Synthesis, Crystal Structures and Reactivity of Rhodium(III) Complexes containing β-Ketophosphine and Phosphino Enolate Ligands†

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The reaction of 3 equivalents of the ketophosphine $Ph_2PCH_2C(O)Ph$ (L) with $RhCl_3{\cdot}3H_2O$ in ethanol yielded $[RhCl_3\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}]$ in the form of the *mer,trans*-(**1**) and *mer,cis*-(**2**) isomers. Complex **2** exhibits fluxional behaviour on the ^1H NMR time-scale as a result of dynamic exchange between the pendant and the co-ordinated keto functions, the activation energy for this process being 75 ± 2 kJ mol^{-1}. Treatment of **2** with $TlPF_6$ in CH_2Cl_2 afforded the cationic complex *trans,cis,cis*-$[RhCl_2\{Ph_2PCH_2C(O)Ph\}_2]PF_6$ **3**, which reacts with excess L to give *mer,cis*-$[RhCl\{Ph_2PCH{\cdots}C(\cdots O)Ph\}\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}]PF_6$ **5**. Complex **5** has an unprecedented ligand set: two ligands L, bound in two different co-ordination modes (terminal through P and chelating), and the corresponding phosphino enolate as the other chelate. In solution, fluxional behaviour is observed by ^{31}P NMR spectroscopy with an activation energy of 56 ± 1 kJ mol^{-1}. The reaction of **3** with NaH afforded $[\{Rh(\mu\text{-}Cl)[Ph_2PCH{\cdots}C(\cdots O)Ph]_2\}_2]$ **6**. The chloride bridges are readily cleaved by $PMePh_2$, affording $[RhCl\{Ph_2PCH{\cdots}C(\cdots O)Ph\}_2(PMePh_2)]$ **7**. Treatment of $[RhCl(PPh_3)_3]$ with 3 equivalents of L in toluene afforded the Rh^{III} complex *mer,cis*-$[RhCl\{Ph_2PCH{\cdots}C(\cdots O)Ph\}_2\{Ph_2PCH_2C(O)Ph\}]$ **8**. Complex **2** and L reacted with NaOMe to afford the tris(enolato) Rh^{III} complex *fac*-$[Rh\{Ph_2PCH{\cdots}C(\cdots O)Ph\}_3]$ **9**, which could be also obtained from $[RhCl(PPh_3)_3]$. The solid-state structures of **3**·CH_2Cl_2, **5** and **8**·CH_2Cl_2 have been determined by single crystal X-ray analysis.

It is well known that the Rh^I–Rh^{III} couple stabilised by phosphines plays an important role in homogeneous catalysis.[2] Chemical modifications of their substituents are expected to lead to new properties. This is for example the case with oxygen functions, such as ethers, esters, ketones or amides, which are potential donors and may be associated with a phosphorus donor in ligands such as $Ph_2PCH_2C(O)OEt$, $Ph_2PCH_2C(O)Ph$ or $Ph_2PCH_2C(O)NPh_2$ which we have studied in previous papers in this series.[1] Such ligands are often characterised by a hemilabile behaviour and, owing to the chelate effect, they generally impart greater stability to their complexes than monodentate phosphines, thus allowing isolation of reactive intermediates.[3] The related four-electron donor anionic phosphino enolate ligand $[Ph_2PCH{\cdots}C(\cdots O)R]^-$ confers special reactivity to its complexes and has been associated with the developments of the nickel-catalysed ethene oligomerisation shell higher olefins process (SHOP).[4]

In view of the widespread applications of functional phosphines, rhodium(III) complexes obtained from hydrated rhodium trichloride have attracted considerable attention. We have previously investigated neutral and cationic rhodium complexes of ethyl(diphenylphosphino)acetate,[5,6] and the co-ordination chemistry of β-ketophosphine ligands with rhodium and iridium has been studied by Shaw and co-workers,[7] while, during the course of this study, Cole-Hamilton and co-workers[8] reported on the co-ordination of the chiral β-ketophosphine (1*R*)-*endo*-(+)-3-diphenylphosphino-1,7,7-trimethyl-2-oxobicyclo[2.2.1]heptane to these metals. We describe here the synthesis of rhodium(III) complexes with the ketophosphine ligand $Ph_2PCH_2C(O)Ph$ (L) and their reactions leading to complexes with the phosphino enolate ligand $[Ph_2PCH{\cdots}C(\cdots O)Ph]^-$.

Results and Discussion

Neutral Complexes.—Addition of (diphenylphosphino)acetophenone (L) (3 equivalents) to $RhCl_3{\cdot}3H_2O$ in warm ethanol solution precipitated an air-stable orange solid. Its ^1H NMR spectrum showed signals assigned to two isomers, **1** (40%) and **2** (60%) (Scheme 1). After recrystallisation from CH_2Cl_2–pentane, **2** was isolated as a yellow powder in 90% yield, whereas **1** was separated manually as red crystals in 2% yield (w.r.t. Rh). Their elemental analyses are in agreement with the formula $[RhCl_3\{Ph_2PCH_2C(O)Ph\}_2]$. The minor isomer was identified as *mer,trans*-$[RhCl_3\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}]$ **1** (*mer,trans* refers to the relative orientation of the chloride and phosphorus atoms, respectively). The ^{31}P NMR spectrum displays a $J(PP)$ coupling constant of 622 Hz which is characteristic of two phosphines in a *trans* position to each other. The IR spectrum shows absorption bands at 1672 and at 1565 cm^{-1} for the free and co-ordinated

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Dedicated to Professor E. Lindner, on the occasion of his 60th birthday.

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Table 1 ^{31}P NMR $J(^{103}Rh^{31}P)$ coupling constants (in Hz) for different phosphine ligands as a function of the *trans* ligand

	Ligand *trans* to phosphine				
Phosphine	P	Cl	O[a]	O[b]	Complex
$PR_nR'_{3-n}$[c]	84–86	110–114			$[RhCl_3\{PR_nR'_{3-n}\}_3]$[d]
Monodentate $Ph_2PCH_2C(O)Ph$	89				**1**
	96				**5**
			124		**2**
Chelating $Ph_2PCH_2C(O)Ph$	87				**1**
	91				**5**
		114			**2**
			122		**3**
Chelating $[Ph_2PCH{=}C({-}O)Ph]^-$		112		132	**6**
			122		**5**
	92			111	**7**
	92			110	**8**
				116	**9**

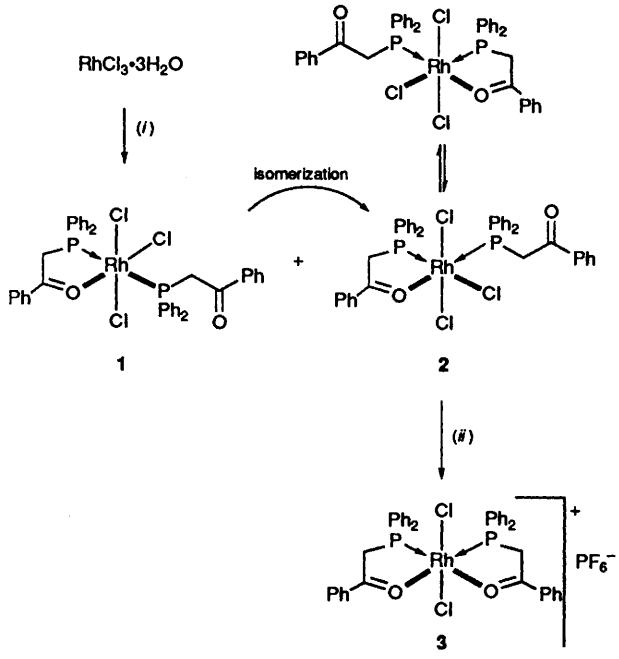
[a] Ketone O atom. [b] Enolate O atom. [c] R = Alkyl, R' = aryl; n = 1–3. [d] Ref. 13.

ketone functions, respectively. Accordingly, two doublets are observed in the ^1H NMR spectrum for the the PCH_2 protons, at δ 4.92 and 4.72 for the chelating and monodentate ligands, respectively. The FIR spectrum contains a strong band at 345 cm^{-1} and two very weak bands for the ν(Rh–Cl) vibrations and is nearly identical to those of the ruthenium complexes *mer*-$[RuCl_3(PMe_2Ph)_3]$[9] and *mer,trans*-$[RuCl_3\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}]$.[1]

Isomerisation of the *mer,trans* isomer **1** to the *mer,cis* isomer **2** occurred within a few hours and was observed by ^{31}P NMR in dichloromethane (Scheme 1). This also occurred during recrystallisation. In the reaction of $RhCl_3{\cdot}3H_2O$ with a camphor-derived β-ketophosphine, it has been reported that the *mer,trans* isomer corresponding to **1** precipitated from ethanol solution, whereas the *mer,cis* isomer was isolated from tetrahydrofuran (thf). The latter isomer was suggested to be thermodynamically favoured.[8] We propose a *mer,cis* geometry for $[RhCl_3\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}]$ **2**; the FIR spectrum shows several bands in the region 350–290 cm^{-1} [three ν(Rh–Cl) bands are expected for a *mer* geometry].[10] The IR (CsI pellet) spectrum of isomer **2** shows the presence of both co-ordinated and free keto groups of the ketophosphine ligands (1575 and 1675 cm^{-1}, respectively). Two different ketophosphine moieties are also detected by NMR; in the ^1H NMR spectrum of **2**, the PCH_2 groups appear as two doublets at δ 4.69 and at 5.29, the latter being assigned to the chelating ligand. Two doublets of doublets are observed in the ^{31}P NMR spectrum. The low field signal at δ 37.4 is assigned to the chelating ketophosphine ligand, and the J(PP) coupling constant of 23 Hz indicates *cis* phosphines.[11] The J(RhP) coupling constant of 114 Hz is typical for a phosphine ligand in *trans* position to a chloride.[13] For the other phosphine, J(RhP) is 124 Hz in keeping with a dative oxygen in the *trans* position.

The ^{103}Rh–^{31}P NMR coupling constants correlate with the *trans* influence.[12] The value for a phosphine *trans* to a dative ketone oxygen atom falls in the range 122–124 Hz (Table 1). The resulting order of *trans* influence: phosphine > chloride > ketone is consistent with previous studies.[12]

Another argument against a *fac* geometry for **2** comes from the difference in chemical shift between the chelated and non-chelated phosphines, defined as the ring contribution to the chemical shift, Δ_R.[13] If **2** had *fac* geometry, both phosphines would have the same ligand in the *trans* position (a chloride), and the difference of 5.4 ppm in chemical shift between these phosphines would equal Δ_R. However, from the data for the *mer,trans* complex **1**, we obtain a value of 9.2 ppm for Δ_R (Table 3). For ketophosphine ruthenium(II) complexes, a ring contribution Δ_R of 13–20 ppm has been determined.[1] Thus after careful examination of the ^{31}P NMR data, a facial geometry can be excluded.



Scheme 1 (*i*) 2 L, EtOH; (*ii*) $+TlPF_6$, $-TlCl$, CH_2Cl_2

It is noteworthy that the crystal structure determinations of complexes similar to $[RhCl_3\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}]$ with a camphor-derived β-ketophosphine[8] or ethyl (diphenylphosphino)acetate,[14] as ligands revealed *mer,cis* isomers. For the last of these complexes, a solution structure with a *fac* arrangement of the chlorides was originally proposed,[5] but owing to the similarity between the ^{31}P NMR data for all these isomers of type $[RhCl_3\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}]$, we believe now that a *mer* arrangement of the chlorides is also present in the ethyl (diphenylphosphino)acetate complex.

Facial isomers of the complexes $[RhCl_3(PR_3)_3]$ are obtained only with small tertiary phosphines such as PMe_3 and usually in poor yield.[15] The steric bulk of (diphenylphosphino)acetophenone of 128°, evaluated from the δ(^{31}P) chemical shift of its *trans*-$[PdCl_2L_2]$ complex,[16] according to Bartik and Himmler,[17] is similar to the values of 128–131° found for the ligands PPh_3, $PEtPh_2$ and PEt_2Ph.

A variable temperature ^1H NMR study in DCl_2CCCl_2D revealed a stereodynamic behaviour for complex **2** (Scheme 1). Above 300 K, the co-ordinated keto group dissociates easily in solution, exchanging with the other keto group. For $[RhCl_3\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}]$ complexes, fluxional behaviour involves the participation of a chloride, as shown for **2** in Scheme 1. This is consistent with the fact that in the meridional complexes $[RhCl_3(PR_3)_3]$ the halide ligand *trans* to the tertiary phosphine is more labile than the other two and can be exchanged with anionic ligands such as NaS_2Y (Y = $CNMe_2$ or PMe_2).[18] The stronger *trans* influence of phosphorus compared to chloride also leads to different Rh–Cl bond lengths of 2.429(3) (*trans* to P) and 2.362(3) Å (*trans* to Cl) (L = PEt_2Ph).[19]

The activation energy for this intramolecular process (no significant concentration effect was noted) could be evaluated using the Eyring equation as 75 ± 2 kJ mol^{-1}. For the analogous complex with ethyl (diphenylphosphino)acetate,[5] the value was 64.3 ± 0.5 kJ mol^{-1}, thus indicating a stronger bonding for the keto function.

Comparison with literature data (see Table 2) for rhodium and ruthenium complexes indicates that for five-membered metallacycles the lability of the dative oxygen metal bond increases in the order ketone < ester < ether. Lindner *et al.*[23] have recently reported the fluxional behaviour and activation parameters of ruthenium(II) complexes containing various ether phosphine ligands.

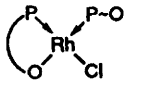
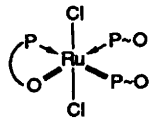
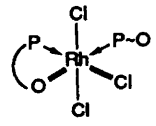
Cationic Complexes.—Addition of $TlPF_6$ to a CH_2Cl_2 solution of **2** led to a complex of formula $[RhCl_2\{Ph_2PCH_2C(O)Ph\}_2]PF_6$ **3**, which was isolated as yellow crystals (Scheme 1). The IR spectrum of the solid shows a single absorption band for the co-ordinated keto group (1570 cm^{-1}). This, together with the absence of a band around 1670 cm^{-1}, suggests that the two keto functions are co-ordinated in equivalent sites. This was confirmed by ^1H NMR spectroscopy, where the PCH_2 protons appear as a filled-in doublet, a pattern frequently observed when two PPh_2Me ligands or PPh_2CH_2 units[24] are in mutually *cis* position.[25] The ^{31}P NMR spectrum contains a doublet with *J*(RhP) 122 Hz, suggesting an oxygen *trans* to phosphorus; however, two Rh–Cl stretching vibrations at 375 and 350 cm^{-1} (CsI) of similar intensity were detected, suggesting mutually *cis* chlorides. However, an X-ray diffraction study revealed *trans* chlorides (see below). It thus appears that the chloride ligand of **2** which is abstracted is the one which participates in the dynamic behaviour of the complex.

The strong binding of the keto groups to the rhodium(III) centre is consistent with the failure of carbon monoxide to open this dative bond although the low affinity of the metal centre toward CO has been invoked to account for the similar lack of reactivity of the corresponding ester phosphine complex,[6] for which a structure with two oxygen atoms occupying mutually *trans* positions was proposed. On the basis of similar spectroscopic data and the crystal structure of **3**, we now propose a structure with *trans* chlorides for the ester phosphine complex.

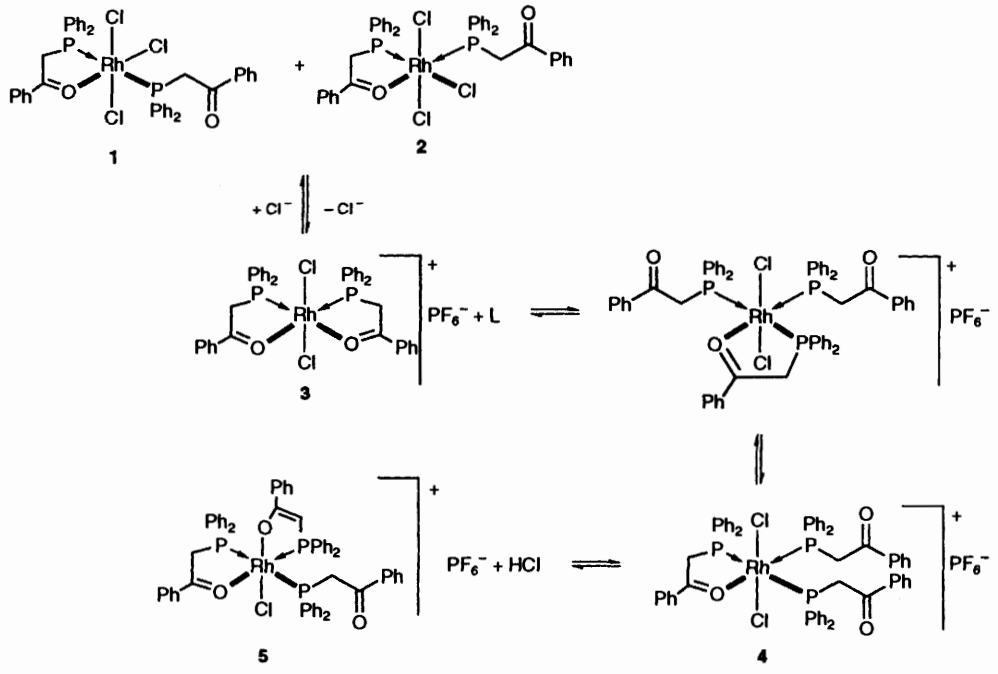
The reaction of a camphor-derived β-ketophosphine rhodium complex similar to **2** with $AgBF_4$ has been reported as not being clean.[8] Recently we have noted considerable differences in the behaviour of thallium and silver halide abstractors, $TlPF_6$ and $AgBF_4$, towards β-ketophosphine cobalt(II) complexes with isolation of the silver complex $[Ag\{Ph_2PCH_2C(O)Ph\}_2]Cl$, as a result of phosphine migration.[26] No significant differences were observed in reactions with the analogous Ni, Pd or Pt complexes.

Phosphino Enolate Complexes.—Addition of an excess of L to **3** in CH_2Cl_2 resulted in a complex equilibrium between neutral and cationic complexes (see Scheme 2) of which only **3** and bright yellow *mer,cis*-$[RhCl\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}]PF_6$ **5** were isolated after one week in 77% yield. The IR spectrum of **5** shows the presence of unco-ordinated and co-ordinated keto functions as well as of the phosphino enolate ligand (1680m, 1567s, 1522m cm^{-1}, respectively), and a single Rh–Cl band at 345 cm^{-1} was detected in the FIR spectrum. The NMR spectra of this complex are temperature dependent. At room temperature, the ^{31}P NMR spectrum displays a doublet of triplets and two broad resonances, which coalesced on raising the temperature to 315 K (T_c). At 250 K, an ABX pattern with additional coupling to rhodium was observed and the resonances at δ 28.7 and 17.0 were well resolved: a *J*(PP) value of 460 Hz indicates two phosphorus atoms in mutually *trans* positions. The difference in chemical shift of 11.7 ppm equals the ring contribution Δ_R and is close to the value obtained for **1** (9.2 ppm). The resonance at δ 36.0 was assigned to the phosphino enolate ligand which is coupled to two P nuclei in a *cis* position, accidentally with the same coupling of 24 Hz. The ^1H NMR spectrum at 296 K (T_c) shows a doublet at δ 5.17 with *J*(PH) 4.4 Hz for the enolate proton and a broad resonance, which on cooling to 253 K resolved into two ABX patterns (X = P in PCH^AH^B) with *J*(PH) 7 and 10 Hz and *J*(HH) 16 and 18 Hz, respectively. These observations are consistent with the lack of any symmetry element in the molecule (see X-ray structure below) and a rapid

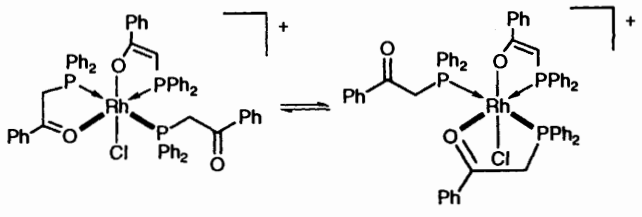
Table 2 Coalescence temperatures and activation energies for stereodynamic processes involving phosphorus–oxygen ligands

Complex[a]	P,O Ligand	Solvent	T_c/K	$\Delta G^{\ddagger b}$/kJ mol^{-1}	Ref.
	L	CD_2Cl_2	> 300	> 57[c]	20
	$(C_6H_{11})_2PCH_2CH_2OMe$	Acetone	292	55 ± 4	21
	L	Toluene	315	63.7 ± 0.7	1
	$Ph_2PCH_2C(O)OEt$	CD_2Cl_2	313	55.6	6
	$Ph_2PCH_2CH_2OMe$	Toluene	258	49.1	22
	L	DCl_2CCCl_2D	373	75 ± 2	This work
	$Ph_2PCH_2C(O)OEt$		325	64.3 ± 0.5	5

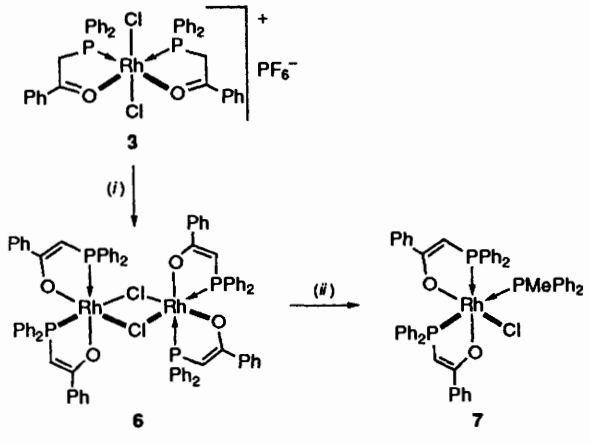
[a] P O represents a chelating P,O ligand, P ~ O a monodentate P,O ligand. [b] Calculated at coalescence temperature (T_c) using the Eyring equation. [c] Calculated with observed δ_ν and estimated T_c.



Scheme 2 Equilibria involving complexes 1–5



Scheme 3 Dynamic behaviour of 5



Scheme 4 (*i*) NaH, thf; (*ii*) $PMePh_2$

exchange between the chelating and non-chelating phosphines in *trans* position, as represented in Scheme 3. The activation energy was evaluated as 56 ± 1 kJ mol^{-1} by ^{31}P NMR and 58 ± 2 kJ mol^{-1} by ^{1}H NMR spectroscopy at variable temperatures. Both the structure and the isolation of this complex are notable. The former because this is the first time that in the same complex a phosphorus–oxygen-type ligand is bound in the monodentate and chelating modes in the presence of its enolate form, and the latter because no obvious base was present to deprotonate the keto phosphine whereas usually relatively strong bases such as NaOMe or NaH have been used to generate the phosphino enolate ligand.

Some light is shed on the formation of **5** by the ^{1}H NMR spectrum of the reaction mixture before layering with pentane. The resonances of **1** (18%), **2** (21%), **3** (4%) and **5** (38%) were identified. In addition a broad resonance at δ 4.47 with a superimposed doublet [J(PH) 9.8 Hz] at δ 4.39 was observed. This may be attributed to fluxional [$RhCl_2\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}_2$] **4** (19%), of which neutral Ru^{II} analogues are known (see Table 2). This complex is in equilibrium with **3** and L. We believe that **4** transforms to **5** by loss of HCl under the action of L as a base. We verified that complex **5** in CH_2Cl_2 was not protonated by $HBr{\cdot}PPh_3$ (NMR evidence). The chloride liberated from **4** will convert **3** to **1** and **2**. In accord with this, complex **5** is present in the ^{1}H NMR spectrum in the same amount as **1** + **2**.

The deprotonation of the co-ordinated ketophosphine by an excess of L is noteworthy and emphasises the stability conferred to a complex by the chelating phosphino enolate ligand in an octahedral geometry. This observation should be related to the very facile conversion of Co^{II} complexes of L into the octahedral Co^{III} phosphino enolate complex [$Co\{Ph_2PCH{\cdots}C(\cdots O)Ph\}_3$].[27] A related deprotonation reaction of a rhodium-co-ordinated ketophosphine has been reported by Shaw and co-workers[7] where treatment of hydrated rhodium trichloride in ethanol at room temperature with 4 equivalents of $Bu^t_2PCH_2C(O)Ph$ gave the neutral complex [$RhCl_2\{Bu^t_2PCH{\cdots}C(\cdots O)Ph\}\{Bu^t_2PCH_2C(O)Ph\}$].

Treating complex **3** with sodium hydride in thf afforded dimeric [$\{Rh(\mu\text{-}Cl)[Ph_2PCH{\cdots}C(\cdots O)Ph]_2\}_2$] **6** (see Scheme 4). Its IR spectrum exhibits a strong band at 1520 cm^{-1} for the enolate ligands and a medium band at 286 cm^{-1}, which may be attributed to bridging chlorides. The ^{31}P NMR spectrum displays doublets of doublets with ^{2}J(PP) 30 Hz, typical for two phosphorus atoms in a *cis* position. The J(RhP) values of 132 (for the low-field signal) and 112 Hz are associated with a phosphorus atom *trans* to a covalent oxygen and a chloride ligand, respectively.

Recently, we have observed that a metal-template effect may lead to highly selective coupling reactions between chlorophosphines and a phosphino enolate moiety co-ordinated to nickel or palladium.[28] A rhodium(I) phosphino enolate complex

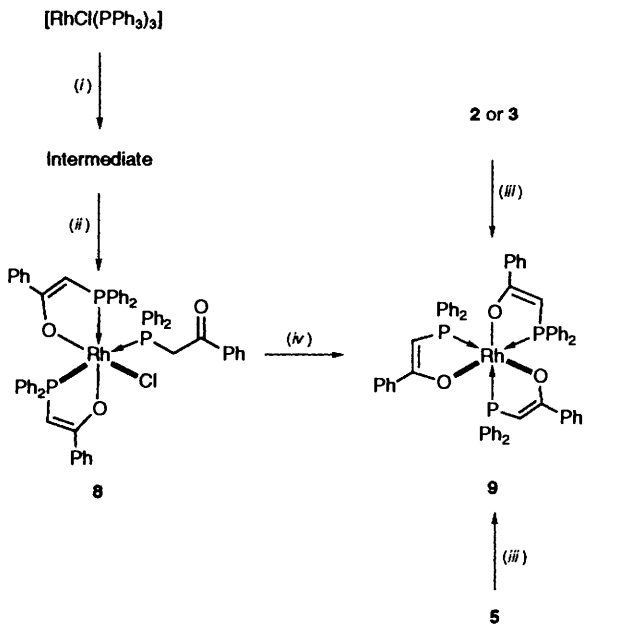
reacted with PPh_2Cl in a similar way.[20] In order to examine the effect of the more oxophilic rhodium(III) on this reaction, complex **6** was treated with PPh_2Cl or $PPhCl_2$ in thf. In the former case, a mixture of complexes was formed, as shown by ^{31}P NMR spectra, which were not further characterised. Signals in the range δ 146–175 indicated the formation of a phosphinite P–O linkage. In the latter case, no reaction occurred as shown by ^{31}P NMR spectra. Possible explanations would be that $PPhCl_2$ is not basic enough to cleave the chloride bridges of **6** and co-ordinate to the metal, which seems necessary for a subsequent reaction to occur, and/or that oxidative addition of a P–Cl bond, which probably represents the next step in this reaction, is obviously less favourable on Rh^{III} than on Ni^{II}, Pd^{II} or Rh^{I}.

When **6** was treated with $PMePh_2$, $[RhCl\{Ph_2PCH{\cdots}C(\cdots O)Ph\}_2(PMePh_2)]$ **7** was isolated. Cleavage of the chloride bridges was indicated by a weak absorption in the IR (CsI) spectrum at 330 cm^{-1} and an ABX pattern with additional coupling to Rh in the ^{31}P NMR spectrum. The ^{31}P NMR data are similar to those for the bis(enolate) complex *mer,cis*-$[RhCl\{Ph_2PCH{\cdots}C(\cdots O)Ph\}_2\{Ph_2PCH_2C(O)Ph\}]$ **8** (see below), suggesting an analogous structure for both complexes. Indeed, a complex analogous to **7** with L in place of $PMePh_2$ was obtained by a completely different route: addition of 3 equivalents of L to a solution of the Rh^{I} complex $[RhCl(PPh_3)_3]$ in toluene afforded yellow crystals in 74% yield (Scheme 5). A crystal structure determination revealed a rhodium(III) complex, *mer,cis*-$[RhCl\{Ph_2PCH{\cdots}C(\cdots O)Ph\}_2\{Ph_2PCH_2C(O)Ph\}]$ **8**. The ring contribution parameter Δ_R for the phosphino enolate chelate can be calculated from the ^{31}P NMR chemical shifts of the *trans* phosphines by internal comparison; the value of 15.8 ppm is greater than those found in **1** and **5** for the keto phosphine.

To examine this reaction more closely, L was added stepwise to a solution of $[RhCl(PPh_3)_3]$. Addition of 1 equivalent of L resulted in the exchange of the phosphine ligand *trans* to chloride with formation of *trans*-$[RhCl\{Ph_2PCH_2C(O)Ph\}(PPh_3)_2]$.[20] Addition of 2 equivalents led to a mixture of complexes, while addition of 3 equivalents of L rapidly yielded a Rh^{III} intermediate (^{31}P NMR) which converted to **8** after a few hours. The spectroscopic data of this intermediate indicate the presence of phosphino enolate and monodentate ketophosphine ligands. Note that a dimeric intermediate $[\{Co(\mu\text{-}Cl)[Ph_2PCH{\cdots}C(\cdots O)Ph][Ph_2PCH_2C(O)Ph]\}_2]$ has been proposed in the formation of cobalt(III) tris(enolate) complexes from Co^{II} precursors by disproportionation.[26] In the present case a disproportionation reaction appears unlikely. Formally the oxidation of rhodium-(I) to -(III) is accompanied by deprotonation of two ketophosphines and formation of hydrogen (not evidenced) [equation (1)].

$$[RhCl(PPh_3)_3] + 3Ph_2PCH_2C(O)Ph \longrightarrow [RhCl\{Ph_2PCH{\cdots}C(\cdots O)Ph\}_2\{Ph_2PCH_2C(O)Ph\}] + H_2 \quad (1)$$

The tris(enolate) complex *fac*-$[Rh\{Ph_2PCH{\cdots}C(\cdots O)Ph\}_3]$ **9** was synthesised in toluene by addition of a slight excess of NaOMe to either **2** or **3**, in the presence of one equivalent of L. The ν(C···O) + ν(C···C) vibration is found at 1522 cm^{-1} and the ^{31}P and ^{1}H NMR spectra show three equivalent phosphino enolate ligands, corresponding to a *fac* structure. It is surprising that the *mer* complexes **5** and **8**, prepared *in situ*, afforded in the presence of free L and NaOMe selectively the *fac* complex **9**. Related complexes with *fac* or *mer* geometries have been obtained recently for Co^{III} and Ru^{II}. Reaction of *trans,mer*-$[RuCl_2\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}_2]$ with NaOMe in toluene afforded selectively Na[*mer*-$Ru\{Ph_2PCH{\cdots}C(\cdots O)Ph\}_3$].[1,26]



Scheme 5 (*i*) 3 L, toluene; (*ii*) a few hours; (*iii*) L, NaOMe, toluene; (*iv*) NaOMe, L, toluene

Table 3 ^{31}P NMR chemical shift of different phosphine ligands as a function of the *trans* ligand

Phosphine	δ_P	Complex
$PMePh_2$	3.6[a]	7
Monodentate	18.7[a]	1
$Ph_2PCH_2C(O)Ph$	32.0[b]	2
	17.0[a]	5
	17.0[a]	8
Chelating	27.9[a]	1
$Ph_2PCH_2C(O)Ph$	37.4[c]	2
	46.5[b]	3
	28.7[a]	5
Chelating	33.1,[a] 26.2[d]	7
$[Ph_2PCH{\cdots}C(\cdots O)Ph]^-$	29.3,[c] 39.1[d]	6
	36.0[b]	5
	32.8,[a] 24.9[d]	8
	27.7[d]	9

[a] Phosphine *trans* to phosphorus. [b] *trans* to ketone oxygen. [c] *trans* to chloride. [d] *trans* to enolate oxygen.

Table 4 Selected bond distances (Å) and angles (°) for **3**

Rh–P(1)	2.258(1)	P(1)–C(1)	1.840(5)
Rh–P(2)	2.260(1)	P(2)–C(21)	1.845(5)
Rh–O(1)	2.093(3)	C(1)–C(2)	1.501(7)
Rh–O(2)	2.107(3)	C(21)–C(22)	1.480(7)
Rh–Cl(1)	2.329(1)	C(2)–O(1)	1.229(6)
Rh–Cl(2)	2.327(1)	C(22)–O(2)	1.239(6)
P(1)–Rh–O(1)	82.56(9)	P(2)–Rh–O(2)	81.20(9)
P(1)–C(1)–C(2)	111.5(3)	P(2)–C(21)–C(22)	101.1(3)
C(1)–C(2)–O(1)	119.3(4)	C(21)–C(22)–O(2)	119.5(4)
Cl(1)–Rh–P(1)	86.17(5)	Cl(2)–Rh–P(2)	86.60(5)
Cl(2)–Rh–P(1)	94.68(5)	Cl(1)–Rh–P(2)	96.12(5)
P(1)–Rh–P(2)	111.07(5)	Cl(1)–Rh–Cl(2)	176.66(5)
O(1)–Rh–O(2)	85.4(1)		

The *trans* influence of various donor groups on the chemical shift of different phosphine types is summarised in Table 3. The ^{31}P NMR resonance of the phosphino enolate ligand is only little affected by the *trans* ligand, possibly owing to electron delocalisation within the chelate.

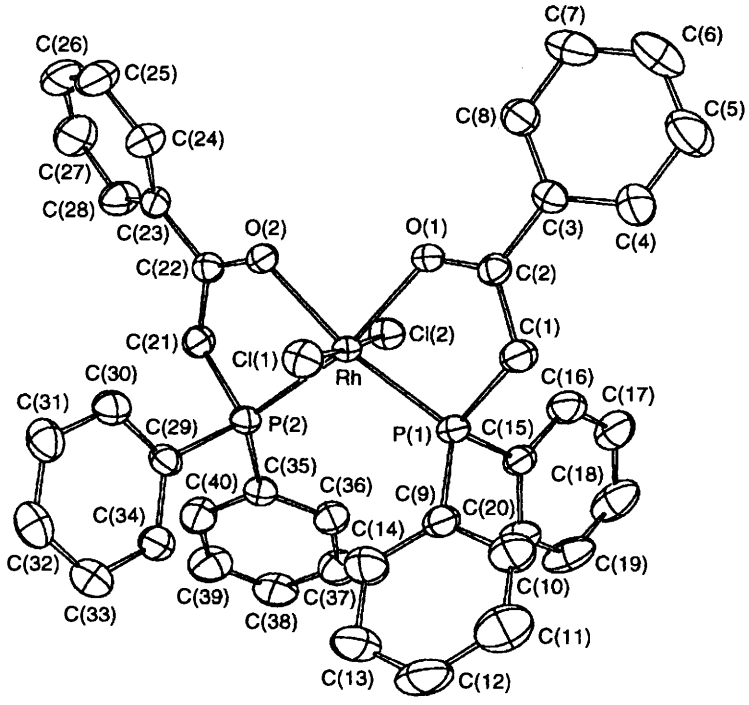


Fig. 1 View of the structure of the cation in $3\cdot CH_2Cl_2$ with the atom numbering scheme. Ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen atoms are omitted

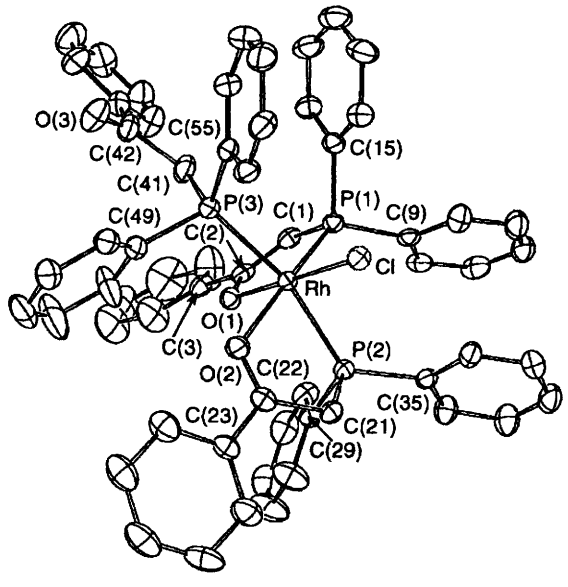


Fig. 2 View of the structure of the cation in **5** with the atom numbering scheme. Details are as for Fig. 1

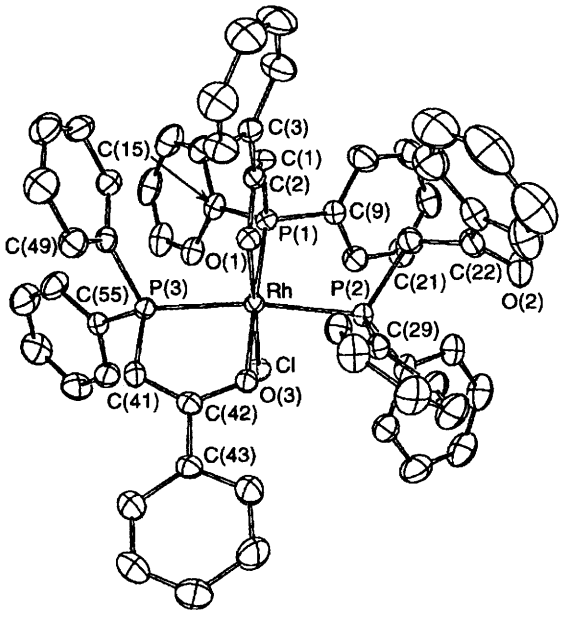


Fig. 3 View of the structure of complex **8** with the atom numbering scheme. Details are as for Fig. 1

Crystal Structure of trans,cis,cis-$[RhCl_2\{Ph_2PCH_2C(O)Ph\}_2]PF_6\cdot CH_2Cl_2$ $3\cdot CH_2Cl_2$.—Fig. 1 shows the molecular structure with the numbering scheme. Selected bond lengths and angles are listed in Table 4. The crystal structure consists of discrete molecular units separated by normal van der Waals contacts. The Rh centre has distorted octahedral geometry with *trans* chloride ligands and two chelating ketophosphine ligands disposed such that the two phosphorus atoms (and keto oxygen atoms) are in a *cis* arrangement. The chelating ligands are very similar in geometry and bond lengths and angles. There are significant angular distortions from the ideal interligand angles (90°) due to the ketophosphine chelate bite angles of 82.56(9) and 81.20(9)°, which together with a minimisation of the steric interactions between the phosphine ligands induces a large value for the P(1)–Rh–P(2) angle [111.07(5)°] and a symmetrical bending of Cl(1) towards O(1) and Cl(2) towards O(2) [Cl(1)–Rh–Cl(2) 176.66(5)°]. The Rh–O(1) and Rh–O(2) bond lengths of 2.093(3) and 2.107(3) Å are much shorter than those [2.190(5) or 2.25(1) Å] in the complexes *mer,cis*-$[RhCl_3(PR_3\text{-}P,O)(PR_3\text{-}P)]$ where PR_3 = $Ph_2PCH_2C(O)OEt$ or (1R)-*endo*-(+)-3-diphenylphosphino-7,7-dimethyl-2-oxobicyclo[2.2.1]heptane, respectively.[8] The C–P and C–C bond lengths in the chelate rings [1.840(5), 1.845(5) and 1.501(7), 1.480(7) Å, respectively] are in agreement with a single bond character and the C–O bond lengths [1.229(6) and 1.239(6) Å] with an appreciable double bond character. The Rh–P(1) and Rh–P(2) bond lengths of 2.258(1) and 2.260(1) Å, respectively, compare with the Rh–P distance of 2.246(2) Å involving the P atom *trans* to O in the ester phosphine complex $[RhCl_3\{Ph_2PCH_2C(O)OEt\}\{Ph_2PCH_2C(O)OEt\}]$, whereas

Table 5 Selected bond distances (Å) and angles (°) for compound **5**

Rh–P(1)	2.232(1)	C(2)–O(1)	1.335(6)
Rh–P(2)	2.367(1)	C(22)–O(2)	1.252(5)
Rh–P(3)	2.401(1)	C(42)–O(3)	1.206(6)
Rh–O(1)	2.027(3)	C(1)–C(2)	1.351(7)
Rh–O(2)	2.173(3)	C(21)–C(22)	1.513(6)
Rh–Cl	2.332(1)	C(41)–C(42)	1.532(7)
P(1)–C(1)	1.748(5)	C(2)–C(3)	1.486(7)
P(2)–C(21)	1.833(5)	C(22)–C(23)	1.459(7)
P(3)–C(41)	1.779(6)	C(42)–C(43)	1.472(8)
P(1)–Rh–P(2)	98.46(4)	Rh–P(1)–C(1)	99.1(1)
P(1)–Rh–P(3)	96.60(4)	Rh–O(1)–C(2)	117.2(3)
P(2)–Rh–P(3)	164.49(3)	P(1)–C(1)–C(2)	116.9(4)
P(1)–Rh–O(1)	84.85(7)	C(1)–C(2)–O(1)	121.8(4)
P(1)–Rh–O(2)	174.9(1)	O(1)–C(2)–C(3)	113.5(5)
P(1)–Rh–Cl	94.04(4)	C(1)–C(2)–C(3)	124.7(5)
P(2)–Rh–O(1)	91.80(9)	Rh–P(2)–C(21)	97.2(1)
P(2)–Rh–O(2)	78.68(9)	Rh–O(2)–C(22)	122.0(3)
P(2)–Rh–Cl	88.14(4)	P(2)–C(21)–C(22)	110.0(3)
P(3)–Rh–O(1)	85.9(1)	C(21)–C(22)–O(2)	118.6(4)
P(3)–Rh–O(2)	86.03(1)	O(2)–C(22)–C(23)	119.1(4)
P(3)–Rh–Cl	94.50(4)	C(21)–C(22)–C(23)	122.2(4)
O(1)–Rh–O(2)	91.0(1)	Rh–P(3)–C(41)	109.7(2)
O(1)–Rh–Cl	178.87(8)	P(3)–C(41)–C(42)	126.1(4)
O(2)–Rh–Cl	90.05(8)	C(41)–C(42)–O(3)	120.4(5)
		O(3)–C(42)–C(43)	122.0(5)
		C(41)–C(42)–C(43)	117.6(5)

Table 6 Selected bond distances (Å) and angles (°) for compound **8**

Rh–P(1)	2.254(1)	O(1)–C(2)	1.319(3)
Rh–P(2)	2.391(1)	O(2)–C(22)	1.214(4)
Rh–P(3)	2.356(1)	O(3)–C(42)	1.305(3)
Rh–O(1)	2.048(2)	C(1)–C(2)	1.362(4)
Rh–O(3)	2.088(2)	C(21)–C(22)	1.518(5)
Rh–Cl	2.342(1)	C(41)–C(42)	1.357(4)
P(1)–C(1)	1.765(3)	C(2)–C(3)	1.475(4)
P(2)–C(21)	1.852(3)	C(22)–C(23)	1.487(5)
P(3)–C(41)	1.762(3)	C(42)–C(43)	1.496(4)
P(1)–Rh–P(2)	96.05(3)	Rh–P(1)–C(1)	100.0(1)
P(1)–Rh–P(3)	100.54(3)	Rh–O(1)–C(2)	117.8(2)
P(2)–Rh–P(3)	161.22(3)	P(1)–C(1)–C(2)	115.7(2)
P(1)–Rh–O(1)	84.02(6)	C(1)–C(2)–O(1)	122.9(2)
P(1)–Rh–O(3)	175.51(5)	O(1)–C(2)–C(3)	113.0(2)
P(1)–Rh–Cl	96.08(3)	C(1)–C(2)–C(3)	124.1(3)
P(2)–Rh–O(1)	86.74(6)	Rh–P(2)–C(21)	115.9(1)
P(2)–Rh–O(3)	81.03(5)	P(2)–C(21)–C(22)	113.3(2)
P(2)–Rh–Cl	94.24(3)	C(21)–C(22)–O(2)	119.8(3)
P(3)–Rh–O(1)	86.30(6)	O(2)–C(22)–C(23)	120.6(3)
P(3)–Rh–O(3)	81.86(5)	C(21)–C(22)–C(23)	119.6(3)
P(3)–Rh–Cl	92.69(3)	Rh–P(3)–C(41)	98.3(1)
O(1)–Rh–O(3)	92.37(7)	Rh–O(3)–C(42)	119.2(2)
O(1)–Rh–Cl	178.99(5)	P(3)–C(41)–C(42)	117.5(2)
O(3)–Rh–Cl	87.57(6)	C(41)–C(42)–O(3)	123.0(3)
		O(3)–C(42)–C(43)	113.6(3)
		C(41)–C(42)–C(43)	123.4(3)

that involving the P atom *trans* to Cl in $[RhCl_3(PEt_2Ph)_3]$ is 2.325(3) Å.[19] The Rh–Cl bond lengths of 2.329(1) and 2.327(1) Å are similar to the *trans* Rh–Cl bonds in trichlorobis[(*o*-methoxyphenyl)dimethylarsine]rhodium(III)[29] [2.33(1), 2.35(1) Å] and in *trans*-$[Rh(py)_4Cl_2]NO_3 \cdot HNO_3$ (py = pyridine) [2.34(1) Å].[30] A chelating mode for L has been observed recently in the related complexes *trans,cis,cis*-$[RuCl_2\{Ph_2PCH_2C(O)Ph\}_2]$ and *cis*-$[Rh\{Ph_2PCH_2C(O)Ph\}_2]PF_6$.[1,20] The PF_6 anion and the CH_2Cl_2 molecule of solvation in **3** are disordered.

Crystal Structures of $[RhCl\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}]PF_6$ **5** *and* $[RhCl\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}_2\{Ph_2PCH_2C(O)Ph\}] \cdot CH_2Cl_2$ **8**$\cdot CH_2Cl_2$.—Figs. 2 and 3 show the molecular structures with the numbering scheme used for these complexes. Selected bond lengths and angles are listed in Tables 5 and 6. Both rhodium(III) complexes have distorted octahedral geometry. They contain monodentate [P(3) in **5** and P(2) in **8**] or chelating ketophosphines [P(2), O(2) in **5**] and the corresponding phosphino enolate [P(1), O(1) in **5** and P(1), O(1) and P(3), O(3) in **8**]. The monodentate phosphines in **5** and **8** are similar and have bond lengths and angles in the normal range. The chelate bite angles for the ketophosphine and the enolate are also in the normal range for both complexes. At 2.332(1) and 2.342(1) Å, the Rh–Cl bond lengths in **5** and **8** respectively, are similar to those in **3**, indicating a similar *trans* influence for the chloride and the enolate oxygen in these complexes. The chelating ketophosphine in **5** has a longer Rh–O(2) bond [2.173(3) Å] than in **3**. This may be related to the stereodynamic behaviour of **5** (see above), which showed the easy rupture of the Rh–O(2) bond. The enolate ligand in **5** has slightly shorter Rh–P(1) [2.232(1) Å] and Rh–O(1) [2.027(3) Å] bonds than the corresponding bonds in **8** involving P(1) *trans* to enolate oxygen, [Rh–P(1) 2.254(1) Å] and O(1) *trans* to Cl, [Rh–O(1) 2.048(2) Å]. The other phosphino enolate ligand in **8** has longer Rh–P [2.356(1) Å] and Rh–O [2.088(2) Å], bonds due to the higher *trans* influence of the phosphorus atoms *trans* to these bonds. The covalent Rh–O bonds in **5** and **8** are shorter than that in $[Rh\{OC(CF_3)_2CH_2C(Me{\cdots}CH{\cdots}CH_2\}(\eta^5\text{-}C_9H_7)]$ [2.081(4) Å] and close to the sum of the covalent radii (1.99 Å), indicating strong bonding.[31] The electron delocalisation within the RhPCCO enolate rings in **5** and **8** is indicated by the C–C and C–O distances in the range 1.351(7)–1.362(4) and 1.305(3)–1.335(6) Å, respectively, whereas in the chelating ketophosphine ligand in **5**, C(21)–C(22) and C(22)–O(2) are 1.513(6) and 1.252(5) Å, respectively. Note than in the octahedral Fe^{II} complex $[Fe\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}_2(CO)_2]$, the phosphorus atoms of the phosphino enolate ligands are *trans* to each other.[32] The PF_6 anion in **5** and the CH_2Cl_2 molecule of solvation in **8** are disordered.

Experimental

(*a*) *Reagents and Physical Measurements*.—All reactions were performed in Schlenk-type flasks under high purity argon (Air Liquide). Rhodium trichloride trihydrate was from Johnson Matthey. Solvents (analytical grade) were dried and distilled under argon: toluene, diethyl ether and thf from sodium–benzophenone, pentane from sodium–potassium, dichloromethane and chloroform over P_2O_5, ethanol from $Mg(OEt)_2$. Elemental analyses (C, H, Cl, P) were performed by the Institut Français du Pétrole and Pascher, Regensburg, Germany. Infrared spectra were recorded in the 4000–200 cm^{-1} region on a Perkin-Elmer 883 spectrometer. Samples were prepared as CsI pellets, Nujol mulls, or in solution in CaF_2 cells. Proton NMR spectra were recorded at 200 MHz on a FT Bruker AC-F 200 and the $^{31}P\text{-}\{^1H\}$ NMR spectra at 81 MHz on a FT Bruker CXP 200 instrument. Chemical shifts are positive downfield relative to external $SiMe_4$ for ^1H and to external 85% H_3PO_4 in water for ^{31}P NMR spectra.

(*b*) *Syntheses*.—The ketophosphine L was prepared by the method previously described,[16] $TlPF_6$ by treating TlOH (from Tl_2SO_4 and BaOH) with $[NH_4]PF_6$.

mer,trans-$[RhCl_3\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}]$ **1**. A solution of L (3.46 g, 11.4 mmol) in EtOH (30 cm^3) was added with stirring to a warm solution of $RhCl_3 \cdot 3H_2O$ (1.00 g, 3.8 mmol) in EtOH (15 cm^3). The product precipitated immediately as an orange solid. After 3 h, the precipitate was collected and washed with Et_2O and pentane. A ^1H NMR spectrum indicated 60% **2** and 40% **1**. Slow diffusion of pentane

into a CH_2Cl_2 solution afforded red crystals of **1** (0.01 g, 2%) and a yellow powder of **2** (3.10 g, 90%).

Data for **1**: (Found: C, 58.4; H, 4.5; Cl, 12.3. $C_{40}H_{34}Cl_3O_2P_2Rh$ requires C, 58.7; H, 4.2; Cl, 13.0%). IR(CsI): ν(CO) 1672m and 1565s, ν(Rh–Cl) 345s, 300w, 260w cm^{-1}; NMR: ^1H (CD_2Cl_2), δ 8.3–7.0 (30 H, m, 6 Ph), 4.92 [2 H, d, J(PH) 8.8, PCH_2 (chelate)] and 4.72 [2 H, dd, ^2J(PH) 10.25 and ^4J(PH) 1.0, PCH_2 (monodentate L)]; ^{31}P-{^1H} (CH_2Cl_2–CD_2Cl_2), δ 27.9 [1 P, dd, J(RhP) 87 and J(PP) 622, P (chelate)] and 18.7 [1 P, dd, J(RhP) 89 Hz, P (monodentate L)].

mer,cis-[$RhCl_3${$Ph_2PCH_2C(O)Ph$}{$Ph_2PCH_2C(O)Ph$}] **2**. This isomer was obtained during the synthesis of **1** (see above) (Found: C, 58.1; H, 4.6; Cl, 12.5. $C_{40}H_{34}Cl_3O_2P_2Rh$ requires C, 58.7; H, 4.2; Cl, 13.0%). IR(CsI): ν(CO) 1675m and 1575s, ν(Rh–Cl) 345s, 293m cm^{-1}; FIR(polyethylene) 350, 340, 305 and 290 cm^{-1}; NMR: ^1H (CD_2Cl_2), δ 8.3–7.0 (30 H, m, 6 Ph), 5.29 [2 H, d, J(PH) 15.1, PCH_2 (chelate)] and 4.69 [2 H, d, J(PH) 11.72, PCH_2 (monodentate L)]; ^{31}P-{^1H} (CH_2Cl_2–CD_2Cl_2), δ 37.4 [1 P, dd, J(RhP) 114 and J(PP) 23, P (chelate) *trans* to Cl] and 32.0 [1 P, dd, J(RhP) 124 Hz, P (monodentate L) *trans* to O].

trans,cis,cis-[$RhCl_2${$Ph_2PCH_2C(O)Ph$}$_2$]PF_6 **3**. Solid $TlPF_6$ (0.05 g, 0.14 mmol) was added to a solution of complex **2** (0.11 g, 0.13 mmol) in CH_2Cl_2 (10 cm^3). The turbid solution was stirred overnight, filtered and evaporated to *ca.* 2 cm^3. A layer of diethyl ether was carefully added and, by slow diffusion at room temperature, yellow X-ray quality crystals of **3** were obtained. These were separated, washed with diethyl ether and dried *in vacuo* (0.11 g, 95%) (Found: C, 50.0; H, 3.6; Cl, 9.8; P, 9.6. $C_{40}H_{34}Cl_2F_6O_2P_3Rh$·0.33$CH_2Cl_2$ requires C, 50.7; H, 3.65; Cl, 9.9; P, 9.7%). IR(CsI): ν(CO) 1570s, ν(PF) 850vs, ν(Rh–Cl) 375m and 350m cm^{-1}; FIR(polyethylene) 375m and 351m cm^{-1}; NMR: ^1H (CD_2Cl_2), δ 8.43–7.33 (30 H, m, 6 Ph) and 5.03 [4 H, d, J(PH) 12.7, PCH_2]; ^{31}P-{^1H} (CH_2Cl_2–CD_2Cl_2), δ 46.5 [2 P, d, J(RhP) 122] and −144.3 [1 P, spt, J(PF) 710 Hz].

mer,cis-[$RhCl${$Ph_2PCH{\cdots}C({\cdots}O)Ph$}{$Ph_2PCH_2C(O)Ph$}-{$Ph_2PCH_2C(O)Ph$}]$PF_5$ **5**. Solid L (0.107 g, 0.35 mmol) was added to a solution of **3** (0.119 g, 0.128 mmol) in CH_2Cl_2 (5 cm^3). After 1 w $CHCl_3$ was added to a CH_2Cl_2 solution and unreacted **3** (0.023 g, 22%) precipitated. The supernatant solution was removed with a pipette and pentane was added to precipitate **5** as yellow needles, which could be recrystallised from CH_2Cl_2–diethyl ether (0.11 g, 77%) (Found: C, 59.0; H, 4.2; Cl, 4.0; P, 10.2. $C_{60}H_{50}ClF_6O_3P_4Rh$·$CH_2Cl_2$ requires C, 59.2; H, 4.2; Cl, 4.8; P, 10.1%). IR: (CD_2Cl_2) 1680m and 1572s, ν(C···O) + ν(C···C) 1525m; (CsI) ν(CO) 1680m and 1567s, ν(C···O) + ν(C···C) 1522m, ν(PF) 850vs, ν(Rh–Cl) 345m cm^{-1}; NMR: ^1H (CD_2Cl_2, 253 K), δ 8.2–6.9 (45 H, m, 9 Ph), 5.17 [1 H, d, J(PH) 4.4, PCH *trans* to O], 4.96 [1 H, br dd, J(PH) + J(HH) 28.3, PCH*H*'], 4.68 [1 H, dd, J(PH) 10.5 and J(HH) 17.8, PCH*H*'], 4.18 [1 H, dd, J(PH) 7.3 and J(HH) 15.6, PCH*H*'] and 2.49 [1 H, dd, J(PH) 7.8 and J(HH) 16.1, PCH*H*']; ^{31}P-{^1H} (CH_2Cl_2–CD_2Cl_2, 250 K), δ 36.0 [1 P, dt, J(RhP) 122 and J(PP) 24, PCH *trans* to O], 28.7 [1 P, dt, J(RhP) 91 and J(PP) 460 and 24, P (chelate)], 17.0 [1 P, dd, J(RhP) 96 and J(PP) 460 and 24, P (monodentate L)] and −144.3 [1 P, spt, J(PF) 710 Hz].

[{$Rh(\mu$-Cl)[$Ph_2PCH{\cdots}C({\cdots}O)Ph$]$_2$}$_2$] **6**. A suspension of **3** (0.09 g, 0.11 mmol) in thf (30 cm^3) was stirred with an excess of NaH (0.01 g, 0.41 mmol) at 50 °C until IR monitoring showed the disappearance of the band at 1570 cm^{-1} and the stabilisation of a strong band at 1520 cm^{-1} (about 2 d). The solution was concentrated and filtered. Upon addition of pentane, yellow microcrystals grew, which could be recrystallised from thf–diethyl ether or CH_2Cl_2–pentane to give **6** as yellow crystals (0.075 g, 92%). Complex **2** could also be used as starting material for this synthesis (Found: C, 63.7; H, 4.7; Cl, 4.8. $C_{80}H_{64}Cl_2O_4P_4Rh_2$ requires C, 64.5; H, 4.3; Cl, 4.75%). IR(thf): ν(C···O) + ν(C···C) 1520s; (CsI) ν(C···O) + ν(C···C) 1520s; ν(Rh–Cl) 286m cm^{-1}; NMR: ^1H (CD_2Cl_2), δ 8.15–7.0 (30 H, m,

Table 7 Crystal data and data collection parameters[a]

Compound	**3**	**5**	**8**
Formula	$C_{40}H_{34}Cl_2F_6O_2P_3Rh$·$CH_2Cl_2$	$C_{60}H_{50}ClF_6O_3P_4Rh$	$C_{60}H_{49}ClO_3P_3Rh$·CH_2Cl_2
M	1012.4	1195.3	1134.3
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
Crystal dimensions/mm	0.20 × 0.26 × 0.36	0.28 × 0.26 × 0.20	0.40 × 0.35 × 0.30
Colour	Yellow-orange	Yellow	Yellow
a/Å	17.107(5)	13.559(4)	12.777(3)
b/Å	19.394(5)	14.036(4)	17.693(5)
c/Å	13.661(4)	16.449(4)	12.490(3)
α/°		71.40(2)	94.31(2)
β/°	108.00(2)	66.26(2)	104.18(2)
γ/°		78.24(2)	77.95(2)
U/Å^3	4310.7	2705.6	2676.2
Z	4	2	2
ρ_{calc}/g cm^{-3}	1.560	1.467	1.407
Linear absorption coefficient μ(Mo-Kα)/cm^{-1}	8.086	5.400	5.965
2θ Range/°	4–48	4–46	4–44
Scan width/°	1.05 + 0.34 tan θ	0.78 + 0.34 tan θ	0.90 + 0.34 tan θ
Octants collected	$\pm h + k + l$	$\pm h \pm k + l$	$\pm h \pm k + l$
No. of data collected	8137	6881	7424
No. of data [$I > 3\sigma(I)$], N_o	5534	5540	6220
$A_{min,max}$	0.94, 1.00	0.91, 1.08	0.96, 1.00
R[b]	0.044	0.039	0.029
R'[c]	0.069	0.063	0.051
p	0.08	0.08	0.08
S[d]	1.542	1.391	1.217
Maximum peak in final difference map/e Å^{-3}	0.21	0.14	0.05

[a] Details in common: T = 295 K; Enraf-Nonius CAD4 diffractometer; Mo-Kα radiation (λ = 0.710 73 Å); ω–2θ scan mode, variable scan speed. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [d] $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{\frac{1}{2}}$ (N_p = no. of parameters).

Table 8 Positional parameters and their estimated standard deviations for **3**·CH_2Cl_2

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh	0.030 84(2)	0.061 01(2)	0.776 61(2)	C(23)	−0.209 3(3)	0.016 6(3)	0.561 2(3)
Cl(1)	0.104 19(7)	0.029 31(7)	0.665 69(8)	C(24)	−0.199 6(3)	−0.046 9(3)	0.519 9(4)
Cl(2)	−0.043 74(7)	0.085 87(7)	0.888 73(9)	C(25)	−0.266 3(4)	−0.081 1(3)	0.457 1(5)
P(1)	0.154 27(7)	0.084 12(6)	0.892 45(9)	C(26)	−0.343 1(4)	−0.054 7(3)	0.437 5(6)
O(1)	0.054 5(2)	−0.037 7(2)	0.840 7(2)	C(27)	−0.354 5(4)	0.006 8(4)	0.480 0(5)
C(1)	0.192 1(3)	−0.004 7(3)	0.921 7(4)	C(28)	−0.287 4(3)	0.044 3(3)	0.541 1(5)
C(2)	0.122 7(3)	−0.055 7(2)	0.896 2(3)	C(29)	−0.001 0(3)	0.176 9(2)	0.572 7(3)
C(3)	0.135 1(3)	−0.127 5(2)	0.933 3(3)	C(30)	−0.026 1(3)	0.132 2(3)	0.488 8(4)
C(4)	0.207 1(4)	−0.148 9(3)	1.004 9(5)	C(31)	−0.005 2(4)	0.147 3(3)	0.401 9(4)
C(5)	0.215 1(4)	−0.215 1(4)	1.039 1(6)	C(32)	0.038 9(3)	0.203 5(3)	0.359 9(4)
C(6)	0.150 7(4)	−0.260 0(3)	1.006 9(5)	C(33)	0.065 8(3)	0.247 8(3)	0.478 4(4)
C(7)	0.078 8(4)	−0.239 6(3)	0.934 3(4)	C(34)	0.045 3(3)	0.234 5(3)	0.567 8(4)
C(8)	0.071 9(3)	−0.174 4(3)	0.898 5(4)	C(35)	−0.029 0(3)	0.239 8(3)	0.750 2(4)
C(9)	0.233 7(3)	0.127 9(3)	0.854 2(3)	C(36)	0.014 9(3)	0.252 5(3)	0.851 3(4)
C(10)	0.316 5(3)	0.114 0(3)	0.905 8(5)	C(37)	0.011 1(4)	0.315 4(3)	0.893 8(4)
C(11)	0.376 4(4)	0.145 3(5)	0.875 4(6)	C(38)	−0.040 8(4)	0.367 3(3)	0.835 8(5)
C(12)	0.357 6(4)	0.194 7(4)	0.798 8(5)	C(39)	−0.084 9(4)	0.354 0(3)	0.738 3(5)
C(13)	0.276 3(4)	0.210 3(4)	0.749 7(5)	C(40)	−0.079 9(4)	0.291 0(3)	0.692 8(4)
C(14)	0.214 2(3)	0.176 2(3)	0.777 6(4)	P(3)	0.594 5(1)	0.086 5(1)	0.753 1(1)
C(15)	0.160 9(3)	0.121 1(3)	1.017 0(3)	F(1)	0.561 9(5)	0.110 6(5)	0.640 9(4)
C(16)	0.137 9(3)	0.082 7(3)	1.088 2(4)	F(2)	0.518 3(3)	0.048 4(5)	0.754 6(6)
C(17)	0.145 8(4)	0.108 9(4)	1.835 5(4)	F(3)	0.627 0(4)	0.075 2(5)	0.865 6(5)
C(18)	0.172 7(4)	0.174 0(4)	1.208 5(4)	F(4)	0.615 3(6)	0.024 3(4)	0.714 5(8)
C(19)	0.193 6(4)	0.214 4(4)	1.136 2(5)	F(5)	0.677 0(4)	0.116 0(4)	0.748 6(5)
C(20)	0.188 3(3)	0.188 2(3)	1.039 4(4)	F(6)	0.571 4(7)	0.148 5(4)	0.784 5(6)
P(2)	−0.025 71(7)	0.157 16(6)	0.689 98(9)	C(41)	0.624 9(9)	0.056 3(6)	0.219 9(9)
O(2)	−0.075 3(2)	0.016 5(2)	0.673 6(2)	Cl(3)	0.594 7(3)	0.068 0(2)	0.091 1(3)
C(21)	−0.133 4(3)	0.127 5(3)	0.645 3(4)	Cl(4)	0.700 1(3)	0.116 1(3)	0.272 8(4)
C(22)	−0.136 4(3)	0.051 9(2)	0.629 8(3)				

Table 9 Positional parameters and their estimated standard deviations for the non-hydrogen atoms in **5**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh	0.299 21(2)	0.160 30(2)	0.634 85(2)	C(33)	0.451 0(4)	0.427 7(4)	0.707 0(4)
Cl	0.360 70(7)	−0.001 73(7)	0.615 83(7)	C(34)	0.433 8(3)	0.335 7(3)	0.703 4(3)
P(1)	0.218 32(8)	0.106 51(8)	0.787 37(7)	C(35)	0.554 5(3)	0.087 0(3)	0.691 2(3)
C(1)	0.172 0(3)	0.223 2(3)	0.812 6(3)	C(36)	0.569 4(3)	−0.013 8(3)	0.694 4(3)
C(2)	0.190 5(3)	0.306 2(3)	0.740 6(3)	C(37)	0.634 5(4)	−0.079 0(4)	0.739 2(4)
O(1)	0.244 9(2)	0.300 1(2)	0.654 1(2)	C(38)	0.685 2(4)	−0.042 4(4)	0.779 8(3)
C(3)	0.149 7(3)	0.411 0(3)	0.747 7(3)	C(39)	0.670 3(4)	0.054 8(4)	0.777 3(3)
C(4)	0.159 0(6)	0.488 0(4)	0.671 2(4)	C(40)	0.602 4(4)	0.122 2(4)	0.734 7(3)
C(5)	0.114 2(7)	0.587 1(5)	0.675 8(6)	P(3)	0.142 11(8)	0.171 33(8)	0.598 24(7)
C(6)	0.065 9(5)	0.606 8(4)	0.756 2(5)	C(41)	0.027 2(3)	0.221 0(4)	0.679 2(3)
C(7)	0.054 6(8)	0.533 9(5)	0.832 5(5)	C(42)	−0.083 2(3)	0.258 3(4)	0.670 4(3)
C(8)	0.099 0(6)	0.433 3(5)	0.831 6(4)	O(3)	−0.100 1(3)	0.252 0(3)	0.605 8(2)
C(9)	0.299 4(3)	0.034 8(3)	0.855 0(3)	C(43)	−0.167 6(4)	0.297 9(4)	0.744 9(3)
C(10)	0.330 6(4)	−0.067 8(4)	0.862 5(3)	C(44)	−0.273 2(4)	0.319 4(4)	0.747 7(4)
C(11)	0.382 9(4)	−0.122 3(4)	0.921 0(3)	C(45)	−0.353 6(4)	0.351 5(5)	0.818 7(5)
C(12)	0.405 2(4)	−0.078 1(4)	0.973 3(3)	C(46)	−0.329 6(5)	0.372 2(5)	0.885 3(4)
C(13)	0.378 5(4)	0.023 1(4)	0.964 2(3)	C(47)	−0.230 7(5)	0.352 1(5)	0.885 4(4)
C(14)	0.325 5(3)	0.080 1(3)	0.906 1(3)	C(48)	−0.147 6(4)	0.315 6(4)	0.816 2(4)
C(15)	0.104 8(3)	0.030 0(3)	0.831 7(3)	C(49)	0.154 8(3)	0.266 6(3)	0.489 7(3)
C(16)	0.115 5(4)	−0.061 1(4)	0.810 6(3)	C(50)	0.167 4(5)	0.363 5(4)	0.482 7(4)
C(17)	0.029 5(4)	−0.118 8(4)	0.846 6(4)	C(51)	0.176 7(7)	0.437 6(5)	0.400 4(5)
C(18)	−0.070 5(4)	−0.084 7(4)	0.903 3(4)	C(52)	0.173 0(5)	0.415 5(5)	0.329 4(4)
C(19)	−0.083 6(4)	0.006 1(4)	0.922 4(4)	C(53)	0.165 0(4)	0.320 8(4)	0.332 3(3)
C(20)	0.004 5(4)	0.061 9(4)	0.888 4(3)	C(54)	0.156 0(3)	0.244 8(4)	0.413 0(3)
P(2)	0.472 81(7)	0.175 27(7)	0.629 07(7)	C(55)	0.108 8(3)	0.058 5(3)	0.587 7(3)
C(21)	0.548 6(3)	0.165 0(3)	0.511 0(3)	C(56)	0.185 5(3)	0.011 0(3)	0.522 8(3)
C(22)	0.482 6(3)	0.217 4(3)	0.451 2(3)	C(57)	0.163 4(3)	−0.075 1(3)	0.510 8(3)
O(2)	0.381 7(2)	0.224 0(2)	0.488 3(2)	C(58)	0.068 2(4)	−0.115 5(3)	0.564 8(3)
C(23)	0.532 7(3)	0.260 1(3)	0.352 1(3)	C(59)	−0.008 3(4)	−0.070 7(4)	0.630 9(4)
C(24)	0.466 3(4)	0.292 9(4)	0.300 3(3)	C(60)	0.012 1(3)	0.016 6(4)	0.641 8(3)
C(25)	0.508 6(5)	0.338 9(4)	0.207 0(3)	P(4)	0.294 5(1)	0.342 5(1)	1.023 9(1)
C(26)	0.616 6(5)	0.353 1(4)	0.166 0(3)	F(1)	0.227 3(6)	0.439 4(5)	1.010 8(7)
C(27)	0.682 3(5)	0.320 4(5)	0.214 0(4)	F(2)	0.385 5(5)	0.406 3(5)	0.963 5(7)
C(28)	0.642 3(4)	0.271 5(4)	0.307 0(3)	F(3)	0.363 9(6)	0.246 9(5)	1.026 8(7)
C(29)	0.492 9(3)	0.299 8(3)	0.627 6(3)	F(4)	0.204 2(6)	0.280 9(5)	1.090 8(8)
C(30)	0.569 1(5)	0.358 8(4)	0.554 3(4)	F(5)	0.279 0(8)	0.327 2(6)	0.949 4(4)
C(31)	0.584 6(5)	0.450 5(4)	0.559 6(5)	F(6)	0.301 5(7)	0.355 1(6)	1.100 5(4)
C(32)	0.529 7(5)	0.483 8(4)	0.633 3(4)				

Table 10 Positional parameters and their estimated standard deviations for **8**·CH_2Cl_2

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh	0.467 52(1)	0.209 40(1)	0.294 82(1)	C(32)	0.880 7(3)	0.334 8(2)	0.407 0(3)
P(1)	0.324 39(5)	0.230 38(4)	0.146 25(5)	C(33)	0.776 6(3)	0.357 8(2)	0.422 4(3)
C(1)	0.294 9(2)	0.332 4(2)	0.149 4(2)	C(34)	0.692 1(2)	0.322 3(2)	0.361 1(3)
C(2)	0.360 4(2)	0.367 0(1)	0.233 0(2)	C(35)	0.682 1(2)	0.126 7(2)	0.155 4(2)
O(1)	0.440 8(1)	0.327 62(9)	0.307 7(1)	C(36)	0.741 3(3)	0.074 6(2)	0.236 4(3)
C(3)	0.350 3(2)	0.451 4(2)	0.249 2(2)	C(37)	0.803 7(3)	0.005 7(2)	0.208 9(3)
C(4)	0.301 8(3)	0.502 6(2)	0.163 2(3)	C(38)	0.803 9(3)	−0.013 3(2)	0.100 6(3)
C(5)	0.298 1(4)	0.581 4(2)	0.181 1(3)	C(39)	0.743 9(3)	0.036 1(2)	0.019 8(3)
C(6)	0.341 1(4)	0.610 4(2)	0.281 8(3)	C(40)	0.682 0(2)	0.106 9(2)	0.045 6(3)
C(7)	0.389 9(3)	0.561 3(2)	0.366 0(3)	P(3)	0.373 52(5)	0.215 68(4)	0.436 67(5)
C(8)	0.395 3(3)	0.482 8(2)	0.350 6(3)	C(41)	0.488 3(2)	0.205 1(2)	0.550 2(2)
C(9)	0.346 7(2)	0.196 5(2)	0.010 3(2)	C(42)	0.589 3(2)	0.196 1(1)	0.528 6(2)
C(10)	0.303 3(3)	0.242 5(2)	−0.081 0(3)	O(3)	0.604 0(1)	0.197 6(1)	0.429 0(1)
C(11)	0.316 7(4)	0.213 7(2)	−0.184 9(3)	C(43)	0.694 3(2)	0.182 9(2)	0.616 1(2)
C(12)	0.372 1(3)	0.141 3(2)	−0.197 4(3)	C(44)	0.791 8(3)	0.184 3(2)	0.587 5(3)
C(13)	0.415 9(3)	0.095 1(2)	−0.107 9(3)	C(45)	0.890 6(3)	0.172 0(3)	0.665 7(3)
C(14)	0.402 9(3)	0.121 9(2)	−0.004 9(2)	C(46)	0.893 7(3)	0.158 8(3)	0.773 9(3)
C(15)	0.199 8(2)	0.193 1(2)	0.141 0(2)	C(47)	0.797 5(3)	0.157 9(2)	0.801 6(3)
C(16)	0.097 2(3)	0.234 6(2)	0.087 7(3)	C(48)	0.699 1(3)	0.168 8(2)	0.725 2(3)
C(17)	0.003 6(3)	0.203 8(2)	0.074 5(3)	C(49)	0.284 7(2)	0.309 8(1)	0.449 1(2)
C(18)	0.012 4(3)	0.131 0(2)	0.115 7(3)	C(50)	0.189 2(2)	0.333 4(2)	0.368 9(2)
C(19)	0.112 3(3)	0.091 3(2)	0.169 1(3)	C(51)	0.122 4(3)	0.404 6(2)	0.378 1(3)
C(20)	0.206 6(2)	0.121 6(2)	0.183 1(3)	C(52)	0.151 3(3)	0.452 8(2)	0.466 5(3)
P(2)	0.605 90(5)	0.217 38(4)	0.199 68(5)	C(53)	0.244 9(3)	0.431 0(2)	0.545 9(3)
C(21)	0.560 8(2)	0.281 1(2)	0.079 1(2)	C(54)	0.313 1(3)	0.359 7(2)	0.437 8(3)
C(22)	0.653 2(2)	0.314 3(2)	0.056 2(2)	C(55)	0.292 2(2)	0.146 1(2)	0.456 9(2)
O(2)	0.716 4(2)	0.275 6(1)	0.005 6(2)	C(56)	0.182 3(2)	0.166 7(2)	0.459 2(3)
C(23)	0.667 0(3)	0.393 4(2)	0.098 1(2)	C(57)	0.125 3(3)	0.111 2(2)	0.472 7(3)
C(24)	0.770 5(3)	0.4 121(2)	0.112 9(3)	C(58)	0.177 2(3)	0.035 9(2)	0.486 5(3)
C(25)	0.787 1(4)	0.485 3(3)	0.146 7(4)	C(59)	0.287 6(3)	0.014 6(2)	0.486 8(3)
C(26)	0.698 1(4)	0.541 9(2)	0.163 6(4)	C(60)	0.343 8(3)	0.070 1(2)	0.472 7(3)
C(27)	0.596 1(4)	0.524 5(2)	0.151 1(4)	Cl	0.496 21(6)	0.074 19(4)	0.282 32(6)
C(28)	0.582 0(3)	0.449 8(2)	0.119 7(3)	C(61)	−0.038 7(6)	0.368 6(5)	0.773 2(8)
C(29)	0.715 2(2)	0.262 0(2)	0.287 4(2)	Cl(1)	0.052 1(2)	0.366 7(1)	0.693 2(2)
C(30)	0.822 8(2)	0.239 9(2)	0.275 0(3)	Cl(2)	−0.002 2(2)	0.412 1(1)	0.903 8(2)
C(31)	0.903 9(3)	0.277 2(2)	0.334 6(3)				

6 Ph), 5.20 [1 H, d, ^2J(PH) 2, PCH *trans* to O] and 4.64 [1 H, dd, ^2J(PH) 6.8 and ^4J(PH) 2, PCH]; ^{31}P-{^{1}H} (thf, C_6D_6), δ 39.1 [1 P, dd, J(RhP) 132, J(PP) 30, P *trans* to O] and 29.3 [1 P, dd, J(RhP) 112 Hz, P *trans* to Cl].

[RhCl{$Ph_2PCH{\cdots}C({\cdots}O)Ph$}$_2$($PMePh_2$)] **7**. The phosphine $PMePh_2$ (22.4 μl, 0.24 mmol) was added *via* a syringe to a stirred solution of **6** (0.18 g, 0.12 mmol) in CH_2Cl_2 (20 cm^3). After 30 min the solution was filtered, concentrated and pentane was added. At −20 °C a yellow precipitate formed, which was filtered off, dried *in vacuo* and recrystallised from CH_2Cl_2–pentane to yield yellow crystals (0.16 g, 70%) (Found: C, 67.2; H, 4.9; Cl, 3.6. $C_{53}H_{45}ClO_2P_3Rh$ requires C, 67.35; H, 4.8; Cl, 3.75%). IR: (CD_2Cl_2) ν(C···O) + ν(C···C) 1518s; (CsI) ν(Rh–Cl) 330w cm^{-1}; NMR: ^{1}H (CD_2Cl_2), δ 8.3–7.0 (40 H, m, 8 Ph), 5.06 [1 H, d, J(PH) 2.2, PCH], 4.81 [1 H, dt, J(PH) 4.4 and 1.5, PCH] and 1.30 [3 H, dd, J(PH) 10.2 and 2.7, PCH_3]; ^{31}P-{^{1}H} (CH_2Cl_2–CD_2Cl_2), δ 33.1 [1 P, ddd, J(RhP) 92, J(PP) 462 and 23, PCH *trans* to P], 26.2 [1 P, dt, J(RhP) 111, J(PP) 26, PCH *trans* to O] and 3.6 [1 P, ddd, J(RhP) 92, J(PP) 462 and 23 Hz, $PMePh_2$].

mer,cis-[RhCl{$Ph_2PCH{\cdots}C({\cdots}O)Ph$}$_2${$Ph_2PCH_2C(O)Ph$}] **8**. A solution of L (0.375 g, 1.23 mmol) in CH_2Cl_2 (5 cm^3) was added to a solution of [RhCl(PPh_3)$_3$] (0.38 g, 0.41 mmol) in toluene–CH_2Cl_2 (37:5 cm^3). The colour changed from red to yellow-orange. The solution was filtered, concentrated and EtOH (30 cm^3) and pentane (65 cm^3) were added. After 4 d at −20 °C the solution was concentrated and pentane added to precipitate a yellow solid which was recrystallised from CH_2Cl_2–pentane to give **8** as yellow crystals (0.32 g, 74%) (Found: C, 68.7; H, 4.8; Cl, 3.5. $C_{60}H_{49}ClO_3P_3Rh$ requires C, 68.7; H, 4.7; Cl, 3.4%). IR: (CsI) ν(CO) 1670m, ν(C···O) + ν(C···C) 1520s, ν(Rh–Cl) 330w; ($CHCl_3$) ν(CO) 1670m, ν(C···O) + ν(C···C) 1521s cm^{-1}; NMR: ^{1}H (CD_2Cl_2), δ 8.3–6.8 (45 H, m, 9 Ph), 5.00 [1 H, m, ^2J(PH) 2.4, PCH], 4.96 [1 H, d, ^2J(PH) 1.95, PCH], 4.80 [1 H, dd, $^2J(PH^A)$ 8.3 and J(HH) 15, PCH^A] and 2.53 [1 H, dd, $^2J(PH^B)$ 8.5 and J(HH) 14.9, PCH^B]; ^{31}P-{^{1}H} (CH_2Cl_2–CD_2Cl_2), δ 32.8 [1 P, ddd, J(RhP) 92 and J(PP) 465 and 25, Ph_2PCH *trans* to P], 24.9 [1 P, dt, J(RhP) 110, J(PP) 26, Ph_2PCH *trans* to O] and 17.0 [1 P, ddd, J(RhP) 92, J(PP) 465 and 26 Hz, P (monodentate L)].

fac-[Rh{$Ph_2PCH{\cdots}C({\cdots}O)Ph$}$_3$] **9**. *Method* (*a*). To a mixture of **2** (0.320 g, 0.39 mmol) and L (0.28 g, 0.78 mmol) in toluene (20 cm^3) was added at −78 °C with stirring NaOMe (1.4 cm^3, 0.5 mol dm^{-3} solution in MeOH). On warming to 20 °C a yellow solution formed, which was stirred overnight, concentrated, filtered and pentane added to precipitate a yellow solid, which was recrystallised from CH_2Cl_2–pentane.

Method (*b*). A solution of L (0.28 g, 0.78 mmol) and [RhCl(PPh_3)$_3$] (0.241 g, 0.26 mmol) in toluene (30 cm^3) was stirred overnight. The solution was filtered, concentrated and pentane added, and the precipitate washed with pentane to eliminate PPh_3. The solid was taken up in toluene (5 cm^3) and NaOMe (slight excess) was added. Sodium chloride was filtered off, toluene was evaporated and the yellow solid recrystallised from CH_2Cl_2–pentane (0.145 g, 55%) (Found: C, 71.0; H, 4.8; P, 9.4. $C_{60}H_{48}O_3P_3Rh$ requires C, 71.15; H, 4.8; P, 9.2%). IR: (CD_2Cl_2) ν(C···O) + ν(C···C) 1522s cm^{-1}; NMR: ^{1}H (CD_2Cl_2), δ 7.8–6.8 (45 H, m, 9 Ph), 4.75 (3 H, s, PCH); ^{31}P-{^{1}H} (CH_2Cl_2–CD_2Cl_2), δ 27.7 [d, J (RhP) 116 Hz].

(*c*) *Crystal Structure Determinations*.—The crystal data and parameters relative to data collection for all structures are

summarised in Table 7. Suitable single crystals of **3**·CH_2Cl_2, **5** or **8**·CH_2Cl_2 were obtained by slow diffusion of pentane in a filtered CH_2Cl_2 or toluene–CH_2Cl_2 solution at 25 °C. For each compound a single crystal was cut out from a cluster of crystals and mounted on a rotation-free goniometer head. A systematic search in reciprocal space using an Enraf-Nonius CAD4-F automatic diffractometer showed that crystals **3**·CH_2Cl_2 and **5**, **8**·CH_2Cl_2 belong to the monoclinic and triclinic systems, respectively. Quantitative data were obtained at room temperature. For all calculations the Enraf-Nonius SDP/VAX package was used.[33] Three standard reflections measured every hour during the entire data collection period showed no significant trend. The raw data were converted to intensities and corrected for Lorentz and polarisation factors. For each compound semi-empirical absorption corrections were applied from the ψ scan data of 4 reflections. The structures were solved using the heavy-atom method. After refinement of the non-hydrogen atoms, a Fourier-difference map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure-factor calculations by their computed coordinates (C–H 0.95 Å) and isotropic thermal parameters such as $B(H) = 1.3\ B(C)$ Å^2 but not refined. Full least-squares refinements; weighting scheme $1/\sigma^2(F^2)$; $\sigma^2(F^2) = \sigma^2_{counts} + (pI)^2$. A final difference map revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients were taken from ref. 34. The final fractional coordinates are listed in Tables 8–10.

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

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References

1 Part 27, P. Braunstein, Y. Chauvin, J. Nähring, Y. Dusausoy, D. Bayeul, A. Tiripicchio and F. Ugozzoli, preceding paper; Part 26, J.-B. Ballif, P. Braunstein, A. D. Burrows, R. D. Adams and W. Wu, *J. Cluster Sci.*, 1994, **5**, 443; Part 25, J. Andrieu, P. Braunstein and A. D. Burrows, *J. Chem. Res.*, 1993, (*S*) 380.
2 J. M. Brégeault, *Catalyse homogène par les complexes des métaux de transition*, Masson, Paris, 1992, pp. 62–65.
3 A. Bader and E. Lindner, *Coord. Chem. Rev.*, 1991, **108**, 27.
4 W. Keim, *Chem. Ing. Tech.*, 1984, **56**, 850; U. Klabunde, T. H. Tulip, D. C. Roe and S. D. Ittel, *J. Organomet. Chem.*, 1987, **334**, 141; W. Keim, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 235; W. Keim, *New J. Chem.*, 1994, **18**, 93; P. Braunstein, Y. Chauvin, S. Mercier, L. Saussine, A. DeCian and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 1994, 2203.
5 P. Braunstein, D. Matt, F. Mathey and D. Thavard, *J. Chem. Res.*, 1978, (*M*) 3041, (*S*) 232.
6 P. Braunstein, D. Matt and Y. Dusausoy, *Inorg. Chem.*, 1983, **22**, 2043.
7 H. D. Empsall, S. Johnson and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 302.
8 D. A. Knight, D. J. Cole-Hamilton, D. C. Cupertino, M. Harman and M. B. Hursthouse, *Polyhedron*, 1992, **11**, 1987.
9 M. M. Taqui Khan and K. V. Reddy, *J. Coord. Chem.*, 1982, 71.
10 B. E. Mann, C. Masters and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1973, 1489.
11 P. S. Pregosin and R. W. Kunz, *^{31}P and ^{13}C NMR of Transition Metal Complexes*, Springer, Berlin, Heidelberg, New York, 1979.
12 T. G. Appleton, H. C. Clark and L. E. Manzer, *Coord. Chem. Rev.*, 1973, **10**, 335.
13 P. L. Goggin and J. R. Knight, *J. Chem. Soc., Dalton Trans.*, 1972, 704; P. E. Garrou, *Inorg. Chem.*, 1975, **14**, 1435; *Chem. Rev.*, 1981, **81**, 229.
14 S.-E. Bouaoud, Ph.D. Thesis, Université de Rennes 1, 1987.
15 P. S. Sheridan, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 4, p. 1029.
16 S.-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *Inorg. Chem.*, 1986, **25**, 3765.
17 T. Bartik and T. Himmler, *J. Organomet. Chem.*, 1985, **293**, 343.
18 D. J. Cole-Hamilton and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 1974, 1818.
19 A. C. Skapski and F. A. Stephens, *J. Chem. Soc., Dalton Trans.*, 1973, 1789.
20 P. Braunstein, Y. Chauvin, J. Nähring, A. DeCian, J. Fischer, A. Tiripicchio and F. Ugozzoli, unpublished work.
21 E. Lindner, Q. Wang, H. A. Mayer, A. Bader, H. Kühbauch and P. Wegner, *Organometallics*, 1993, **12**, 3291.
22 E. Lindner and B. Karle, *Z. Naturforsch., Teil B*, 1990, **45**, 1108.
23 E. Lindner, A. Möckel, H. A. Mayer, H. Kühbauch, R. Fawzi and M. Steimann, *Inorg. Chem.*, 1993, **32**, 1266.
24 D. A. Redfield and J. H. Nelson, *Inorg. Chem.*, 1973, **12**, 15.
25 A. W. Verstuyft, D. A. Redfield, L. W. Cary and J. H. Nelson, *Inorg. Chem.*, 1977, **16**, 2776.
26 P. Braunstein, D. G. Kelly, Y. Dusausoy, D. Bayeul, M. Lanfranchi and A. Tiripicchio, *Inorg. Chem.*, 1994, **33**, 233.
27 P. Braunstein, D. G. Kelly, A. Tiripicchio and F. Ugozzoli, *Inorg. Chem.*, 1993, **32**, 4845.
28 P. Braunstein, D. Matt, D. Nobel and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 1987, 1530; P. Braunstein, D. Matt, D. Nobel, F. Balegroune, D. Grandjean and J. Fischer, *J. Chem. Soc., Dalton Trans.*, 1988, 353; F. Balegroune, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *Inorg. Chem.*, 1988, **27**, 3320.
29 R. Graziani, G. Bombieri, L. Volponi and C. Panattoni, *J. Chem. Soc., Chem. Commun.*, 1967, 1284.
30 G. C. Dobinson, R. Mason and D. R. Russell, *J. Chem. Soc., Chem. Commun.*, 1967, 62.
31 P. Caddy, M. Green, J. A. K. Howard, J. M. Squire and N. J. White, *J. Chem. Soc., Dalton Trans.*, 1981, 400.
32 P. Braunstein, S. Coco Cea, A. DeCian and J. Fischer, *Inorg. Chem.*, 1992, **31**, 4203.
33 B. A. Frenz, in *Computing in Crystallography*, eds. H. Schenk, R. Olthof-Hazekamp, H. van Koningveld and G. C. Bassi, Delft University Press, Delft, 1978, pp. 64–71.
34 D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography*, Kynoch, Birmingham, 1974, vol. 4, Tables 2.2b and 2.3.1.

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