

Redox-active catecholate complexes of rhodium hydrotris(pyrazolyl)-borates

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The complexes $[\text{Rh}(\text{CO})\text{LTp}']$ $\{\text{L} = \text{CO}$ or PPh_3 , $\text{Tp}' = \text{hydrotris}(3,5\text{-dimethylpyrazolyl})\text{borate}\}$ reacted with the *ortho*-quinone $o\text{-C}_6\text{Cl}_4\text{O}_2$ (*o*-chloranil; 3,4,5,6-tetrachloro-1,2-benzoquinone) to give $[\text{Rh}\{\text{C}(\text{O})\text{OC}_6\text{Cl}_4\text{O}\}\text{LTp}']$ ($\text{L} = \text{CO}$, **1**; $\text{L} = \text{PPh}_3$, **2**). X-Ray structural studies on **2** reveal CO insertion into one Rh–O bond of a rhodium–catecholate ring. Loss of the inserted CO on UV irradiation (of **1**) or thermolysis (of **2**) gives $[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)\text{LTp}']$ ($\text{L} = \text{CO}$ **3** or PPh_3 , **4**); thermal substitution of the CO ligand of $[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{CO})\text{Tp}']$ with L provides a second route to $[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{PPh}_3)\text{Tp}']$ as well as $[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)\text{LTp}']$ $\{\text{L} = \text{AsPh}_3$, **5**, $\text{P}(\text{OPh})_3$, **6** or py , **7** $\}$ which are oxidised by $[\text{NO}]^+$ to the monocations $[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)\text{LTp}']^+ \mathbf{4^+-7^+}$. X-Ray structural studies on the redox pair $[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{PPh}_3)\text{Tp}']^z$ ($z = 0, \mathbf{4}$ or $1, \mathbf{4^+}$) are consistent with catecholate ligand-based oxidation; the ESR spectra of the paramagnetic cations $\mathbf{4^+-7^+}$ suggest little delocalisation of unpaired electron density from the semiquinone ligand to the $\text{Rh}^{\text{III}}\text{LTp}'$ unit.

Introduction

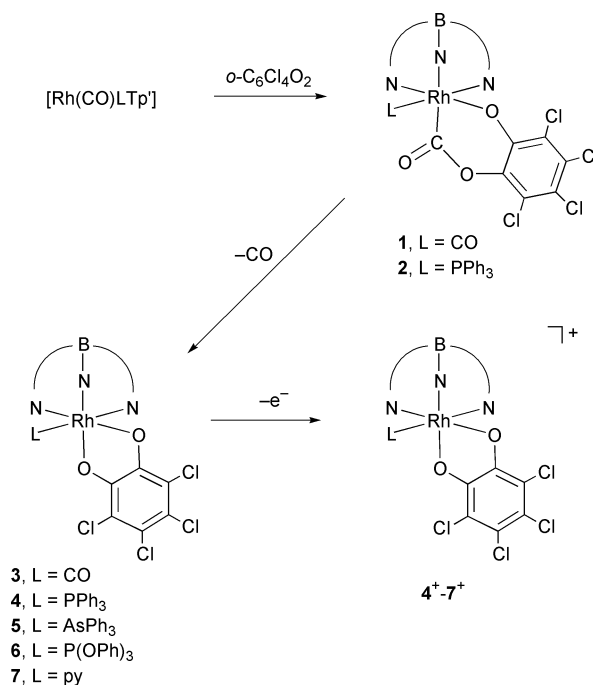
Our recent studies have shown that one-electron oxidation of the κ^2 -rhodium(I) species $[\text{Rh}(\text{CO})\text{LTp}']$ $\{\text{Tp}' = \text{the hydrotris}(\text{pyrazolyl})\text{borate ligand } [\text{HBR}_3]^-; \text{R} = 3,5\text{-dimethylpyrazolyl}\}$ gives stable κ^3 -rhodium(II) complexes $[\text{Rh}(\text{CO})\text{LTp}']^+$ in which the Rh^{II} is stabilised by the formation of a third Rh–N bond, in the axial site of a square pyramidal structure.¹ The isolation of such stable rhodium(II) complexes is noteworthy and contrasts with the behaviour of the analogous cyclopentadienyl species $[\text{Rh}(\text{CO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$ which, on oxidation, gave the fulvalene-bridged dication $[\text{Rh}_2(\text{CO})_2(\text{PPh}_3)_2(\eta^5\text{:}\eta^5\text{-C}_{10}\text{H}_8)]^{2+}$,² although the intermediate rhodium(II) cation $[\text{Rh}(\text{CO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]^+$ was not detected spectroscopically the sterically protected derivative $[\text{Rh}(\text{CO})(\text{PPh}_3)(\eta\text{-C}_5\text{Ph}_5)]^+$ was fully characterised.³ Stable paramagnetic rhodium complexes were also obtained by one-electron oxidation of the rhodium(III) catecholate complexes $[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)\text{L}(\eta\text{-C}_5\text{R}_5)]$ ($\text{L} = \text{PPh}_3$, py , *etc.*; $\text{R} = \text{H}$ or Me). The cations $[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)\text{L}(\eta\text{-C}_5\text{R}_5)]^+$ were, however, best formulated as semiquinone rhodium(III) complexes although delocalisation of unpaired electron density onto both Rh and L was evident from the ESR spectra.⁴

An analogy is often drawn^{5,6} between $\eta\text{-C}_5\text{R}_5$ and hydrotris(pyrazolyl)borate ligands but, as noted above, there is a significant difference between the redox chemistry of $[\text{Rh}(\text{CO})\text{LTp}']$ and $[\text{Rh}(\text{CO})\text{L}(\eta\text{-C}_5\text{H}_5)]$. We now therefore compare the reactions of the *ortho*-quinone $o\text{-C}_6\text{Cl}_4\text{O}_2$ (*o*-chloranil; 3,4,5,6-tetrachloro-1,2-benzoquinone) with $[\text{Rh}(\text{CO})\text{LTp}']$ and $[\text{Rh}(\text{CO})\text{L}(\eta\text{-C}_5\text{R}_5)]$.⁴ Although the chemistry is generally analogous, the Tp' ligand stabilises the carbonyl insertion products $[\text{Rh}\{\text{C}(\text{O})\text{OC}_6\text{Cl}_4\text{O}\}\text{LTp}']$ and allows the isolation of the stable but substitutionally labile carbonyl $[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{CO})\text{Tp}']$. Moreover, structural studies of the redox pair $[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{PPh}_3)\text{Tp}']^z$ ($z = 0$ or 1) and the ESR spectra of $[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{PPh}_3)\text{Tp}']^+$ are consistent with increased localisation of unpaired electron density on the semiquinone ligand of the paramagnetic cations.

Results and discussion

Synthesis

The reaction of $[\text{Rh}(\text{CO})\text{LTp}']$ ($\text{L} = \text{CO}$ or PPh_3) with 3,4,5,6-tetrachloro-1,2-benzoquinone (*o*-chloranil) in the absence of light gave bright yellow (**1**, $\text{L} = \text{CO}$) or orange (**2**, $\text{L} = \text{PPh}_3$) solids (Scheme 1), characterised by elemental analysis and IR



Scheme 1 $\text{BN}_3 = \text{hydrotris}(3,5\text{-dimethylpyrazolyl})\text{borate}$.

(Table 1) and NMR (Table 2) spectroscopy. The IR spectra in CH_2Cl_2 show ketonic carbonyl bands in the region $1700\text{--}1740\text{ cm}^{-1}$ and, in the case of **1**, a band at 2108 cm^{-1} corresponding

Table 1 Analytical and IR spectroscopic data for rhodium hydrotris(pyrazolyl)borate complexes

Complex	Colour	Yield (%)	Analysis (%) ^a			IR ν/cm^{-1}		$\nu(\text{BH})$	E°/V^c	$\lambda_{\text{max}}/\text{nm}$
			C	H	N	$\nu(\text{CO})$	$\nu(\text{BH})$			
$[\text{Rh}\{\text{C}(\text{O})\text{OC}_6\text{Cl}_4\text{O}\}(\text{CO})\text{Tp}']$ 1	Bright yellow	54	39.4 (39.4)	3.3 (3.1)	12.0 (12.0)	2108, 1736, 1719	2558	—	—	306, 392
$[\text{Rh}\{\text{C}(\text{O})\text{OC}_6\text{Cl}_4\text{O}\}(\text{PPh}_3)\text{Tp}']$ 2	Orange-yellow	68	50.2 (50.2)	3.8 (3.9)	8.6 (8.7)	1709, 1696	2558	—	—	324, 425
$[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{CO})\text{Tp}']$ 3	Orange-brown	44	39.4 (39.2)	3.3 (3.3)	12.4 (12.5)	2120	2557	1.05	—	319, 426
$[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{PPh}_3)\text{Tp}']$ 4	Red	49	48.5 (48.4)	4.0 (4.0)	8.8 (8.5)	—	2553	0.77	—	317, 479
$[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{AsPh}_3)\text{Tp}']$ 5	Pink-purple	26	49.6 (49.2)	3.6 (3.9)	8.5 (8.8)	—	2548	0.76	—	323, 494
$[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{P}(\text{OPh})_3)\text{Tp}']$ 6	Orange	67	48.7 (49.0)	3.9 (3.9)	8.7 (8.8)	—	2547	0.81	—	323s 417
$[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{py})\text{Tp}']$ 7	Yellow	65	43.1 (43.1)	3.4 (3.8)	13.1 (13.5)	—	2546	0.78	—	325, ca. 380
$[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{PPh}_3)\text{Tp}']$ 8	Purple	81	40.4 (40.3)	3.4 (3.4)	6.9 (6.9)	—	2564	0.77	—	325, 502, 685
$[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{AsPh}_3)\text{Tp}']$ 9	Purple	29	39.7 (39.7)	2.8 (3.3)	7.3 (7.7)	—	2561	0.76	—	328, 497, 711
$[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{P}(\text{OPh})_3)\text{Tp}']$ 10	Brown	35	41.6 (41.5)	2.9 (3.4)	7.2 (7.4)	—	2565	0.80	—	324, 482, 664
$[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{py})\text{Tp}']$ 11	Purple	68	34.3 (34.0)	3.0 (3.1)	10.3 (10.3)	—	2562	0.77	—	325, 489, 689

^a Calculated values in parentheses. ^b In CH_2Cl_2 . ^c Potentials for reversible oxidation of the neutral complexes or reduction of the cationic complexes, at a platinum disk electrode in CH_2Cl_2 .

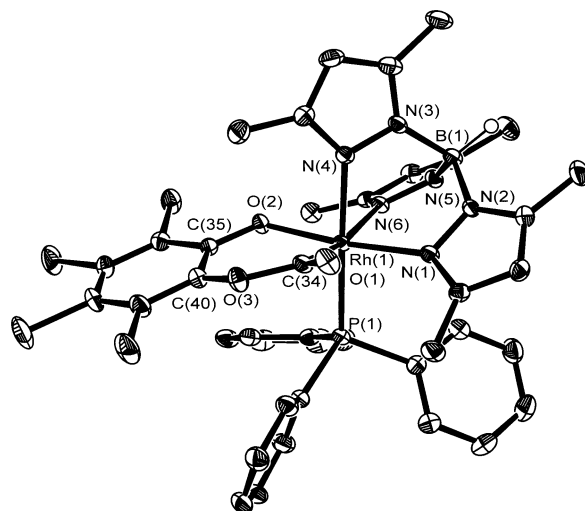


Fig. 1 The molecular structure of complex **2**. Hydrogen atoms have been omitted for clarity (in all structures shown).

to a terminal CO bound to Rh; the spectra of **1** and **2** (and of all the complexes reported herein) also show $\nu(\text{BH})$ bands corresponding unambiguously to κ^3 co-ordination of the Tp' ligand to rhodium, in both solution and the solid state.⁷ The spectroscopic data suggest that **1** and **2** are analogous to the products of the reactions between $[\text{Rh}(\text{CO})\text{L}(\eta\text{-C}_5\text{R}_5)]$ ($\text{L} = \text{CO}$ or PPh_3 , $\text{R} = \text{H}$ or Me) with $o\text{-C}_6\text{Cl}_4\text{O}_2$,⁴ i.e. that **1** and **2** are $[\text{Rh}\{\text{C}(\text{O})\text{OC}_6\text{Cl}_4\text{O}\}\text{LTp}']$. This suggestion was borne out by an X-ray structural study of complex **2**.

The structure of complex **2** is shown in Fig. 1 and important bond lengths and angles, together with those for the two crystallographically independent molecules of $[\text{Rh}\{\text{C}(\text{O})\text{OC}_6\text{Cl}_4\text{O}\}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$ for comparison,⁴ are given in Table 3. The rhodium atom of **2** is essentially octahedral, co-ordinated to $\kappa^3\text{-Tp}'$ and PPh_3 ligands and bound to oxygen and carbon atoms as part of a $\text{Rh}\{\text{C}(\text{O})\text{OC}_6\text{Cl}_4\text{O}\}$ metallacycle; the metallacycle is formed, at least formally, by the insertion of CO into one Rh–O bond of a rhodium catecholate ring. Within the $\text{Rh}\{\text{C}(\text{O})\text{OC}_6\text{Cl}_4\text{O}\}$ metallacycle the C(34)–O(1) and C(34)–O(3) lengths [1.199(3) and 1.409(2) Å] are normal for carbon–oxygen double and single bonds [1.23(1) and 1.43(1) Å].⁸ The C_6 ring is planar with C–C distances which vary between 1.379(3) and 1.411(3) Å.

Though the structure of complex **2** is generally similar to that of $[\text{Rh}\{\text{C}(\text{O})\text{OC}_6\text{Cl}_4\text{O}\}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$, there are some small differences in the conformation of the metallacycle which is more flattened in **2** than in the $\eta\text{-C}_5\text{H}_5$ complex. In **2** the Rh–N(6) bond *trans* to the ketonic carbonyl group [2.247(2) Å] is significantly longer than Rh–N(1) [2.091(2) Å], *trans* to oxygen, and Rh–N(4) [2.108(2) Å], *trans* to phosphorus, in accord with the high *trans* influence of the σ -bound carbon ligand. The Rh–P(1) distance [2.364(1) Å] in **2** is longer [*cf.* 2.298(3) Å], and the Rh–O(2) distance shorter [2.022(2), *cf.* 2.079(6) Å] than the corresponding lengths in $[\text{Rh}\{\text{C}(\text{O})\text{OC}_6\text{Cl}_4\text{O}\}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$.⁴

Complexes **1** and **2** are significantly more stable than their cyclopentadienyl analogues. Both are stable in solution (in the absence of air) whereas solid $[\text{Rh}\{\text{C}(\text{O})\text{OC}_6\text{Cl}_4\text{O}\}(\text{CO})(\eta\text{-C}_5\text{R}_5)]$ ($\text{R} = \text{H}$ or Me) rapidly loses two molecules of CO on dissolution, to give $[\{\text{Rh}(\text{O}_2\text{C}_6\text{Cl}_4)(\eta\text{-C}_5\text{R}_5)\}_n]$, and $[\text{Rh}\{\text{C}(\text{O})\text{OC}_6\text{Cl}_4\text{O}\}(\text{PPh}_3)(\eta\text{-C}_5\text{R}_5)]$ gives $[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{PPh}_3)(\eta\text{-C}_5\text{R}_5)]$, albeit more slowly.⁴ Decarbonylation occurs on UV irradiation for 6 hours (for **1**) or heating under reflux (for **2**). Moreover, **1** only loses the CO group inserted into the Rh–O bond, giving orange-brown $[\text{Rh}(o\text{-O}_2\text{C}_6\text{Cl}_4)(\text{CO})\text{Tp}']$ **3** the C_5R_5 analogues of which were not observed. (Subsequent heating of a toluene solution of **3** under reflux for five days resulted in decarbonylation to give a black solution containing unidentified products perhaps analogous to

Table 2 Proton, ^{13}C - $\{^1\text{H}\}$ and ^{31}P NMR spectroscopic data for rhodium hydrotris(pyrazolyl)borate complexes^a

Complex	^1H	^{13}C - $\{^1\text{H}\}$	^{31}P
[Rh{C(O)OC ₆ Cl ₄ O}(CO)Tp'] 1	5.97 (s, 1H, Tp' CH), 5.94 (s, 1H, Tp' CH), 5.91 (s, 1H, Tp' CH), 2.47 (s, 3H, Tp' CCH ₃), 2.42 (s, 6H, Tp' CCH ₃), 2.41 (s, 3H, Tp' CCH ₃), 2.21 (s, 3H, Tp' CCH ₃), 2.20 (s, 3H, Tp' CCH ₃)	180.0 (d, J_{CRh} 59, CO), 173.2 {d, J_{CRh} 35, C(O)C ₆ Cl ₄ O}, 152.1, 151.8, 151.4, 146.9, 146.1, 145.6 (Tp' CCH ₃), 152.1, 141.3, 127.1, 123.1, 122.1, 120.5 {C(O)C ₆ Cl ₄ O}, 108.9, 108.5, 107.5 (Tp' CH), 15.7, 14.2, 13.6, 13.2, 12.9, 12.4 (s, Tp' CH ₃)	—
[Rh{C(O)OC ₆ Cl ₄ O}(PPh ₃)Tp']·0.33 CH ₂ Cl ₂ 2	7.38–6.87 {m, 15H, P(C ₆ H ₅) ₃ }, 5.80 (s, 1H, Tp' CH), 5.75 (s, 1H, Tp' CH), 5.15 (s, 1H, Tp' CH), 2.53 (s, 3H, Tp' CCH ₃), 2.31 (s, 3H, Tp' CCH ₃), 2.30 (s, 3H, Tp' CCH ₃), 1.99 (s, 3H, Tp' CCH ₃), 1.73 (s, 3H, Tp' CCH ₃), 1.42 (s, 3H, Tp' CCH ₃)	174.5 {dd, J_{CRh} 39, J_{CP} 12, C(O)C ₆ Cl ₄ O}, 155.6, 152.1 (Tp' CCH ₃), 150.9 {C(O)C ₆ Cl ₄ O}, 150.7 (d, J 5, Tp' CCH ₃), 146.4, 145.1 (Tp' CCH ₃), 144.8 (d, J 3, Tp' CCH ₃), 140.3 {s, C(O)C ₆ Cl ₄ O}, 134.7 {d, J_{CP} 10, P(C ₆ H ₅) ₃ }, 130.8 {d, J_{CP} 3, P(C ₆ H ₅) ₃ }, 130.7 {d, J_{CP} 47, P(C ₆ H ₅) ₃ }, 128.3 {d, J_{CP} 11, P(C ₆ H ₅) ₃ }, 125.7, 123.7, 120.9, 117.1 {C(O)C ₆ Cl ₄ O}, 108.7, 108.6 (Tp' CH), 108.1 (d, J 4, Tp' CH), 18.3, 13.1, 13.0, 12.9, 12.8, 12.7 (Tp' CH ₃)	20.7 (d, J_{PRh} 121)
[Rh(<i>o</i> -O ₂ C ₆ Cl ₄)(CO)Tp'] 3	5.99 (s, 2H, Tp' CH) 5.82 (s, 1H, Tp' CH), 2.64 (s, 6H, Tp' CCH ₃), 2.42 (s, 6H, Tp' CCH ₃), 2.37 (s, 3H, Tp' CCH ₃), 1.92 (s, 3H, Tp' CCH ₃)	176.6 (d, J_{CRh} 58, CO), 158.4 (C ₆ Cl ₄ O ₂), 153.1, 152.46, 146.9, 145.2 (Tp' CCH ₃), 118.6 (s, C ₆ Cl ₄ O ₂), 116.5 (d, J 2, C ₆ Cl ₄ O ₂), 109.0, 108.8 (Tp' CH), 13.3, 12.7, 12.3 (Tp' CH ₃)	—
[Rh(<i>o</i> -O ₂ C ₆ Cl ₄)(PPh ₃)Tp']·CH ₂ Cl ₂ 4	7.36–6.87 {m, 15H, P(C ₆ H ₅) ₃ }, 5.64 (d, 1H, J 1, Tp' CH), 5.53 (s, 2H, Tp' CH), 2.36 (s, 6H, Tp' CCH ₃), 2.20 (s, 3H, Tp' CCH ₃), 1.91 (s, 6H, Tp' CCH ₃), 1.81 (s, 3H, Tp' CCH ₃)	160.0 (d, J 1, C ₆ Cl ₄ O ₂), 155.9 (Tp' CCH ₃), 150.4 (d, J 5, Tp' CCH ₃), 147.0 (Tp' CCH ₃), 144.5 (d, J 3, Tp' CCH ₃), 135.2 {d, J_{CP} 9, P(C ₆ H ₅) ₃ }, 131.1 {d, J_{CP} 48, P(C ₆ H ₅) ₃ }, 130.9 {d, J_{CP} 2, P(C ₆ H ₅) ₃ }, 128.2 {d, J_{CP} 10, P(C ₆ H ₅) ₃ }, 117.3, 116.7 (C ₆ Cl ₄ O ₂), 110.0 (Tp' CH), 107.9 (d, J 5, Tp' CH), 13.5, 12.9, 12.8, 12.8 (Tp' CH ₃)	8.6 (d, J_{PRh} 124)
[Rh(<i>o</i> -O ₂ C ₆ Cl ₄)(AsPh ₃)Tp'] 5	7.4–7.0 {m, 15H, As(C ₆ H ₅) ₃ }, 5.67 (s, 1H, Tp' CH), 5.56 (s, 2H, Tp' CH), 2.39 (s, 6H, Tp' CCH ₃), 2.25 (s, 3H, Tp' CCH ₃), 1.98 (s, 6H, Tp' CCH ₃), 1.85 (s, 3H, Tp' CCH ₃)	160.1 (C ₆ Cl ₄ O ₂), 155.9, 151.1, 146.9, 145.0 (Tp' CCH ₃), 134.4 {As(C ₆ H ₅) ₃ }, 132.9 {d, J 1, As(C ₆ H ₅) ₃ }, 130.5, 128.8 {As(C ₆ H ₅) ₃ }, 117.3, 116.6 (C ₆ Cl ₄ O ₂), 109.7, 108.4 (Tp' CH), 13.8, 12.9, 12.8, 12.6 (Tp' CH ₃)	—
[Rh(<i>o</i> -O ₂ C ₆ Cl ₄){P(OPh) ₃ }Tp'] 6	7.05–6.61 {m, 15H, P(OC ₆ H ₅) ₃ }, 5.82 (s, 2H, Tp' CH), 5.67 (d, 1H, J 3, Tp' CH), 2.72 (s, 6H, Tp' CCH ₃), 2.24 (s, 6H, Tp' CCH ₃), 2.21 (s, 3H, Tp' CCH ₃), 1.86 (s, 3H, Tp' CCH ₃)	159.9 (C ₆ Cl ₄ O ₂), 155.3 (Tp' CCH ₃), 150.8 {d, J_{CP} 14, P(OC ₆ H ₅) ₃ }, 150.7 (d, J 8, Tp' CCH ₃), 146.5 (Tp' CCH ₃), 144.3 (d, J 6, Tp' CCH ₃), 129.8, 125.2 {P(OC ₆ H ₅) ₃ }, 119.9 {d, J_{CP} 5, P(OC ₆ H ₅) ₃ }, 117.2, 116.3 (C ₆ Cl ₄ O ₂), 110.1 (Tp' CH), 107.8 (d, J 8, Tp' CH), 14.0, 12.7, 12.6 (Tp' CH ₃)	74.6 (d, J_{PRh} 204)
[Rh(<i>o</i> -O ₂ C ₆ Cl ₄)(py)Tp'] 7	8.3–7.0 (m, 5H, NC ₅ H ₅), 5.86 (s, 2H, Tp' CH), 5.75 (s, 1H, Tp' CH), 2.48 (s, 6H, Tp' CCH ₃), 2.38 (s, 3H, Tp' CCH ₃), 1.76 (s, 3H, Tp' CCH ₃), 1.72 (s, 6H, Tp' CCH ₃)	159.7 (C ₆ Cl ₄ O ₂), 154–152 (broad s, NC ₅ H ₅), 153.1, 152.1, 145.9, 145.6 (Tp' CCH ₃), 139.0 (s, NC ₅ H ₅), 127–125 (broad s, NC ₅ H ₅), 117.3 (C ₆ Cl ₄ O ₂), 117.2 (d, J 1, C ₆ Cl ₄ O ₂), 109.1, 108.9 (Tp' CH), 13.5, 13.0, 12.7, 12.0 (Tp' CH ₃)	—

^a Chemical shift (δ) in ppm, J values in Hz, spectra in CD₂Cl₂.

[{Rh(O₂C₆Cl₄)(η -C₅R₅)₃}]_n.) Decarbonylation of **2** gives [Rh(*o*-O₂C₆Cl₄)(PPh₃)Tp'] **4** which is, however, analogous to [Rh(*o*-O₂C₆Cl₄)(PPh₃)(η -C₅R₅)].

The high energy of the $\nu(\text{CO})$ band of complex **3** (2120 cm⁻¹) suggested carbonyl substitution would readily occur and, indeed, heating with PPh₃ in toluene at 70 °C provided a second route to **4**, as well as to [Rh(*o*-O₂C₆Cl₄)LTp'] {L = AsPh₃ **5**, P(OPh)₃ **6** or py **7**}. Complexes **3–7** were characterised by elemental analysis and IR, UV-visible (Table 1) and NMR spectroscopy (Table 2); in contrast to the η -C₅R₅ analogues, no spectroscopic evidence was found for dissociation of the ligand, L, in solution. (The molecular structure of **4** is discussed below, together with that of the monocation **4**⁺.)

The most intense absorption in the electronic spectra of complexes **1–7** lies between 306 and 325 nm, in the UV region, and is virtually independent of the nature of the ligand L. A very similar absorption occurs for the cations **4**⁺–**7**⁺ (324–328 nm) (see below). The only absorption in the visible region is highly dependent on L, occurring from approximately 380 nm for the bright yellow pyridine complex **7** to 494 nm for the pink triphenylarsine complex **5**. This absorption is, in each case,

approximately 70–100 nm shorter in wavelength than that of the η -C₅H₅ analogue which ranges from 475 nm for the pyridine complex to 558 nm for the AsPh₃ complex.⁴ The dependence of energy on L suggests the absorption derives from catecholate-to-L charge transfer.

Voltammetric studies

The cyclic voltammograms of the insertion products **1** and **2**, in CH₂Cl₂ at a platinum electrode, are relatively uninformative, each showing an irreversible oxidation wave {(E_{p})_{ox} = 1.47 and 1.25 V respectively} and, for **1**, an irreversible reduction wave (at ca. -1.5 V); each process is accompanied by ill defined product waves. Unlike [Rh{C(O)OC₆Cl₄O}(PPh₃)(η -C₅Me₅)] **2** does not show a product wave corresponding to the formation of the ligand decarbonylation product **4**, perhaps a further indication of the greater stability of the Rh{C(O)OC₆Cl₄O} metallacycle in the Tp' complex.

By contrast, each of complexes **3–7** shows one reversible one-electron oxidation wave with no evidence for dissociation of L from [Rh(*o*-O₂C₆Cl₄)LTp'] (cf. the detection of the oxidation

Table 3 Selected bond lengths (Å) and angles (°) for complex **2** and the two crystallographically independent molecules, **A** and **B**, of $[\text{Rh}(\text{C}(\text{O})\text{OC}_6\text{Cl}_4\text{O})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]^a$

	2	A	B
Rh(1)–N(1)	2.091(2)	—	—
Rh(1)–N(4)	2.108(2)	—	—
Rh(1)–N(6)	2.247(2)	—	—
Rh(1)–P(1)	2.364(1)	2.302(3)	2.294(3)
Rh(1)–O(2)	2.022(2)	2.079(6)	2.078(4)
Rh(1)–C(34)	1.969(2)	1.986(11)	2.001(12)
C(35)–O(2)	1.316(3)	1.322(9)	1.309(7)
C(40)–O(3)	1.369(3)	1.341(17)	1.373(12)
C(34)–O(3)	1.409(2)	1.401(9)	1.423(7)
C(34)–O(1)	1.199(3)	1.207(16)	1.192(13)
C(35)–C(36)	1.409(4)	1.427(26)	1.403(14)
C(36)–C(37)	1.391(3)	1.413(17)	1.363(9)
C(37)–C(38)	1.392(4)	1.376(31)	1.398(16)
C(38)–C(39)	1.379(4)	1.365(28)	1.401(16)
C(39)–C(40)	1.405(3)	1.428(12)	1.371(9)
C(40)–C(35)	1.411(3)	1.427(19)	1.395(14)
O(2)–Rh(1)–C(34)	91.5(1)	85.2(3)	87.7(3)
C(34)–Rh(1)–P(1)	95.8(1)	89.4(3)	88.7(3)
P(1)–Rh(1)–O(2)	93.3(1)	87.1(2)	84.6(2)

^a Data from ref. 4.

waves for $[\{\text{Rh}(\text{O}_2\text{C}_6\text{Cl}_4)(\eta\text{-C}_5\text{R}_5)\}_n]$ in the CV of $[\text{Rh}(\text{o-O}_2\text{-C}_6\text{Cl}_4)\text{L}(\eta\text{-C}_5\text{R}_5)]$. The oxidation potentials, E° , are 120–190 mV more positive than those of the $\eta\text{-C}_5\text{H}_5$ analogues, suggesting the $\eta\text{-C}_5\text{H}_5$ ligand to be more electron-donating than Tp' when bound to the $\text{Rh}(\text{o-O}_2\text{C}_6\text{Cl}_4)\text{L}$ fragment. As Bergman and co-workers have recently pointed out,⁹ the relative donor abilities of cyclopentadienyl and hydrotris(pyrazolyl)borate ligands seem to depend on the metal centre to which they are bound so that no useful generalisations can yet be made. This is strikingly underlined by comparing the redox behaviour of the catecholate complexes with that of the related species $[\text{Rh}(\text{CO})(\text{PPh}_3)\text{Tp}']^1$ and $[\text{Rh}(\text{CO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]^2$ which are oxidised at 0.31 and *ca.* 0.47 V (albeit irreversibly) respectively. Thus, Tp' appears to be more electron donating than $\eta\text{-C}_5\text{H}_5$ when bound to $\text{Rh}(\text{CO})(\text{PPh}_3)$.

Apart from the carbonyl **3**, the dependence of E° on L for complex **4–7** is small, varying by only 50 mV from L = AsPh_3 to $\text{P}(\text{O}i\text{Pr})_3$. This may suggest less delocalisation over the $\text{Rh}(\text{O}_2\text{C}_6\text{Cl}_4)\text{L}$ unit than for $[\text{Rh}(\text{o-O}_2\text{C}_6\text{Cl}_4)\text{L}(\eta\text{-C}_5\text{H}_5)]$ for which the variation in E° is 110 mV for L = AsPh_3 to $\text{P}(\text{O}i\text{Pr})_3$.⁴

Chemical oxidation reactions

Chemical oxidation of $[\text{Rh}(\text{o-O}_2\text{C}_6\text{Cl}_4)\text{LTp}']$ with $[\text{NO}][\text{PF}_6]$ gave the cations $[\text{Rh}(\text{o-O}_2\text{C}_6\text{Cl}_4)\text{LTp}']^+ \{ \text{L} = \text{PPh}_3 \textbf{4}^+, \text{AsPh}_3 \textbf{5}^+, \text{P}(\text{O}i\text{Pr})_3 \textbf{6}^+ \text{ or } \text{py} \textbf{7}^+ \}$, characterised as brown or purple $[\text{PF}_6]^-$ salts (Table 1), which are reversibly reduced at potentials essentially identical to those for the oxidation of **4–7**. Each of the cations **4⁺–7⁺** exhibits strong UV-visible absorptions at 324–328 and 482–502 nm, similar to those of the neutral complexes **1–7**. An additional band at 664–711 nm may arise from rhodium to semiquinone charge transfer.

The $\nu(\text{BH})$ stretches of cations **4⁺–7⁺** lie between 2561 and 2564 cm^{-1} , 10–20 cm^{-1} higher in energy than those of the corresponding neutral complexes **4–7**. Much larger shifts in $\nu(\text{BH})$ (*ca.* 85–90 cm^{-1}) are observed on oxidation of $[\text{Rh}(\text{CO})\text{L}(\kappa^2\text{-Tp}')]$ to $[\text{Rh}(\text{CO})\text{L}(\kappa^3\text{-Tp}')^+]$.¹

The isotropic ESR spectra of cations **4⁺–7⁺** are very similar, consisting of narrow lines with g_{iso} ranging from 2.000 (L = PPh_3 or py) to 2.002 $\{ \text{L} = \text{P}(\text{O}i\text{Pr})_3 \}$, close to the free electron value and to that of the uncomplexed $\text{o-C}_6\text{Cl}_4\text{O}_2^-$ radical anion (2.0053),¹⁰ indicating that the unpaired electron resides mainly on the O-donor ligand of a rhodium(III) semiquinone complex. Unlike the cyclopentadienyl analogues,⁴ which generally show hyperfine coupling to both rhodium and the P- or As-donor

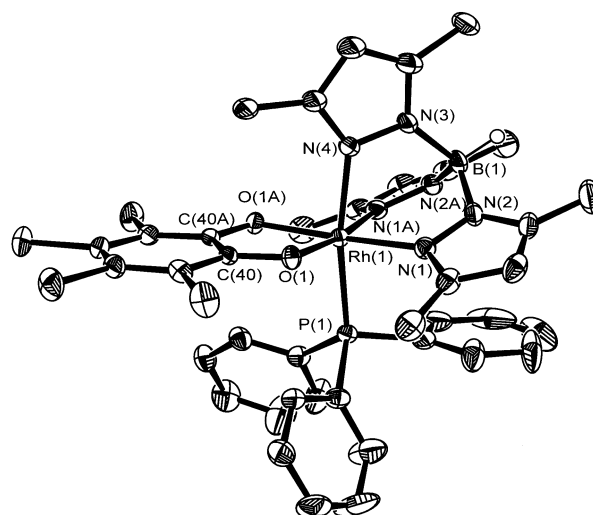


Fig. 2 The molecular structure of complex **4**.

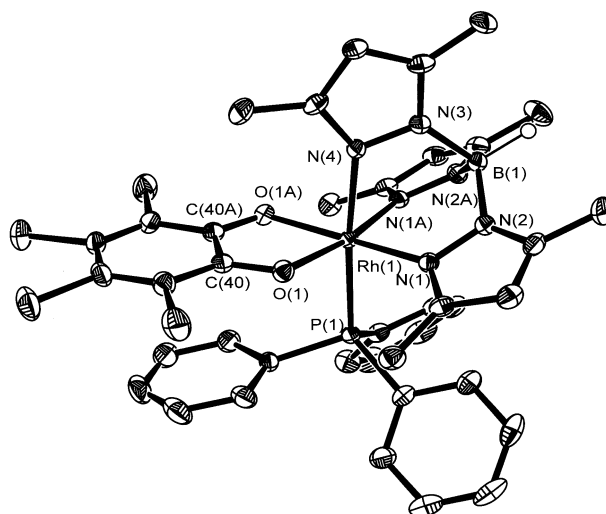


Fig. 3 The molecular structure of complex **4⁺**.

atom, only $[\text{Rh}(\text{o-O}_2\text{C}_6\text{Cl}_4)\{\text{P}(\text{O}i\text{Pr})_3\}\text{Tp}']^+ \textbf{6}^+$ shows resolved coupling to phosphorus; at 6 G this is considerably less than observed for $[\text{Rh}(\text{o-O}_2\text{C}_6\text{Cl}_4)\{\text{P}(\text{O}i\text{Pr})_3\}(\eta\text{-C}_5\text{H}_5)]^+ (20.8 \text{ G})$, lending support to the electrochemical results described above which suggested less delocalisation of unpaired electron density from the semiquinone ligand to Rh^{III} in $[\text{Rh}(\text{o-O}_2\text{C}_6\text{Cl}_4)\text{LTp}']^+$ than in $[\text{Rh}(\text{o-O}_2\text{C}_6\text{Cl}_4)\text{L}(\eta\text{-C}_5\text{H}_5)]^+$.

Structures of complexes **4** and **4⁺**

The molecular structures of complexes **4** and **4⁺** are shown in Figs. 2 and 3 and important bond lengths and angles are given in Table 4, together with selected data for the redox pair $[\text{Ru}(\text{o-O}_2\text{C}_6\text{Cl}_4)(\text{CO})_2(\text{PPh}_3)_2]^z$ ($z = 0$ or 1)¹¹ for comparison.

Both complexes **4** and **4⁺** are octahedral with the metal bound to a $\kappa^3\text{-Tp}'$ ligand, PPh_3 , and an O, O' -chelate. In each case, a plane of symmetry bisects the O, O' -chelate; in contrast to **2**, the $\text{Rh}(\text{o-O}_2\text{C}_6\text{Cl}_4)$ metallacycle is nearly planar in both **4** and **4⁺**. The C–O bond distances define the bonding in the $\text{Rh}(\text{o-O}_2\text{C}_6\text{Cl}_4)$ units. Thus, in **4** the C(40)–O(1) bond length [1.339(4) Å] is typical of the complexed catecholate dianion $\text{o-C}_6\text{Cl}_4\text{O}_2^{2-}$ (1.33–1.35 Å) whereas in **4⁺** the C–O length is significantly shorter [1.293(4) Å] and typical of the co-ordinated semiquinone radical anion $\text{o-C}_6\text{Cl}_4\text{O}_2^-$ (1.26–1.30 Å).¹²

As in complex **2**, the Rh–N(4) bond *trans* to PPh_3 in both **4** and **4⁺** [2.130(4) and 2.143(3) Å respectively] is longer than Rh–N(1) which is *trans* to oxygen [2.080(3) and 2.039(2) Å], presumably as a result of *trans* influence effects. The Rh–N

Table 4 Selected bond lengths (Å) and angles (°) for [Rh(*o*-O₂C₆-Cl₄)(PPh₃)Tp'] **4** and [Rh(*o*-O₂C₆Cl₄)(PPh₃)Tp']⁺[PF₆]⁻ **4**⁺[PF₆]⁻ and for *trans*-[Ru(CO)₂(PPh₃)₂(O₂C₆Cl₄)]^z (*z* = 0 or 1)^a

	4	4 ⁺	Ru, <i>z</i> = 0	Ru, <i>z</i> = 1
Rh–N(1)	2.080(3)	2.039(2)	—	—
Rh–N(4)	2.130(4)	2.143(3)	—	—
M–P(1)	2.357(1)	2.390(1)	2.434(2)	2.420(2)
			2.414(2)	2.437(2)
M–O(1)	2.021(2)	2.048(2)	2.062(3)	2.098(3)
	—	—	2.065(3)	2.088(3)
C(40)–O(1)	1.339(4)	1.293(4)	1.334(5)	1.291(5)
	—	—	1.326(5)	1.289(5)
C(40)–C(40A)	1.383(4)	1.454(6)	1.417(7)	1.439(7)
P–C _{av}	1.830(4)	1.831(3)	1.829(5)	1.826(5)
O(1)–M–O(1A)	83.49(13)	80.97(12)	80.9(1)	78.4(1)
O(1)–M–P(1)	96.0(1)	92.66(6)	92.3(2)	90.6(2)
N(1)–M–N(4)	83.75(11)	84.36(9)	—	—
N(1)–M–N(1A)	96.1(2)	96.28(14)	—	—

^a Data from ref. 11.

bonds are slightly shorter in **4**⁺ than in **4** perhaps as a consequence of some of the positive charge residing on rhodium. The Rh–P bond is longer in the cation [2.390(1) compared to 2.357(1) Å] as is Rh–O [2.048(2) compared to 2.021(2) Å]. The increase on oxidation in the Rh–P bond length (0.033 Å) is greater than that observed on oxidation of [Ru(*o*-O₂C₆Cl₄)(CO)₂(PPh₃)₂] (*ca.* 0.005 Å)¹¹ and towards the lower end of the range observed for metal–phosphine complex redox pairs {increases range from 0.012(2) to 0.117(4) Å}.¹³ The lack of any observable change in the mean P–C bond lengths on oxidation is in accord with our overall view that oxidation is primarily confined to the catecholate ligand of **4**.

Conclusion

The reaction of [Rh(CO)LTp'] with *o*-C₆Cl₄O₂ gives the carbonyl insertion products [Rh{C(O)OC₆Cl₄O}LTp'] (L = CO **1** or PPh₃ **2**) which are considerably more stable to heat and UV light than the η-C₅R₅ analogues. The complexes [Rh(*o*-O₂C₆Cl₄)LTp'] {L = CO **3**, PPh₃ **4**, AsPh₃ **5**, P(OPh)₃ **6** or py **7**} are formed by decarbonylating **1** or **2** either thermally or by UV irradiation, or by the reaction of [Rh(*o*-O₂C₆Cl₄)(CO)Tp'] **3** with L. Oxidation of **4**–**7** gave stable monocations in which the unpaired electron is localised on the O, O'-donor ligand.

Experimental

The preparation, purification and reactions of the complexes

Table 5 Crystal and refinement data for [Rh{C(O)OC₆Cl₄O}(PPh₃)Tp']·2CH₂Cl₂ **2**·2CH₂Cl₂, [Rh(*o*-O₂C₆Cl₄)(PPh₃)Tp']·CH₂Cl₂ **4**·CH₂Cl₂ and [Rh(*o*-O₂C₆Cl₄)(PPh₃)Tp']⁺[PF₆]⁻·3CH₂Cl₂ **4**⁺[PF₆]⁻·3CH₂Cl₂

	2 ·2 CH ₂ Cl ₂	4 ·CH ₂ Cl ₂	4 ⁺ [PF ₆] ⁻ ·3CH ₂ Cl ₂
Formula	C ₄₂ H ₄₁ BCl ₈ N ₆ O ₃ PRh	C ₄₀ H ₃₉ BCl ₆ N ₆ O ₂ PRh	C ₄₂ H ₄₃ BCl ₁₀ F ₆ N ₆ O ₂ P ₂ Rh
Formula weight	1106.10	993.16	1307.98
Crystal system	Triclinic	Orthorhombic	Orthorhombic
Space group (no.)	<i>P</i> $\bar{1}$ (2)	<i>Pnma</i> (62)	<i>Pnma</i> (62)
<i>a</i> /Å	11.724(1)	21.053(4)	26.150(1)
<i>b</i> /Å	12.302(2)	14.046(4)	13.756(3)
<i>c</i> /Å	18.348(2)	14.439(3)	14.601(1)
<i>α</i> /°	93.077(9)		
<i>β</i> /°	97.73(3)		
<i>γ</i> /°	114.924(8)		
<i>V</i> /Å ³	2303.5(4)	4269.9(17)	5252.4(13)
<i>Z</i>	2	4	4
<i>μ</i> /mm ⁻¹	0.916	0.856	0.959
Reflections collected	24121	26097	32291
Independent reflections	10422	5068	6252
Final <i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)]	0.034	0.046	0.0435

described were carried out under an atmosphere of dry nitrogen using dried, distilled and deoxygenated solvents; reactions were monitored by IR spectroscopy where necessary. Unless stated otherwise complexes (i) were purified by dissolution in CH₂Cl₂, filtration of the solution through Celite, addition of *n*-hexane to the filtrate and reduction of the volume of the mixture *in vacuo* to induce precipitation, and (ii) are stable under nitrogen and dissolve in polar solvents such as CH₂Cl₂, acetone and thf to give moderately air-stable solutions. Photolysis reactions were carried out in silica tubes placed *ca.* 20 cm from a 500 W mercury vapour lamp as a source of UV irradiation.

The compounds [Rh(CO)₂Tp']¹⁴ and [Rh(CO)(PPh₃)Tp']¹ were prepared by published methods. IR spectra were recorded on a Nicolet 5ZDX FT spectrometer and UV-visible spectra on a Perkin-Elmer Lambda 2 UV/VIS spectrometer. X-Band ESR spectra were recorded on a Bruker 300ESP spectrometer equipped with a Bruker variable temperature accessory and a Hewlett-Packard 5350B microwave frequency counter. The field calibration was checked by measuring the resonance of the dp^{ph} (diphenylpicrylhydrazyl) radical before each series of spectra. NMR spectra were recorded on JEOL GX270, GX400 and I300 spectrometers with SiMe₄ as an internal standard. All spectrometers operated in the Fourier transform mode, with field stability maintained by an external lock system. Electrochemical studies were carried out in CH₂Cl₂ as previously described.¹⁵ Under the conditions used, *E*^{o'} for the one-electron oxidations of [Fe(η-C₅H₅)₂] and [Fe(η-C₅H₄COMe)₂], added to the test solutions as internal calibrants for complexes **3**–**7** and **4**⁺–**7**⁺ respectively, are 0.47 and 0.97 V. Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Preparations

[Rh{C(O)OC₆Cl₄O}(CO)Tp'] 1. A solution of [Rh(CO)₂Tp'] (0.20 g, 0.44 mmol) and *o*-C₆Cl₄O₂ (0.11 g, 0.44 mmol) in toluene (45 cm³) was stirred in the absence of light for 20 min and then evaporated to dryness *in vacuo*. Purification of the resulting solid (three times) gave the product as a bright yellow solid, yield 165 mg (54%).

[Rh{C(O)OC₆Cl₄O}(PPh₃)Tp']·0.33 CH₂Cl₂ 2. A solution of [Rh(CO)(PPh₃)Tp'] (0.20 g, 0.29 mmol) and *o*-C₆Cl₄O₂ (71 mg, 0.29 mmol) in *n*-hexane (180 cm³) was stirred in the absence of light for 20 min. The pale yellow mother liquors were decanted from a bright orange-yellow solid which was purified and then dried *in vacuo*, yield 183 mg (68%).

[Rh(*o*-O₂C₆Cl₄)(CO)Tp'] 3. A mixture of [Rh(CO)₂Tp'] (1.5 g, 3.3 mmol) and *o*-C₆Cl₄O₂ (0.81 g, 3.3 mmol) in toluene (150

cm³) was stirred in a silica tube for 30 min in the absence of light and then irradiated under UV light for 6 h. The resulting orange-red solution was evaporated to dryness *in vacuo* to give an orange-brown solid which was dissolved in CH₂Cl₂ (80 cm³), filtered through Celite, and concentrated *in vacuo* before *n*-hexane was added to give an orange-brown solid. The product was purified, washed with *n*-hexane and dried *in vacuo*, yield 0.97 g (44%).

[Rh(*o*-O₂C₆Cl₄)(PPh₃)Tp']·CH₂Cl₂ 4·CH₂Cl₂. A solution of [Rh(CO)(PPh₃)Tp'] (0.10 g, 0.145 mmol) and *o*-C₆Cl₄O₂ (36 mg, 0.145 mmol) in toluene (70 cm³) was stirred for 20 min in the absence of light. The resulting orange-brown solution was heated under reflux for 40 min and then evaporated to dryness *in vacuo*. The product was purified (twice) to give a brick red solid, yield 64 mg (49%).

[Rh(*o*-O₂C₆Cl₄)(AsPh₃)Tp'] 5. A solution of [Rh(*o*-O₂C₆Cl₄)(CO)Tp'] 3 (0.20 g, 0.30 mmol) in toluene (50 cm³) was added dropwise over 4 h to a solution of AsPh₃ (0.273 g, 0.89 mmol) in toluene (30 cm³) at 70 °C. After stirring the mixture for 30 h at 70 °C, the solution was evaporated to dryness *in vacuo*. The resulting oily red solid was washed with *n*-hexane and purified (twice) to give a pink-purple solid, yield 74 mg (26%).

[Rh(*o*-O₂C₆Cl₄)(P(OPh)₃)Tp'] 6. A solution of [Rh(*o*-O₂C₆Cl₄)(CO)Tp'] 3 (0.20 g, 0.30 mmol) and P(OPh)₃ (80 µl, 0.30 mmol) in toluene (50 cm³) was stirred at 70 °C for 1 h and then evaporated to dryness *in vacuo*. The resulting solid was purified to give a pale orange solid, yield 190 mg (67%).

[Rh(*o*-O₂C₆Cl₄)(py)Tp'] 7. A solution of [Rh(*o*-O₂C₆Cl₄)(CO)Tp'] 3 (0.20 g, 0.30 mmol) and pyridine (30 µl, 0.37 mmol) in toluene (50 cm³) was stirred for 3 h at 70 °C and then evaporated to dryness *in vacuo*. The residue was dissolved in CH₂Cl₂, filtered through Celite, and then *n*-hexane was added and the solution concentrated *in vacuo*. The resulting bright yellow precipitate was purified using CH₂Cl₂–Et₂O, yield 140 mg (65%).

[Rh(*o*-O₂C₆Cl₄)(PPh₃)Tp'][(PF₆)₂·2 CH₂Cl₂ 4⁺[PF₆]⁻·2 CH₂Cl₂. Solid [NO][PF₆] (26 mg, 0.15 mmol) was added to a CH₂Cl₂ (30 cm³) solution of complex 4 (0.10 g, 0.10 mmol). After 1 h the purple solution was filtered through Celite and *n*-hexane was added to give deep purple crystals, yield 100 mg (81%). [Rh(*o*-O₂C₆Cl₄)(py)Tp'][(PF₆)₂·CH₂Cl₂ 7⁺[PF₆]⁻·CH₂Cl₂ was prepared similarly. The complexes [Rh(*o*-O₂C₆Cl₄)LTp'][(PF₆)₂·*x* CH₂Cl₂ {L = AsPh₃, *x* = 1.5, 5⁺; L = P(OPh)₃, *x* = 0.5, 6⁺} were isolated similarly after further purification using CH₂Cl₂–*n*-hexane and CH₂Cl₂–Et₂O respectively.

Crystal structure determinations of [Rh{C(O)OC₆Cl₄O}-(PPh₃)Tp']·2 CH₂Cl₂ 2·2 CH₂Cl₂, [Rh(*o*-O₂C₆Cl₄)(PPh₃)Tp']·CH₂Cl₂ 4·CH₂Cl₂ and [Rh(*o*-O₂C₆Cl₄)(PPh₃)Tp'][(PF₆)₂·3 CH₂Cl₂ 4⁺[PF₆]⁻·3 CH₂Cl₂

Crystals of the three compounds suitable for X-ray diffraction studies were grown by allowing concentrated CH₂Cl₂ solutions

to diffuse slowly into *n*-hexane at –10 °C. All X-ray diffraction measurements were made at 173 K. Many of the other details of the structure analyses are presented in Table 5. Molecules of 4 and 4⁺ lie on mirror planes with one pyrazolyl ring and one phosphine ring in the plane and hydrogens on the methyl groups of the pyrazolyl disordered over the plane. One dichloromethane solvate in 2·2 CH₂Cl₂ was disordered and refined anisotropically with two site occupancies for the carbon and hydrogens in the ratio 62 : 38(1). Refinement of the anion in 4⁺[PF₆]⁻·3CH₂Cl₂ was hampered by disorder since its site (in a general position of the space group) is also 50% occupied by a dichloromethane solvate molecule whose carbon atom lies at the same position as the phosphorus atom of the anion. The B–H hydrogen atom in each structure was located in the electron density map and the co-ordinates refined freely.

CCDC reference numbers 155162–155164.

See <http://www.rsc.org/suppdata/dt/b0/b010061g/> for crystallographic data in CIF or other electronic format.

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