Co-ordination of Highly Substituted Alkenes to Transition-metal Complexes: Preparation and Crystal and Molecular Structures of the Complexes [{RhCl(Ph₂PO₂CCH=CMe₂)}₂] and [{RhCl(Ph₂PO₂CCH=CHCH=CHMe)}₂] ‡

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Reaction of Ph_2PCl with $RR'C=CR''C(X)OH$ in the presence of triethylamine produces $Ph_2POC(X)CR''=CRR'$ (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 = H₂, R = R' = Me, R'' = H) in high yield. These ligands react with [(RhClL₂)₂] (L = C₂H₄ or cyclo-octene) to give high yields of [{RhCl(Ph₂POC(X)CR''=CRR')}₂] in which the ligands are bound through phosphorus and the double bond. The new compounds have been fully characterised by spectroscopic means, as well as by the crystal structures of [{RhCl(Ph₂PO₂CCH=CMe₂)}₂] and [{RhCl(Ph₂PO₂CCH=CHCH=CH-Me)}₂]. Crystal data: for [{RhCl(Ph₂PO₂CCH=CMe₂)}₂], monoclinic, a = 8.485(1), b = 28.070(3), c = 14.253(1) Å, β = 93.96(1)°, space group $P2_1/n$; for [{RhCl(Ph₂PO₂CCH=CHCH=CHMe)}₂], monoclinic, a = 17.372(2), b = 22.070(1), c = 9.986(2) Å, β = 104.51(1)°, space group $P2_1/a$. Both complexes contain dimeric structures with bridging chlorine atoms. Each rhodium atom is in an approximately square-planar configuration, and is bonded to two chlorine, one phosphorus atom, and one π-bonded C=C double bond, the phosphorus and π system being part of a chelate ring structure. In [{RhCl(Ph₂PO₂CCH=CHCH=CHMe)}₂] the α,β unsaturated linkage is bonded to the rhodium only, the γ,δ double bond being free.

We have recently attempted to co-ordinate highly substituted alkenes to transition elements in order to study their further reactions with, *e.g.*, small molecules or nucleophiles. Using [Fe(cp)(CO)₂]⁺ as a substrate (cp = η⁵-C₅H₅) proved unsuccessful for substituted acrylic acids and esters, all the isolated products having the acid or ester co-ordinated through an oxygen atom.[1] We therefore considered the possibility of stabilising the binding of the double bond by co-ordinating it in a chelate ring since most of the rather scarce examples of binding of highly substituted alkenes do involve attachment of a remote atom as well. For example, co-ordination of the double bond of α-amidoacrylic acids to rhodium is stabilised by co-ordination of the amido oxygen atom and it has been shown that such bidentate co-ordination is of considerable importance in asymmetric hydrogenation reactions.[2] Other examples of chelate stabilisation of the co-ordination of highly functionalised alkenes include [Co(cp){Ph₂PC₆H₄C(CO₂Me)=CH(CO₂-Me)}][3] obtained from thermolysis of [Co(cp)(PPh₃)-(MeO₂CC≡CCO₂Me)],[{RhCl(Me₂C=CHCMe₂CH₂OH)}₂]⁴ and the related [{PtCl(Me₂C=CHCMe₂CH₂O)}₂]⁴ in which binding is through the double bond and O, [Ir(CO)(PPh₃)₂-(O₂CCH₂CH=CHPh)],[5] and iridium complexes of terpinen-4-ol (*p*-menth-1-en-4-ol).[6]

All of the examples quoted rely on the serendipitous presence of a co-ordinating atom in a suitable position relative to the double bond. Our approach to the problem, however, involves the intended incorporation of a co-ordinating atom by formation of the mixed anhydrides of diphenylphosphinous

acid and the acrylic acid or, for allyl alcohols, by formation of a suitable phosphinite [see equation (1), X = O or H₂]. Although

$$RR'C=CR''C(X)OH + Ph_2PCl \xrightarrow{NEt_3}$$
$$RR'C=CR''C(X)OPPh_2 + [NEt_3H]Cl \quad (1)$$
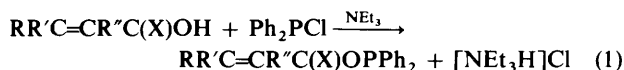
phosphinites of this kind have been prepared before, the mixed anhydrides had not previously been reported and, indeed, reports in the literature suggest that they may not be easy to make. Thus, acrylic acids react with Et₂PCl in the absence of triethylamine at higher temperatures to give Et₂P(O)CH₂CH₂-C(O)Cl where significant rearrangement has occurred.[7] The only known examples of mixed anhydrides of carboxylic acids and phosphinous acids are Ph₂PO₂CR (R = Me, CF₃, C₂F₅, or C₃F₇).[8,9] These compounds have been fully characterised but, at least for R = CₙF₂ₙ₊₁, rearrange to give Ph₂P(O)C(O)R on standing in solution. For R = Me, there is some evidence that Ph₂P(O)C(O)Me rearranges to give Ph₂PO₂CMe.[10]

Complexes which contain tertiary phosphines with unsaturated side chains are comparatively well established, although in most cases the double bonds bear only one or occasionally two substituents.[11] The only examples of a co-ordinated mixed anhydride or phosphinite in which chelate binding has been observed are [{RhCl(Ph₂POCH₂CH=CH₂)}₂],[12] [RhCl(Ph₂-POCH₂CH=CH₂)₂],[13] [Rh(cp)(Ph₂POCH₂CH=CH₂)],[14] and [RhX₂(cp)(Ph₂POCH₂CH=CH₂)][14] (X = Cl or Br) and more recently a series of complexes of the general form [Mo(CO)₄(Me₂POCH₂CR''=CRR')] (R,R',R'' = alkyl or aryl), prepared by transesterification of [Mo(CO)₄(Me₂POC₅H₄N)] with allylalkoxides.[15] Monodentate (with binding through phosphorus) complexes of Ph₂PO₂CMe have also been prepared for various transition metals.[8]

Results and Discussion

Preparation and Characterisation of Ph₂POC(X)CR''= CRR'.—Reaction of acrylic acids or allyl alcohols with Ph₂PCl in the presence of NEt₃ in diethyl ether at 0 °C gives colourless

Table 1. Analytical and i.r. data for new compounds*

Compound	Analysis (%) Required C	H	Found C	H	I.r. (cm^{-1}) ν(C=O)	ν(C=C)	ν(P–O)	ν(Rh–Cl)
$Ph_2PO_2CCHCMe_2$	71.9	6.0	71.2	6.1	1 692s (1 712)	1 640s (1 633)	735s	
$Ph_2PO_2CCHCHMe$	71.1	5.5	70.6	5.5	1 705s (1 700)	1 645s (1 650)	736s	
$Ph_2POCH_2CHCMe_2$						1 660w (1 660)	738s	
$Ph_2PO_2CCHCHCHCHMe$	72.9	5.7	72.2	5.5	1 692s (1 680)	1 638s (1 631)	740s	
						1 608s (1 600)		
$Ph_2PO_2CCMeCHPh$	76.3	5.5	75.9	5.4	1 685s (1 666)	1 620m (1 613)	739s	
[{RhCl($Ph_2PO_2CCHCMe_2$)}$_2$]	48.3	4.0	48.4	4.1	1 748s			276w
[{RhCl($Ph_2PO_2CCHCHMe$)}$_2$]	49.9	4.7	49.6	4.5	1 760s			270w
[{RhCl($Ph_2POCH_2CHCMe_2$)}$_2$]	46.7	3.6	46.9	3.9				274w
[{RhCl($Ph_2PO_2CCHCHCHCHMe$)}$_2$]	49.7	3.9	49.6	3.9	1 762s	1 630m		280w
[{RhCl($Ph_2PO_2CCMeCHPh$)}$_2$]	54.5	3.9	54.2	3.8	1 745s			265w

* Values in parentheses are those for the free acid.

Table 2. Proton and ^{31}P n.m.r. data for new compounds

| Compound	^{1}H Chemical shifts* δ(Me)	δ(H)	Coupling (J/Hz)	δ(^{31}P)†
$Ph_2PO_2CCH^cCMe_2{}^{a,b}$	^{a}1.83 (d), ^{b}2.00 (s)	^{c}5.71 (m)	$^4J(Me^aH^c)$ 1.2	96.2
$Ph_2PO_2CCH^cCH^bMe^a$	^{a}1.92 (d)	^{b}7.08 (dq), ^{c}6.02 (dq)	$^2J(H^bH^c)$ 15.5, $^3J(Me^aH^b)$ 6.0, $^4J(Me^aH^c)$ 1.0	98.9
$Ph_2POCH_2{}^{d,e}CH^cCMe_2{}^{a,b}$	^{a}2.00 (s), ^{b}2.14 (s)	^{c}5.83 (t), ^{d,e}4.69 (dd)	$^3J(H^cH^{d,e})$ 5.3, $^3J(PH^{d,e})$ 9.7	112.3
$Ph_2PO_2CCH^cCH^dCH^cCH^bMe^a$	^{a}1.83 (d)	^{b,c}6.22 (m), ^{d}7.32 (m), ^{e}5.88 (d)	$^3J(Me^aH^b)$ 5.5, $^3J(H^dH^c)$ 15	99.6
$Ph_2PO_2CCMe^bCH^aPh$	^{a}2.20 (s)	^{b}7.88 (s)		100.6
[{RhCl($Ph_2PO_2CCH^c=CMe_2{}^{a,b}$)}$_2$]	^{a}1.30, ^{b}1.45 (d)	^{c}2.76 (br m)	$^4J(Me^aH^c)$ 3.3	134.5 (183.2)
[{RhCl($Ph_2PO_2CCH^c=CH^bMe^a$)}$_2$]	^{a}1.41 (d)	^{b,c}3.0—3.8 (m)	$^3J(Me^aH^b)$ 6.0	133.2 (176), 131.9 (176)
[{RhCl($Ph_2POCH_2{}^{d,e}CH^c=CMe_2{}^{a,b}$)}$_2$]	^{a}1.13 (br s), ^{b}1.41 (s)	^{c}3.11 (br s), ^{d}3.91 (br dd), ^{e}4.17 (dd)	$^2J(H^eH^d)$ 4.7, $^3J(PH^d)$ 35, $^3J(PH^e)$ 10	165 (209.9)
[{RhCl($Ph_2PO_2CCH^c=CH^dCH^c=CH^bMe^a$)}$_2$]	^{a}1.53 (d)	^{b}6.00 (dq), ^{c}5.42 (dd), ^{d}4.04 (t), ^{e}2.71 (d)	$^3J(Me^aH^b)$ 5.0, $^3J(H^bH^c)$ 15, $^3J(H^cH^d)$ 10, $^3J(H^dH^e)$ 10	134.5 (176.6)
[{RhCl($Ph_2PO_2CCMe^a=CH^bPh$)}$_2$]	^{a}1.62 (s)	^{b}4.41		132 (173.8)

* In p.p.m. to high frequency of SiMe$_4$ (CD$_2$Cl$_2$, 25 °C). † In p.p.m. to high frequency of 85% H$_3$PO$_4$; J(Rh–P)/Hz in parentheses.

solutions from which the desired $Ph_2POC(X)CR''=CRR'$ (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) can be crystallised after removal of [NEt$_3$H]Cl. These compounds have been fully characterised by microanalysis and i.r. (Table 1), and n.m.r. spectroscopy (Table 2).

In all cases, the mixed anhydrides of diphenylphosphinous acid and acrylic acids show two strong absorptions in their i.r. spectra near 1 600 cm^{-1} which are similar to those observed for the free acrylic acids and their methyl esters and are assigned to ν(C=O) and ν(C=C), although there may be some mixing of the two vibrations. For $Ph_2POCH_2CH=CMe_2$, ν(C=C) is at 1 660 cm^{-1}. The ^{1}H n.m.r. spectra are similar to those of the free acid, while in each case the ^{31}P-{^{1}H} n.m.r. spectrum shows a singlet at ca. 100 p.p.m.

The compounds are stable in solution at room temperature and are indefinitely stable in the solid state under nitrogen. In air, the crystalline materials rapidly become oily. We have not noticed any tendency for the mixed anhydrides to undergo oxygen migration or Arbuzov-type rearrangements. They do, however, undergo transesterification with other carboxylic

acids and we have measured the equilibrium constant for reaction (2) as 0.6 at 25 °C in benzene. This facile

$$Ph_2PO_2CCH=CMe_2 + HO_2CMe \rightleftharpoons$$
$$Ph_2PO_2CMe + HO_2CCH=CMe_2 \quad (2)$$
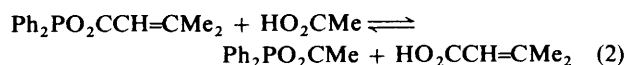
transesterification reaction means that the Ph_2P group can be considered to be a protecting group for the carboxylic acid function.

Chelate Co-ordination of $Ph_2POC(X)CR''=CRR'$.—In an attempt to use the Ph_2P-protected acrylic acids and allyl alcohol as a means of co-ordinating the alkenes, which in many cases are highly substituted and would not normally co-ordinate to a transition metal, we have treated them with an equimolar quantity of $\frac{1}{2}$[(RhClL$_2$)$_2$], L = C$_2$H$_4$ or cyclo-octene. In all cases, reaction occurs readily and orange crystalline complexes of stoicheiometry [{RhCl[$Ph_2POC(X)$-CR''=CRR']}$_2$] are obtained.

In each case, where R'' = H, the ^{1}H n.m.r. spectrum shows that the resonance from this proton is shifted to high field (δ ca. 3.5 p.p.m.) consistent with co-ordination of the double bond and

the [31]P n.m.r. spectrum shows strong Rh–P coupling (*ca.* 180 Hz) consistent with co-ordination of the phosphorus atom. Furthermore, in the i.r. spectra there is only one absorption [v(C=O)] near 1 600 cm^{-1} for the mixed anhydrides and the position of this band (*ca.* 1 750 cm^{-1}) is about half-way between what has been observed for five- (1 780 cm^{-1}) and six- (1 730 cm^{-1}) membered lactone rings.[16] The shift of the [31]P n.m.r. resonance to high field is also consistent with a ring structure.[17]

For [{RhCl(Ph$_2$POCH$_2$CH=CMe$_2$)}$_2$], the lack of v(C=C) near 1 600 cm^{-1}, together with the high-field shift of the vinylic proton (δ 3.11) and the high-frequency shift of the phosphorus atom are all consistent with chelate binding of the allyl-phosphinite.

The observation of only one doublet in the [31]P n.m.r. spectrum for each of the complexes, except [{RhCl(Ph$_2$-PO$_2$CCH=CHMe)}$_2$], indicates that only one of the six possible isomers is present and *X*-ray studies of [{RhCl(Ph$_2$PO$_2$CCH=CMe$_2$)}$_2$] show that this has mutually *trans* phosphorus atoms, (**1**). The identity of the second isomer of [{RhCl(Ph$_2$PO$_2$-CCH=CMe$_2$)}$_2$] is unknown but may have *cis* phosphorus atoms, (**2**).

For [{RhCl(Ph$_2$PO$_2$CCH=CHCH=CHMe)}$_2$], [1]H n.m.r. studies suggest that the major product has binding through the α,β unsaturated linkage and that the γ,δ double bond is unco-ordinated, as is observed crystallographically, but a minor isomer with a ^{1}H resonance at δ 0.89 is also observed. This resonance is in the region expected for an *endo* proton of a co-ordinated diene so we tentatively assign this as having the structure shown in (**3**) but cannot rule out the possibility of bridge cleavage by the extra double bond to give monomeric (**4**).

(1)

(2)

n = 2 (**3**)
n = 1 (**4**)
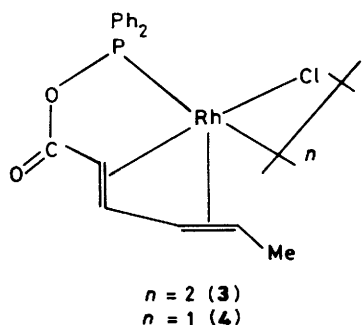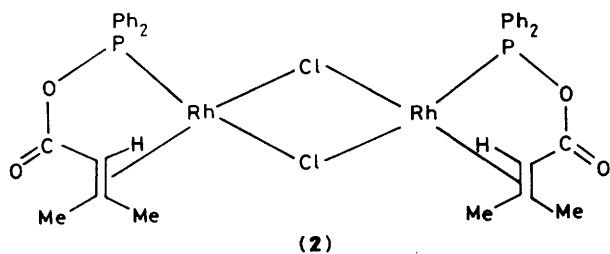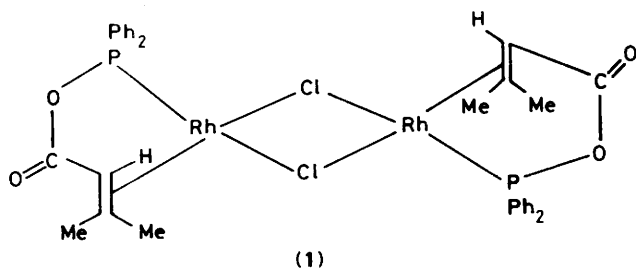
The spectroscopic data described above are all consistent with binding of Ph$_2$POC(X)CR″=CRR′ through the phosphorus atom and the double bond and this is confirmed by *X*-ray studies of the complexes with R = R′ = Me, R″ = H and with R = R″ = H, R′ = CH=CHMe.

X-Ray Crystallographic Studies.—(*a*) [{RhCl(Ph$_2$PO$_2$CCH=CMe$_2$)}$_2$]. The main features of the solid-state structure of [{RhCl(Ph$_2$PO$_2$CCH=CMe$_2$)}$_2$] are shown in Figure 1 and selected bond lengths and angles in Table 3. Each rhodium atom is in an approximately square-planar configuration, being bonded to two chlorine, one phosphorus, and one π-bonded C=C double bond. However, in the dimeric unit, both square-planar arrangements are not perfect, since the four groups bonded to a rhodium atom do not strictly lie in the same plane.

An interesting feature is that this double square-planar structure is bent with a dihedral angle at Cl of 120.8(1)°. This value is comparable with that of 122.6(2)° observed in [Rh$_2$Cl$_2${P(OPh)$_3$}$_2$(C$_8$H$_{12}$)][18] but is significantly higher than the 115.8° value observed for [{RhCl(C$_6$H$_{10}$)$_2$}$_2$].[19,20] Although common, this bent, bridged geometry is not general for di-μ-chloro complexes of Rh[I]; indeed the 1,5-cyclo-octadiene complex [{RhCl(C$_8$H$_{12}$)}$_2$] has been shown to contain a strictly planar Rh–Cl$_2$–Rh bridge.[21]

The Rh···Rh distance is 3.172(4) Å for [{RhCl(Ph$_2$-PO$_2$CCH=CMe$_2$)}$_2$]. This value is similar to those found in most other structures of bent di-μ-chloro complexes of Rh[I] and may be considered as indicative of a weak metal–metal interaction. It is also of interest to note that the structure of the present complex (as that of [Rh$_2$Cl$_2${P(OPh)$_3$}$_2$(C$_8$H$_{12}$)][18]) is different from that of [{RhCl(CO)$_2$}$_2$][22] which has been postulated as having an octahedral stereochemistry on the basis of a short (3.31 Å) intermolecular Rh–Rh distance. In the present structure, the closest approach of two Rh atoms belonging to closest separate molecules is greater than 5 Å. Thus the observed bent structure can be attributed to intramolecular metal–metal interaction. This interaction enforces an angle of only 82.2(3)° at Cl and 82.3(3)° at Rh, both significantly less than would be expected on the basis of geometrical arguments.

The binding of the double bond to rhodium appears to be quite strong despite the presence of the *gem*-dimethyl groups, with Rh–C distances of 2.111(39) and 2.160(36) Å. These compare with distances of *ca.* 2.19 Å for simple ethene complexes of rhodium(I).[23,24] Similarly, the double bond is lengthened to 1.437(54) Å and is comparable with those that have been observed for C$_2$H$_4$ (1.36—1.42 Å)[23,24] or C$_2$F$_4$ (1.40 Å)[23] complexes of rhodium. The degree of lengthening of this bond gives a crude measure of the strength of interaction between the metal and the alkene, and confirms the strong interaction in this case. The slight pyramidalisation at C(2) is also consistent with a strong rhodium–alkene interaction.

The requirements of the five-membered ring containing Rh(1), P(1), O(2), C(4), and C(3) lead to a slight compression of the formally *sp^2* angles at C(4) [117.8(40)°] and O(2) [115.1(23)°].

(*b*) [{RhCl(Ph$_2$PO$_2$CCH=CH–CH=CHMe)}$_2$]. The main features of the solid-state structure of [{RhCl(Ph$_2$PO$_2$-CCH=CH–CH=CHMe)}$_2$] are shown in Figure 2 and selected bond lengths and angles in Table 4. The complex has a structure very similar to that of [{RhCl(Ph$_2$PO$_2$CCH=CMe$_2$)}$_2$] except that there is significantly less steric crowding at C(4) so that the Rh(1)–C(4) distance is rather shorter [2.106(10) Å] than the analogous distance [2.160(36) Å] in [{RhCl(Ph$_2$PO$_2$CCH=CMe$_2$)}$_2$] and the α,β alkene is almost symmetrically bound to the rhodium atom. There is no evidence for binding of the γ,δ double bond to the rhodium atom in the solid state and the stereochemistry about both double bonds is the same (*Z*) as in the parent 2,4-hexadienoic acid.

Table 3. Selected bond lengths* (Å) and angles (°) for [{RhCl(Ph₂PO₂CCH=CMe₂)}₂]

Rh(1)–Rh(2)	3.172(4)	Rh(2)–Cl(2)	2.475(9)	C(1)–C(2)	1.515(50)	C(4)–O(1)	1.209(44)
Rh(1)–Cl(1)	2.451(9)	Rh(1)–P(1)	2.153(10)	C(2)–C(3)	1.437(54)	C(4)–O(2)	1.372(45)
Rh(1)–Cl(2)	2.400(9)	Rh(1)–C(2)	2.160(36)	C(2)–C(5)	1.519(52)	Rh(1)–C(3)	2.111(39)
Rh(2)–Cl(1)	2.375(10)	P(1)–O(2)	1.656(26)	C(3)–C(4)	1.483(54)		

Rh(2)–Rh(1)–Cl(1)	47.9(2)	Cl(2)–Rh(1)–P(1)	94.1(4)	Rh(1)–C(3)–C(2)	72.2(22)	P(1)–O(2)–C(4)	115.1(23)
Rh(2)–Rh(1)–Cl(2)	50.4(2)	Cl(2)–Rh(1)–C(2)	157.1(11)	Rh(1)–C(3)–C(4)	112.3(28)	C(2)–Rh(1)–C(3)	39.3(15)
Cl(1)–Rh(1)–Cl(2)	82.3(3)	Cl(2)–Rh(1)–C(3)	163.5(12)	C(3)–C(4)–O(1)	120.9(30)	C(1)–C(2)–C(3)	124.0(37)
Cl(1)–Rh(1)–P(1)	168.2(4)	P(1)–Rh(1)–C(2)	92.6(11)	C(3)–C(4)–O(2)	124.2(42)	C(1)–C(2)–C(5)	112.2(38)
Cl(1)–Rh(1)–C(2)	95.0(11)	P(1)–Rh(1)–C(3)	82.9(11)	O(1)–C(4)–O(2)	117.8(40)	C(3)–C(2)–C(5)	116.8(38)
Cl(1)–Rh(1)–C(3)	97.5(11)						

Torsion angles (°)

Cl(1)–Rh(1)–Rh(2)–Cl(2)	124.7(1)	C(5)–Rh(1)–C(4)–C(3)	119.9(7)	C(2)–C(3)–C(4)–Rh(1)	116.9(7)	Rh(1)–C(5)–C(6)–O(2)	32.8(8)
Cl(1)–Rh(1)–Rh(2)–P(2)	169.9(1)	P(1)–Rh(1)–C(5)–C(4)	94.6(4)	C(2)–C(3)–C(4)–C(5)	163.2(8)	C(4)–C(5)–C(6)–O(1)	129.6(9)
C(4)–Rh(1)–P(1)–O(2)	45.0(3)	P(1)–Rh(1)–C(5)–C(6)	20.1(5)	Rh(1)–C(4)–C(5)–C(6)	106.0(7)	C(4)–C(5)–C(6)–O(2)	46.9(9)
C(5)–Rh(1)–P(1)–O(2)	5.2(3)	C(4)–Rh(1)–C(5)–C(6)	114.7(7)	C(3)–C(4)–C(5)–Rh(1)	103.3(7)	C(5)–C(6)–O(2)–P(1)	28.1(7)
P(1)–Rh(1)–C(4)–C(3)	158.7(5)	C(1)–C(2)–C(3)–C(4)	177.9(8)	C(3)–C(4)–C(5)–C(6)	150.7(7)	O(1)–C(6)–O(2)–P(1)	155.0(6)
P(1)–Rh(1)–C(4)–C(5)	81.5(4)	Rh(1)–P(1)–O(2)–C(6)	10.4(4)	Rh(1)–C(5)–C(6)–O(1)	150.7(7)		

* For one side of the dimer, the other ligand parameters being very similar.
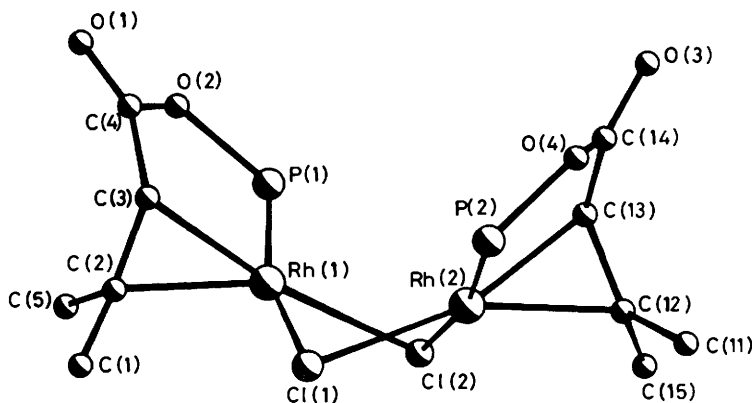

Figure 1. Solid-state structure and atom numbering scheme for [{RhCl(Ph₂PO₂CCH=CMe₂)}₂]. Phenyl rings and hydrogen atoms are omitted for clarity
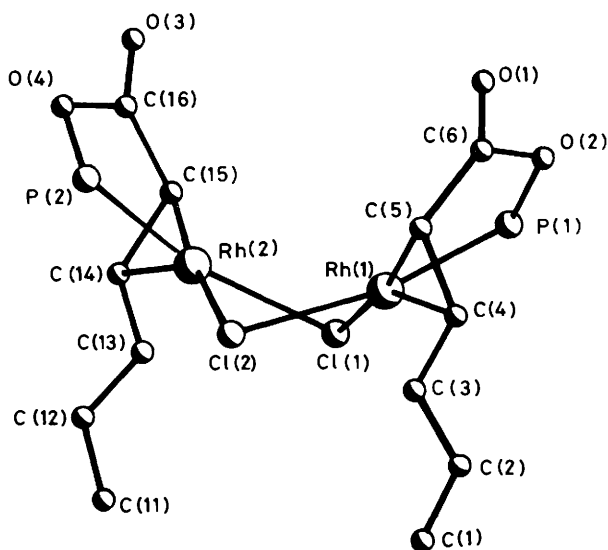
Figure 2. Solid-state structure and atom numbering scheme for [{RhCl(Ph₂PO₂CCH=CHCH=CHMe)}₂]. Phenyl rings and hydrogen atoms are omitted for clarity

Once again, the angles at O(2) [114.7(6)°] and at C(6) [114.9(9)°] within the ring are significantly compressed from the sp^2 values of 120°.

Experimental

Microanalyses were by Elemental Micro Analysis Ltd. or University of Liverpool microanalytical service (C and H). I.r. spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer 577 grating spectrometer, ^{1}H and ^{31}P n.m.r. spectra on a Bruker WM250 spectrometer (University of Liverpool), operating in the Fourier-transform mode with proton-noise decoupling (^{31}P). Fast atom bombardment mass spectra were recorded on a VG7070E mass spectrometer (University of Liverpool). Standard Schlenk-line and catheter-tubing techniques were employed and all solvents were carefully dried by (a) distillation from sodium diphenylketyl [diethyl ether, tetrahydrofuran, and light petroleum (b.p. 40—60 °C)] or (b) distillation from CaH₂ (dichloromethane). Chlorodiphenylphosphine was distilled under reduced pressure and stored under nitrogen. Triethylamine was distilled from CaH₂ prior to use.

Purification of Unsaturated Acids and Alcohols.—In order to remove traces of water from the unsaturated acids prior to the

Table 4. Selected bond lengths * (Å) and angles (°) for [{RhCl(Ph$_2$PO$_2$-CCH=CH-CH=CHMe)}$_2$]

Rh(1)–Rh(2)	3.134(1)	C(6)–O(1)	1.189(12)
Rh(1)–Cl(1)	2.380(2)	C(6)–O(2)	1.405(12)
Rh(1)–Cl(2)	2.448(3)	C(1)–C(2)	1.521(17)
Rh(2)–Cl(1)	2.447(3)	C(2)–C(3)	1.323(15)
Rh(2)–Cl(2)	2.372(2)	C(3)–C(4)	1.459(14)
Rh(1)–P(1)	2.155(3)	C(4)–C(5)	1.434(15)
Rh(1)–C(4)	2.106(10)	C(5)–C(6)	1.451(15)
Rh(1)–C(5)	2.101(10)	P(1)–O(2)	1.653(6)
Rh(2)–Rh(1)–Cl(1)	50.5(1)	C(1)–C(2)–C(3)	124.3(13)
Rh(2)–Rh(1)–Cl(2)	48.4(1)	C(2)–C(3)–C(4)	122.2(11)
Cl(1)–Rh(1)–Cl(2)	84.6(1)	Rh(1)–C(4)–C(3)	111.8(7)
Cl(1)–Rh(1)–P(1)	97.7(1)	Rh(1)–C(4)–C(5)	69.9(6)
Cl(2)–Rh(1)–C(4)	146.8(3)	C(3)–C(4)–C(5)	124.2(10)
Cl(1)–Rh(1)–C(5)	173.4(3)	Rh(1)–C(5)–C(4)	70.2(6)
Cl(2)–Rh(1)–P(1)	167.1(1)	Rh(1)–C(5)–C(6)	113.1(7)
Cl(2)–Rh(1)–C(4)	98.1(3)	C(4)–C(5)–C(6)	119.7(11)
Cl(2)–Rh(1)–C(5)	94.1(3)	C(5)–C(6)–O(1)	127.0(10)
P(1)–Rh(1)–C(4)	86.9(3)	C(5)–C(6)–O(2)	114.9(9)
P(1)–Rh(1)–C(5)	82.2(3)	O(1)–C(6)–O(2)	118.0(10)
C(4)–Rh(1)–C(5)	39.9(4)	P(1)–O(2)–C(6)	114.7(6)

* For one side of the dimer, the other ligand parameters being very similar.

preparation of the corresponding phosphinite esters it was necessary to recrystallise the acids from weak solutions of the anhydrides. The anhydride solutions were prepared, in general, by standing a 20% ether solution of the unsaturated acid over phosphorus(v) oxide for 30 min. The filtered solution of the acid in the presence of the anhydride was then evaporated to give a saturated solution of the acid, which slowly crystallised upon cooling the solution.

The unsaturated alcohol Me$_2$C=CHCH$_2$OH was dried by standing over molecular sieves (4A) followed by distillation under reduced pressure and was stored under dinitrogen.

Phosphinite Esters.—(*i*) Ph$_2$PO$_2$CCH=CMe$_2$. To a rapidly stirring solution of Me$_2$C=CHCO$_2$H (10.0 g, 0.1 mmol) in diethyl ether (150 cm^3) at −20 °C and under an atmosphere of dinitrogen, Ph$_2$PCl (22.0 g, 0.1 mol) was slowly added over a period of 5 min. To this mixture was added NEt$_3$ (10 g, 0.1 mol) in diethyl ether (50 cm^3) over a period of 10 min. On addition, an immediate reaction occurred with concurrent precipitation of [NEt$_3$H]Cl (13.7 g, 99.5%). The mixture was stirred for 15 min before being filtered quickly under dinitrogen to obtain a clear solution. The diethyl ether was then evaporated to approximately 30 cm^3 whereupon a white microcrystalline solid separated. This was isolated, washed with cold light petroleum spirit (3 × 30 cm^3) at −40 °C, and dried *in vacuo*. Yield 22.4 g (79%). Mass spectrum (*m/z*): 284 ([Ph$_2$PO$_2$CCH=CMe$_2$]$^+$, *M*$^+$), 256 ([*M* − CO]$^+$), 201 ([Ph$_2$PO]$^+$), 183 ([Ph$_2$P]$^+$), and 100 ([Me$_2$C=CHCO$_2$H]$^+$).

(*ii*) Ph$_2$PO$_2$CCH=CHMe. This was prepared as in (*i*) using MeCH=CHCO$_2$H (1 g, 0.01 mol), Ph$_2$PCl (2.2 g, 0.01 mol), and NEt$_3$ (1.0 g, 0.01 mol) in diethyl ether (40 cm^3). Yield 2.3 g (86%). The product was found to be thermally sensitive above −10 °C, and developed an oily yellow appearance within a few minutes. Mass spectrum (*m/z*): 270 (*M*$^+$), 255 ([*M* − Me]$^+$), 242 ([*M* − CO]$^+$), 201 ([Ph$_2$PO]$^+$), 183 ([Ph$_2$P]$^+$), and 86 ([MeCH=CHCO$_2$H]$^+$).

(*iii*) Ph$_2$PO$_2$CCH=CHCH=CHMe. This was prepared as in (*i*) except that the solvent was changed to tetrahydrofuran (60 cm^3) because of the low solubility of the acid in diethyl ether. The preparation used MeCH=CHCH=CHCO$_2$H (5 g, 0.044

mol), Ph$_2$PCl (9.84 g, 0.044 mol), and NEt$_3$ (4.5 g, 0.044 mol). Yield 12.5 g (95%). Mass spectrum (*m/z*): 296 (*M*$^+$), 268 ([*M*$^+$ − CO]$^+$), 201 ([Ph$_2$PO]$^+$), 183 ([Ph$_2$P]$^+$), 95 {[MeCH=CHCH=CHC(O)]$^+$}, and 67 ([MeCH=CHCH=CH]$^+$).

(*iv*) Ph$_2$PO$_2$CCMe=CHPh. This was prepared as in (*iii*) using PhCH=CMeCO$_2$H (2 g, 0.012 mol), Ph$_2$PCl (2.72 g, 0.012 mol), and NEt$_3$ (1.25 g, 0.012 mol) in tetrahydrofuran solution (50 cm^3). Yield 4 g (94%). Mass spectrum (*m/z*): 346 (*M*$^+$), 201 {[Ph$_2$P(O)]$^+$}, and 162 ([PhCH=CMeCO$_2$H]$^+$).

(*v*) Ph$_2$POCH$_2$CH=CMe$_2$. This was prepared as in (*i*) from Me$_2$C=CHCH$_2$OH (1 g, 0.01 mol), Ph$_2$PCl (2.6 g, 0.01 mol), and NEt$_3$ (1.0 g, 0.01 mol) in diethyl ether (40 cm^3). The filtered solution was evaporated to give a colourless liquid. Yield 3.0 g (95%). No analysis was obtained for this compound. Mass spectrum (*m/z*): 270 (*M*$^+$), 255 ([*M* − Me]$^+$), 202 {[Ph$_2$P(O)-H]$^+$}, 201 ([Ph$_2$PO]$^+$), and 183 ([Ph$_2$P]$^+$).

Rhodium Complexes.—(*vi*) [{RhCl(Ph$_2$PO$_2$CCH=CMe$_2$)}$_2$]. *Method* (*a*). To a suspension of [{RhCl(C$_8$H$_{14}$)$_2$}$_2$]^{25} (0.3 g, 0.42 mmol) in dichloromethane* (15 cm^3) was added a solution of Ph$_2$PO$_2$CCH=CMe$_2$ (0.24 g, 0.85 mmol) in dichloromethane* (15 cm^3). On addition an immediate reaction was observed and the [{RhCl(C$_8$H$_{14}$)$_2$}$_2$] rapidly dissolved to give a red-orange solution. The solution was filtered and the solvent was removed by evaporation under reduced pressure to approximately 3 cm^3. Light petroleum was added quickly to this concentrated solution to afford bright orange needles. The orange crystals required no further purification but could be recrystallised from dichloromethane, tetrahydrofuran, or benzene. Yield 0.32 g (90%).

Method (*b*). As for (*a*) but using [{RhCl(C$_2$H$_4$)$_2$}$_2$]^{26} (0.3 g).

(*vii*) [{RhCl(Ph$_2$PO$_2$CCH=CHMe)}$_2$]. The complex was prepared as in (*vi*), but using [{RhCl(C$_8$H$_{14}$)$_2$}$_2$] (0.2 g, 2.8 mmol) and Ph$_2$PO$_2$CCH=CHMe (0.15 g, 5.6 mmol). Yield 0.2 g (88%).

(*viii*) [{RhCl(Ph$_2$PO$_2$CCH=CHCH=CHMe}$_2$]. The complex was prepared as in (*vi*), but using [{RhCl(C$_8$H$_{14}$)$_2$}$_2$] (0.3 g, 0.42 mmol) and Ph$_2$PO$_2$CCH=CHCH=CHMe (0.25 g, 0.84 mmol). It was precipitated as a bright orange solid upon addition of excess of light petroleum, and recrystallised from dichloromethane–light petroleum as bright red-orange needles. Yields of crude product 0.34 g (94%); recrystallised material 0.15 g (41%). A further crop of product could be recovered from the filtrate by addition of excess of light petroleum. Yield 0.15 g (41%).

(*ix*) [{RhCl(Ph$_2$PO$_2$CCMe=CHPh)}$_2$]. The complex was prepared as in (*vi*), but using [{RhCl(C$_8$H$_{14}$)$_2$}$_2$] (0.1 g, 0.14 mmol) and Ph$_2$PO$_2$CCMe=CHPh (0.1 g, 0.28 mmol) in tetrahydrofuran solution (20 cm^3). It was isolated as a bright orange solid by precipitation with excess of light petroleum.

(*x*) [{RhCl(Ph$_2$POCH$_2$CH=CMe$_2$)}$_2$]. The complex was prepared as described in (*vi*), but using [{RhCl(C$_8$H$_{14}$)$_2$}$_2$] (0.1 g, 0.14 mmol) in dichloromethane and Ph$_2$POCH$_2$-CH=CMe$_2$ (0.075 g, 0.28 mmol) in dichloromethane solution (20 cm^3). The product was isolated as a mustard-yellow solid by precipitation with excess of light petroleum. Yield 0.1 g (87%).

Crystallography.—[{RhCl(Ph$_2$PO$_2$CCH=CMe$_2$)}$_2$]. Long thin needles were obtained from dichloromethane–light petroleum at 25 °C. Crystal dimensions, 0.3 × 0.1 × 0.1 mm.

Crystal data. C$_{34}$H$_{34}$Cl$_2$O$_4$P$_2$Rh$_2$, *M* = 845, monoclinic, *a* = 8.485(1), *b* = 28.070(3), *c* = 14.253(1) Å, β = 93.96(1)°, *U* = 3 386.6 Å^3, space group P2$_1$/n, *D*$_m$ = 1.65 g cm^{-3}, *Z* = 4, *D*$_c$ = 1.66 g cm^{-3}, Cu-*K*$_α$ radiation, λ = 1.5419 Å, μ = 36.42 cm^{-1}, *F*(000) = 1 696.

* Tetrahydrofuran was also used as a solvent in some preparations.

Table 5. Atom co-ordinates

For [{RhCl(Ph$_2$PO$_2$CCH=CMe$_2$)}$_2$]

Atom	x	y	z	Atom	x	y	z
Rh(1)	0.082 9(1)	0.179 5(0)	0.377 6(1)	C(34)	0.669 6	0.272 8	0.312 1
Rh(2)	0.151 4(1)	0.102 9(0)	0.221 9(1)	C(35)	0.527 5	0.274 6	0.357 3
Cl(1)	−0.057 9(3)	0.107 2(1)	0.323 9(2)	C(36)	0.432 1(7)	0.234 3(2)	0.359 4(5)
Cl(2)	0.106 2(3)	0.189 9(1)	0.212 0(2)	C(11)	0.171 1(16)	0.043 7(4)	0.040 5(7)
P(1)	0.248 9(3)	0.235 2(1)	0.416 9(2)	C(12)	0.228 4(13)	0.091 1(3)	0.085 5(6)
P(2)	0.214 6(3)	0.033 1(1)	0.270 6(2)	C(13)	0.359 7(12)	0.095 6(4)	0.152 2(6)
C(1)	−0.055 9(15)	0.233 3(4)	0.546 2(7)	C(14)	0.456 2(16)	0.052 8(4)	0.177 7(8)
C(2)	−0.026 1(12)	0.183 6(4)	0.509 9(6)	C(15)	0.184 5(16)	0.133 0(4)	0.018 2(7)
C(3)	0.124 2(12)	0.159 9(4)	0.520 2(7)	O(3)	0.589 1(11)	0.046 6(3)	0.161 6(7)
C(4)	0.264 6(13)	0.184 1(4)	0.566 0(7)	O(4)	0.380 7(8)	0.016 8(2)	0.224 2(4)
C(5)	−0.172 1(14)	0.152 3(4)	0.509 7(8)	C(41)	−0.068 6	−0.011 1	0.224 1
O(1)	0.339 0(10)	0.169 4(3)	0.635 4(5)	C(42)	−0.169 7	−0.050 2	0.213 1
O(2)	0.310 9(8)	0.226 4(2)	0.528 3(4)	C(43)	−0.111 3	−0.096 1	0.229 3
C(21)	0.237 0	0.326 9	0.494 4	C(44)	0.048 1	−0.103 0	0.256 5
C(22)	0.191 3	0.374 7	0.492 3	C(45)	0.149 2	−0.063 9	0.267 5
C(23)	0.102 2	0.392 7	0.414 3	C(46)	0.090 9(7)	−0.017 9(2)	0.251 3(4)
C(24)	0.058 8	0.362 9	0.338 5	C(51)	0.400 0	0.063 9	0.424 4
C(25)	0.104 5	0.315 2	0.340 6	C(52)	0.446 7	0.066 8	0.520 0
C(26)	0.193 6(8)	0.297 2(2)	0.418 6(4)	C(53)	0.369 5	0.039 6	0.584 7
C(31)	0.478 7	0.192 9	0.317 8	C(54)	0.245 6	0.009 5	0.553 8
C(32)	0.620 7	0.190 2	0.274 1	C(55)	0.198 9	0.006 7	0.458 2
C(33)	0.716 2	0.230 6	0.272 1	C(56)	0.276 1(7)	0.033 9(2)	0.393 5(4)

For [{RhCl(Ph$_2$PO$_2$CCH=CHCH=CHMe)}$_2$]

Atom	x	y	z	Atom	x	y	z
Rh(1)	0.330 2(0)	0.340 4(0)	−0.069 4(1)	C(36)	0.355 5(2)	0.458 6(2)	−0.278 8(5)
Rh(2)	0.430 9(0)	0.227 6(0)	0.061 5(1)	C(11)	0.715 3(6)	0.263 2(5)	0.380 9(11)
Cl(1)	0.470 1(1)	0.331 1(1)	0.020 7(2)	H(11)	0.764 3(56)	0.240 4(41)	0.416 0(90)
Cl(2)	0.322 1(1)	0.274 6(1)	0.123 9(2)	H(12)	0.710 4(44)	0.275 4(35)	0.461 8(85)
P(1)	0.331 8(1)	0.379 8(1)	−0.266 1(2)	H(13)	0.727 2(39)	0.295 5(34)	0.329 7(71)
P(2)	0.383 1(1)	0.137 7(1)	0.559 9(2)	C(12)	0.649 5(4)	0.222 9(3)	0.308 6(7)
C(1)	0.198 4(9)	0.467 2(5)	0.256 3(10)	C(13)	0.607 5(4)	0.229 9(3)	0.179 9(7)
C(2)	0.215 1(5)	0.455 5(4)	0.116 1(8)	C(14)	0.545 0(4)	0.187 2(3)	0.113 1(7)
C(3)	0.213 7(4)	0.401 3(5)	0.059 0(7)	H(16)	0.544 4(25)	0.156 8(22)	0.163 5(47)
C(4)	0.227 6(4)	0.392 6(4)	−0.077 9(7)	C(15)	0.511 2(4)	0.184 8(3)	−0.031 1(7)
C(5)	0.207 1(4)	0.338 6(4)	−0.158 9(7)	H(17)	0.528 0(28)	0.206 2(22)	−0.082 6(50)
H(7)	0.183 0(31)	0.308 7(26)	−0.122 4(53)	C(16)	0.480 4(4)	0.127 6(3)	−0.099 2(7)
C(6)	0.187 1(4)	0.342 4(3)	−0.308 7(8)	O(3)	0.493 1(4)	0.106 6(3)	−0.201 4(6)
O(1)	0.130 2(3)	0.321 6(3)	−0.387 1(5)	O(4)	0.430 8(3)	0.095 8(2)	−0.033 4(5)
O(2)	0.239 6(2)	0.377 3(2)	−0.363 4(4)	C(41)	0.405 8	0.032 2	0.215 3
C(21)	0.418 7	0.283 8	−0.331 1	C(42)	0.412 3	0.000 5	0.338 4
C(22)	0.461 8	0.253 4	−0.410 9	C(43)	0.406 6	0.031 2	0.457 5
C(23)	0.474 0	0.280 5	−0.530 1	C(44)	0.394 3	0.093 7	0.453 5
C(24)	0.443 1	0.338 0	−0.569 5	C(45)	0.387 8	0.125 5	0.330 4
C(25)	0.400 0	0.368 4	−0.489 6	C(46)	0.393 5(3)	0.094 7(2)	0.211 3(4)
C(26)	0.387 8	0.341 3	−0.370 4	C(51)	0.223 7	0.104 9	0.015 4
C(31)	0.431 2	0.477 8	−0.207 4	C(52)	0.144 5	0.103 3	−0.060 7
C(32)	0.453 4	0.538 2	−0.214 7	C(53)	0.123 2	0.127 7	−0.193 7
C(33)	0.399 8	0.579 5	−0.293 4	C(54)	0.180 9	0.153 8	−0.250 6
C(34)	0.324 1	0.560 3	−0.364 7	C(55)	0.260 0	0.155 5	−0.174 4
C(35)	0.302 0	0.499 9	−0.357 4	C(56)	0.281 4(3)	0.131 0(2)	−0.041 4(4)

Intensity data were recorded on a CAD4 diffractometer measuring to $\theta_{max.} = 65°$. These were merged to give 5 740 unique reflections with correction for absorption being made empirically[27] (minimum 0.6031, maximum 0.9987). The structure was solved by Patterson and Fourier methods. The positions and anisotropic vibrational parameters of all non-phenyl and -hydrogen atoms were refined. The methyl, phenyl, and vinylic hydrogen atoms were constrained to idealised geometries (C–H 1.08 Å). Phenyl rings were constrained to D_{6h} symmetry (C–C 1.395 Å).

The final R factor was 0.064 and R' ($= [\Sigma w|\Delta F|^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$) 0.057 for 4 071 reflections having $F > 4.5\sigma(F)$. The largest peaks in the final difference map were 1.5—2.0 e Å^{-3} in the vicinity of the rhodium and chlorine atoms, presumably as a result of absorption along the crystal axis. The fractional co-ordinates are in Table 5.

[{RhCl(Ph$_2$PO$_2$CCH=CHCH=CHMe)}$_2$]. Small cubes were obtained from dichloromethane–light petroleum at 25 °C. Crystal dimensions, 0.2 × 0.2 × 0.1 mm.

Crystal data. C$_{36}$H$_{34}$Cl$_2$O$_4$P$_2$Rh$_2$, M = 868, monoclinic, a = 17.372(2), b = 22.070(1), c = 9.986(2) Å, β = 104.51(1)°, U = 3 707.68 Å^3, space group $P2_1/a$, D_m = 1.54 g cm^{-3}, Z = 4, D_c = 1.55 g cm^{-3}, Mo-K_α radiation, λ = 0.7107 Å, μ = 36.42 cm^{-1}, $F(000)$ = 1 744.

Intensity data were recorded on a CAD4 diffractometer measuring in four octants of reciprocal space to $\theta_{max.} = 25°$. These were merged to give 5 130 unique reflections with correction for absorption being made empirically[27] (minimum

0.9642, maximum 0.9995). The structure was solved by Patterson and Fourier methods using full-matrix least-squares refinement and anisotropic vibrational parameters for all non-phenyl and -hydrogen atoms. The phenyl hydrogen, methyl hydrogen on C(1), and vinylic hydrogen atoms on C(2), C(3), C(12), and C(13) were all constrained to idealised geometries (C–H 1.08 Å) whilst all other hydrogen atoms were allowed to refine freely, this giving the best model for the electron densities in these regions. Phenyl rings were constrained as for $[\{RhCl(Ph_2PO_2CCH=CMe_2)\}_2]$.

The final R factor was 0.039 and R' was 0.0408 for 3 812 reflections having $F > 4\sigma(F)$. The largest peaks in the final difference map were 0.5—0.8 e $Å^{-3}$ in the vicinity of the phenyl rings. The fractional co-ordinates are in Table 5.

Computations were made using the program SHELX 76[28] on IBM 4341 and 3083 computers.

Acknowledgements

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