Co-ordination, Isomerisation and Disruption of the Ligands $Ph_2PO_2C(CH_2)_nCH{=}CH_2$ (n = 0 or 1). X-Ray Crystal and Molecular Structure of Chloro(tetraphenyldiphosphoxane-κ^2P,P')(triphenylphosphine)rhodium(I)–Tetrahydrofuran (1/1)†

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Reaction of Ph_2PCl with $CH_2{=}CHCO_2H$ and $CH_2{=}CHCH_2CO_2H$ in the presence of triethylamine produces $Ph_2PO_2CCH{=}CH_2$ (L) and $Ph_2PO_2CCH_2CH{=}CH_2$ (L′) respectively. Both are found to undergo further intermolecular reaction to produce $Ph_2PP(O)Ph_2$. Reaction of L with $[RhCl(PPh_3)_3]$, 1 mol L per 1 mol Rh, produces $[RhCl(PPh_3)L]$ which reverts back to $[RhCl(PPh_3)_3]$ if left in solution. The compound $[RhCl(PPh_3)L]$ contains a bidentate L ligand co-ordinated *via* the phosphorus atom and the double bond. A similar reaction of L′ with $[RhCl(PPh_3)_3]$ produces $[RhCl(PPh_3)(Ph_2PO_2CCH{=}CHMe)]$, involving metal-promoted double-bond migration in the L′ ligand. Reaction of 2 mol of L per mol of rhodium produces $[RhCl(PPh_3)(Ph_2POPPh_2)]$ involving a metal-promoted disruption of the L ligand to bidentate tetraphenyldiphosphoxane. Reaction of $[RhCl(PPh_3)(Ph_2POPPh_2)]$ with $TlPF_6$ produces $[Rh(PPh_3)_2(Ph_2POPPh_2)][PF_6]$. However addition of $TlPF_6$ to the reaction solution of the above 2:1 reaction of L and $[RhCl(PPh_3)_3]$ results in the isolation of $[Rh(PPh_3)_3(O_2CCH_2CH_2PPh_3)][PF_6]$, a complex containing a triphenylphosphoniopropionate ligand, the formation of which involves a major alteration of the L ligand. Reaction, 1 mol ligand per 1 mol Rh, of L and L′ with $[\{RhCl(C_8H_{14})_2\}_2]$ produces complexes of the form $[(RhClL'')_2]$, where L″ = L or L′ in which the mixed anhydride ligand is co-ordinated *via* the phosphorus atom and the double bond. Reaction of 2 mol of L per mol of Rh with $[\{RhCl(C_8H_{14})_2\}_2]$ produces $[RhClL_2]$ and $[(RhClL)_2(Ph_2POPPh_2)]$ as its major products. The former is a five-co-ordinate complex containing two bidentate L ligands, the later a binuclear complex containing a tetraphenyldiphosphoxane bridge between the metal centres each of which has a bidentate L ligand co-ordinated to it. All L ligands in these complexes are co-ordinated *via* the phosphorus atom and the double bond. The complexes have been characterised by spectroscopic means and by an X-ray crystal structure of $[RhCl(PPh_3)(Ph_2POPPh_2)]\cdot$thf (thf = tetrahydrofuran). The crystals are triclinic, space group $P\bar{1}$ with a = 11.294(4), b = 11.475(6), c = 17.144(9) Å, α = 102.31(4), β = 102.71(4), γ = 74.11(4)°, and Z = 2. The structure was obtained from 2329 reflections measured on an automatic diffractometer and refined to an R' value of 0.075. The RhPOP ring is essentially planar with very small angles at Rh (68.4°) and O (95.4°) so that the two ring phosphorus atoms are brought very close together (2.457 Å). Calculations confirm that, despite this short P···P distance, there is no bonding interaction.

Reactions of compounds with general formula $RR'C{=}CR''C(X)OH$ with Ph_2PCl in the presence of NEt_3, at 0 °C and under nitrogen, produce compounds of the form $Ph_2POC(X)CR''{=}CR'R$ (X = O, R = R′ = Me, R″ = H; R = R″ = H, R′ = Me; R = R″ = H, R′ = CH=CHMe; R = Ph, R′ = H, R″ = Me; X = H_2, R = R′ = Me, R″ = H).[1] These compounds were found to be stable in solution at room temperature and indefinitely stable in the solid state under a dinitrogen atmosphere, whilst in air the materials rapidly became oily. No tendency for the compounds to undergo oxygen migrations or Arbuzov-type rearrangements was observed. Subsequent reaction of these isolated ligands with equimolar quantities of 0.5 $[\{RhCl(C_2H_4)_2\}_2]$ or 0.5 $[\{RhCl(C_8H_{14})_2\}_2]$ (C_8H_{14} = cyclooctene) in all cases produced complexes of the form $[\{RhCl[Ph_2POC(X)CR''{=}CR'R]\}_2]$ in which the mixed anhydride ligands were co-ordinated *via* the phosphorus atom and double bond.[1] Equimolar reaction of $[RhCl(PPh_3)_3]$ and $Ph_2PO_2CCR''{=}CRR'$ produced $[RhCl(PPh_3)_n(Ph_2PO_2CCR''{=}CRR')]$, n = 1 or 2.[2] For n = 2 the complexes contained a mixed anhydride ligand co-ordinated *via* the phosphorus atom alone, whilst for n = 1 the complexes contained a bidentate mixed anhydride ligand co-ordinated *via* the phosphorus atom and the double bond. Treatment of $[RhCl(PPh_3)_n(Ph_2PO_2CCR''{=}CR'R)]$ with $TlPF_6$ or $AgSbF_6$ led in all cases to complexes of the form $[Rh(PPh_3)_2(Ph_2PO_2CCR''{=}CR'R)]^+$ in which the mixed anhydride was bound through the phosphorus atom and the carbonyl oxygen atom.[2] It has also been reported that catalytic hydrogenation of highly functionalised acrylic acids could be achieved using these complexes in which both the metal centre and the phosphorus atom of the mixed anhydride are involved in catalytically important steps. Specifically, base-catalysed *trans* esterification of the co-ordinated $Ph_2PO_2CCR''HCR'RH$ by $^-O_2CCR''{=}CR'R$ allows loss of the hydrogenated product and introduction of a new

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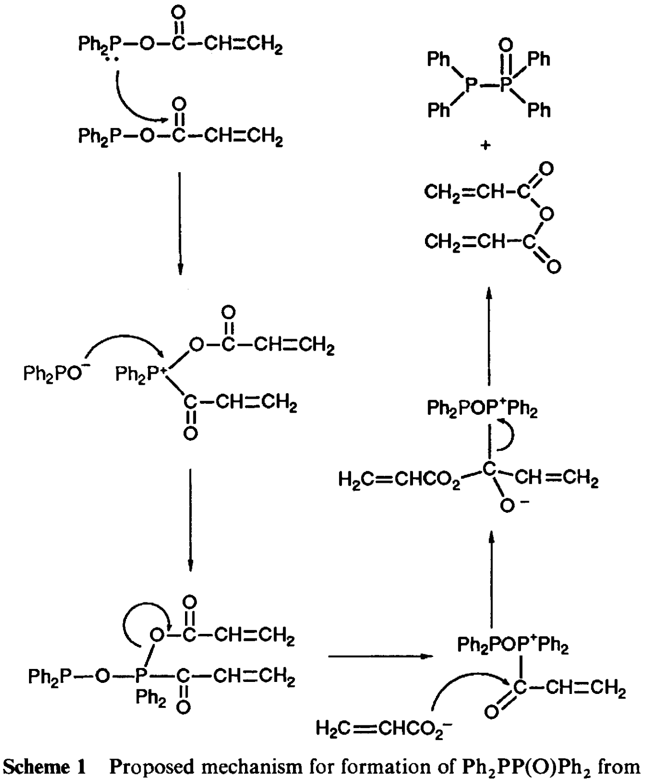
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Phosphorus-31 NMR data for new ligands and rhodium complexes[a]

	δ			J/Hz					
Compound	P_A	P_B	P_C	RhP_A	RhP_B	RhP_C	P_AP_B	P_AP_C	P_BP_C
L	100.1 (s)								
L′	100.5 (s)								
$Ph_2PP(O)Ph_2$	37.2 (d)	−22.9 (d)					227.2		
$Ph_3P^+CH_2CH_2CO_2^-$	24.7 (s)								
$[RhCl(PPh_3)L]$	27.5 (dd)	116 (dd)		122	133		424		
$[RhCl(PPh_3)(Ph_2POPPh_2)]$	25.1 (ddd)	106.5 (ddd)	81.2 (ddd)	132	170	125	30	382	122
2 $[(RhClL_2)_2]$	132.4 (d)			172					
3 $[(RhClL_2)_2]$	115.5 (d)			96					
4 $[(RhClL_2)_2]$	125.8 (dd)	131.6 (dd)		123	127		20		
$[(RhClL')_2]$	149.3 (d)			196					
$[RhClL_2]$	109.2 (d)			96					
$[RhClL_2]$[b,c]	110.8	109.2		86	104		512		
$[(RhClL)_2(Ph_2POPPh_2)]$[c,d]	136.5 (dd)	131.8 (dt)	131.8 (t)	155	149	149	25	0	30
$[Rh(PPh_3)_2(Ph_2POPPh_2)]PF_6$[c,e,f]	28.5	28.5	100.2	135	135	124	25	−35	259
$[Rh(PPh_3)_3(O_2CCH_2CH_2PPh_3)]PF_6$[e]	51.3 (dt)	34.8 (dd)	22.2 (s)	177	152	0	42	0	0

[a] In CD_2Cl_2 at 298 K unless otherwise stated; chemical shifts to high frequency of external 85% H_3PO_4; for assignments see structures and schemes. [b] At 263 K. [c] Coupling constants from simulation, signs are relative. [d] $\delta(P_D)$ 136.5 (dd), $J(RhP_D)$ 155, $J(P_AP_D) = J(P_BP_D) = 0$, $J(P_CP_D) = 25$ Hz. [e] Septet at δ −144 from PF_6^-. [f] $\delta((P_D)$ 100.2, $J(RhP_D)$ 124, $J(P_AP_D) = 259$, $J(P_BP_D) = -35$, $J(P_CP_D) = 122$ Hz.



Scheme 1 Proposed mechanism for formation of $Ph_2PP(O)Ph_2$ from $Ph_2PO_2CCH{=}CH_2$ (L)

substrate molecule.[3] We now report an extension in the range of these mixed anhydrides to include $Ph_2PO_2CCH{=}CH_2$ and $Ph_2PO_2CCH_2CH{=}CH_2$ and the associated co-ordination chemistry of these ligands to rhodium centres. This differs from that of their more substituted analogues. Preliminary results of part of this work have been communicated.[4]

Results and Discussion

Preparation and Properties of $Ph_2PO_2CCH{=}CH_2$ *and* $Ph_2PO_2CCH_2CH{=}CH_2$.—Reaction of 1 mol dm^{-3} tetrahydrofuran (thf) solutions of propenoic and but-3-enoic acids with 1 mol dm^{-3} solutions of Ph_2PCl and NEt_3, at 0 °C and under nitrogen, gives colourless solutions of $Ph_2PO_2CCH{=}CH_2$ (L) and $Ph_2PO_2CCH_2CH{=}CH_2$ (L′) respectively, upon removal of $[NEt_3H]Cl$ by filtration. Unlike those mixed anhydrides already reported[1] it proved impossible to isolate these ligands; attempts to do so resulted in the isolation of a colourless precipitate which analysed as $Ph_2PP(O)Ph_2$, tetraphenyldiphosphane monoxide.[5,6] Phosphorus-31 NMR studies of fresh solutions of L or L′ (see Table 1) showed that ≈40% conversion into $Ph_2PP(O)Ph_2$ occurs over 24 h if the ligands are left in dilute thf solution at 0 °C and under nitrogen. The reaction was shown to be unaffected by NEt_3 or Ph_2PCl and is thought to take place *via* a disproportionation reaction. A possible mechanism is shown in Scheme 1. All reactions of these mixed anhydrides involved the use of the freshly prepared dilute L and L′ solutions, adding them directly to precooled solutions of the metal reagents directly after removal of the $[NEt_3H]Cl$ by filtration.

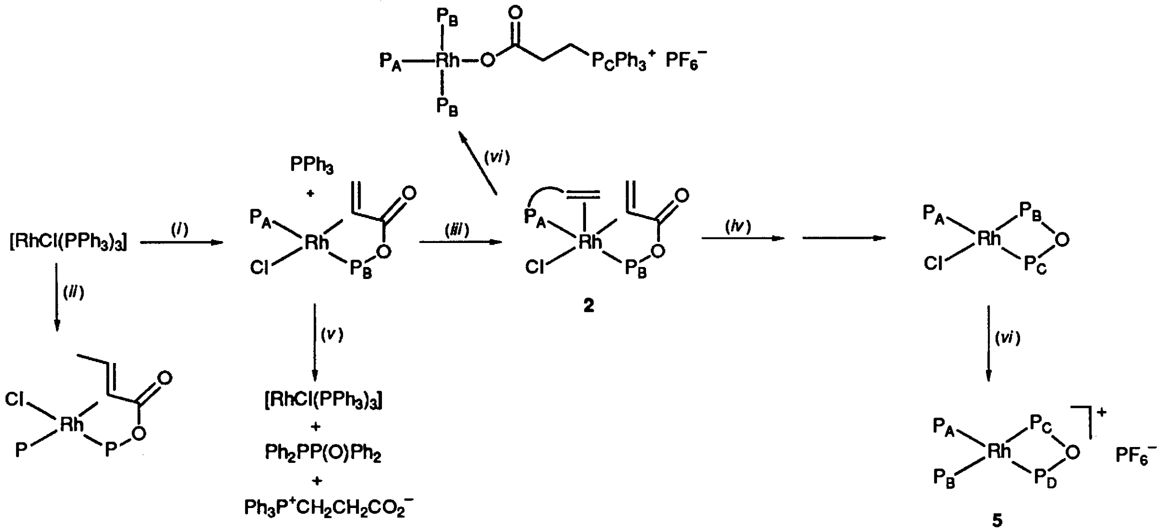
Reactions of L *and* L′ *with* $[RhCl(PPh_3)_3]$.—(*i*) 1 *mol of rhodium*: 1 *mol of mixed anhydride*. The complex $[RhCl(PPh_3)_3]$ and L were allowed to react in a 1:1 molar ratio and the reaction monitored at 10 min intervals using ^{31}P NMR spectroscopy. After 10 min ^{31}P NMR data (Table 1) showed a species giving rise to two doublets of doublets. We have not been able to isolate this complex in a pure state, although addition of light petroleum at this stage precipitates a yellow solid which contains mostly this compound. Infrared and ^1H NMR studies (Table 2) suggest that it contains a mixed anhydride ligand bound though P and the double bond[3] so we assign this complex as $[RhCl(PPh_3)L]$. Similar complexes have been obtained[3] from reactions of $[RhCl(PPh_3)_3]$ with $Ph_2PO_2CCH{=}CHR$ (R = Me or CH=CHMe). For $[RhCl(PPh_3)L]$ the high value of J_{PP} suggests mutually *trans* P atoms. Other complexes of this stoichiometry usually have mutually *cis* P atoms but for $[RuCl(PPh_3)(Ph_2PO_2CCH{=}CHMe)]$ there is a minor isomer with mutually *trans* P atoms which exchanges rapidly with the major isomer (*cis* P) at room temperature.[7] It appears that steric factors play a major role in determining the stereochemistry of these complexes with the isomer with *trans* P atoms being preferred in the absence of major steric interactions, but addition of substituents on the double bond causes an unacceptable interaction with the PPh_3 ligand and this is relieved by the complex adopting a geometry in which the double bond becomes *trans* to PPh_3 (*i.e.* *cis* P atoms).

On further standing at 0 °C the resonances from $[RhCl(PPh_3)L]$ decayed although not completely and were replaced by those of $[RhCl(PPh_3)_3]$, $Ph_2PP(O)Ph_2$ and the zwitterion $Ph_3P^+CH_2CH_2CO_2^-$.[8] It appears that some of the PPh_3

Table 2 Infrared and ^{1}H NMR data for new compounds[a]

Compound	δ H_a	δ H_b	δ H_c	ν(C=O)	ν_{asym}(POP)	ν(Rh–Cl)
$[RhCl(PPh_3)L]$	4.01 (m)		4.51 (m)	1740s		290w
$[RhCl(PPh_3)(Ph_2POPPh_2)]$					800m	290w
$[(RhClL)_2]$	3.0 (m)		3.7 (m)	1750s		300w
$[(RhClL')_2]$[b]	5.6 (m)		2.7 (m)	1755s		295w
$[RhClL_2]$[c]	3.1 (m), 3.2 (m)	3.45, 3.55 (m)	3.9 (m)	1740s, 1760s		280w
$[(RhClL)_2(Ph_2POPPh_2)]$[d]	3.0 (m)		3.41 (m)	1740s	855s	280w
$[Rh(PPh_3)_2(Ph_2POPPh_2)][PF_6]$					830s	
$[Rh(PPh_3)_3(O_2CCH_2CH_2PPh_3)][PF_6]$[e]	1.67 (m)	1.00 (m)		1620m		
$Ph_3P^+CH_2CH_2CO_2^-$[e]	3.4 (m)	2.7 (m)		1593m, 1583m		

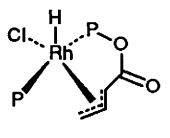
[a] Proton NMR spectra in CD_2Cl_2 at 298 K, chemical shifts to high frequencies of $SiMe_4$; IR (maxima) in cm^{-1}; H_a, H_b are protons on terminal C atom, H_c is on other vinyl C atom. All compounds show broad resonances from Ph near δ 7. All isolated complexes contain thf (1 molecule). [b] Methylene protons at δ 3.05 (dm). [c] At 263 K. [d] ν_{sym}(POP) at 770w cm^{-1}. [e] H_a adjacent to CO_2^- group.



Scheme 2 Reactions of $[RhCl(PPh_3)_3]$ with L′ or L. (*i*) L (1 equivalent), 0 °C, thf, 10 min; (*ii*) L′ (1 equivalent), 0 °C. thf; (*iii*) L (1 equivalent), 0 °C, thf, 10 min; (*iv*) PPh_3, 0 °C, thf, several hours or standing solution from (*iii*) prepared *in situ* for several days; (*v*) thf, 0 °C several hours; (*vi*) $TlPF_6$ (slightly < 1 equivalent); 0 °C, thf, 1 h. Phenyl groups have been omitted for clarity; P⌒= indicates mixed anhydride bound through P and the double bond

released during the early stages of the reaction attacks free or bound L to give $Ph_3PCH_2CH_2CO_2$, a reaction which we have shown separately occurs for the free mixed anhydride, whilst the rest reco-ordinates to rhodium to regenerate $[RhCl(PPh_3)_3]$ (see Scheme 2).

A similar reaction of L′ with $[RhCl(PPh_3)_3]$ produced the known[2] $[RhCl(PPh_3)(Ph_2PO_2CCH{=}CHMe)]$, which is also formed from $[RhCl(PPh_3)_3]$ and $Ph_2PO_2CCH{=}CHMe$.[2] The formation of this complex from L′ involves a metal-promoted isomerisation of the double bond. Similar double-bond migrations have been reported, *e.g.* $Ph_2P(CH_2)_3CH{=}CH_2$ undergoes isomerisation on co-ordination to $[RhCl_2(CO)_4]$, although more forcing conditions are required.[9] The isomerisation of L′, as with related reactions, probably occurs *via* a π-allyl intermediate of the type **1**.



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Because related complexes are active for the catalytic hydrogenation of acrylate anions,[3] it seemed possible that this double-bond migration might also be rendered catalytic. However, under various conditions only stoichiometric reactions could be observed, presumably because $CH_2{=}CHCH_2CO_2^-$ does not displace $MeCH{=}CHCO_2^-$ from the complex in which the mixed anhydride is bound through both the P atom and the double bond. In the catalytic hydrogenation reaction the product mixed anhydride (*e.g.* $Ph_2PO_2CCH_2CH_2Me$) is bound through only P or possibly P and the carbonyl oxygen and is displaced by a potentially chelating ligand.[10]

(*ii*) 1 *mol of* $[RhCl(PPh_3)_3]$: 2 *mol of mixed anhydride*. The complex $[RhCl(PPh_3)_3]$ was treated with 2 mol equivalents of L. After standing for several days at 3 °C, bright orange crystals were obtained. X-Ray analysis (see below) showed that the complex was $[RhCl(PPh_3)(Ph_2POPPh_2)]$, containing a tetraphenyldiphosphoxane ligand, the anhydride of diphenylphosphinous acid. Phosphorus-31 NMR (Table 1) and mass spectral (see Experimental section) studies were totally consistent with this formulation and the ^{31}P chemical shifts and coupling constants were very similar to those reported for the analogous $[RhCl(PPh_3)(Ph_2PCH_2PPh_2)]$.[11] Unusually for transition-metal phosphorus compounds, one of the phosphorus atoms exhibits two large values of J_{PP} (122 and 382 Hz). This resonance is from the ring P atom *trans* to PPh_3 so there is the usual large *trans* P–P coupling and a large coupling to the other ring P atom, mostly *via* the O atom. Complexes containing the Ph_2POPPh_2 ligand have been reported[12–14] for transition-metal carbonyls and unidentate, bridging or chelating modes of bonding have been identified. In these cases the complexes have usually been formed from reactions of metal carbonyls with $Ph_2PP(O)Ph_2$.

Since $Ph_2PP(O)Ph_2$ is formed slowly from L on standing under the reaction conditions in the absence of metal complexes, it seemed possible that $[RhCl(PPh_3)(Ph_2POPPh_2)]$ might have been formed by a reaction of $Ph_2PP(O)Ph_2$. Confirmation that the formation of $[RhCl(PPh_3)(Ph_2POPPh_2)]$ is not from a reaction of $Ph_2PP(O)Ph_2$ comes from the observation that reactions of $[RhCl(PPh_3)_3]$ with $Ph_2PP(O)Ph_2$ under similar conditions do not produce $[RhCl(PPh_3)(Ph_2POPPh_2)]$ but two other unidentified complexes.[15,*]

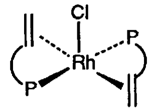
Monitoring the reaction of $[RhCl(PPh_3)_3]$ with 2 molar equivalents of L by ^{31}P NMR spectroscopy shows that several intermediates are involved. Within a few minutes of mixing, the major signals are from *trans*-$[RhCl(PPh_3)L]$ (see above), PPh_3 and $Ph_2PO_2CCH{=}CH_2$. The resonances from this metal complex are then gradually replaced by signals identical to those obtained from $[RhClL_2]$ (see below). At least one and probably two metal-containing intermediates are observed on the way to $[RhCl(PPh_3)(Ph_2POPPh_2)]$, but since we have not identified these we cannot speculate further on the mechanism of disruption of the mixed anhydride except to suggest that it almost certainly occurs within the co-ordination sphere of the metal and involves attack of PPh_3 on $[RhClL_2]$ (see later).

The reactions between $[RhCl(PPh_3)_3]$ and L or L′ are summarised in Scheme 2.

Reactions of L *and* L′ *with* $[\{RhCl(C_8H_{14})_2\}_2]$.—(*i*) 1 *mol of* L *or* L′ *with* 0.5 $[\{RhCl(C_8H_{14})_2\}_2]$. Ligand L or L′ was added to a thf solution containing $[\{RhCl(C_8H_{14})_2\}_2]$ (anhydride: Rh = 1:1). As with other mixed anhydrides,[1] the major products were $[(RhClL_2)_2]$, L = L or L′, with binding *via* the phosphorus atom and the double bond. Using L, minor products, $[RhClL_2]$ and $[(RhClL)_2Ph_2POPPh_2]$ (see below) were also formed. It is interesting that double-bond migration does *not* occur for L′ in this system.

(*ii*) 2 *mol of* L *with* 0.5 $[\{RhCl(C_8H_{14})_2\}_2]$. Addition of L to $[\{RhCl(C_8H_{14})_2\}_2]$ (L:Rh = 2:1) produced a colourless precipitate and a yellow solution from which yellow crystallites deposited on standing at 3 °C for several days. The white precipitate analyses as $[RhClL_2]$ and the observation of a single doublet in the ^{31}P NMR spectrum at room temperature suggests that it is either five-co-ordinate or fluxional or both. Infrared, ^1H and ^{31}P NMR studies at low temperature show that both L ligands are bound through both P and the double bond. The non-equivalence of the phosphorus atoms at low temperature, the observation of ν(Rh–Cl) at 280 cm^{-1}, and the low conductivity in CH_2Cl_2 confirm that the complex is five-co-ordinate and fluxional. Other similar complexes, *e.g.* $[RhCl(Ph_2PXCH_2CH{=}CH_2)_2]$, X = O[16] or CH_2,[17] are also five-co-ordinate and, for X = CH_2, the structure is known[18] to be distorted trigonal bipyramidal with one P atom and Cl occupying the axial positions, although the distortion is such that it could also be considered a square-pyramidal complex with a double bond in the apical position and mutually *cis* P atoms in the basal plane along with Cl and the other double bond. In these complexes, the chemical shifts of the two phosphorus atoms are very different from one another and the value of J_{PP} is typical of that for mutually *cis* P atoms.[19] In contrast, the very large value of J_{PP} (512 Hz) for $[RhClL_2]$ and the near concidence of the chemical shifts of the two P atoms at low temperature suggests a square-pyramidal geometry with the two phosphorus atoms mutually *trans* in the basal plane, one connected to a double bond in the apical position and the other to a double bond in the basal plane, **2** (Schemes 2 and 3). The compound $[RhClL_2]$ is also produced from 0.5 $[\{RhCl(C_2H_4)_2\}_2]$ and L.

Two other species are observable at low temperature in the ^{31}P NMR spectrum of $[RhClL_2]$. One gives rise to a doublet at δ 115.5, J_{PP} = 9 Hz, which exchanges with the main ABX resonances described above and can be attributed, assuming square-pyramidal geometry, to **3**. The other gives two doublets of doublets, at δ 131.6 (J_{RhP} = 127) and 125.8 (J_{RhP} = 123, J_{PP} = 20 Hz), which broaden on warming to room temperature. This may well be a further isomer, **4**, with mutually *cis* P atoms. Overall, apart from differences in chemical shifts, the spectrum is somewhat similar to that of $[RhCl(Ph_2POCH_2CH{=}CH_2)_2]$. for which two or three isomers have also been proposed.[16]



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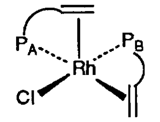

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The yellow crystallites obtained from the reaction of L with $[\{RhCl(C_8H_{14})_2\}_2]$, (L:Rh = 2:1) analyse as $[(RhClL)_2(Ph_2POPPh_2)]$ and this formulation is supported by mass spectroscopic studies. The ^{31}P NMR spectrum consists of an apparent doublet of triplets at δ 131.8 and an apparent doublet of doublets at δ 136.5. This can be simulated as an AA′MM′XX′ spin system with the values of coupling constants shown in Table 1. Long-range P–Rh couplings are close to 0 for all P atoms. The low value of $J(P_AP_B)$ and $J(P_CP_D)$ means that the phosphorus atoms are mutually *cis* on each rhodium, as in **6** (Scheme 3). Infrared studies confirm the bridging nature of Ph_2POPPh_2: ν_{asym}(POP) is at 855 cm^{-1}, *cf.* reported values of 775–800 for chelating and *ca.* 860 cm^{-1} for bridging, *e.g.* in $[\{W(CO)_5\}_2Ph_2POPPh_2]$,[12] or unidentate[13] binding.

The compound $[RhClL_2]$ is stable in solution or in the solid state, but reacts with PPh_3 to give $[RhCl(PPh_3)(Ph_2POPPh_2)]$, and $Ph_3P^+CH_2CH_2CO_2^-$, confirming that $[RhClL_2]$ is a plausible intermediate in the formation of $[RhCl(PPh_3)(Ph_2POPPh_2)]$ from $[RhCl(PPh_3)_3]$ and L.

Reactions of L and L′ with $[\{RhCl(C_8H_{14})_2\}_2]$ are summarised in Scheme 3.

Reactions with $TlPF_6$.—(*i*) $[RhCl(PPh_3)(Ph_2POPPh_2)]$. Reaction of $[RhCl(PPh_3)(Ph_2POPPh_2)]$ with slightly less than 1 equivalent of $TlPF_6$ produced, after work-up, a yellow solid analysing as $[Rh(PPh_3)(Ph_2POPPh_2)]PF_6$, always in less than 50% yield. A similar reaction using $[RhCl(PPh_3)(Ph_2POCCH{=}CHMe)]$ also produced a bis(PPh_3) complex, $[Rh(PPh_3)_2(Ph_2PO_2CCH{=}CHMe)]PF_6$, again in < 50% yield.[2] The compound $[Rh(PPh_3)_2(Ph_2POPPh_2)]^+$ is assigned structure **5** (Scheme 2) on the basis of its ^{31}P NMR spectrum which can be analysed as an AA′MM′X spin system (Table 1).

(*ii*) *With a mixture of* $[RhCl(PPh_3)_3]$ *and* L (1:2). Addition of $TlPF_6$ to a solution prepared from $[RhCl(PPh_3)_3]$ and L (1:2) gives a different product, $[Rh(PPh_3)_3(O_2CCH_2CH_2PPh_3)]PF_6$. The ^{31}P NMR spectrum of this complex shows resonances of PF_6^- as well as signals for the various different co-ordinated P atoms with the expected multiplicities. The resonance from the P atom of the $Ph_3P^+CH_2CH_2CO_2^-$ ligand appears as a singlet at δ 22.2, close to the position (δ 23.9) observed for the phosphorus atom of the same ligand in $[RuCl\{(Ph_2PO)_2H\}(PPh_3)(O_2CCH_2CH_2PPh_3)]$ which we have prepared from a similar reaction with $[RuCl_2(PPh_3)_3]$ and has been crystallographically characterised.[20] The presence of the zwitterion in the $[Rh(PPh_3)_3(O_2CCH_2CH_2PPh_3)]PF_6$ is further confirmed by the observation of multiplet resonances at δ 1.6 and 1.0 in the ^1H NMR spectrum arising from the methylene protons. These resonances are shifted upfield from those for the free zwitterion, as has previously been observed on complexation with Sn[21] or Ru.[20]

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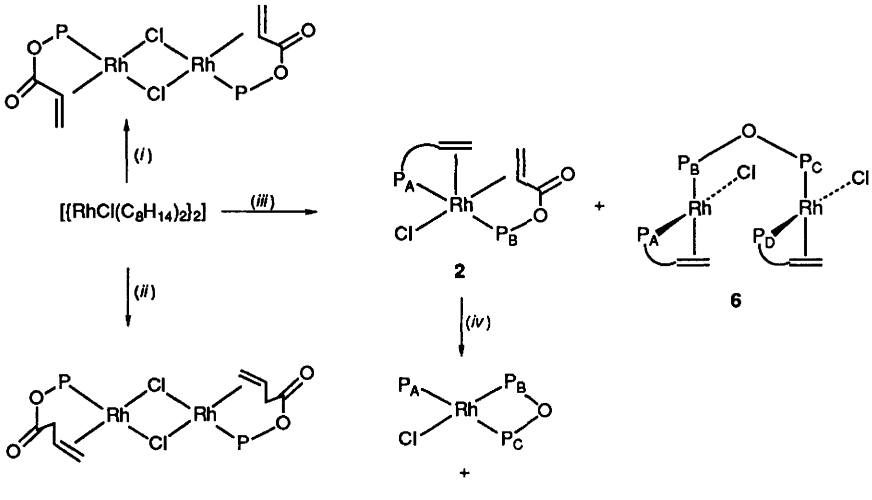
[*] Under reflux, $[RhCl(PPh_3)(Ph_2POPPh_2)]$ is a product of this reaction.[15]



Scheme 3 Reactions of $[\{RhCl(C_8H_{14})_2\}_2]$ with L′ or L. (*i*) L, Rh:L = 1:1, thf, 0 °C, 15 min; (*ii*) as (*i*) but L′; (*iii*) as (*i*) but Rh:L = 1:2, 2 h; (*iv*) $3PPh_3$, 0 °C, thf, several hours. Other details as in Scheme 2

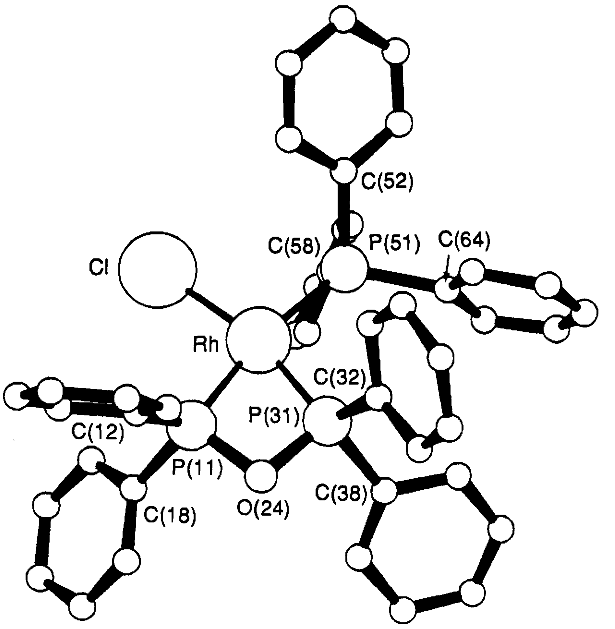


Fig. 1 X-Ray structure and numbering scheme for $[RhCl(PPh_3)(Ph_2POPPh_2)]$·thf (the thf molecule and H atoms are omitted for clarity)

Table 3 Selected bond lengths (Å) and angles (°) for $[RhCl(PPh_3)(Ph_2POPPh_2)]$

Rh–Cl	2.394(6)	Rh–P(51)	2.356(4)
Rh–P(31)	2.156(5)	P(11)–O(24)	1.648(12)
Rh–P(11)	2.215(4)	P(31)–O(24)	1.674(10)
Cl–Rh–P(51)	91.1(2)	Rh–P(11)–O(24)	97.3(4)
Cl–Rh–P(11)	97.4(2)	Rh–P(31)–O(24)	98.8(4)
P(11)–Rh–P(31)	68.4(2)	P(11)–O(24)–P(31)	95.4(5)
P(31)–Rh–P(51)	103.1(2)		

Since we have shown that L reacts with PPh_3 to give the zwitterion, $Ph_3P^+CH_2CH_2CO_2^-$, as the major product, it seems probable that the complex is formed by co-ordination of this zwitterion to rhodium on removal of Cl^- from $[RhCl(PPh_3)_3]$.

X-Ray Crystal Structure of $[RhCl(PPh_3)(Ph_2POPPh_2)]$.—The structure of $[RhCl(PPh_3)(Ph_2POPPh_2)]$ obtained by X-ray crystallography is shown in Fig. 1. Selected bond lengths and angles are in Table 3. The rhodium is co-ordinated to three phosphorus atoms and the chloride in a severely distorted square-planar arrangement. The Rh–Cl and Rh–P(Ph_3) bond lengths are as expected and similar to those in *e.g.* $[RhCl(PPh_3)_3]$.[22] The major feature of interest, however, is the four-membered Rh–P–O–P ring. Because of the very narrow bite angle of the chelating ligand, the P–Rh–P angle is only 68.4(2)°.

This small angle is compensated for in the rhodium co-ordination sphere by there being angles considerably >90° for Cl–Rh–P(11) and P(31)–Rh–P(51). Steric interactions between PPh_3 and the adjacent Ph_2P group of the chelating ligand make the largest angle P(31)–Rh–P(51) at 103.1(2)°. The four-membered ring is almost planar, with the oxygen atom lying only 0.083 Å out of the P(31)–Rh–P(11) plane but has a very acute angle at oxygen [95.4(5)°]. This angle is much less than those observed in related complexes of Cr or Mo (100.2 and 103.3° respectively)[13] and smaller than is generally found in chelating dppm ($Ph_2PCH_2PPh_2$) complexes.[11]

Comparison of the other ring angles with those in $[M(CO)_4(Ph_2POPPh_2)]$ shows that it is the M–P–O angles that are relatively invariant (at ≈97°) and that the angles at O and the metal distort to accommodate differences in *e.g.* M–P bond length.[4]

The net effect of this distortion of the angles in the Rh–P–O–P ring is to bring the two ring phosphorus atoms into very close proximity (2.457 Å).

MNDO Calculations on* $[RhCl(PPh_3)(Ph_2POPh_2)]$.—Although the P···P distance in the Ph_2POPPh_2 ligand of $[RhCl(PPh_3)(Ph_2POPh_2)]$, 2.457(7) Å, is longer than typical values[23] of P–P distances in molecules of types $X_3P–PX_3$ and $X_2P–PX_2$, it is only *ca.* 0.1 Å longer than the longest P–P bond distance so far recorded in a molecular compound, 2.360(3) Å in α-P_4S_4.[24] This distance is however very much less than the sum of either the van der Waals radii, 3.70 Å,[25] or even the one-angle radii, 2.92 Å,[26] for two phosphorus atoms. We have therefore investigated, by computational methods, the possibility of some bonding interaction between the two phosphorus atoms in this ligand.

An MNDO[27] bond-order calculation for a free Ph_2POPPh_2 molecule with experimental (from the complex) bond lengths, bond angles, and torsional angles averaged to C_{2v} symmetry gave calculated P–O and P···P bond orders of 0.934 and 0.018 respectively indicative of essentially zero bonding interaction between the two phosporus atoms.

There are two clearly identifiable phosphorus lone-pair

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* MNDO is Modified Neglect of Diatomic Differential Overlap.

orbitals, of a_1 and b_2 symmetry respectively, each composed of a mixture of phosphorus 3s and 3p orbitals, but largely uncontaminated by contributions from either oxygen or carbon. The a_1 and b_2 orbitals, which may be visualised as in-phase and out-of-phase lone-pair combinations in the POP plane, subtend angles of 26.1 and 77.4°, which may be compared with the experimental P–Rh–P angle of 68.4(2)°. Since both lone-pair contributions point in the direction of the metal atom in the complex and are not located between the two phosphorus atoms, we can conclude that there is negligible P–P bonding interaction.

Similar calculations were made on the related molecule Me_2POPMe_2, in which the geometry of the central C_2POPC_2 core was fixed at the C_{2v}-averaged geometry employed for Ph_2POPPh_2 but the remaining parameters were all optimised. The calculated P–O and P···P bond orders were 0.939 and 0.016, little different from those found for Ph_2POPPh_2. When the geometry of Me_2POPMe_2 were fully optimised, without constraints, the C_{2v} skeletal symmetry was retained, but the P–O–P angle increased from 95.4 to 115.8°, with a fall in $\Delta H_f°$ of some 31 kJ mol^{-1}: at this geometry the calculated P–O and P···P bond orders are 0.919 and 0.009 respectively. The results indicate a comparably soft skeleton-bending potential function, with very little variation in electronic structure with skeletal angle.

Experimental

Microanalyses were by the University of St. Andrews microanalytical service. NMR spectra were recorded on a Brüker Associates AM 300 spectrometer operating in the Fourier-transform mode with (for ^{31}P) proton-noise decoupling, IR spectra on Perkin-Elmer 1310 or 1710 (Fourier-transform) spectrometers on Nujol mulls between caesium iodide plates.

All manipulations were carried out under dry oxygen-free nitrogen using standard Schlenk-line and catheter-tubing techniques. All solvents were purified by distillation from calcium hydride (CH_2Cl_2) or sodium diphenylketyl [toluene, light petroleum (b.p. 40–60 °C), diethyl ether and tetrahydrofuran (thf)].

The complexes $[RhCl(PPh_3)_3]$,[28] $[\{RhCl(C_8H_{14})_2\}_2]$,[29] $[\{RhCl(C_2H_4)_2\}_2]$[30] and $Ph_2PP(O)Ph_2$[31] were prepared by standard literature methods.

(*i*) *Diphenylphosphino propenoate*, $Ph_2PO_2CCH{=}CH_2$ (L).—Equal volumes (0.54 cm^3) of separate solutions containing $H_2C{=}CHCO_2H$, Ph_2PCl and NEt_3 each in thf (1 mol dm^{-3}) were added sequentially to thf (20 cm^3) precooled to 0 °C. After stirring for 5 min the colourless solution was filtered to remove $[NEt_3H]Cl$ and used directly for subsequent reactions. Phosphorus-31 NMR studies showed that this solution contained only $Ph_2PO_2CCH{=}CH_2$ but that after 1 h at 3 °C *ca.* 5% conversion into $Ph_2PP(O)Ph_2$ had occurred. This rose to *ca.* 40% in 24 h. Diphenylphosphino but-3-enoate, $Ph_2PO_2CCH_2CH{=}CH_2$ (L′), was similarly prepared using $H_2C{=}CHCH_2CO_2H$ in place of $H_2C{=}CHCO_2H$.

(*ii*) *Chloro(diphenylphosphino propenoate)(triphenylphosphine)rhodium*(I).—A cooled solution (0 °C) of $[RhCl(PPh_3)_3]$ (0.5 g, 0.54 mmol) in thf (20 cm^3) was added to a cooled solution (0 °C) of $Ph_2PO_2CCH{=}CH_2$ (0.54 mmol) in thf, which had been preformed using the method described above. After a reaction period of 5–10 min the volume of the filtered reaction solution was reduced to approximately 5 cm^3 and then added to a large volume of cold petroleum. This produced a yellow precipitate which contained $[RhCl(PPh_3)L]$ as its major product. This complex was contaminated with $[RhCl(PPh_3)_3]$ and $Ph_3P^+CH_2CH_2CO_2^-$, but was identified by spectroscopic means.

(*iii*) $[RhCl(PPh_3)(Ph_2PO_2CCH{=}CHMe)]$ *from* $[RhCl(PPh_3)_3]$ *and* L′.—A solution of L′ (0.54 mmol) in thf (30 cm^3) was added to a cooled solution (0 °C) of $[RhCl(PPh_3)_3]$ (0.5 g, 0.54 mmol) in thf (20 cm^3). After filtration, the volume of the reaction solution was reduced to *ca.* 5 cm^3 and light petroleum was added dropwise to produce an orange microcrystalline solid. This was collected and recrystallised from CH_2Cl_2–diethyl ether. Yield 0.28 g (77%). The complex was identified as $[RhCl(PPh_3)(Ph_2PO_2CCH{=}CHMe)]$ by comparison of its ^1H and ^{31}P NMR spectra with those of an authentic sample.[2]

(*iv*) *Chloro(tetraphenyldiphosphoxane)(triphenylphosphine)rhodium*(I)*–Tetrahydrofuran*(1/1).—*Method* 1. To a cooled (0 °C) solution of $[RhCl(PPh_3)_3]$ (0.5 g, 0.54 mmol) in thf (20 cm^3) was added a cooled solution of L (0.28 g, 1.08 mmol). After stirring at 0 °C for 1.2 h, the orange solution was filtered, reduced in volume to *ca.* 10 cm^3 and allowed to stand at 3 °C for several days. The orange crystals that were formed were collected and dried *in vacuo*. Yield 0.3 g (78%) (Found: C, 64.3; H, 5.0. $C_{46}H_{43}ClO_2P_3Rh$ requires C, 64.3; H, 5.0%).

Method 2. The complex $[RhClL_2]$ (0.4 g, 0.6 mmol) in thf (25 cm^3) was treated with PPh_3 (0.48 g, 1.3 mmol). After stirring at 0 °C for 1 h, the solution was filtered and allowed to stand at −3 °C for several days. Phosphorus-31 NMR studies showed that it contained only $[RhCl(PPh_3)(Ph_2POPPh_2)]$, PPh_3 and $Ph_3P^+CH_2CH_2CO_2^-$.

(*v*) *Di-μ-chloro-bis[(diphenylphosphino propenoate)rhodium*(I)].—To a suspension of $[\{RhCl(C_8H_{14})_2\}_2]$ (0.3 g, 0.42 mmol) in thf (20 cm^3) was added a cooled solution of L (0.85 mmol) in thf (20 cm^3). The solution quickly became clear and after filtration was evaporated to 5 cm^3. Addition of light petroleum (10 cm^3) produced a bright orange precipitate. This was collected, dissolved in thf (10 cm^3), filtered to remove small amounts of $[RhClL_2]$ and allowed to stand at −3 °C for several days. Small amounts of $[(RhClL)_2(Ph_2POPPh_2)]$ which crystallised were removed by filtration and the complex was obtained as orange microcrystals by careful addition of light petroleum. These were collected and dried *in vacuo*. Yield 0.26 g (55%).

Di-μ-chloro-bis[(diphenylphosphino but-3-enoate)rhodium(I)]*–Tetrahydrofuran* (1/1) was prepared similarly using L′ (0.85 mmol). The initial bright orange precipitate was washed with diethyl ether (5 × 5 cm^3) and dried *in vacuo*. Yield 0.3 g (60%) (Found: C, 48.8; H, 3.9. $C_{36}H_{38}Cl_2O_5P_2Rh_2$ requires C, 48.6; H, 4.3%).

(*vi*) *Chlorobis(diphenylphosphino propenoate)rhodium*(I)*–Tetrahydrofuran* (1/1).—This was prepared as in (*v*) using L (1.7 mmol) in thf (20 cm^3). A white precipitate rapidly formed and, after stirring for 2 h, this was collected, washed with cold thf and dried *in vacuo* (Found: C, 55.8; H, 4.4. $C_{36}H_{38}ClO_5P_2Rh$ requires C, 55.4; H, 4.0%). The complex was also prepared as above but using $[\{RhCl(C_2H_4)_2\}_2]$ (0.3 g, 0.8 mmol) and L (1.6 mmol). Yield 0.13 g (50%). Fast atom bombardment (FAB) mass spectrum: *m/z* 650 (M^+), 615 ($M - Cl^+$), 560 $\{[RhL(Ph_2PO)]^+\}$ and 489 $\{[Rh(PPh_2)(Ph_2PO)]^+\}$.

(*vii*) *μ-Tetraphenyldiphosphoxane-bis[chloro(diphenylphosphino propenoate)rhodium*(I)]*–Tetrahydrofuran* (1/1).—After removal of the white precipitate produced in (*vi*), the yellow supernatant was evaporated to *ca.* 6 cm^3 and allowed to stand at 3 °C for several days. The yellow crystals that formed were collected and dried *in vacuo* (Found: C, 55.9; H, 4.7. $C_{58}H_{54}ClO_6P_4Rh_2$ requires C, 55.8; H, 4.4%). FAB mass spectrum: *m/z* 1175 (M^+), 1140 ($M - Cl^+$), 919 ($M - L^+$), 745 ($M - RhCl_2L^+$) and 339 $\{[RhCl(Ph_2PO)]^+\}$.

(*viii*) *(Tetraphenyldiphosphoxane)bis(triphenylphosphine)rhodium*(I) *Hexafluorophosphate–Tetrahydrofuran* (1/1).—To $[RhCl(PPh_3)(Ph_2POPPh_2)]$ (0.2 g, 0.25 mmol) in thf (20 cm^3)

Table 4 Coordinates (× 10^4) for non-hydrogen atoms of [RhCl(PPh$_3$)(Ph$_2$POPPh$_2$)] with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Rh	5 967(1)	8 782(1)	2 173(1)
Cl	4 749(4)	7 317(4)	2 035(3)
P(11)	4 553(4)	10 441(4)	2 573(3)
C(12)	3 125(14)	11 192(15)	1 952(10)
C(13)	1 971(18)	11 065(15)	2 036(11)
C(14)	899(18)	11 614(17)	1 565(11)
C(15)	927(19)	12 314(18)	1 029(13)
C(16)	2 052(22)	12 488(18)	951(12)
C(17)	3 119(18)	11 911(15)	1 417(11)
C(18)	4 074(13)	10 611(17)	3 536(10)
C(19)	3 837(15)	9 598(18)	3 754(12)
C(20)	3 459(18)	9 689(24)	4 479(14)
C(21)	3 295(19)	10 716(26)	5 009(14)
C(22)	3 519(20)	11 748(21)	4 787(14)
C(23)	3 885(20)	11 680(20)	4 052(12)
O(24)	5 418(9)	11 438(8)	2 714(6)
P(31)	6 653(4)	10 420(4)	2 384(3)
C(32)	6 851(14)	11 082(15)	1 544(11)
C(33)	7 215(16)	12 180(16)	1 656(12)
C(34)	7 228(17)	12 653(18)	997(14)
C(35)	6 894(17)	12 075(20)	242(14)
C(36)	6 529(18)	11 008(19)	101(11)
C(37)	6 504(15)	10 491(16)	747(12)
C(38)	7 875(16)	10 832(14)	3 200(11)
C(39)	7 648(18)	11 390(18)	3 937(12)
C(40)	8 607(24)	11 653(20)	4 586(12)
C(41)	9 800(20)	11 302(23)	4 453(15)
C(42)	10 069(18)	10 795(17)	3 711(13)
C(43)	9 120(17)	10 514(15)	3 073(11)
P(51)	7 727(4)	7 200(4)	1 891(3)
C(52)	7 549(14)	6 201(14)	926(10)
C(53)	6 360(15)	6 277(15)	416(11)
C(54)	6 220(19)	5 536(18)	−330(12)
C(55)	7 227(21)	4 718(16)	−618(11)
C(56)	8 364(16)	4 664(16)	−107(13)
C(57)	8 544(17)	5 380(14)	605(11)
C(58)	8 213(16)	6 120(19)	2 626(11)
C(59)	8 862(30)	4 987(21)	2 528(13)
C(60)	9 309(30)	4 243(25)	3 086(18)
C(61)	9 067(28)	4 654(34)	3 799(21)
C(62)	8 442(41)	5 740(45)	3 923(22)
C(63)	8 063(29)	6 585(26)	3 349(18)
C(64)	9 244(16)	7 653(17)	1 852(12)
C(65)	9 187(16)	8 151(18)	1 237(13)
C(66)	10 283(30)	8 488(22)	1 177(17)
C(67)	11 244(27)	8 233(27)	1 748(23)
C(68)	11 288(22)	7 687(28)	2 366(22)
C(69)	10 260(22)	7 387(17)	2 475(14)
C(71)	2 734(41)	15 208(40)	3 835(36)
C(72)	4 377(58)	14 743(38)	3 132(36)
O(73)	3 577(48)	15 989(28)	4 054(19)
C(74)	3 176(57)	14 656(38)	3 019(30)
C(75)	4 899(51)	5 538(75)	3 798(47)

was added TlPF$_6$ (0.1 g, 0.22 mmol). After stirring for 15 min, the fine precipitate of TlCl was allowed to settle for 15 min before the solution was filtered through 'hiflo' Celite. The solution was then evaporated to *ca.* 5 cm^3 and treated with light petroleum (10 cm^3). The yellow solid was collected and recrystallised from CH$_2$Cl$_2$. Yield 0.1 g (40%) (Found: C, 62.5; H, 4.8. C$_{58}$H$_{54}$Cl$_2$O$_6$P$_4$Rh$_2$ requires C, 62.5; H, 4.8%). FAB mass spectrum: *m*/*z* 1013 (M^+), 766 {[Rh(PPh$_3$)(PPh$_2$)$_3$]$^+$}, 751 (M − PPh$_3^+$), 627 (M − Ph$_2$POPPh$_2^+$) and 350 {[Rh(PPh$_3$)(Ph$_2$PO)]$^+$}.

(*ix*) *Tris*(*triphenylphosphine*)(*triphenylphosphoniopropionate*)-*rhodium*(I) *Hexafluorophosphate–Tetrahydrofuran* (1/1).—A solution obtained as in (*iv*) was treated with TlPF$_6$ (0.22 g, 0.5 mmol) after stirring for 1 h at 0 °C. After stirring for 1 h, the fine white precipitate of TlCl was allowed to settle, the solution was filtered and evaporated to *ca.* 10 cm^3. Bright yellow crystallites were formed on standing for 3 °C for 1 d. These were collected and dried *in vacuo*. Yield 0.33 g (64%) (Found: C, 66.0; H, 4.7. C$_{79}$H$_{68}$F$_6$O$_3$P$_5$Rh requires C, 65.8; H, 5.0%). FAB mass spectrum: *m*/*z* 961 (M − PPh$_3^+$) and 889 {[Rh(PPh$_3$)$_3$]$^+$}; many other lower fragments are observed including 627 {[Rh(PPh$_3$)$_2$]$^+$} and 365 {[Rh(PPh$_3$)]$^+$}.

(*x*) *Reaction of* L *with* PPh$_3$.—A solution of L (0.54 mmol) in thf (20 cm^3) was treated with PPh$_3$ (0.14 g, 0.54 mmol) and stirred for 0.5 h at 0 °C. The white solid which precipitated was collected and shown to contain Ph$_3$P$^+$CH$_2$CH$_2$CO$_2^-$ and Ph$_2$PP(O)Ph$_2$. The zwitterion was obtained pure by recrystallisation of the solid from thf. It was identified by comparison with an authentic sample prepared by the literature method.[6]

Crystallography.—Crystals were obtained as described above. *Crystal data*. C$_{42}$H$_{35}$ClOP$_3$Rh·C$_4$H$_8$O, M = 859.1, triclinic, space group $P\bar{1}$, a = 11.294(4), b = 11.475(6), c = 17.144(9) Å, α = 102.31(4), β = 102.71(4), γ = 74.11(4)°, U = 2056.68 Å^3, Z = 2, D_c = 1.270 g cm^{-3}, Mo-Kα radiation, λ = 0.710 69 Å, μ = 5.6 cm^{-1}, F(000) = 878.00.

Intensity data were collected on a Nicolet P3 diffractometer. 6160 Unique reflections were collected (insufficient overlaps to get a valid R_{int}) of which 2329 with $F \geqslant 6\sigma F$ were used in the refinement, 2θ_{max} 50°. Range of indices $0 \leqslant h \leqslant 13$, $-15 \leqslant k \leqslant 15$, $-23 \leqslant l \leqslant 23$. The structure was solved by Patterson methods. Least-squares refinement of the metal and phosphorus atoms was carried out and the remaining non-hydrogen atoms were located in the subsequent Fourier difference maps. Isotropic vibrational parameters were refined until all of the non-hydrogen atoms were located, after which the anisotropic vibrational parameters were assigned and refined to convergence. The hydrogen atoms of the phenyl groups were included with isotropic thermal parameters in calculated positions (C–H bond length fixed at 1.09 Å). The assignments of the oxygen atoms were checked by assigning them as carbon atoms. This however produced an increase in the thermal parameters of this species indicating that the oxygen assignment was the correct one. The thf was found to show some disorder which was not included in the model. Final refinement (minimising $w||F_o| - |F_c||^2$), 486 refined parameters, R' = 0.0746, $w = 1.9641/[\sigma^2(F) + 0.000\,618F^2]$, mean shift/e.s.d. = 0.008, maximum shift/e.s.d. = 0.05, maximum difference peak = 0.873, maximum negative peak = 1.427 e Å^{-3}; R = 0.0718 for 2329 reflections. Final atomic coordinates are given in Table 4. Computer programs employed were SHELX 76,[32] SHELXS[33] and XANADU.[34]

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

Calculations.—All calculations were made using the MNDO method[27] as implemented in the MOPAC system:[35] the PRECISE option was used throughout and the atomic parameters were those previously published.[27,36]

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