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Isomerism in Carbonyldihalogenotris(phosphine)ruthenium(II) Complexes: Photochemical and Thermal Rearrangements

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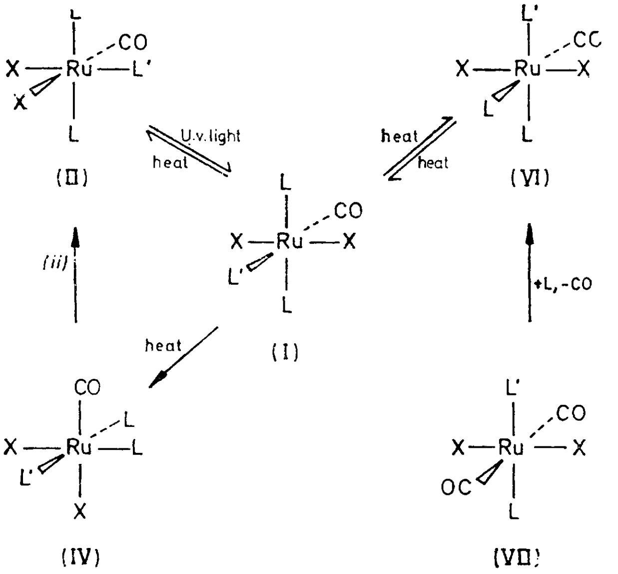
Four isomers of the complexes [$Ru(CO)Cl_2(PMe_2Ph)_2L'$] [(I), (II), (IV), and (VI); L' = $P(OMe)_3$ or $PPh(OMe)_2$] can be isolated and characterized. Isomer (II) is obtained, directly or indirectly, by heating any of the other three isomers, but irradiation of (II) leads specifically to isomer (I). A separate equilibrium exists between (I) and (VI). Isomers (I) and (II) of complexes [$Ru(CO)X_2(PMe_2Ph)_3$] (X = Cl, Br, or I) can be similarly interconverted. Kinetic study of the rearrangement (I) ⟶ (II) for [$Ru(CO)Cl_2(PMe_2Ph)_3$] indicates that the initial step involves loss of a PMe_2Ph ligand: the five-co-ordinate intermediate obtained can either react directly with PMe_2Ph to form isomer (II) or rearrange prior to reaction with PMe_2Ph. Evidence of the lability of the bonds to both types of phosphorus ligand in the various isomers of the complexes [$Ru(CO)Cl_2(PMe_2Ph)_2L'$] [L' = $P(OMe)_3$ or $PPh(OMe)_2$] suggests that mechanisms involving initial dissociation of a phosphorus ligand may also be involved in their interconversions.

In a recent paper [1] we reported that complexes [$Ru(CO)_2X_2L_2$] (L = ligand with phosphorus donor atom, X = halogen) of structure (II) (see Scheme 1, L' = CO) can be converted in solution into isomers of structure (I) by u.v. irradiation, and that the process can be reversed by heating the solution. Studies of the thermal rearrangement (I) ⟶ (II) revealed that it occurs by two competing routes, one direct and one by way of a third isomer of structure (IV). The mechanisms proposed for the thermal conversions (I) ⟶ (II) and (I) ⟶ (IV) ⟶ (II) are shown in Scheme 2 (L' = CO throughout): it can be seen that the reactions involve dissociation of a carbonyl ligand (L') as a first step.



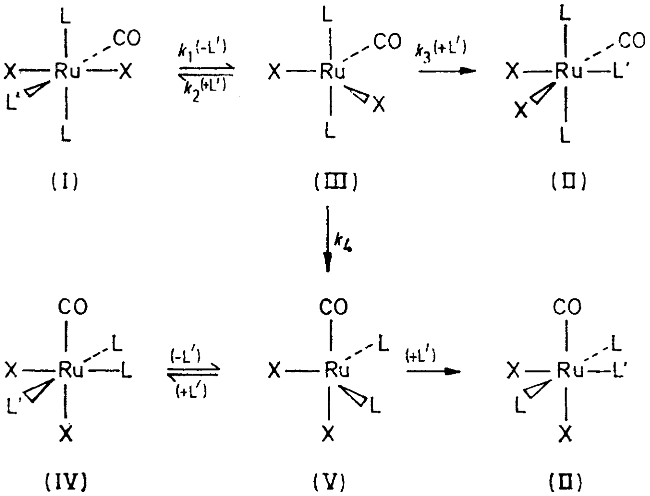
SCHEME 1 Interconversions of isomers of complexes [$Ru(CO)X_2L_2L'$], and preparative route to isomer (VI).

We have found that a somewhat related set of light- and heat-induced rearrangements connects four isomers of complexes [$Ru(CO)X_2(PMe_2Ph)_2L'$] (L' = ligand with phosphorus donor atom). This paper describes a study of the rearrangements and suggests mechanisms for them.

RESULTS AND DISCUSSION

Details of the preparation and i.r. and n.m.r. spectra of isomers (I), (II), and (IV) of complexes [$Ru(CO)Cl_2(PMe_2Ph)_2L'$] [L' = PMe_2Ph, $P(OMe)_3$, $PPh(OMe)_2$, or $PPh_2(OMe)$] (for structures see Scheme 1) have been given in a previous paper.[1] Complexes [$Ru(CO)X_2(PMe_2Ph)_3$] (X = Br or I) of structure (II) were prepared from the corresponding chloro-complex by treatment with the appropriate halide ions [2]: details of their i.r. and n.m.r. spectra are given in Table 1.

Irradiation of benzene solutions of the isomers of structure (II) converted them into those of structure (I) in good yield. (The method could not be used for [$Ru(CO)Cl_2(PMe_2Ph)_2\{PPh_2(OMe)\}$] because of the insolubility of isomer (II) in suitable solvents.) The reverse reaction, (I) ⟶ (II), could be brought about by heating in 2-methoxyethanol, chlorobenzene, or light petroleum {this reaction has previously been reported, for [$Ru(CO)Cl_2(PMe_2Ph)_3$] only, by Jenkins *et al.*[2]}: conversion into isomer (II) was essentially quantitative, except that in the case of the complexes containing two different phosphorus ligands a little disproportionation to



SCHEME 2 Proposed mechanisms for conversion of isomers (I) and (IV) of complexes [$Ru(CO)X_2L_2L'$] into isomer (II).

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[1] C. F. J. Barnard, J. A. Daniels, J. Jeffery, and R. J. Mawby, *J.C.S. Dalton*, 1976, 953.

[2] J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1787.

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products such as $[Ru(CO)Cl_2(PMe_2Ph)_3]$ and $[Ru(CO)Cl_2(PMe_2Ph)L'_2]$ occurred.

TABLE 1

Infrared [a] and n.m.r.[b] spectra of the complexes

Complex	Structure	$\bar{\nu}$(C–O)/cm^{-1}	δ/p.p.m.	Assignment
$[RuBr_2(CO)(PMe_2Ph)_3]$	(I)	1 979	1.66 (t, 12) [c]	P*Me*$_2$Ph (L)
			1.38 (d, 6)	P*Me*$_2$Ph (L′)
$[Ru(CO)I_2(PMe_2Ph)_3]$	(I)	2 004	1.75 (t, 12) [c]	P*Me*$_2$Ph (L)
			1.63 (d, 6)	P*Me*$_2$Ph (L′)
$[RuBr_2(CO)(PMe_2Ph)_3]$	(II)	1 933	2.05 (t, 6) [c]	P*Me*$_2$Ph (L)
			2.02 (t, 6)	
			1.43 (d, 6)	P*Me*$_2$Ph (L′)
$[Ru(CO)I_2(PMe_2Ph)_3]$	(II)	1 943 [c]	2.29 (t, 6)[d]	P*Me*$_2$Ph (L)
			2.26 (t, 6)	
			1.43 (d, 6)	P*Me*$_2$Ph (L′)
$[Ru(CO)Cl_2(PMe_2Ph)_2\{P(OMe)_3\}]$	(VI)	1 994 [d]	3.68 (d, 9) [e]	P(O*Me*)$_3$ (L′)
			1.74 (d, 6)	P*Me*$_2$Ph [f]
			1.38 (dd, 6)	P*Me*$_2$Ph [g]
$[Ru(CO)Cl_2(PMe_2Ph)_2\{PPh(OMe)_2\}]$	(VI)	2 001	3.56 (d, 6) [e]	PPh(O*Me*)$_2$ (L′)
			1.52 (d, 6)	P*Me*$_2$Ph [f]
			1.50 (dd, 6)	P*Me*$_2$Ph [g]

[a] In the C–O stretching region only. Nujol mulls except where otherwise stated. [b] Resonances due to phenyl protons are not included. Multiplicities and relative areas are given in parentheses after the chemical-shift values: d = doublet, dd = doublet of doublets, and t = triplet. [c] In benzene solution. [d] In chloroform solution (for n.m.r. spectra, $CDCl_3$). [e] In chlorobenzene solution. [f] This ligand is *trans* to CO (see Scheme 1). [g] This ligand is *trans* to L′ (see Scheme 1).

In order to obtain information about the mechanism of the rearrangement (I) ⟶ (II), a study was made of the isomerization of $[Ru(CO)Cl_2(PMe_2Ph)_3]$ in chlorobenzene solution. Since complexes $[Ru(CO)_2X_2L_2]$ had been found[1] to undergo a similar rearrangement by a dissociative mechanism, it seemed likely that the mechanism of this reaction would also be dissociative in nature. Such a mechanism might involve the loss of a PMe_2Ph ligand as a first step: to check on this possibility n.m.r. spectroscopy was used to determine the effect on the rate of isomerization at 373 K of adding free PMe_2Ph to the solution. Two solutions were used: each contained the same concentration of isomer (I) of $[Ru(CO)Cl_2(PMe_2Ph)_3]$, but one also contained free PMe_2Ph. The only resonances observed in the spectra of the reaction mixtures were those attributable to isomers (I) and (II) of $[Ru(CO)Cl_2(PMe_2Ph)_3]$ and, in one case, free PMe_2Ph. In each case conversion into isomer (II) was quantitative, but rearrangement was markedly slower in the solution containing free PMe_2Ph.

This suggests that the initial step in the rearrangement of isomer (I) of $[Ru(CO)Cl_2(PMe_2Ph)_3]$ is indeed the loss of a PMe_2Ph ligand. This could, however, either be that *trans* to CO (marked L′ in Scheme 1) or one of the pair of mutually *trans* PMe_2Ph ligands (marked L). Evidence as to the relative lability of the two types of Ru–P bond was obtained by studying the reaction of isomer (I) of $[Ru(CO)Cl_2(PMe_2Ph)_3]$ with excess of $P(OMe)_3$. Replacement of the ligand marked L′ would give isomer (I) of $[Ru(CO)Cl_2(PMe_2Ph)_2\{P(OMe)_3\}]$, while replacement of one of those marked L would give isomer (VI) [see Scheme 1, L = PMe_2Ph, L′ = $P(OMe)_3$, and X = Cl]. We had prepared both these isomers and (see below) found them to be of very similar thermodynamic stability. The reaction of isomer (I) of $[Ru(CO)Cl_2(PMe_2Ph)_3]$ with $P(OMe)_3$ (in chlorobenzene at 294 K), however, yields only isomer (I) of $[Ru(CO)Cl_2(PMe_2Ph)_2\{P(OMe)_3\}]$, and therefore appears to be kinetically controlled, indicating that the bond to the PMe_2Ph ligand marked L′ in isomer (I) of $[Ru(CO)Cl_2(PMe_2Ph)_3]$ is more labile than those to the PMe_2Ph ligands marked L. Since PMe_2Ph appears to have a greater *trans*-labilizing effect than CO in complexes of Ru^{II},[2] this is surprising, but it presumably reflects the much greater relief of steric strain within the molecule when the ligand L′ is removed.

A kinetic study of the rearrangement of isomer (I) of $[Ru(CO)Cl_2(PMe_2Ph)_3]$ in the presence of varying concentrations of free PMe_2Ph, using visible spectroscopy to monitor the reaction, revealed that it is first order in the concentration of isomer (I), and that the value for the first-order rate constant $k_{obs.}$ (see Table 2) decreases with increasing PMe_2Ph concentration, but approaches a limiting minimum value beyond which further addition of PMe_2Ph has no effect.

TABLE 2

Observed rate constants for the rearrangement of isomer (I) of $[Ru(CO)Cl_2(PMe_2Ph)_3]$ in the presence of PMe_2Ph *

$[PMe_2Ph]$/mol dm^{-3}	$10^4k_{obs.}/s^{-1}$
6.60×10^{-5}	3.05
2.23×10^{-4}	2.27
1.11×10^{-3}	1.55
3.04×10^{-3}	1.50
1.42×10^{-2}	1.49

* In chlorobenzene solution at 368 K. Values accurate to (at worst) ±5%. Initial concentration of isomer (I) *ca.* 6×10^{-3} mol dm^{-3}.

These results are compatible with the mechanism shown in Scheme 2 (L = L′ = PMe_2Ph, X = Cl). Loss from (I) of the PMe_2Ph ligand marked L′ yields the same intermediate, (III), as that formed in the first step of the rearrangement of isomer (I) of complexes $[Ru(CO)_2X_2L_2]$.[1] This may then pick up L′ to reform (I) or to give (II), or it may rearrange to (V) prior to attack by L′. Either of the two paths of attack on (V) shown in Scheme 2 will yield isomer (II), since for the complexes

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$[Ru(CO)X_2(PMe_2Ph)_3]$ structures (II) and (IV) are identical.

Using the steady-state approximation for the concentration of intermediates (III) and (V), the rate expression (1) is obtained which gives the required first-order

$$-\frac{d[(I)]}{dt} = \frac{k_1[(I)](k_3[L'] + k_4)}{(k_2 + k_3)[L'] + k_4} \qquad (1)$$

dependence on the concentration of isomer (I) and a first-order rate constant as in (2). As the concentration

$$k_{obs.} = \frac{k_1(k_3[L'] + k_4)}{(k_2 + k_3)[L'] + k_4} \qquad (2)$$

of free PMe_2Ph (L') is increased, $k_{obs.}$ should decrease towards a limiting value $k_1k_3/(k_2 + k_3)$. This fits the observed kinetic behaviour of the system: in effect, increase of the concentration of free PMe_2Ph increases the likelihood that (III) will be attacked before it can rearrange, until at high PMe_2Ph concentrations the rearrangement (III) ⟶ (V) can be neglected.*

An n.m.r. study was then made of the rearrangement of isomer (I) of the complexes $[Ru(CO)Cl_2(PMe_2Ph)_2L']$ $[L' = P(OMe)_3$, $PPh(OMe)_2$, or $PPh_2(OMe)]$. When isomer (I) of $[Ru(CO)Cl_2(PMe_2Ph)_2\{P(OMe)_3\}]$ was heated at 353 K in chlorobenzene solution, resonances attributable to isomer (II) appeared at once and increased in area throughout the reaction. Resonances due to some other species were also observed, however: this complex appeared to reach equilibrium with isomer (I), and thereafter the relative concentrations of the two remained unaltered as conversion into isomer (II) proceeded. The new species was not, as might have been expected, isomer (IV) of $[Ru(CO)Cl_2(PMe_2Ph)_2\{P(OMe)_3\}]$ but was tentatively assigned structure (VI) [see Scheme 1, L = PMe_2Ph, L' = $P(OMe)_3$, and X = Cl], an assignment which was confirmed by preparing this isomer of $[Ru(CO)Cl_2(PMe_2Ph)_2\{P(OMe)_3\}]$ from $[Ru(CO)_2Cl_2(PMe_2Ph)\{P(OMe)_3\}]$ [structure (VII)] [1] and comparing n.m.r. spectra (see Table 1).

On heating a chlorobenzene solution of the isolated sample of isomer (VI) at 353 K, the equilibrium between (VI) and (I) was again set up, but there was a significant delay in the formation of (II) suggesting that (II) is formed from (I) and not directly from (VI). On this basis, formation of (VI) during the rearrangement (I) ⟶ (II) for $[Ru(CO)Cl_2(PMe_2Ph)_2\{P(OMe)_3\}]$ appears to be a diversion rather than a first step in the rearrangement.

Similar results were obtained when $[Ru(CO)Cl_2(PMe_2Ph)_2\{PPh(OMe)_2\}]$ was studied. Details of the n.m.r. spectrum of isomer (VI) of this complex, formed during the rearrangement of isomer (I) and also prepared independently from $[Ru(CO)_2Cl_2(PMe_2Ph)\{PPh(OMe)_2\}]$ [structure (VII)],[1] are given in Table 1. Use of n.m.r. spectroscopy to study the rearrangement of isomer (I) of $[Ru(CO)Cl_2(PMe_2Ph)_2\{PPh_2(OMe)\}]$ was ruled out by the insolubility of isomer (II) of this complex.

Attempts were made, by determining the effect on the rate of rearrangement of adding free L' to the solution, to obtain evidence that the rearrangement (I) ⟶ (II) for the complexes $[Ru(CO)Cl_2(PMe_2Ph)_2L']$ [L' = $P(OMe)_3$ or $PPh(OMe)_2$] involves dissociation of the ligand L'. Unfortunately this caused partial replacement of PMe_2Ph by L'. Conversely, addition of free PMe_2Ph caused partial conversion into $[Ru(CO)Cl_2(PMe_2Ph)_3]$. From these results we conclude that both types of Ru–P bond are somewhat labile under the conditions used for the rearrangement, a conclusion supported by the observation that some disproportionation accompanies the rearrangement.

TABLE 3

Analytical data

Complex	Structure	Colour	M.p. (T/K)	Analysis (%)			
				Found		Calc.	
				C	H	C	H
$[RuBr_2(CO)(PMe_2Ph)_3]$	(I)	Yellow	418—421	42.7	4.70	42.7	4.75
$[Ru(CO)I_2(PMe_2Ph)_3]$	(I)	Orange-red	479—481	37.45	4.10	37.65	4.15
$[RuBr_2(CO)(PMe_2Ph)_3]$	(II)	Colourless	465—468	42.8	4.70	42.7	4.75
$[Ru(CO)I_2(PMe_2Ph)_3]$	(II)	Yellow	489—491	37.8	4.10	37.65	4.15
$[Ru(CO)Cl_2(PMe_2Ph)_2\{P(OMe)_3\}]$	(VI)	Yellow	424—425	40.15	5.05	40.0	5.20
$[Ru(CO)Cl_2(PMe_2Ph)_2\{PPh(OMe)_2\}]$	(VI)	Yellow	424—427	46.6	5.05	46.45	5.15

In view of the results obtained with $[Ru(CO)Cl_2(PMe_2Ph)_3]$, however, it is likely that a mechanism of the type illustrated in Scheme 2 [L = PMe_2Ph, L' = $P(OMe)_3$ or $PPh(OMe)_2$, X = Cl] may also apply here, although there is no direct evidence for the involvement of the species (V) and (IV). Failure to observe isomer (IV) of these complexes during the rearrangement (I) ⟶ (II) does not, however, rule out its involvement in the rearrangement, since separate experiments with isolated samples of isomer (IV) of $[Ru(CO)Cl_2(PMe_2Ph)_2L']$ [L' = $P(OMe)_3$ or $PPh(OMe)_2$] showed that the rate of conversion (IV) ⟶ (II) is appreciably faster than that for the overall rearrangement (I) ⟶ (II). No species other than (IV) and (II) (apart from small quantities of disproportionation products) was observed during the conversion. Experiments involving treatment of [IV; L = PMe_2Ph, L' = $PPh(OMe)_2$, X = Cl]

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* The intermediates (III) and (V) are represented as having trigonal-bipyramidal geometry [despite the fact that several isolable five-co-ordinate complexes of d^6 metal ions have been found to be closer to square-pyramidal than to trigonal-bipyramidal geometry (see, for example, P. R. Hoffmann and K. G. Caulton, *J. Amer. Chem. Soc.*, 1975, **97**, 4221)] because the kinetic data cannot be fitted satisfactorily to any reasonably simple scheme involving intermediates of square-pyramidal geometry.

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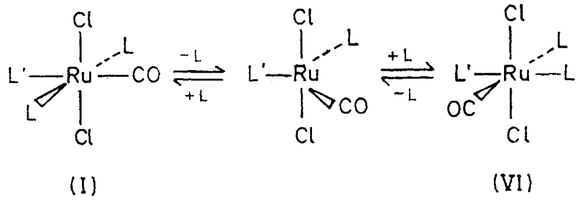
with either PMe_2Ph or $PPh(OMe)_2$ established that the bonds to both the mutually *trans* phosphorus ligands are labile (as is implied by the formation of disproportionation products during the rearrangement). Either of these ligands may be lost in the first step of the rearrangement: Scheme 2 envisages the loss of L′ {as previously proposed[1] with L′ = CO for the corresponding rearrangement of complexes $[Ru(CO)_2X_2L_2]$}, but a parallel mechanism involving loss of L is equally plausible.

The mechanism by which isomers (I) and (VI) of the complexes $[Ru(CO)Cl_2(PMe_2Ph)_2L']$ [L′ = $P(OMe)_3$ or $PPh(OMe)_2$] come into equilibrium cannot involve (III) (see Schemes 1 and 2) as an intermediate since this would allow direct conversion of (VI) into (II) which apparently (see above) does not occur. Treatment of either isomer with excess of L′ caused partial replacement of PMe_2Ph by L′, indicating that the bonds to the PMe_2Ph ligands are somewhat labile. This makes it possible to suggest a mechanism of the type shown in Scheme 3 [L = PMe_2Ph, L′ = $P(OMe)_3$ or $PPh(OMe)_2$] for the equilibration of the two isomers. One of the surprising features of the behaviour of the four observed isomers of these complexes is that whereas (I) and (VI) are evidently of roughly equal stability, the similarly related pair (II) and (IV) are not, so that on heating any one of the isomers (I), (VI), and (IV) there is ultimately complete conversion into (II).



SCHEME 3 Suggested mechanism for interconversion of isomers (I) and (VI) of complexes $[Ru(CO)Cl_2L_2L']$.

The photochemical conversion of the complexes of structure (II) into their isomers of structure (I) is the most striking of the rearrangements in that it leads specifically to one of the three isomers of higher energy, (I), (IV), and (VI). The mechanism probably involves initial light-induced cleavage of one of the metal–ligand bonds. Ultraviolet light is known to promote phosphorus ligand exchange in transition-metal complexes,[3] and it is possible that the ligand lost in this instance is L′ (see Scheme 2), generating the intermediate (III). This, under the mild conditions used (room temperature or below) would pick up L′ preferentially *trans* to CO rather than *trans* to halide ion because of the greater *trans*-directing effect of the former ligand (see discussion in refs. 1 and 4). Ultraviolet light is, however, also known to cleave metal–carbonyl bonds,[5] and an analogous mechanism could be put forward on the basis of initial dissociation of the carbonyl ligand.

EXPERIMENTAL

All the work described in this paper took place under an atmosphere of dry nitrogen. Infrared spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer, and n.m.r. spectra on a Varian A60A 60 MHz spectrometer, using a V-6057 variable-temperature accessory. Kinetic data for the rearrangement of isomer (I) of $[Ru(CO)Cl_2(PMe_2Ph)_3]$ were obtained by monitoring the change in absorbance of the reaction solution at 430 nm, using a Unicam SP 800 spectrophotometer. Linear plots of log(absorbance) against time were obtained for at least three half-lives, and the values given for the observed first-order rate constant in Table 2 were obtained from a least-mean-squares treatment of absorbance and time data.

Complexes $[Ru(CO)X_2(PMe_2Ph)_3]$ (X = Br *or* I), *Configuration* (II).—These were prepared from the chloro-complex of this configuration as described by Jenkins *et al.*[2]

Irradiation of Complexes of Configuration (II).—$[Ru(CO)Cl_2(PMe_2Ph)_3]$. A solution of $[Ru(CO)Cl_2(PMe_2Ph)_3]$ [isomer (II), 0.15 g] in benzene (2 cm^3) was irradiated for 24 h (for details of the irradiation apparatus see ref. 1). After removal of the solvent under reduced pressure, the residue was recrystallized from ethanol, giving crystals of isomer (I) of $[Ru(CO)Cl_2(PMe_2Ph)_3]$. The complexes $[Ru(CO)X_2(PMe_2Ph)_3]$ (X = Br or I) were similarly converted from structure (II) into (I). In the case of the complexes $[Ru(CO)Cl_2(PMe_2Ph)_2L']$ [L′ = $P(OMe)_3$ or $PPh(OMe)_2$] the products were obtained in crystalline form on concentrating the benzene solutions by evaporation of the solvent under reduced pressure. The crystals were washed with a little acetone and then with light petroleum (b.p. 313—333 K).

Complexes $[Ru(CO)Cl_2(PMe_2Ph)_2L']$, *Configuration* (VI).—$[Ru(CO)Cl_2(PMe_2Ph)_2\{P(OMe)_3\}]$. To a solution of $[Ru(CO)_2Cl_2(PMe_2Ph)\{P(OMe)_3\}]$ [configuration (VII), 0.10 g][1] in chlorobenzene (10 cm^3) was added PMe_2Ph (0.042 g). After 2 h at 313 K the solution was cooled to room temperature and concentrated by passing a stream of nitrogen over it. The crystals obtained were washed thoroughly with light petroleum (b.p. 313—333 K). The same method was used to obtain $[Ru(CO)Cl_2(PMe_2Ph)_2\{PPh(OMe)_2\}]$ from $[Ru(CO)_2Cl_2(PMe_2Ph)\{PPh(OMe)_2\}]$ (0.10 g) and PMe_2Ph (0.039 g).

Preparations of other complexes mentioned in the paper are given in ref. 1.

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