Fluxional Behaviour of Bis- and Tris-(ether phosphine)ruthenium(II) Chloro and Acetato Complexes†

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The syntheses of bis- and tris-[(2-methoxyethyl)diphenylphosphine]ruthenium(II) complexes with chloro, acetato, and trifluoroacetato ligands are described. The complexes are *mer*-[RuCl$_2$(P–O)(PO)$_2$], *fac*-[RuCl(P–O)$_2$(PO)]X (X = Cl, SbF$_6$, or BPh$_4$), *fac*-[Ru(P–O)$_3$][SbF$_6$]$_2$, [RuCl(P–O)$_2$]SbF$_6$, *fac*-[Ru(O$_2$CCH$_3$)$_2$(PO)$_3$], *fac*-[Ru(O$_2$CCH$_3$)(P–O)(PO)$_2$]X (X = O$_2$CCH$_3$ or BPh$_4$), [RuX$_2$(O,P)$_2$] (X = O$_2$CCH$_3$ or O$_2$CCF$_3$), [RuCl(O$_2$CCH$_3$)(O,P)$_2$] and *mer*-[RuH(O$_2$CCH$_3$)(PO)$_3$]; PO represents the ligand which is co-ordinated *via* phosphorus only (ether function free), P–O ligand which is co-ordinated in the bidentate chelating mode *via* phosphorus and oxygen, and O,P is used where the mode of co-ordination is not certain. The mechanism of the fluxional behaviour of these complexes in solution has been investigated by the use of temperature-programmed ^{31}P and ^{13}C n.m.r. and by nuclear Overhauser enhancement spectroscopy ^{31}P n.m.r. studies. Fluxional processes occur through exchange between the bidentate (P- and O-bonded) and the monodentate (P-bonded) co-ordination modes of the ether phosphine ligands, as the labile metal–oxygen bonds are broken and reformed. A second type of fluxional process is observed in the six-co-ordinate tris(ether phosphine) complexes due to Berry-type rearrangements of five-co-ordinate intermediates formed upon opening of a metal–oxygen bond. In several of the complexes both types of fluxional process are operating simultaneously. Other complexes show different types of fluxional behaviour in polar and in non-polar solvents, due to ionic dissociation of chloride and acetate ligands in the polar solvents. Some reactions of the complexes are also discussed.

The catalytic properties of tertiary phosphine complexes of platinum metals are well known. In recent years special attention has been focused on complexes of tertiary phosphines containing additional donor functions, particularly oxygen, which are capable of labile addition to the metal centre.[2–6] The interest in such 'hemilabile' ligands stems from the fact that the co-ordinated oxygen can dissociate from the metal in solution so leaving a vacant co-ordination site for substrate binding catalytic action. Some studies of such complexes have also revealed fluxional behaviour in solution.[3,7] The work of this group to date has mainly concerned complexes of rhodium,[8–10] cobalt,[11] platinum,[12] and ruthenium[7,13,14] with ether phosphines, and their potential as homogeneous catalysts for the hydrocarbonylation of methanol.[15,16] Among the ether phosphine ligands which we have used is (2-methoxyethyl)-diphenylphosphine, Ph$_2$PCH$_2$CH$_2$OCH$_3$.[17] We present here further studies of the co-ordination chemistry of this ligand with ruthenium(II). In particular, we give details of investigations, using ^{1}H, ^{31}P, and ^{13}C n.m.r. spectroscopy, of the behaviour in solution of chloro- and acetato-complexes of ruthenium(II) with the ligand. It emerges that the fluxional behaviour of these complexes involving the 'hemilabile'· ligands is strongly dependent on the ionizing power of the solvent, and on the mode of co-ordination of the anionic ligands.

Results and Discussion

Three equivalents of Ph$_2$PCH$_2$CH$_2$OCH$_3$ react with commercial 'RuCl$_3$·3H$_2$O' in refluxing methoxyethanol to form *trans,cis,cis*-[RuCl$_2$(P–O)$_2$][14] (1), where P–O represents the ligand bonded in a bidentate manner. This complex may also be

prepared by treating [RuCl$_2$(PPh$_3$)$_3$][18–20] with 2 equivalents of ligand in dichloromethane (Scheme 1). Complex (1) reacts with excess of ligand in dichloromethane to give *mer*-[RuCl$_2$(P–O)(PO)$_2$] (2) (PO indicates ligand bonded through P only), obtained as a red solid by evaporation of this solution to low volume and addition of diethyl ether. The i.r. spectrum of (2) shows an absorption due to v_{asym}(C$_2$O) which is diagnostic of the co-ordinated ether function (Table 4).[14] When complex (2) is dissolved in dichloromethane or toluene the equilibrium (1) is established with complex (1) and free ligand.

$$[RuCl_2(P-O)(PO)_2](2) \rightleftharpoons$$
$$[RuCl_2(P-O)_2] (1) + Ph_2PCH_2CH_2OCH_3 \quad (1)$$
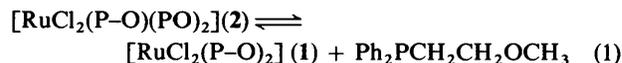
This equilibrium is observed in the ^{31}P-{^{1}H} n.m.r. spectrum of a dichloromethane or toluene solution of complex (2), where a singlet at 62 p.p.m. due to complex (1) and a singlet of half the intensity due to free ligand are observed together with the signals arising from (2).[19] Addition of a large excess of ligand to the solution pushes the equilibrium to the left, almost suppressing the formation of complex (1). Conductivity measurements for complex (2) in dichloromethane solution show that ionic dissociation is minimal. A variable-temperature ^{31}P-{^{1}H} n.m.r. study of complex (2) in toluene containing excess of ligand is shown in Figure 1. At 203 K a doublet of doublets at low field and an AB pattern at higher field are observed (Table 2). We assign the low-field signal to a unique

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† This paper is regarded as Part 25 of the series 'Novel Basic Ligands for the Homogeneous Catalytic Carbonylation of Methanol.' Part 24 is ref. 1.
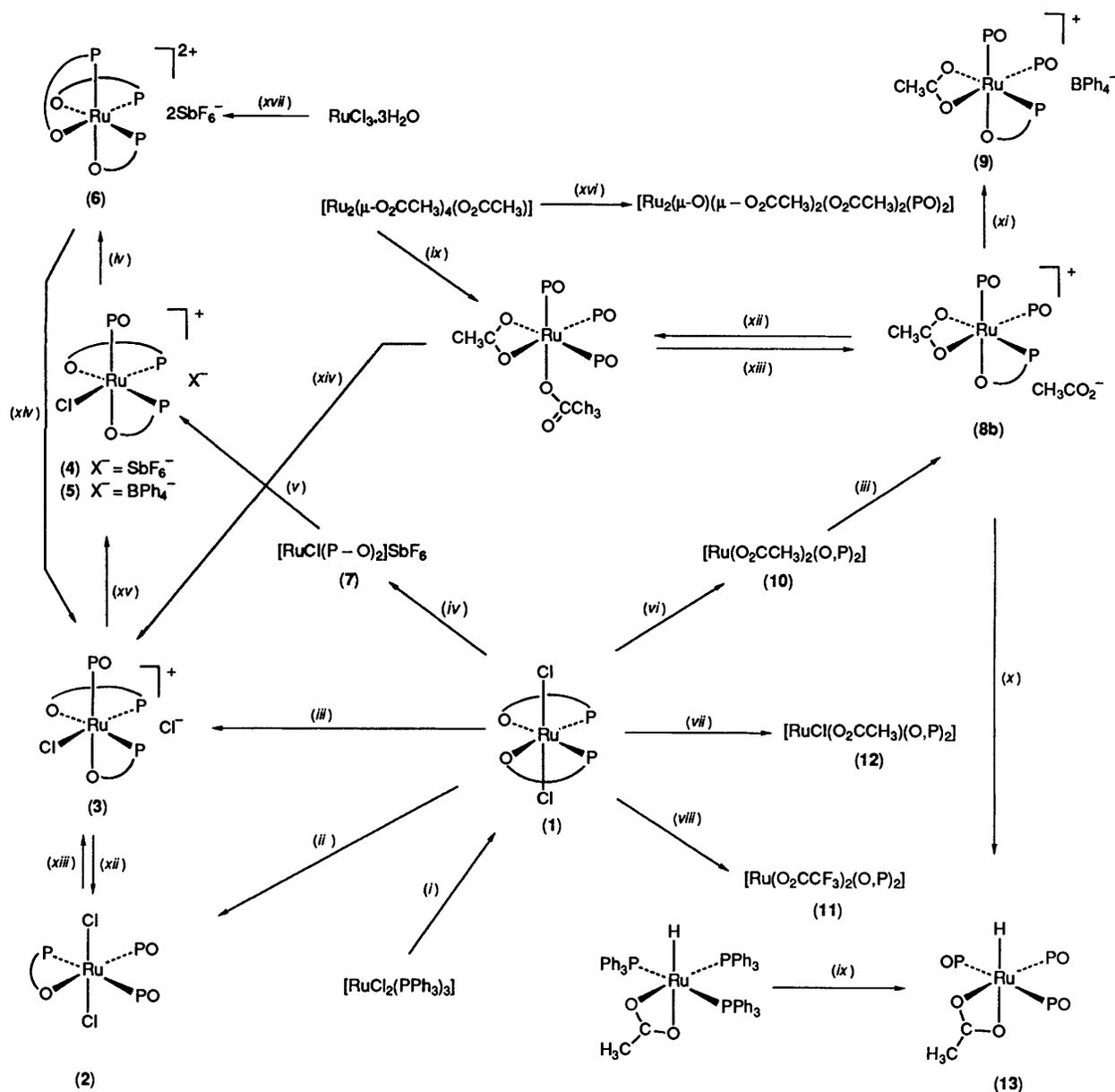
Scheme 1. Synthetic routes to the complexes. (*i*) 2 $Ph_2PCH_2CH_2OCH_3$, CH_2Cl_2; (*ii*) excess of ligand, CH_2Cl_2; (*iii*) ligand, CH_3OH; (*iv*) $AgSbF_6$; (*v*) ligand; (*vi*) 2 AgO_2CCH_3; (*vii*) AgO_2CCH_3; (*viii*) 2 AgO_2CCF_3; (*ix*) excess of ligand; (*x*) Pr^nOH, 90 °C; (*xi*) $NaBPh_4$; (*xii*) CH_2Cl_2; (*xiii*) CH_3OH; (*xiv*) HCl, CH_3OH; (*xv*) $NaBPh_4$, $AgSbF_6$; (*xvi*) excess of ligand, O_2; (*xvii*) 3 $AgSbF_6$, 4 $Ph_2PCH_2CH_2OCH_3$

phosphine which is *trans* to a co-ordinated ether function and *cis* to the pair of mutually *trans* phosphines which generate the AB pattern. The higher-field part of this AB pattern is due to a monodentate ether phosphine, while the lower field part is due to a bidentate chelating ether phosphine.[21,22] On raising the temperature to 258 K the AB part of the spectrum coalesces to a broad signal, and at 313 K the signal due to the unique phosphine also coalesces. The variable-temperature behaviour of this complex is thus very similar to that observed for the isostructural dihydride $[RuH_2(P-O)(PO)_2]$.[7] It is thought that in both complexes the first coalescence is due to an interchange between monodentate and bidentate co-ordination of the mutually *trans* phosphines [species (**I**) and (**III**) in Scheme 2]. The second coalescence, which makes all three phosphines equivalent on the n.m.r. time-scale, can be explained in terms of a Berry-type exchange mechanism [(**I**)—(**VII**) and (**I**)—(**VIII**) in Scheme 2] involving a trigonal-bipyramidal intermediate (**IV**). This is similar to the mechanism proposed by Hoffman

and Caulton[19] for the exchange of the three phosphines in $[RuCl_2(PPh_3)_3]$, and in the ether phosphine complexes it is thought to be working in conjunction with the ring-opening and -closing mechanism for exchange of the *trans* phosphines. For the dichloride complex (**2**) the first exchange process has a slightly higher calculated free energy of activation[23] (49.1 kJ mol^{-1}) than for the dihydride, whereas the free energy of activation for the second process (56.9 kJ mol^{-1}) is about the same in both complexes.

Prolonged stirring of the red solid (**2**) in refluxing methanol yields a deep yellow solution, the molecular conductivity of which is as expected for a 1:1 electrolyte containing chloride in conjunction with a large cation.[24] Subsequent evaporation of this solution to low volume, or addition of a non-polar solvent, causes the reprecipitation of complex (**2**). The $^{31}P-\{^1H\}$ n.m.r. spectrum of the yellow solution at 243 K (Figure 2) shows three doublets of doublets due to inequivalent phosphines, with $^2J_{PP}$ values typical of *cis* coupling on Ru^{II}.[19] We attribute this

Table 1. Analytical and physical data

| Complex | Colour | M.p. (decomp.)/°C | Analysis (%)[a] | | | | Λ_M/Ω^{-1} cm^2 mol^{-1} |
			C	H	Cl	F	
(2) mer-[RuCl$_2$(P–O)(PO)$_2$]	Red	130—132	60.45 (59.75)	5.70 (5.70)	8.15 (7.85)		0.5[b]
(3) fac-[RuCl(P–O)$_2$(PO)]Cl[c]	Deep yellow	—					82[d]
(4) fac-[RuCl(P–O)$_2$(PO)]SbF$_6$	Yellow	154—156	48.00 (48.90)	4.65 (4.65)	3.35 (3.20)	10.55 (10.30)	
(5) fac-[RuCl(P–O)$_2$(PO)]BPh$_4$	Pale yellow	138—140	69.65 (69.65)	6.20 (5.60)	3.40 (3.00)		
(6) fac-[Ru(P–O)$_3$][SbF$_6$]$_2$	Yellow	147—149	40.70 (41.40)	4.15 (3.95)		17.45 (17.45)	
(7) [RuCl(P–O)$_2$]SbF$_6$[e]	Yellow	79—81	41.55 (41.85)	4.10 (4.00)	4.35 (4.10)	14.30 (13.25)	
(8a) fac-[Ru(O$_2$CCH$_3$)$_2$(PO)$_3$]	Yellow	165—167	61.55 (61.80)	6.20 (6.05)			4.3[b]
(8b) fac-[Ru(O$_2$CCH$_3$)(P–O)(PO)$_2$]O$_2$CCH$_3$[c]	Yellow	—					58[d]
(9) fac-[Ru(O$_2$CCH$_3$)(P–O)(PO)$_2$]BPh$_4$	Pale yellow	81—83	70.00 (70.10)	6.25 (6.45)			
(10) [Ru(O$_2$CCH$_3$)$_2$(O,P)$_2$]	Deep orange	147—149	56.65 (57.70)	5.95 (5.70)			
(11) [Ru(O$_2$CCF$_3$)$_2$(O,P)$_2$]	Deep yellow	133—149	47.05 (46.95)	4.35 (4.45)		14.05 (14.85)	
(12) [RuCl(O$_2$CCH$_3$)(O,P)$_2$]	Pale red	156—158	55.70 (56.20)	5.35 (5.45)	5.60 (5.20)		
(13) mer-[RuH(O$_2$CCH$_3$)(O,P)$_3$]	Yellow	41—43	64.65 (63.15)	6.40 (6.20)			

[a] Calculated values are given in parentheses. [b] 10^{-3} mol dm^{-3} solution in dichloromethane at 20 °C. [c] Exists only in solution (see Results and Discussion). [d] 10^{-3} mol dm^{-3} solution in methanol at 20 °C.

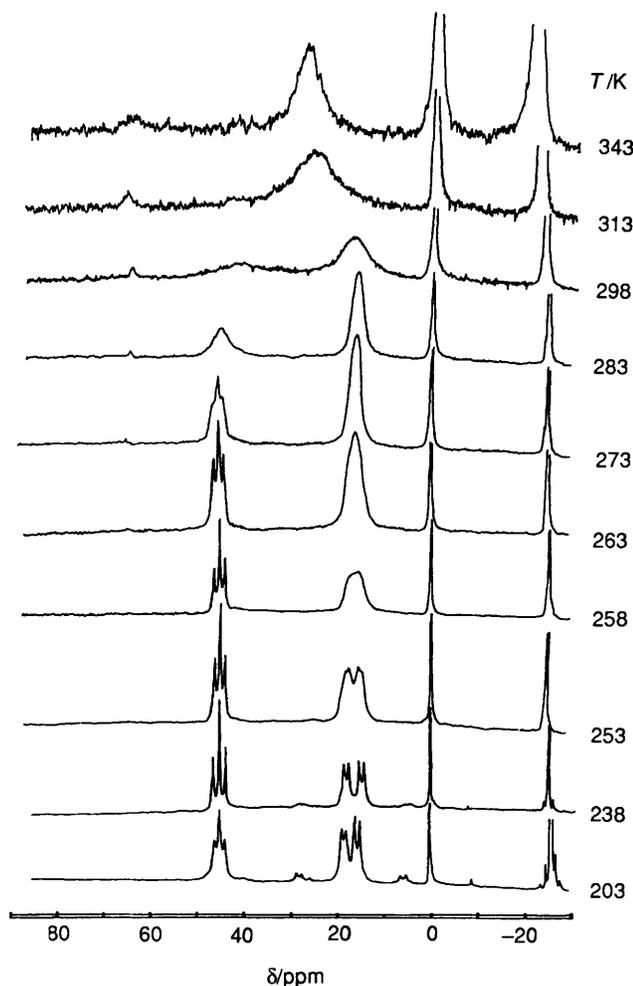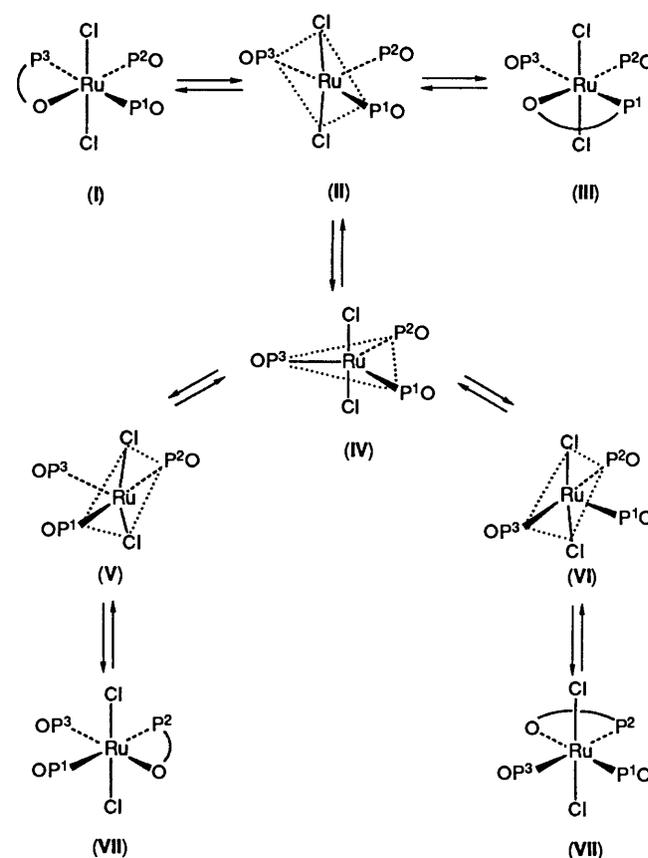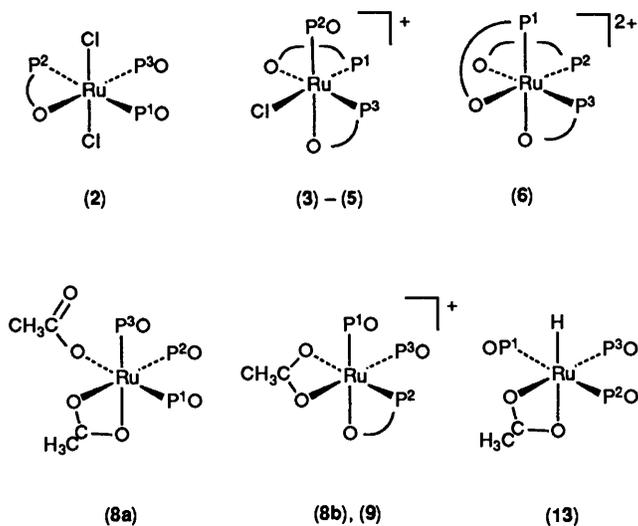**Figure 1.** ^{31}P-{^{1}H} N.m.r. variable-temperature study of mer-[RuCl$_2$(P–O)(PO)$_2$] (2) in toluene solution, in the presence of ca. 1 equivalent of excess of free ligand. The highest-field singlet is due to free ligand, the second highest is that due to standard. The small low-field signal observable at higher temperatures is due to trans,cis,cis-[RuCl$_2$(P–O)$_2$] (1)

Scheme 2. Mechanism for interchange of only trans phosphines (I)—(III) and for interchange of cis and trans phosphines, (I)—(VII), (I)—(VIII), in mer-[RuCl$_2$(P–O)(PO)$_2$] (2). The labels P^1, P^2, P^3 in this and subsequent Schemes follow the movements of the individual ether phosphine molecules, rather than identifying atomic environments

spectrum to the yellow, six-co-ordinate facial tris(phosphine) cation fac-[RuCl(P–O)$_2$(PO)]$^+$ [Scheme 3, species (III)]. The

chloride salt of this cation, i.e. fac-[RuCl(P–O)$_2$(PO)]Cl (3), is only stable in polar solvents at relatively low concentrations. Under less-ionizing conditions the chloride counter ion reco-ordinates and the resulting complex isomerizes to the red meridional isomer (2). This interpretation is substantiated by the fact that complex (2) reacts with 1 equivalent of either AgSbF$_6$ or NaBPh$_4$ to give the yellow solids fac-[RuCl-(P–O)$_2$(PO)]SbF$_6$ (4) and fac-[RuCl(P–O)$_2$(PO)]BPh$_4$ (5),

Table 2. ^{31}P-$\{^1H\}$ N.m.r. data

(2)   (3) – (5)   (6)

(8a)   (8b), (9)   (13)

			$^2J_{PP}/Hz$		
Complex (solvent)	T/K	δ^a/p.p.m.	P^1P^2	P^2P^3	P^3P^1
(2) (toluene)^b	203	12.3 (dd, P^1), 20.6 (dd, P^2), 44.8 (dd, P^3)	313	32	32
	258	16.1 (br, c, P^1, P^2), 44.7 (t, P^3)		32	32
	343	25.6 (br, c, P^1, P^2, P^3)			
(3) (CH$_3$OH)	243	43.3 (dd, P^1), 35.9 (dd, P^2), 49.0 (dd, P^3)^d			
(4) (CH$_2$Cl$_2$) c	298	43.4 (br, c, P^1, P^2, P^3)			
(5) (acetone)	333	44.5 (s, c, P^1, P^2, P^3)			
(6) (acetone)	243^e	51.9 (s, P^1, P^2, P^3)			
(8a) (CH$_2$Cl$_2$)^f	203	30.4 (d, P^1, P^2), 32.6 (t, P^3)	34	32	34
	295	31.3 (s, c, P^1, P^2, P^3)			
(8b) (CH$_3$OH)	243	39.3 (dd, P^1), 49.8 (dd, P^2), 34.2 (dd, P^3)	33	33	33
	338^g	40.6 (br, P^1), 43.2 (br, c, P^2, P^3)			
(9) (1-Chloropentane) c	363^g	43.5 (br, c, P^1, P^2, P^3)			
(13)^h (CH$_2$Cl$_2$)	243	28.2 (d, P^1, P^2), 56.2 (t, P^3)		29	29
(acetone)	308	29.9 (d, P^1, P^2), 59.3 (t, P^3)		29	29
(7) (THF)^i	243	66.9 (d), 60.0 (d)	43		
(10) (CH$_3$OH)^i	203	67.0 (dd), 58.3 (d), 53.4 (d), 46.3 (s)			
	313	56.7 (c), 57.2 (c)			
(11) (CH$_3$OH)^i	223	55.4 (d), 52.8 (d)			
	313	54.0 (br, c)			
(12) (CH$_3$OH)^i	203	67.0 (dd), 58.4 (d), 52.7 (d)			
	308	57.6 (s, c)			

^{a} Measured at 32.39 MHz except where mentioned. Phosphines labelled in parentheses: see diagrams for assignment of labels P^1, P^2, P^3. s = Singlet, d = doublet, dd = doublet of doublets (or pseudo-triplet), br = broad, and c = coalesced signal due to exchange process. ^{b} In the presence of excess of ligand. ^{c} The ^{31}P-$\{^1H\}$ n.m.r. data are similar for this group of compounds, neglecting small chemical shift differences due to solvent effects. ^{d} Tentative assignments of P^1, P^2, P^3 for this complex. ^{e} The same sharp singlet appears at 193 and at 308 K. ^{f} Measured at 101.26 MHz. ^{g} Only complex (9) measured at this temperature. ^{h} Proton n.m.r. data for complex (13), hydride region: doublet of triplets δ −20.49 p.p.m.; $^2J(P^1-H)$ = $^2J(P^2-H)$ = 25.0, $^2J(P^3-H)$ = 31.6 Hz. ^{i} Structure not yet assigned.

respectively. The i.r. spectra of complexes (4) and (5) show $\nu_{asym}(C_2O)$ bands attributable to both co-ordinated and unco-ordinated ether functions. Both of these complexes dissolve in methanol or in dichloromethane to give solutions whose ^{31}P-$\{^1H\}$ n.m.r. spectra are identical to that of complex (2) in methanol.

The ^{13}C-$\{^1H\}$ n.m.r. spectrum of complex (5) in dichloromethane at 203 K contains a signal for the methylene carbon α to oxygen of the unco-ordinated ether function, and also a signal of approximately twice the intensity due to this carbon in the co-ordinated ether function (Table 3).[21,25,26] For the methyl group one signal for the unco-ordinated and two signals of equal intensity for the co-ordinated oxygen are observed. The

reason for the inequivalence of these methyl groups α to co-ordinated oxygen in complex (5) is not clear, but it may be due to the presence of structurally inequivalent methyl positions arising from the different conformations of the co-ordinated ether groups.[2,21,27] The inequivalence of the three phosphorus atoms in the ^{31}P-$\{^1H\}$ n.m.r. spectra of these complexes favours the configuration (III) over the symmetrical configuration (I) shown in Scheme 3, since if the latter configuration were present it would give an A$_2$X pattern. ^{31}P-$\{^1H\}$ N.m.r. variable-temperature measurements for complexes (3), (4), and (5) in methanol, acetone, and dichloromethane, respectively, show almost identical behaviour. The three signals observed at 243 K broaden at higher temperatures and all three coalesce at 298 K,
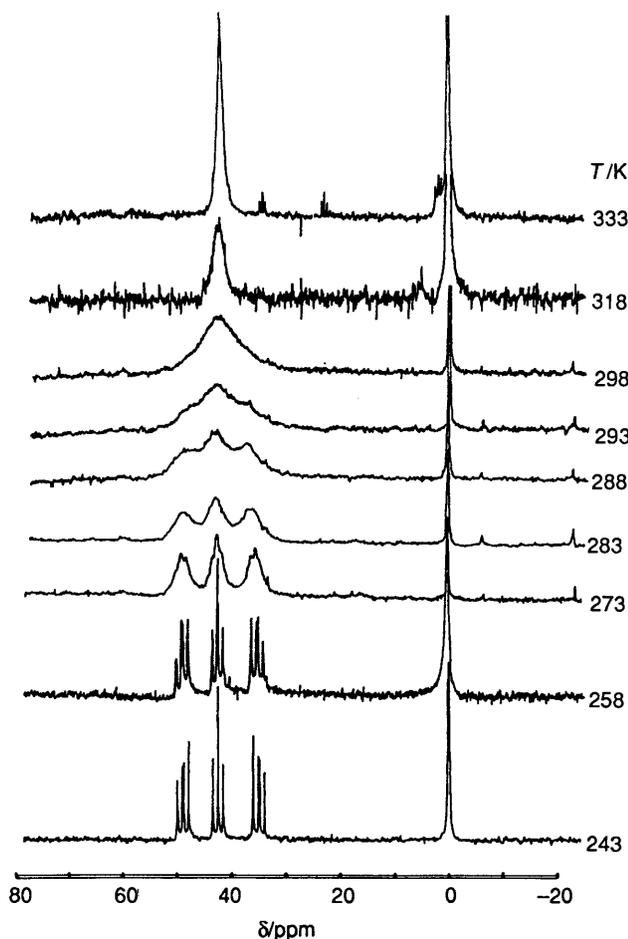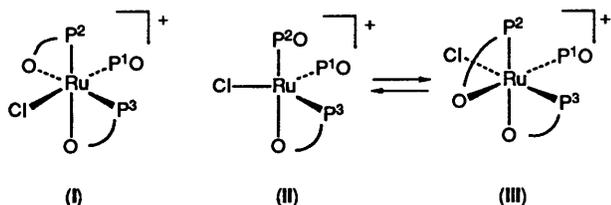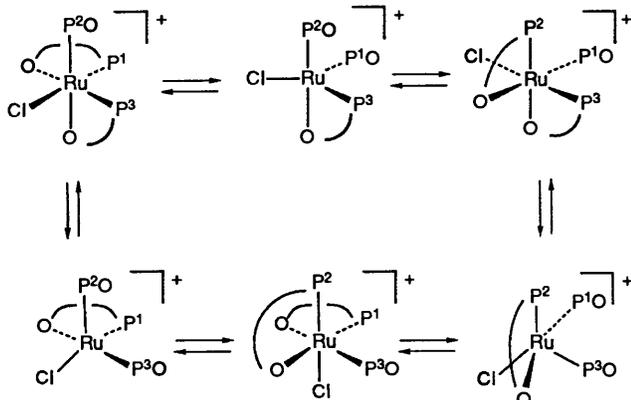
Figure 2. $^{31}P-\{^1H\}$ N.m.r. variable-temperature study of *fac*-[RuCl-(P–O)$_2$(PO)]SbF$_6$ (4) in acetone. The highest-field singlet is standard

Scheme 3. Non-formation of the symmetric isomer (I) of *fac*-[RuCl(P–O)$_2$(PO)]$^+$, (3)—(5). The presence of a freely rotating monodentate ligand behind the metal, and its absence in front [as seen in the intermediate (II)], would favour the formation of (III)

Scheme 4. Mechanism for interchange of the three phosphines in *fac*-[RuCl(P–O)$_2$(PO)]$^+$ (3)—(5)

becoming a sharp singlet at 333 K (Table 2, Figure 2). This coalescence is also observed in the $^{13}C-\{^1H\}$ and ^1H n.m.r. spectra of complex (5). We propose a mechanism for this coalescence process (Scheme 4) whereby opening of one of the co-ordinated ether functions leads to a square-pyrimidal or trigonal-bipyramidal five-co-ordinate intermediate, followed by closure of the hitherto open ether function to yield a structure identical to the first, but in which all three phosphines have been exchanged. This mechanism is consistent with the result of a two-dimensional Nuclear Overhauser enhancement spectroscopy (NOESY) ^{31}P n.m.r. experiment which was carried out for complex (4) at 243 K. This type of two-dimensional n.m.r. experiment is especially suited to elucidate slow molecular dynamic processes.[28] Thus, the observation of symmetrical off-diagonal correlations for all three phosphorus nuclei is due to an exchange mechanism in which all three phosphines are involved as described above. If the intermediate is considered to be the trigonal-bipyramidal[19,29] structure (II) (Scheme 3), then the presence of a unidentate ether phosphine on the far side of the intermediate as seen in the Scheme, and its absence on the near side, may explain why the symmetrical isomer (I) is not formed.

Complex (1) reacts with AgSbF$_6$ in dichloromethane to give a yellow solution from which the salt, [RuCl(P–O)$_2$]SbF$_6$ (7), is subsequently isolated. The i.r. spectrum of this complex showed a strong $\nu_{asym}(C_2O)$ band for the co-ordinated ether, and no bands attributable to unco-ordinated ether. The $^{31}P-\{^1H\}$ n.m.r. spectrum of a tetrahydrofuran (thf) solution of this complex shows an AB pattern. Although the exact structure of complex (7) has not yet been fully established, a five-co-ordinate configuration containing co-ordinated chloride and two chelating ether phosphine ligands seems to be most likely. Solutions of (7) react readily with free ligand to give complex (4).

Complex (4) reacts readily with a further equivalent of AgSbF$_6$ in dichloromethane to give [Ru(P–O)$_3$][SbF$_6$]$_2$ (6). This complex may also be prepared by treating RuCl$_3$·3H$_2$O directly with 3 equivalents of AgSbF$_6$ followed by reaction with excess of ligand. A single-crystal X-ray diffraction study of (6) proved the ether phosphines to be in the facial configuration as illustrated in Scheme 1. However, the structure was found to be disordered and could not be well resolved.[30] The $^{31}P-\{^1H\}$ n.m.r. spectrum of complex (6) recorded in acetone at 243 K shows one sharp singlet at 51.9 p.p.m., which remains sharp on either lowering the temperature to 193 K or raising it to 308 K, indicating the absence of fluxional behaviour in solution. The $^{13}C-\{^1H\}$ n.m.r. spectrum measured at 306 K shows signals corresponding to chelating ether phosphine. No signals due to carbons α to unco-ordinated ether oxygen are observed. Upon the addition of a methanolic solution of HCl to a solution of (6) in methanol, immediate reconversion into complex (3) occurs.

A methanolic solution of the dichloride (1) reacts with 2 equivalents of silver acetate, 2 equivalents of silver trifluoroacetate, or 1 equivalent of silver acetate to give [Ru(O$_2$CCH$_3$)$_2$(O,P)$_2$] (10), [Ru(O$_2$CCF$_3$)$_2$(O,P)$_2$] (11), and [RuCl(O$_2$CCH$_3$)(O,P)$_2$] (12), respectively, where O,P indicates that the mode of co-ordination of the ligand is uncertain. Under anaerobic conditions, tetra-μ-acetato-acetatodiruthenium(II,III), [Ru$_2$(μ-O$_2$CCH$_3$)$_4$(O$_2$CCH$_3$)], reacts with excess of ligand in refluxing methanol to give a solution from which *fac*-[Ru(O$_2$CCH$_3$)$_2$(PO)$_3$] (8a) is eventually isolated. Complex (8a) was also prepared by treating (10) with a further equivalent of ligand. It has low conductivity in dichloromethane.

The $^{31}P-\{^1H\}$ n.m.r. spectrum of the diacetato complex (8a) in dichloromethane, measured at 203 K and 101.26 MHz (the spectrum at 32.39 MHz is strongly second order), shows a triplet and a doublet of twice the intensity (Table 2). On increasing the temperature to 243 K the triplet and the doublet coalesce to form a broad signal, which at higher temperatures

Table 3. Selected ^{13}C-(^{1}H) and ^{1}H n.m.r. chemical shift values[a]

| | | ^{13}C-{^{1}H}, δ/p.p.m. | | | | | | | | ^{1}H, δ | | | |
| | | CH$_2$OCH$_3$ | | CH$_2$OCH$_3$ | | CH$_3$CO$_2$ | | CH$_3$CO$_2$ | | CH$_2$OCH$_3$ | | CH$_3$CO$_2$ | |
Complex (solvent)	T/K	mono.	chel.	mono.	chel.	mono.	chel.	mono	chel.	mono	chel.	mono	chel.
(5) (CD$_2$Cl$_2$)	193	68.4	72.3	58.2	62.2, 59.8					2.92	3.21		
	306	72.0[b]		59.9[b]						3.12[b]			
(6) (CD$_2$Cl$_2$)	306		72.9								3.51		
(8a) (CD$_2$Cl$_2$)	203	68.0		57.8		25.1	26.5	176.7	189.2	2.97		1.96	2.07
	283	68.6		57.9		26.1[b]		183.5[b]		2.98		2.04[b]	
(8b) (CD$_3$OD)	243	69.0	74.0	58.5	61.8	24.2[c]	24.9	180.0[c]	192.8	2.98	3.52	1.88[c]	1.78
	306	69.0	73.0[b]	58.6	60.5[b]	24.2[c]	24.9	180.0[c]	192.8	2.96	3.2[b] (br)	1.88[c]	1.78

[a] mono. = Monodentate ether phosphine or acetate ligands, chel. = bidentate chelating ether phosphine or acetate ligand. [b] Coalesced signal due to monodentate/bidentate exchange process. [c] Ionic acetate in solution.

becomes a sharp singlet. The values of the coupling constants indicate mutual *cis* coupling of all three phosphorus atoms, and hence a facial configuration for the complex. The free energy of activation for the exchange process leading to this coalescence has been calculated as $\Delta G^{\neq} = 46.3$ kJ mol^{-1}. The ^{13}C-{^{1}H} n.m.r. spectrum of complex (8a) in CD$_2$Cl$_2$ (Table 3) shows ether-phosphine methyl and methylene signals at chemical shifts which indicate that all three ether oxygens are unco-ordinated at all temperatures measured (203—303 K). At 203 K, two signals of approximately equal intensity due to the carboxylate carbon of monodentate and of bidentate acetate are observed.[31] These signals become broad on raising the temperature, coalescing at *ca.* 258 K to become a single sharp resonance at 283 K. The signals due to the methyl groups of the two acetates show similar behaviour (Table 3). The free energy of activation of the process by which the signals due to the two acetates coalesce has been estimated to be *ca.* 49 kJ mol^{-1}, suggesting that it is the same process by which the three phosphines coalesce. The i.r. spectrum of complex (8a) indicates the presence of both monodentate and bidentate acetates,[32–34] as well as the absence of chelating ether oxygen (Table 4).

The above spectroscopic data indicate that for complex (8a) the co-ordination sites on one octahedral face are occupied by three monodentate phosphine ligands, while the other three sites are shared by a monodentate and a bidentate acetate,[35,36] as illustrated in Scheme 1. A dynamic process by which the two acetates interchange between monodentate and bidentate co-ordination modes is directly observed in the ^{13}C-{^{1}H} n.m.r. spectra. This process also explains the corresponding coalescence of signals due to the three phosphines in the ^{31}P-{^{1}H} spectra.[37] Furthermore, it is thought that the opening of a bidentate acetate is the rate-determining step in the exchange process.

On dissolving complex (8a) in methanol a yellow solution is formed, whose conductivity corresponds to the value expected for a 1:1 electrolyte containing acetate in conjunction with a large cation.[24] The ^{31}P-{^{1}H} n.m.r. spectrum of this solution at 243 K shows three doublets of doublets with mutual *cis*-coupling constants, indicating the presence of three chemically inequivalent phosphorus atoms in facial configuration. On treating a methanolic solution of complex (8a) with 1 equivalent of NaBPh$_4$, a bright yellow precipitate, *fac*-[Ru(O$_2$CCH$_3$)(P–O)(PO)$_2$]BPh$_4$ (9), is formed. The i.r. spectrum of this complex (Table 4) shows v(CO$_2$) bands for chelating acetate only, and v$_{asym}$(C$_2$O) bands due to both monodentate and chelating ether phosphine. The ^{31}P-{^{1}H} n.m.r. spectrum of complex (9) at 243 K (Figure 3) in either

dichloromethane or 1-chloropentane is the same as that of complex (8a) in methanol. This indicates that the complex species in methanolic solutions of (8a) is the cation *fac*-[Ru(O$_2$CCH$_3$)(P–O)(PO)$_2$]$^+$, and also that it is not a meth-anolic solvate of the type, *fac*-[Ru(O$_2$CCH$_3$)(P–O)(PO)$_2$-(CH$_3$OH)]$^+$,[37] since microanalytical and i.r. data for complex (9) show no evidence for the presence of methanol. We have designated the complex salt *fac*-[Ru(O$_2$CCH$_3$)(P–O)(PO)$_2$]-O$_2$CCH$_3$, which like complex (3) only exists in solution in polar solvents, as complex (8b). As with complex (3), under less-ionizing conditions (8b) reco-ordinates the ionic acetate to form (8a).

From the variable-temperature ^{31}P-{^{1}H} n.m.r. spectra of complex (9) in 1-chloropentane (Figure 3) it can be seen that the highest- and lowest-field signals coalesce at *ca.* 338 K, while the signal at intermediate field coalesces at the higher temperature of *ca.* 363 K, making all three phosphines equivalent on the n.m.r. time-scale. The variable-temperature ^{31}P-{^{1}H} n.m.r. spectra of complex (8b) in methanol followed a similar pattern. Thus, the one-dimensional spectra shown in Figure 3 suggest that the interchange of the three phosphines involves two separate mechanisms with different activation energies. This was verified by two-dimensional NOESY ^{31}P n.m.r. experiments on complex (8b) at different temperatures. The off-diagonal correlations of the low- and the high-field signals are due to exchange of these two phosphines at 243 K, while the phosphine at intermediate field shows no correlation and thus is not involved in the exchange at this temperature. At 263 K this phosphine also builds up cross-peaks indicating the start of the second exchange mechanism. Further evidence that two separate exchange mechanisms are involved comes from the ^{13}C-{^{1}H} n.m.r. spectrum of complex (8b) (Table 3). At 306 K the α-methyl and α-methylene carbons of one of the unco-ordinated ether functions show broad signals coalesced with those of the co-ordinated ether function, while the signals due to the second unco-ordinated ether function of the unique phosphine remain sharp. The first exchange involves the two ether phosphine ligands P-bonded *trans* to the bidentate acetate, which interchange between monodentate and chelating modes by way of opening and closing of the metal–oxygen (ether) bond *trans* to the third phosphine. The free energy of activation for this exchange has been estimated to be *ca.* 63.3 kJ mol^{-1}, and it occurs in conjunction with a second process whereby migration of the acetate to a new position relative to the three phosphines causes all three phosphines to become equivalent on the n.m.r. time-scale at elevated temperatures. The free energy of activation for this second process has been

Table 4. I.r.[a] and far-i.r.[b] spectroscopic data $(v_{max.}/cm^{-1})^c$

Complex	$v_{asym}(C_2O)$(ether) mono.	chel.	$v_{asym}(CO_2)$(carboxylate) mono.	chel.	$v_{sym}(CO_2)$(carboxylate) mono.	chel.	v(RuCl)
(2)	1 096 (sh)	1 067m					324s
(4)	ca. 1 100[d]	1 070s					309m
(5)	ca. 1 100[d]	1 063s					308m
(6)		1 056s					
(7)		1 061s					
(8a)	1 094 (sh)		1 626s	1 472s	1 317s	1 357s	
(9)	ca. 1 100[d]	1 056m		1 579m		1 465s	
(10)	ca. 1 100[d]	1 065 (sh)	1 600s	1 522m	1 412m	1 455s	
(11)	ca. 1 100[d]	1 052m	1 687s		1 403m		
(12)	ca. 1 100[d]	1 071m		1 529m		1 453s	311m
(13)	ca. 1 100[d]			1 537m		1 446s	e

[a] As KBr disc. [b] As polyethylene disc. [c] mono. = Monodentate ether phosphine or carboxylate, chel. = bidentate chelating ether phosphine or carboxylate. [d] Band obscured by P–C$_{aryl}$ vibration at ca. 1 100 cm^{-1}. [e] v(Ru–H) at 1 973w cm^{-1}.

estimated to be ca. 72.6 kJ mol^{-1}. It is of note that when a solution of complex (8a) in propan-1-ol is heated to 90 °C for several minutes substantial conversion into the hydride, mer-[RuH(O$_2$CCH$_3$)(PO)$_3$] (13), occurs.

The ^{31}P-{^{1}H} n.m.r. spectra of the methanolic solutions of the bis(ether phosphine) complexes [Ru(O$_2$CCH$_3$)$_2$(O,P)$_2$] (10), [Ru(O$_2$CCF$_3$)$_2$(O,P)$_2$] (11), and [RuCl(O$_2$CCH$_3$)(O,P)$_2$] (12) show evidence of complicated fluxional behaviour. In addition, the i.r. spectrum of (10) contains v(CO$_2$) bands due to both monodentate and chelating acetate.[33] This behaviour is in contrast with that found for the related species [Ru(O$_2$-CCH$_3$)$_2$(PPh$_3$)$_2$],[38] which has a rigid structure wherein both acetates are bidentate. The v_{asym}(C$_2$O) bands for co-ordinated ether functions are seen in the i.r. spectra of complexes (10) and (12) (Table 4).[14] We suspect that, in solutions of these complexes, acetate and ether functions are in competition to form the chelating mode and that this competition is giving rise to the observed fluxionality. The behaviour of complexes (10)—(12) in solution is under further investigation.

Complex (10) reacts with ligand in methanol to form the tris(phosphine) complex (8b). In addition, when a methanolic solution of complex (10) is exposed to air the solution changes from deep orange to deep purple. A similar purple solution is formed when [Ru$_2$(μ-O$_2$CCH$_3$)$_4$(O$_2$CCH$_3$)] is treated with ligand in the presence of air. Although the purple species has not yet been isolated in a pure state, the u.v.–visible spectra of the solutions and a mass-spectral molecular ion corresponding to [Ru$_2$O(O$_2$CCH$_3$)$_4$(O,P)$_2$]$^+$ strongly suggest that it may be an ether phosphine analogue of the proposed diruthenium(III,III) triphenylphosphine complex [Ru$_2$(μ-O)(μ-O$_2$CCH$_3$)$_2$(O$_2$CCH$_3$)$_2$(PPh$_3$)$_2$].[38,39]

We have found that mer-[RuH(O$_2$CCH$_3$)(PPh$_3$)$_3$][40,41] reacts with excess of ligand to give the extremely air-sensitive hydride mer-[RuH(O$_2$CCH$_3$)(PO)$_3$] (13). The structural analogy of complex (13) with its triphenylphosphine precursor is confirmed by the facts that their ^{31}P-{^{1}H} n.m.r. spectra show similar spin systems, and that there is no evidence for chelation of any ether phosphines in (13). The ^{1}H n.m.r. spectrum of complex (13) showed a doublet of triplets for the hydride ligand at −20.49 with a pattern of $^2J_{PH}$ values (Table 2) again similar to that obtained for [RuH(O$_2$CCH$_3$)(PPh$_3$)$_3$].[19]

Experimental

All operations were carried out under dry, oxygen-free argon using the usual Schlenk techniques. Solvents were purified by standard methods and stored under argon. Infra-red and far-i.r.

spectra were recorded with Bruker IFS 48 and IFS 114 C spectrophotometers, ^{31}P-{^{1}H} n.m.r. spectra at 32.39 and at 101.26 MHz with Bruker WP 80 and AC 250 spectrometers, respectively. The ^{31}P chemical shifts were recorded in p.p.m. downfield from 1% H$_3$PO$_4$ in (CD$_3$)$_2$CO or 85% H$_3$PO$_4$ in D$_2$O. The two-dimensional NOESY ^{31}P n.m.r. spectra were recorded on a Bruker AC 80 (32.44 MHz) spectrometer equipped with an Aspect 3000 computer and standard Bruker software. The temperature was controlled with a B-VT 1000 unit. The ^{13}C-{^{1}H} and ^{1}H n.m.r. spectra were recorded at 20.15 and at 80.13 MHz, respectively, on a Bruker AC 80 spectrometer. Chemical shifts for ^{13}C and ^{1}H are in p.p.m. downfield from SiMe$_4$. Field desorption (f.d.) and fast atom bombardment (f.a.b.) mass spectra were recorded on a Varian MAT 711 A mass spectrometer. Elemental analyses were carried out using a Carlo Erba 1106 analyser, and conductance measurements were made on a WTW DIGI 610 conductivity bridge.

(2-Methoxyethyl)diphenylphosphine,[17] mer-[RuCl$_2$-(PPh$_3$)$_3$],[18] [Ru$_2$(μ-O$_2$CCH$_3$)$_4$(O$_2$CCH$_3$)],[42] and mer-[RuH-(O$_2$CCH$_3$)(PPh$_3$)$_3$][43] were prepared according to the literature methods.

trans,cis,cis-[RuCl$_2$(P–O)$_2$] (1) (Alternative Preparation).[14]—The ligand Ph$_2$PCH$_2$CH$_2$OCH$_3$ (0.513 g, 2.1 mmol) was added to [RuCl$_2$(PPh$_3$)$_3$] (0.959 g, 1.0 mmol) in dichloromethane (20 cm^3), and the dark brown solution refluxed for 10 min. The resulting dark red solution was evaporated to low volume in vacuo. Diethyl ether (50 cm^3) was then added with stirring, causing precipitation of the red product. The solid was filtered off, washed several times with ether, and then dried in vacuo. Yield 0.560 g (85%).

mer-[RuCl$_2$(P–O)(PO)$_2$] (2).—Complex (1) (0.660 g, 1.0 mmol) and the ligand (0.448 g, 2.0 mmol) were dissolved in dichloromethane (20 cm^3) and refluxed for 10 min. No colour change was observed. The solution was cooled and evaporated in vacuo to low volume. Addition of n-hexane (20 cm^3) yielded the red product, which was washed several times with n-hexane and then dried in vacuo. Yield 0.630 g (70%).

fac-[RuCl(P–O)$_2$(PO)]Cl (3).—Solutions of this salt were prepared by refluxing a suspension of complex (1) (0.660 g, 1.0 mmol) in methanol (50 cm^3) with ligand (0.244 g, 1.0 mmol) for 0.5 h, the red solid slowly dissolving to give a deep yellow solution.

fac-[RuCl(P–O)$_2$(PO)]SbF$_6$ (4).—Method (a). A suspension of complex (1) (0.660 g, 1.0 mmol) with ligand (0.224 g, 1.0
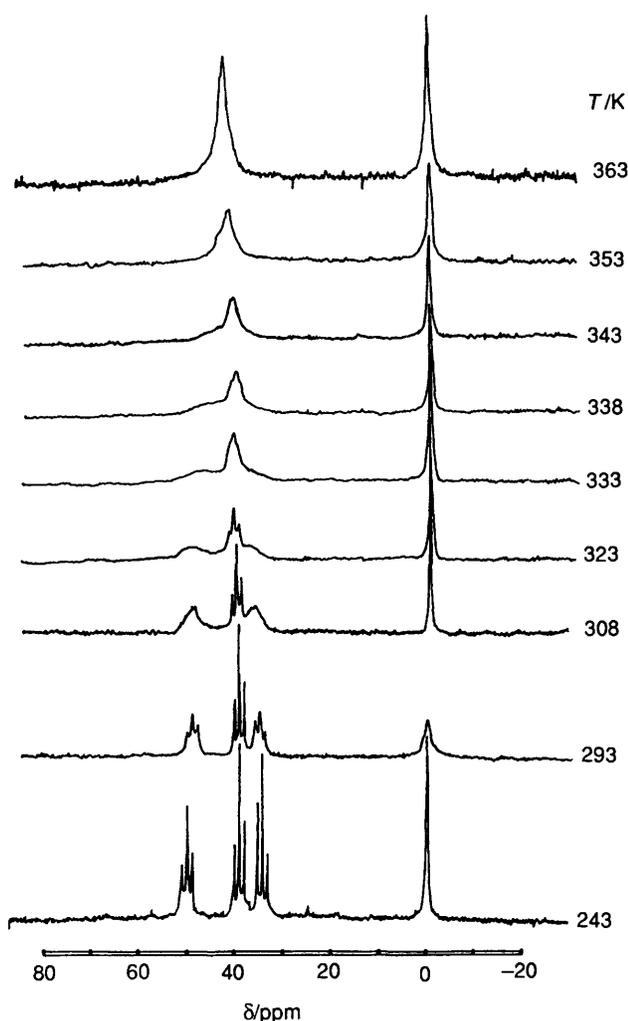
Figure 3. ^{31}P-$\{^1H\}$ N.m.r. variable-temperature study of *fac*-[Ru(O$_2$CCH$_3$)(P–O)(PO)$_2$]BPh$_4$ (9) in 1-chloropentane. The highest-field singlet is standard

mmol) in methanol (50 cm^3) was refluxed for 0.5 h to give a yellow solution. After cooling to room temperature a solution of AgSbF$_6$ (0.343 g, 1.0 mmol) in methanol (5 cm^3) was added dropwise. The AgCl was removed by centrifugation, and the yellow solution was evaporated to low volume *in vacuo*. The yellow solid which formed was filtered off, washed several times with diethyl ether, and then dried *in vacuo*. Yield 0.622 g (60%).

Method (*b*). Ligand (0.244 g, 1.0 mmol) was added to a solution of [RuCl(P–O)$_2$]SbF$_6$ (7) (0.860 g, 1.0 mmol) in thf (20 cm^3). After stirring for 0.5 h the solution was evaporated *in vacuo* to low volume. Addition of diethyl ether induced the precipitation of complex (4). Yield 0.440 g (40%). Mass spectrum (f.d.): *m/z* 868, [RuCl(P–O)$_2$(PO)]$^+$.

fac-[RuCl(P–O)$_2$(PO)]BPh$_4$ (5).—A suspension of complex (1) (0.660 g, 1.0 mmol) with ligand (0.244g, 1.0 mmol) in methanol (30 cm^3) was refluxed for 0.5 h and then cooled to room temperature. To the resulting yellow solution was added, with stirring, a methanolic solution (5 cm^3) of NaBPh$_4$ (0.324 g, 1.0 mmol). The yellow precipitate which formed immediately was filtered off, washed with methanol, and dried *in vacuo*. Yield 0.77 g (65%). Mass spectrum (f.d.): *m/z* 868, [RuCl(P–O)$_2$(PO)]$^+$.

fac-[Ru(P–O)$_3$][SbF$_6$]$_2$ (6).—*Method* (*a*). To a solution of *fac*-[RuCl(P–O)$_2$(PO)]SbF$_6$ (4) (1.104 g, 1.0 mmol) in

dichloromethane (50 cm^3) was added a solution of AgSbF$_6$ (0.343 g, 1.0 mmol) in dichloromethane. After stirring for 0.5 h the AgCl precipitate was removed, and the solution was then evaporated to low volume *in vacuo*. Addition of diethyl ether caused precipitation of the product, which was washed with ether and then dried *in vacuo*. Yield 0.720 g (55%). Crystals of this complex were obtained from a solution in dichloromethane–chloroform which was allowed to stand under argon.

Method (*b*). To a solution of RuCl$_3$·3H$_2$O (0.261 g, 1.0 mmol) in ethanol was added an ethanolic solution of AgSbF$_6$ (1.030 g, 3.0 mmol). The mixture was stirred for 0.5 h and the precipitate of AgCl removed by centrifugation. Ligand (0.978 g, 4.0 mmol) was then added to the brown filtrate and the mixture was refluxed for 1 h. When the resulting bright yellow solution was evaporated to low volume *in vacuo* and then cooled to −30 °C the product precipitated. Mass spectrum (f.d.): *m/z* 1 069, [Ru(P–O)$_3$(SbF$_6$)]$^+$.

[RuCl(P–O)$_2$]SbF$_6$ (7).—A solution of AgSbF$_6$ (0.343 g, 1.0 mmol) in thf (5 cm^3) was added dropwise to a solution of complex (1) (0.660 g, 1.0 mmol) in thf (50 cm^3) which had been cooled to 0 °C. After stirring in darkness at 0 °C for 1 h the AgCl was removed by centrifugation. The yellow filtrate was evaporated *in vacuo* to low volume, and addition of diethyl ether precipitated the product as a yellow powder. The solid was washed with ether and then dried *in vacuo*. Yield 0.267 g (31%). Mass spectrum (f.d.): *m/z* 625, [RuCl(P–O)$_2$]$^+$.

fac-[Ru(O$_2$CCH$_3$)$_2$(PO)$_3$] (8a).—The complex [Ru$_2$(μ-O$_2$-CCH$_3$)$_4$(O$_2$CCH$_3$)] (0.257 g, 0.5 mmol) and ligand (*ca.* 1.2 g, 5.0 mmol) were dissolved in methanol (15 cm^3) and the mixture refluxed until the dark brown solution turned first to dark green and then to deep yellow (*ca.* 1 h). The methanol was removed *in vacuo*, and the resulting brown tar was redissolved in dichloromethane (5 cm^3). Addition of diethyl ether (50 cm^3) caused precipitation of a crude product. The product was reprecipitated from dichloromethane using diethyl ether. The solid was collected by filtration, washed with ether, and then dried *in vacuo*. Yield 0.740 g (79%). Mass spectrum (f.a.b.): *m/z* 893, [Ru(O$_2$CCH$_3$)(P–O)(PO)$_2$]$^+$.

Solutions of the salt *fac*-[Ru(O$_2$CCH$_3$)(P–O)(PO)$_2$]O$_2$-CCH$_3$ (8b) were prepared by dissolving *fac*-[Ru(O$_2$CCH$_3$)$_2$-(PO)$_3$] (8a) in methanol.

fac-[Ru(O$_2$CCH$_3$)(P–O)(PO)$_2$]BPh$_4$ (9).—The complex *fac*-[Ru(O$_2$CCH$_3$)$_2$(PO)$_3$] (8a) (0.476 g, 0.5 mmol) was dissolved in methanol (5 cm^3), and to this solution was added, with stirring, a solution of NaBPh$_4$ (0.171 g, 0.5 mmol) in methanol (5 cm^3). A yellow precipitate formed immediately. After cooling the mixture to 0 °C the precipitate was filtered off, washed with two portions (5 cm^3) of cold methanol, and then dried *in vacuo*. Yield 0.478 g (78%). The salt (9) is insoluble in cold methanol but soluble in dichloromethane and diethyl ether.

[Ru(O$_2$CCH$_3$)$_2$(O,P)$_2$] (10).—Complex (1) (0.330 g, 0.5 mmol) was stirred at 50 °C in methanol (5 cm^3) with finely ground AgO$_2$CCH$_3$ (0.330 g, 1.0 mmol) for 0.5 h. The AgCl was filtered off, and the resulting orange-brown filtrate evaporated to dryness *in vacuo*. The brown solid was taken up in dichloromethane (5 cm^3) and then n-hexane (20 cm^3) was added. The dichloromethane was evaporated *in vacuo*, and when the remaining hexane solution was cooled to 0 °C the crude product precipitated. The solid was removed by filtration and then dried *in vacuo*. The crude solid was reprecipitated from dichloromethane using n-hexane to give the product as a dark orange-brown solid. Yield 0.160 g (45%). Mass spectrum (f.d.): *m/z* 708, [Ru(O$_2$CCH$_3$)$_2$(O,P)$_2$]$^+$. The solid decomposes

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to a tar after several weeks, even under an atmosphere of argon.

[Ru(O$_2$CCF$_3$)$_2$(O,P)$_2$] (11).—Complex (1) (0.330 g, 0.5 mmol) was stirred at 50 °C in thf (5 cm^3) with AgO$_2$CCF$_3$ (0.221 g, 1.0 mmol) for 0.5 h. The AgCl was removed by filtration, and n-heptane (20 cm^3) was added to the filtrate. The thf was removed *in vacuo* and the product precipitated. The solid was washed with n-hexane and then dried *in vacuo*. Yield 0.260 g (63%). Complex (11) appears to be more stable than (10).

[RuCl(O$_2$CCH$_3$)(O,P)$_2$] (12).—Complex (1) (0.660 g, 1.0 mmol) was stirred in methanol (30 cm^3) at 50 °C with AgO$_2$CCH$_3$ (0.166 g, 1.0 mmol) for 0.5 h. The AgCl was removed by filtration and the red filtrate was evaporated *in vacuo* to low volume. Diethyl ether (40 cm^3) was added and the product formed as a red-orange powder. The solid was filtered off, washed with ether, and then dried *in vacuo*. Yield 0.27 g (40%). Mass spectrum (f.d.): *m/z* 683, [RuCl(O$_2$CCH$_3$)(O,P)$_2$]$^+$.

mer-[RuH(O$_2$CCH$_3$)(PO)$_3$] (13).—The ligand (0.976 g, 4.0 mmol) was added to a suspension of *mer*-[RuH(O$_2$CCH$_3$)(PPh$_3$)$_3$] (0.948 g, 1.0 mmol) in methanol (50 cm^3). The mixture was refluxed until all the solids dissolved to give a yellow solution, which was subsequently evaporated to dryness *in vacuo*. The resulting yellow tar was dissolved in n-hexane (100 cm^3) at 40 °C, and the solution cooled to −40 °C. The yellow solid which precipitated was collected by filtration and washed several times with n-hexane at −40 °C. This crude product was redissolved in n-hexane containing further ligand (*ca.* 0.5 g, 2 mmol), and the mixture refluxed for 0.5 h. The resulting solution was then cooled to −40 °C to give the product as a yellow powder. The solid was washed with n-hexane at −40 °C and then dried *in vacuo*. The solutions and solid are extremely air-sensitive. Yield 0.206 g (23%). Mass spectrum (f.d.): *m/z* 894, [RuH(O$_2$CCH$_3$)(PO)$_3$]$^+$.

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