Impact of Dioxygen and Carboxylic Acids on the Transformation of Rhodium(I) to Rhodium(III) Complexes†

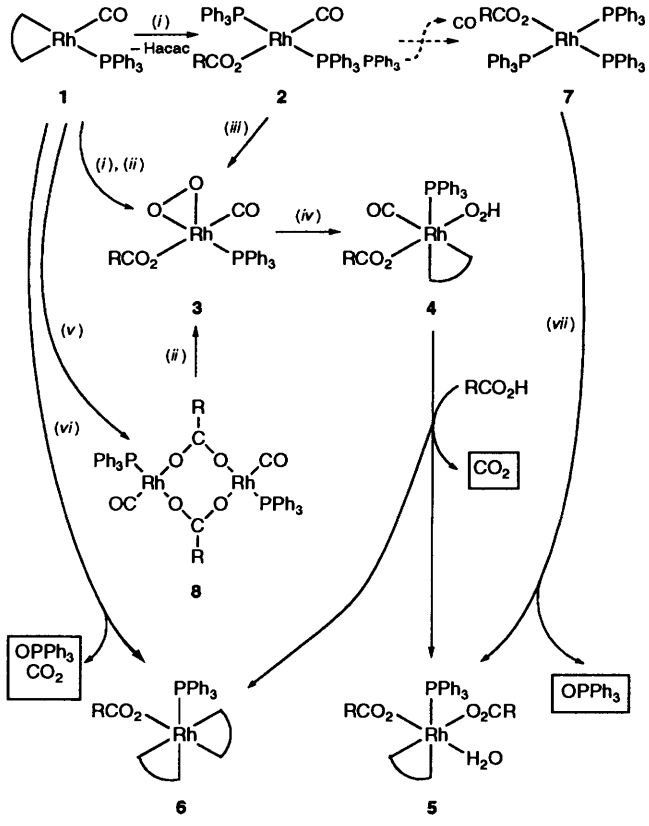
Ewa Mieczyńska, Anna M. Trzeciak, Józef J. Ziółkowski and Tadeusz Lis
Institute of Chemistry, University of Wrocław, F. Joliot-Curie 14 str., 50-383 Wrocław, Poland

The reaction of the hydroformylation catalyst precursor $[Rh(acac)(CO)(PPh_3)]$ (acac = acetylacetonate) with dioxygen and salicylic acid led to the formation of the rhodium(III) complexes $[Rh(acac)(HOC_6H_4CO_2)_2(PPh_3)(H_2O)]$ and $[Rh(acac)_2(HOC_6H_4CO_2)(PPh_3)]$. The structures of the latter complexes were characterized spectroscopically (^1H and ^{31}P NMR) as well as by X-ray crystallography. Dioxygen activation by Rh' proceeds through peroxo $[Rh(O_2)(HOC_6H_4CO_2)(CO)(PPh_3)]$ and hydrogen dioxide $[Rh(O_2H)(acac)(HOC_6H_4CO_2)(CO)(PPh_3)]$ complexes identified by IR, UV/VIS and ^{31}P NMR methods. Oxidation of CO to CO_2 occurs in the inner co-ordination sphere of rhodium.

The activity of rhodium(I) phosphine hydroformylation catalysts usually decreases in the presence of dioxygen.[1,2] This is caused by the oxidation of triphenylphosphine to triphenylphosphine oxide which has a detrimental effect on the catalytic system. Elimination of phosphine ligand from the co-ordination sphere converts the rhodium complexes into forms which are catalytically active in isomerization rather than hydroformylation reactions of olefins.[2] On the other hand it is well known that dioxygen treatment is successful in reactivating rhodium catalysts after prolonged use.[3] In this paper we present the results of studies on reaction of the hydroformylation precatalyst $[Rh(acac)(CO)(PPh_3)]$ **1** (acac = acetylacetonate), with dioxygen in the presence of salicylic acid. We expected that it would be possible to explain the effect of both dioxygen and the carboxylic acid on the real rhodium catalyst. The inspiration for this work was the identification of the rhodium(III) complex $[Rh(acac)(HOC_6H_4CO_2)_2(PPh_3)(H_2O)]$ as one of the products of reaction of **1** with salicylic acid.[4]

Results and Discussion

The results of the investigations of the system containing complex **1**, salicylic acid and dioxygen are shown in Scheme 1. Complex **1** does not react with dioxygen, even in the presence of triphenylphosphine, although that reaction was expected, since the peroxo-complex $[Rh(O_2)(acac)(PPh_3)_2]$ obtained from $[Rh(acac)(PPh_3)_2]$ is well known and structurally characterized.[5] However, the reaction does occur when salicylic acid is added. The presence of triphenylphosphine effects only the initial stage of the reaction, and the final reaction products are always the complexes $[Rh(acac)(HOC_6H_4CO_2)_2(PPh_3)(H_2O)]$ **5** and $[Rh(acac)_2(HOC_6H_4CO_2)(PPh_3)]$ **6**. Immediately after addition of salicylic acid to a solution of complex **1**, salicylate complexes without acetylacetonate ligand are formed: $[Rh(HOC_6H_4CO_2)(CO)(PPh_3)_2]$ **2** in the presence of phosphine or $[\{Rh(HOC_6H_4CO_2)(CO)(PPh_3)\}_2]$ **8** in the absence of phosphine, respectively. These complexes show quite different reactivities towards dioxygen. Thus **8** reacts with dioxygen giving the peroxo complex $[Rh(O_2)(HOC_6H_4CO_2)(CO)(PPh_3)]$ **3**. This was demonstrated by UV/VIS (Fig. 1), IR [ν(O–O) 813 cm^{-1}, Fig. 2] and ^{31}P NMR spectroscopy [δ 41, J(Rh–P) = 157.4 Hz]. Complex **2** reacts with dioxygen only in the presence of an excess of free salicylic acid, producing the same peroxo complex **3**. This reaction however does not occur when phosphine is added to the solution.



Scheme 1 R = HOC_6H_4. (*i*) 3–9 equivalents RCO_2H, PPh_3; (*ii*) O_2; (*iii*) O_2, RCO_2H; (*iv*) Hacac; (*v*) $3RCO_2H$; (*vi*) 3Hacac, $3RCO_2H$, O_2, PPh_3; (*vii*) $3RCO_2H$, 3Hacac, O_2

Passing dioxygen through a solution of complex **1** containing salicylic acid results in the formation of not only the peroxo complex **3**, but also of a hydrogen dioxide complex of formula $[Rh(O_2H)(acac)(HOC_6H_4CO_2)(CO)(PPh_3)]$ **4**. Complex **4** was characterized by ^{31}P NMR spectroscopy [δ 28.4, d, J(Rh–P) = 94 Hz]. Infrared and ^{31}P NMR data obtained for complexes **3** and **4** are in good agreement with those reported for similar complexes: $[Rh(O_2)(acac)(PPh_3)_2]$, ^{31}P NMR,[5]

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

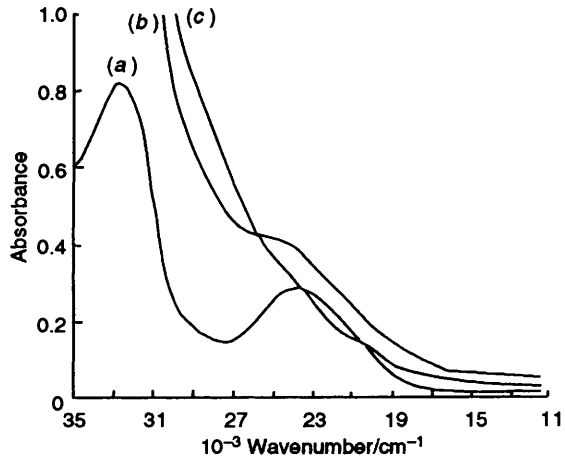


Fig. 1 The UV/VIS spectra measured during the reaction of $[\{Rh(HOC_6H_4CO_2)(CO)(PPh_3)\}_2]$ **8** with O_2 in toluene. Reaction times: (*a*) 0, (*b*) 16 and (*c*) 48 and 90 min

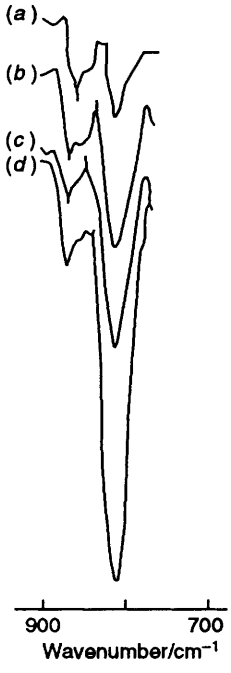


Fig. 2 Infrared spectra (700–900 cm^{-1}) measured during the reaction of complex **8** with O_2 in toluene. Reaction times: (*a*) 0, (*b*) 16, (*c*) 48 and (*d*) 90 min

δ 37.2 [J(Rh–P) = 148.5] and 28.6 [J(Rh–P) = 138.3]; IR[5] ν(O–O) 875 cm^{-1}; $[RhCl(O_2H)(acac)(PPh_3)]$, ^{31}P NMR,[6,7] δ 24.7 [J(Rh–P) = 99.6 Hz]; IR,[6,7] ν(O–O) 813 cm^{-1}. Both complexes contribute to the mechanism of oxidation of Rh^{I} to Rh^{III} in a way similar to that described for $[RhCl(acac)_2(PPh_3)]$ formation.[7]

It is worthwhile mentioning that the oxidation of rhodium in our system is accompanied by the oxidation of the CO ligand to CO_2 (after 5 h *ca.* 98% CO_2 is produced). Such a reaction is rather rare,[8] contrary to the oxidation of triphenylphosphine to triphenylphosphine oxide which is well known for many rhodium complexes.[5–9] However in our system phosphine oxidation is much slower than that of carbon monoxide. Therefore, the final reaction products, complexes **5** and **6**, contain co-ordinated phosphine. It was found that the oxidation of triphenylphosphine occurs more easily in ethanol than in benzene. Reaction of **1** with dioxygen in the presence of salicylic acid and phosphine in ethanol is much faster but less selective than in benzene. After 90 min of reaction mainly $OPPh_3$ and

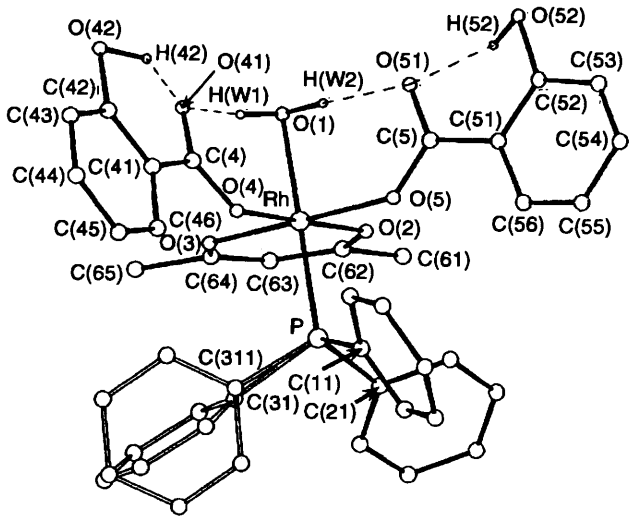


Fig. 3 Structure and numbering scheme of $[Rh(acac)(HOC_6H_4CO_2)_2(PPh_3)(H_2O)]$ **5**

Table 1 Phosphorus-31 and ^1H NMR data for rhodium(III) complexes (in C_6D_6)

	^1H NMR		^{31}P NMR	
Complex	δ_{CH_3}	δ_{CH}	δ	J(Rh–P)/Hz
5	1.66	5.04	30.8	134.7
6a	1.68, 1.76, 2.03, 2.12	4.86, 5.5	25.9	128.9
6b	1.51, 1.65, 2.07, 2.2	4.94, 5.32	27.7	130.8

traces of **5** are observed in the products. A shorter time is not sufficient for total conversion of the transient complex **2**.

Particularly interesting is the formation of complex **6** with two acetylacetonate ligands besides that of **5** from **4** (when no excess of acetylacetonate). According to ^1H NMR measurements, **6** exists in solution as two isomeric forms **a** and **b**. This is demonstrated by the two doublets for the methyl groups as well as two signals for the methine protons having different chemical shifts (Table 1). In both isomers the acetylacetonate ligands are inequivalent (Table 1). As a consequence, both the remaining ligands $HOC_6H_4CO_2^-$ and PPh_3 should be located in *cis* position, as are Cl^- and PPh_3 in $[RhCl(acac)_2(PPh_3)]$.[7] X-Ray crystallographic studies of **6** (Fig. 4) show the possibility of isomers in solution.

The reaction of complex **1** with dioxygen and salicylic acid in the presence of free Hacac leads to the formation of only complex **6**. Increase in the salicylic acid concentration even to the ratio $[HOC_6H_4CO_2H]:[Rh] = 9:1$ did not change the product composition and a mixture of **5** and **6** was obtained. Complex **5** may also be obtained independently from the reaction of $[Rh(HOC_6H_4CO_2)(PPh_3)_3]$ **7** with salicylic acid and acetylacetone. This reaction probably proceeds *via* the peroxo complex $[Rh(O_2)(HOC_6H_4CO_2)(PPh_3)_3]$, by analogy to $[RhCl(O_2)(PPh_3)_3]$.[10]

Important conclusions concerning the stability of the Rh–acac and $Rh–O_2CC_6H_4OH$ bonds are as follows: even very small amounts of salicylic acid added to rhodium(I) complexes in an oxygen-free atmosphere are enough to replace acetylacetonate ligand; on the contrary, in rhodium(III) complexes, acetylacetonate ligand is not substituted even when an excess of salicylic acid is applied; at comparable concentrations of acetylacetone and salicylic acid, complexes **6a** and **6b** with two inequivalent acetylacetonate ligands

are formed; Rh^{I}–acac bonding is weaker than Rh^{III}–acac bonding.

Crystal Structures of $[Rh(acac)(HOC_6H_4CO_2)_2(PPh_3)(H_2O)]$ **5** *and* $[Rh(acac)_2(HOC_6H_4CO_2)(PPh_3)]$ **6**.—Very few rhodium(III) carboxylate complexes have been characterized by X-ray crystallography.[11–15] The molecular structures of **5** and **6** are presented in Figs. 3 and 4 and selected interatomic distances and angles are listed in Tables 2 and 3. In both complexes the co-ordination geometry around rhodium atom is approximately octahedral with the O_{acac}–Rh–O_{sal} angles varying from 83.9 to 96.1°. Similar slight distortion caused by the presence of the chelate ligand was observed in other rhodium–acetylacetonate complexes (Table 4).[16–19]

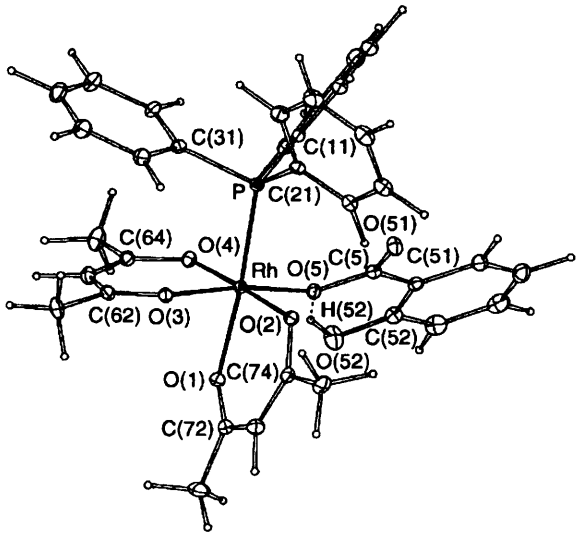


Fig. 4 Structure and numbering scheme of $[Rh(acac)_2(HOC_6H_4CO_2)(PPh_3)]$ **6**

Table 2 Selected interatomic distances (Å) and angles (°) for $[Rh(acac)(HOC_6H_4CO_2)_2(PPh_3)(H_2O)]$ **5**

Rh–P	2.262(1)	Rh–O(1)	2.154(5)
Rh–O(2)	1.982(4)	Rh–O(3)	1.964(4)
Rh–O(4)	2.047(4)	Rh–O(5)	2.025(4)
O(1)–Rh–P	176.9(2)	O(2)–Rh–P	92.9(2)
O(3)–Rh–P	94.4(2)	O(4)–Rh–P	86.3(2)
O(5)–Rh–P	86.1(2)	O(2)–Rh–O(1)	84.8(2)
O(3)–Rh–O(1)	83.8(2)	O(4)–Rh–O(1)	96.1(2)
O(5)–Rh–O(1)	95.7(2)	O(3)–Rh–O(2)	95.5(2)
O(4)–Rh–O(2)	177.2(2)	O(5)–Rh–O(2)	85.0(2)
O(4)–Rh–O(3)	87.3(2)	O(5)–Rh–O(3)	179.3(2)
O(5)–Rh–O(4)	92.2(2)		

Table 3 Selected interatomic distances (Å) and angles (°) for $[Rh(acac)_2(HOC_6H_4CO_2)(PPh_3)]$ **6**

Rh–P	2.277(2)	Rh–O(1)	2.063(3)
Rh–O(2)	1.990(3)	Rh–O(3)	1.980(3)
Rh–O(4)	2.000(3)	Rh–O(5)	2.022(3)
O(1)–Rh–P	174.7(1)	O(2)–Rh–P	92.4(1)
O(3)–Rh–P	91.9(1)	O(4)–Rh–P	89.7(1)
O(5)–Rh–P	96.0(1)	O(2)–Rh–O(1)	91.8(2)
O(3)–Rh–O(1)	85.3(2)	O(4)–Rh–O(1)	86.1(2)
O(5)–Rh–O(1)	86.7(2)	O(3)–Rh–O(2)	84.6(2)
O(4)–Rh–O(2)	177.9(2)	O(5)–Rh–O(2)	96.1(2)
O(4)–Rh–O(3)	95.2(2)	O(5)–Rh–O(3)	172.0(2)
O(5)–Rh–O(4)	83.9(2)		

The Rh^{III}–O_{acac} bonds in complexes **5** and **6** (Tables 2 and 3) are shorter than the corresponding bonds in rhodium(I) complexes (2.029–2.087 Å).[20,21] This is in agreement with our earlier conclusion that Rh^{I}–O_{acac} bonds in these complexes are weaker than those of Rh^{III}–O_{acac}. However this is not a general behaviour for rhodium–acetylacetonate complexes, as shown by the data in Table 4.

In complex **6** the Rh–O(1) bond *trans* to PPh_3 is 2.063(3) Å, the longest Rh–O_{acac} distance in **5** and **6**. This may be explained by the *trans* effect of PPh_3. A similar effect was observed in $[Rh(acac)(CO)(PPh_3)]$,[20] where the corresponding Rh–O (*trans* to PPh_3) distance is 2.087(4) Å whereas in $[Rh(acac)(CO)_2]$[21] it is only 2.040(4) Å. In complex **5** the *trans* influence of PPh_3 is demonstrated by a lengthening of the Rh–O(1) bond. Compared with $[Rh(acac)(H_2O)(C_{10}H_{12}F_6)]$[17] {$C_{10}H_{12}F_6$ = 7,8-bis(trifluoromethyl)bicyclo-[4.2.2]dec-7-ene-2,5-diyl} however this effect is probably diminished by hydrogen-bond formation (Table 5).

The Rh–P distance in complex **5** is 2.262(1) Å while in **6** it is 2.277(2) Å. Both these interatomic distances are more close to those in rhodium(I) complexes $[Rh(L–L)(CO)(PPh_3)]$ (L–L = chelate ligand) [2.232(1)–2.261(2) Å][22–25] than to those in rhodium(III) complexes which are usually longer, *e.g.* 2.395 and 2.388 Å in $[Rh(acac)I_2(PPh_3)_2]$[20] and 2.35 Å in $[RhMeI_2(PPh_3)_2(C_6H_6)]$.[26] This can be explained as a consequence of the low *trans* influence of oxygen-containing ligands.

In complex **6** the angle between the planes formed by the two acetylacetonate ligands is 68(1)°. The carboxylate group and the carbon ring of the salicylate ligand are almost coplanar. In complex **5** both carboxylate groups of the salicylate ligands are not coplanar with the corresponding carbon rings and the angles between the planes are 7.2(8) and 2.9(8)° respectively. This distortion of the salicylate ligand in **5** can be explained by the formation of two hydrogen bonds between the carbonyl oxygen of the carboxyl group with the water molecule and the α-hydroxyl group of the salicylate ligand. The angle between the planes through the carboxyl groups is equal to 102(1)°. The salicylate ligands are arranged towards the rhodium atom in such a way that the torsion angles Rh–O(4)–C(4)–O(41) and Rh–O(5)–C(5)–O(51) are −2.7(10) and 8.6(15)°, respectively. In complex **6** only one intramolecular hydrogen bond was found between the oxygen atom of the carboxylate group co-ordinated to rhodium and the α-hydroxyl group of the salicylate ligand (Table 5).

Table 4 Distances (Å) Rh–O_{acac} and angles (°) O_{acac}–Rh–O_{acac} in known complexes of Rh^{III} with acetylacetonate ligands

Compound	Rh–O_{acac}	O_{acac}–Rh–O_{acac}
$[Rh(acac)_3]$[16]	1.981, 1.992	95.5
	1.999, 1.999	95.1
	1.990, 1.991	95.4
$[Rh(acac)(H_2O)(C_{10}H_{12}F_6)]$[17]	2.18(1), 2.05(1)	86.5(5)
$[Rh(acac)I_2(PPh_3)_2]$[18]	2.07(2), 2.07(2)	90.2(8)
$[Rh_2(C_5Me_5)_2(acac)_2][BF_4]_2$[19]	2.103(4), 2.101(4)	86.8(2)

Table 5 Intramolecular hydrogen-bond distances (Å) and angles (°) in complexes **5** and **6**

	Distances		
D–H···A	H···A	D···A	Angle
Complex **5**			
O(42)–H(42)···O(41)	1.74(8)	2.565(8)	141(7)
O(52)–H(52)···O(51)	1.73(9)	2.535(12)	138(8)
O(1)–H(W1)···O(41)	1.73(4)	2.679(7)	164(6)
O(1)–H(W2)···O(51)	1.70(5)	2.635(8)	160(6)
Complex **6**			
O(52)–H(52)···O(5)	1.64(3)	2.527(5)	150(4)

Table 6 Fractional atomic coordinates for complex **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh	0.324 13(4)	0.579 69(3)	0.189 05(2)	C(35)*	0.715 1(7)	0.592 6(5)	0.073 1(3)
P	0.540 87(13)	0.542 71(9)	0.225 09(6)	C(36)*	0.652 0(7)	0.602 1(5)	0.123 6(3)
O(1)	0.121 3(5)	0.621 6(3)	0.154 0(3)	C(311)*	0.616 8(8)	0.513 2(6)	0.162 7(4)
O(2)	0.350 8(4)	0.687 3(3)	0.235 8(2)	C(321)*	0.754 6(8)	0.500 4(6)	0.179 7(4)
O(3)	0.347 8(5)	0.624 7(3)	0.107 0(2)	C(331)*	0.822 9(8)	0.482 8(6)	0.132 2(4)
O(4)	0.297 3(4)	0.465 7(3)	0.145 1(2)	C(341)*	0.753 4(8)	0.478 0(6)	0.067 7(4)
O(41)	0.096 3(5)	0.484 6(3)	0.080 5(3)	C(351)*	0.615 6(8)	0.490 7(6)	0.050 7(4)
O(42)	−0.022 2(6)	0.361 4(4)	0.014 4(3)	C(361)*	0.547 3(8)	0.508 3(6)	0.098 2(4)
O(5)	0.297 5(4)	0.532 4(3)	0.273 0(2)	C(4)	0.197 5(7)	0.441 5(4)	0.101 6(3)
O(51)	0.089 3(5)	0.570 9(4)	0.266 6(4)	C(41)	0.204 2(7)	0.356 5(4)	0.077 0(3)
O(52)	−0.016 5(8)	0.539 9(6)	0.359 7(6)	C(42)	0.093 4(8)	0.321 2(5)	0.035 1(4)
C(11)	0.568 8(6)	0.449 5(4)	0.275 1(3)	C(43)	0.098 8(9)	0.239 4(5)	0.012 7(4)
C(12)	0.685 9(7)	0.440 7(5)	0.322 2(4)	C(44)	0.212 1(9)	0.195 1(5)	0.031 0(5)
C(13)	0.708 4(9)	0.366 5(6)	0.358 7(4)	C(45)	0.323 1(9)	0.229 3(5)	0.071 6(5)
C(14)	0.616 7(9)	0.305 5(5)	0.349 4(4)	C(46)	0.319 9(8)	0.310 7(5)	0.095 1(4)
C(15)	0.499 7(8)	0.314 1(5)	0.303 3(4)	C(5)	0.196 6(6)	0.540 1(5)	0.296 0(4)
C(16)	0.475 0(6)	0.386 3(4)	0.265 4(4)	C(51)	0.210 7(8)	0.508 3(5)	0.362 0(4)
C(21)	0.634 1(6)	0.623 7(4)	0.276 6(3)	C(52)	0.104 1(11)	0.509 5(6)	0.391 5(6)
C(22)	0.598 7(7)	0.641 9(5)	0.332 9(3)	C(53)	0.123 6(18)	0.479 0(9)	0.453 6(9)
C(23)	0.663 9(8)	0.703 4(6)	0.372 6(4)	C(54)	0.235 2(18)	0.448 6(8)	0.485 3(8)
C(24)	0.764 4(9)	0.745 1(6)	0.357 2(4)	C(55)	0.342 1(11)	0.447 3(5)	0.458 3(5)
C(25)	0.797 2(12)	0.728 7(7)	0.301 1(6)	C(56)	0.330 4(9)	0.475 9(5)	0.398 1(4)
C(26)	0.735 4(10)	0.666 2(6)	0.261 9(5)	C(61)	0.399 0(8)	0.827 0(5)	0.255 5(4)
C(31)*	0.635 8(7)	0.533 6(5)	0.161 2(3)	C(62)	0.377 6(7)	0.754 9(5)	0.210 2(4)
C(32)*	0.682 8(7)	0.455 6(5)	0.148 2(3)	C(63)	0.386 9(8)	0.763 8(5)	0.147 2(4)
C(33)*	0.745 8(7)	0.446 1(5)	0.097 7(3)	C(64)	0.370 7(8)	0.704 7(5)	0.101 2(4)
C(34)*	0.762 0(7)	0.514 6(5)	0.060 1(3)	C(65)	0.381 1(9)	0.726 5(6)	0.034 3(4)

* Occupancy factor 0.5.

Table 7 Fractional atomic coordinates for complex **6**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh	0.298 94(2)	−0.128 19(3)	0.072 94(1)	C(32)	0.117 92(31)	−0.172 3(5)	0.204 03(20)
P	0.254 60(7)	−0.022 43(11)	0.156 88(5)	C(33)	0.085 66(37)	−0.274 1(6)	0.240 01(23)
O(1)	0.331 61(22)	−0.238 9(3)	−0.001 39(12)	C(34)	0.144 41(40)	−0.352 9(6)	0.276 09(22)
O(2)	0.423 93(19)	−0.055 4(3)	0.089 31(13)	C(35)	0.234 31(39)	−0.335 1(6)	0.277 54(22)
O(3)	0.346 89(19)	−0.287 9(3)	0.121 78(12)	C(36)	0.267 63(33)	−0.236 4(5)	0.241 41(20)
O(4)	0.174 77(19)	−0.205 3(3)	0.053 95(12)	C(61)	0.354 49(36)	−0.515 4(5)	0.155 03(24)
O(5)	0.253 56(19)	0.019 6(3)	0.012 79(12)	C(62)	0.303 21(33)	−0.400 0(5)	0.122 80(19)
O(51)	0.306 30(24)	0.208 6(4)	0.061 01(13)	C(63)	0.215 27(33)	−0.421 2(5)	0.098 79(20)
O(52)	0.172 19(29)	0.032 7(4)	−0.093 82(16)	C(64)	0.156 15(32)	−0.328 0(5)	0.068 70(20)
C(11)	0.163 24(28)	0.099 9(4)	0.142 03(18)	C(65)	0.061 64(33)	−0.369 7(6)	0.049 25(24)
C(12)	0.159 52(34)	0.216 9(5)	0.177 21(22)	C(71)	0.422 39(42)	−0.356 2(6)	−0.063 16(25)
C(13)	0.087 81(40)	0.304 8(6)	0.167 24(26)	C(72)	0.412 56(39)	−0.260 1(5)	−0.010 53(21)
C(14)	0.018 97(39)	0.276 2(6)	0.122 14(29)	C(73)	0.488 58(35)	−0.204 1(6)	0.021 11(22)
C(15)	0.021 36(35)	0.161 5(6)	0.087 15(24)	C(74)	0.491 01(32)	−0.105 8(5)	0.066 58(19)
C(16)	0.094 06(31)	0.072 7(5)	0.096 24(21)	C(75)	0.580 07(29)	−0.048 9(6)	0.092 82(22)
C(21)	0.339 70(28)	0.065 3(5)	0.208 05(18)	C(5)	0.265 41(29)	0.151 4(5)	0.017 17(18)
C(22)	0.406 21(28)	0.141 8(5)	0.185 43(19)	C(51)	0.224 91(28)	0.230 8(5)	−0.036 57(18)
C(23)	0.467 04(31)	0.215 3(5)	0.224 66(21)	C(52)	0.181 27(33)	0.168 6(6)	−0.087 90(21)
C(24)	0.461 57(38)	0.213 0(6)	0.285 89(23)	C(53)	0.145 43(36)	0.249 4(7)	−0.136 05(24)
C(25)	0.394 96(40)	0.139 4(6)	0.309 07(21)	C(54)	0.152 94(37)	0.388 1(7)	−0.133 75(25)
C(26)	0.333 97(35)	0.066 3(6)	0.270 94(21)	C(55)	0.195 72(37)	0.451 9(6)	−0.084 04(26)
C(31)	0.208 90(29)	−0.151 4(5)	0.204 71(17)	C(56)	0.231 79(33)	0.373 0(6)	−0.035 37(21)

Experimental

The rhodium(I) complexes were obtained as described in the literature: $[Rh(acac)(CO)(PPh_3)]$ **1**,[27] $[Rh(HOC_6H_4CO_2)(CO)(PPh_3)_2]$ **2**,[4] $[Rh(acac)(HOC_6H_4CO_2)_2(PPh_3)(H_2O)]$ **5**,[4] $[\{Rh(HOC_6H_4CO_2)(CO)(PPh_3)\}_2]$ **8**.[4] Benzene was distilled over sodium. Ethanol was distilled before use.

$[Rh(acac)_2(HOC_6H_4CO_2)(PPh_3)]$ **6**.—A solution of complex **1** (0.11 g) in benzene (3 cm^3), triphenylphosphine (0.058 g) and a three-fold excess of salicylic acid and acetylacetone were added to a glass reactor. Dioxygen was passed through the solution at 70 °C for 2 h, then the solvent was evaporated to dryness. The precipitate was washed with ethanol and dried in a vacuum. The product, a yellow powder, is stable in air. Yield *ca.* 78% [Found (Calc.): C, 59.2 (60.0); H, 4.90 (4.85)%].

$[Rh(HOC_6H_4CO_2)(PPh_3)_3]$ **7**.—To $[RhH(PPh_3)_4]$[28] (0.3 g) in ethanol (10 cm^3), was added salicylic acid (1.18 g) and the mixture heated under reflux for *ca.* 1 h. The orange precipitate of complex **7** was washed with ethanol and dried in a vacuum. Yield 67% [Found (Calc.): C, 71.00 (71.00); H, 4.80 (4.85)%].

Crystallography.—Crystal data for complex **5**. Dark yellow crystals, $C_{37}H_{34}O_9PRh$, M = 765.56, monoclinic, space group $P2_1/n$, a = 10.31(1), b = 16.07(2), c = 21.36(2) Å, β = 103.82(8)°, U = 3437(7) $Å^3$, Z = 4, D_c = 1.462(3) g cm^{-3},

D_m = 1.44 g cm^{-3}, $F(000)$ = 1552, T = 293(2) K, μ(Cu-Kα) = 50.2 cm^{-1}, λ(Cu-Kα) = 1.5418 Å.

Crystal data for complex **6**. Dark yellow crystals, $C_{35}H_{34}O_7PRh$, M = 700.54, monoclinic, space group $P2_1/c$, a = 14.918(6), b = 9.734(4), c = 22.034(9) Å, β = 96.28(3)°, U = 3180(3) Å^3, Z = 4, D_c = 1.463(2) g cm^{-3}, D_m = 1.446 g cm^{-3}, $F(000)$ = 1440, T = 299(1) K, μ(Mo-Kα) = 6.25 cm^{-1}, λ(Mo-Kα) = 0.710 69 Å.

Data collection and processing. For both crystals the preliminary data were recorded by photographic methods. Intensities were collected with a KUMA KM4 four-circle diffractometer in the ω–2θ mode (with crystals of dimensions 0.4 × 0.3 × 0.1 mm for **5** and 0.4 × 0.2 × 0.2 mm for **6**) and Cu-Kα (for **5**) and Mo-Kα (for **6**) radiation; 6945 ($4 < 2\theta < 150°$) and 6323 ($4 < 2\theta < 54°$) reflections were measured respectively, of which 4474 and 3401 with $I > 3\sigma(I)$ were used for calculations. The structures were solved by the Patterson method and refined by full-matrix least-squares calculations using SHELX 76.[29] Atomic scattering factors and anomalous dispersion terms used in the refinement were taken from ref. 30. The carbon-bonded hydrogen atoms were included in geometrically calculated positions with d(C–H) = 1.08 Å. The hydrogen atoms from the hydroxyl groups were found from difference maps and refined with d(O–H) = 0.97 Å. One of the phenyl rings in **5** is statistically disordered in two positions. A weighting scheme of the form $w = 1/\sigma^2(F_o)$ was applied for both structures. Final R [$= (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$] and R' [$= \Sigma w(|F_o| - |F_c|)/\Sigma wF_o$] values are 0.0463 and 0.0496 for **5** and 0.0298 and 0.0297 for **6**. For the last cycle of refinement the maximum value of the ratio Δ/σ was 0.12 for **5** and 0.22 for **6**, and the final difference maps showed a general background within −0.63 and 0.58 and −0.30 and 0.30 e Å^{-3} for **5** and **6**, respectively. The final positional parameters for the non-hydrogen atoms are given in Tables 6 and 7.

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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