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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*-$[Ru(O_2CCH_3)_2(PO)_3]$, *fac*-$[Ru(O_2CCH_3)(P–O)(PO)_2]X$ (X = O_2CCH_3 or BPh_4), $[RuX_2(O,P)_2]$ (X = O_2CCH_3 or O_2CCF_3), $[RuCl(O_2CCH_3)(O,P)_2]$ and *mer*-$[RuH(O_2CCH_3)(PO)_3]$; 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, $Ph_2PCH_2CH_2OCH_3$.[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 ^1H, ^{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 $Ph_2PCH_2CH_2OCH_3$ react with commercial '$RuCl_3·3H_2O$' 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 $\nu_{asym}(C_2O)$ 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 $^{31}P-\{^1H\}$ 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 $^{31}P-\{^1H\}$ 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

† 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.

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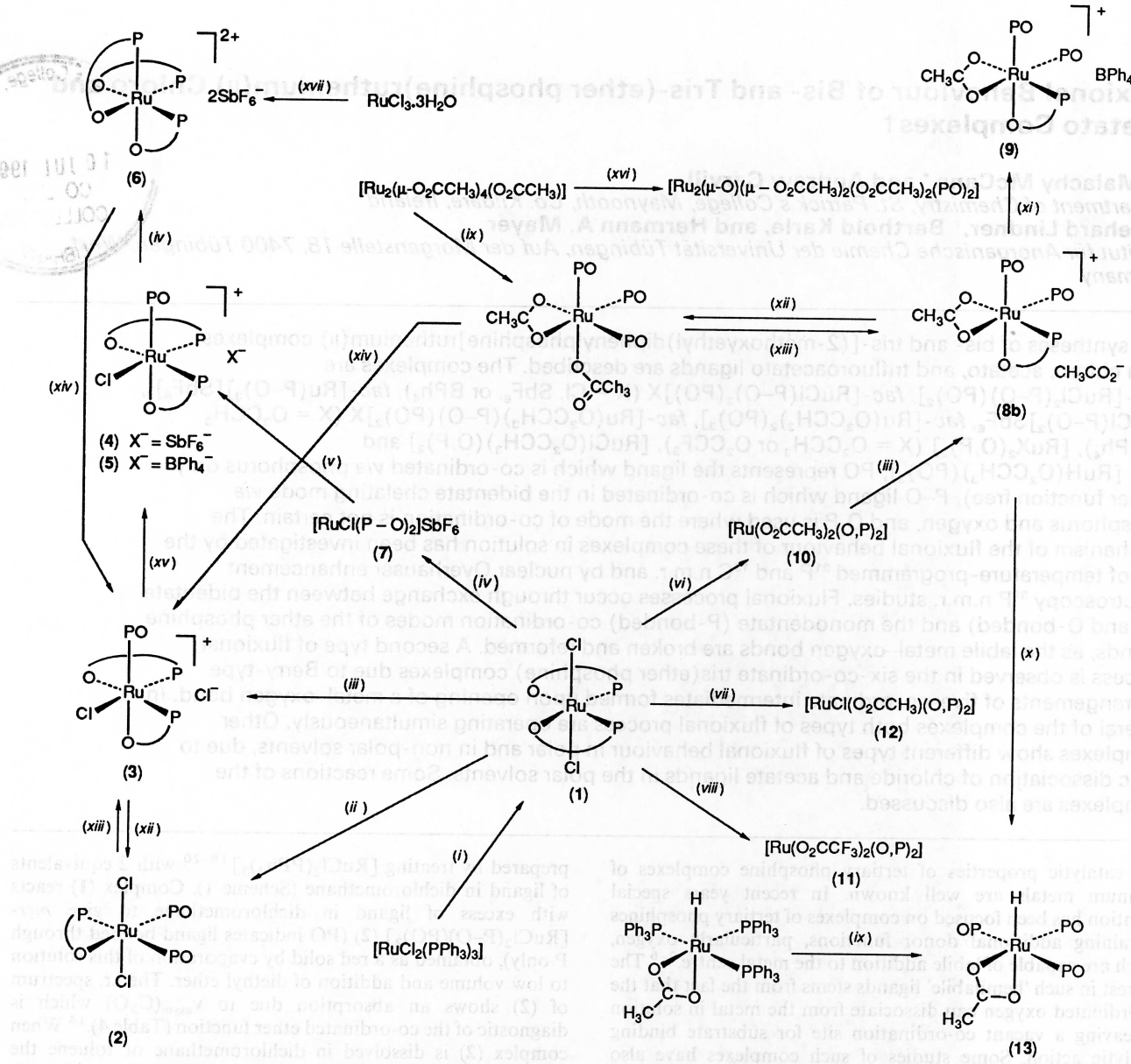


Scheme 1. Synthetic routes to the complexes. (*i*) 2 $Ph_2PCH_2CH_2OCH_3$, CH_2Cl_2; (*ii*) excess of ligand, CH_2Cl_2; (*iii*) ligand, CH_3OH; (*iv*) AgSbF ligand; (*vi*) 2 AgO_2CCH_3; (*vii*) AgO_2CCH_3; (*viii*) 2 AgO_2CCF_3; (*ix*) excess of ligand; (*x*) Pr^nOH, 90 °C; (*xi*) $NaBPh_4$; (*xii*) CH_2Cl_2; (*xiii*) CH_3 (*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 phosphine $[RuCl_2(PPh_3)_3]$, and in the ether phosphine complexes thought to be working in conjunction with the ring-opening -closing mechanism for exchange of the *trans* phosphines. the dichloride complex (**2**) the first exchange process ha slightly higher calculated free energy of activation[23] (49. mol⁻¹) than for the dihydride, whereas the free energy activation for the second process (56.9 kJ mol⁻¹) is about same in both complexes.

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

Table 1. Analytical and physical data

Complex	Colour	M.p. (decomp.)/°C	Analysis (%)[a] C	H	Cl	F	Λ_M/Ω^{-1} cm^2 mol^{-1}
(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*-[$Ru(O_2CCH_3)_2(PO)_3$]	Yellow	165—167	61.55 (61.80)	6.20 (6.05)			4.3[b]
(8b) *fac*-[$Ru(O_2CCH_3)(P{-}O)(PO)_2]O_2CCH_3$[c]	Yellow	—					58[d]
(9) *fac*-[$Ru(O_2CCH_3)(P{-}O)(PO)_2]BPh_4$	Pale yellow	81—83	70.00 (70.10)	6.25 (6.45)			
(10) [$Ru(O_2CCH_3)_2(O,P)_2$]	Deep orange	147—149	56.65 (57.70)	5.95 (5.70)			
(11) [$Ru(O_2CCF_3)_2(O,P)_2$]	Deep yellow	133—149	47.05 (46.95)	4.35 (4.45)		14.05 (14.85)	
(12) [$RuCl(O_2CCH_3)(O,P)_2$]	Pale red	156—158	55.70 (56.20)	5.35 (5.45)	5.60 (5.20)		
(13) *mer*-[$RuH(O_2CCH_3)(O,P)_3$]	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.

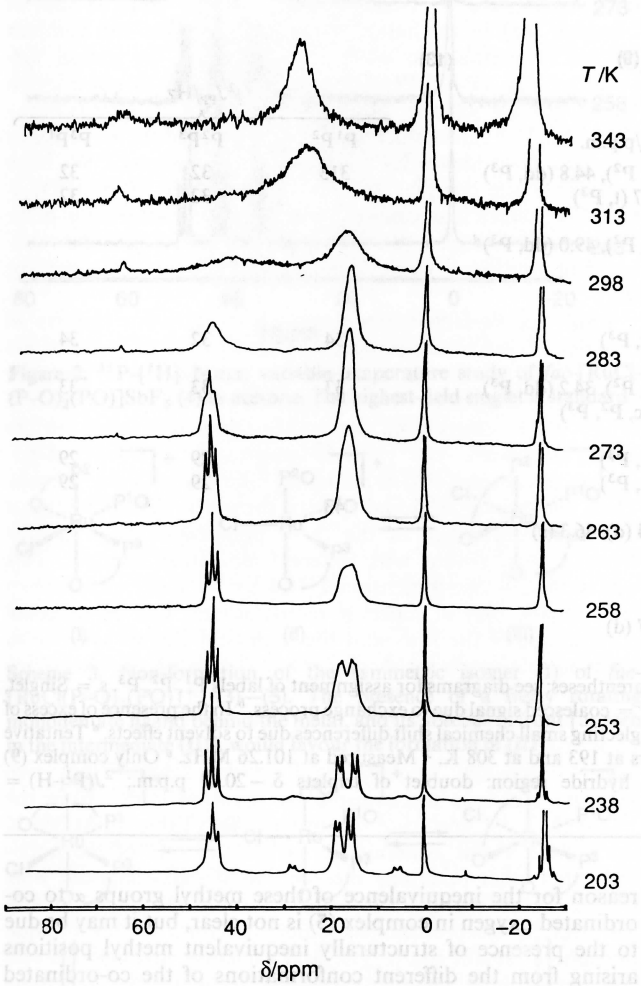
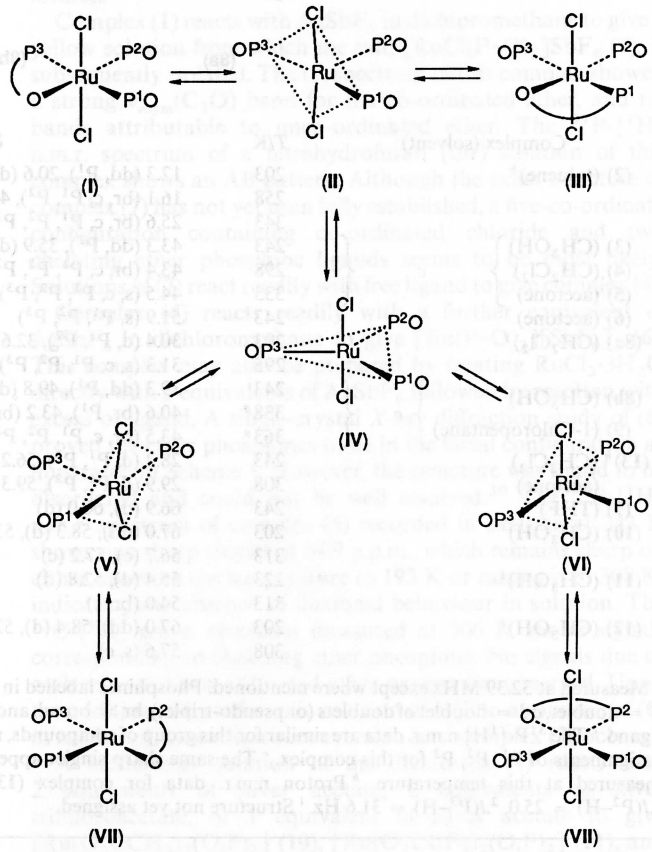


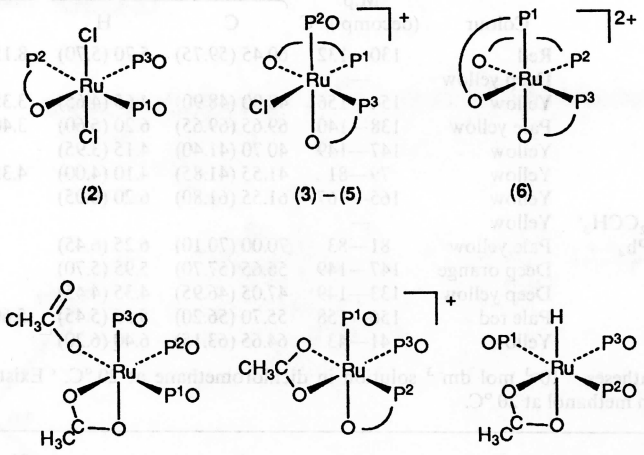
Figure 1. $^{31}P\text{-}\{^1H\}$ N.m.r. variable-temperature study of *mer*-[$RuCl_2(P{-}O)(PO)_2$] (2) in toluene solution, in the presence of *ca.* 1 equivalent of excess of free ligand. The highest-field singlet is due to free ligand, the second highest is that due to standard. The small low-field 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-{^{1}H} N.m.r. data



Complex (solvent)		T/K	δ[a]/p.p.m.	$^{2}J_{PP}$/Hz 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_3OH)	c	243	43.3 (dd, P^1), 35.9 (dd, P^2), 49.0 (dd, P^3)[d]			
(4) (CH_2Cl_2)	c	298	43.4 (br, c, P^1, P^2, P^3)			
(5) (acetone)	c	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_2Cl_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_3OH)	c	243	39.3 (dd, P^1), 49.8 (dd, P^2), 34.2 (dd, P^3)	33	33	33
(9) (1-Chloropentane)	c	338[g]	40.6 (br, P^1), 43.2 (br, c, P^2, P^3)			
		363[g]	43.5 (br, c, P^1, P^2, P^3)			
(13)[h] (CH_2Cl_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_3OH)[i]		203	67.0 (dd), 58.3 (d), 53.4 (d), 46.3 (s)			
		313	56.7 (c), 57.2 (c)			
(11) (CH_3OH)[i]		223	55.4 (d), 52.8 (d)			
		313	54.0 (br, c)			
(12) (CH_3OH)[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-{^{1}H} 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.; $^{2}J(P^1–H) = {}^{2}J(P^2–H) = 25.0$, $^{2}J(P^3–H) = 31.6$ 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-{^{1}H} n.m.r. spectra are identical to that of complex (2) in methanol.

The ^{13}C-{^{1}H} 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-{^{1}H} 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_2X pattern. ^{31}P-{^{1}H} 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,

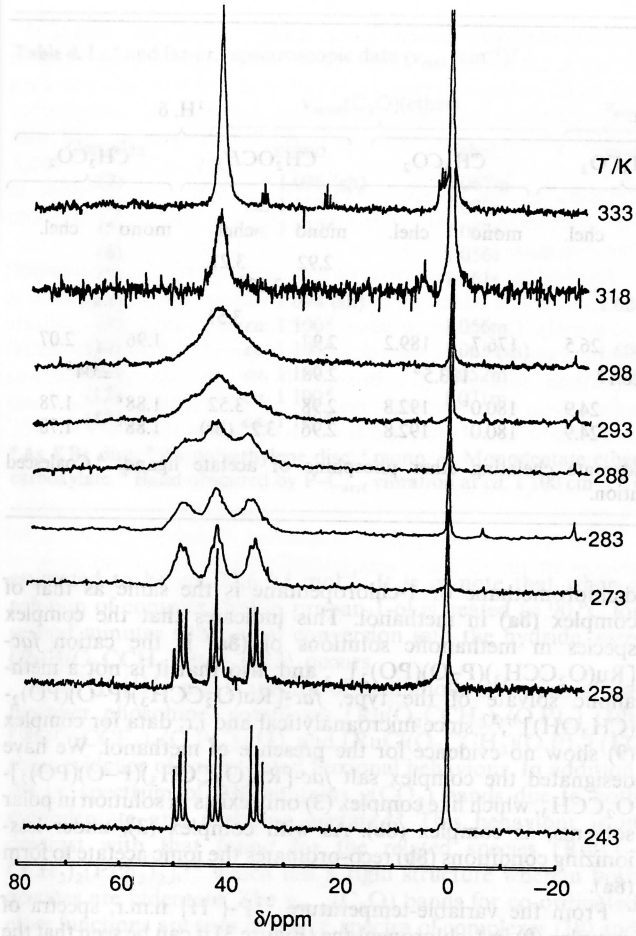
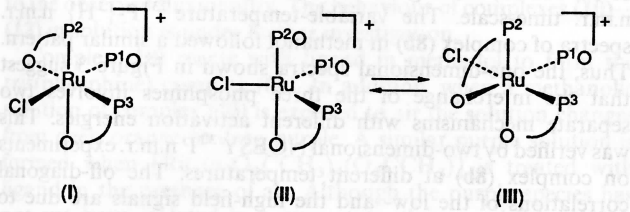
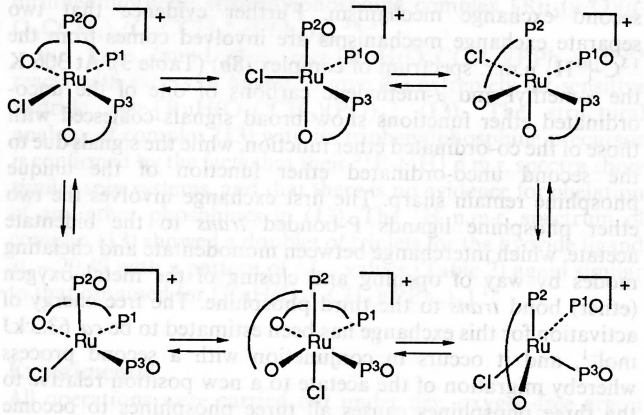


Figure 2. $^{31}P-\{^1H\}$ N.m.r. variable-temperature study of *fac*-[RuCl(P–O)$_2$(PO)]SbF$_6$ (**4**) in acetone. The highest-field singlet is standard



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 $RuCl_3 \cdot 3H_2O$ 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

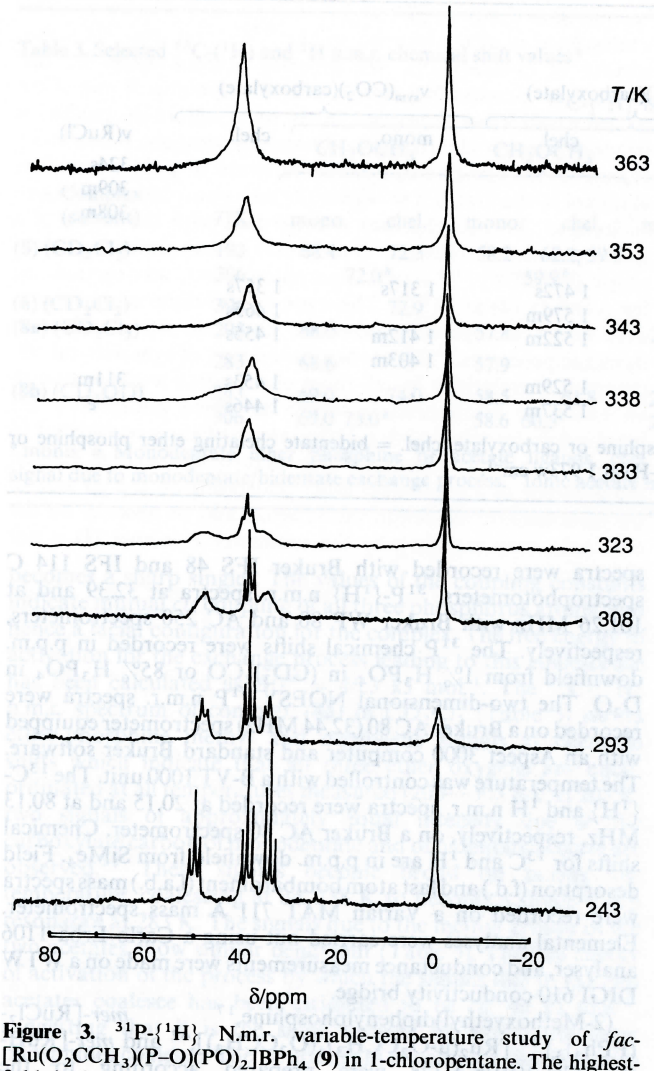


Figure 3. $^{31}P-\{^1H\}$ N.m.r. variable-temperature study of *fac*-$[Ru(O_2CCH_3)(P-O)(PO)_2]BPh_4$ (**9**) in 1-chloropentane. The highest-field singlet is standard

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 A (0.343 g, 1.0 mmol) in dichloromethane. After stirring fo the AgCl precipitate was removed, and the solution wa evaporated to low volume *in vacuo*. Addition of diethy caused precipitation of the product, which was washe ether and then dried *in vacuo*. Yield 0.720 g Crystals of this complex were obtained from a solu dichloromethane–chloroform which was allowed to under argon.

Method (*b*). To a solution of $RuCl_3 \cdot 3H_2O$ (0.261 g, 1.0 in ethanol was added an ethanolic solution of $AgSbF_6$ (1 3.0 mmol). The mixture was stirred for 0.5 h and the prec of AgCl removed by centrifugation. Ligand (0.978 g, 4.0 was then added to the brown filtrate and the mixtu refluxed for 1 h. When the resulting bright yellow solutio evaporated to low volume *in vacuo* and then cooled to − the product precipitated. Mass spectrum (f.d.): *m/z* $[Ru(P-O)_3(SbF_6)]^+$.

$[RuCl(P-O)_2]SbF_6$ (**7**).—A solution of $AgSbF_6$ (0.343 mmol) in thf (5 cm^3) was added dropwise to a solut complex (**1**) (0.660 g, 1.0 mmol) in thf (50 cm^3) which had cooled to 0 °C. After stirring in darkness at 0 °C for 1 AgCl was removed by centrifugation. The yellow filtrat evaporated *in vacuo* to low volume, and addition of d ether precipitated the product as a yellow powder. The was washed with ether and then dried *in vacuo*. Yield 0 (31%). Mass spectrum (f.d.): *m/z* 625, $[RuCl(P-O)_2]^+$.

fac-$[Ru(O_2CCH_3)_2(PO)_3]$ (**8a**).—The complex $[Ru_2($ $CCH_3)_4(O_2CCH_3)]$ (0.257 g, 0.5 mmol) and ligand (*ca.* 5.0 mmol) were dissolved in methanol (15 cm^3) and the m refluxed until the dark brown solution turned first to dark and then to deep yellow (*ca.* 1 h). The methanol was remo *vacuo*, and the resulting brown tar was redissolve dichloromethane (5 cm^3). Addition of diethyl ether (50 caused precipitation of a crude product. The product reprecipitated from dichloromethane using diethyl ether solid was collected by filtration, washed with ether, and dried *in vacuo*. Yield 0.740 g (79%). Mass spectrum (f.a.b. 893, $[Ru(O_2CCH_3)(P-O)(PO)_2]^+$.

Solutions of the salt *fac*-$[Ru(O_2CCH_3)(P-O)(PO)_2$ CCH_3 (**8b**) were prepared by dissolving *fac*-$[Ru(O_2CC$ $(PO)_3]$ (**8a**) in methanol.

fac-$[Ru(O_2CCH_3)(P-O)(PO)_2]BPh_4$ (**9**).—The comple $[Ru(O_2CCH_3)_2(PO)_3]$ (**8a**) (0.476 g, 0.5 mmol) was diss in methanol (5 cm^3), and to this solution was added, stirring, a solution of $NaBPh_4$ (0.171 g, 0.5 mmol) in meth (5 cm^3). A yellow precipitate formed immediately. After co the mixture to 0 °C the precipitate was filtered off, washed two portions (5 cm^3) of cold methanol, and then dried *in v* Yield 0.478 g (78%). The salt (**9**) is insoluble in cold meth but soluble in dichloromethane and diethyl ether.

$[Ru(O_2CCH_3)_2(O,P)_2]$ (**10**).—Complex (**1**) (0.330 g mmol) was stirred at 50 °C in methanol (5 cm^3) with f ground AgO_2CCH_3 (0.330 g, 1.0 mmol) for 0.5 h. The AgC filtered off, and the resulting orange-brown filtrate evapor to dryness *in vacuo*. The brown solid was taken u dichloromethane (5 cm^3) and then n-hexane (20 cm^3) added. The dichloromethane was evaporated *in vacuo*, when the remaining hexane solution was cooled to 0 °C crude product precipitated. The solid was removed by filtra and then dried *in vacuo*. The crude solid was reprecipit from dichloromethane using n-hexane to give the product dark orange-brown solid. Yield 0.160 g (45%). Mass spect (f.d.): *m/z* 708, $[Ru(O_2CCH_3)_2(O,P)_2]^+$. The solid decomp

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

$[Ru(O_2CCF_3)_2(O,P)_2]$ (**11**).—Complex (**1**) (0.330 g, 0.5 mmol) was stirred at 50 °C in thf (5 cm^3) with AgO_2CCF_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**).

$[RuCl(O_2CCH_3)(O,P)_2]$ (**12**).—Complex (**1**) (0.660 g, 1.0 mmol) was stirred in methanol (30 cm^3) at 50 °C with AgO_2CCH_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, $[RuCl(O_2CCH_3)(O,P)_2]^+$.

mer-$[RuH(O_2CCH_3)(PO)_3]$ (**13**).—The ligand (0.976 g, 4.0 mmol) was added to a suspension of *mer*-$[RuH(O_2CCH_3)(PPh_3)_3]$ (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, $[RuH(O_2CCH_3)(PO)_3]^+$.

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References

1 Part 24, E. Lindner and H. Norz, *Z. Naturforsch., Teil B*, 1989, **44**, 1493.
2 J. C. Jeffrey and T. B. Rauchfuss, *Inorg. Chem.*, 1979, **18**, 2658.
3 P. Braunstein, D. Matt, and Y. Dusausoy, *Inorg. Chem.*, 1983, **22**, 2043.
4 H. D. Empsall, S. Johnson, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 302.
5 N. W. Alcock, A. W. G. Platt, and P. Pringle, *J. Chem. Soc., Dalton Trans.*, 1987, 2273.
6 M. M. Taqui Khan and Md. K. Nazeeruddin, *Inorg. Chim. Acta*, 1988, **147**, 33.
7 E. Lindner and U. Schober, *Inorg. Chem.*, 1988, **27**, 212.
8 E. Lindner and B. Andres, *Chem. Ber.*, 1987, **120**, 761.
9 E. Lindner and B. Andres, *Chem. Ber.*, 1987, **121**, 829.
10 E. Lindner and H. Norz, *Chem. Ber.*, 1990, **123**, 459.
11 E. Lindner, U. Schober, E. Glaser, H. Norz, and P. Wegner, *Z. Naturforsch., Teil B*, 1987, **42**, 1527.
12 E. Lindner and R. Speidel, *Z. Naturforsch., Teil B*, 1989, **44**, 437.
13 E. Lindner, U. Schober, and M. Stängle, *J. Organomet. Chem.*, 1987, **331**, C13.
14 E. Lindner, U. Schober, R. Fawzi, W. Hiller, U. Englert, and P. Wegner, *Chem. Ber.*, 1987, **120**, 1621.
15 E. Lindner, A. Sickinger, and P. Wegner, *J. Organomet. Chem.*, 1988, **349**. 75.
16 E. Lindner, A. Bader, H. Bräunling, and R. Jira, *J. Mol. Catal.*, 1990, **57**, 291.
17 W. E. McEwen, A. Blair Janes, J. W. Knapczyk, V. L. Kyllingstad, W. I. Shiau, S. Shore, and J. H. Smith, *J. Am. Chem. Soc.*, 1978, **100**, 7304.
18 T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1966, **28**, 945.
19 P. R. Hoffman and K. G. Caulton, *J. Am. Chem. Soc.*, 1975, **97**, 4221.
20 S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 778.
21 E. Lindner, H. A. Mayer, and P. Wegner, *Chem. Ber.*, 1986, **119**, 2616.
22 P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229.
23 H. Günther, 'NMR Spektroskopie,' 2nd edn., Thieme Verlag, Stuttgart, 1983, p. 92.
24 P. W. Atkins, *Physical Chemistry*, 2nd ed. Oxford, 1982.
25 S. Meyer, Dissertation, University of Tübingen, 1987.
26 D. M. Roundhill, S. G. N. Roundhill, W. B. Beaulieu, and U. Bagghi, *Inorg. Chem.*, 1980, **19**, 3365.
27 T. B. Rauchfuss, F. T. Patino, and D. M. Roundhill, *Inorg. Chem.*, 1975, **14**, 652.
28 J. Jeener, B. H. Meier, P. Bachmann, and R. R. Ernst, *J. Chem. Phys.*, 1979, **71**, 4546.
29 A. Mezzetti, A. Del Zotto, P. L. Rigo, and N. Bresciani Pahor, *J. Chem. Soc., Dalton Trans.*, 1989, 1045.
30 B. Karle, Dissertation, University of Tübingen, 1990.
31 B. E. Mann and B. F. Taylor, '^{13}C NMR Data for Organometallic Compounds,' Academic Press, London, 1981.
32 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227.
33 R. C. Mehrotra and R. Bohra, 'Metal Carboxylates,' Academic Press, London, 1983, pp. 48—60.
34 A. Dobson and S. D. Robinson, *Inorg. Chem.*, 1977, **16**, 137.
35 R. H. Crabtree and A. J. Pearman, *J. Organomet. Chem.*, 1978, **157**, 335.
36 A. R. Al-Ohaly, R. A. Head, and J. F. Nixon, *J. Chem. Soc., Dalton Trans.*, 1978, 889.
37 C. J. Creswell, A. Dobson, D. S. Moore, and S. D. Robinson, *Inorg. Chem.*, 1979, **18**, 2055.
38 R. W. Mitchell, A. Spencer, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1973, 846.
39 P. Neubold, K. Wieghardt, B. Nuber, and J. Weiss, *Inorg. Chem.*, 1989, **28**, 459.
40 D. Rose, J. D. Gilbert, R. P. Richardson, and G. Wilkinson, *J. Chem. Soc. A*, 1969, 2610.
41 A. C. Skapski and F. A. Stephens, *J. Chem. Soc., Dalton Trans.*, 1974, 390.
42 M. Mukaida, T. Nomura, and T. Ishimori, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 2143.
43 S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1973, 1912.

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