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

Pierre Braunstein,[a] Yves Chauvin,[b] Jens Nähring,[a,b] Yves Dusausoy,[c] Daniel Bayeul,[c] Antonio Tiripicchio[d] and Franco Ugozzoli[d]

[a] *Laboratoire de Chimie de Coordination, Associé au CNRS (URA 416), Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cédex, France*

[b] *Institut Français du Pétrole, B. P. 311, F-92506 Rueil-Malmaison Cédex, France*

[c] *Laboratoire de Minéralogie et Cristallographie, Associé au CNRS (URA 162), Université de Nancy 1, B. P. 239, F-54037 Nancy Cédex, France*

[d] *Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze 78, I-43100 Parma, Italy*

Reaction of 1, 2 or 3 equivalents of (diphenylphosphino)acetophenone, $Ph_2PCH_2C(O)Ph$ (L), with $[RuCl_2(PPh_3)_3]$ in toluene afforded selectively *trans,mer*-$[RuCl_2\{Ph_2PCH_2C(O)Ph\}(PPh_3)_2]$ **1**, *trans,cis,cis*-$[RuCl_2\{Ph_2PCH_2C(O)Ph\}_2]$ **2** or *trans,mer*-$[RuCl_2\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}_2]$ **3**, respectively. Complex **1** hydrogenates and isomerises hex-1-ene at atmospheric hydrogen pressure, whereas **2** is inactive. Complex **3** exhibits a dynamic behaviour on the ^1H NMR time-scale which corresponds to exchange between chelating and terminally bound phosphines. The activation energy of this process was calculated to be 63.7 ± 0.7 kJ mol^{-1}. Reaction of **3** with $TlPF_6$ in CH_2Cl_2 gave *mer*-$[RuCl\{Ph_2PCH_2C(O)Ph\}_2\{Ph_2PCH_2C(O)Ph\}]PF_6$ **9** which reacted with a second equivalent of $TlPF_6$ in MeCN to give the dicationic complex *trans,cis,cis*-$[Ru\{Ph_2PCH_2C(O)Ph\}_2(NCMe)_2][PF_6]_2$ **10**. The *fac* and *mer* isomers of the tris(enolato) Ru^{II} complex $[Na][Ru\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}_3]$ **11a** and **11b** were obtained by reaction of **9** with NaH in tetrahydrofuran (thf). Treatment of **3** with NaOMe in toluene afforded selectively **11b**, which has been crystallised by addition of 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5) to give $[Na(15\text{-crown-}5){\cdot}H_2O]$[*mer*-$Ru\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}_3]{\cdot}$thf **12**. Protonation of **11b** with $HBF_4{\cdot}Et_2O$ gave the neutral intermediate *mer*-$[Ru\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}_2\{Ph_2PCH_2C(O)Ph\}]$ **13**, characterised spectroscopically, and the final product *mer*-$[Ru\{Ph_2PCH_2C(O)Ph\}_3][BF_4]_2$ **14**. Treatment of $[RuCl_3(AsPh_3)_2(MeOH)]$ with 2 equivalents of L yielded the ruthenium(III) complex *mer,trans*-$[RuCl_3\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}]$ **15**, which was easily reduced to the ruthenium(II) complex **2**. The solid state structures of complexes **2**, **10** and **12** have been determined by single crystal X-ray analysis. The co-ordination of the metal in **2** and **10** is slightly distorted octahedral with the two phosphorous atoms (and oxygen atoms) in a *cis* position and the chloride and acetonitrile ligands, respectively, in a *trans* position. In the chiral anion of complex **12** the distorted octahedral structure has a meridional arrangement of the P atoms and electronic delocalisation occurs within the chelating phosphino enolate ligands.

The synthesis and properties of ruthenium phosphine complexes have been intensively investigated owing to their role in the homogeneous hydrogenation of olefins.[2] Chiral bidentate phosphine ligands such as 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl bound to ruthenium catalyse the asymmetric hydrogenation of 2-substituted β-keto ester derivatives.[3] Heterodifunctional ligands containing a strong and a weak donor group have been found to confer interesting properties to their metal complexes, such as the selective binding to metal ions of different types (hard *vs.* soft), dynamic behaviour *via* reversible dissociation of the weaker metal–ligand bond, or stereoelectronic control of the co-ordination sphere of the metal resulting in, *e.g.*, unique catalytic properties.[4] We have previously shown that in the Ru^{II} ester phosphine complex *trans*-$[RuCl_2\{Ph_2PCH_2C(O)OEt\}\{Ph_2PCH_2C(O)OEt\}_2]$, dynamic exchange occurs between the co-ordinated and unco-ordinated ester functions.[5] The heterodifunctional nature of this P,O ligand associated with a labile oxygen–metal bonding also accounts for the reversible binding of carbon monoxide by *trans*-$[RuCl_2(CO)\{Ph_2PCH_2C(O)OEt\}\{Ph_2PCH_2C(O)OEt\}]$.[5,6] We were thus interested in a comparative study of ruthenium complexes with the β-ketophosphine ligand $Ph_2PCH_2C(O)Ph$ and its derived phosphino enolate.

Results and Discussion

Neutral Ruthenium(II) *Complexes*.—The addition of one equivalent of $Ph_2PCH_2C(O)Ph$ (L) to a toluene solution of $[RuCl_2(PPh_3)_3]$ resulted in partial ligand exchange and afforded the air-stable dark-red complex *trans,mer*-

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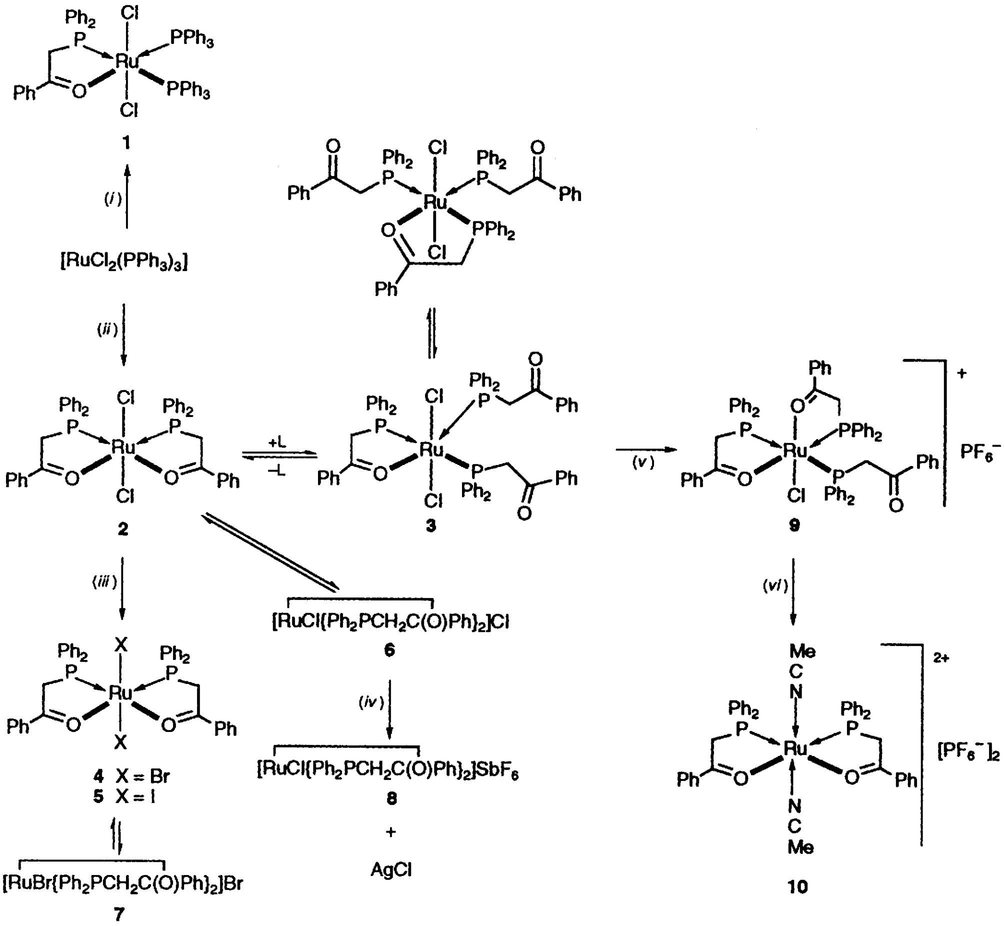
† Complexes of Functional Phosphines. Part 27.[1]

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: bar ≈ 10^5 Pa.



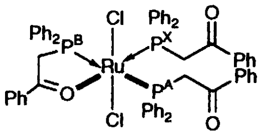
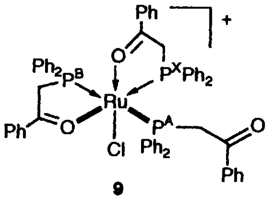
Scheme 1 (*i*) +L, −PPh_3; (*ii*) +2 L, −3 PPh_3; (*iii*) excess of NaBr or KI; (*iv*) $AgSbF_6$; (*v*) $TlPF_6$; (*vi*) $TlPF_6$ in MeCN, −L, −Cl^-

$[RuCl_2\{Ph_2PCH_2C(O)Ph\}(PPh_3)_2]$ **1** (*trans,mer* refers to the relative position of the chloride and phosphorus atoms, respectively) (Scheme 1). Its FIR spectrum shows a medium absorption at 325 cm^{-1} indicative of a *trans* arrangement of the chlorides.[5] The IR spectrum (CsI, Nujol mull or toluene solution) showed an absorption around 1570 cm^{-1} for the co-ordinated keto function. In the ^{31}P-$\{^1H\}$ NMR spectrum an ABX pattern is observed with coupling constants indicative of a meridional arrangement, consistent with the structure drawn. Recently the chelating P,N ligand *ortho*-diphenylphosphino-*N*,*N*-dimethylaniline was reported to give the five-co-ordinate complex $[RuCl_2\{Ph_2PC_6H_4(NMe_2)\text{-}o\}\{P(C_6H_4Me\text{-}p)_3\}]$. This compound forms under 1 bar hydrogen an η^2-H_2 complex, which on treatment with base is converted to the chlorohydrido complex $[Ru(H)Cl\{Ph_2PC_6H_4(NMe_2)\text{-}o\}\{P(C_6H_4Me\text{-}p)_3\}]$, of catalytic relevance.[7] However, when $[RuCl_2(PPh_3)_3]$ was treated with 2 equivalents of L in toluene or dichloromethane, complete ligand exchange occurred which yielded *trans,cis,cis*-$[RuCl_2\{Ph_2PCH_2C(O)Ph\}_2]$ **2**, the ^{31}P-$\{^1H\}$ NMR spectrum of which shows a singlet at δ 70.6 due to equivalent phosphorus atoms. The difference of 88.6 ppm in chemical shift between the free and the co-ordinated ligand is in part due to the formation of a five-membered chelate ring. The presence of a 'filled-in doublet' in the ^1H NMR spectrum for the PCH_2 protons indicates a *cis* arrangement of the phosphorus atoms.[8] Complexes of this type have been reported with ether phosphine ligands.[4] To test for the possible formation of hydride complexes, a toluene or a dichloromethane solution of **2** was placed under 8 bar of hydrogen, but no hydride resonance was detected by ^1H NMR spectroscopy. From the ^{31}P NMR data for complexes **1** and **2** we conclude that there is no detectable dissociation of phosphine at 25 °C for concentrations of 0.01–0.1 mol dm^{-3}. For $[RuCl_2(PPh_3)_3]$ a concentration-dependent phosphine dissociation was observed: *ca.* 5 at 0.1 and 30% at 0.01 mol dm^{-3}.[9]

The bromo- and iodo-derivatives of compounds **2**, *trans,cis,cis*-$[RuBr_2\{Ph_2PCH_2C(O)Ph\}_2]$ **4** and *trans,cis,cis*-$[RuI_2\{Ph_2PCH_2C(O)Ph\}_2]$ **5** were isolated by metathetical anion exchange using a twenty- or five-fold excess of NaBr or KI, respectively, in CH_2Cl_2 (see Experimental section).

The *bis*(chelate) complex **2** reacted with excess L in toluene to give *trans,mer*-$[RuCl_2\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}_2]$ **3** as a red crystalline solid after recrystallisation. Its ^{31}P NMR spectrum at 250 K is almost identical to that of complex **1** and indicates a *mer* geometry for the phosphorus atoms. The IR spectrum in CsI shows absorptions for unco-ordinated and co-ordinated keto functions at 1672 and 1573 cm^{-1}, respectively. When complex **3** was dissolved in toluene or CH_2Cl_2 an equilibrium was established with complex **2** and free L, Scheme 1. Related chemistry has been observed previously for analogous ruthenium complexes with ester- and ether-phosphines.[6,10] Furthermore, a variable-temperature ^{31}P-$\{^1H\}$ NMR study of complexes analogous to **3** with the functional ligands $Ph_2PCH_2C(O)OEt$ or $Ph_2PCH_2CH_2OMe$ revealed dynamic behaviour, with the exchange of monodentate and chelating *trans* phosphines.[5,10] The free energies of activation reported were 55.6 and 49.1 kJ mol^{-1} respectively. We have measured a value of 63.7 ± 0.7 kJ mol^{-1} for **3**,[11] indicating stronger bonding to the metal by the keto function than the ester or ether group (dissociative pathway) or less propensity of the unco-ordinated keto group to co-ordinate to the metal and displace the bound keto function in a seven-co-ordinate transition state (associative pathway). The cleavage of the M–O (ketone) bond has also been found to be more difficult than M–O (ester) in

Table 1 Selected ^{31}P NMR parameters

Compound	δ_C [a]	δ_L [b]	Δ_C [c]	Δ_R [d]	Non-chelated analogue
$[RuCl_2(PEtPh_2)_3]$	30.4 [e]	−13.5 [f]	43.9	—	
1	37.3 [f]	−19.7 [f]	57.0	13.1	$PEtPh_2$
2	70.6 [g]	−18.0 [g]	88.6	20.0	P^X in 3
 3	20.8 (P^A) [f]	−19.7 [f]	40.5		
	37.3 (P^B) [f]		57.0	16.5	P^A in 3
				13.1	$PEtPh_2$
	48.9 (P^X) [f]		68.6	—	
				—	
 9	27.8 (P^A) [f]	−19.7 [f]	47.5		
	41.7 (P^B) [f]		61.4	13.9	P^A in 9
	54.5 (P^X) [f]		74.2	5.6	P^X in 3

[a] The chemical shift in the complex. [b] The chemical shift in the free ketophosphine. [c] The co-ordination chemical shift (= $\delta_C - \delta_L$). [d] The ring contribution, defined as the co-ordination chemical shift of a chelated phosphine complex minus the co-ordination chemical shift of an equivalent phosphorus in a non-chelated analogue. [e] Phosphorus *trans* to $PEtPh_2$, in $CDCl_3$. [f] In CD_2Cl_2. [g] In C_6D_6.

complexes of formula *mer,cis*-$[RhCl_3\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}]$.[12]

In Ni, Pd and Pt complexes containing two P-bound $Ph_2PCH_2C(O)Ph$ ligands, thermal cleavage of the P–CH_2 bond has been previously shown to lead to acetophenone and chelating $Ph_2PCH{=}C(Ph)OPPh_2$.[13] No reaction occurred on refluxing solutions of 2 in toluene or ethanol demonstrating a stabilisation of the P–CH_2 bond upon chelation. However, refluxing solutions of 3 in toluene or *p*-xylene yielded a mixture of compounds: acetophenone was detected by ^1H NMR and the ^{31}P NMR signals observed in the range δ 160–140 suggest formation of phosphine–phosphinite ligands by cleavage of the P–CH_2 bond. Phosphine–phosphinite complexes were also obtained from refluxing a mixture of $[RuCl_2(PPh_3)_3]$ with 4 equivalents of L in hexane–ethanol. The presence of two isomers containing a P(O) phosphorus atom was inferred from the ^{31}P NMR spectrum which contained two triplets at δ 147 and 151, respectively. These isomers could not be separated by recrystallisation from CH_2Cl_2–pentane.

The ^{31}P NMR chemical shifts of complexes 1–3 are given in Table 1. Whereas the co-ordination chemical shift $\Delta_C = \delta_C - \delta_L$ measures a net change in the chemical shift upon complexation of a ligand, the 'ring-contribution' parameter Δ_R, defined as the difference between the co-ordination chemical shift, Δ_C, of a chelating phosphine and that of a non-chelated analogue,[14] is characteristic of the effect of chelation. Values were obtained from internal comparison of the ^{31}P NMR chemical shifts in complexes 3 and 9 (see below), and by comparison with $[RuCl_2(PEtPh_2)_3]$[9] where $PEtPh_2$ was taken as the closest non-chelating analogue to the ketophosphine $Ph_2PCH_2C(O)Ph$ (Table 1). The values of Δ_R for L were in the range δ 5.6–20 against 9–12 for rhodium(III) complexes.[12]

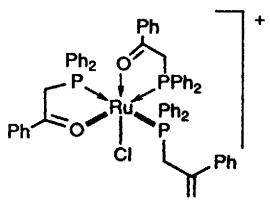
Cationic Ruthenium(II) *Complexes.*—Crystals of 2 obtained from CH_2Cl_2–pentane take much longer to solubilise in toluene than those obtained from chlorobenzene–pentane. We ascribe this difference to partial dissociation of a chloride ligand of 2 in CH_2Cl_2 leading to the ionic complex $[RuCl\{Ph_2PCH_2C(O)Ph\}_2]Cl$ 6. Indeed, the 400 MHz ^1H NMR spectrum of 2 in CH_2Cl_2 contains, in addition to the 'filled-in doublet' due to the PCH_2 protons of 2, four doublets of doublets with typical $^2J(PH)$ and $^2J(HH)$ couplings.[15] We assign them to the diastereotopic methylene protons PCH^AH^B and $P'CH^{A'}H^{B'}$ of 6. In CD_2Cl_2 *ca.* 40% of 6 is present. The ^{31}P-{^1H} NMR spectrum contains resonances for 6 which are typical of non-equivalent phosphines (AB pattern), with *J*(PP) 36.5 Hz characteristic of a *cis* geometry. However the detailed structure cannot be given unambiguously. Related five-co-ordinate Ru^{II} complexes with diphosphines $R_2P(CH_2)_nPR_2$ forming at least a five-membered ring (R = Et, C_6H_{11}, $n = 2$; R = Ph, n = 2, 3 or 4)[16] or an ether phosphine[10] have also been reported but the latter resisted full structural elucidation. The formation of the bromo- and iodo-derivatives of 2 is likely to proceed *via* the five-co-ordinated species $[RuCl\{Ph_2PCH_2C(O)Ph\}_2]^+$ which would readily undergo halide metathesis. The neutral complex 4 in CH_2Cl_2 formed 20% of the ionic species $[RuBr\{Ph_2PCH_2C(O)Ph\}_2]Br$ 7, whereas 5 did not dissociate iodide (NMR evidence). For the complexes *trans,cis,cis*-$[RuX_2\{Ph_2PCH_2C(O)Ph\}_2]$ (X = Cl, Br or I) in CH_2Cl_2 the strength of the Ru–X bond increases in the order Cl < Br < I.

The ionic complex $[RuCl\{Ph_2PCH_2C(O)Ph\}_2]SbF_6$ 8 was prepared from 2 using the halide abstractor $AgSbF_6$ in tetrahydrofuran (thf). In co-ordinating solvents isomers are present and the ^{31}P NMR data of a $(CD_3)_2CO$ solution of 8 showed an AB pattern for the major isomer (80%) with *J*(PP) in the typical range for *cis*-phosphines. The ^1H NMR spectra in CD_3CN contained characteristic patterns for the PCH^AH^B and $P'CH^{A'}H^{B'}$ protons. Reaction of the ketophosphine with 8 led mainly to $[RuCl\{Ph_2PCH_2C(O)Ph\}_2\{Ph_2PCH_2C(O)Ph\}]SbF_6$ the cation of which was identified by comparison of its ^{31}P NMR spectrum with that of $[RuCl\{Ph_2PCH_2C(O)Ph\}_2\{Ph_2PCH_2C(O)Ph\}]PF_6$ 9 prepared by reaction of complex 3 with $TlPF_6$ (Scheme 1). In the ^1H NMR spectrum of 9, the three PCH_2 groups appear as complex multiplets owing to inequivalence (ABX spin systems). The ^{31}P NMR data contains an ABX pattern which indicates three phosphorus atoms in a meridional arrangement with a 'triplet' (overlapping doublet

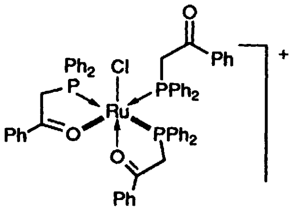
Table 2 The ^{31}P NMR chemical shifts of different phosphine ligands as a function of the *trans* ligand

Ligand	δ_P	Complex
PPh_3	20.8[a], 43.5[b]	1
Monodentate $Ph_2PCH_2C(O)Ph$	20.8[a], 48.9[b]	3
	27.8[a]	9
Chelating $Ph_2PCH_2C(O)Ph$	37.3[a]	1
	70.6[b]	2
	37.3[a]	3
	41.7[a], 54.5[b]	9
Chelating $Ph_2PC(H){=}C(Ph)O^-$	35.9[a], 46.6[c]	11b
	44.6[c]	11a

[a] Ligand *trans* to P. [b] *trans* to ketone oxygen [c] *trans* to enolato oxygen.



9a

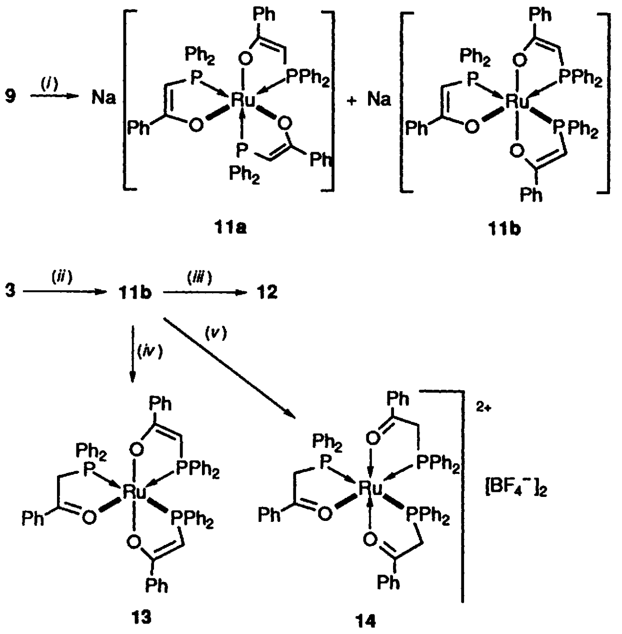


9b

of doublets) at δ 54.5 for the *cis* P atom whereas the *trans* P nuclei show a coupling of 320 Hz. In contrast to **3** this complex does not display dynamic behaviour at room temperature. Comparison of its ^{31}P NMR data with those of complexes having P- and P,O-bound phosphines (Table 2) suggests structure **9a** rather than **9b** with the *cis* P atoms each being part of a chelate ring. The analogous ether phosphine complex with $Ph_2PCH_2CH_2OMe$ adopts a facial geometry.[10b]

The IR data for the Ru–Cl bonds *trans* to the oxygen donor in **9** and *trans* to chloride in complexes **1–3** have a similar strength [ν(Ru–Cl) 315 *vs. ca.* 325 cm^{-1}, respectively]. Chloride abstraction by $TlPF_6$ is facile in the case of **2** and **3**, whereas it is solvent dependent for **9**. In CH_2Cl_2 at 25 °C or in acetone at 50 °C only mixtures were obtained, as shown by ^{31}P NMR spectroscopy, which contained mainly the starting material. A minor product at δ 57.2 was later identified as the dicationic *fac*-$[Ru\{Ph_2PCH_2C(O)Ph\}_3]^{2+}$ (see below). However, the reaction with an excess of $TlPF_6$ at 50 °C in MeCN, where the solvation energy terms are higher than in acetone or CH_2Cl_2, afforded yellow crystals of the dicationic complex *trans,cis,cis*-$[Ru\{Ph_2PCH_2C(O)Ph\}_2(NCMe)_2][PF_6]_2$ **10**. These reactions are a good example of the importance of solvation effects in driving substitution reactions involving charged leaving groups.[17] Removal of the chloride ion was confirmed by elemental analysis. The IR spectrum shows strong absorptions for bidentate β-ketophosphine ligands and the hexafluorophosphate anion at 1564 and 838 cm^{-1}, respectively, and the ^{31}P NMR spectrum in acetonitrile shows a singlet (chelating L) and a septet (PF_6), indicating equivalent ketophosphines. A single crystal X-ray study of **10** confirmed the *cis* arrangement of the bidentate ketophosphine ligands (see below). These reactions are summarised in Scheme 1.

Phosphino Enolate Ruthenium(II) *Complexes*.—Treatment of the ionic complex **9** with NaH in thf afforded the yellow isomers *fac*- and *mer*-$Na[Ru\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}_3]$ **11a** and **11b**, respectively (Scheme 2). The ratio of **11a** to **11b** depended strongly on the reaction temperature: 9:1 at 25 °C, but 1:4 at 50 °C as indicated by ^1H and ^{31}P NMR spectroscopy. The facial isomer gave one ^{31}P-$\{^1H\}$ NMR signal at δ 44.6 due to equivalent phosphorus atoms and a singlet at δ 5.45 in the ^1H NMR spectrum for the enolate protons. The spin system for the phosphorus atoms of the meridional isomer leads to an ABX pattern, with an apparent triplet for the *cis* P nucleus at δ 42.6 (X part). The triplet at δ 37.0 (AB part) results from a signal separation comparable to the values of $J(P^AP^X)$ and $J(P^BP^X)$ couplings of 29 Hz for the *trans* P nuclei. In benzene a doublet at δ 35.9 is observed for the *trans* P nuclei. Three signals are found in the ^1H NMR (benzene) at δ 5.94, 5.65 and 5.49 for the enolate protons; the most deshielded signal is assigned to the chemically dissimilar PCH proton of the phosphino enolate *cis* to the other phosphorus atoms.



Scheme 2 (*i*) NaH, thf; (*ii*) NaOMe, toluene; (*iii*) 15-crown-5; (*iv*) H_2O; (*v*) HBF_4

Heating a toluene solution of a 1:1 mixture of **11a** and **11b** to 100 °C in C_7D_8 led slowly to a 2:1 *mer*:*fac* isomer ratio (^1H NMR). For the analogous neutral cobalt(III) tris(enolato) complexes *mer*- and *fac*-$[Co\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}_3]$, conversion was also found to occur slowly in refluxing toluene.[18]

In order to obtain selectively one isomer of the anion $[Ru\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}_3]^-$, $[RuCl_2(PPh_3)_3]$ was treated with 3 equivalents of L and NaOMe in toluene. The intermediate complex **3** already has the phosphorus atoms in a *mer* arrangement and indeed, **11b** was isolated in high yield with only traces of the *fac* isomer. By adding 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5) to a solution of **11b** crystals could be grown from thf–ether–pentane, which proved suitable for X-ray diffraction, and this established their formulation as $[Na(15\text{-crown-}5){\cdot}H_2O]$-$[mer\text{-}Ru\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}_3]{\cdot}thf$ **12** (Figs. 3 and 4).

On standing, a yellow benzene solution of **11b** slowly turns violet. The formation of a neutral [bis(enolato) ketophosphine] complex $[Ru\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}_2\{Ph_2PCH_2C(O)Ph\}]$ **13** was indicated by ^1H, ^{31}P NMR and IR spectroscopic methods (Scheme 2). Traces of water are likely to be the proton source, as KBr pellets of **11b** turned violet with moisture and developed an absorption at 1575 cm^{-1} due to chelating ketophosphine. Addition of HCl (ether solution) to a yellow toluene solution of **11b** resulted in a colour change to violet, suggesting again formation of **13**. On further addition, an orange precipitate appeared, which produced a red solution, from which **2** could be isolated. These observations are consistent with a stepwise protonation reaction. Similarly, a CH_2Cl_2 solution of complex **11b** became first dark violet upon dropwise addition of 3 equivalents $HBF_4{\cdot}Et_2O$, consistent with formation of **13**, then red and finally orange. Filtration and layering with diethyl ether yielded orange crystals of the bis-cationic complex *mer*-$[Ru\{Ph_2PCH_2C(O)Ph\}_3][BF_4]_2$ **14** (Scheme 2). The $^{31}P-\{^1H\}$ NMR spectrum showed an ABX spectrum for **14** and a small peak at δ 57.2 due to *fac*-$[Ru\{Ph_2PCH_2C(O)Ph\}_3]^{2+}$ (see above). Thus the protonation takes place with retention of the geometry around the metal centre. It is interesting that the analogous ether phosphine complex with $Ph_2PCH_2CH_2OMe$ adopts a facial geometry.[10b]

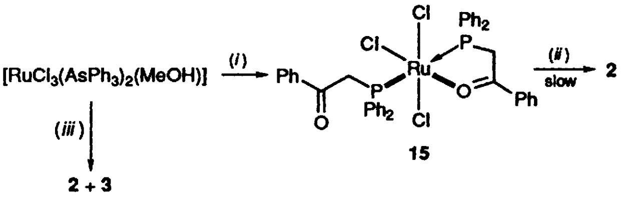
Complex **11b** is more reactive towards HBF_4 than the related cobalt(III) tris(enolate) complex $[Co\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}_3]$ and this is likely to be the result of the negative charge of the former.

Ruthenium(III) *Complexes*.—When 2 equivalents of L were treated in warm toluene with $[RuCl_3(AsPh_3)_2(MeOH)]$, green crystals were obtained in 35% yield after work-up (Scheme 3). Elemental analysis indicated the formula $[RuCl_3L_2]$. Owing to paramagnetism, no valuable NMR information could be obtained. Infrared absorptions at 1670 and 1555 cm^{-1} were characteristic of unco-ordinated and co-ordinated keto groups, respectively. The FIR spectrum shows a strong band at 333 cm^{-1} and two very weak bands for the ruthenium–chloride stretches. Frequencies and intensities of the FIR spectrum were nearly identical to those of the analogous rhodium and ruthenium complexes *mer,trans*-$[RhCl_3\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}]$[12] and *mer*-$[RuCl_3(PMe_2Ph)_3]$.[19] Thus we propose the same octahedral geometry for the ruthenium complex with a meridional arrangement for the chlorides, *trans* phosphines and the sixth co-ordination site occupied by the keto function: *mer,trans*-$[RuCl_3\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}]$ **15**. The corresponding complex with the ester phosphine $Ph_2PCH_2C(O)OEt$ has been shown by X-ray diffraction to also have a *mer,trans* structure.[6]

Complex **15** is easily reduced: a green CH_2Cl_2 or toluene solution slowly becomes red and *trans,cis,cis*-$[RuCl_2\{Ph_2PCH_2C(O)Ph\}_2]$ **2**, identified by its ^1H NMR spectrum, is formed. Refluxing a solution of $[RuCl_3(AsPh_3)_2(MeOH)]$ and 3 equivalents of L in benzene for 2 h also resulted in reduction with formation of **2** and **3**. This behaviour is in contrast to the reported stability of *mer*-$[RuCl_3L'_3]$ complexes towards reduction. They are synthesised from $[RuCl_3(AsPh_3)_2(MeOH)]$ and 4 equivalents of L′ (L′ = PPh_3, $PMePh_2$, $PEtPh_2$ or PMe_2Ph) in refluxing benzene and can be recrystallised unchanged from CH_2Cl_2–pentane. Reduction occurred only when a ten-fold excess of $PMePh_2$ was used, leading to $[RuCl_2(PMePh_2)_3]$.[19] We conclude that the ketophosphine L in **15** makes reduction of the metal centre easier compared to aryl- and alkylaryl-phosphines in the *mer*-$[RuCl_3L'_3]$ complexes. That reduction of **15** occurs readily could possibly explain why only a mixture of Ru^{II} and Ru^{III} complexes was formed in its reaction with $TlPF_6$ in acetone, instead of a bis(chelated) Ru^{III} complex. These reactions are summarised in Scheme 3.

Hydrogenation of Hex-1-*ene*.—Under the conditions used (see Experimental section), the mono(ketophosphine) complex **1** is a very slow hydrogenation catalyst: the average rate of hydrogen uptake was *ca.* 0.1 cm^3 min^{-1} while the bis(chelate) complex **2** was inactive. Isomerisation of hex-1-ene to only *trans*-hex-2-ene occurred at about the same rate. For comparison, a hydrogen absorption of 260 cm^3 min^{-1} has been measured for $[Ru(H)Cl(PPh_3)_3]$, which is obtained under catalytic conditions by hydrogenolysis from $[RuCl_2(PPh_3)_3]$, the parent compound of **1**. No isomerisation of hex-1-ene has been observed in kinetic experiments with $[Ru(H)Cl(PPh_3)_3]$, but after 15 hours under nitrogen 7% of hex-1-ene was isomerised to only *trans*-hex-2-ene.[20]

The inactivity of **2** contrasts with the results reported with the bis(diphosphine) complex *cis*-$[RuCl_2(dcpe)_2]$ [dcpe = bis(dicyclohexylphosphino)ethane]. In its red dichloromethane solution the latter is in equilibrium with ionic penta-co-ordinated $[RuCl(dcpe)_2]Cl$ which, under an atmosphere of hydrogen, forms colourless $[RuCl(dcpe)_2(\eta^2\text{-}H_2)]^+$.[16] Subsequent reaction with base (NaOEt) under hydrogen leads to the homogeneous hydrogenation catalyst precursor *trans*-$[Ru(H)Cl(dcpe)_2]$.[21]



Scheme 3 (*i*) 2 L; (*ii*) in CH_2Cl_2 or toluene; (*iii*) 3 L, benzene, 2 h reflux

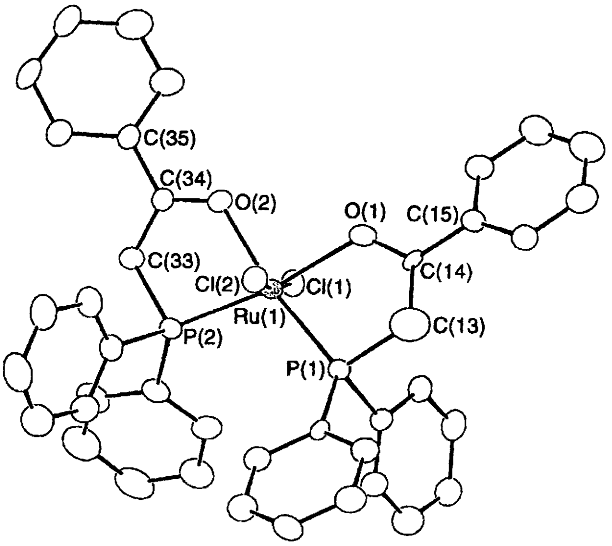


Fig. 1 View of the structure of complex **2** with the atom numbering scheme

A dichloromethane solution of **2** containing about 40% $[RuCl\{Ph_2PCH_2C(O)Ph\}_2]Cl$ failed to add hydrogen even under a pressure of 0.8 MPa (^1H NMR monitoring) and preserved its red colour. Apparently, co-ordination by two (diphenylphosphino)acetophenone ligands does not provide enough electron density to the metal to activate hydrogen. For the related rhodium(I) complexes $[Rh\{Ph_2PCH_2C(O)Ph\}_2]^+$[22] and $[Rh\{Ph_2PCH_2CH_2(O)R\}_2]$ (R = furfuryl)[23] the inactivity observed with hydrogen was also explained by the low basicity of the phosphines. In contrast, the corresponding rhodium complex with the more basic ether phosphine $(C_6H_{11})_2PCH_2CH_2OMe$ oxidatively adds H_2, O_2 and MeI.[24]

Crystal Structure of trans,cis,cis-$[RuCl_2\{Ph_2PCH_2C(O)Ph\}_2]$ **2**.—The molecular structure of the complex is shown in Fig. 1 and selected bond lengths and angles are listed in Table 3. The crystal structure consists of discrete molecular units separated by normal van der Waals contacts. The Ru centre is in a distorted octahedral environment with *trans* chloride ligands and two chelating ketophosphine ligands the phosphorus atoms (and oxygen atoms) of which are *cis* to each other. The chelating ligands have the same structural features. The five atoms Ru, P(1), P(2), O(1) and O(2) are almost coplanar (distances to the mean plane less than 0.1 Å), and the C(13) and C(33) carbon atoms are in a symmetrical position with respect to this plane (+0.59 and −0.54 Å, respectively). There are significant angular distortions from the ideal interligand angles (90°) due to the chelating phosphine bite angles of 82.0(2) and 82.1(2)° and to symmetrical bending of

Table 3 Selected bond distances (Å) and angles (°) for **2**

Ru–P(1)	2.226(2)	P(1)–C(13)	1.862(9)
Ru–P(2)	2.231(2)	P(2)–C(33)	1.864(8)
Ru–O(1)	2.156(5)	C(13)–C(14)	1.47(1)
Ru–O(2)	2.150(5)	C(33)–C(34)	1.48(1)
Ru–Cl(1)	2.401(2)	C(14)–O(1)	1.24(1)
Ru–Cl(2)	2.402(2)	C(34)–O(2)	1.23(1)
P(1)–Ru–O(1)	82.0(2)	Ru–P(1)–C(13)	100.0(3)
P(1)–Ru–P(2)	108.15(7)	Ru–O(1)–C(14)	120.9(5)
P(2)–Ru–O(2)	82.1(2)	P(1)–C(13)–C(14)	110.7(6)
P(1)–Ru–Cl(1)	98.65(8)	O(1)–C(14)–C(13)	120.4(7)
P(1)–Ru–Cl(2)	86.03(8)	Ru–P(2)–C(33)	99.4(3)
P(2)–Ru–Cl(1)	89.15(8)	Ru–O(2)–C(34)	121.2(5)
P(2)–Ru–Cl(2)	95.63(8)	P(2)–C(33)–C(34)	110.1(6)
Cl(1)–Ru–Cl(2)	172.0(1)	O(2)–C(34)–C(33)	120.3(7)
Cl(1)–Ru–O(1)	86.6(2)		
Cl(1)–Ru–O(2)	86.0(2)		

Cl(1) towards O(1) and Cl(2) towards O(2) [Cl(1)–Ru–Cl(2) 172.0(1)°]. The distortion of the chelate angle is compensated for by the large P(1)–Ru–P(2) angle [108.15(7)°] which also decreases the steric interactions between the phenyl substituents. The similar Ru–Cl(1) and Ru–Cl(2) distances of 2.401(2) and 2.402(2) Å are in the range found for *trans* ClRuCl arrangements in Ru^{II} phosphine complexes;[5,25] those of Ru–P(1) and Ru–P(2) [2.226(2) and 2.231(2) Å] are comparable to those in [$RuCl_2\{Ph_2PCH_2CH_2C(O)Me\}_2$] [2.224(2) Å][26] and considerably shorter than the average Ru–P distance usually found in six-co-ordinate Ru^{II} complexes with mutually *trans* phosphines[25] (around 2.4 Å) and in *trans*-[$RuCl_2\{Ph_2PCH_2C(O)OEt\}\{Ph_2PCH_2C(O)OEt\}_2$] where the Ru–P (chelate) distance is 2.363(1) Å;[5] the short Ru–P distance [2.266(1) Å, P *trans* to O] has been associated with the low *trans* influence of the ester oxygen. In **2** the Ru–O distances [2.156(5) and 2.150(5) Å] are shorter than that in [$Ru(SnCl_3)(CO)(PPh_3)_2(OCMe_2)$]·$Me_2CO$ [2.194(8) Å][27a] and close to the expected value for a Ru–O single bond (sum of the covalent radii 1.99 Å).[27b] This indicates a fairly strong interaction between the keto oxygen and the neutral metal centre. Comparison with Ru–O distances in the ester chelate [2.230(3) Å],[5] the ether phosphine complexes [$RuCl_2\{Ph_2P(o\text{-}C_4H_6OMe)\}_2$] (average 2.278 Å)[28] and the ether phosphine complex [$RuCl_2\{Ph_2PCH_2CH_2(O)Me\}_2$] [average 2.263(4) Å] shows that the Ru^{II}–O distance increases in the order ketone < ester < ether. Interestingly, we note that the Ru–O distance in *mer*-[$RuCl_3\{Ph_2PCH_2C(O)OEt\}\{Ph_2PCH_2C(O)OEt\}$] is only slightly shorter [2.143(5) Å].[29] The P–C and C–C bond lengths in the chelate rings [1.862(9), 1.864(9) and 1.47(1), 1.48(1) Å, respectively] in **2** are in agreement with a single bond character and those of the C–O bond [1.24(1) and 1.23(1) Å] with an appreciable double-bond character. Similar values have been found for this ligand in *trans,cis,cis*-[$RhCl_2\{Ph_2PCH_2C(O)Ph\}_2$]$PF_6$ and in *cis*-[$Rh\{Ph_2PCH_2C(O)Ph\}_2$]PF_6.[12,22]

Crystal Structure of trans,cis,cis-[$Ru\{Ph_2PCH_2C(O)Ph\}_2(NCMe)_2$][$PF_6$]$_2$ **10**.—A view of the molecular structure is shown in Fig. 2. The relatively poor quality of the crystals limited the quality of the structure, which will therefore not be discussed in detail. However, it establishes the spatial arrangement of the ligands. Selected bond lengths and angles are listed in Table 4. The structure of **10** is related to that of **2** with chloride ligands replaced by acetonitrile donors. There are significant differences between the Ru–O distances: 2.20(1) and 2.13(1) Å, and the Ru–N distances are also different with values of 2.09(1) and 1.98(1) Å.

Table 4 Selected bond distances (Å) and angles (°) for **10**

Ru–P(1)	2.276(6)	P(1)–C(13)	1.86(2)
Ru–P(2)	2.254(6)	P(2)–C(33)	1.84(2)
Ru–O(1)	2.20(1)	C(13)–C(14)	1.63(2)
Ru–O(2)	2.13(1)	C(33)–C(34)	1.38(2)
Ru–N(1)	2.09(1)	C(14)–O(1)	1.22(3)
Ru–N(2)	1.98(1)	C(34)–O(2)	1.26(2)
N(1)–C(43)	1.07(2)	C(14)–O(15)	1.43(2)
N(2)–C(41)	1.17(2)	C(34)–C(35)	1.53(2)
C(43)–C(44)	1.43(2)	C(41)–C(42)	1.47(2)
P(1)–Ru–P(2)	106.2(2)	Ru–P(1)–C(13)	103.1(6)
O(1)–Ru–O(2)	92.6(5)	Ru–P(2)–C(33)	97.5(5)
N(1)–Ru–N(2)	173.3(4)	Ru–O(1)–C(14)	120.7(9)
P(1)–Ru–O(1)	80.6(4)	Ru–O(2)–C(34)	121.9(8)
P(1)–Ru–O(2)	172.4(3)	P(1)–C(13)–C(14)	103(1)
P(2)–Ru–O(1)	172.6(4)	P(2)–C(33)–C(34)	115(1)
P(2)–Ru–O(2)	80.9(3)	C(33)–C(34)–O(2)	118(1)
O(1)–Ru–N(1)	83.9(5)	C(13)–C(14)–O(1)	121(1)
O(1)–Ru–N(2)	89.9(5)		
O(2)–Ru–N(1)	92.1(4)		
O(2)–Ru–N(2)	85.6(5)		

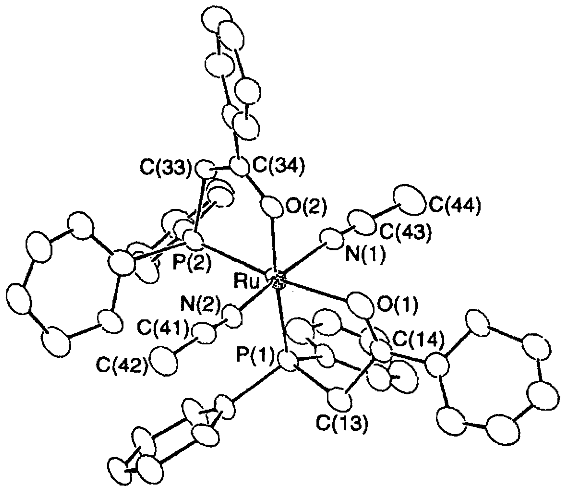


Fig. 2 View of the structure of the dication in complex **10** with the atom numbering scheme

Crystal Structure of [Na(15-crown-5)·H_2O][*mer*-$Ru\{Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O)Ph\}_3$]·thf **12**.—In the crystals, [*mer*-$Ru\{Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O)Ph\}_3$]$^-$ anions, [Na(15-crown-5)·H_2O]$^+$ cations and tetrahydrofuran molecules of solvation are present. Views of the anion and of the cation are shown in Figs. 3 and 4, respectively, together with the atom numbering schemes; selected bond distances and angles are given in Table 5. The anion is chiral by virtue of the heterobidentate nature of the chelating ligands. As the compound crystallises in a centrosymmetric space group, both Δ and Λ enantiomers of the anion are present in the crystals. The Ru atom displays an octahedral co-ordination involving three P and three O atoms from three chelating phosphino enolate ligands, which form five-membered rings with the metal. In all three rings, the metal atom is only slightly displaced out of the almost planar PCCO moiety. The octahedral co-ordination around the Ru atom is only slightly distorted and the interligand bond angles are in the range 81.3(2)–100.3(2)°. No particular strain is associated with the chelating ligands, as their bite angles in the range 81.3(2)–83.0(2)° are favourable for this co-ordination mode. The Ru–P(2) and Ru–P(3) bonds, *trans* to one another, have comparable lengths of 2.326(3) and 2.338(4) Å, respectively, whereas the Ru–P(1) bond distance, 2.242(3) Å, *trans* to an oxygen atom, is much shorter. The mutually *trans* ruthenium–

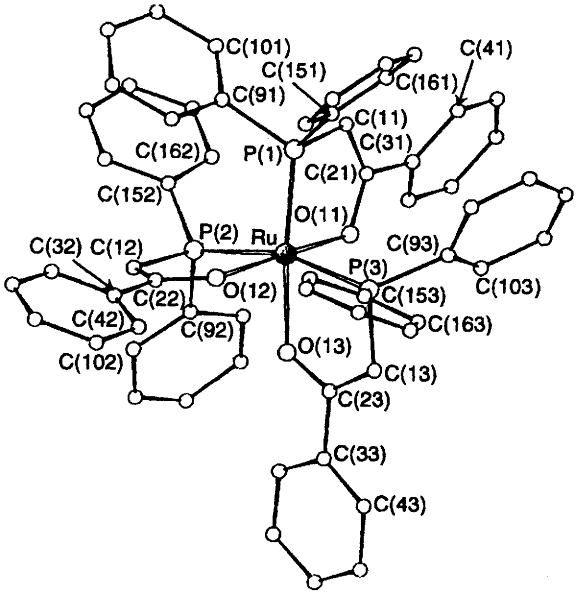


Fig. 3 View of the structure of the anion in complex **12** with the atom numbering scheme

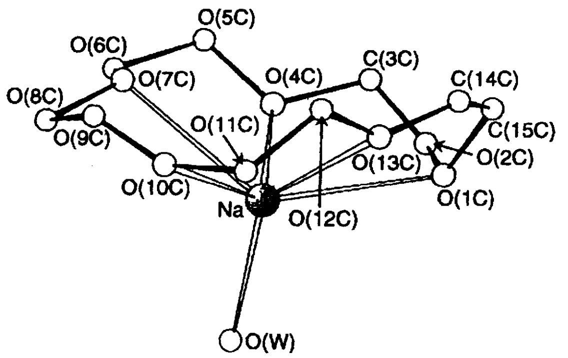


Fig. 4 View of the structure of the cation in complex **12** with the atom numbering scheme

Table 5 Selected bond distances (Å) and angles (°) for **12**

Ru–P(1)	2.242(3)	Ru–P(2)	2.326(3)
Ru–P(3)	2.338(4)	Ru–O(11)	2.107(7)
Ru–O(12)	2.095(7)	Ru–O(13)	2.120(7)
P(1)–C(11)	1.771(12)	O(11)–C(21)	1.308(14)
C(11)–C(21)	1.358(18)	C(21)–C(31)	1.497(17)
P(2)–C(12)	1.742(12)	O(12)–C(22)	1.306(15)
C(12)–C(22)	1.372(16)	C(22)–C(32)	1.477(17)
P(3)–C(13)	1.771(11)	O(13)–C(23)	1.298(16)
C(13)–C(23)	1.330(15)	C(23)–C(33)	1.536(15)
Na–O(1C)	2.603(16)	Na–O(4C)	2.477(15)
Na–O(7C)	2.585(19)	Na–O(10C)	2.617(18)
Na–O(13C)	2.474(17)	Na–O(W)	2.259(10)
P(1)–Ru–P(2)	96.8(1)	P(1)–Ru–P(3)	99.4(1)
P(2)–Ru–P(3)	163.2(1)	P(1)–Ru–O(11)	83.0(2)
P(1)–Ru–O(12)	100.3(2)	P(1)–Ru–O(13)	171.0(2)
P(2)–Ru–O(11)	95.6(2)	P(2)–Ru–O(12)	81.6(2)
P(2)–Ru–O(13)	83.4(2)	P(3)–Ru–O(11)	90.8(2)
P(3)–Ru–O(12)	91.1(2)	P(3)–Ru–O(13)	81.3(2)
O(11)–Ru–O(12)	175.9(3)	O(11)–Ru–O(13)	88.0(3)
O(12)–Ru–O(13)	88.6(3)	Ru–P(1)–C(11)	102.1(4)
Ru–O(11)–C(21)	115.3(6)	P(1)–C(11)–C(21)	112.5(8)
Ru–P(2)–C(12)	101.3(4)	Ru–P(3)–C(13)	99.3(4)
Ru–O(12)–C(22)	117.1(7)	Ru–O(13)–C(23)	117.9(7)
O(11)–C(21)–C(11)	127.0(10)	O(11)–C(21)–C(31)	114.6(9)
P(2)–C(12)–C(22)	113.5(8)	O(12)–C(22)–C(12)	126.4(11)
P(3)–C(13)–C(23)	116.4(9)	O(13)–C(23)–C(13)	124.9(11)
C(11)–C(21)–C(31)	118.4(11)	O(13)–C(23)–C(33)	112.1(9)
O(12)–C(22)–C(32)	111.6(10)	C(12)–C(22)–C(32)	122.0(10)
C(13)–C(23)–C(33)	123.0(10)	O(10C)–Na–O(W)	119.9(5)
O(13C)–Na–O(W)	138.9(5)	O(7C)–Na–O(W)	108.9(5)
O(10C)–Na–O(13C)	69.1(6)	O(7C)–Na–O(10C)	68.7(6)
O(7C)–Na–O(13C)	111.3(6)	O(4C)–Na–O(13C)	113.5(5)
O(4C)–Na–O(W)	90.5(4)	O(4C)–Na–O(7C)	65.6(6)
O(4C)–Na–O(10C)	131.3(6)	O(1C)–Na–O(13C)	67.1(6)
O(1C)–Na–O(W)	97.1(5)	O(1C)–Na–O(7C)	123.8(6)
O(1C)–Na–O(10C)	135.9(6)	Na–O(1C)–C(15C)	106.7(17)
O(1C)–Na–O(4C)	65.1(5)		

oxygen bonds Ru–O(11) and Ru–O(12), have comparable distances of 2.107(7) and 2.095(7) Å, respectively, whereas Ru–O(13) [2.120(7) Å] *trans* to a phosphorus atom, is slightly longer. A shorter Ru–O distance has been reported in [{Ru(μ-Cl)[$Ph_2PCH\cdots C(\cdots O)Ph$](CO)$_2$}$_2$] [2.065(3) Å, *trans* to CO].[30] From the values of the O–C, C–C and C–P bond distances in the chelate rings [in the range 1.298(16)–1.308(14), 1.330(15)–1.372(16) and 1.742(12)–1.771(12) Å, respectively], it can be noted that the C–C bond displays an appreciable double-bond character although electron delocalisation occurs within the P–C$\cdots$C$\cdots$O system. The structure of the anion in **12** is very similar to that found in the neutral *mer*-[Co{$Ph_2PCH\cdots C(\cdots O)Ph$}$_3$].[18]

In the [Na(15-crown-5)·H_2O]$^+$ cation, Na$^+$ interacts with all five oxygen atoms of the 15-crown-5 molecule [Na–O distances in the range 2.474(17)–2.617(18) Å] and completes its octahedral co-ordination with a water molecule [Na–O(W) 2.259(10) Å].

Experimental

(*a*) *Reagents and Physical Measurements*.—All reactions were performed by using Schlenk-type flasks under argon and standard high vacuum-line techniques. All solvents were analytical grade and distilled under argon from sodium–benzophenone (toluene, diethyl ether, thf), sodium–potassium (pentane), P_2O_5 (dichloromethane) or CaH_2 (acetonitrile). IR spectra were recorded in the 4000–200 cm^{-1} region on a Perkin-Elmer 883 spectrometer. Samples were prepared as Nujol mulls, CsI discs or in solution between CaF_2 plates. Proton NMR spectra were recorded at 200 MHz on a FT Bruker AC-F 200, at 400 MHz on a FT Bruker MSL 400 and ^{31}P-{^{1}H} spectra at 81 MHz on a FT Bruker CXP 200 instrument. Elemental analyses were performed by the Institut Français du Pétrole and ATX. Hex-1-ene (Aldrich) was freed from peroxides by passage through an alumina column and distilled from sodium.

(*b*) *Syntheses*.—The compound $Ph_2PCH_2C(O)Ph$ (L) was prepared by the method previously described[13a] and the complexes [$RuCl_3(AsPh_3)_2(MeOH)$] and [$RuCl_2(PPh_3)_3$] were prepared as described in the literature.[31]

trans,mer-[$RuCl_2${$Ph_2PCH_2C(O)Ph$}(PPh_3)$_2$] **1**. Solid L (0.142 g, 0.47 mmol) was added at 25 °C to a stirred dark brown solution of [$RuCl_2(PPh_3)_3$] (0.47 g, 0.49 mmol) in toluene (20 cm^3). A colour change to dark red occurred instantaneously and after stirring for 10 min pentane was added. The red precipitate was filtered off and recrystallised from toluene–pentane. Dark red crystals were separated, washed with pentane and dried under vacuum to yield product **1** (0.393 g, 80%) (Found: C, 67.0; H, 4.6. $C_{56}H_{47}Cl_2OP_3Ru$ requires C, 67.2; H, 4.7%). IR: (CsI) ν(CO) 1570s and ν(Ru–Cl) 325m; (C_7H_8) ν(CO) 1572m cm^{-1}; NMR: ^{1}H (C_6D_6), δ 8.7–6.0 (45 H, m, 9 Ph) and 4.33 [2 H, d, *J*(PH) 9.8, PCH_2]; ^{31}P-{^{1}H} (C_7H_8–C_6D_6), δ 43.5 [1 P, t, *J*(PP) 30.5, PPh_3 *trans* to oxygen], 37.3 [1 P, dd, *J*(PP) 339 and 30.5, PCH_2] and 20.8 [1 P, dd, *J*(PP) 339 and 30.5 Hz, PPh_3 *trans* to P].

trans, cis, cis-[$RuCl_2${$Ph_2PCH_2C(O)Ph$}$_2$] **2**. A solution of L

(1.04 g, 3.4 mmol) in CH_2Cl_2 (15 cm^3) was added to a solution of $[RuCl_2(PPh_3)_3]$ (1.63 g, 1.7 mmol) in CH_2Cl_2 (20 cm^3). The solution changed colour immediately from dark brown to red. After being stirred for 10 min, the solution was concentrated and **2** precipitated by addition of pentane (50 cm^3) as an air-stable red powder, which was washed with pentane and dried *in vacuo*. Recrystallisation from chlorobenzene–pentane yielded red crystals (0.988 g, 75%) (Found: C, 60.9; H, 4.5. $C_{40}H_{34}Cl_2O_2P_2Ru$ requires C, 61.5; H, 4.4%). IR: (CsI) ν(CO) 1570s and ν(Ru–Cl) 330m; (C_7H_8) ν(CO) 1570s cm^{-1}; NMR: ^1H (C_6D_6), δ 8.5–6.6 (30 H, m, 6 Ph) and 4.30 [2 H, 'filled-in' d, *J*(PH) 11.4 Hz, PCH_2]; ^{31}P-{^1H} (C_7H_8–C_6D_6), δ 70.6 (s).

trans,mer-$[RuCl_2\{Ph_2PCH_2C(O)Ph\}\{Ph_2PCH_2C(O)Ph\}_2]$ **3**. Solid L (0.152 g, 0.50 mmol) was added at 25 °C under stirring to a dark red suspension of **2** (0.39 g, 0.50 mmol) in toluene (20 cm^3). The homogeneous red solution was stirred for 30 min, pentane was added and the product was filtered off. It was washed with pentane and recrystallised from toluene–pentane to give dark red crystals, which were separated, washed with pentane and dried under vacuum to yield **3** (0.488 g, 90%) (Found: C, 66.6; H, 4.85; Cl, 6.55. $C_{60}H_{51}Cl_2O_3P_3Ru$ requires C, 66.4; H, 4.75; Cl, 6.55%). IR: (CsI) ν(CO) 1672s and 1573s, ν(Ru–Cl) 322m; (Nujol) ν(CO) 1666m and 1567s cm^{-1}; NMR: ^1H (C_6D_6, 253 K), δ 7.9–6.7 (45 H, m, 9 Ph), 4.60 [2 H, d, *J*(PH) 6.3, PCH_2], 4.46 [2 H, d, *J*(PH) 8.3, PCH_2] and 4.22 [2 H, d, *J*(PH) 9.8 Hz, PCH_2]; ^{31}P-{^1H} (C_7H_8–C_6D_6, 250 K), δ 48.9 [1 P, t, *J*(PP) 30.5, P(monodentate L) with P *trans* to O], 37.3 [1 P, dd, *J*(PP) 339 and 30.5, P(chelate)] and 20.8 [1 P, dd, *J*(PP) 339 and 30.5 Hz, P(monodentate L) with P *trans* to P].

trans,cis,cis-$[RuBr_2\{Ph_2PCH_2C(O)Ph\}_2]$ **4**. Complex **2** (0.14 g, 0.18 mmol) and NaBr (0.37 g, 3.6 mmol) were stirred in CH_2Cl_2 (10 cm^3) for 4 d, filtered, heptane added and the solution concentrated *in vacuo* to yield **4** as a red solid isolated by filtration (0.156 g, 89%) (Found: C, 54.9; H, 3.8. $C_{40}H_{34}Br_2O_2P_2Ru$ requires C, 55.25; H, 3.95%). IR: (KBr) ν(CO) 1565s; (CD_2Cl_2) ν(CO) 1570s cm^{-1}; NMR: ^1H (CD_2Cl_2), δ 8.5–6.6 (30 H, m, 6 Ph) and 4.69 [2 H, 'filled-in' d, *J*(PH) 11.7 Hz, PCH_2]; ^{31}P-{^1H} (CH_2Cl_2–CD_2Cl_2), 73.2 (s) + peaks of **7**; (C_7H_8–C_6D_6), δ 74.7(s).

trans,cis,cis-$[RuI_2\{Ph_2PCH_2C(O)Ph\}_2]$ **5**. Complex **2** (0.15 g, 0.19 mmol) and KI (0.17 g, 1.0 mmol) were stirred in CH_2Cl_2 (20 cm^3) for 4 d. The filtered solution was evaporated to dryness and the solid obtained was recrystallised from PhCl–pentane to yield red crystals (0.162 g, 78%) (Found: C, 51.0; H, 3.4. $C_{40}H_{34}I_2O_2P_2Ru{\cdot}C_6H_5Cl$ requires C, 51.3; H, 3.65%). IR: (CsI) ν(CO) 1564s; (CD_2Cl_2) ν(CO) 1567s cm^{-1}; NMR: ^1H (CD_2Cl_2), δ 8.5–6.6 (30 H, m, 6 Ph) and 4.81 [2 H, 'filled-in' d, *J*(PH) 10.7 Hz, PCH_2]; ^{31}P-{^1H} (CH_2Cl_2–CD_2Cl_2), δ 74.7 (s); (C_7H_8–C_6D_6), δ 76.4 (s).

$[RuCl\{Ph_2PCH_2C(O)Ph\}_2]Cl$ **6**. See text. Selected data: NMR: ^1H (CD_2Cl_2, 400 MHz): δ 4.79 [1 H, ABX system, *J*(PH^A) 10.7 and *J*(HH) 17.4, PCH^A] and 4.33 [1 H, ABX system, *J*(PH^B) 10.4 and *J*(HH) 17.4, PCH^B], 4.52 [1 H, A′B′X′ system, *J*($PH^{A'}$) 11.7 and *J*(HH) 17.0, $PCH^{A'}$] and 4.42 [1 H, A′B′X′ system, *J*($PH^{B'}$) 10.9 and *J*(HH) 17.0, $PCH^{B'}$]; ^{31}P-{^1H} (CD_2Cl_2), δ 70.8 [1 P, d, *J*(PP) 36.5] and 66.6 [1 P, d, *J*(PP) 36.6 Hz].

$[RuBr\{Ph_2PCH_2C(O)Ph\}_2]Br$ **7**. See text. Selected data: ^{31}P-{^1H} NMR (CH_2Cl_2–CD_2Cl_2), δ 69.9 [1 P, d, *J*(PP) 34.1] and 68.7 [1 P, d, *J*(PP) 33.9 Hz].

$[RuCl\{Ph_2PCH_2C(O)Ph\}_2]SbF_6$ **8**. The salt $AgSbF_6$ (0.086 g, 0.25 mmol) was added to a solution of **2** (0.19 g, 0.245 mmol) in thf (5 cm^3). Slowly the colour changed from red to orange-red. The turbid solution was filtered over Celite, evaporated to *ca*. 4 cm^3, and addition of diethyl ether precipitated an orange solid (0.204 g, 85%) (Found: C, 48.6; H, 3.45; Cl, 4.1. $C_{40}H_{34}ClF_6O_2P_4RuSb$ requires C, 49.0; H, 3.5; Cl, 3.6%). IR (CsI): ν(CO) 1568s, ν(SbF_6) 838vs, ν(Ru–Cl) 315 (br); NMR: ^1H (CD_3CN), superposition of ABX systems for the PCH_2 protons; ^{31}P-{^1H} [$(CD_3)_2CO$], see text, δ 74.4 [1 P, d, *J*(PP) 41] and 66.3 [1 P, d, *J*(PP) 36 Hz].

mer-$[RuCl\{Ph_2PCH_2C(O)Ph\}_2\{Ph_2PCH_2C(O)Ph\}]PF_6$ **9**. A suspension of $TlPF_6$ (0.042 g, 0.12 mmol) in CH_2Cl_2 (5 cm^3) was added to a solution of **2** (0.094 g, 0.12 mmol) and L (0.037 g, 0.12 mmol) in CH_2Cl_2 (5 cm^3). Overnight the colour changed from red to orange-red. The turbid solution was filtered over Celite, evaporated to *ca*. 2 cm^3, and addition of pentane precipitated the product as an orange powder, which was washed with pentane (0.139 g, 97%) (Found: C, 59.8; H, 4.3. $C_{60}H_{51}ClF_6O_3P_4Ru$ requires C, 60.3; H, 4.3%). IR: (CsI) ν(CO) 1677s and 1568s, ν(PF_6) 838vs, ν(Ru–Cl) 315 (br); (Nujol) ν(CO) 1669s and 1564s cm^{-1}; NMR: ^1H (CD_2Cl_2), δ 8.0–6.9 (45 H, m, 9 Ph), 5.03 [1 H, m, *J*(PH) 6.1 and *J*(HH) 15.9, PCH], 4.86 [1 H, m, *J*(PH) 11.7 and *J*(HH) 17.1, PCH], 4.37 [1 H, m, *J*(PH) 10.2 and *J*(HH) 17.6, PCH], 4.05 [1 H, m, *J*(PH) 10.1 and *J*(HH) 18.2, PCH], 2.60–2.41 (2 H, complex m, PCH); ^{31}P-{^1H} (CH_2Cl_2–CD_2Cl_2), δ 54.5 [1 P, t, *J*(PP) 28, P(chelate) *trans* to oxygen], 41.7 [1 P, dd, *J*(PP) 320 and 29, P(chelate) *trans* to P], 27.8 [1 P, dd, *J*(PP) 320 and 28, P(monodentate L)] and −141.1 [1 P, spt, *J*(PF) 707 Hz, PF_6].

trans,cis,cis-$[Ru\{Ph_2PCH_2C(O)Ph\}_2(NCMe)_2][PF_6]_2$ **10**. Thallium hexafluorophosphate (0.064 g, 0.18 mmol) was added to a stirred solution of **9** (0.10 g, 0.085 mmol) in MeCN (10 cm^3) and the reaction mixture was heated to reflux. After 2 h the colour had changed from orange to yellow and the heating was stopped. The cold solution was filtered over Celite, evaporated to *ca*. 3 cm^3, and diethyl ether was added until the solution was cloudy. Air-stable yellow crystals formed overnight at −20 °C and were separated manually from an orange byproduct (0.064 g, 70%) (Found: C, 48.4; H, 3.6; N, 2.4. $C_{44}H_{40}F_{12}N_2O_2P_4Ru$ requires C, 48.85; H, 3.7; N, 2.6%). IR [poly(chlorotrifluoroethylene)]: ν(CO) 1564s, ν(PF_6) 838vs; ^{31}P-{^1H} NMR (CD_3CN): δ 59.3 [2 P, s, PCH_2(chelate) *trans* to oxygen] and −141.3 [2 P, spt, *J*(PF) 707 Hz].

$[Na][fac\text{-}Ru\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}_3]$ **11a**. An excess of NaH (0.036 g, 1.5 mmol) was added at room temperature to a stirred solution of **9** (0.19 g, 0.16 mmol) in thf (10 cm^3). A slow colour change developed over 9 h from red-violet to grey-green, yellow-green and to yellow. Filtration over Celite, evaporation to *ca*. 2 cm^3 and addition of pentane precipitated the yellow product, which was recrystallised from thf–pentane or CH_2Cl_2–pentane. The product distribution was 90% **11a** and 10% **11b**, (0.14 g, 85%). IR (thf): ν(C${\cdots}$O) + ν(C${\cdots}$C) 1530s cm^{-1}; NMR: ^1H (C_6D_6): 8.15–6.75 (45 H, m, aromatic), 5.45 (3 H, s, PCH); ^{31}P-{^1H} (thf–C_6D_6), 44.6 (s).

$[Na{\cdot}2thf][mer\text{-}Ru\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}_3]$ **11b·2thf**. *Method* (*a*). The same procedure was followed as for **11a**, but at 50 °C, the solution changing from black to yellow within 1 h. The product distribution was 80% **11b** and 20% **11a** (82%).

Method (*b*). Solid L (1.01 g, 3.3 mmol) was added to a stirred hot solution of $[RuCl_2(PPh_3)_3]$ (1.06 g, 1.1 mmol) in toluene (20 cm^3). After 3 min, NaOMe (7.94 cm^3 of a 0.46 mol dm^{-3} solution in MeOH) was added dropwise and the solution became red-violet and then yellow. It was concentrated, filtered over Celite, pentane was added and at −20 °C the yellow product precipitated. It was recrystallised from thf–pentane or chlorobenzene–pentane (0.91 g, 80%) (Found: C, 69.7; H, 5.4; P, 8.4. $C_{60}H_{48}NaO_3P_3Ru{\cdot}2thf$ requires C, 69.3; H, 5.5; P, 7.9%) IR (thf): ν(C${\cdots}$O) + ν(C${\cdots}$C) 1530s cm^{-1}; NMR: ^1H (C_6D_6), δ 8.10–6.60 (45 H, m, aromatic), 5.94 (1 H, s, PCH *trans* to O), 5.65 (1 H, s, PCHCO with O *trans* to O) and 5.49 (1 H, s, PCH); ($CDCl_3$), δ 5.65 (1 H, s, PCH *trans* to O), 5.36 (1 H, s, PCHCO with O *trans* to O), 5.23 (1 H, s, PCH), 3.30 (4 H, m, thf) and 1.62 (4 H, m, thf); ^{31}P-{^1H} (C_6D_6–C_7H_8), δ 46.6 [1 P, t, ^2J(PP) 30.5, P *trans* to O], 35.9 [1 P, d, ^2J(PP) 32, P *trans* to P]; (thf–C_6D_6), δ 42.6 [1 P, t, ^2J(PP) 30.5] and 37.0 [1 P, t, 2 overlapping d, ^2J(PP) 29.0 Hz].

$[Na(15\text{-}crown\text{-}5){\cdot}H_2O][mer\text{-}Ru\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}_3]{\cdot}thf$ **12**. The crown ether 15-crown-5 (30 μl, 0.15 mmol) was

Table 6 Crystal data and data collection parameters[a]

	2	**10**	**12**
Formula	$C_{40}H_{34}Cl_2O_2P_2Ru$	$C_{44}H_{40}F_{12}N_2O_2P_4Ru$	$C_{70}H_{70}NaO_9P_3Ru{\cdot}C_4H_8O$
M	780.74	1081.77	1344.40
Space group	$P2_1/n$	Cc	$P2_1/c$
Crystal dimensions/mm	0.1 × 0.2 × 0.1	0.2 × 0.3 × 0.2	0.23 × 0.26 × 0.32
Colour, habit	Red, pinacoïds	Yellow	Orange
a/Å	13.922(5)	23.105(4)	14.367(6)
b/Å	11.437(1)	9.615(1)	21.463(8)
c/Å	25.301(4)	24.103(5)	23.226(8)
β/°	95.32(2)	118.88(2)	105.76(2)
U/Å^3	4011(1)	4688.6(7)	6893(5)
ρ_{calc}/g cm^{-3}	1.293	1.53	1.295
F(000)	1592	2184	2808
Diffractometer	Enraf-Nonius CAD4		Philips PW 1100
μ(Mo-Kα)/cm^{-1}	4.92	5.54	3.51
Scan mode	ω–2θ	ω–2θ	θ–2θ
2θ Range/°	4–40	4–42	6–54
Step width/°	0.04	0.04	0.01
Scan width/°	0.9 + 0.35 tan θ	1.0 + 0.35 tan θ	1.2 + 0.35 tan θ
Scan speed/° min^{-1}	0.25–0.5	0.25–0.50	2.5–12
No. of data collected	4848	4207	15 016
No. of unique data used [$I > 3\sigma(I)$], N	3554	3648	4917[b]
R[c]	0.051	0.067	0.067
R'[d]	0.049	0.075	0.060

[a] Details in common: $T = 295$ K; Mo-Kα radiation (λ = 0.710 73 Å); monoclinic; $Z = 4$. [b] $I > 2\sigma(I)$. [c] $[\Sigma(||F_o| - |F_c||)/\Sigma|F_o|^2]^{\frac{1}{2}}$. [d] $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

added dropwise with a microsyringe to a solution of **11b** (0.15 g, 0.146 mmol) in thf (2 cm^3). The orange thf solution was layered with Et_2O (1 cm^3) and pentane (9 cm^3), and overnight beautiful orange crystals grew, which were suitable for X-ray analysis.

mer-[Ru{$Ph_2PCH\overset{\cdots}{-}C(\overset{\cdots}{-}O)Ph$}$_2${$Ph_2PCH_2C(O)Ph$}] **13**.

On standing for some days a yellow solution of **11b** became slowly violet with formation of **13**. Selected data: IR (thf): ν(CO) 1575m and ν($C\overset{\cdots}{-}O$) + ν($C\overset{\cdots}{-}C$) 1515s cm^{-1}; NMR: ^{1}H (C_6D_6), δ 5.73 [1 H, d, J(PH) 2.4, PCH *trans* to O], 5.53 [1 H, d, J(PH) 1.0, PCH], 3.96 and 3.88 [2 H, ABX system, J(PH) 9.0 and J(HH) 16.5, PCH_2CO with O *trans* to P]; ^{31}P-{^{1}H} (C_6D_6–C_7H_8), δ 49.4 [1 P, t, J(PP) 33, PCH *trans* to O], 39.5 [1 P, dd, J(PP) 305 and 32] and 34.6 [1 P, dd, J(PP) 305 and 35 Hz].

mer-[Ru{$Ph_2PCH_2C(O)Ph$}$_3$][BF_4]$_2$ **14**. To a stirred solution of **11b** (0.054 g, 0.052 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise with a microsyringe $HBF_4{\cdot}Et_2O$ (19 μl, 0.16 mmol). The dark red solution changed colour to dark violet, then red and finally orange. A white precipitate of $NaBF_4$ appeared. The solution was concentrated, filtered and layered with Et_2O. Orange crystals formed rapidly at the interface (0.05 g, 81%) (Found: C, 60.5; H, 4.2; F, 12.7. $C_{60}H_{51}B_2F_8O_3P_3Ru$ requires C, 60.7; H, 4.3; F, 12.8%). IR: (CsI) ν(CO) 1560s, ν(BF_4) 1060s; (CD_2Cl_2) ν(CO) 1556s cm^{-1}; NMR: ^{1}H (CD_2Cl_2), δ 8.7–6.0 (m, 45 H, 9 Ph), 4.9–4.7 [2 H, ABX system, J(PH) 9.0 and J(HH) 18.3, PCH_2], 4.52 and 4.44 [2 H, ABX system, J(PH) 8.6 and J(HH) 19.1, PCH_2], 4.19 and 4.00 [2 H, ABX system, J(PH) 10.7 and J(HH) 18.7, PCH_2]; ^{31}P-{^{1}H} (CH_2Cl_2–CD_2Cl_2), δ 60.0 [1 P, t, J(PP) 26.3 and 27.1, P *trans* to O], 45.6 [1 P, dd, J(PP) 295, P *trans* to P] and 42.8 [1 P, dd, J(PP) 295 Hz, P *trans* to P].

fac-[Ru{$Ph_2PCH_2C(O)Ph$}$_3$]$^{2+}$. Selected data: ^{31}P-{^{1}H} NMR (CH_2Cl_2–CD_2Cl_2), δ 57.2.

mer,trans-[$RuCl_3${$Ph_2PCH_2C(O)Ph$}{$Ph_2PCH_2C(O)Ph$}] **15**. Solid L (0.245 g, 0.795 mmol) was added to a stirred suspension of [$RuCl_3(AsPh_3)_2MeOH$] (0.337 g, 0.396 mmol) in warm toluene (25 cm^3). After 1 h the brown solution was filtered, concentrated and pentane was added to precipitate a green solid, which was recrystallised from CH_2Cl_2–pentane to yield green crystals (0.115 g, 35%) (Found: C, 58.9; H, 4.4; Cl, 13.0; P, 6.5. $C_{40}H_{34}O_2P_2Ru$ requires C, 58.9; H, 4.2; Cl, 13.0; P, 7.6%). IR: (CsI) ν(CO) 1670s, 1555vs, ν(Ru–Cl) 330s; (Nujol) ν(CO) 1657m, 1550s cm^{-1}. FIR (polyethylene) 333vs, 297w and 266w cm^{-1}.

(*c*) *Catalysis*.—The catalytic hydrogenations were carried out in a thermostatted double-jacket glass reactor (50 cm^3). The catalyst precursor was weighed in. Two vacuum–hydrogen cycles were applied, and toluene (5 cm^3), ethanol (5 cm^3) and hex-1-ene (1 cm^3) were added by syringe. The solution was stirred with a magnetic stirring bar and the clock was started at the same time. The reaction could be followed by pressure decrease in the hydrogen reservoir. Samples were taken by a syringe through a septum and analysed on a Girdel serie 330 gas chromatograph with a flame ionisation detector and a PONA column at 60 °C.

At 25 °C under 1 bar of hydrogen with 5 mmol dm^{-3} catalyst precursor and 0.8 mol dm^{-3} hex-1-ene, no conversion was found for complex **2** after 1 h. Under the same conditions, 8% conversion was observed with **1**. The product distribution was 41% hexane and 59% *trans*-hex-2-ene.

(*d*) *Crystal Structure Determinations*.—The crystal data and parameters relative to data collection for all structures are summarised in Table 6.

Complexes **2** *and* **10**. Intensities were corrected for Lorentz-polarisation effects, and an empirical absorption correction was applied after isotropic convergence.[32,33] The structure was solved by direct methods and successive Fourier-difference syntheses and refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms, except for the fluorine atoms which were refined isotropically owing to their large amplitudes of thermal vibration. Hydrogen atoms were placed in calculated positions (C–H 1.08 Å) then refined with fixed distances and were assigned an isotropic thermal parameter of 5 Å^2.[34] The weighting scheme used in the final cycles of refinement was 0.0519/[$\sigma^2(F)$ + 0.00001 F^2] for **2** and 1.0/[$\sigma^2(F)$ + 0.000 122 F^2] for **10**. The neutral scattering factors used for all atoms and anomalous dispersion coefficients were obtained from standard sources.[35]

Table 7 Atomic coordinates with estimated standard deviations (e.s.d.s) in parentheses for **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	0.359 43(4)	0.058 90(5)	0.130 47(3)	C(18)	0.648 5(7)	0.506 7(8)	0.037 3(5)
Cl(1)	0.268 9(2)	0.210 6(2)	0.168 86(9)	C(19)	0.616 6(7)	0.490 9(7)	0.087 5(5)
Cl(2)	0.469 6(2)	−0.079 9(2)	0.098 2(1)	C(20)	0.556 4(6)	0.399 1(7)	0.096 1(4)
P(1)	0.304 0(1)	0.083 4(2)	0.045 80(9)	C(21)	0.136 3(5)	−0.060 1(6)	0.164 7(4)
P(2)	0.267 1(1)	−0.073 8(2)	0.165 95(9)	C(22)	0.087 4(6)	0.011 3(7)	0.128 4(4)
O(1)	0.457 6(3)	0.194 8(4)	0.111 1(2)	C(23)	−0.011 6(6)	0.025 5(8)	0.127 8(5)
O(2)	0.439 7(4)	0.046 3(4)	0.207 0(2)	C(24)	−0.062 0(7)	−0.035 6(9)	0.163 1(6)
C(1)	0.283 1(5)	−0.036 9(6)	−0.001 4(3)	C(25)	−0.011 1(7)	−0.106 7(9)	0.202 3(5)
C(2)	0.232 8(6)	−0.134 1(7)	0.013 5(4)	C(26)	0.087 9(6)	−0.119 5(7)	0.201 6(5)
C(3)	0.208 0(6)	−0.222 4(7)	−0.022 7(4)	C(27)	0.286 0(5)	−0.229 4(6)	0.159 8(3)
C(4)	0.232 6(6)	−0.214 2(7)	−0.071 1(4)	C(28)	0.217 2(7)	−0.306 1(7)	0.136 3(4)
C(5)	0.286 9(7)	−0.120 1(8)	−0.088 1(5)	C(29)	0.235 5(8)	−0.426 0(7)	0.134 1(4)
C(6)	0.309 6(6)	−0.030 6(7)	−0.050 7(4)	C(30)	0.321 2(8)	−0.469 5(7)	0.153 3(5)
C(7)	0.202 1(5)	0.180 0(6)	0.023 4(3)	C(31)	0.390 5(8)	−0.396 3(8)	0.175 8(5)
C(8)	0.122 0(6)	0.141 6(7)	−0.007 2(4)	C(32)	0.370 2(7)	−0.277 3(7)	0.178 8(4)
C(9)	0.048 5(7)	0.216 5(8)	−0.025 2(5)	C(33)	0.307 7(5)	−0.051 9(6)	0.237 5(3)
C(10)	0.052 7(6)	0.333 1(8)	−0.011 2(4)	C(34)	0.407 7(5)	−0.007 0(6)	0.243 6(3)
C(11)	0.133 1(7)	0.371 1(7)	0.021 5(4)	C(35)	0.467 1(6)	−0.017 4(7)	0.294 4(4)
C(12)	0.206 2(6)	0.296 5(7)	0.039 6(4)	C(36)	0.457 8(6)	−0.112 5(7)	0.328 4(4)
C(13)	0.408 3(6)	0.161 3(7)	0.021 0(3)	C(37)	0.518 0(7)	−0.121 3(8)	0.375 5(4)
C(14)	0.463 8(5)	0.224 1(6)	0.064 4(3)	C(38)	0.584 9(8)	−0.036 4(9)	0.388 6(5)
C(15)	0.528 3(5)	0.323 3(6)	0.055 0(3)	C(39)	0.591 3(9)	0.057 8(9)	0.356 8(5)
C(16)	0.559 7(5)	0.339 4(7)	0.004 7(4)	C(40)	0.537 0(7)	0.066 3(7)	0.307 7(5)
C(17)	0.622 1(6)	0.434 2(8)	−0.002 9(4)				

Table 8 Atomic coordinates with e.s.d.s in parentheses for **10**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	0.309	−0.003 30(6)	0.423	C(23)	0.242 4(9)	0.518(1)	0.294 6(8)
P(1)	0.283 5(2)	0.137 6(5)	0.483 9(2)	C(24)	0.185 9(9)	0.485(2)	0.249 0(9)
P(2)	0.333 1(2)	0.138 7(5)	0.362 5(2)	C(25)	0.168 9(8)	0.344(1)	0.233 6(8)
O(1)	0.281 5(6)	−0.162(1)	0.471 7(6)	C(26)	0.213 5(7)	0.252(1)	0.264 4(7)
O(2)	0.335 0(5)	−0.156(1)	0.374 7(5)	C(27)	0.416 8(8)	0.210(1)	0.397 1(9)
N(1)	0.208 6(7)	−0.014(1)	0.354 6(7)	C(28)	0.438 2(7)	0.286(1)	0.454 4(8)
N(2)	0.401 8(6)	−0.015(1)	0.490 2(7)	C(29)	0.503 0(9)	0.343(2)	0.484(1)
C(41)	0.458 4(8)	−0.027(1)	0.525 3(8)	C(30)	0.547 2(7)	0.295(1)	0.455 4(8)
C(42)	0.528 5(7)	−0.015(1)	0.572 4(8)	C(31)	0.525 3(8)	0.203(1)	0.407 8(9)
C(43)	0.157(1)	−0.018(1)	0.323 4(9)	C(32)	0.462 3(7)	0.181(1)	0.371 3(8)
C(44)	0.088 0(8)	−0.047(2)	0.285 4(9)	C(33)	0.326 6(7)	0.008(1)	0.303 8(6)
C(1)	0.337 9(7)	0.283(1)	0.524 8(7)	C(34)	0.338 8(6)	−0.127(1)	0.325 5(6)
C(2)	0.323 8(8)	0.415(1)	0.506 5(9)	C(35)	0.365 9(7)	−0.237(1)	0.298 0(8)
C(3)	0.365 4(7)	0.523(1)	0.530 2(7)	C(36)	0.404 2(8)	−0.348(1)	0.335 5(8)
C(4)	0.431 1(7)	0.498(1)	0.582 6(8)	C(37)	0.426 6(7)	−0.453(1)	0.321 2(7)
C(5)	0.446 2(8)	0.368(1)	0.606 3(8)	C(38)	0.412 2(7)	−0.452(1)	0.256 7(8)
C(6)	0.397 8(8)	0.253(1)	0.576 1(8)	C(39)	0.369 7(9)	−0.341(2)	0.209 5(9)
C(7)	0.199 4(6)	0.202(1)	0.446 4(7)	C(40)	0.347 3(9)	−0.232(1)	0.235 9(8)
C(8)	0.175 9(8)	0.292(1)	0.397 4(9)	P(3)	0.144 8(3)	−0.098 6(6)	0.137 2(3)
C(9)	0.113 2(8)	0.334(1)	0.364 6(8)	F(1)	0.189 1(9)	−0.132(2)	0.209 0(8)
C(10)	0.073 0(9)	0.307(2)	0.380 5(8)	F(2)	0.087 6(8)	−0.187(1)	0.147 1(8)
C(11)	0.091 8(8)	0.230(1)	0.437(1)	F(3)	0.171 2(8)	−0.229(1)	0.115 7(9)
C(12)	0.156 2(7)	0.165(1)	0.465 6(7)	F(4)	0.091 1(6)	−0.105(1)	0.064 9(6)
C(13)	0.292 0(9)	0.020(1)	0.548 8(8)	F(5)	0.205 7(8)	−0.055(1)	0.134 5(7)
C(14)	0.268 8(6)	−0.129(1)	0.513 6(7)	F(6)	0.131 5(8)	0.053(1)	0.145 6(8)
C(15)	0.249 4(8)	−0.237(1)	0.542 2(8)	P(4)	0.475 4(3)	0.104 3(6)	0.210 1(3)
C(16)	0.265 1(9)	−0.232(2)	0.607(1)	F(7)	0.437 0(6)	0.125(1)	0.134 4(7)
C(17)	0.250(1)	−0.346(2)	0.632(1)	F(8)	0.458 7(5)	0.253(1)	0.217 4(6)
C(18)	0.218 5(8)	−0.451(2)	0.603 0(8)	F(9)	0.409 8(8)	0.020(1)	0.194 2(7)
C(19)	0.196 6(8)	−0.455(1)	0.544 2(8)	F(10)	0.506 8(6)	−0.037(1)	0.195 8(6)
C(20)	0.212 8(7)	−0.346(1)	0.503 8(8)	F(11)	0.541 4(7)	0.135(1)	0.217 9(7)
C(21)	0.274 7(7)	0.277(1)	0.313 5(7)	F(12)	0.498 9(7)	0.044(1)	0.278 5(7)
C(22)	0.291 9(8)	0.420(1)	0.335(1)				

Complex **12**. No correction for absorption was applied. Only the observed reflections were used in the structure solution and refinement. The structure was solved by Patterson and Fourier methods. From the Δ*F* map the presence of a tetrahydrofuran molecule of solvation was revealed. The refinement was carried out by full-matrix least squares first with isotropic and then with anisotropic thermal parameters in the last cycles for the non-hydrogen atoms of the anion excepting the carbon atoms of the phenyl groups and the Na atom of the cation. Because of the high thermal parameters of the atoms of the thf molecule of solvation, the identification of its oxygen atom was uncertain and therefore the molecule was treated as all-carbon. All hydrogen atoms (except those of the solvent molecule) were placed at their geometrically calculated positions (C–H 0.96 Å)

Table 9 Fractional atomic coordinates (× 10^4) with e.s.d.s in parentheses for the non-hydrogen atoms of **12**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ru	6 996(1)	−363(1)	7 917(1)	P(3)	6 997(2)	48(2)	6 985(1)
P(1)	5 426(2)	−610(2)	7 730(1)	O(13)	8 511(5)	−276(4)	8 056(3)
O(11)	7 104(5)	−1 275(3)	7 606(3)	C(23)	8 822(7)	−74(5)	7 615(6)
C(21)	6 300(9)	−1 596(5)	7 473(5)	C(13)	8 261(7)	84(5)	7 079(5)
C(11)	5 414(8)	−1 396(5)	7 496(5)	C(33)	9 931(8)	−45(5)	7 778(5)
C(31)	6 390(9)	−2 243(6)	7 253(5)	C(43)	10 426(9)	211(5)	7 384(5)
C(41)	5 648(10)	−2 541(6)	6 838(6)	C(53)	11 460(9)	217(6)	7 560(5)
C(51)	5 732(10)	−3 170(6)	6 651(6)	C(63)	11 929(9)	18(5)	8 092(6)
C(61)	6 571(10)	−3 450(6)	6 873(6)	C(73)	11 484(9)	−200(6)	8 500(6)
C(71)	7 379(10)	−3 214(7)	7 289(6)	C(83)	10 432(9)	−245(5)	8 314(5)
C(81)	7 256(9)	−2 576(6)	7 470(5)	C(93)	6 484(8)	−406(6)	6 307(5)
C(91)	4 840(7)	−571(5)	8 345(5)	C(103)	6 967(10)	−925(7)	6 209(6)
C(101)	4 352(7)	−1 072(5)	8 504(5)	C(113)	6 514(12)	−1 327(8)	5 720(7)
C(111)	3 947(8)	−1 011(5)	8 986(5)	C(123)	5 656(12)	−1 159(8)	5 351(7)
C(121)	4 025(8)	−467(6)	9 287(5)	C(133)	5 146(11)	−687(7)	5 447(6)
C(131)	4 509(7)	46(5)	9 139(5)	C(143)	5 544(9)	−299(6)	5 936(6)
C(141)	4 926(7)	−7(5)	8 665(5)	C(153)	6 557(7)	829(5)	6 727(5)
C(151)	4 456(8)	−234(6)	7 162(5)	C(163)	6 636(8)	1 056(6)	6 170(5)
C(161)	3 954(11)	−592(7)	6 689(7)	C(173)	6 356(9)	1 672(6)	6 004(6)
C(171)	3 238(12)	−274(8)	6 225(7)	C(183)	6 008(9)	2 029(6)	6 345(6)
C(181)	3 073(10)	317(8)	6 288(6)	C(193)	5 917(10)	1 836(7)	6 897(7)
C(191)	3 561(11)	706(7)	6 730(7)	C(203)	6 184(9)	1 208(6)	7 085(6)
C(201)	4 290(9)	381(7)	7 172(6)	Na	10 386(4)	2 162(3)	3 102(3)
P(2)	7 430(2)	−624(2)	8 927(1)	O(1C)	9 056(11)	2 572(9)	2 182(7)
O(12)	6 985(5)	534(3)	8 271(3)	C(2C)	8 437(18)	2 028(11)	2 035(10)
C(22)	7 181(8)	582(5)	8 852(6)	C(3C)	8 164(15)	1 711(10)	2 406(10)
C(12)	7 410(7)	103(5)	9 257(5)	O(4C)	8 907(10)	1 513(6)	2 807(7)
C(32)	7 111(8)	1 234(6)	9 040(6)	C(5C)	8 658(14)	1 189(9)	3 227(9)
C(42)	7 245(10)	1 729(8)	8 694(7)	C(6C)	9 488(15)	1 055(9)	3 704(9)
C(52)	7 166(11)	2 346(8)	8 876(8)	O(7C)	10 022(13)	1 545(8)	3 972(7)
C(62)	6 887(11)	2 480(8)	9 359(8)	C(8C)	10 939(16)	1 624(10)	4 365(10)
C(72)	6 744(9)	2 019(7)	9 719(6)	C(9C)	11 220(15)	2 299(10)	4 519(9)
C(82)	6 858(9)	1 397(6)	9 562(6)	O(10C)	11 346(12)	2 612(9)	4 141(8)
C(92)	8 676(8)	−933(5)	9 217(5)	C(11C)	11 318(14)	3 241(10)	3 999(8)
C(102)	9 279(9)	−695(5)	9 735(5)	C(12C)	10 424(17)	3 426(11)	3 726(11)
C(112)	10 233(9)	−979(6)	9 941(6)	O(13C)	10 051(13)	3 286(7)	3 172(8)
C(122)	10 501(10)	−1 457(6)	9 636(6)	C(14C)	9 159(17)	3 346(9)	2 786(10)
C(132)	9 863(10)	−1 695(6)	9 130(6)	C(15C)	8 777(19)	3 069(14)	2 331(13)
C(142)	8 912(9)	−1 435(5)	8 900(5)	O(W)	11 133(5)	1 525(3)	2 594(3)
C(152)	6 813(7)	−1 189(5)	9 287(5)	C(1S)	−32(15)	4 237(10)	721(8)
C(162)	6 673(8)	−1 792(6)	9 052(5)	C(2S)	347(17)	3 607(12)	994(10)
C(172)	6 254(8)	−2 249(6)	9 341(6)	C(3S)	−711(18)	3 489(10)	732(10)
C(182)	6 011(8)	−2 085(6)	9 850(6)	C(4S)	−1 442(15)	3 876(11)	273(9)
C(192)	6 154(9)	−1 524(6)	10 088(6)	C(5S)	−1 057(17)	4 509(11)	404(9)
C(202)	6 557(8)	−1 055(6)	9 803(5)				

and refined 'riding' on the corresponding carbon atoms. In the final cycles of refinement a weighting scheme, $w = [\sigma^2(F_o)]^{-1}$ was used; at convergence *K* was 0.956. The atomic scattering factors, corrected for the real and the imaginary parts of anomalous dispersion, were taken from ref. 35.

All calculations for the structure determination were carried out on the GOULD POWERNODE 6040 of the Centro di Studio per la Strutturistica Diffrattometrica del Consiglio Nationale della Ricerce, Parma, using the SHELX 76 and SHELXS 86 computer programs.[34]

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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