Mechanism of Light- and Heat-induced Rearrangements of Complexes of Ruthenium(II)

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Complexes *cis*-$[Ru(CO)_2L_2X_2]$ (L = ligand with phosphorus or arsenic donor atom, X = halogen) are converted to their all-*trans*-isomers by u.v. irradiation; the process can be reversed by heating. Similar rearrangements occur with complexes $[Ru(CO)_2LL'Cl_2]$ containing two different phosphorus ligands L and L'. Studies of the thermal rearrangements of complexes all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2X_2]$ and all-*trans*-$[Ru(CO)_2(PMePh_2)_2X_2]$ show that they occur by two competing routes, one direct and one by way of a third isomer, the all-*cis*-isomer. Evidence from these studies and from the stereochemistry of carbonyl-substitution reactions of the various isomers of $[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ is presented to support mechanisms for the photochemical and thermal isomerizations which involve dissociation of a carbonyl ligand as a first step During the isomerizations, partial loss of CO from solution causes the formation of complexes $[\{Ru(CO)L_2X_2\}_2]$ as by-products.

SOME time ago, we reported [1] that the complex *cis*-$[Ru(CO)_2(PPh_3)_2I_2]$ rearranges in solution under the influence of daylight to all-*trans*-$[Ru(CO)_2(PPh_3)_2I_2]$ (for structures, see Scheme 1, where L = PPh_3 and X = I), and that the reaction can be reversed by heating the solution. We have now found that this reversible isomerization is general to a range of complexes $[Ru(CO)_2L_2X_2]$ (L = ligand with phosphorus or arsenic donor atom; X = Cl, Br, or I), although in most cases the conversion of *cis*-isomer to all-*trans*-isomer requires u.v. radiation rather than daylight. We have also discovered that—in some cases, at least—the thermal rearrangement of all-*trans*-isomer back to *cis*-isomer goes by way of a third isomer.

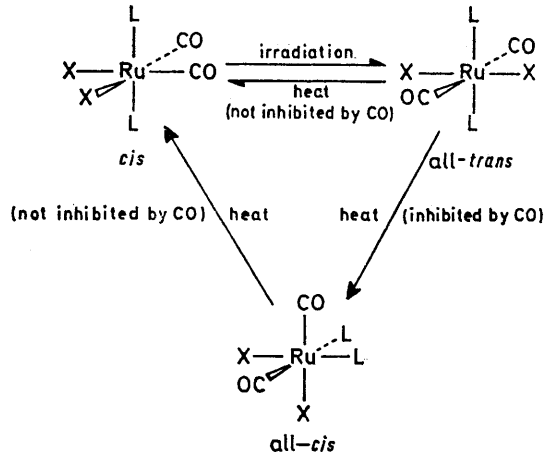
This paper examines the mechanism of the isomerizations in the light of evidence from these and related reactions.

RESULTS AND DISCUSSION

Details of the i.r. and n.m.r. spectra of the complexes described in this paper are given in Tables 1 and 2 respectively.

[1] J. Jeffery and R. J. Mawby, *J. Organometallic Chem.*, 1972, **40**, C42.

(1) *Preparation of Complexes* cis-$[Ru(CO)_2L_2X_2]$ *and Their Photochemical Conversion into All-*trans*-isomers.*—



SCHEME 1 Rearrangements of complexes $[Ru(CO)_2L_2X_2]$: experimental observations

containing the ligands PMe_2Ph, $PMePh_2$, $P(CH_2Ph)Ph_2$, and $P(OMe)_2Ph$ follows from the observation of two C–O stretching bands of similar intensity (*i.e.* mutually *cis*-carbonyl ligands) in their i.r. spectra and 'triplet' resonances for the methyl or methylene protons (*i.e.* mutually *trans*-phosphorus ligands) in their n.m.r. spectra. The similarity of the i.r. spectra of the complexes containing PPh_3 and $AsPh_3$ to those of the others suggests that these complexes also have the *cis*-stereochemistry.

Two further complexes, with the same stereochemistry but containing two different phosphorus ligands, were prepared by treating a carbonylated solution of $RuCl_3 \cdot 3H_2O$ in 2-methoxyethanol first with 1 mol equivalent of PMe_2Ph and then with $P(OMe)_2Ph$ or $P(OMe)_3$. The i.r. spectra of these complexes, *cis*-$[Ru(CO)_2(PMe_2Ph)\{P(OMe)_2Ph\}Cl_2]$ and *cis*-$[Ru(CO)_2(PMe_2Ph)\{P(OMe)_3\}Cl_2]$, are similar to those of the complexes described above, but the n.m.r. spectra are more complicated (since the two mutually *trans*-phosphorus ligands are different,

TABLE 1

I.r. spectra of complexes in the C–O stretching region [a]

Complex	Isomer	ν_{C-O}/cm^{-1}	Isomer	ν_{C-O}/cm^{-1}	Isomer	ν_{C-O}/cm^{-1}
$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$	*cis*	2 058, 1 994	all-*trans*	2 012	all-*cis*	2 082, 1 998
$[Ru(CO)_2(PMe_2Ph)_2Br_2]$	*cis*	2 057, 1 992	all-*trans*	2 012	all-*cis*	2 078, 1 995
$[Ru(CO)_2(PMe_2Ph)_2I_2]$	*cis*	2 054, 1 993	all-*trans*	2 005	all-*cis*	2 070, 2 000
$[Ru(CO)_2(PMePh_2)_2Cl_2]$	*cis*	2 059, 1 996	all-*trans*	2 014	all-*cis*	2 090, 2 000
$[Ru(CO)_2(PMePh_2)_2Br_2]$	*cis*	2 059, 1 994	all-*trans*	2 007	all-*cis*	2 085, 2 002
$[Ru(CO)_2(PMePh_2)_2I_2]$	*cis*	2 056, 1 994	all-*trans*	1 997	all-*cis*	2 078, 2 000
$[Ru(CO)_2\{P(CH_2Ph)Ph_2\}_2Cl_2]$	*cis*	2 059, 1 997	all-*trans* [b]	2 023		
$[Ru(CO)_2\{P(CH_2Ph)Ph_2\}_2Br_2]$	*cis*	2 058, 1 997	all-*trans* [b]	2 020		
$[Ru(CO)_2\{P(CH_2Ph)Ph_2\}_2I_2]$	*cis*	2 056, 1 995	all-*trans* [b]	2 017		
$[Ru(CO)_2(PPh_3)_2Cl_2]$	*cis*	2 059, 1 997	all-*trans* [c]	2 011		
$[Ru(CO)_2(PPh_3)_2Br_2]$	*cis*	2 058, 1 996	all-*trans* [c]	2 008		
$[Ru(CO)_2(PPh_3)_2I_2]$	*cis*	2 055, 1 994	all-*trans* [b]	1 998		
$[Ru(CO)_2(AsPh_3)_2Cl_2]$	*cis*	2 060, 1 998	all-*trans* [c]	2 013		
$[Ru(CO)_2(AsPh_3)_2Br_2]$	*cis*	2 058, 1 998	all-*trans* [c]	2 007		
$[Ru(CO)_2(AsPh_3)_2I_2]$	*cis*	2 055, 1 996	all-*trans* [b]	1 997		
$[Ru(CO)_2\{P(OMe)_2Ph\}_2Cl_2]$	*cis*	2 070, 2 012	all-*trans*	2 033		
$[Ru(CO)_2(PMe_2Ph)\{P(OMe)_2Ph\}Cl_2]$	*cis*	2 069, 2 005	all-*trans*	2 026		
$[Ru(CO)_2(PMe_2Ph)\{P(OMe)_3\}Cl_2]$	*cis*	2 074, 2 010	all-*trans*	2 030		
$[Ru(CO)(PMe_2Ph)_3Cl_2]$	(II) [d]	1 952	(I)	1 980	(IV) [d]	1 952
$[Ru(CO)(PMe_2Ph)_2\{P(OMe)_3\}Cl_2]$	(II)	1 980	(I)	2 010	(IV)	1 965
$[Ru(CO)(PMe_2Ph)_2\{P(OMe)_2Ph\}Cl_2]$	(II)	1 972	(I)	2 005	(IV)	1 960
$[Ru(CO)(PMe_2Ph)_2\{P(OMe)Ph_2\}Cl_2]$	(II)	1 963	(I)	1 988	(IV)	1 962
$[Ru(CO)(PMe_2Ph)_2(PMePh_2)Cl_2]$					(IV)	1 958
$[Ru(CO)(PMe_2Ph)_2(PPh_3)Cl_2]$					(IV)	1 960
$[Ru(CO)(PMe_2Ph)_2(py)Cl_2]$			(I)	1 960	(IV)	1 948
$[Ru(CO)(PMe_2Ph)_2(NH_3)Cl_2]$			(I)	1 952		
$[Ru(CO)(PMe_2Ph)_2(pip)Cl_2]$ [e]			(I)	1 955		
$[Ru(CO)(PMe_2Ph)_2(NCMe)Cl_2]$	(II)	1 960				
$[Ru(CO)(PMe_2Ph)_2(NCPh)Cl_2]$	(II)	1 955				
$[Ru(CO)(PMe_2Ph)_2(SMe_2)Cl_2]$	(II)	1 950				
$[Ru(CO)(PMe_2Ph)_2(OSMe_2)Cl_2]$	(II)	1 985				
$[Ru(CO)(PMe_2Ph)_2(C_2H_4)Cl_2]$	(II)	1 970				
$[\{Ru(CO)(PMe_2Ph)_2Cl_2\}_2]$					(VI)	1 978
$[\{Ru(CO)(PMe_2Ph)_2Br_2\}_2]$					(VI)	1 977
$[\{Ru(CO)(PMe_2Ph)_2I_2\}_2]$					(VI)	1 970

[a] In $CHCl_3$ solution except where otherwise stated. [b] Nujol mull. [c] Not isolated in a pure state: see text. [d] For this complex, isomers (II) and (IV) are the same compound. [e] pip = piperidine.

The complexes *cis*-$[Ru(CO)_2L_2X_2]$, several of which have previously been described in the literature,[2-4] were prepared by published methods (with minor modifications where necessary). The stereochemistry of the complexes

the simple 'virtual coupling' situation described by Harris [5,6] and illustrated by the work of Shaw [7] does not apply here). The resonance for the methyl protons of

[2] J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1787.
[3] R. Colton and R. H. Farthing, *Austral. J. Chem.*, 1967, **20**, 1283.
[4] W. Hieber and P. John, *Chem. Ber.*, 1970, **103**, 2161.
[5] R. K. Harris, *Canad. J. Chem.* 1964, **42**, 2275.
[6] R. K. Harris, *Inorg. Chem.*, 1966, **5**, 701.
[7] J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 1963, 279; and many subsequent papers by Shaw and his co-workers.

TABLE 2

N.m.r. spectra of complexes [c]

Complex	Isomer	δ/p.p.m. PMe$_2$Ph	Others
[Ru(CO)$_2$(PMe$_2$Ph)$_2$Cl$_2$]	*cis* [e]	1.75 (t)	
[Ru(CO)$_2$(PMe$_2$Ph)$_2$Br$_2$]	*cis* [e]	1.85 (t)	
[Ru(CO)$_2$(PMe$_2$Ph)$_2$I$_2$]	*cis* [e]	2.07 (t)	
[Ru(CO)$_2$(PMePh$_2$)$_2$Cl$_2$]	*cis* [e]		PMePh$_2$: 2.32 (t)
[Ru(CO)$_2$(PMePh$_2$)$_2$Br$_2$]	*cis* [e]		PMePh$_2$: 2.47 (t)
[Ru(CO)$_2$(PMePh$_2$)$_2$I$_2$]	*cis* [e]		PMePh$_2$: 2.73 (t)
[Ru(CO)$_2${P(CH$_2$Ph)Ph$_2$}$_2$Cl$_2$]	*cis* [f]		P(CH$_2$Ph)Ph$_2$: 4.51 (t)
[Ru(CO)$_2${P(CH$_2$Ph)Ph$_2$}$_2$Br$_2$]	*cis* [f]		P(CH$_2$Ph)Ph$_2$: 4.63 (t)
[Ru(CO)$_2${P(CH$_2$Ph)Ph$_2$}$_2$I$_2$]	*cis* [f]		P(CH$_2$Ph)Ph$_2$: 4.91 (t)
[Ru(CO)$_2${P(OMe)$_2$Ph}$_2$Cl$_2$]	*cis* [e]		P(OMe)$_2$Ph: 3.68 (t)
[Ru(CO)$_2$(PMe$_2$Ph){P(OMe)$_2$Ph}Cl$_2$]	*cis* [g]	1.84 (dd, 6)	P(OMe)$_2$Ph: 3.77 (d, 6) [h]
[Ru(CO)$_2$(PMe$_2$Ph){P(OMe)$_3$}Cl$_2$]	*cis* [g]	1.85 (dd, 6)	P(OMe)$_3$: 3.76 (d, 9) [h]
[Ru(CO)$_2$(PMe$_2$Ph)$_2$Cl$_2$]	all-*trans* [e]	1.62 (t)	
[Ru(CO)$_2$(PMe$_2$Ph)$_2$Br$_2$]	all-*trans* [e]	1.72 (t)	
[Ru(CO)$_2$(PMe$_2$Ph)$_2$I$_2$]	all-*trans* [e]	1.92 (t)	
[Ru(CO)$_2$(PMePh$_2$)$_2$Cl$_2$]	all-*trans* [e]		PMePh$_2$: 2.06 (t)
[Ru(CO)$_2$(PMePh$_2$)$_2$Br$_2$]	all-*trans* [e]		PMePh$_2$: 2.18 (t)
[Ru(CO)$_2$(PMePh$_2$)$_2$I$_2$]	all-*trans* [e]		PMePh$_2$: 2.38 (t)
[Ru(CO)$_2$(P(OMe)$_2$Ph}$_2$Cl$_2$]	all-*trans* [e]		P(OMe)$_2$Ph: 3.49 (t)
[Ru(CO)$_2$(PMe$_2$Ph){P(OMe)$_2$Ph}Cl$_2$]	all-*trans* [g]	1.78 (dd, 6)	P(OMe)$_2$Ph: 3.63 (d, 6) [h]
[Ru(CO)$_2$(PMe$_2$Ph){P(OMe)$_3$}Cl$_2$]	all-*trans* [g]	1.79 (dd, 6)	P(OMe)$_3$: 3.67 (d, 9) [h]
[Ru(CO)$_2$(PMe$_2$Ph)$_2$Cl$_2$]	all-*cis* [g]	1.78 (d, 3); 1.74 (d, 3) 1.31 (d, 3); 1.17 (d, 3)	
[Ru(CO)$_2$(PMe$_2$Ph)$_2$Br$_2$]	all-*cis* [g]	1.98 (d, 3); 1.88 (d, 3) 1.37 (d, 3); 1.23 (d, 3)	
[Ru(CO)$_2$(PMe$_2$Ph)$_2$I$_2$]	all-*cis* [g]	2.24 (d, 3); 2.03 (d, 3) 1.41 (d, 3); 1.27 (d, 3)	
[Ru(CO)$_2$(PMePh$_2$)$_2$Cl$_2$]	all-*cis* [g]		PMePh$_2$: 2.25 (d, 3); 1.50 (d, 3)
[Ru(CO)$_2$(PMePh$_2$)$_2$Br$_2$]	all-*cis* [g]		PMePh$_2$: 2.43 (d, 3); 1.54 (d, 3)
[Ru(CO)$_2$(PMePh$_2$)$_2$I$_2$]	all-*cis* [g]		PMePh$_2$: 2.71 (d, 3); 1.63 (d, 3)
[Ru(CO)(PMe$_2$Ph)$_3$Cl$_2$]	(I) [g]	1.63 (t, 12)	PMe$_2$Ph (L′): 1.30 (d, 6)
[Ru(CO)(PMe$_2$Ph)$_2$(P(OMe)$_3$}Cl$_2$]	(I) [g]	1.86 (t, 12)	P(OMe)$_3$: 3.46 (d, 9)
[Ru(CO)(PMe$_2$Ph)$_2$(P(OMe)$_2$Ph}Cl$_2$]	(I) [g]	1.73 (t, 12)	P(OMe)$_2$Ph: 3.39 (d, 6)
[Ru(CO)(PMe$_2$Ph)$_2$(P(OMe)Ph$_2$}Cl$_2$]	(I) [g]	1.71 (t, 12)	P(OMe)Ph$_2$: 3.11 (d, 3)
[Ru(CO)(PMe$_2$Ph)$_2$(py)Cl$_2$]	(I) [e]	1.63 (t)	
[Ru(CO)(PMe$_2$Ph)$_2$(NH$_3$)Cl$_2$]	(I) [e]	1.80 (t)	
[Ru(CO)(PMe$_2$Ph)$_2$(pip)Cl$_2$] [i]	(I) [e]	1.73 (t)	
[Ru(CO)(PMe$_2$Ph)$_3$Cl$_2$]	(II) [g]	1.85 (t, 6); 1.79 (t, 6)	PMe$_2$Ph (L′): 1.09 (d, 6)
[Ru(CO)(PMe$_2$Ph)$_2$(P(OMe)$_3$}Cl$_2$]	(II) [g]	1.98 (t, 6); 1.91 (t, 6)	P(OMe)$_3$: 3.14 (d, 9)
[Ru(CO)(PMe$_2$Ph)$_2$(P(OMe)$_2$Ph}Cl$_2$]	(II) [g]	1.91 (t, 6); 1.87 (t, 6)	P(OMe)$_2$Ph: 3.08 (d, 6)
[Ru(CO)(PMe$_2$Ph)$_2$(NCMe)Cl$_2$]	(II) [e]	2.01 (t, 6); 1.86 (t, 6)	NCMe: 0.29 (t, 3)
[Ru(CO)(PMe$_2$Ph)$_2$(NCPh)Cl$_2$]	(II) [e]	2.07 (t, 6); 1.92 (t, 6)	
[Ru(CO)(PMe$_2$Ph)$_2$(SMe$_2$)Cl$_2$]	(II) [e]	1.93 (t, 6); 1.83 (t, 6)	SMe$_2$: 1.13 (s, 6)
[Ru(CO)(PMe$_2$Ph)$_2$(OSMe$_2$)Cl$_2$]	(II) [e]	1.93 (t, 6); 1.81 (t, 6)	OSMe$_2$: 2.09 (s, 6)
[Ru(CO)(PMe$_2$Ph)$_2$(C$_2$H$_4$)Cl$_2$]	(II) [e]	1.99 (t, 6); 1.92 (t, 6)	C$_2$H$_4$: 2.26 (t, 4)
[Ru(CO)(PMe$_2$Ph)$_2$(P(OMe)$_3$}Cl$_2$]	(IV) [g]	1.64 (d, 3); 1.57 (d, 3) [a] 1.81 (dd, 3); 1.55 (dd, 3) [b]	P(OMe)$_3$: 3.83 (d, 9) [h]
[Ru(CO)(PMe$_2$Ph)$_2$(P(OMe)$_2$Ph}Cl$_2$]	(IV) [g]	1.65 (d, 3); 1.56 (d, 3) [a] 1.80 (dd, 3); 1.51 (dd, 3) [b]	P(OMe)$_2$Ph: 3.98 (d, 3) [h] 3.53 (d, 3) [h]
[Ru(CO)(PMe$_2$Ph)$_2$(P(OMe)Ph$_2$}Cl$_2$]	(IV) [g]	1.72 (d, 3); 1.59 (d, 3) [a] 1.82 (dd, 3); 1.61 (dd, 3) [b]	P(OMe)Ph$_2$: 3.29 (d, 3) [h]
[Ru(CO)(PMe$_2$Ph)$_2$(PMePh$_2$)Cl$_2$]	(IV) [g]	1.26 (d, 3); 1.21 (d, 3) [a] 1.86 (dd, 3); 1.83 (dd, 3) [b]	PMePh$_2$: 2.40 (dd, 3)
[Ru(CO)(PMe$_2$Ph)$_2$(PPh$_3$}Cl$_2$]	(IV) [g]	1.39 (d, 3); 1.30 (d, 3) [a] 1.92 (dd, 3); 1.87 (dd, 3) [b]	
[Ru(CO)(PMe$_2$Ph)$_2$(py)Cl$_2$]	(IV) [g]	2.11 (d, 3); 1.99 (d, 3) 1.23 (d, 3); 1.19 (d, 3)	
[{Ru(CO)(PMe$_2$Ph)$_2$Cl$_2$}$_2$]	(VI) [f]	1.68 (d, 6); 1.60 (d, 6)	

[a] This ligand is *trans* to Cl$^-$ (see Scheme 2). [b] This ligand is *trans* to L′ (see Scheme 2). [c] Resonances due to aromatic and amine protons are not included. Multiplicities and relative areas are given in brackets after the chemical shift values: s = singlet, d = doublet, dd = doublet of doublets, t = triplet. [e] In benzene solution. [f] In $CDCl_3$ solution. [g] In chlorobenzene solution. [h] A further small coupling {^5J(P–H) < 1 Hz} to the ^{31}P nucleus in the *trans*-PMe$_2$Ph ligand was detected by the ' wiggle beat ' method. [i] pip = piperidine.

the PMe$_2$Ph ligand is in each case a doublet of doublets (coupling to the ^{31}P nucleus in the PMe$_2$Ph ligand and to that in the other phosphorus ligand), while that for the methyl protons in the P(OMe)$_2$Ph or P(OMe)$_3$ ligand appears to be a doublet (coupling to ' their own ' ^{31}P nucleus only), although a tiny further splitting caused by the ^{31}P nucleus in the PMe$_2$Ph ligand can be detected by the ' wiggle beat ' method.[8]

U.v. irradiation of the complexes *cis*-[Ru(CO)$_2$L$_2$X$_2$] in tetrahydrofuran, chloroform, benzene, or acetone solution yields the all-*trans*-isomers, which can in most cases be isolated in good yield: in some instances n.m.r. spectra and analytical data indicate the presence of solvent of crystallization. For L = PPh$_3$ or AsPh$_3$, the complexes with X = Cl or Br cannot be isolated in a pure

[8] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, ' High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, Oxford, 1965, p. 43.

state because of the rapidity of the thermal reconversion into the *cis*-isomers. Again, the n.m.r. spectra of the complexes with L = PMe_2Ph, $PMePh_2$, or $P(OMe)_2Ph$ [those containing $P(CH_2Ph)Ph_2$ are too insoluble to allow n.m.r. spectra to be obtained] contain triplet resonances for the methyl protons, establishing that the phosphorus ligands are still mutually *trans*, but the i.r. spectra exhibit only a single C–O stretching band, showing that the carbonyl ligands are now also mutually *trans*.

The complexes *cis*-$[Ru(CO)_2(PMe_2Ph)\{P(OMe)_2Ph\}Cl_2]$ and *cis*-$[Ru(CO)_2(PMe_2Ph)\{P(OMe)_3\}Cl_2]$ can also be converted into all-*trans*-isomers by this method, although a small amount of disproportionation by phosphorus ligand exchange occurs during irradiation.

Many of these all-*trans*-isomers have not been previously reported.

(2) *Thermal Reconversion of Complexes All*-trans-$[Ru(CO)_2L_2X_2]$ *into* cis-*Isomers*.—All the all-*trans*-complexes, including $[Ru(CO)_2(PMe_2Ph)\{P(OMe)_2Ph\}Cl_2]$ and $[Ru(CO)_2(PMe_2Ph)\{P(OMe)_3\}Cl_2]$, are reconverted into their *cis*-isomers when heated in chloroform or chlorobenzene solution (in the case of complexes with L = PPh_3 or $AsPh_3$, rearrangement occurs at a significant rate at room temperature, the rate decreasing in the order X = Cl > Br > I). I.r. and n.m.r. studies were made of the thermal rearrangement of the complexes all-*trans*-$[Ru(CO)_2L_2X_2]$ (L = PMe_2Ph or $PMePh_2$; X = Cl, Br, or I) in the absence of light. In every case, although some *cis*-$[Ru(CO)_2L_2X_2]$ appeared to be formed directly from all-*trans*-$[Ru(CO)_2L_2X_2]$, it was clear that some other species was being formed in the solution, and that this species was then undergoing a further rearrangement to form the *cis*-isomer.

The i.r. spectra of all the intermediates contain two C–O stretching bands of similar intensity; the n.m.r. spectra of those formed from the complexes all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2X_2]$ contain four doublets of equal area in the methyl proton region, while those from all-*trans*-$[Ru(CO)_2(PMePh_2)_2X_2]$ contain two such doublets. None of the intermediates could be obtained in a pure state from the reaction mixtures, but on the basis of the spectroscopic data they were tentatively identified as the (previously unknown) all-*cis*-isomers of these complexes (see Scheme 1: note that the carbonyl ligands are mutually *cis*, that the ligands L are mutually *cis* and inequivalent, and that neither Ru–P bond lies in a plane of symmetry, so for complexes with L = PMe_2Ph the two methyl groups on a given PMe_2Ph ligand are also inequivalent).

Subsequently we discovered that, although the major product present in a chloroform solution of $[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ after u.v. irradiation of the *cis*-isomer is the all-*trans*-isomer, essentially quantitative conversion into the all-*cis*-isomer can be achieved by then leaving the solution in the dark for 24 h at 313 K. Under these mild conditions, no further conversion into *cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ occurs. The all-*cis*-isomer of $[Ru(CO)_2(PMePh_2)_2Cl_2]$ was obtained in a similar manner, and bromo- and iodo-analogues were prepared by treating them with bromide and iodide ion respectively; the halogen exchange occurs under mild conditions and with retention of stereochemistry. Comparison of the i.r. and n.m.r. spectra of solutions of the isolated all-*cis*-complexes with those of the intermediates in the thermal rearrangement of all-*trans*-$[Ru(CO)_2L_2X_2]$ to *cis*-$[Ru(CO)_2L_2X_2]$ confirmed that the intermediates were the all-*cis*-isomers, and when the isolated complexes were heated in solution, they underwent the expected rearrangement to *cis*-$[Ru(CO)_2L_2X_2]$.

It was found that the formation of the all-*cis*-isomers during the thermal rearrangement of the all-*trans*-complexes is severely inhibited by the presence of free CO in the solution, but that the rate of appearance of *cis*-$[Ru(CO)_2L_2X_2]$ in the early stages of the reaction remains unchanged. Separate experiments indicated that the rate of conversion of all-*cis*-$[Ru(CO)_2L_2X_2]$ into *cis*-$[Ru(CO)_2L_2X_2]$ is unaffected by the presence of free CO. As indicated in Scheme 1, therefore, there are two routes for the thermal rearrangement of complexes *trans*-$[Ru(CO)_2L_2X_2]$, one (which is not inhibited by CO) direct to the *cis*-isomers, and one by way of the all-*cis*-isomers: in the latter case the first step of the rearrangement *is* inhibited by CO and the second is not.

Of the various reactions involved, the most intriguing is the two-step rearrangement of the all-*trans* to the *cis*-complexes by way of the all-*cis*-isomers, because the overall rearrangement seems much simpler than those involved in the individual steps. Since the first step is inhibited by CO, it seemed likely that its mechanism might involve initial loss and subsequent recapture of a carbonyl ligand. For this reason, we decided to study the stereochemistry of simple carbonyl-substitution reactions of the all-*trans*- and all-*cis*-isomers of $[Ru(CO)_2(PMe_2Ph)_2Cl_2]$.

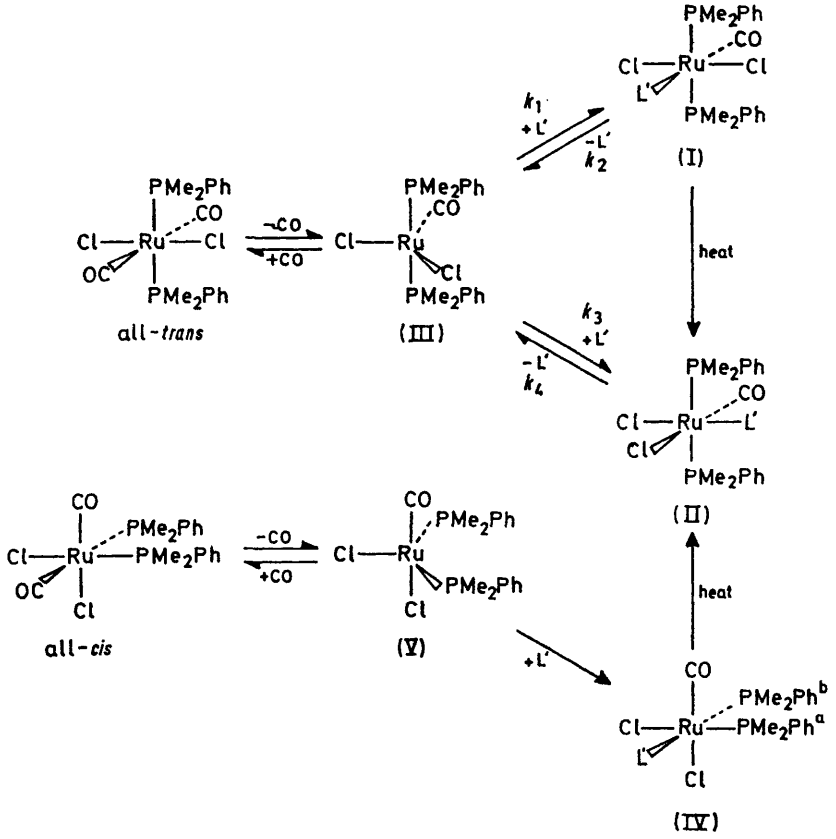
(3) *Carbonyl-substitution Reactions of all*-trans-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$.—This complex reacts, under mild conditions, with a wide range of ligands L′ to give monosubstituted products $[Ru(CO)(PMe_2Ph)_2L'Cl_2]$. Kinetic study of the reactions with various ligands L′ containing phosphorus donor atoms established that the reaction rate is independent of the choice and the concentration of the ligand L′, and that the entropy of activation is large and positive, as expected for a mechanism involving an initial dissociation of a carbonyl ligand [experimental details and kinetic data have been deposited as a Supplementary publication, SUP No. 21718 (2 pp)].*

The stereochemistry of the products varies according to the nature of the ligand L′. The reactions with phosphorus ligands, pyridine, ammonia, and piperidine yield products assigned structure (I) (see Scheme 2), since their n.m.r. spectra contain a single triplet resonance for the methyl protons in the PMe_2Ph ligands, establishing that they are still mutually *trans* and that the Ru–P bonds lie in a plane of symmetry through the molecule. The stereochemistry of these reactions seems

* For details of the Supplementary publications scheme see Notice to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue. (Items less than 10 pp. are supplied as full-size copies.)

to be kinetically controlled: studies of the complexes containing ligands L′ with phosphorus donor atoms established that they rearrange on heating in solution to isomers of structure (II). The n.m.r. spectra of these isomers contain two triplet resonances for the methyl protons in the PMe_2Ph ligands (ligands mutually *trans*, but the Ru–P bonds not in a plane of symmetry through the molecule). Isomer (II) of $[Ru(CO)(PMe_2Ph)_2\{P(OMe)Ph_2\}Cl_2]$ was too insoluble for an n.m.r. spectrum to be obtained.

In the case of the reactions of all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ with acetonitrile, benzonitrile, dimethyl sulphide, dimethyl sulphoxide, and ethylene, products of



SCHEME 2 Stereochemistry of carbonyl substitution reactions of $[Ru(CO)_2(PMe_2Ph)_2Cl_2]$

structure (II) are formed directly. Treatment of any of these complexes with PMe_2Ph, however, yields isomer (I) of $[Ru(CO)(PMe_2Ph)_3Cl_2]$, despite the fact that substitution with retention of stereochemistry would yield the thermodynamically preferred isomer (II). Similarly, if CO is passed through solutions of the complexes with L′ = SMe_2 or C_2H_4, the all-*trans*-isomer of $[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ is regenerated, whereas retention of stereochemistry would give the more stable *cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$.

All these observations are compatible with a scheme (Scheme 2) in which dissociation of a carbonyl ligand from all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ yields a five-coordinate species (III) (most easily visualized as having trigonal bipyramidal geometry). On the basis of the principle of microscopic reversibility, a ligand with a large *trans*-labilizing effect should also be kinetically *trans*-directing,[9,10] so the kinetically preferred direction of attack on (III) should be *trans* to CO rather than *trans* to Cl^- ($k_1 > k_3$). It is, however, also to be expected that k_2 will be much larger than k_4. Hence ligands L′ which bind strongly to the ruthenium (phosphorus ligands and amines), and for which $k_1[L'] > k_2$, will form products of structure (I) initially, although these may then rearrange when heated to structure (II). Ligands which bind less strongly and for which $k_1[L'] < k_2$ will form products of structure (II) directly. But, in these latter cases, replacement of L′ by PMe_2Ph or CO will give isomer (I) of $[Ru(CO)(PMe_2Ph)_3Cl_2]$ and all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ respectively because, after formation of the intermediate (III) by the loss of L′, subsequent attack by PMe_2Ph or CO will follow the kinetically preferred route.

(4) *Carbonyl-substitution Reactions of all*-cis-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$.—This complex reacts with a variety of ligands L′ containing phosphorus donor atoms to give products $[Ru(CO)(PMe_2Ph)_2L'Cl_2]$ assigned structure (IV) (see Scheme 2) on the basis of their n.m.r. spectra. In the special case where L′ = PMe_2Ph, structure (IV) is identical with (II), and indeed the product is identical

[9] D. M. Blake and M. Kubota, *J. Amer. Chem. Soc.*, 1970, **92**, 2578.

[10] G. Wright, R. W. Glyde, and R. J. Mawby, *J.C.S. Dalton*, 1973, 220.

with that described in the previous section. In all other cases, the methyl protons in PMe_2Ph^a in structure (IV) give rise to two doublets of equal area, while those in PMe_2Ph^b give a similar pattern but with a small extra doublet splitting due to the ^{31}P nucleus in L′. The resonances due to the methyl protons in the ligands L′ are as expected, except that it is interesting to note that the splitting from the ^{31}P nucleus in PMe_2Ph^b is easily detected where L′ = $PMePh_2$ but vanishingly small where L′ = $P(OMe)_nPh_{3-n}$ (n = 1, 2, or 3) {*cf.* section (1)}. A complex $[Ru(CO)(PMe_2Ph)_2(py)Cl_2]$, probably also of structure (IV), is obtained when all-*cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ is treated with pyridine.

Again the stereochemistry of the reactions appears to be kinetically controlled: studies of the complexes with L′ = $P(OMe)_nPh_{3-n}$ indicated that when heated in solution they are quantitatively converted into the isomers of structure (II). Initial formation of isomer (IV) can be attributed (as illustrated in Scheme 2) to loss of the carbonyl ligand opposite to the *trans*-labilizing PMe_2Ph ligand, giving intermediate (V). This will pick up L′ preferentially *trans* to PMe_2Ph rather than *trans* to Cl^-, giving (IV) rather than (II).

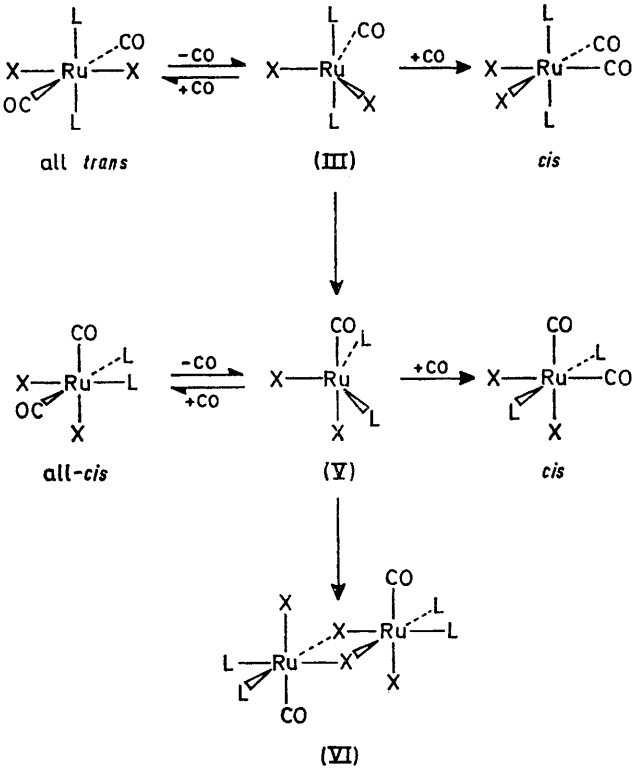
(5) *Mechanisms for the Isomerizations of Complexes* $[Ru(CO)_2L_2X_2]$.—The observations on the stereochemistry of the substitution reactions of all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ can be used as a basis for a mechanism for the direct rearrangement of the complexes all-*trans*-$[Ru(CO)_2L_2X_2]$ to their *cis*-isomers (and for the reverse process). If loss of CO from all-*trans*-$[Ru(CO)_2L_2X_2]$ to form intermediate (III) is the first step, the kinetically preferred pick-up of CO *trans* to the remaining carbonyl ligand will lead back to the all-*trans*-isomer, but the slower attack *trans* to halide ion will give the *cis*-isomer. This is shown in Scheme 3.

This mechanism is compatible with the finding that the direct conversion of all-*trans*-isomers into *cis*-isomers is not inhibited by free CO, since the rate of reaction of intermediate (III) by the two competing pathways will be similarly affected by variation in CO concentration.

The bonds to the carbonyl ligands in *cis*-$[Ru(CO)_2L_2X_2]$ are not thermally labile {for example, *cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ can be recovered unchanged after being heated with PMe_2Ph at 353 K for several hours}, but may well be cleaved by irradiation {a comparable case is that of $[Fe(CO)_5]$, which is inert to CO exchange in the dark but undergoes rapid exchange under irradiation [11]}. Light-induced cleavage of a metal–carbonyl bond in *cis*-$[Ru(CO)_2L_2X_2]$ would yield intermediate (III) which, at the low temperatures used for the irradiation experiments, would combine with CO to give almost exclusively all-*trans*-$[Ru(CO)_2L_2X_2]$.

The experiments with $[Ru(CO)_2(PMe_2Ph)\{P(OMe)_2Ph\}Cl_2]$ and $[Ru(CO)_2(PMe_2Ph)\{P(OMe)_3\}Cl_2]$ [see section (1)] indicate that the metal–phosphorus bonds are also somewhat sensitive to u.v. irradiation, but the extent of disproportionation is small and it seems likely that cleavage of these bonds is a side reaction rather than a crucial step in the isomerization mechanism.

In view of the inhibition by free CO of the conversion of all-*trans*-$[Ru(CO)_2L_2X_2]$ into all-*cis*-$[Ru(CO)_2L_2X_2]$, it seems probable that loss of CO to form the intermediate (III) is also the first step in this reaction. On this basis, the formation of the all-*cis*-isomer probably results from



SCHEME 3 Mechanisms for the thermal rearrangements of complexes $[Ru(CO)_2L_2X_2]$

the rearrangement of (III) to (V) (see Scheme 3), in which the ligands L are in equatorial positions (this can be achieved by the Berry mechanism [12]). The rearrangement allows the CO to re-enter *trans* to one of the ligands L [this is kinetically favoured since these ligands have a larger *trans*-effect in ruthenium(II) complexes than either CO or halide ion [2]] giving the all-*cis*-isomer. The inhibition of the isomerization by CO can be attributed to the fact that the rearrangement of (III) into (V), which occurs at a rate which is independent of CO concentration, must compete with the two other modes of reaction of (III), both of which are accelerated by increasing the CO concentration.

As shown by the carbonyl-substitution reactions described in the previous section, the bond to the carbonyl ligand *trans* to L in the all-*cis*-complexes is labile. Thus, as indicated in Scheme 3, when the all-*cis* complexes are heated in solution the slower process of attack on (V) *trans* to halide ion will ultimately lead to quantitative conversion into the *cis*-isomers. As mentioned earlier, this step is not inhibited by CO: this is in agreement with the suggested mechanism since an increase in

[11] D. F. Keeley and R. E. Johnson, *J. Inorg. Nuclear Chem.*, 1959, **11**, 33.
[12] R. S. Berry, *J. Chem. Phys.*, 1960, **32**, 933.

the CO concentration must have an equal effect on both paths of reaction of intermediate (V).

We are not clear as to the mechanism of the ' post-irradiation ' rearrangement of the complexes all-*trans*-$[Ru(CO)_2L_2Cl_2]$ (L = PMe_2Ph or $PMePh_2$) to all-*cis*-isomers under mild conditions in chloroform solution, mentioned in section (2). Both the solvent and the irradiation are crucial factors: rearrangement does not occur at this temperature if the prior photochemical conversion of the *cis*-isomers has been performed in acetone or benzene, nor does a chloroform solution of one of the all-*trans*-isomers which has not been irradiated show this effect. Experiments with scavengers suggest that radicals may be involved: thus the radical-trap cyclohexene, which does not inhibit the photochemical conversion of *cis*-isomers into all-*trans*-isomers in chloroform, *does* inhibit the subsequent rearrangement to all-*cis*-isomers.

(6) *Loss of Carbon Monoxide during Isomerizations.*—The mechanisms proposed for the various rearrangements of the complexes $[Ru(CO)_2L_2X_2]$ all involve dissociation of a carbonyl ligand as a key step, and there should be some tendency for CO to be lost from the solution during the rearrangements. This would leave some of the five-co-ordinate species $[Ru(CO)L_2X_2]$ in solution.

It was found that a solid is slowly deposited from the mother liquor remaining from the irradiative conversion of *cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ into the all-*trans*-isomer in acetone. The solid has the empirical formula $[Ru(CO)(PMe_2Ph)_2Cl_2]$, and molecular-weight measurements (although of limited accuracy owing to the poor solubility of the compound) showed that the molecular unit is $[\{Ru(CO)(PMe_2Ph)_2Cl_2\}_2]$. The i.r. spectrum (one band in the C–O stretching region) and a rather poor n.m.r. spectrum (apparently two doublet resonances of equal area for the methyl protons) indicate that the complex has structure (VI) (see Scheme 3: L = PMe_2Ph; X = Cl). This stereochemistry is that to be expected from the combination of two molecules of $[Ru(CO)(PMe_2Ph)_2Cl_2]$ of structure (V), left in solution by loss of CO, with a chloride ligand on each molecule acting as a nucleophile attacking the other molecule in the kinetically preferred direction *trans* to a PMe_2Ph ligand.

As expected, treatment of a solution of $[\{Ru(CO)(PMe_2Ph)_2Cl_2\}_2]$ with CO yields all-*cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$. The process can be reversed by passing nitrogen through a benzene solution of all-*cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$. Complexes $[Ru(CO)(PMe_2Ph)_2L'Cl_2]$ of structure (IV) (see Scheme 2), obtainable by treating all-*cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ with ligands L' [see section (4)], can be more rapidly prepared from $[\{Ru(CO)(PMe_2Ph)_2Cl_2\}_2]$ and L'.

From $[\{Ru(CO)(PMe_2Ph)_2Cl_2\}_2]$, the corresponding bromo- and iodo-complexes can be prepared by metathesis reactions under mild conditions. Careful study by i.r. spectroscopy of the thermal rearrangement of the complexes all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2X_2]$ (X = Cl, Br, or I) in solution under an atmosphere of nitrogen revealed that, although the major end-products are the expected *cis*-isomers, small quantities of the dimeric species $[\{Ru(CO)(PMe_2Ph)_2X_2\}_2]$ are formed in each case. Since the metal–carbonyl bonds in *cis*-$[Ru(CO)_2(PMe_2Ph)_2X_2]$ are not labile in the absence of irradiation, it is clear that the dimeric species are formed by loss of CO during the rearrangements which lead from the *trans* to the *cis*-isomers. As pointed out at the start of this section, such a result is exactly what one would expect on the basis of the mechanisms proposed for the rearrangements.

EXPERIMENTAL

Except where otherwise stated, all the work described below was performed under an atmosphere of dry nitrogen, and light petroleum used in preparative work had a boiling range of 353—373 K. Analytical data for all the complexes are collected in Table 3.

Complexes cis-$[Ru(CO)_2L_2Cl_2]$.—cis-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$. This compound was prepared in 2-methoxyethanol solution by the method described by Jenkins *et al.*[2] Concentration of the solution under reduced pressure usually yielded a crystalline product; occasionally an oil was obtained which could be induced to crystallize by seeding (yield 88%). This method was also used to prepare *cis*-$[Ru(CO)_2(PMePh_2)_2Cl_2]$: in this case the product was obtained in crystalline form as soon as the 2-methoxyethanol solution was allowed to cool (yield 67%).

cis-$[Ru(CO)_2\{P(CH_2Ph)Ph_2\}_2Cl_2]$, *cis*-$[Ru(CO)_2(PPh_3)_2Cl_2]$, *and* cis-$[Ru(CO)_2(AsPh_3)_2Cl_2]$. These compounds were prepared by the method described by Colton and Farthing [3] for *cis*-$[Ru(CO)_2(PPh_3)_2Cl_2]$, and were recrystallized from chloroform–ethanol mixtures (yields 50—80%).

cis-$[Ru(CO)_2\{P(OMe)_2Ph\}_2Cl_2]$. Carbon monoxide was passed through a solution of $RuCl_3 \cdot 3H_2O$ (1.00 g) in refluxing 2-methoxyethanol (50 ml) for 5 h. The ligand $P(OMe)_2Ph$ (1.29 g) was then added and heating continued for 0.1 h. After removal of the solvent under reduced pressure, the oily residue was induced to crystallize by treatment with a light petroleum (b.p. 313—333 K)–ethanol mixture (yield 55%).

cis-$[Ru(CO)_2(PMe_2Ph)\{P(OMe)_2Ph\}Cl_2]$. The method used to prepare this compound was the same as that for *cis*-$[Ru(CO)_2\{P(OMe)_2Ph\}_2Cl_2]$, except that the carbonylated solution of $RuCl_3 \cdot 3H_2O$ was treated with PMe_2Ph (0.53 g) and heated for a further 1.5 h prior to the addition of $P(OMe)_2Ph$ (0.65 g) (yield 50%). The complex *cis*-$[Ru(CO)_2(PMe_2Ph)\{P(OMe)_3\}Cl_2]$ was prepared in the same way (yield 57%).

Complexes cis-$[Ru(CO)_2L_2X_2]$ (X = Br *or* I). These complexes were prepared from their chloro-analogues by the methods described by Jenkins *et al.* [2] for *cis*-$[Ru(CO)_2(PMe_2Ph)_2X_2]$, except that the complexes other than *cis*-$[Ru(CO)_2(PMe_2Ph)_2X_2]$ could be obtained in crystalline form simply by cooling the reaction solutions (yields 40—60%).

Complexes all-trans-$[Ru(CO)_2L_2X_2]$ (X = Cl, Br, *or* I). These complexes were obtained by irradiation of solutions of the corresponding *cis*-isomers. The solution were placed in Pyrex tubes, shaped to maximise the surface area exposed to the light, and irradiated with a Hanovia 125W mercury-arc lamp placed 0.1 m from the tubes. During irradiation the tubes were air-cooled. The complexes all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2X_2]$ and all-*trans*-$[Ru(CO)_2\{P(OMe)_2Ph\}_2Cl_2]$ were prepared in acetone, while chloroform was used as the solvent for all-*trans*-$[Ru(CO)_2(PMePh_2)_2X_2]$ and benzene for all-*trans*-$[Ru(CO)_2(PMe_2Ph)\{P(OMe)_2Ph\}Cl_2]$; in all cases, crystals were obtained when the volume of the

solution was reduced under a nitrogen stream. The complexes all-*trans*-$[Ru(CO)_2(PPh_3)_2I_2]$, all-*trans*-$[Ru(CO)_2(AsPh_3)_2I_2]$ (both prepared in tetrahydrofuran), and all-*trans*-$[Ru(CO)_2\{P(CH_2Ph)Ph_2\}_2X_2]$ (prepared in chloroform) crystallized from solution during irradiation: these products contained solvent of crystallization. In the case of all-*trans*-$[Ru(CO)_2(PMe_2Ph)\{P(OMe)_3\}Cl_2]$, prepared in benzene, it was necessary to remove the solvent under reduced pressure and subject the residue to low-temperature crystallization from ethanol. Yields from irradiations were usually between 50 and 80%.

similarly prepared, but at a temperature of 298 K (yields 60 and 75% respectively).

Complexes $[Ru(CO)(PMe_2Ph)_2L'Cl_2]$, *Configuration* (*I*).—$[Ru(CO)(PMe_2Ph)_3Cl_2]$. To a stirred solution of all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ (0.10 g) in benzene (15 ml) was added PMe_2Ph (0.03 g). After 16 h at 313 K the solution was evaporated to dryness under reduced pressure. The residue was recrystallized from ethanol (yield 75%). The complexes $[Ru(CO)(PMe_2Ph)_2L'Cl_2]$ [L′ = $P(OMe)_3$, $P(OMe)_2Ph$, or $P(OMe)Ph_2$] were prepared in the same way: the first was recrystallized from diethyl ether (yield 48%)

TABLE 3

Analytical data

Complex	Found Isomer	Found %C	Found H%	Found Isomer	Found %C	Found %H	Found Isomer	Found %C	Found %H	Required %C	Required %H
$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$	*cis*	43.05	4.25	all-*trans*	42.45	4.35	all-*cis*	42.6	4.45	42.88	4.40
$[Ru(CO)_2(PMe_2Ph)_2Br_2]$	*cis*	36.3	3.7	all-*trans*	36.7	3.7	all-*cis*	37.0	3.8	36.44	3.74
$[Ru(CO)_2(PMe_2Ph)_2I_2]$	*cis*	31.4	3.15	all-*trans*	31.4	3.2	all-*cis*	31.9	3.35	31.46	3.23
$[Ru(CO)_2(PMePh_2)_2Cl_2]$	*cis*	53.35	4.2	all-*trans*	53.15	4.2	all-*cis*	53.0	4.15	53.51	4.17
$[Ru(CO)_2(PMePh_2)_2Br_2]$	*cis*	46.75	3.6	all-*trans*	46.55	3.65	all-*cis*	46.25	3.9	46.88	3.65
$[Ru(CO)_2(PMePh_2)_2I_2]$	*cis*	41.45	3.2	all-*trans*	41.3	3.15	all-*cis*	42.05	3.45	41.45	3.23
$[Ru(CO)_2\{P(CH_2Ph)Ph_2\}_2Cl_2]$ [a]	*cis*	61.7	4.85							61.54	4.39
				(all-*trans*	58.75	4.2)				(59.04)	(4.22)
$[Ru(CO)_2\{P(CH_2Ph)Ph_2\}_2Br_2]$ [a]	*cis*	55.15	3.9							55.25	3.94
				(all-*trans*	52.45	3.9)				(53.27)	(3.81)
$[Ru(CO)_2\{P(CH_2Ph)Ph_2\}_2I_2]$ [a]	*cis*	50.45	3.65							49.86	3.56
				(all-*trans*	48.5	3.4)				(48.28)	(3.45)
$[Ru(CO)_2(PPh_3)_2I_2]$ [b]	*cis*	48.9	3.3							48.79	3.23
				(all-*trans*	50.05	3.9)				(50.06)	(3.80)
$[Ru(CO)_2(AsPh_3)_2I_2]$ [b]	*cis*	44.1	3.05							44.60	2.95
				(all-*trans*	46.15	3.55)				(46.05)	(3.50)
$[Ru(CO)_2\{P(OMe)_2Ph\}_2Cl_2]$	*cis*	38.25	4.0	all-*trans*	38.05	3.95				38.04	3.90
$[Ru(CO)_2(PMe_2Ph)\{P(OMe)_2Ph\}Cl_2]$	*cis*	40.45	4.15	all-*trans*	40.6	4.15				40.31	4.13
$[Ru(CO)_2(PMe_2Ph)\{P(OMe)_3\}Cl_2]$	*cis*	31.85	4.05	all-*trans*	32.1	3.95				31.85	4.11
$[Ru(CO)(PMe_2Ph)_3Cl_2]$	(II)	48.95	5.45	(I)	48.7	5.3				48.87	5.41
$[Ru(CO)(PMe_2Ph)_2\{P(OMe)_3\}Cl_2]$	(II)	39.15	5.2	(I)	39.9	5.1	(IV)	39.6	5.05	40.01	5.20
$[Ru(CO)(PMe_2Ph)_2\{P(OMe)_2Ph\}Cl_2]$	(II)	47.05	5.15	(I)	46.75	5.2	(IV)	46.35	4.95	46.45	5.15
$[Ru(CO)(PMe_2Ph)_2\{P(OMe)Ph_2\}Cl_2]$	(II)	52.05	4.95	(I)	52.5	5.05	(IV)	52.05	4.9	52.03	5.09
$[Ru(CO)(PMe_2Ph)_2(PMePh_2)Cl_2]$							(IV)	53.7	5.2	53.26	5.21
$[Ru(CO)(PMe_2Ph)_2(PPh_3)Cl_2]$							(IV)	56.75	5.2	56.91	5.05
$[Ru(CO)(PMe_2Ph)_2(py)Cl_2]$ [c]				(I)	47.75	4.85	(IV)	47.7	4.75	47.57	4.90
$[Ru(CO)(PMe_2Ph)_2(NH_3)Cl_2]$ [d]				(I)	41.5	5.0				41.39	5.11
$[Ru(CO)(PMe_2Ph)_2(pip)Cl_2]$ [e]				(I)	47.6	5.95				47.06	5.92
$[Ru(CO)(PMe_2Ph)_2(NCMe)Cl_2]$ [f]	(II)	44.15	4.75							44.11	4.87
$[Ru(CO)(PMe_2Ph)_2(NCPh)Cl_2]$ [g]	(II)	50.0	4.65							49.75	4.70
$[Ru(CO)(PMe_2Ph)_2(SMe_2)Cl_2]$	(II)	41.9	5.15							42.38	5.24
$[Ru(CO)(PMe_2Ph)_2(OSMe_2)Cl_2]$	(II)	41.1	5.0							41.16	5.09
$[Ru(CO)(PMe_2Ph)_2(C_2H_4)Cl_2]$	(II)	45.1	5.0							45.25	5.20
$[\{Ru(CO)(PMe_2Ph)_2Cl_2\}_2]$							(VI)	42.75	4.6	42.87	4.66
$[\{Ru(CO)(PMe_2Ph)_2Br_2\}_2]$							(VI)	36.05	4.0	36.12	3.92
$[\{Ru(CO)(PMe_2Ph)_2I_2\}_2]$							(VI)	30.85	3.25	30.97	3.36

[a] The all-*trans*-isomer contains one-third of a molecule of $CHCl_3$ of crystallization. [b] The all-*trans*-isomer contains one molecule of tetrahydrofuran of crystallization. [c] %N Found: isomer (I), 2.55; isomer (IV), 2.6. %N required, 2.52. [d] %N Found, 2.65. %N required, 2.83. [e] %N Found, 2.6. %N required, 2.50, pip = piperidine. [f] %N Found, 2.8. %N required, 2.71. [g] %N Found, 2.45. %N required, 2.42.

Complexes all-cis-$[Ru(CO)_2L_2X_2]$.—*all*-cis-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$. A solution of *cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ (0.10 g) in chloroform (10 ml) was irradiated for 24 h, and then kept at 313 K in the absence of light for 16 h. The solvent was removed under reduced pressure and the residue recrystallized from an ethanol–light petroleum (b.p. 313–333 K) mixture (yield 75%). The complex all-*cis*-$[Ru(CO)_2(PMePh_2)_2Cl_2]$ was similarly prepared (yield 77%).

all-cis-$[Ru(CO)_2(PMe_2Ph)_2Br_2]$. A solution of all-*cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ (0.10 g) in chloroform (15 ml) was stirred at 313 K with NaBr (0.20 g) for 4 h. The reaction mixture was filtered and the product obtained in crystalline form by concentrating the filtrate under reduced pressure (yield 60%). The analogous iodo-complex was obtained in the same way using NaI (0.30 g) (yield 75%). The complexes all-*cis*-$[Ru(CO)_2(PMePh_2)_2X_2]$ (X = Br or I) were and the others (at 273 K) from benzene–light petroleum mixtures (yields 79 and 63% respectively).

$[Ru(CO)(PMe_2Ph)_2(py)Cl_2]$. Pyridine (0.5 ml) was added to a solution of all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ (0.10 g) in acetone (15 ml). After 5 h at 313 K the solution was concentrated under a stream of nitrogen. The yellow crystals obtained were recrystallized from dichloromethane–light petroleum (yield 85%). The complexes $[Ru(CO)(PMe_2Ph)_2L'Cl_2]$ (L′ = NH_3 or piperidine) were similarly prepared (the ammonia for the former preparation was added as a concentrated aqueous solution) but did not require recrystallization (yields 85 and 90% respectively).

Complexes $[Ru(CO)(PMe_2Ph)_2L'Cl_2]$, *Configuration* (*II*).—$[Ru(CO)(PMe_2Ph)_3Cl_2]$. Isomer (I) of $[Ru(CO)(PMe_2Ph)_3Cl_2]$ (0.40 g) was heated under reflux in 2-methoxyethanol (30 ml) for 2 h. Water (70 ml) was added to the solution

and the precipitated product was recrystallized from methanol (yield 50%).

$[Ru(CO)(PMe_2Ph)_2\{P(OMe)_3\}Cl_2]$. Isomer (I) of this complex was heated under reflux in light petroleum (b.p. 393—433 K, 30 ml) for 2 h. The product was obtained on cooling the solution (yield 55%). The same method was used to prepare $[Ru(CO)(PMe_2Ph)_2\{P(OMe)_2Ph\}Cl_2]$ and $[Ru(CO)(PMe_2Ph)_2\{P(OMe)Ph_2\}Cl_2]$, except that the latter product was insoluble even in the refluxing solvent (yields 55 and 90% respectively).

$[Ru(CO)(PMe_2Ph)_2(NCMe)Cl_2]$. To a stirred solution of all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ (0.10 g) in chloroform (15 ml) was added MeCN (0.5 ml). After 9 h at 313 K, the solution was concentrated under a stream of nitrogen and the residue recrystallized from a chloroform–light petroleum mixture (yield 85%). The complexes $[Ru(CO)(PMe_2Ph)_2L'Cl_2]$ ($L' = NCPh$, SMe_2, or $OSMe_2$) were prepared in the same way, except that the last of them was obtained as an oil on removal of the reaction solvent; this was solidified by trituration with diethyl ether–light petroleum (yields 85, 72, and 65% respectively).

$[Ru(CO)(PMe_2Ph)_2(C_2H_4)Cl_2]$. Ethylene was bubbled through a solution of all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ (0.10 g) in chloroform (15 ml) at 313 K for 72 h. The solvent was removed under reduced pressure and the residue recrystallized from an ethylene-saturated mixture of acetone and light petroleum (yield 75%).

Complexes $[Ru(CO)(PMe_2Ph)_2L'Cl_2]$, *Configuration* (*IV*).—$[Ru(CO)(PMe_2Ph)_2(py)Cl_2]$. A stirred solution of all-*cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ (0.10 g) in chloroform (15 ml) was treated with pyridine (0.5 ml). After 5 h at 293 K the solvent was removed under reduced pressure and the residue recrystallized from a chloroform–light petroleum mixture (yield 70%). The complexes $[Ru(CO)(PMe_2Ph)_2L'Cl_2]$ where L′ is a ligand with a phosphorus donor atom could be obtained in this way but were more satisfactorily prepared from $[\{Ru(CO)(PMe_2Ph)_2Cl_2\}_2]$.

$[Ru(CO)(PMe_2Ph)_3Cl_2]$. To a solution of $[\{Ru(CO)(PMe_2Ph)_2Cl_2\}_2]$ [structure (VI), 0.05 g] in chloroform (10 ml) was added PMe_2Ph (0.015 g). After 0.1 h the solution was concentrated under a stream of nitrogen to give a crystalline product (yield 83%). The same method was used to prepare the complexes $[Ru(CO)(PMe_2Ph)_2L'Cl_2]$ [$L' = P(OMe)_3$, $P(OMe)_2Ph$, $P(OMe)Ph_2$, $PMePh_2$, and PPh_3] in yields between 70 and 90%.

Complexes $[\{Ru(CO)(PMe_2Ph)_2X_2\}_2]$ (X = Cl, Br, *or* I), *Configuration* (*VI*).—$[\{Ru(CO)(PMe_2Ph)_2Cl_2\}_2]$. The mother liquor from a preparation of all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ by irradiation of the *cis*-isomer in acetone was stored for several days. The dimeric species $[\{Ru(CO)(PMe_2Ph)_2Cl_2\}_2]$ was slowly precipitated from the solution. It could not be satisfactorily recrystallized. The same product could be obtained by bubbling nitrogen through a solution of all-*cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ (0.10 g) in benzene (15 ml) at 313 K for 24 h (yield 95%).

$[\{Ru(CO)(PMe_2Ph)_2Br_2\}_2]$. A chloroform solution (15 ml) of $[\{Ru(CO)(PMe_2Ph)_2Cl_2\}_2]$ (0.10 g) was stirred with LiBr (0.18 g) at 313 K for 5 h. After filtration, the product was obtained by concentration of the filtrate under reduced pressure (yield 80%). The complex $[\{Ru(CO)(PMe_2Ph)_2I_2\}_2]$ was obtained in the same way using NaI (0.30 g) (yield 85%).

Instruments used in the work described above were: Varian A60A 60 MHz n.m.r. spectrometer; Perkin-Elmer 257 grating i.r. spectrometer; Perkin-Elmer 240 elemental analyser; Mechrolab vapour pressure osmometer, model 301A.

We thank Mrs. Judith Foggin for experimental assistance, and the S.R.C. for maintenance grants (to C. F. J. B., J. A. D., and J. J.).

[5/1672 *Received*, 29*th August*, 1975]