Reactions of $[RuCl_2(PPh_3)_4]$ with Mixed Anhydrides of Diphenylphosphinous and Acrylic Acids; Structure of $[RuCl\{(Ph_2PO)_2H\}(PPh_3)(O_2CCH_2CH_2PPh_3)]\cdot C_4H_8O$†

Derek J. Irvine,[a] **Sheila A. Preston,**[a] **David J. Cole-Hamilton***,[a] **and John C. Barnes**[b]
[a] *Chemistry Department, University of St. Andrews, St. Andrews, Fife, KY16 9ST, UK*
[b] *Chemistry Department, University of Dundee, Perth Road, Dundee, Tayside DD1 4HN, UK*

Reactions of $[RuCl_2(PPh_3)_4]$ with 1 mol equivalent of $Ph_2PO_2CCH{=}CR'R''$ produce $[RuCl_2(PPh_3)_2(Ph_2PO_2CCH{=}CR'R'')]$ (R′, R″ = H or Me), although for R′ = H, R″ = H or Me the major product is $[RuCl\{(Ph_2PO)_2H\}(PPh_3)(O_2CCH_2CHR''PPh_3)]$, which for R″ = H has been crystallographically characterized. Using 2 mol equivalents of $Ph_2PO_2CCR{=}CR'R''$ the products are $[RuCl_2(Ph_2PO_2CCR{=}CR'R'')_2]$ (R = H, R′ = R″ = Me; R = Me, R′ = H, R″ = Ph) or $[RuCl_2(PPh_3)(Ph_2PO_2CCH{=}CH_2)(Ph_2POPPh_2)]$. The complexes have all been characterized spectroscopically and the mixed anhydride ligands are generally co-ordinated through P and O, apparently for steric reasons. Binding through P and the C=C appears to occur in $[RuCl_2(PPh_3)_2(Ph_2POCH_2CH{=}CMe_2)]$, prepared from $[RuCl_2(PPh_3)_4]$ and $Ph_2POCH_2CH{=}CMe_2$, whilst unidentate binding *via* the P atom is observed for the mixed anhydride in $[RuCl_2(PPh_3)(Ph_2PO_2CCH{=}CH_2)(Ph_2POPPh_2)]$. Crystal data for $[RuCl\{(Ph_2PO)_2H\}(PPh_3)(O_2CCH_2CH_2PPh_3)]$: orthorhombic, space group $P2_12_12_1$, with a = 15.16(3), b = 23.05(3), c = 17.08(4) Å and Z = 4. The structure was obtained from 6558 reflections measured on an automatic diffractometer and refined to an R value of 0.076. The main features of the structure include the zwitterionic triphenylphosphoniopropionate betaine ligand binding *via* the carboxylate in a chelating fashion and the planar RuPOHPO ring of the bis(diphenylphosphinito)hydrogenate ligand. The O ··· O distance in this ligand is 2.382(12) Å indicative of strong hydrogen bonding.

During studies of the co-ordination chemistry of compounds of the form $Ph_2PO_2CCR{=}CR'R''$ (R, R′, R″ are H, alkyl or aryl) with rhodium we have demonstrated that these mixed anhydrides can bind *via* the P atom alone, as in $[RhCl(PPh_3)_2(Ph_2PO_2CCR{=}CR'R'')]$ (R = H, R′ = R″ = Me; R = Me; R′ = H, R″ = Ph; or R = R′ = H, R″ = CH=CHMe,[1] *via* the phosphorus atom and the double bond, as in $[RhCl(PPh_3)(Ph_2PO_2CCR{=}CR'R'')]$ (R = R′ = H, R″ = H, Me or CH=CHMe)[1] or in dimers of the form $[\{RhCl(Ph_2PO_2CCR{=}CR'R'')\}_2]$;[2] or *via* the P atom and the carbonyl O atom as in $[Rh(PPh_3)_2(Ph_2PO_2CCR{=}CR'R'')]^+$ (for all R, R′, R″ studied).[1] The phosphinite $Ph_2POCH_2CH{=}CMe_2$ forms a dimer $[\{RhCl(Ph_2POCH_2CH{=}CMe_2)\}_2]$ with binding through the P atom and the double bond.[2] In addition to simple co-ordination of the mixed anhydride ligands, various alterations can be observed under certain conditions. Thus, $[RhCl(PPh_3)_3]$ reacts with $Ph_2PO_2CCH_2CH{=}CH_2$ to give exclusively $[RhCl(PPh_3)(Ph_2PO_2CCH{=}CHMe)]$ in which the double bond has migrated along the chain,[3] whilst reaction of $[RhCl(PPh_3)_3]$ with excess (2 mol equivalents) of $Ph_2PO_2CCH{=}CH_2$ gives $[RhCl(PPh_3)(Ph_2POPPh_2)]$ *via* a complex sequence of reactions.[3,4] Finally, reaction of $TlPF_6$ with a solution produced from reaction of $[RhCl(PPh_3)_3]$ with 1 mol equivalent of $Ph_2PO_2CCH{=}CH_2$ gives $[Rh(PPh_3)_3(O_2CCH_2CH_2PPh_3)]PF_6$, containing the unusual zwitterionic ligand which has been shown to be produced in a reaction of free $Ph_2PO_2CCH{=}CH_2$ with PPh_3 prior to co-ordination to the metal.[3]

Many of the mixed anhydride complexes (*viz.* those containing PPh_3) are active catalysts for the hydrogenation of acrylic acids in the presence of base[5] and detailed mechanistic studies have shown that these reactions involve catalytically important steps at the metal (alkene co-ordination, H–H activation, insertion and reductive elimination) but also at the P atom. The product ($R'R''CHCHRCO_2^-$) is released and substrate ($R'R''C{=}CRCO_2^-$) is reintroduced into the cycle *via* a base-catalysed transesterification at the co-ordinated P atom of the mixed anhydride.[5,6]

We now report reactions of the mixed anhydride ligands with $[RuCl_2(PPh_3)_4]$ in which, in addition to simple co-ordination, three different types of disruption of the ligand are observed.

Results and Discussion

(*a*) $[RuCl_2(PPh_3)_4]$ *and* $Ph_2PO_2CCR{=}CR'R''$ (1:2).—The complex $[RuCl_2(PPh_3)_4]$ reacts with 2 mol equivalents of $Ph_2PO_2CCR{=}CR'R''$ (R = H, R′ = R″ = Me; R = Me, R′ = H, R″ = Ph) to give bright red crystalline complexes which analyse as $[RuCl_2(Ph_2PO_2CCR{=}CR'R'')_2]$. For both these complexes spectroscopic data suggest that the mixed anhydrides are bound through the P atoms and the O atoms of the carbonyl group, unlike their rhodium counterparts where this kind of binding is generally observed only in cationic compounds where the metal is more positive and hence more oxophilic.[1] Thus, there is no ν(C=O) near 1670 cm^{-1} in the IR spectra (Table 1) of these ruthenium complexes, whilst a feature at *ca.* 1600 cm^{-1} can be assigned to ν(C=O) of an ester carbonyl bound through the oxygen atom; ν(C=C) is observed near 1620 cm^{-1}, *cf.* 1585 [ν(C=O)] and 1628 [ν(C=C)] cm^{-1} for $[Rh(PPh_3)_2(Ph_2PO_2CCH{=}CMe_2)]^+$.[1] More evidence for this mode of binding[2] is obtained from the NMR data, since the resonances from the phosphorus atoms appear at very high field (δ *ca.* 186) (Table 2), consistent with their being in a five-membered ring.[7] Finally, the vinylic protons give resonances (Table 1) in the olefinic region, confirming that co-ordination of

---

† [Bis(diphenylphosphinito)hydrogenato-κ^2*P*,*P*′]chloro(triphenylphosphine)(3-triphenylphosphoniopropionate-κ^2*O*,*O*′)ruthenium(II)–tetrahydrofuran (1/1).

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

Table 1 Selected IR and ^{1}H NMR data for the ligands and ruthenium complexes

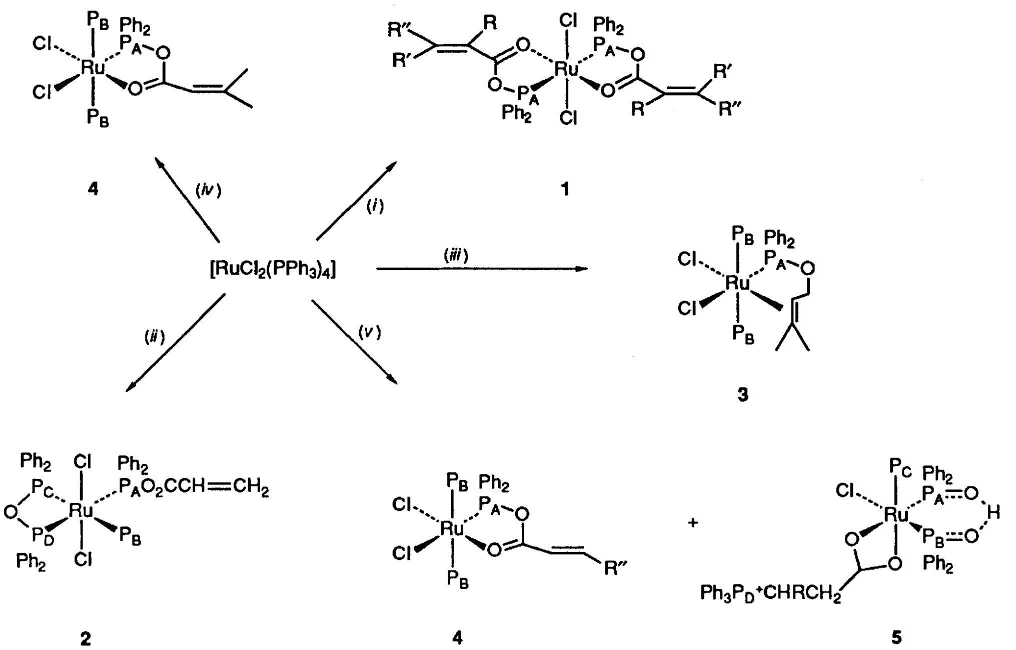
	IR/cm^{-1}				^{1}H NMR	
Compound	ν(C=O)	ν(C=C)	ν(Ru–Cl)	ν(P–O)	δ(Me)	δ(H)
$Ph_3P^+CH^b_2CH^a_2CO_2^-$	1593, 1583					3.4 (m, H^a), 2.7 (m, H^b)
$Ph_3PCH^bMeCH^a_2CO_2^-$	1588 (br)				1.4	3.0 (m, H^a), 4.7 (m, H^b) 2.25 (m, H^b)
$[RuCl_2(Ph_2PO_2CCMe{=}CHPh)_2]$	1590	1620	340			
$[RuCl_2(Ph_2PO_2CCH{=}CMe_2)_2]$	1600	1630	347		1.98 (d),^{a} 2.03 (d)^a	6.19 (m)
$[RuCl_2(PPh_3)_2(Ph_2PO_2CCH{=}CMe_2)]$		1637	340		2.2 (d), 1.9 (d)	5.75 (m)
$[RuCl_2(PPh_3)(Ph_2PO_2CCH{=}CH_2)(Ph_2POPPh_2)]$	1710	1580	330	830, 780		*b*
$[RuCl_2(PPh_3)_2(Ph_2POCH^a_2CH^b{=}CMe_2)]$		1670w			1.1 (d), 1.4 (d)	3.5 (m, H^a), 4.6 (m, H^b)
$[RuCl\{(Ph_2PO)_2H\}(PPh_3)(O_2CCH^a_2CH^b_2PPh_3)]$	1550		340, 300	770, 755		1.55 (m, H^a), 1.20 (m, H^b)
$[RuCl\{(Ph_2PO)_2H\}(PPh_3)(O_2CCH^a_2CH^bMePPh_3)]$	1550		335, 290	830, 780	0.5	2.85 (m, H^a), 2.5 (m, H^a), 1.6 (m, H^b)

^{a} $^4J_{HH}$ = 1.0 Hz. ^{b} Obscured by phenyl resonances.

Table 2 Phosphorus-31 data for new ligands and ruthenium complexes^a

	δ				*J*/Hz		
Compound	P_A	P_B	P_C	P_D	P_AP_B	P_AP_B	P_BP_C
$Ph_3P^+CH_2CH_2CO_2^-$	24.7						
$Ph_3P^+CHMeCH_2CO_2^-$	30.1						
$[RuCl_2(Ph_2PO_2CCMe{=}CHPh)_2]$	186.6						
$[RuCl_2(Ph_2PO_2CCH{=}CMe_2)_2]$	185.6						
$[RuCl_2(PPh_3)_2(Ph_2PO_2CCH{=}CMe_2)]$	153.3 (t)	29.3 (d)			30.6		
$[RuCl_2(PPh_3)_2(Ph_2PO_2CCH{=}CH_2)]$	153.3 (t)	29.2 (d)			30.6		
$[RuCl_2(PPh_3)_2(Ph_2PO_2CCH{=}CHMe)]$	153.0 (t)	29.2 (d)			30.6		
$[RuCl_2(PPh_3)(Ph_2PO_2CCH{=}CH_2)(Ph_2POPPh_2)]^b$	84.5 (dt)	18.7 (dt)	111.2 (ddd)	106.8 (ddd)	26.8	35.1	305.4
$[RuCl_2(PPh_3)_2(Ph_2POCH_2CH{=}CMe_2)]$	163.0 (t)	29.4 (d)			30.3		
$[RuCl\{(Ph_2PO)_2H\}(PPh_3)(O_2CCH_2CH_2PPh_3)]$	112.0 (br)		52.7 (t)	23.9 (s)		43.8	43.8
(248 K)	115.4 (dd)	110.8 (t)	51.6 (dd)	23.0 (s)	46.1	38.6	47.3
$[RuCl\{(Ph_2PO)_2H\}(PPh_3)(O_2CCH_2CHMePPh_3)]$	110.0 (br)		53.8 (t)	28.9 (s)		43.8	43.8
(248 K)	111.2 (dd)	110.7 (t)	52.7 (dd)	28.7 (s)	47.7	38.6	49.7

^{a} In CD_2Cl_2 at 298 K; chemical shifts to high frequency of 85% H_3PO_4; for assignments see Scheme 1. ^{b} Other *J*: P_AP_D, 329.3; P_BP_D, 28.2; P_CP_D, 89.9 Hz.



Scheme 1 Reactions of $[RuCl_2(PPh_3)_4]$ with mixed anhydrides; P = PPh_3. (*i*) $Ph_2PO_2CCR{=}CR'R''$, R = H, R′ = R″ = Me or R = Me, R′ = H, R″ = Ph (1:2); (*ii*) $Ph_2PO_2CCH{=}CH_2$ (1:2); (*iii*) $Ph_2POCH_2CH{=}CMe_2$; (*iv*) $Ph_2PO_2CCH{=}CMe_2$ (1:1); (*v*) $Ph_2PO_2CCH{=}CHR''$, R″ = Me or H (1:1)

the double bond does not occur. A single ν(Ru–Cl) at ≈340 cm^{-1} shows that the complexes have mutually *trans* Cl atoms, and the presence of only one ν(C=O) and only one ν(C=C) suggest that the phosphorus atoms are also mutually *trans* as in

1, Scheme 1. This stereochemistry is also likely on steric grounds since it places the bulky Ph_2P groups as far away from one another as possible. Braunstein *et al.*[8] have reported various complexes of $Ph_2PCH_2CO_2Et$, including $[RuCl_2(Ph_2PCH_2CO_2Et)_3]$ in which one of the phosphine ligands is bound through P and O whilst the other two are bound only through P. As in **1**, the chlorine atoms are mutually *trans*.

Using the less highly substituted mixed anhydride, $Ph_2PO_2CCH{=}CH_2$, in reaction with $[RuCl_2(PPh_3)_4]$ (2:1 mol ratio), a different kind of complex is formed. This pale yellow compound analyses as $[RuCl_2(Ph_2POPPh_2)(PPh_3)(Ph_2PO_2CCH{=}CH_2)]$ and exhibits a single ν(Ru–Cl) in the far-IR spectrum, suggesting mutually *trans* Cl atoms. The ^{31}P NMR spectrum is consistent with this, with large couplings being observed between the mutually *trans* P atoms (> 300 Hz) and a coupling of *ca.* 90 Hz between the P atoms of the Ph_2POPPh_2 ligand; *cf.* 120 Hz for $[RhCl(PPh_3)(Ph_2POPPh_2)]$.[3,4] The phosphorus resonance of the mixed anhydride ligand is at δ 84.5, consistent with bonding through only the P atom,[1] and this is confirmed by the IR and ^1H NMR (all vinyl resonances obscured by the phenyl resonances) spectra (see Table 1). We, therefore, assign the complex structure **2**.

In an attempt to force a mixed anhydride or similar ligand to bind to ruthenium through P and the double bond, $[RuCl_2(PPh_3)_4]$ was treated with 2 mol equivalents of the unsaturated phosphinite, $Ph_2POCH_2CH{=}CMe_2$. A dark green product analysing as $[RuCl_2(PPh_3)_2(Ph_2POCH_2CH{=}CMe_2)]$ was obtained. The ^{31}P resonance from the P atom of the phosphinite is at δ 163, similar to the position found for $[\{RhCl(Ph_2POCH_2CH{=}CMe_2)\}_2]$ (δ 165),[2] suggesting binding through P and the double bond and this is supported by the ^1H NMR spectrum, in which the vinylic proton resonates at δ 4.58 (*cf.* δ 5.8 for the free ligand[2] and 3.1 for chelate binding in $[\{RhCl(Ph_2POCH_2CH{=}CMe_2)\}_2]$). Although the shift to high field for this vinylic proton is small compared with that in the rhodium complex, similar shifts are observed for the vinylic protons in $[RhCl(PPh_3)(Ph_2PO_2CCH{=}CHMe)]$, for which binding through P and the double bond has been confirmed crystallographically[1] (δ 4.98 and 4.37, *cf.* 7.08 and 6.02 for the free ligand and 3.0–3.8 for the ligand in $[\{RhCl(Ph_2PO_2CCH{=}CHMe)\}_2]$.[2] We, therefore, assign $[RuCl_2(PPh_3)_2(Ph_2POCH_2CH{=}CMe_2)]$ structure **3**, although a very weak feature at 1670 cm^{-1} in the IR spectrum [ν(C=C)?] may indicate unidentate binding of the mixed anhydride through only the P atom.

(*b*) $[RuCl_2(PPh_3)_4]$ *and* $Ph_2PO_2CCR{=}CR'R''$ (1:1).—The reaction of equimolar proportions of $[RuCl_2(PPh_3)_4]$ and $Ph_2PO_2CCH{=}CMe_2$ gives a brown complex which analyses as $[RuCl_2(PPh_3)_2(Ph_2PO_2CCH{=}CMe_2)]$. The P atom of the mixed anhydride ligand occurs at δ 153.3, between the positions usually observed for chelate binding through P and the double bond (δ 130)[1,2] or P and O (δ 180).[1] A weak band at 1637 cm^{-1} is assigned to ν(C=C) of a mixed anhydride bound through P and O whilst the ^1H NMR resonance from the vinylic proton (δ 5.75) is close to that of the free ligand (δ 5.71)[2] confirming that the double bond is unco-ordinated. We, therefore, assign this complex as having binding of the mixed anhydride through P and O. The P–P coupling constant indicates that the P atom of the mixed anhydride is *cis* to the P atoms of the PPh_3 ligands, whilst the equivalence of the P atoms of the PPh_3 ligands shows that they must be mutually *trans* as in **4**. The brown colour is unusual for six-co-ordinate complexes of ruthenium(II), but may be related to the presence of chromophores in the ligands.

In contrast, reactions of $[RuCl_2(PPh_3)_4]$ with molar equivalent quantities of the less-substituted mixed anhydrides, $Ph_2PO_2CCH{=}CHR''$ (R″ = Me or H), give two products. The minor ones, which have not been obtained analytically pure, have very similar spectroscopic properties to $[RuCl_2(PPh_3)_2(Ph_2PO_2CCH{=}CMe_2)]$ so are assigned as $[RuCl_2(PPh_3)_2(Ph_2PO_2CCH{=}CHR'')]$ (R″ = H or Me) with structure **4**. The major products, which appear as yellow precipitates upon allowing the reactions to stand at −3 °C for several days, are quite different and X-ray diffraction studies (see below) have shown that for R″ = H the product is $[RuCl\{(Ph_2PO)_2H\}(PPh_3)(O_2CCH_2CH_2PPh_3)]$ with structure **5**. The spectroscopic properties of this complex and its analogue with R″ = Me are entirely consistent with this structure being maintained in solution at low temperature. Thus, the ^{31}P NMR spectrum at −25 °C exhibits four resonances, one of which, a singlet at *ca.* δ 25 can be assigned to the unco-ordinated P atom of the zwitterionic ligand. For the free ligands, this resonance appears at very similar chemical shifts (Table 2). The coupling constants for the other P atoms are all as expected for mutually *cis* P atoms and the non-equivalence of the P atoms of the $(Ph_2PO)_2H$ ligand is also consistent with structure **5**, as are the values of ν(C=O) for the carboxylate group (≈1550 cm^{-1} indicating bidentate binding). The methylene protons of the zwitterionic ligand R″ = H) resonate as multiplets at δ 1.55 and 1.20 (*cf.* 3.4 and 2.7 for the free ligand). Similar shifts are observed for the methylene protons for R″ = Me (Table 2) and of $[Rh(PPh_3)_3(O_2CCH_2CH_2PPh_3)]^+$.[3] The presence of the $(Ph_2PO)_2H$ ligand is less easy to identify spectroscopically, although the chemical shifts of the P atoms (δ *ca.* 110) are similar to those of related ruthenium complexes containing this ligand (*cf.* δ 123.1 for $[Ru(S_2PMe_2)\{(Ph_2PO)_2H\}(PPh_3)]$).[9] The low value of J_{PP} rules out the presence of Ph_2POPPh_2 or a related ligand. The ^{31}P NMR spectra of these complexes indicate fluxional behaviour such that the two phosphorus atoms of the $(Ph_2PO)_2H$ ligand exchange with one another at higher temperatures. Coupling to the PPh_3 ligand is not lost so the mechanism of this exchange is not dissociative. Various other mechanisms are possible, but perhaps the most probable would involve the deco-ordination of one oxygen atom of the zwitterionic ligand to give a five-co-ordinate complex, which is fluxional or in which the two P atoms of the $(Ph_2PO)_2H$ ligand are symmetry related. Fluxionality has been observed in other complexes of $(Ph_2PO)_2H$, *e.g.* $[Rh_2Cl_5\{(Ph_2PO)_2H\}_2]$, although the exact mechanism remains obscure.[10]

Reactions to form the various complexes described above are outlined in Scheme 1.

X-Ray Crystal Structure of $[RuCl\{(Ph_2PO)_2H\}(PPh_3)(O_2CCH_2CH_2PPh_3)]$.—The structure of $[RuCl\{(Ph_2PO)_2H\}(PPh_3)(O_2CCH_2CH_2PPh_3)]$ is shown in Fig. 1, with selected bond lengths and angles in Table 3. Overall, the ruthenium atom is in a distorted-octahedral environment with the P atoms bound to the ruthenium in a mutually *fac* orientation. The chloride ion is *trans* to one of the phosphorus atoms of the $(Ph_2PO)_2H$ ligand whilst the other two co-ordination sites are occupied by the oxygen atoms of a triphenylphosphoniopropionate betaine ligand bound in a chelating manner. Although this is the first reported structure of a complex containing this zwitterionic ligand, the ligand has been known for some time[11] and complexes of it with *e.g.* Sn have been reported.[12] There has been some controversy as to the exact nature of this compound, with both the zwitterionic form and an ylide tautomer, $Ph_3P{=}CHCH_2CO_2H$, having been proposed.[12] The zwitterionic structure was supported by co-ordination to Sn, where a bridging bonding mode was proposed on the basis of infrared data.[12] The crystal structure of $[RuCl\{(Ph_2PO)_2H\}(PPh_3)(O_2CCH_2CH_2PPh_3)]$ unequivocally confirms the zwitterionic formulation for $Ph_3P^+CH_2CH_2CO_2^-$, whilst the similarity of its spectroscopic properties in the co-ordinated or unco-ordinated states allows us to conclude that it also has the zwitterionic structure in the free state. The bond lengths and angles of the carboxylate moiety are similar to those found in other carboxylate complexes of ruthenium *e.g.* $[RuCl(O_2CMe)(CO)(PPh_3)_2]$,[13] $[RuH(O_2CMe)(PPh_3)_3]$[14] or $[Ru(O_2CMe)(p\text{-}MeC_6H_4NCH)(CO)(PPh_3)_2]$[15] although the RuOCO ring is more distorted with the RuO bond *trans* to the $Ph_2PO \cdots H$ ligand [2.382(8) Å] being significantly longer than those in related ruthenium carboxylate complexes[13–15] and than that

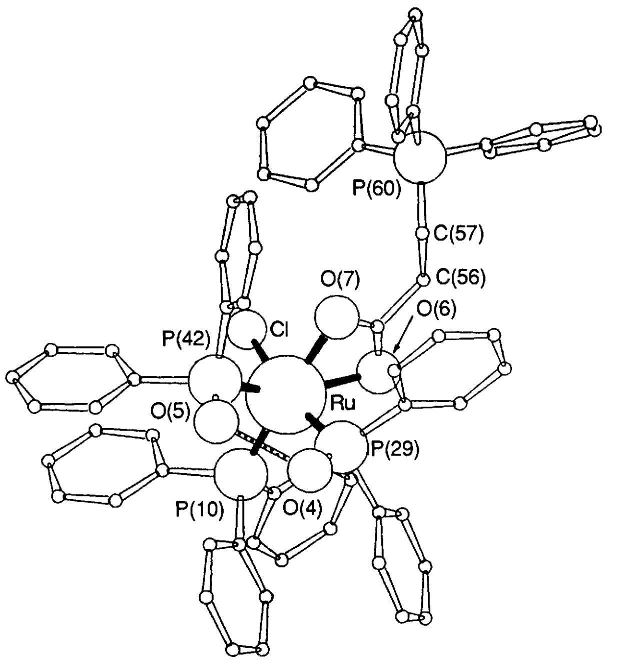


Fig. 1 Structure and numbering scheme for $[RuCl\{(Ph_2PO)_2H\}(PPh_3)(O_2CCH_2CH_2PPh_3)]$

Table 3 Selected bond lengths (Å) and angles (°) for $[RuCl\{(Ph_2PO)_2H\}(PPh_3)(O_2CCH_2CH_2PPh_3)]$

Ru–Cl	2.496(4)	P(29)–O(4)	1.558(10)
Ru–P(42)	2.238(4)	O(4) ··· O(5)	2.382(12)
Ru–P(29)	2.296(3)	O(7)–C(55)	1.255(17)
Ru–P(10)	2.287(4)	O(6)–C(55)	1.246(18)
Ru–O(6)	2.382(8)	C(55)–C(56)	1.501(20)
Ru–O(7)	2.165(9)	C(56)–C(57)	1.519(20)
P(42)–O(5)	1.544(11)	C(57)–P(60)	1.811(14)
Cl–Ru–O(7)	82.0(2)	P(10)–Ru–P(29)	95.8(1)
Cl–Ru–O(6)	82.1(2)	P(10)–Ru–P(42)	95.1(1)
Cl–Ru–P(42)	99.4(1)	P(29)–Ru–P(42)	89.9(1)
Cl–Ru–P(10)	91.2(1)	Ru–O(7)–C(55)	95.9(8)
O(7)–Ru–O(6)	56.9(3)	Ru–O(6)–C(55)	86.1(8)
O(7)–Ru–P(29)	89.2(2)	O(6)–C(55)–O(7)	120.7(13)
O(7)–Ru–P(42)	96.2(3)	O(6)–C(55)–C(56)	120.8(12)
O(7)–Ru–P(10)	167.6(3)	O(7)–C(55)–C(56)	118.5(13)
O(6)–Ru–P(29)	86.0(2)	C(55)–C(56)–C(57)	112.0(12)
O(6)–Ru–P(10)	112.1(2)	C(56)–C(57)–P(60)	115.1(10)
O(6)–Ru–P(42)	152.8(2)		

trans to the PPh_3 ligand [2.165(9) Å] suggesting a much higher *trans* influence for the $Ph_2PO \cdots H$ ligand than for PPh_3. This difference in bond length is reflected in minor distortions in the ring angles. The O(7)–Ru–O(6) angle [56.9(3)°][15] is somewhat less than that found in $[RuCl(O_2CMe)(CO)(PPh_3)_3]$ [60.3(2)°][13] or $[Ru(O_2CMe)(p\text{-}MeC_6H_4NCH)(CO)(PPh_3)_2]$ [58.7(3)°] but similar to that in $[RuH(O_2CMe)(PPh_3)_3]$ [57.6(4)°].[14] The bond lengths and angles around the unco-ordinated P atom are essentially identical to those found in the phosphonium cations of $[PEtPh_3][tcnq]$[16] (tcnq is α,α,α′,α′-tetracyano-*p*-quinodimethanide) and $[PPrPh_3][CuBr_2]$.[17]

As with other metal complexes containing $(Ph_2PO)_2H$,[18] the RuPOOP ring of the $(Ph_2PO)_2H$ ligand is essentially planar (root mean square deviation from the plane 0.096 Å). The O ··· O distance of 2.382(12) Å is typical for this type of ligand and would usually indicate a strong (symmetrical) hydrogen bond, although some X-ray[18] and neutron[19] diffraction data suggest that in these particular compounds the hydrogen bonds are not symmetrical or may even be absent.

Mechanistic Considerations.—In all cases, where the mixed anhydride ligands, $Ph_2PO_2CCR{=}CR'R''$, remain intact (with the exception of **2**) binding to ruthenium is observed to be bidentate through the phosphorus and oxygen atoms. This behaviour contrasts with that in neutral rhodium complexes where binding is through P alone or through P and the double bond.[1,2] Binding through P and O has only previously been observed in *cationic* rhodium complexes,[1] presumably because the positive charge on the metal centre renders it more oxophilic. Steric effects may also be important for these complexes since they contain two triphenylphosphine ligands in addition to the bidentate mixed anhydride. For the ruthenium complexes it seems likely that steric effects dominate the choice of co-ordination mode since in all cases the metal centre is six-co-ordinate (rather than four-co-ordinate for Rh^I). In complexes where there are highly substituted double bonds in the mixed anhydride ligands (**1** or **4**, R = H, R′ = R″ = Me) bidentate binding through P and the double bond would not be expected, whilst where there are less-substituted double bonds (**4**, R = R′ = H, R″ = H or Me) there are at least two other bulky ligands around the metal centre in addition to the two chlorides. The observation of bidentate binding of the mixed anhydrides in these complexes, rather than of unidentate binding through just P, might be expected since this allows the ruthenium centre to achieve the favourable 18e count {as in *e.g.* $[RuCl_2(CO)(PPh_3)_3]$}.

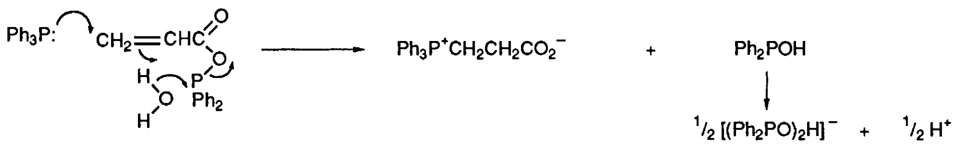
For $[RuCl_2(Ph_2POPPh_2)(PPh_3)(Ph_2PO_2CCH{=}CH_2)]$ the 18e configuration of the metal is achieved with binding of the mixed anhydride ligand only through P. In related ruthenium complexes, containing the $Ph_2PCH_2CO_2Et$ ligand, binding through P and O is also observed,[8] although the strength of the Ru–O interaction is generally weak ($\Delta G^{\ddagger}$ for exchange of bi- and uni-dentate co-ordination = 55.6 kJ mol^{-1}) and complexes containing unidentate $Ph_2PCH_2CO_2Et$ are readily formed.[8]

The structures of complexes **2** and **4** demonstrate three other possible fates for the mixed anhydride ligands in addition to simple co-ordination. We have already reported[3,4] that reaction of 2 mol equivalents of $Ph_2PO_2CCH{=}CH_2$ with $[RhCl(PPh_3)_3]$ leads to $[RhCl(PPh_3)(Ph_2POPPh_2)]$, *via* a coupling of two mixed anhydrides co-ordinated to rhodium. A similar mechanism is presumably responsible for the formation of the Ph_2POPPh_2 ligand in **2**, although it is perhaps a little surprising that the complex also contains an unchanged $Ph_2PO_2CCH{=}CH_2$ ligand when the ratio of mixed anhydride:Ru was only 2:1. We note, however, that the yield of this complex is relatively low.

The zwitterionic ligand in **5** has also been observed to form in the reaction of $TlPF_6$ with a mixture of $[RhCl(PPh_3)_3]$ and $Ph_2PO_2CCH{=}CH_2$.[3] Its origin in **5** is probably similar to that in the rhodium complex and we have shown that $Ph_2PO_2CCH{=}CH_2$ reacts with PPh_3 to give $Ph_3P^+CH_2CH_2CO_2^-$ together with $Ph_2PP(O)Ph_2$ as the major products.[3] Since $[RuCl_2(PPh_3)_4]$ releases one PPh_3 group on dissolution in organic solvents, indeed it has been suggested that it is not co-ordinated in the solid state,[20] it is not surprising that the zwitterion forms in the reaction solution and its complexation would then be expected (carboxylates readily metathesize Ru–Cl bonds). The formation of the $(Ph_2PO)_2H$ ligand in this system is perhaps a little more surprising, since we have not previously observed this ligand to be formed from mixed anhydride compounds. It is possible that Ph_2POH is the other product in the formation of the zwitterion, particularly if traces of water are present and this is then likely to be the source of the $(Ph_2PO)_2H$ ligand (see Scheme 2). Failure to observe zwitterionic ligands for the more substituted mixed anhydrides arises because the latter are unreactive towards PPh_3.[3]

Experimental

Microanalyses were by the University of St. Andrews Materials Analysis Service, infrared spectra were recorded on a Perkin-



Scheme 2 Possible mechanism for the formation of $[(Ph_2PO)_2H]^-$ and $Ph_3P^+CH_2CH_2CO_2^-$ from $Ph_2PO_2CCH{=}CH_2$

Table 4 Coordinates ($\times 10^4$) for non-hydrogen atoms for $[RuCl\{(Ph_2PO)_2H\}(PPh_3)(O_2CCH_2CH_2PPh_3)]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Ru	2 123(1)	7 912(1)	7 685(1)	C(43)	1 728(6)	7 390(5)	5 733(5)
Cl	632(2)	7 472(2)	7 868(2)	C(44)	2 060(6)	7 479(5)	4 981(5)
O(4)	4 133(7)	8 287(5)	7 066(6)	C(45)	1 513(6)	7 406(5)	4 332(5)
O(5)	3 359(7)	7 692(4)	6 156(6)	C(46)	634(6)	7 244(5)	4 435(5)
P(10)	1 522(2)	8 711(2)	7 096(2)	C(47)	302(6)	7 155(5)	5 187(5)
C(11)	843(6)	9 153(4)	7 784(5)	C(48)	849(6)	7 228(5)	5 836(5)
C(12)	782(6)	8 996(4)	8 571(5)	C(49)	2 747(6)	6 728(4)	6 815(6)
C(13)	348(6)	9 358(4)	9 100(5)	C(50)	2 115(6)	6 349(4)	7 118(6)
C(14)	−26(6)	9 877(4)	8 842(5)	C(51)	2 351(6)	5 783(4)	7 317(6)
C(15)	35(6)	10 034(4)	8 055(5)	C(52)	3 218(6)	5 596(4)	7 214(6)
C(16)	469(6)	9 672(4)	7 526(5)	C(53)	3 850(6)	5 975(4)	6 911(6)
C(17)	2 264(6)	9 244(4)	6 619(6)	C(54)	3 614(6)	6 540(4)	6 712(6)
C(18)	2 319(6)	9 823(4)	6 855(6)	O(6)	2 061(6)	7 972(4)	9 076(5)
C(19)	2 884(6)	10 203(4)	6 466(6)	C(55)	2 296(7)	7 454(7)	9 075(8)
C(20)	3 395(6)	10 006(4)	5 841(6)	O(7)	2 504(6)	7 205(4)	8 448(5)
C(21)	3 340(6)	9 428(4)	5 605(6)	C(56)	2 345(9)	7 115(7)	9 824(8)
C(22)	2 775(6)	9 047(4)	5 993(6)	C(57)	2 848(10)	6 550(6)	9 724(8)
C(23)	4 389(5)	1 366(4)	1 350(5)	P(60)	2 293(2)	5 911(2)	10 094(2)
C(24)	4 274(5)	1 224(4)	563(5)	C(61)	1 194(5)	5 853(5)	9 678(6)
C(25)	4 974(5)	1 284(4)	39(5)	C(62)	968(5)	6 162(5)	9 005(6)
C(26)	5 788(5)	1 488(4)	302(5)	C(63)	135(5)	6 093(5)	8 671(6)
C(27)	5 903(5)	1 630(4)	1 089(5)	C(64)	−472(5)	5 714(5)	9 010(6)
C(28)	5 203(5)	1 569(4)	1 613(5)	C(65)	−247(5)	5 404(5)	9 683(6)
P(29)	3 520(2)	8 287(2)	7 798(2)	C(66)	587(5)	5 474(5)	10 016(6)
C(30)	4 176(6)	7 904(4)	8 555(5)	C(67)	2 881(5)	5 845(4)	11 602(6)
C(31)	4 654(6)	7 424(4)	8 294(5)	C(68)	2 172(5)	6 004(4)	11 129(6)
C(32)	5 149(6)	7 098(4)	8 823(5)	C(69)	1 429(5)	6 263(4)	11 460(6)
C(33)	5 166(6)	7 251(4)	9 613(5)	C(70)	1 396(5)	6 364(4)	12 265(6)
C(34)	4 688(6)	7 731(4)	9 874(5)	C(71)	2 106(5)	6 205(4)	12 738(6)
C(35)	4 193(6)	8 057(4)	9 345(5)	C(72)	2 848(5)	5 946(4)	12 407(6)
C(36)	3 574(7)	9 046(3)	8 154(6)	C(73)	2 946(6)	5 282(4)	9 853(6)
C(37)	3 000(7)	9 259(3)	8 723(6)	C(74)	3 634(6)	5 332(4)	9 315(6)
C(38)	3 026(7)	9 844(3)	8 932(6)	C(75)	4 130(6)	4 845(4)	9 112(6)
C(39)	3 627(7)	10 216(3)	8 571(6)	C(76)	3 938(6)	4 308(4)	9 449(6)
C(40)	4 202(7)	10 003(3)	8 001(6)	C(77)	3 251(6)	4 258(4)	9 987(6)
C(41)	4 175(7)	9 418(3)	7 792(6)	C(78)	2 755(6)	4 745(4)	10 190(6)
P(42)	2 510(2)	7 478(2)	6 564(2)				

Elmer 1310 grating spectrometer on Nujol mulls between caesium iodide plates, NMR spectra on a Brüker Associates AM300 spectrometer operating in the Fourier-transform mode with, for ^{31}P, proton noise decoupling. Fast atom bombardment (FAB) mass spectra were obtained from the SERC Mass Spectrometry service based in Swansea.

Solvents were purified by distillation from sodium diphenylketyl [thf, diethyl ether, toluene and light petroleum, (b.p. 40–60 °C)] or $CaH_2(CH_2Cl_2)$. All manipulations were carried out under dry oxygen-free nitrogen (purified by passing over a column of Cr^{2+} on silica gel) using standard Schlenk-line and catheter-tubing techniques. All taps were greaseless and all Quickfit joints were sealed using poly(tetrafluoroethylene) sleeves. Grease was not used.

The complex $[RuCl_2(PPh_3)_4]$[21] and $Ph_2PO_2CCR{=}CR'R''$[2] were prepared by standard literature methods, although for R = R′ = H, R″ = H or Me the mixed anhydrides were not isolated but used as freshly prepared solutions, as previously described.[3]

Dichlorobis(diphenylphosphino 3-*Methylbut*-2-*enoate*-κ²P,O)-*ruthenium*(II).—To a solution of $[RuCl_2(PPh_3)_4]$ (0.43 g, 0.35 mmol) in CH_2Cl_2 (20 cm³) was added $Ph_2PO_2CCH{=}CMe_2$ (0.2 g, 0.7 mmol) in CH_2Cl_2 (10 cm³). The initially brown solution immediately became bright red. The solution was filtered, evaporated *in vacuo* to *ca.* 5 cm³ and treated with light petroleum–diethyl ether (1:1) to produce a red crystalline product which was collected, washed with light petroleum (2 × 10 cm³) and dried *in vacuo*. Yield 0.21 g (80%) (Found: C, 55.6; H, 4.6. $C_{34}H_{34}Cl_2O_4P_2Ru$ requires C, 55.1; H, 4.6%). *Dichlorobis(diphenylphosphino* E-2-*methyl*-3-*phenylprop*-2-*enoate*-κ²P,O)*ruthenium*(II) was similarly prepared as red crystals but using $Ph_2PO_2CCMe{=}CHPh$ (0.25 g, 0.72 mmol). Yield 0.26 g (85%) (Found: C, 60.9; H, 4.5. $C_{44}H_{38}Cl_2O_4P_2Ru$ requires C, 61.1; H, 4.4%). *Dichloro*(3-*methylbut*-2-*enyl diphenylphosphinite*)*bis*(*triphenylphosphine*)*ruthenium*(II) was similarly prepared from $[RuCl_2(PPh_3)_4]$ (0.63 g, 0.52 mmol) and $Ph_2POCH_2CH{=}CMe_2$ (0.28 g, 1.04 mmol). Yield 0.43 g (83%) (Found: C, 65.4; H, 5.0. $C_{53}H_{49}Cl_2OP_3Ru$ requires C, 65.8; H, 5.1%).

Dichloro(diphenylphosphino 3-*Methylbut*-2-*enoate*-κ²P,O)*bis*-(*triphenylphosphine*)*ruthenium*(II).—To $[RuCl_2(PPh_3)_4]$ (0.5 g, 0.41 mmol) in CH_2Cl_2 (30 cm³) was added $Ph_2PO_2CCH{=}CMe_2$ (0.11 g, 0.41 mmol). After stirring for 1 h the solution was filtered and concentrated to 5 cm³. Upon careful addition of light petroleum a black microcrystalline solid was obtained.

This was collected and washed with cold (−10 °C) thf. Yield 0.28 g (70%) (Found: C, 64.7; H, 4.4. $C_{53}H_{47}Cl_2O_2P_3Ru$ requires C, 64.9; H, 4.8%).

*Dichloro(diphenylphosphino but-2-enoate-*κP*)(tetraphenyldiphosphoxane-*κ^{2}P,P′*)(triphenylphosphine)ruthenium*(II)*–Tetrahydrofuran* (1/1).—To a cooled (0 °C) solution of $[RuCl_2(PPh_3)_4]$ (0.61 g, 0.5 mmol) in thf (10 cm^3) was added a cooled solution of $Ph_2PO_2CCH{=}CH_2$ (1 mmol) in thf (10 cm^3) prepared from Ph_2PCl, $CH_2{=}CHCO_2H$ and NEt_3. The resulting yellow solution was evaporated to *ca.* 5 cm^3 and allowed to stand at −3 °C for several days. The resulting yellow solid was collected, washed with diethyl ether (3 × 50 cm^3) and dried *in vacuo*. Yield 0.29 g (51%) (Found: C, 63.3; H, 4.9. $C_{57}H_{48}Cl_2O_3P_4Ru{\cdot}C_4H_8O$ requires C, 63.8: H, 4.9%). Proton NMR studies confirm the presence of 1 mol equivalent of thf. [*Bis(diphenylphosphinito)hydrogenato-*κ^{2}P,P″]*chloro(triphenylphosphine)(3-triphenylphosphoniopropionate-*κ^{2}O,O′*)-ruthenium*(II)*–tetrahydrofuran* (1/1) and [*bis(diphenylphosphinito)hydrogenato-*κ^{2}P,P″]*chlorotriphenylphospine(3-triphenylphosphoniobutanoate-*κ^{2}O,O′*)ruthenium*(II)*–tetrahydrofuran* (1/1) were similarly prepared from $[RuCl_2(PPh_3)_4]$ (0.61 g, 0.5 mmol) and $Ph_2PO_2CCH{=}CHR''$ (R″ = H or Me) (0.5 mmol). On standing at 0 °C for several days, dark solids, which have not been obtained pure, identified spectroscopically as $[RuCl_2(PPh_3)_2(Ph_2PO_2CCH{=}CHR'')]$ were obtained. The filtrates from these precipitates gradually precipitated the final products as yellow crystals. For R″ = H these were characterized crystallographically and the structure of the product for R″ = Me was established by the similarity of its spectral properties to those of the crystallographically characterized product.

Crystallography.—Crystals of $[RuCl\{(Ph_2PO)_2H\}(PPh_3)(O_2CCH_2CH_2PPh_3)]$ were obtained by slow growth from a concentrated CH_2Cl_2 solution at −3 °C.

Crystal data. $C_{63}H_{55}ClO_4P_4Ru{\cdot}C_4H_8O$, $M = 1208.65$, orthorhombic, space group $P2_12_12_1$, $a = 15.16(3)$, $b = 23.05(3)$, $c = 17.08(4)$ Å, $U = 5968.40$ Å^3, $Z = 4$, $D_c = 1.35$ g cm^{-3}, μ(Mo-Kα) = 3.99 cm^{-1}, $F(000) = 2480$, λ = 0.710 69 Å.

The crystal (0.20 × 0.35 × 0.43 mm) used for data collection showed no significant change in the intensities of three standard reflections during data collection (Stoe STADI 2 diffractometer). Unit-cell dimensions were refined from 20 accurately centred reflections with $\theta \approx 12°$. Data were collected for layers 0–14 of an *a*-axis-mounted crystal for an octant of reciprocal space to $\theta = 25°$. Ranges of indices $0 \leqslant h \leqslant 14$, $-2 \leqslant k \leqslant 30$, $-2 \leqslant l \leqslant 21$. 6558 Reflections collected, 4920 unique ($R_{int} = 0.056$); 4203 had $F_o > 6\sigma(F_o)$ and were used in the refinement. Data were corrected for the Lorentz and polarization terms but not for absorption.

The structure was solved by Patterson and Fourier methods (SHELX). Phenyl rings were included as rigid hexagon (C_6H_5) units with isotropic thermal parameters; other hydrogen atoms were placed on calculated positions except for that of the phosphinito-groups, which was not included. Anisotropic thermal parameters were used for the remaining non-hydrogen atoms. The disordered thf molecule was represented by eight isotropic atoms with site occupancy factor 0.5 in an approximately spherical cavity centred at 0.1809, 0.1737 and 0.7656.

Final refinement [minimizing $\Sigma w||F_o| - |F_c||^2$, 283 refined parameters, $R' = 0.102$, $w = 2.3253/\sigma(F)^2 + 0.001\ 713F^2$], mean shift/e.s.d. = 0.062, maximum shift/e.s.d. = 0.199 (excluding instability at disordered solvent molecule), maximum difference peak = 0.70 e Å^{-3}, maximum negative peak = 0.85 e Å^{-3}; $R = 0.076$. Final atomic coordinates are given in Table 4. Computer programs employed were SHELX 76,[22] SHELXS,[23] PLUTO[24] and XANADU.[25]

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

Acknowledgements

We thank BP Research International and the SERC for a studentship to (D. J. I.), Johnson Matthey plc for general loans of ruthenium salts, and the SERC Mass Spectroscopy Service for FAB mass spectra.

References

1 A. F. Borowski, A. Iraqi, D. C. Cupertino, D. J. Irvine, D. J. Cole-Hamilton, M. Harmon and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1990, 29.

2 D. C. Cupertino and D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, 1987, 443.

3 D. J. Irvine, C. Glidewell, D. J. Cole-Hamilton and J. C. Barnes, *J. Chem. Soc., Dalton Trans.*, 1991, 1765.

4 D. J. Irvine, D. J. Cole-Hamilton, J. C. Barnes and P. K. G. Hodgson, *Polyhedron*, 1989, 1575.

5 S. A. Preston, D. C. Cupertino, P. Palma-Ramirez and D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, 1986, 977.

6 A. Iraqi, N. R. Fairfax, S. A. Preston, D. C. Cupertino, D. J. Irvine and D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, 1991, 1929.

7 P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229.

8 P. Braunstein, D. Matt and D. Nobel, *J. Chem. Soc., Dalton Trans.*, 1986, 415.

9 I. W. Robertson and T. A. Stephenson, *Inorg. Chim. Acta*, 1980, **45**, L215.

10 J. A. S. Duncan, T. A. Stephenson, M. D. Walkinshaw, D. Heddon and D. M. Roundhill, *J. Chem. Soc., Dalton Trans.*, 1984, 801.

11 V. S. Tsuvin, L. V. Zhegalina and L. N. Kruitskii, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1973, **43**, 436.

12 S. W. Ng and J. J. Zuckerman, *J. Organomet. Chem.*, 1982, **234**, 257 and refs. therein.

13 R. Sanchez Delgado, U. Thewalt, N. Valencia, A. Andriollo, R.-L. Marquez-Silva, J. Puga, H. Schöllhorn, H.-P. Klein and B. Fontal, *Inorg. Chem.*, 1986, **25**, 1097.

14 A. C. Skapski and F. A. Stephens, *J. Chem. Soc., Dalton Trans.*, 1974, 390.

15 G. R. Clark, J. M. Waters and K. R. Whittle, *J. Chem. Soc., Dalton Trans.*, 1975, 2556.

16 R. J. Fleming, M. A. Shaikh, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1979, **32**, 2187.

17 S. Andersson and S. Jagner, *Acta Chem. Scand., Ser. A*, 1985, **39**, 577.

18 See ref. 10 and refs. therein.

19 E. D. Schlemper and C. K. Fair, *Acta Crystallogr., Sect. B*, 1977, **33**, 2482 and refs. therein.

20 P. W. Armit, A. S. F. Boyd and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 1975, 1663.

21 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1966, **28**, 945.

22 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.

23 G. M. Sheldrick, SHELXS, Program for crystal structure determination, University of Göttingen, 1986.

24 W. D. S. Motherwell and W. Clegg, PLUTO, Program for plotting molecular and crystal structures, University of Cambridge, 1978.

25 P. Roberts and G. M. Sheldrick, XANADU, Program for molecular geometry calculations, University of Cambridge, 1975.

Received 18*th March* 1991; *Paper* 1/01295I