)	6 314(7)
C(1)	3 343(6)	3 889(8)	1 406(9)	C(14)	9 307(6)	8 506(6)	5 502(7)
C(2)	3 482(7)	3 048(11)	1 377(12)	C(15)	9 221(5)	7 559(7)	4 456(6)
C(3)	3 159(9)	1 985(11)	399(16)	C(16)	8 756(5)	6 597(6)	4 162(6)
C(4)	2 703(9)	1 761(10)	−519(13)	C(17)	8 365(5)	6 648(6)	4 991(6)
C(5)	2 529(6)	2 509(9)	−565(10)	Cl(5)	7 934(2)	7 606(2)	7 035(2)
C(6)	2 856(6)	3 856(6)	421(8)	Cl(6)	8 924(2)	9 736(2)	7 618(2)
Cl(1)	4 075(2)	3 424(4)	2 565(4)	Cl(7)	9 892(2)	9 672(2)	5 848(3)
Cl(2)	3 306(3)	1 020(3)	472(5)	Cl(8)	9 684(2)	7 503(2)	3 415(2)
Cl(3)	2 357(4)	448(3)	−1 685(4)	O(3)	7 936(4)	5 748(4)	4 807(4)
Cl(4)	2 014(2)	2 231(2)	−1 692(2)	O(4)	8 713(3)	5 698(4)	3 159(4)
O(1)	2 730(4)	4 332(4)	373(4)	C(18)	7 000(6)	5 496(8)	1 652(7)
O(2)	3 653(4)	4 891(5)	2 302(5)	C(19)	6 554(5)	4 463(8)	1 030(7)
C(7)	2 001(8)	5 173(15)	3 731(14)	C(20)	6 028(5)	4 366(8)	1 702(9)
C(8)	1 484(7)	4 561(10)	2 684(12)	C(21)	6 125(7)	5 369(10)	2 744(8)
C(9)	1 153(6)	5 260(13)	2 631(11)	C(22)	6 740(7)	6 074(8)	2 730(8)
C(10)	1 508(8)	6 281(11)	3 609(13)	C(0)	7 361(5)	4 878(6)	3 794(6)
C(11)	2 031(9)	6 213(15)	4 319(11)	O(0)	6 912(4)	4 258(4)	3 847(5)
C	2 543(5)	5 290(7)	1 276(6)	C(23) *	9 444(10)	9 349(12)	−93(11)
O	2 350(4)	5 801(5)	1 030(4)	Cl(9)	9 629(11)	10 655(12)	525(10)

* Occupancy 0.5.

(0.22 g, 0.75 mmol) in n-hexane (20 cm^3) was added solid *o*-chloranil (0.18 g, 0.73 mmol). After 20 min the yellow-brown precipitate was removed by filtration, washed with n-hexane, and dried *in vacuo* to give the *product*, yield 0.32 g (79%). The complex is air-sensitive, and rapidly decarbonylates in solvents, such as CH_2Cl_2, in which it is soluble. The orange-red complex [Rh(CO){*o*-C(O)OC$_6$Cl$_4$O}(η-C$_5$H$_5$)] (1; R = H, L = CO) (yield 50%) was prepared by the same method and has similar properties.

With [Rh(CO)(PPh$_3$)(η-C$_5$H$_5$)]: *synthesis of the complex* [Rh(PPh$_3$){*o*-C(O)OC$_6$Cl$_4$O}(η-C$_5$H$_5$)] (1; R = H, L = PPh$_3$). To a stirred solution of [Rh(CO)(PPh$_3$)(η-C$_5$H$_5$)] (0.16 g, 0.35 mmol) in CH_2Cl_2 (10 cm^3) was added *o*-chloranil (0.09 g, 0.35 mmol) in the same solvent (10 cm^3). On adding n-hexane to the yellow-orange solution an amber precipitate was formed which was purified to give the yellow, solid product, yield 0.22 g (89%). The complex slowly decarbonylates when dissolved in solvents such as CH_2Cl_2 or acetone, giving [Rh(PPh$_3$)(*o*-O$_2$C$_6$Cl$_4$)(η-C$_5$H$_5$)] (2; R = H, L = PPh$_3$). The yellow complex [Rh(PPh$_3$){*o*-C(O)OC$_6$Cl$_4$O}(η-C$_5$Me$_5$)] (1; R = Me, L = PPh$_3$) was prepared by the same method and has similar properties to (1; R = H, L = PPh$_3$).

The Protonation of [Rh(PPh$_3$){*o*-C(O)OC$_6$Cl$_4$O}(η-C$_5$H$_5$)]: *preparation of* [Rh{*o*-OC$_6$Cl$_4$(OH)}(CO)(PPh$_3$)(η-C$_5$H$_5$)][BF$_4$].—To a stirred suspension of [Rh(PPh$_3$){*o*-C(O)OC$_6$Cl$_4$O}(η-C$_5$H$_5$)] (0.26 g, 0.37 mmol) in diethyl ether (40 cm^3) was added dropwise $HBF_4\cdot OEt_2$ until the reaction was complete. After stirring for 1 h the solvent was decanted from the precipitate which was then washed with diethyl ether (2 × 25 cm^3) and dried *in vacuo* to give a red-purple solid, yield 0.22 g (76%). The solid complex is stable under nitrogen but decomposes in solvents in which it is soluble, such as CH_2Cl_2 and thf.

(η-*Cyclopentadienyl*)(*tetrachloro*-o-*catecholato*)*rhodium*, [Rh(*o*-O$_2$C$_6$Cl$_4$)(η-C$_5$H$_5$)] (2; R = H).—*Method* (*a*). *o*-Chloranil (1.26 g, 5.13 mmol) was added to a stirred solution of [Rh(η^4-cod)(η-C$_5$H$_5$)] (1.42 g, 5.13 mmol) in CH_2Cl_2 (80 cm^3). The intense blue-black solution was filtered and reduced in volume (10 cm^3) *in vacuo*. On addition of n-hexane (50 cm^3) the product was precipitated as a blue-black solid, yield 2.01 g (95%).

Method (*b*). A mixture of [Rh(CO)$_2$(η-C$_5$H$_5$)] (0.21 g, 0.94 mmol) and *o*-chloranil (0.24 g, 0.97 mmol) in CH_2Cl_2 (160 cm^3) was heated under reflux for 6 h. Treatment of the blue-black solution as above gave the product, 0.28 g (72%). The complex [Rh(o-$O_2C_6Cl_4$)(η-C_5Me_5)] (2; R = Me) was prepared similarly, as a deep purple solid (79%) with similar properties to (2; R = H).

*(η-Cyclopentadienyl)(tetrachloro-*o*-catecholato)(triphenylphosphine)rhodium*, [Rh(PPh_3)(o-$O_2C_6Cl_4$)(η-C_5H_5)] (3; R = H, L = PPh_3).—Triphenylphosphine (0.82 g, 3.13 mmol) was added to [Rh(o-$O_2C_6Cl_4$)(η-C_5H_5)] (1.29 g, 3.12 mmol) in CH_2Cl_2 (30 cm^3) to give a red-purple solution. After filtration, n-hexane (100 cm^3) was added and the volume of the solution reduced *in vacuo* to give a purple precipitate. After purification the yield was 1.79 g (85%). The complexes [RhL(o-$O_2C_6Cl_4$)(η-C_5R_5)] [3; R = H, L = $AsPh_3$, P(OPh)$_3$, or py; R = Me, L = PPh_3 or $AsPh_3$] were prepared similarly as air-stable solids.

*(η-Cyclopentadienyl)(tetrachloro-*o*-benzosemiquinone)(triphenylphosphine)rhodium Hexafluorophosphate*, [Rh(PPh_3)(o-$O_2C_6Cl_4$)(η-C_5H_5)][PF_6] (4; R = H, L = PPh_3).—To Ag[PF_6] (0.42 g, 1.66 mmol) in CH_2Cl_2 (40 cm^3), was added [Rh(PPh_3)(o-$O_2C_6Cl_4$)(η-C_5H_5)] (1.12 g, 1.66 mmol). After stirring for 5 min the deep purple solution was filtered through Kieselguhr, and n-hexane (100 cm^3) was added to the filtrate to precipitate the product. Purification gave a deep purple solid, yield 1.03 g (76%). The complexes [RhL(o-$O_2C_6Cl_4$)(η-C_5R_5)][PF_6] [4; R = H, L = $AsPh_3$, P(OPh)$_3$, or py; R = Me, L = PPh_3 or $AsPh_3$] were prepared by the same method and have similar properties.

*Acetonitrile(η-cyclopentadienyl)(tetrachloro-*o*-benzosemiquinone)rhodium Hexafluorophosphate*, [Rh(NCMe)(o-$O_2C_6Cl_4$)(η-C_5Me_5)][PF_6] (4; R = Me, L = NCMe).—To a stirred solution of [NO][PF_6] (30 mg, 0.17 mmol) in acetonitrile (20 cm^3) was added [Rh(o-$O_2C_6Cl_4$)(η-C_5Me_5)] (83 mg, 0.17 mmol). After 20 min the red-brown solution was filtered and then evaporated to dryness. Extraction of the residue with CH_2Cl_2 (10 cm^3) and addition of n-hexane (80 cm^3) to the filtered extract gave the product as a purple *solid*, yield 53 mg (46%).

Structure Determination of [Rh(PPh_3){o-C(O)OC_6Cl_4O}(η-C_5H_5)]·0.25CH_2Cl_2 (1; R = H, L = PPh_3).—Light-sensitive, orange plates of (1; R = H, L = PPh_3), as its dichloromethane solvate, were grown from a dichloromethane–n-hexane mixture. A single crystal of dimensions *ca.* 0.5 × 0.25 × 0.075 mm was mounted in a thin-walled glass capillary under N_2. Preliminary oscillation and Weissenberg photography established an approximate cell volume and indicated the space group to be $P\bar{1}$ (no. 2). A full hemisphere of intensity data, in the range $4 < 2\theta < 45°$, was collected at 295 K on a Nicolet *P*3*m* diffractometer. Integrated intensities were measured by the θ—2θ scan technique with scan widths 2.0° + $\Delta_{\alpha1\alpha2}$ (difference in 2θ of Mo-$K_{\alpha1}$ and Mo-$K_{\alpha2}$ wavelengths) and scan speeds varying between 2.0 and 29.3° min^{-1} based on a 2-s prescan of the reflection. For the reflections in the range $40 < 2\theta < 45°$ only those with counts greater than 15 in the 2-s prescan were measured. Of the total 6 439 independent measured intensities only those 5 296 data with $I \geqslant 1.5\sigma(I)$ were used in structure solution and refinement. Check reflections 8 -5 4 and 2 -3 6, measured every 50 reflections, showed a *ca.* 10% loss in intensity during the 191 h of data collection. A suitable correction for this decay was therefore applied. A correction for *X*-ray absorption effects was applied by a semi-empirical method based on 242 azimuthal scan data (maximum and minimum transmission coefficients 0.899 and 0.675).

Crystal data. $C_{30}H_{20}Cl_4O_3PRh\cdot0.25CH_2Cl_2$, $M = 724.9$, triclinic, $a = 15.420(5)$, $b = 16.677(8)$, $c = 15.587(7)$ Å, $\alpha = 128.89(3)$, $\beta = 90.83(3)$, $\gamma = 99.83(3)°$, $U = 3\,035(2)$ Å^3, $Z = 4$, $D_c = 1.63$ g cm^{-3}, $F(000) = 1\,471$, space group $P\bar{1}$ (no. 2), Mo-K_α *X*-radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 9.87 cm^{-1}, $T = 295$ K.

Structure solution and refinement. The structure was solved by heavy-atom methods; the unique rhodium atoms were located by inspection of the Patterson function and the remaining non-hydrogen atoms, including those of the solvent which is disordered about a crystallographic inversion centre, were located in subsequent Fourier difference maps. Refinement was by blocked-cascade least squares, all non-hydrogen atoms being allowed anisotropic thermal parameters. Hydrogen atoms were restricted to idealised geometries (C–H 0.96 Å) and isotropic thermal parameters fixed to *ca.* 1.2 times that of the carbon atoms to which they were attached. Individual weights were ascribed according to the scheme $w = [\sigma^2(F_o) + 0.0007(F_o)^2]^{-1}$ and refinement converged at $R = 0.0527$ ($R' = 0.0523$), $S = 1.41$.* The final electron-density difference synthesis showed no features of modulus >1 e Å^{-3}, all large features being in regions of no chemical significance.

All computing was carried out within the laboratory on a Data General Eclipse computer using the SHELXTL system of programs with scattering factors, corrected for anomalous dispersion, taken from ref. 28. Table 6 lists the atomic positional parameters for (1; R = H, PPh_3)·0.25CH_2Cl_2.

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* $R = \Sigma|F_o - |F_c||/\Sigma|F_o|$; $R' = \Sigma w^{\frac{1}{2}}|F_o - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$; $S = [\Sigma w(F_o - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$.

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