

Nuclear Magnetic Resonance Studies on Metal Complexes. Part III.* Dimethylphenylphosphine Complexes of Ruthenium(II)

By J. M. Jenkins, M. S. Lupin, and B. L. Shaw

New complexes are described of types $[\text{RuX}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{or SCN}$), $[\text{RuXCl}(\text{CO})(\text{PMe}_2\text{Ph})_3]$ ($\text{X} = \text{Br}, \text{or I}$), $[\text{RuHX}(\text{CO})(\text{PMe}_2\text{Ph})_3]$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$), and $[\text{RuX}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$). Results for the methyl resonance spectra are given, the spectra being very useful in determining stereochemistry. Empirical shielding constants are calculated for the effects on the τ -values of the methyl resonances on replacing Cl by Br or I. Resonance results for the ruthenium hydrides are reported as are infrared and dipole moment measurements. The *trans*-effects of carbon monoxide, tertiary phosphine, and chloride ligands in ruthenium(II) complexes are discussed.

THE reactions of tertiary phosphine-ruthenium trichloride complexes with alcohols, usually in the presence of a base, or the reactions of tertiary phosphines with ruthenium halogenocarbonyl complexes give very stable carbonyl or hydridocarbonyl complexes of the type $[\text{RuCl}_2(\text{CO})(\text{PR}_3)_3]$, $[\text{RuHCl}(\text{CO})(\text{PR}_3)_3]$, or $[\text{RuCl}_2(\text{CO})_2(\text{PR}_3)_2]$.¹⁻⁵ The configurations of the diethylphenylphosphine and triethylphosphine complexes were assigned by Chatt and Shaw² from infrared and dipole-moment results and for the hydridocarbonyl complexes from the nuclear magnetic resonance pattern of the hydridic hydrogen.

We have shown that the proton magnetic resonance spectra of dimethylphenylphosphine-metal complexes

are extremely useful in determining stereochemistry^{6,7} and we have now examined the nuclear magnetic resonance spectra of some ruthenium-dimethylphenylphosphine complexes.

Preparation of Complexes.—*Monocarbonyl complexes.* Treatment of ruthenium trichloride in boiling ethanol with carbon monoxide followed by the addition of dimethylphenylphosphine gave a yellow monocarbonyl complex $[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$. This complex is assigned configuration (I), from its low dipole moment (3.7 D),² proton magnetic resonance spectrum (discussed below), and by analogy with the corresponding PEt_3 and PEt_2Ph complexes;² similarly for the other PMe_2Ph -ruthenium complexes. The yellow complex

* Part II, J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. (A)*, 1966, 1407.

¹ J. Chatt and B. L. Shaw, *Chem. and Ind.*, 1960, 931; 1961, 290.

² J. Chatt, B. L. Shaw, and A. E. Field, *J. Chem. Soc.*, 1964, 3466.

³ L. Vaska, *Chem. and Ind.*, 1961, 1402.

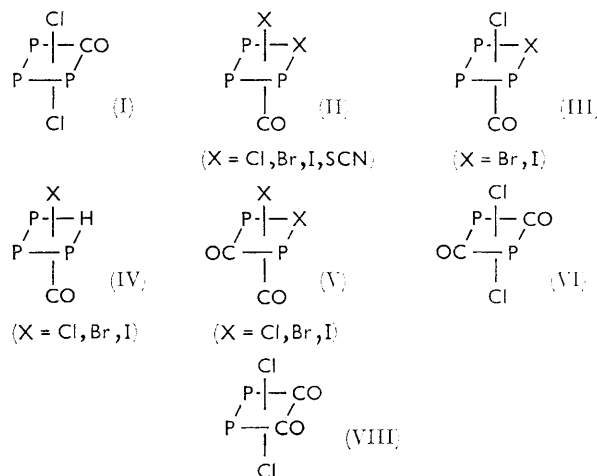
⁴ L. Vaska and J. W. Diluzio, *J. Amer. Chem. Soc.*, 1961, **83**, 1262.

⁵ A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1966, **28**, 945.

⁶ J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 1963, 291.

⁷ J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. (A)*, 1966, 770, 1407.

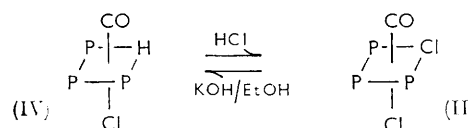
$[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (I), isomerises above its melting point (165°) or on recrystallisation from a high-boiling solvent such as 2-methoxyethanol (b. p. 124°) to a colourless monocarbonyl complex of configuration (II) ($\text{X} = \text{Cl}$) which has a higher dipole moment (7.45 D). The colourless mono carbonyl complex can be prepared directly by the action of dimethylphenylphosphine on ruthenium trichloride in boiling 2-methoxyethanol for 1 hr., followed by treatment of the resulting orange solution with carbon monoxide for 7 hr. Alternatively, it is formed by the action of carbon monoxide on the binuclear salt $[\text{Ru}_2\text{Cl}_3(\text{PMe}_2\text{Ph})_6]\text{Cl}$ in boiling 2-methoxyethanol.



Treatment of the monocarbonyl complex $[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (II), with lithium bromide or sodium iodide in acetone at room temperature caused the chlorine atom *trans* to the phosphine ligand to be substituted (by Br or I) much more quickly than the chlorine *trans* to carbon monoxide. Thus after reaction times of 18 hr. the complexes $[\text{RuXCl}(\text{CO})(\text{PMe}_2\text{Ph})_3]$ ($\text{X} = \text{Br}$ or I) of configuration (III) were obtained in good yields. Prolonged treatment (6 weeks) of the dichlorocarbonyl complex $[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (II) ($\text{X} = \text{Cl}$), with sodium iodide in acetone at room temperature gave the di-iodo-complex $[\text{RuI}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (II) ($\text{X} = \text{I}$). Under more vigorous conditions, e.g., in boiling 2-methoxyethanol, metathetical replacement of both chlorine atoms occurred after ca. 10 hr. and the dibromo-, di-iodo-, and dithiocyanato-complexes $[\text{RuX}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (II) ($\text{X} = \text{Br, I, or SCN}$), were so obtained. No replacement of the chlorine atoms of the yellow dichloro-complex $[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (I), occurred on treatment with sodium iodide for 18 hr., but after 7 weeks the di-iodo-complex $[\text{RuI}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (II), was obtained.

Hydridocarbonyl complexes. The hydridocarbonyl complex $[\text{RuHCl}(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (IV), was prepared by the action of aqueous potassium hydroxide on the complex $[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$

configuration (II), in boiling ethanol. The hydride ligand is labile to acids and with hydrochloric acid hydrogen is evolved and the colourless monocarbonyl complex $[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (II), is regenerated.



Treatment of the hydridocarbonyl complex $[\text{RuHCl}(\text{CO})(\text{PMe}_2\text{Ph})_3]$ with lithium bromide or sodium iodide in boiling ethanol gave the corresponding bromo- or iodo-hydridocarbonyl complexes in good yields.

Dicarbonyl complexes. Two isomeric dicarbonyl complexes of the type $[\text{RuCl}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$ were obtained, a colourless *cis* form of configuration (V) and a yellow less stable *trans* form of configuration (VI). The *cis*-dicarbonyl complex was obtained by prolonged (20 hr.) treatment of ruthenium trichloride in boiling 2-methoxyethanol with carbon monoxide, giving a pale yellow solution which, when treated with dimethylphenylphosphine, gave the colourless *cis*-dicarbonyl complex $[\text{RuCl}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$. Metatheses with lithium bromide or sodium iodide are slow even in boiling 2-methoxyethanol.

The yellow *trans* isomer, configuration (VI), was prepared by treating ruthenium trichloride in boiling ethanol with carbon monoxide for 5 hr. followed by the addition of dimethylphenylphosphine to the red solution. A mixture of the yellow monocarbonyl complex $[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$ and the yellow dicarbonyl complex $[\text{RuCl}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$ was obtained from which

TABLE 1
Carbonyl stretching frequencies of some ruthenium complexes

Complex	Con-figuration	$\nu(\text{C}=\text{O})$ (cm^{-1})	
		Nujol	Chloroform
$[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$	I	1961	1961
$[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$	II	1923	1949
$[\text{RuBr}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$	II	1938	1953
$[\text{RuI}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$	II	1945	1953
$[\text{Ru}(\text{SCN})_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$...	II	1968	1970
$[\text{RuBrCl}(\text{CO})(\text{PMe}_2\text{Ph})_3]$	III	1912, 1938	1945
$[\text{RuICl}(\text{CO})(\text{PMe}_2\text{Ph})_3]$	III	1912, 1934	1949
$[\text{RuHCl}(\text{CO})(\text{PMe}_2\text{Ph})_3]$ * a ...	IV	1887, 1905	1916 †
$[\text{RuHBr}(\text{CO})(\text{PMe}_2\text{Ph})_3]$ * b ...	IV	1898, 1919	1923
$[\text{RuHI}(\text{CO})(\text{PMe}_2\text{Ph})_3]$ * c ...	IV	1908, 1923	1930
<i>cis</i> - $[\text{RuCl}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$...	V	1972, 2037	1990, 2055
<i>cis</i> - $[\text{RuBr}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$...	V	1968, 2037	1984, 2045
<i>cis</i> - $[\text{RuI}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$...	V	1968, 2037	1980, 2041
<i>trans</i> - $[\text{RuCl}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$	VI	1996	2008

* $\nu(\text{Ru}-\text{H})$ (cm^{-1}). a, 1835 (Nujol); 1866 (benzene); b, 1862, 1866 (Nujol); 1866 (chloroform); c, 1880 (Nujol); 1880 (chloroform). † In benzene.

the yellow dicarbonyl complex was isolated by repeated crystallisation from benzene. This *trans* isomer is thermally less stable than the *cis* (dipole moment 4.5 D) and is readily isomerised to it on heating to 190° .

All the carbonyl complexes prepared showed strong infrared absorptions in the range $1900\text{--}2050\text{ cm}^{-1}$ due to carbonyl stretching modes. The carbonyl stretching frequencies are given in Table 1.

trans-Effects in Ruthenium(II) Complexes.—In the preparative work we generally found the lability of a chlorine towards substitution by bromide or iodide to depend mainly on the *trans* ligand. Thus chlorine *trans* to dimethylphenylphosphine substitutes much more rapidly than chlorine *trans* either to carbon monoxide or to another chlorine, *i.e.*, in octahedral ruthenium(II) complexes carbon monoxide has a low *trans*-effect but tertiary phosphines have a high *trans*-effect.

This is in contrast to platinum(II) complexes where both carbon monoxide and tertiary phosphines have

high *trans*-effect of the hydride ion.¹¹ The complex $[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (II), shows two very strong bands, at 288 and 229 cm^{-1} , in its infrared absorption spectrum. These are absent from spectra of the corresponding dibromo- or di-iodo-complexes and are therefore assigned to $\nu(\text{Ru}-\text{Cl})$. In complexes of type $[\text{RuClX}(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (III) ($\text{X} = \text{Br}, \text{I}, \text{or } \text{NO}_3$) (prepared by treating $[\text{RuHCl}(\text{CO})(\text{PMe}_2\text{Ph})_3]$ with dilute nitric acid) only one band due to ruthenium-chlorine stretching is observed: the band is at 288, 283, and 294 cm^{-1} , respectively, for $\text{X} = \text{Br}, \text{I}, \text{and } \text{NO}_3$. A stretching frequency of 229

TABLE 2

Nuclear magnetic resonance for some ruthenium complexes. Methyl resonances of monocarbonyl complexes, in chloroform unless indicated. Coupling constants (J ; c./sec.) measured to ± 0.5 c./sec.; τ -values ± 0.01

Compound	Configuration	τ	Triplet $J(\text{P}^1, {}^3\text{H})$ (c./sec.)	τ	Doublet $J(\text{P}^2\text{--H})$ (c./sec.)
$[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$	I	8.29	3.5	8.73	8
$[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$	II	8.10 †		8.77	10
$[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]^*$	II	8.12 †		8.92	10
$[\text{RuBr}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$	II	7.96 †		8.67	10.5
$[\text{RuI}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$	II	7.73	3.5	8.58	10
		7.76	3.5		
$[\text{Ru}(\text{SCN})_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$	III	8.18 †		8.84	9.5
$[\text{RuBrCl}(\text{CO})(\text{PMe}_2\text{Ph})_3]$	III	8.01 †		8.80	10
$[\text{RuICl}(\text{CO})(\text{PMe}_2\text{Ph})_3]$	III	7.88	4	8.81	10
$[\text{RuHCl}(\text{CO})(\text{PMe}_2\text{Ph})_3]$	IV	8.27 †		8.90	7
$[\text{RuHCl}(\text{CO})(\text{PMe}_2\text{Ph})_3]^*$	IV	8.29	3.5	8.85	7.5
$[\text{RuHBr}(\text{CO})(\text{PMe}_2\text{Ph})_3]$	IV	8.18	3	8.80	7
		8.27	3		
$[\text{RuHBr}(\text{CO})(\text{PMe}_2\text{Ph})_3]^*$	IV	8.24	3	8.80	7
		8.27	3		
$[\text{RuHI}(\text{CO})(\text{PMe}_2\text{Ph})_3]$	IV	8.12	3	8.69	6
		8.22	3		
$[\text{RuHI}(\text{CO})(\text{PMe}_2\text{Ph})_3]^*$	IV	8.20 †		8.69	7

* In benzene. † Partially resolved quartet.

high *trans*-effects.⁸ According to the theories of Chatt and his co-workers⁹ and of Orgel¹⁰ of the high *trans*-effects of π -bonding ligands in planar platinum(II) complexes, removal of electron density from the non-bonding d -orbitals above and below the plane facilitates attack by a nucleophile in an $\text{S}_{\text{N}}2$ process. In an octahedral complex the presence of the two extra ligands will greatly hinder this attack; hence the Chatt-Orgel theory readily explains the low *trans*-effect of carbon monoxide in these ruthenium(II) complexes. Tertiary phosphines which are much better σ -donors of electrons than carbon monoxide presumably cause strong polarisations across the complex, which greatly weaken the ruthenium-chlorine bonds in *trans* positions and facilitate substitution (as in the Grinberg theory of the *trans*-effect).⁸ The high dipole moment (7.45 D) of the complex $[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (II) (Table 7), suggests a strong electron drift along the vector $\text{P} \rightarrow \text{Ru} \rightarrow \text{Cl}$ making the chlorine more negatively charged, more weakly bonded, and more likely to come off as chloride ion. An inductive electron-release mechanism is believed to be the cause of the very

cm^{-1} is very low for a platinum-metal-chlorine bond and suggests that in this ruthenium chloride complex the chlorine *trans* to phosphine is weakly bonded. Chatt and his co-workers¹² found fairly low platinum-chlorine stretching frequencies for platinum(II) complexes where a tertiary phosphine was the *trans*-ligand; *e.g.*, for *trans*- $[\text{PtCl}_2(\text{PEt}_3)_2]$ $\nu(\text{Pt}-\text{Cl}) = 340$ cm^{-1} , for *cis*- $[\text{PtCl}_2(\text{PEt}_3)_2]$ $\nu(\text{Pt}-\text{Cl}) = 303$ and 281 cm^{-1} . Similarly for *mer*- $[\text{IrCl}_3(\text{PMe}_2\text{Ph})_3]$ $\nu(\text{Ir}-\text{Cl})$ for chlorine *trans* to chlorine is 315 cm^{-1} but for chlorine *trans* to phosphine it is 276 cm^{-1} and this chlorine is very much more labile to substitution.¹³

Stereochemistry determined by Nuclear Magnetic Resonance of Methyl Groups.—When two dimethylphenylphosphine ligands are mutually *trans* the methyl resonance is a 1:2:1 triplet or a multiplet owing to "virtual coupling" with both phosphorus nuclei but a dimethylphenylphosphine ligand without a dimethylphenylphosphine ligand in a *trans*-position shows a 1:1 doublet methyl resonance.^{6,7} The resonance results for the complexes are in Tables 2 and 3.

The methyl resonance of the yellow monocarbonyl

⁸ See F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," Wiley, New York, 1958, pp. 172–192.

⁹ J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 1955, 4456.

¹⁰ L. E. Orgel, *J. Inorg. Nuclear Chem.*, 1956, 2, 137.

¹¹ F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 1961, 2207.

¹² D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 1964, 734.

¹³ J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.*, 1965, 6789.

complex $[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$ consists of a 1:2:1 triplet and 1:1 doublet of relative intensities 2:1 confirming the assigned configuration (I). The methyl resonance of the colourless monocarbonyl consists of a partially resolved quartet and a 1:1 doublet confirming

TABLE 3

Methyl resonances of dicarbonyl complexes in chloroform

Compound	Triplet (τ)	$J(\text{P-H})$ (c./sec.)
<i>cis</i> - $[\text{RuCl}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$	7.99	4.5
<i>cis</i> - $[\text{RuBr}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$	7.85	4
<i>cis</i> - $[\text{RuI}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$	7.63	4
<i>trans</i> - $[\text{RuCl}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$	8.03	4

the assigned configuration (II). The quartet arises because there is no plane of symmetry through the two *trans*-phosphorus atoms, therefore the methyl groups on the same phosphorus atom are not equivalent and the quartet is formed from two overlapping 1:2:1 triplets. The quartet is approximately 1:3:3:1 with only the top half of each peak being resolved from the rest. The yellow monocarbonyl complex has a plane of symmetry through the *trans*-phosphorus atoms (Figure)



Showing symmetry looking down line P-Ru-P of the two isomers of formula $[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$. A plane of symmetry can be drawn through this line for the monocarbonyl of configuration (I) but not for the isomer of configuration (II).

and the methyl groups on the same phosphorus are equivalent so that a well defined triplet is observed. The di-iodo-complex $[\text{RuI}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (II) ($X = \text{I}$), shows two distinct 1:2:1 triplets with equal coupling, $J(\text{P-H}) = 3.5$ c./sec. separated by 9 c./sec., whilst the other complexes of configuration (II) ($X = \text{Br}$ or SCN) show quartet methyl resonances. The methyl resonance of the bromochloro-complex $[\text{RuBrCl}(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (III), also consists of a quartet and a 1:1 doublet but the methyl resonance of the iodochloro-complex $[\text{RuICl}(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (III), consists of a partially resolved 1:2:1 triplet and a 1:1 doublet, the triplet being due to accidental superimposition of the two triplets of the non-equivalent methyl groups. The methyl resonances of the hydridocarbonyl complexes $[\text{RuHX}(\text{CO})(\text{PMe}_2\text{Ph})_3]$ consist either of a quartet and a doublet, or two distinct triplets close together and a doublet, in agreement with the assigned configuration (IV) (the iodide shows two triplets in chloroform solution but these merge into a quartet in benzene solution). The hydridic resonance confirms this stereochemistry and is discussed below.

The methyl proton resonance of the dicarbonyl complex $[\text{RuCl}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$, configuration (V), consists of a narrow 1:2:1 triplet, $J(\text{P-H}) = 4$ c./sec., owing to the two phosphine ligands' being mutually *trans*.

Previously² dicarbonyl complexes of this type with other tertiary phosphines had been assigned the configuration (VII), but we now consider that this was in error and that they have configuration (V). The dimethylphenylphosphine complex $[\text{RuCl}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$, configuration (V), shows two very strong infrared carbonyl stretching frequencies which are of similar frequency to those of the dicarbonyl complexes described previously.² It also has a similar dipole moment (4.5 D).

The methyl proton resonance of the *trans*-isomer $[\text{RuCl}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$ configuration (VI), consists of a 1:2:1 triplet, $J(\text{P-H}) = 4$ c./sec. This configuration is confirmed by the presence of only one strong infrared absorption band in the carbonyl region.

Factors affecting Chemical Shifts.—For the series $[\text{RuX}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (II) ($X = \text{Cl}$, Br , I , or SCN), the τ -values of the doublet resonance due to the phosphine ligand *trans* to the ligand X decrease in the order $X = \text{SCN} > \text{Cl} > \text{Br} > \text{I}$ and the τ -values of the triplet resonance, due to the mutually *trans*-phosphines, also decrease in the same order (Table 2). Similarly in the series of *cis*-dicarbonyl complexes

$[\text{RuX}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$, configuration (V) ($X = \text{Cl}$, Br , or I), the τ -value of the triplet resonance decreases in the order $\text{Cl} > \text{Br} > \text{I}$. These orders suggest that the main factor lowering τ is removal of electron density from the methyl groups by back donation of electrons from ruthenium to halogen; this probably increases in the order $\text{Cl} < \text{Br} < \text{I}$.¹⁴ In the series of complexes of type $[\text{RuXCl}(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (III) ($X = \text{H}$, Cl , Br , or I), the τ -value for the doublet resonance of the phosphine *trans* to the X -ligand decreases in the order $\text{H} > \text{I} > \text{Br} > \text{Cl}$, that is, in order of increasing electronegativity of X , but the decrease is small except for the hydride ligand, suggesting that the electronegative effect is not a major factor.

It is possible to calculate empirical shielding constants for the effects on the methyl resonances of replacing Cl by Br or I in the series of complexes of type $[\text{RuXCl}(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (III), and of type $[\text{RuHX}(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (IV). Thus for the complexes of type $[\text{RuXCl}(\text{CO})(\text{PMe}_2\text{Ph})_3]$ replacement of Cl *trans* to a phosphine ligand by Br increases τ of the doublet by 0.03 and decreases that of the triplet by 0.09. For complexes of type $[\text{RuHX}(\text{CO})(\text{PMe}_2\text{Ph})_3]$ replacement of Cl *trans* to carbon monoxide by Br decreases τ of the doublet by 0.10 and decreases the triplet resonance by 0.04. Similarly changes in τ -values when Cl is replaced by I can be calculated; the results are in Table 4.

Table 5 compares the observed τ -values for complexes of types $[\text{RuX}_2\text{CO}(\text{PMe}_2\text{Ph})_3]$, configuration (II), and $[\text{RuX}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$, configuration (V) ($X = \text{Br}$ or I), with those calculated from the corresponding chloro-complexes, using the constants given in Table 4, e.g., the calculation of the triplet resonance of the complex $[\text{RuBr}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (II), from the dichloro-complex is $8.10 - 0.09 - 0.04 = 7.97$ (Found:

¹⁴ I. Leden and J. Chatt, *J. Chem. Soc.*, 1955, 2936.

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7.96). Agreement between observed and calculated values is good.

The hydride ligand causes high τ -values for both the multiplet and doublet resonances of $[\text{RuHX}(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (IV) ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$), possibly because of its low electronegativity, and inability to accept back-donation of electrons.

TABLE 4

Shielding constants for the effect on the methyl resonance τ -value of replacing chlorine by bromine or iodine in some halogenocarbonyl(dimethylphenylphosphine)ruthenium(II) complexes

		Cl by Br	Cl by I
Effect of replacing chlorine in } <i>trans</i> -position to phosphine	Doublet	+0.03	+0.04
	Triplet	-0.09	-0.22
Effect of replacing chlorine in } <i>trans</i> -position to carbon monoxide	Doublet	-0.10	-0.21
	Triplet	-0.04	-0.10

TABLE 5

Comparison of observed τ -values with those calculated from corresponding chloro-complexes by use of the constants given in Table 4

Compound	Con-figuration	Doublet		Triplet	
		Obs.	Calc.	Obs.	Calc.
$[\text{RuBr}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$...	(II)	8.67	8.70 *	7.96	7.97 *
$[\text{RuI}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$	(II)	8.58	8.60 *	7.73	7.78 *
$[\text{RuBr}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$...	(V)	—	—	7.85	7.86 †
$[\text{RuI}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$	(V)	—	—	7.63	7.67 †

* Calculated from τ -values for $[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$, configuration (II). † Calculated from τ -values for $[\text{RuCl}_2(\text{CO})_2(\text{PMe}_2\text{Ph})_2]$, configuration (V).

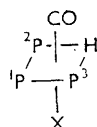
Nuclear Magnetic Resonance of the Hydride Ligand.—As in other transition-metal hydride complexes the chemical shift of the hydridic hydrogens is large (τ 16.6—17.7) and the resonances are split by coupling with the phosphorus nuclei. The resonances consist of two 1:2:1 triplets [$J(\text{H}-\text{P}^1) = J(\text{H}-\text{P}^3)$, 26.5—27 c./sec.; $J(\text{H}-\text{P}^2)$, 105—113 c./sec.], the coupling constants with phosphorus in a *trans* position are large, but with phosphorus in *cis* positions are much smaller, thus confirming the configuration (IV) (Table 6.)

TABLE 6

Hydride resonances of hydrido-carbonyl complexes in benzene *

	τ	$J(\text{P}^1, \text{H})$ (c./sec.)	$J(\text{P}^2, \text{H})$ (c./sec.)
$[\text{RuHCl}(\text{CO})(\text{PMe}_2\text{Ph})_3]$...	16.6	26.5	105
$[\text{RuHBr}(\text{CO})(\text{PMe}_2\text{Ph})_3]$...	17.0	26.5	113
$[\text{RuHI}(\text{CO})(\text{PMe}_2\text{Ph})_3]$...	17.7	27	108

* Phosphorus atoms number as follows



EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are corrected. All reactions involving free tertiary phosphines or hydrido-complexes were carried out

under nitrogen. Ruthenium trichloride trihydrate was purchased from Johnson Matthey Ltd.

Preparation of Monocarbonyl Complexes.—*Dichloro(carbonyl)tris(dimethylphenylphosphine)ruthenium(II)*, configuration (I) $[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$. Carbon monoxide was passed through a boiling solution of ruthenium trichloride trihydrate (0.96 g.) in ethanol (25 ml.) for 5½ hr. Dimethylphenylphosphine (1.81 g.) was added to the cold blood-red solution which was then boiled under reflux for 5 min. The product which separated was recrystallised from ethanol to give the complex as yellow prisms (1.39 g.), m. p. 164—165° (Found: C, 49.2; H, 5.4. $\text{C}_{25}\text{H}_{33}\text{Cl}_2\text{OP}_3\text{Ru}$ requires C, 48.9; H, 5.4%).

Dichloro(carbonyl)tris(dimethylphenylphosphine)ruthenium(II), configuration (II) $[\text{RuCl}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$. Dimethylphenylphosphine (3.95 g.) was added to ruthenium trichloride trihydrate (8.79 g.) in 2-methoxyethanol (65 ml.) and the mixture was heated under reflux for 1 hr. Carbon monoxide was then passed through the refluxing solution for 7 hr.; the solution had become pale yellow. The solvent was evaporated off under reduced pressure to give an off-white solid which on recrystallisation from methanol gave the *dichloro-complex* as colourless prisms (9.79 g.), m. p. 179—181° (Found: C, 48.7; H, 5.35%).

Dibromo(carbonyl)tris(dimethylphenylphosphine)ruthenium(II), configuration (II) $[\text{RuBr}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$. A solution of dichloro(carbonyl)tris(dimethylphenylphosphine)ruthenium(II), configuration (II), (0.50 g.) and lithium bromide (2.5 g.) in 2-methoxyethanol (30 ml.) was heated under reflux for 9½ hr. The yellow solution was cooled and diluted with water. The precipitate was crystallised from ethanol to give the *dibromo-complex* as yellow prisms (0.42 g.), m. p. 193—197.5° (Found: C, 43.0; H, 4.7%; M, osmometric in chloroform, 681. $\text{C}_{25}\text{H}_{33}\text{Br}_2\text{OP}_3\text{Ru}$ requires C, 42.7; H, 4.8%; M, 703).

Di-iodo(carbonyl)tris(dimethylphenylphosphine)ruthenium(II), configuration (II) $[\text{RuI}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$. A solution of the dichloro-complex (0.30 g.) and sodium iodide (1.6 g.) in 2-methoxyethanol (25 ml.) was heated under reflux for 10 hr. The solution was cooled and diluted with water and the precipitate was recrystallised from ethanol to give the required product as *yellow prisms* (0.20 g.), m. p. 215—216° (Found: C, 38.2; H, 4.35. $\text{C}_{25}\text{H}_{33}\text{I}_2\text{OP}_3\text{Ru}$ requires C, 37.65; H, 4.2%).

Dithiocyanato(carbonyl)tris(dimethylphenylphosphine)ruthenium(II), configuration (II) $[\text{Ru}(\text{SCN})_2(\text{CO})(\text{PMe}_2\text{Ph})_3]$. A solution of the dichloro-complex (0.20 g.) and potassium thiocyanate (1.5 g.) in 2-methoxyethanol (30 ml.) was heated under reflux for 4½ hr. The colourless solution was cooled and diluted with water and the precipitate was recrystallised from ethanol to give the *dithiocyanato-complex* as white needles (0.14 g.), m. p. 188—200° (Found: C, 49.1; H, 5.0; N, 4.2. $\text{C}_{27}\text{H}_{33}\text{N}_2\text{OP}_3\text{RuS}_2$ requires C, 49.1; H, 5.1; N, 4.3%).

Iodochloro(carbonyl)tris(dimethylphenylphosphine)ruthenium(II), configuration (III) $[\text{RuI}(\text{Cl})(\text{CO})(\text{PMe}_2\text{Ph})_3]$. Sodium iodide (0.71 g.) was added to a suspension of dichloro(carbonyl)tris(dimethylphenylphosphine)ruthenium(II), configuration (II) (0.30 g.), in acetone (15 ml.) and the mixture was shaken at room temperature for 18 hr. The yellow solution was treated with benzene (25 ml.) and water (25 ml.) and the benzene extract was evaporated to dryness under reduced pressure to give a yellow solid. This was recrystallised twice from dichloromethane-light petroleum (b. p. 60—80°) to give the required product

as yellow prisms (0.21 g.), m. p. 203–220° (Found: C, 42.6; H, 4.6%; *M*, osmometric in chloroform, 693. $C_{25}H_{33}ClIOP_3Ru$ requires C, 42.5; H, 4.7%; *M*, 706).

Bromochloro(carbonyl)tris(dimethylphenylphosphine)ruthenium(II), configuration (III) $[RuBrCl(CO)(PMe_2Ph)_3]$. Lithium bromide (0.45 g.) was added to a suspension of dichloro(carbonyl)tris(dimethylphenylphosphine)ruthenium(II), configuration (II) (0.30 g.), in acetone (15 ml.) and the mixture was shaken at room temperature for 25 hr. The mixture was then treated with benzene (25 ml.) and water (25 ml.). The benzene extract when evaporated to dryness gave a yellow solid which was recrystallised twice from dichloromethane–light petroleum (b. p. 60–80°) to give the *bromochloro-complex* as pale yellow prisms (0.24 g.), m. p. 176–194° (decomp.) (Found: C, 45.7; H, 5.3. $C_{25}H_{33}BrClOP_3Ru$ requires C, 45.5; H, 5.1%).

Isomerisation of Dichloro(carbonyl)tris(dimethylphenylphosphine)ruthenium(II), Configuration (I), to *Dichloro(carbonyl)tris(dimethylphenylphosphine)ruthenium(II)*, Configuration (II).—The yellow isomer, configuration (I) (0.20 g.),

nium(II) $[RuHI(CO)(PMe_2Ph)_3]$. Sodium iodide (1.50 g.) was added to a solution of the hydriochloro-complex (0.48 g.) in ethanol (25 ml.) and the mixture was heated under reflux for 1½ hr. The solvent was evaporated off under reduced pressure and the water-insoluble portion was recrystallised from ethanol to give the required product as colourless prisms (0.48 g.), m. p. 150–155° (decomp.) (Found: C, 44.5; H, 5.2. $C_{25}H_{34}IOP_3Ru$ requires C, 44.7; H, 5.1%).

Dicarbonyl Complexes.—*cis-Dichloro(dicarbonyl)bis(dimethylphenylphosphine)ruthenium(II)*, configuration (V) $[RuCl_2(CO)_2(PMe_2Ph)_2]$. Carbon monoxide was passed through a boiling solution of ruthenium trichloride trihydrate (0.94 g.) in 2-methoxyethanol (25 ml.) for 3½ hr. Dimethylphenylphosphine (0.98 g.) was added to the hot solution and carbon monoxide was passed through the boiling solution for a further 19 hr.; the solution had become pale yellow. The solvent was evaporated off under reduced pressure to give a gum which when treated with ethanol–water at 0° gave the product as colourless prisms

TABLE 7

Dipole moments of some ruthenium(II) complexes in benzene at 25°

Compound	Configuration	$\Delta\epsilon/\omega$	$-\Delta\nu/\omega$	τ^P	ϵ^P	σ^P	μ (D)
$[RuCl_2(CO)(PMe_2Ph)_3]$	(I)	2.999					
		3.026	(0.43)	468	(159)	286	3.7 *
$[RuCl_2(CO)(PMe_2Ph)_3]$	(II)	10.54					
		10.69	(0.43)	1334	(159)	1151	7.45 *
$[RuHCl(CO)(PMe_2Ph)_3]$	(IV)	2.793					
		2.81	(0.36)	431	(164)	242	3.4 *
<i>cis</i> - $[RuCl_2(CO)_2(PMe_2Ph)_2]$	(V)	4.783					
		5.04	(0.43)	547	(123)	417	4.5 *

* Calculated from estimated values of densities and refractivities, shown in parentheses. The margin of error is $< \pm 0.2$ D.

was heated in carbon monoxide to 170°. After cooling, the off-white product was recrystallised (twice) from methanol to give white prisms (0.15 g.), m. p. 179–181°, identical (infrared) with authentic dichloro(carbonyl)tris(dimethylphenylphosphine)ruthenium(II), configuration (II).

Hydriodicarbonyl complexes.—*Hydriodochloro(carbonyl)tris(dimethylphenylphosphine)ruthenium(II)* $[RuHCl(CO)(PMe_2Ph)_3]$. Aqueous potassium hydroxide (7.0 ml.; 1*M*) was added to a solution of dichloro(carbonyl)tris(dimethylphenylphosphine)ruthenium(II), configuration (II) (2.84 g.), in hot ethanol (60 ml.) and the mixture was heated under reflux for 4½ hr. The solvent was removed by evaporation under reduced pressure and the water-insoluble portion of the residue recrystallised from aqueous methanol to give the *hydriodochlorocarbonyl-complex* as colourless prisms (2.17 g.), m. p. 135–140° (decomp.) (Found: C, 51.85; H, 5.9%; *M*, osmometric in chloroform, 544. $C_{25}H_{34}ClOP_3Ru$ requires C, 51.7; H, 5.9%; *M*, 580).

Hydriodibromo(carbonyl)tris(dimethylphenylphosphine)ruthenium(II) $[RuHBr(CO)(PMe_2Ph)_3]$. A solution of hydriodochloro(carbonyl)tris(dimethylphenylphosphine)ruthenium(II) (0.40 g.) in ethanol (20 ml.) was treated with lithium bromide (1.0 g.) and the mixture heated under reflux for 4 hr. The solvent was removed by evaporation under reduced pressure and the water-insoluble portion of the residue was recrystallised from methanol to give the required product as colourless needles (0.27 g.), m. p. 126–129° (Found: C, 48.0; H, 5.6. $C_{25}H_{34}IOP_3Ru$ requires C, 48.1; H, 5.5%).

Hydriodiodo(carbonyl)tris(dimethylphenylphosphine)ruthenium(II) $[RuHI(CO)(PMe_2Ph)_3]$. Sodium iodide (1.50 g.)

was added to a solution of the hydriochloro-complex (0.48 g.) in ethanol (25 ml.) and the mixture was heated under reflux for 1½ hr. The solvent was evaporated off under reduced pressure and the water-insoluble portion was recrystallised from ethanol to give the required product as colourless prisms (0.48 g.), m. p. 150–155° (decomp.) (Found: C, 44.5; H, 5.2. $C_{25}H_{34}IOP_3Ru$ requires C, 44.7; H, 5.1%).

cis-Dibromo(dicarbonyl)bis(dimethylphenylphosphine)ruthenium(II), configuration (V) $[RuBr_2(CO)_2(PMe_2Ph)_2]$. A solution of *cis*-dichloro(dicarbonyl)bis(dimethylphenylphosphine)ruthenium(II) (0.29 g.) and lithium bromide (2.13 g.) in 2-methoxyethanol was heated under reflux for 17 hr. The solution was cooled, water added, and the precipitate recrystallised from light petroleum (b. p. 80–100°) to give the required product as colourless prisms (0.24 g.), m. p. 171.5–173.5° (decomp.) (Found: C, 37.0; H, 4.0. $C_{18}H_{22}Br_2O_2P_2Ru$ requires C, 36.4; H, 3.8%).

cis-Diiodo(dicarbonyl)bis(dimethylphenylphosphine)ruthenium(II), configuration (V) $[RuI_2(CO)_2(PMe_2Ph)_2]$. A solution of the *cis*-dichlorodicarbonyl complex (0.61 g.) and sodium iodide (2.5 g.) in 2-methoxyethanol (30 ml.) was heated under reflux for 17 hr. The solution was cooled, water added, and the precipitate recrystallised from ethanol to give the required product as pale yellow plates (0.51 g.), m. p. 211–213° (Found: C, 31.7; H, 3.4%; *M*, osmometric in chloroform, 671. $C_{18}H_{22}I_2O_2P_2Ru$ requires C, 31.45; H, 3.15%; *M*, 687).

trans-Dichloro(dicarbonyl)bis(dimethylphenylphosphine)ruthenium(II) $[RuCl_2(CO)_2(PMe_2Ph)_2]$. Carbon monoxide was passed through a boiling solution of ruthenium trichloride trihydrate (1.01 g.) in 2-methoxyethanol (25 ml.) for 3½ hr. The solution was cooled, dimethylphenylphosphine (1.29 g.) added, and then carbon monoxide was passed through the yellow solution at 20° for 12 hr. The resultant

solid (1.5 g.) was shown to be a mixture of dichloro(carbonyl)tris(dimethylphosphine)ruthenium(II), configuration (I), and *trans*-dichloro(dicarbonyl)bis(dimethylphenylphosphine)ruthenium(II) by its infrared spectrum. Repeated fractional crystallisations from cold benzene gave the required *trans*-dichloro-complex as yellow plates (0.05 g.), m. p. 132–152° (decomp.) (Found: C, 42.9; H, 4.4%).

Isomerisation of trans-Dichloro(dicarbonyl)bis(dimethylphenylphosphine)ruthenium(II) to the cis-Isomer.—The *trans*-isomer (0.03 g.) was heated to 190° *in vacuo*. The resultant pale orange liquid was recrystallised from methanol-water to give white prisms (0.02 g.) identical with a sample of the *cis*-isomer.

Determination of Dipole Moments.—These were determined as described previously¹⁵ except that a WTW Dipole Meter and a 50 ml. dipole cell were used. Values of $-\Delta V/\omega$,

which are needed only approximately, were assumed to be the same as for the analogous diethylphenylphosphine complexes.² Electron polarisations were estimated from values for diethylphenylphosphine complexes and group refractivities.¹⁵ Atom polarisation was assumed to be 15% of electron polarisation.

Nuclear Magnetic Resonance Spectra.—These were recorded at ca. 34° on a Perkin-Elmer R10 spectrometer.

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SCHOOL OF CHEMISTRY, THE UNIVERSITY,
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¹⁵ J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1959, 705; 1959, 4020.