

## Linkage Isomerism in Rhodium(I) Complexes of Mixed Anhydrides of Diphenylphosphinous and Acrylic Acids: Crystal and Molecular Structure of $[\text{RhCl}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHMe})]^\dagger$

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Reactions of  $[\text{RhCl}(\text{PPh}_3)_3]$  with mixed anhydrides  $\text{Ph}_2\text{PO}_2\text{CCR}=\text{CR}'\text{R}''$  ( $\text{R} = \text{R}' = \text{H}$ ,  $\text{R}'' = \text{Me}$  or  $\text{CH}=\text{CHMe}$ ;  $\text{R} = \text{H}$ ,  $\text{R}' = \text{R}'' = \text{Me}$ ;  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{H}$ ,  $\text{R}'' = \text{Ph}$ ) give complexes  $[\text{RhCl}(\text{PPh}_3)_n(\text{Ph}_2\text{PO}_2\text{C}-\text{CR}=\text{CR}'\text{R}'')]$  ( $n = 1$ ,  $\text{R} = \text{R}' = \text{H}$ ,  $\text{R}'' = \text{Me}$  or  $\text{CH}=\text{CHMe}$ ;  $n = 2$ ,  $\text{R} = \text{H}$ ,  $\text{R}' = \text{R}'' = \text{Me}$ ;  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{H}$ ,  $\text{R}'' = \text{Ph}$ ;  $\text{R} = \text{R}' = \text{H}$ ,  $\text{R}'' = \text{CH}=\text{CHMe}$ ). For  $n = 1$ , the mixed anhydride is bound to the metal *via* the phosphorus atom and the double bond, whilst for  $n = 2$  binding is through phosphorus alone. Treatment of  $[\text{RhCl}(\text{PPh}_3)_n(\text{Ph}_2\text{PO}_2\text{CCR}=\text{CR}'\text{R}'')]$  with  $\text{TIPF}_6$  or  $\text{AgSbF}_6$  leads in all cases to complexes  $[\text{Rh}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCR}=\text{CR}'\text{R}'')]^\ddagger$  in which the mixed anhydride is bound through the phosphorus atom and the carbonyl oxygen atom. Spectroscopic diagnostics for the various different bonding modes are discussed, whilst their occurrence is rationalised largely on steric grounds. The *X*-ray crystal structure of  $[\text{RhCl}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHMe})]$  is described along with its curious fluxional behaviour. Crystals of this complex are monoclinic (space group  $P2_1/n$ ), with  $a = 19.954(4)$ ,  $b = 13.250(4)$ ,  $c = 11.425(1)$  Å,  $\beta = 91.66(2)^\circ$ , and  $Z = 4$ . The structure was obtained from 3 721 observed intensities measured on an automatic diffractometer and refined to an *R* value of 0.0358. The complex is distorted square planar about rhodium with the co-ordination sites being occupied by the two phosphorus atoms, the chloride, and the C=C of the mixed anhydride. The two phosphorus atoms are mutually *cis*. The C=C bond length is 1.393(9) Å, and there is significant pyramidalisation at the carbon atoms of the double bond, suggesting a fairly strong interaction between the double bond and the rhodium atom.

We have recently reported<sup>1</sup> that catalytic hydrogenation of highly functionalised acrylic acids can be achieved using bifunctional catalysts in which both the metal centre and the phosphorus atom of a mixed anhydride of the acrylic acid and diphenylphosphinous acid are involved in catalytically important steps. Specifically, base-catalysed *trans* esterification of the co-ordinated  $\text{Ph}_2\text{PO}_2\text{CCR}-\text{CR}'\text{R}''\text{H}$  ( $\text{R}$ ,  $\text{R}'$ ,  $\text{R}''$  are alkyl or aryl) by  $^-\text{O}_2\text{CCR}=\text{CR}'\text{R}''$  allows loss of the hydrogenated product and introduction of a new substrate molecule. We have argued that this type of catalyst is more efficient than simple catalysts {e.g.  $[\text{RhCl}(\text{PPh}_3)_3]$ } for hydrogenation of these highly substituted double bonds because co-ordination of the double bond is stabilised by chelation. We have observed<sup>2</sup> this type of bonding in complexes of the form  $[\{\text{RhCl}(\text{Ph}_2\text{PO}_2\text{CCR}=\text{CR}'\text{R}'')\}_2]$ .

We now report that mixed anhydrides of this kind are capable of binding to rhodium in three different ways and that small changes in the steric or electronic properties of the metal can lead to changes in the mode of co-ordination.

### Results

Reaction of  $[\text{RhCl}(\text{PPh}_3)_3]$  with 1 mol equivalent of  $[\text{Ph}_2\text{PO}_2\text{CCR}=\text{CR}'\text{R}'']$  leads to the isolation of complexes of composition  $[\text{RhCl}(\text{PPh}_3)_n(\text{Ph}_2\text{PO}_2\text{CCR}=\text{CR}'\text{R}'')]$  ( $n = 2$ ,  $\text{R} = \text{H}$ ,  $\text{R}' = \text{R}'' = \text{Me}$ ;  $\text{R} = \text{R}' = \text{H}$ ,  $\text{R}'' = \text{CH}=\text{CHMe}$ ;  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{H}$ ,  $\text{R}'' = \text{Ph}$ ;  $n = 1$ ,  $\text{R} = \text{R}' = \text{H}$ ,  $\text{R}'' = \text{Me}$  or  $\text{CH}=\text{CHMe}$ ). In general, only one product is observed, although in the case of the mixed anhydride with hexa-2,4-dienoic acid, in addition to the compounds described above, a third compound,  $[\text{RhCl}(\text{PPh}_3)(\text{Ph}_2\text{POPPh}_2)]^3$  is also formed.

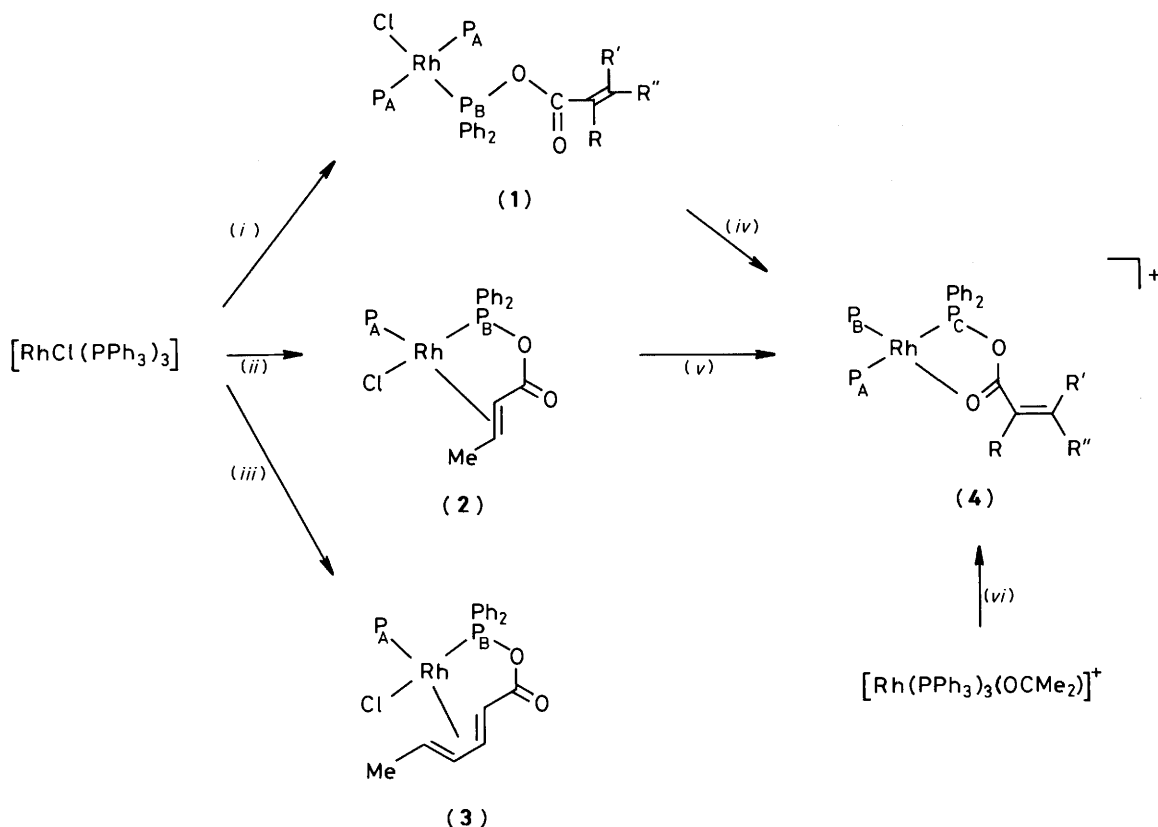
Treatment of the complexes  $[\text{RhCl}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCR}=\text{CR}'\text{R}'')]$  with 1 equivalent of  $\text{TIPF}_6$  or  $\text{AgSbF}_6$  leads to complexes of formula  $[\text{Rh}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCR}=\text{CR}'\text{R}'')]\text{Y}$  ( $\text{Y} = \text{SbF}_6$  or  $\text{PF}_6$ ). A similar reaction using  $[\text{RhCl}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHMe})]$  gives an intractable orange tar, but using a deficiency of  $\text{TIPF}_6$ ,  $[\text{Rh}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHMe})]\text{PF}_6$  is isolated but always in yields <50%. The complex  $[\text{Rh}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CMe}_2)]\text{PF}_6$  can also be obtained from reactions of  $[\text{Rh}(\text{PPh}_3)_3(\text{OCMe}_2)]\text{PF}_6^\ddagger$  with  $\text{Ph}_2\text{PO}_2\text{CCH}=\text{CMe}_2$ . These reactions are outlined in the Scheme.

*Spectroscopic Studies.*—(a)  $[\text{RhCl}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCR}=\text{CR}'\text{R}'')]$ . I.r. (Table 1) and  $^1\text{H}$  n.m.r. spectra (Table 2) of these complexes show features which are very similar to those present in the starting mixed anhydrides,<sup>2</sup> whilst the  $^{31}\text{P}$  n.m.r. spectra are very similar to that of  $[\text{RhCl}(\text{PPh}_3)_3]$ . Two strong peaks near  $1700\text{ cm}^{-1}$  in the i.r. spectra suggest that neither the C=O nor the C=C bond is perturbed much on co-ordination so that unidentate bonding through the phosphorus atom has occurred. The presence of resonances near  $\delta 5$  for the vinylic protons also suggests that the double bond is not bound to the metal. We therefore assign structure (I) (Scheme) to these complexes.

<sup>†</sup> Chloro(diphenylphosphino *E*-but-2-enoate-*C*<sup>3</sup>*P*)(triphenylphosphine)rhodium(I).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.

<sup>‡</sup> Related complexes have recently been reported.<sup>4</sup>



**Scheme.** Reactions of  $[\text{RhCl}(\text{PPh}_3)_3]$  with mixed anhydrides of diphenylphosphinous and acrylic acids.  $\text{P} = \text{PPh}_3$ ; (i) 1 mol  $\text{Ph}_2\text{PO}_2\text{CCR}=\text{CR}''$  ( $\text{R} = \text{H}$ ,  $\text{R}' = \text{R}'' = \text{Me}$ ;  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{H}$ ,  $\text{R}'' = \text{Ph}$ ;  $\text{R} = \text{R}' = \text{H}$ ,  $\text{R}'' = \text{CH}=\text{CHMe}$ ); (ii) 1 mol  $\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHCH}=\text{CHMe}$ ; (iii) 1 mol  $\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHCH}=\text{CHMe}$ ; (iv) 1 mol  $\text{TiPF}_6$  or  $\text{AgSbF}_6$ ; (v)  $<1$  mol  $\text{TiPF}_6$ ; (vi) 1 mol  $\text{Ph}_2\text{PO}_2\text{CCH}=\text{CMe}_2$

**Table 1.** Selected i.r. data ( $\text{cm}^{-1}$ ) for rhodium(I) complexes

Complex	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{C})$	$\nu(\text{Rh}-\text{Cl})$
$[\text{RhCl}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CMe}_2)]$	1 708	1 635	290
$[\text{RhCl}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHCH}=\text{CHMe})]$	1 710	1 640, 1 610	275
$[\text{RhCl}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCMe}=\text{CHPh})]^*$	1 685	1 620	
$[\text{RhCl}(\text{PPh}_3)(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHMe})]$	1 740		282
$[\text{RhCl}(\text{PPh}_3)(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHCH}=\text{CHMe})]$	1 760		270
$[\text{Rh}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CMe}_2)]^+$	1 585	1 628	
$[\text{Rh}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHMe})]^+$	1 583	1 641	
$[\text{Rh}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCMe}=\text{CHPh})]^+$	1 565(br)	1 613	

\* In  $\text{CH}_2\text{Cl}_2$ .

**Table 2.** Proton n.m.r. data for rhodium complexes<sup>a</sup>

Complex	$\delta$ (Me)	$\delta$ (H)	Coupling ( $J/\text{Hz}$ )			
			$\text{H}_a\text{H}_b$	$\text{H}_b\text{H}_c$	$\text{H}_a\text{H}_c$	$\text{PH}_c$
$[\text{RhCl}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CMe}_2)^{a,b}]$	<sup>a</sup> 1.9 (d), <sup>b</sup> 2.1 (s)	<sup>c</sup> 5.7 (q)	0	0	4	0
$[\text{RhCl}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCMe}=\text{CH}^b\text{Ph})]$	<sup>a</sup> 1.48 (s)	<sup>b</sup>				
$[\text{RhCl}(\text{PPh}_3)(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CH}^b\text{Me}^a)]$	<sup>a</sup> 1.69 (br)	<sup>b</sup> 4.75 (br), <sup>c</sup> 4.07 (br)		<sup>c</sup>		
$[\text{RhCl}(\text{PPh}_3)(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CH}^b\text{Me}^a)]^d$	<sup>a</sup> 1.88 (d)	<sup>b</sup> 4.98 (ddq), <sup>c</sup> 4.37 (dd)	6.4	4.9	0	11.2
$[\text{RhCl}(\text{PPh}_3)(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CH}^a\text{CH}^b=\text{CH}^b\text{Me}^a)]$	<sup>a</sup> 1.14 (br)	<sup>b</sup> 0.23 (br), <sup>c</sup> 5.67 (br), <sup>d</sup> 5.05 (br), <sup>e</sup> 2.42 (br)		<sup>c</sup>		
$[\text{Rh}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CMe}_2)^{a,b}]^+$	<sup>a</sup> 1.1 (d), <sup>b</sup> 1.75 (d)	<sup>c</sup> 5.7 (m)		1.6	1.6	
$[\text{Rh}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CH}^b\text{Me}^a)]^+$	<sup>a</sup> 1.7 (dd)	<sup>b</sup> 6.37 (dq), <sup>c</sup> 5.66 (dq)	7	16	1.6	0
$[\text{Rh}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCMe}=\text{CH}^b\text{Ph})]^+$	<sup>a</sup> 1.8 (s)	<sup>b</sup>				

<sup>a</sup> Measured in  $\text{CD}_2\text{Cl}_2$  at 298 K. Chemical shifts are relative to  $\text{SiMe}_4$  (phenyl resonances are observed for all complexes at  $\delta$  6.8–7.8). <sup>b</sup> Obscured by phenyl resonances. <sup>c</sup> Not observed. <sup>d</sup> At 238 K.

(b)  $[\text{RhCl}(\text{PPh}_3)(\text{Ph}_2\text{PO}_2\text{CR}=\text{CR}'')]$ . Complexes of this form show only one absorption in their i.r. spectra near 1 750

$\text{cm}^{-1}$  and we have previously shown<sup>2</sup> that this can be attributed to  $\nu(\text{C}=\text{O})$  of a mixed anhydride bound through the phosphorus

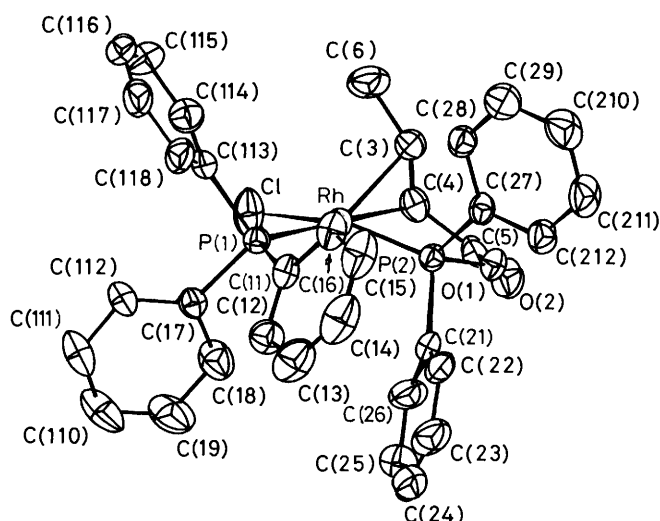


Figure. Solid-state structure and numbering scheme for  $[\text{RhCl}(\text{PPh}_3)(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHMe})]$

atom and the double bond, as in (2) (Scheme). Consistent with this assignment are the marked shift to high field of the vinylic protons in the  $^1\text{H}$  n.m.r. spectra and the substantial downfield shift (Table 3) for the phosphorus atom of the  $\text{Ph}_2\text{PO}_2\text{CCR}=\text{CR}'\text{R}''$  ligand on account of the formation of a five and a half membered ring.<sup>2,5</sup> For  $[\text{RhCl}(\text{PPh}_3)(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHCH}=\text{CHMe})]$ , the  $^1\text{H}$  n.m.r. spectrum includes a resonance at very high field ( $\delta$  0.23). This high-field shift is similar to those observed for *endo* protons of *e.g.* 1,3-butadiene<sup>6</sup> complexed to transition metals and therefore suggests that the complex is five-co-ordinate, with the ligand being bound by the phosphorus atom and by both double bonds in the chain, (3). This bonding is probably responsible for the slightly different P–P and P–Rh couplings for this complex from those for  $[\text{RhCl}(\text{PPh}_3)(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHMe})]$ . A similar bonding mode is also observed for the minor isomer of  $[\{\text{RhCl}(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHCH}=\text{CHMe})\}_2]$ .<sup>2</sup>

For  $[\text{RhCl}(\text{PPh}_3)(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHMe})]$ , the  $^{31}\text{P}$  n.m.r. spectrum at low temperature (below  $-20^\circ\text{C}$ ) consists of two doublets of doublets whose chemical shifts (141.9 and 25.6 p.p.m.) and coupling constants [ $J(\text{PP}) = 29.5$ ,  $J(\text{Rh}-\text{P}) = 162.6$  and  $152.5$  Hz] are consistent with *cis* phosphorus atoms and the  $\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHMe}$  ligand being bonded through P and the double bond, as is observed in the solid-state structure (see below). The low-temperature  $^1\text{H}$  n.m.r. spectrum (Table 2) is also consistent with this structure, although  $J(\text{H}_\text{b}\text{H}_\text{c})$  (4.9 Hz) is smaller than might be expected for *trans* hydrogen atoms. This is perhaps attributable to significant pyramidalisation at the carbon atoms on co-ordination.

On warming, both of the spectra change so that at room temperature the  $^{31}\text{P}$  spectrum consists of a broad resonance near 140 and a sharp doublet [ $J(\text{PP})$  is lost at  $0^\circ\text{C}$ ] at 25.5 p.p.m. In the  $^1\text{H}$  n.m.r. spectrum, all the signals broaden and that from the methyl groups is gradually replaced by a resonance at higher field ( $\delta$  1.72 p.p.m.). At room temperature, the  $^1\text{H}$  n.m.r. spectrum consists of broad resonances at 4.81, 4.25, and 1.72. The broadness of the  $^1\text{H}$  resonances from  $[\text{RhCl}(\text{PPh}_3)(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHCH}=\text{CHMe})]$  may reflect fluxionality in this complex also.

(c)  $[\text{Rh}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCR}=\text{CR}'\text{R}'')]\text{Y}$ . Cationic complexes of the form  $[\text{Rh}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCR}=\text{CR}'\text{R}'')]^+$  have quite different spectroscopic properties from those of formula  $[\text{RhCl}(\text{PPh}_3)_n(\text{Ph}_2\text{PO}_2\text{CCR}=\text{CR}'\text{R}'')]$  ( $n = 1$  or  $2$ ). There are no strong bands in their i.r. spectra near  $1700\text{ cm}^{-1}$ , although in each case there are features near  $1600\text{ cm}^{-1}$ . The peak at

$\approx 1630\text{ cm}^{-1}$  attributed to  $\nu(\text{C}=\text{C})$  is in a similar position to that for the free ligand, whilst its weakness is consistent with their being much less intensity borrowing from  $\nu(\text{C}=\text{O})$  than is observed for the other complexes. The strong absorption at  $\approx 1585\text{ cm}^{-1}$  is attributed to  $\nu(\text{C}=\text{O})$ . The vinylic protons resonate near  $\delta$  5 in the  $^1\text{H}$  n.m.r. spectrum, suggesting that the double bond is not bound to the metal, whilst the phosphorus atom of the mixed anhydride resonates at very high frequency ( $\approx 175$  p.p.m.) suggesting that it is contained in a five-membered ring.<sup>5</sup> These results are all consistent with binding through the phosphorus atom and the ester oxygen [as in (4) in the Scheme] so that the complexes are reminiscent of complexes of ethyl diphenylphosphino acetate reported by Braunstein *et al.*<sup>7</sup>

*X-Ray Studies of  $[\text{RhCl}(\text{PPh}_3)(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHMe})]$ .*—The X-ray structure of  $[\text{RhCl}(\text{PPh}_3)(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHMe})]$  has been determined since its formation and behaviour are somewhat different from those of the other complexes prepared in this study. Selected bond lengths and angles are collected in Table 4.

The structure (Figure) consists of discrete monomers in which the rhodium atom is in a distorted square planar environment with the four co-ordination positions occupied by the two phosphorus atoms, the chloride, and the double bond of the mixed anhydride. The triphenylphosphine and the double bond are mutually *trans* whilst the double bond retains its *E* configuration on co-ordination. Although rather shorter than that found in  $[\{\text{RhCl}(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CMe}_2)\}_2]$ ,<sup>2</sup> the C=C bond length [ $1.393(9)\text{ \AA}$ ] is typical for double bonds bound to  $\text{Rh}^{\text{I}}$  ( $1.36$ – $1.42\text{ \AA}$  for ethene)<sup>8,9</sup> as are the Rh–C bond lengths in the metallocyclopropane ring. The carbon atom of the methyl group does not lie in the same plane as that containing the two carbon atoms of the double bond and the carbon atom of the carboxylate group [dihedral angle C(6)–C(3)–C(4)–C(5)  $155^\circ$ ], suggesting significant pyramidalisation at the carbon atoms of the double bond and this pyramidalisation is also suggested by the angle between the substituents on each C atom of the double bond, although large uncertainties in the positions of the vinylic hydrogen atoms mean that these data are less than conclusive.

## Discussion

The products of reactions of  $[\text{RhCl}(\text{PPh}_3)_3]$  with mixed anhydrides of diphenylphosphinous and acrylic acids appear to be determined largely by steric factors. Thus, if the acrylic acid has three substituents (including the carboxylate group) on the double bond, as in 3-methylbut-2-enoic acid ( $\text{R} = \text{H}$ ,  $\text{R}' = \text{R}'' = \text{Me}$ ) or 2-methyl-3-phenylpropenoic acid ( $\text{R} = \text{Me}$ ,  $\text{R}' = \text{H}$ ,  $\text{R}'' = \text{Ph}$ ), bonding is only through phosphorus, whilst if the double bond is less substituted, as in but-2-enoic acid ( $\text{R} = \text{R}' = \text{H}$ ,  $\text{R}'' = \text{Me}$ ) or hexa-2,4-dienoic acid ( $\text{R} = \text{R}' = \text{H}$ ,  $\text{R}'' = \text{CH}=\text{CHMe}$ ), chelate binding through P and the double bond is observed, although for hexa-2,4-dienoic acid, with its larger substituent on the double bond, binding only through P is also possible.

Treatment of any of these compounds with  $\text{TlPF}_6$  or  $\text{AgSbF}_6$  removes the chloride and leads to products in which the mixed anhydride is bound in a third way, through P and O, even if as in the but-2-enoic acid case it is bound through P and the double bond in the starting complex. This different bonding mode probably arises because of both steric and electronic factors. The presence of two triphenylphosphine molecules as well as the  $\text{Ph}_2\text{P}$  group of the mixed anhydride will lead to severe steric congestion around the metal so that the mixed anhydride will bond in such a way that it minimises further steric interaction (*i.e.* through O). Furthermore, the presence of the positive charge on the metal (and loss of the  $\pi$ -donor Cl ligand) will make the metal centre harder and more oxophilic, thus providing

**Table 3.**  $^{31}\text{P}$  N.m.r. data for rhodium complexes<sup>a</sup>

Complex	$\delta$			Coupling (J/Hz)					
	P <sub>A</sub>	P <sub>B</sub>	P <sub>C</sub>	RhP <sub>A</sub>	RhP <sub>B</sub>	RhP <sub>C</sub>	P <sub>A</sub> P <sub>B</sub>	P <sub>A</sub> P <sub>C</sub>	P <sub>B</sub> P <sub>C</sub>
[RhCl(PPh <sub>3</sub> ) <sub>2</sub> (Ph <sub>2</sub> PO <sub>2</sub> CCH=CMe <sub>2</sub> )]	32.4 (dd)	49.1 (d)		143	191		38		
[RhCl(PPh <sub>3</sub> ) <sub>2</sub> (Ph <sub>2</sub> PO <sub>2</sub> CCH=CHCH=CHMe)]	33.4 (dd)	47.8 (dt)		144	191		38		
[RhCl(PPh <sub>3</sub> ) <sub>2</sub> (Ph <sub>2</sub> PO <sub>2</sub> CCMe=CHPh)]	31.7 (dd)	48.4 (dt)		145	193		40		
[RhCl(PPh <sub>3</sub> ) <sub>2</sub> (Ph <sub>2</sub> PO <sub>2</sub> CCH=CHMe)]	25.5 (d)	140 (br)		147					
[RhCl(PPh <sub>3</sub> ) <sub>2</sub> (Ph <sub>2</sub> PO <sub>2</sub> CCH=CHMe)] <sup>b</sup>	25.6 (dd)	142.1 (dd)		153	164		30		
[RhCl(PPh <sub>3</sub> ) <sub>2</sub> (Ph <sub>2</sub> PO <sub>2</sub> CCH=CHCH=CHMe)]	22.5 (dd)	121.7 (dd)		167	138		23		
[Rh(PPh <sub>3</sub> ) <sub>2</sub> (Ph <sub>2</sub> PO <sub>2</sub> CCH=CMe <sub>2</sub> )] <sup>+</sup>	28.7 (ddd)	52.0 (ddd)	173.8 (ddd)	137	185	162	37	320	37
[Rh(PPh <sub>3</sub> ) <sub>2</sub> (Ph <sub>2</sub> PO <sub>2</sub> CCH=CHMe)] <sup>+</sup>	29.5 (ddd)	51.5 (ddd)	177.3 (ddd)	137	185	163	37	323	37
[Rh(PPh <sub>3</sub> ) <sub>2</sub> (Ph <sub>2</sub> PO <sub>2</sub> CCMe=CHPh)] <sup>+</sup>	27.0 (ddd)	48.5 (ddd)	175.2 (ddd)	136	185	164	36	323	36

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub> at 298 K. Chemical shifts are in p.p.m. to high frequency of external 85% H<sub>3</sub>PO<sub>4</sub>. For assignments see Scheme. <sup>b</sup> At 238 K.

**Table 4.** Selected bond lengths (Å) and angles (°) for [RhCl(PPh<sub>3</sub>)<sub>2</sub>(Ph<sub>2</sub>PO<sub>2</sub>CCH=CHMe)]

P(1)–Rh	2.348(3)	P(2)–Rh	2.171(3)
Cl–Rh	2.392(3)	C(3)–Rh	2.142(8)
C(4)–Rh	2.147(7)	O(1)–P(2)	1.670(6)
C(4)–C(3)	1.393(9)	C(6)–C(3)	1.497(10)
C(5)–C(4)	1.469(9)	O(1)–C(5)	1.382(8)
O(2)–C(5)	1.200(7)	H(3)–C(3)	1.02(6)
H(4)–C(4)	0.84(5)	H(61)–C(6)	1.01(6)
H(62)–C(6)	0.98(9)	H(63)–C(6)	0.91(7)
P(2)–Rh–P(1)	98.7(2)	Cl–Rh–P(1)	89.0(2)
Cl–Rh–P(2)	162.4(1)	C(3)–Rh–P(1)	142.7(2)
C(3)–Rh–P(2)	84.6(3)	C(3)–Rh–Cl	98.9(2)
C(4)–Rh–P(1)	178.4(2)	C(4)–Rh–P(2)	82.8(3)
C(4)–Rh–Cl	89.3(3)	C(4)–Rh–C(3)	37.9(2)
C(11)–P(1)–Rh	118.4(2)	C(17)–P(1)–Rh	111.9(2)
C(113)–P(1)–Rh	115.3(2)	C(21)–P(2)–Rh	114.6(2)
C(27)–P(2)–Rh	126.7(2)	O(1)–P(2)–Rh	104.4(2)
O(1)–P(2)–C(21)	99.5(3)	O(1)–P(2)–C(27)	97.5(3)
C(4)–C(3)–Rh	71.3(4)	C(6)–C(3)–Rh	110.6(6)
C(6)–C(3)–C(4)	122.9(7)	C(3)–C(4)–Rh	70.8(4)
C(5)–C(4)–Rh	109.7(5)	C(5)–C(4)–C(3)	120.7(6)
O(1)–C(5)–C(4)	115.2(6)	O(2)–C(5)–C(4)	126.2(7)
O(2)–C(5)–O(1)	118.6(6)	C(5)–O(1)–P(2)	117.5(4)
H(3)–C(3)–Rh	113(4)	H(3)–C(3)–C(4)	116(4)
H(3)–C(3)–C(6)	114(4)	H(4)–C(4)–Rh	115(3)
H(4)–C(4)–C(3)	120(3)	H(4)–C(4)–C(5)	113(3)
H(61)–C(6)–C(3)	107(3)	H(62)–C(6)–C(3)	110(4)
H(62)–C(6)–H(61)	118(6)	H(63)–C(6)–C(3)	101(5)
H(63)–C(6)–H(61)	102(5)	H(63)–C(6)–H(62)	117(6)

an additional, electronic, driving force for oxygen co-ordination.

The fluxionality of the complex [RhCl(PPh<sub>3</sub>)<sub>2</sub>(Ph<sub>2</sub>PO<sub>2</sub>CCH=CHMe)] is unusual since it appears to indicate that the phosphorus atom of the mixed anhydride is either lost from the metal at higher temperatures, or that there is an equilibrium between two species in which the coupling constant between the two phosphorus atoms is of opposite sign. A full interpretation of these results is hampered by our inability to obtain spectra at temperatures >40 °C on account of substantial complex decomposition.

## Experimental

Microanalyses were by the University of St. Andrews micro-analytical service. N.m.r. spectra were recorded on Brüker Associates WP80, WM250, and AM300 spectrometers operating in the Fourier-transform mode with (for  $^{31}\text{P}$ ) proton noise decoupling. I.r. spectra were recorded on a Perkin-Elmer 257 or 1310 spectrometer as 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<sub>2</sub>Cl<sub>2</sub>) or sodium diphenylketyl [toluene, light petroleum (b.p. 40–60 °C), diethyl ether, and tetrahydrofuran (thf)].

The complex [RhCl(PPh<sub>3</sub>)<sub>3</sub>]<sup>10</sup> and the mixed anhydrides of diphenylphosphinous and acrylic acids<sup>2</sup> were made by literature procedures.

(i) *Chloro(diphenylphosphino E-but-2-enoate)(triphenylphosphine)rhodium(I)*.—To a cooled (0 °C) solution of [RhCl(PPh<sub>3</sub>)<sub>3</sub>] (0.50 g, 0.54 mmol) in thf (70 cm<sup>3</sup>) was added a cooled (–40 °C) solution of Ph<sub>2</sub>PO<sub>2</sub>CCH=CHMe (0.18 g, 0.65 mmol) in diethyl ether (17 cm<sup>3</sup>). On addition, a slow reaction occurred and the solution gradually became orange. The solution was stirred for 30–40 min, and the solvent evaporated under vacuum to ca. 6 cm<sup>3</sup>, when an orange–yellow material began to precipitate. It was further concentrated to ca. 2 cm<sup>3</sup> before slowly adding (–40 °C) light petroleum (b.p. 40–60 °C) (ca. 20 cm<sup>3</sup>). The resulting suspension was allowed to settle overnight at –30 °C before filtration. The product was washed with cold (–40 °C) light petroleum (3 × 10 cm<sup>3</sup>) prior to drying under vacuum. Yield 0.29 g (80%). Orange crystals suitable for crystallographic analysis were obtained from dichloromethane and diethyl ether. Yield 0.18 g (49.6%) (Found: C, 60.8; H, 4.4; Rh, 15.1. C<sub>34</sub>H<sub>30</sub>ClO<sub>2</sub>P<sub>2</sub>Rh requires C, 60.9; H, 4.5; Rh, 15.3%).

(ii) *Chloro(diphenylphosphino E,E-hexa-2,4-dienoate)(triphenylphosphine)rhodium(I)*.—To a solution of [RhCl(PPh<sub>3</sub>)<sub>3</sub>] (0.2 g, 0.22 mmol) in dichloromethane–tetrahydrofuran (20 cm<sup>3</sup>, ratio 1:1) was added a solution of Ph<sub>2</sub>PO<sub>2</sub>CCH=CHCH=CHMe (0.06 g, 0.22 mmol) in thf (10 cm<sup>3</sup>). On addition, an immediate reaction was observed and the solution became orange. The solution was stirred for 15 min before being filtered. The solvent was then removed by evaporation to approximately 2 cm<sup>3</sup> and light petroleum was added to give a bright orange solid. The solid was recrystallised from dichloromethane–light petroleum. Yield 0.05 g (35%). The complex was contaminated with [RhCl(PPh<sub>3</sub>)<sub>2</sub>(Ph<sub>2</sub>PO<sub>2</sub>CCH=CHCH=CHMe)] and [RhCl(PPh<sub>3</sub>)<sub>2</sub>(Ph<sub>2</sub>POPPH<sub>2</sub>)] but was identified by its spectroscopic properties.

(iii) *Chloro(diphenylphosphino 3-methylbut-2-enoate)bis(triphenylphosphine)rhodium(I)*.—To a suspension of [RhCl(PPh<sub>3</sub>)<sub>3</sub>] (0.5 g, 0.54 mmol) in thf (20 cm<sup>3</sup>) was added a solution of Ph<sub>2</sub>PO<sub>2</sub>CCH=CMe<sub>2</sub> (0.15 g, 0.54 mmol) in thf (10 cm<sup>3</sup>). On addition, an immediate reaction occurred and the solution became orange, whilst the [RhCl(PPh<sub>3</sub>)<sub>3</sub>] rapidly dissolved to give a homogeneous solution. The solution was stirred for 5 min, filtered, and the solvent was evaporated to

**Table 5.** Fractional atomic co-ordinates ( $\times 10^4$ ) for  $[\text{RhCl}(\text{PPh}_3)(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHMe})]$ 

Atom	x	y	z	Atom	x	y	z
Rh	-1 621.9(1)	1 523.8(2)	1 404.8(3)	C(118)	-835(2)	4 917(2)	1 808(2)
P(1)	-972(1)	2 937(1)	935(1)	C(113)	-891(2)	3 895(2)	2 083(2)
P(2)	-2 344(1)	1 590(1)	-53(1)	C(22)	-2 101(1)	2 199(2)	-2 395(2)
Cl	-739(1)	978(1)	2 718(1)	C(23)	-1 757(1)	2 116(2)	-3 437(2)
C(12)	-831(1)	3 756(2)	-1 324(2)	C(24)	-1 291(1)	1 343(2)	-3 574(2)
C(13)	-1 066(1)	4 291(2)	-2 305(2)	C(25)	-1 169(1)	653(2)	-2 670(2)
C(14)	-1 693(1)	4 755(2)	-2 300(2)	C(26)	-1 513(1)	736(2)	-1 629(2)
C(15)	-2 087(1)	4 684(2)	-1 313(2)	C(21)	-1 979(1)	1 509(2)	-1 491(2)
C(16)	-1 853(1)	4 150(2)	-332(2)	C(28)	-3 229(1)	3 018(2)	768(2)
C(11)	-1 225(1)	3 686(2)	-337(2)	C(29)	-3 827(1)	3 565(2)	753(2)
C(18)	-16(1)	1 703(2)	-6(3)	C(210)	-4 280(1)	3 475(2)	-195(2)
C(19)	626(1)	1 445(2)	-359(3)	C(211)	-4 136(1)	2 837(2)	-1 126(2)
C(110)	1 168(1)	2 075(2)	-81(3)	C(212)	-3 538(1)	2 290(2)	-1 110(2)
C(111)	1 069(1)	2 962(2)	548(3)	C(27)	-3 085(1)	2 381(2)	-163(2)
C(112)	427(1)	3 220(2)	901(3)	C(3)	-2 462(2)	1 060(3)	2 398(4)
C(17)	-115(1)	2 590(2)	623(3)	C(4)	-2 192(2)	214(3)	1 862(4)
C(114)	-866(2)	3 586(2)	3 251(2)	C(5)	-2 514(2)	-218(3)	803(4)
C(115)	-784(2)	4 298(2)	4 143(2)	C(6)	-2 346(3)	1 295(4)	3 669(4)
C(116)	-727(2)	5 319(2)	3 868(2)	O(1)	-2 735(1)	477(2)	-23(2)
C(117)	-753(2)	5 629(2)	2 700(2)	O(2)	-2 610(2)	-1 098(2)	614(3)

approximately  $2 \text{ cm}^3$ . A bright orange crystalline material then precipitated. The solid was collected, washed with light petroleum ( $2 \times 10 \text{ cm}^3$ ), and dried *in vacuo*. A second crop of crystals was obtained from the filtrate by addition of excess light petroleum. Combined yield 0.49 g (95%). The solid was recrystallised from dichloromethane–light petroleum to afford the pure complex as orange crystals. Yield 0.44 g (85%). The complex was slightly air-sensitive, and became dull orange when exposed to air over a few days (Found: C, 67.0; H, 5.0; P, 10.0.  $\text{C}_{53}\text{H}_{47}\text{ClO}_2\text{P}_3\text{Rh}$  requires C, 67.0; H, 5.0; P, 9.8%).

(iv) *Chloro(diphenylphosphino E-2-methyl-3-phenylpropenoate)bis(triphenylphosphine)rhodium(I)*.—A solution of  $\text{Ph}_2\text{PO}_2\text{-CMeC}=\text{CHPh}$  (0.143 g, 41.3 mmol) in thf ( $20 \text{ cm}^3$ ) was added slowly at room temperature to a suspension of  $[\text{RhCl}(\text{PPh}_3)_3]$  (0.382 g, 41.3 mmol) in thf ( $15 \text{ cm}^3$ ). The mixture was stirred for 40 min and then reduced to  $3 \text{ cm}^3$ . Light petroleum ( $50 \text{ cm}^3$ ) was added to give an orange powder that was filtered off and dried *in vacuo*. Yield 0.33 g (81%) (Found: C, 68.6; H, 5.0.  $\text{C}_{53}\text{H}_{49}\text{ClO}_2\text{P}_3\text{Rh}$  requires C, 69.0; H, 4.9%).

(v) *Chloro(diphenylphosphino E,E-hexa-2,4-dienoate)bis(triphenylphosphine)rhodium(I)*.—To a suspension of  $[\text{RhCl}(\text{PPh}_3)_3]$  (0.2 g, 0.22 mmol) in dichloromethane and diethyl ether ( $30 \text{ cm}^3$ , ratio 1:4) was added a solution of  $\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHCH}=\text{CHMe}$  (0.06 g, 0.22 mmol) in diethyl ether ( $15 \text{ cm}^3$ ) and the mixture was stirred for 5 h. The  $[\text{RhCl}(\text{PPh}_3)_3]$  slowly dissolved with concurrent precipitation of a light orange solid. The solid was collected, washed with diethyl ether ( $2 \times 5 \text{ cm}^3$ ), and recrystallised from dichloromethane–light petroleum to afford a bright orange solid. Yield 0.08 g (40%). The complex was contaminated by  $[\text{RhCl}(\text{PPh}_3)(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CHCH}=\text{CHMe})]$  and  $[\text{RhCl}(\text{PPh}_3)(\text{Ph}_2\text{POPPH}_2)]$ , but was identified by its spectroscopic properties.

\* From this solution red crystals precipitated on addition of diethyl ether. The crystals were collected and when dried under vacuum cracked instantly with the formation of an air-sensitive red–brown powder that showed ( $^1\text{H}$  n.m.r.,  $\text{CD}_2\text{Cl}_2$ ,  $25^\circ\text{C}$ )  $\delta$  2.09 (s, 6 H) and 7.5–6.9 (m, 45 H) suggesting the composition  $[\text{Rh}(\text{PPh}_3)_3(\text{OCMe}_2)]^+ [\text{PF}_6]^-$ .

(vi) *Diphenylphosphino 3-methyl-but-2-enoatebis(triphenylphosphine)rhodium(I) hexafluorophosphate*.—*Procedure (a)*. A suspension of  $[\text{RhCl}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CMe}_2)]$  (0.50 g, 0.53 mmol) and  $\text{TlPF}_6$  (0.19 g, 0.53 mmol) in dichloromethane ( $20 \text{ cm}^3$ ) was stirred for *ca.* 30 min, after which time the solution gradually paled to yellow–orange with concurrent precipitation of  $\text{TiCl}$ . The solution was filtered and the solvent was evaporated to *ca.*  $2 \text{ cm}^3$ . On addition of small portions ( $5 \text{ cm}^3$ ) of diethyl ether ( $40 \text{ cm}^3$ ) a yellow crystalline material was formed. This was collected, washed with diethyl ether ( $3 \times 7 \text{ cm}^3$ ), and dried *in vacuo*. The product was recrystallised as yellow needles from acetone–diethyl ether. Yield 0.36 g (65%) (Found: C, 59.7; H, 4.5; P, 11.8; Rh, 9.3.  $\text{C}_{53}\text{H}_{47}\text{F}_6\text{O}_2\text{P}_2\text{Rh}$  requires C, 60.2; H, 4.5; P, 11.7; Rh, 9.7%).

*Procedure (b)*. A suspension of  $[\text{RhCl}(\text{PPh}_3)_3]$  (0.10 g, 0.11 mmol) and  $\text{TlPF}_6$  (0.038 g, 0.11 mmol) in dried acetone ( $5 \text{ cm}^3$ ) was stirred for *ca.* 30 min to give an orange–red solution\* from which a white precipitate of  $\text{TiCl}$  was removed by filtration. To this solution solid  $\text{Ph}_2\text{PO}_2\text{CCH}=\text{CMe}_2$  (0.031 g, 0.11 mmol) was added causing lightening of the reaction solution. After *ca.* 15 min diethyl ether (*ca.*  $15 \text{ cm}^3$ ) was added slowly to the yellow–orange solution to afford a yellow microcrystalline solid which was collected, washed with diethyl ether, and dried *in vacuo*. I.r. and  $^1\text{H}$  n.m.r. spectra of this material were identical with those of the product obtained in procedure (a).

The following complexes were similarly prepared using procedure (a).

*Diphenylphosphino 3-methylbut-2-enoatebis(triphenylphosphine)rhodium(I) tetrafluoroborate*. Using  $[\text{RhCl}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CMe}_2)]$  (0.25 g, 0.26 mmol) and  $\text{AgBF}_4$  (0.05 g, 0.26 mmol). Yield 0.09 g (34%) (Found: C, 63.0; H, 5.0.  $\text{C}_{53}\text{H}_{47}\text{BF}_4\text{O}_2\text{P}_3\text{Rh}$  requires C, 63.7; H, 4.7%).

*Diphenylphosphino 3-methylbut-2-enoatebis(triphenylphosphine)rhodium(I) hexafluoroantimonate*. As above for  $\text{AgBF}_4$ , but using  $\text{AgSbF}_6$ ; or from  $[\text{RhCl}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCH}=\text{CMe}_2)]$  (0.2 g, 0.21 mmol) and  $\text{KSbF}_6$  (0.06 g, 0.21 mmol) in tetrahydrofuran ( $20 \text{ cm}^3$ ) for 3 h. The yellow product was precipitated with excess of diethyl ether and recrystallised from  $\text{CH}_2\text{Cl}_2$ –diethyl ether. Yield 0.16 g (67%).

*Diphenylphosphino E-2-methyl-3-phenylpropenoatebis(triphenylphosphine)rhodium(I) hexafluorophosphate*. Using  $[\text{RhCl}(\text{PPh}_3)_2(\text{Ph}_2\text{PO}_2\text{CCMe}=\text{CHPh})]$ , formed *in situ* from  $[\text{RhCl}(\text{PPh}_3)_3]$  (0.56 g, 0.6 mmol) and  $\text{Ph}_2\text{PO}_2\text{CCMeCHPh}$

(0.21 g, 0.6 mmol) in thf (35 cm<sup>3</sup>), and TlPF<sub>6</sub> (0.21 g, 0.6 mmol). Precipitation of the product was with light petroleum. Yield ≈ 80% (Found: C, 60.1; H, 4.4. C<sub>58</sub>H<sub>49</sub>F<sub>6</sub>O<sub>2</sub>P<sub>4</sub>Rh requires C, 62.3; H, 4.4%\*).

*Diphenylphosphino E-but-2-enoatebis(triphenylphosphine)-rhodium(I) hexafluorophosphate.* From [RhCl(PPh<sub>3</sub>)(Ph<sub>2</sub>PO<sub>2</sub>CCH=CHMe)] (0.1 g, 0.15 mmol) and TlPF<sub>6</sub> (0.038 g, 0.11 mmol)† in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>). Precipitation was with diethyl ether and the yellow product was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>-diethyl ether. Yield 0.031 g (20%) (Found: C, 59.5; H, 4.3. C<sub>52</sub>H<sub>45</sub>F<sub>6</sub>O<sub>2</sub>P<sub>4</sub>Rh requires C, 59.9; H, 4.3%).

*Crystallography.—Crystal data.* [RhCl(PPh<sub>3</sub>)(Ph<sub>2</sub>PO<sub>2</sub>-CCH=CHMe)]. C<sub>34</sub>H<sub>30</sub>ClO<sub>2</sub>P<sub>2</sub>Rh, *M* = 670.9, monoclinic, *a* = 19.954(4), *b* = 13.250(4), *c* = 11.425(1) Å, β = 91.66(2)°, *U* = 3 020(1) Å<sup>3</sup>, space group *P2<sub>1</sub>/n*, *D<sub>c</sub>* = 1.48 g cm<sup>-3</sup>, *Z* = 4, Mo-*K<sub>α</sub>* radiation, λ = 0.7107 Å, μ = 7.783 cm<sup>-1</sup>, *F*(000) = 1 368.

*Data collection.*<sup>11</sup> CAD4 diffractometer using graphite-monochromated Mo-*K<sub>α</sub>* radiation; ω-2θ scan mode, ω scan width = 0.85 + 0.15 tan θ, ω scan speed = 1.35–6.77° min<sup>-1</sup>, 1.5 < θ < 25°. 5 310 Unique reflections were measured, of which 3 721 were observed [*F<sub>o</sub>* > 3σ(*F<sub>o</sub>*)]. The data were corrected for absorption empirically.<sup>12</sup> Weighting scheme, 1/[σ<sup>2</sup>*F<sub>o</sub>* + 0.000196 *F<sub>o</sub>*<sup>2</sup>].

*Structure solution and refinement.* Standard heavy-atom method. All non-hydrogen atoms were refined anisotropically. Phenyl rings were refined as rigid hexagons with C–C distances of 1.395 Å.

Final *R* value = 0.0358, *R'* = 0.0361. Final atomic coordinates are given in Table 5. Programs and computers used and sources of scattering factor data were as in ref. 11.

Hydrogens on phenyl rings were inserted in idealised posi-

tions and refined as parts of rigid groups with group *U<sub>iso</sub>* parameters. Those on atoms C(3)–C(6) were located experimentally and freely refined with individual *U<sub>iso</sub>* parameters.

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

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\* The microanalytical data for this complex were consistently low but its identification was confirmed spectroscopically.

† Using a 1:1 molar ratio, it was not possible to isolate a crystalline product.