

656. *The Formation of Hydrido- and Carbonyl Complexes of Ruthenium by Reaction of Certain of its Complexes with Alcohols.*

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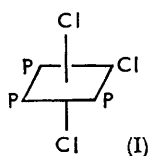
Ruthenium chloride-tertiary phosphine complexes are shown to react with alcohols, especially in the presence of a base, to give very stable hydrido-carbonyl or carbonyl complexes of ruthenium; in the process, the alcohol is degraded, *e.g.*, ethanol gives methane. A mechanism is suggested for the reaction. New ruthenium carbonyl-tertiary phosphine and -tertiary arsine complexes have been prepared by the direct action of carbon monoxide on ruthenium complexes. Bromo- and iodo-complexes were also prepared. Infrared, nuclear magnetic resonance, and dipole-moment data are given.

DURING the study of complexes formed by transition-metal halides with tertiary phosphines and arsines, we discovered that many of them react with alcohols, especially in the presence of a base.¹ Two types of reaction occur: (1) reduction, often with the replacement of the halide ion in the complex by hydride ion and the consequent formation of a hydrido-complex together with the aldehyde or ketone corresponding to the alcohol; or (2) carbonylation of the metal to form a carbonyl complex and a degraded fragment of the alcohol, *e.g.*, methane from ethanol. Sometimes both reactions occur together to give hydridocarbonyl complexes.

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

These are general reactions of tertiary phosphine and similar complexes of Group VIII metals except iron, cobalt, and nickel, and here we shall describe the reactions of ruthenium complexes with alcohols. Hydridocarbonylation is the predominant reaction and provides a convenient route to several new and very stable hydridocarbonyl and carbonyl complexes, some of which can also be prepared by the direct action of carbon monoxide at 1 atm. Direct carbonylation also gives carbonyl complexes not obtained by reaction with alcohols, and these will also be described here.

For this work, the complexes of tertiary mono-phosphines and -arsines with ruthenium di- and tri-chlorides were needed. Several phosphine complexes are known for ruthenium dichloride; these are of the type $[\text{Ru}_2\text{Cl}_3(\text{PR}_3)_6]\text{Cl}$, and were previously obtained by the prolonged action of the phosphine on ruthenium trichloride in boiling methanol.² We find that boiling 2-methoxyethanol is a much better solvent, giving a more rapid reaction and better yields. It is interesting that, although these binuclear complexes will not react with an excess of the tertiary phosphine to give mono-nuclear complexes $[\text{RuCl}_2(\text{PR}_3)_4]$, we were unable to obtain the analogous binuclear tertiary arsine complexes. Exactly analogous preparative methods yielded only the mononuclear complex of dimethylphenylarsine, as a mixture of orange *cis*- and red *trans*- $[\text{RuCl}_2(\text{AsMe}_2\text{Ph})_4]$, which were readily separated. Dimethylphenylphosphine gave a binuclear salt under the same conditions. Previously, ruthenium trichloride complexes of the type $[\text{RuCl}_3(\text{MR}_3)_3]$ were known with methylphenylarsine and with triphenylphosphine.^{3,4} We have obtained tertiary phosphine complexes of ruthenium(III) by a novel reaction. Ruthenium trichloride trihydrate in ethanol was shaken under carbon monoxide until a blood-red solution was obtained, and this on treatment with diethylphenylphosphine evolved carbon monoxide with the separation of $[\text{RuCl}_3(\text{PEt}_2\text{Ph})_3]$, whilst some



trans- $[\text{RuCl}_2(\text{CO})_2(\text{PEt}_2\text{Ph})_2]$ remained in solution. The dipole moment (6.85 D) and magnetic moment (2.1 B.M.) show that the complex $[\text{RuCl}_3(\text{PEt}_2\text{Ph})_3]$ has the configuration (I) and contains trivalent ruthenium. The corresponding diethylphenylarsine complex was obtained directly on adding the arsine to a solution of ruthenium trichloride trihydrate in 2-methoxyethanol, which had been boiled for 1 hour.

The reactions of alcohols and carbon monoxide with the ruthenium complexes are classified below according to the number of carbon monoxide groups which appear in the product. For convenience of operation, mixed aliphatic-aromatic phosphines and arsines were used. They give the most tractable products, those of the purely aromatic ligands being rather poorly soluble, and those of the aliphatic too soluble, for easy recrystallisation.

Monocarbonyl Complexes.—The salt $[\text{Ru}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6]\text{Cl}$ reacted with ethanol in the presence of potassium hydroxide to give the hydrido-carbonylruthenium(II) complex $[\text{RuHCl}(\text{CO})(\text{PEt}_2\text{Ph})_3]$ and methane. The reaction can be represented as



but is accompanied by side-reactions, since acetaldehyde is formed slowly by catalytic dehydrogenation of ethanol.⁵ Methane was identified by means of its infrared spectrum and confirmed by gas chromatography, which showed that other simple hydrocarbons, *e.g.*, ethane and ethylene, had not been formed. The infrared spectrum of the hydrido-carbonyl complex in hexane showed strong bands at 1910 cm^{-1} [$\nu(\text{C}\equiv\text{O})$] and 1880 cm^{-1} [$\nu(\text{Ru}-\text{H})$]. The dipole moment (3.2 D) suggested the configuration (II), which was confirmed by nuclear magnetic resonance. The hydridic hydrogen has a large chemical shift (τ 17.1) in benzene, with the resonance split into two 1 : 2 : 1 triplets by coupling with the phosphorus nuclei [$J(\text{H}-\text{P}^1) = J(\text{H}-\text{P}^2)$, 24 c./sec.; $J(\text{H}-\text{P}^2)$, 107 c./sec.].

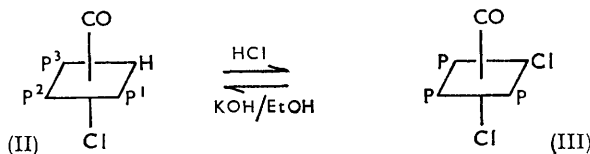
² Chatt and Hayter, *J.*, 1961, 896.

³ Dwyer, Humpolitz, and Nyholm, *Proc. Roy. Soc. N.S.W.*, 1946, 80, 217.

⁴ Vaska, *Chem. and Ind.*, 1961, 1402.

⁵ Chatt and Thornton, unpublished results.

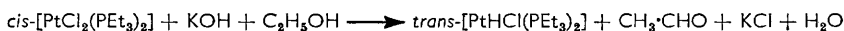
As with other transition-metal hydrides stabilised by tertiary phosphines, we find strong coupling between hydrogen and phosphorus in the *trans*-position and much weaker coupling when in the *cis*-position.⁶



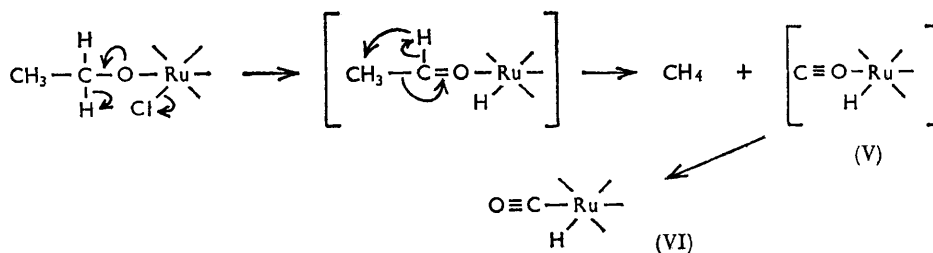
The hydride ligand is labile to acids. With hydrochloric acid, hydrogen is evolved and a white carbonyl complex $[\text{RuCl}_2(\text{CO})(\text{PEt}_2\text{Ph})_3]$ of configuration (III) (dipole moment 7.5 D) is formed; this, with ethanol and potassium hydroxide, regenerates the hydrido-carbonyl complex (II).

Treatment of the hydrido-carbonyl complex $[\text{RuHCl}(\text{CO})(\text{PEt}_2\text{Ph})_3]$ with lithium bromide or sodium iodide gave only partial replacement of the chlorine, or led to decomposition. Nevertheless, the bromo- or iodo-hydridocarbonyl complexes were readily prepared by treating the chloro-bridged complex $[\text{Ru}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6]\text{Cl}$ with lithium bromide or sodium iodide in the high-boiling basic alcohol 2-diethylaminoethanol, but similar treatment with lithium bromide in 2-methoxyethanol gave $[\text{RuBr}_2(\text{CO})(\text{PEt}_2\text{Ph})_3]$. The nuclear magnetic resonance spectrum of $[\text{RuHBr}(\text{CO})(\text{PEt}_2\text{Ph})_3]$ in benzene solution gave, for the hydridic hydrogen: τ 17.65; $J(\text{H}-\text{P}^1) = J(\text{H}-\text{P}^3)$, 25 c./sec.; and $J(\text{H}-\text{P}^2)$, 106 c./sec. Attempts to prepare analogous arsine complexes by treating either *cis*- or *trans*- $[\text{RuCl}_2(\text{AsMe}_2\text{Ph})_4]$ with alkali in ethanol led to decomposition, and no hydrido-carbonyl or carbonyl complexes of ruthenium were isolated.

The hydride-transfer reaction⁷ is promoted by bases



and we have suggested that the initial step is the formation of an ethoxide complex, followed by the transfer of hydrogen as hydride ion from the α -carbon atom of the ethoxide ligand to the platinum and liberation of acetaldehyde. We suggest that, similarly, in the base-promoted hydridocarbonylation reaction with the ruthenium complex, the initial step is the formation of an ethoxide-ruthenium complex. This is followed by hydride-transfer to the ruthenium to give the acetaldehyde complex (IV), which then breaks down to give methane and the carbonyl complex (VI), possibly by way of an isocarbonyl complex (V), rather than to eliminate acetaldehyde:



This second step is favoured by the great stability of the ruthenium carbonyl complex and also by the presence of a vacant ligand position (due to the splitting of the halogen bridge) which the carbon monoxide can occupy. The pyrolytic or photochemical decomposition of acetaldehyde to methane and carbon monoxide is known to be a free-radical process⁸

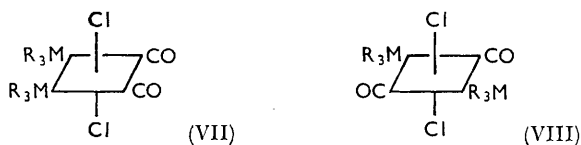
⁶ Shaw and Sheppard, unpublished results.

⁷ Chatt and Shaw, *J.*, 1962, 5075.

⁸ Steacie, "Atomic and Free Radical Reactions," Reinhold, New York, 1954.

and it is possible that co-ordination of acetaldehyde to ruthenium promotes decomposition to these products, although the mechanism is probably not a free-radical one.

Several new carbonyl complexes were prepared by the action of carbon monoxide on ruthenium complexes. The shaking of a solution of ruthenium trichloride trihydrate in 2-methoxyethanol with carbon monoxide for 11 days at 20°, followed by the addition of diethylphenylphosphine, gave $[\text{RuCl}_2(\text{CO})(\text{PEt}_2\text{Ph})_3]$ of configuration (III); in ethanol as solvent, the product was the red ruthenium(III) complex $[\text{RuCl}_3(\text{PEt}_2\text{Ph})_3]$, as described above. Prolonged shaking of an ethanolic suspension of the binuclear complex $[\text{Ru}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6]\text{Cl}$ with carbon monoxide at 20° also gave the monocarbonyl complex $[\text{RuCl}_2(\text{CO})(\text{PEt}_2\text{Ph})_3]$; this was also formed by heating a 2-methoxyethanolic solution of ruthenium trichloride with ethylene, followed by the addition of the phosphine. In the absence of an ethylene atmosphere, no carbonyl complex was formed; possibly, a ruthenium(II)-ethylene complex, similar to that described by Halpern and his co-workers,⁹ forms as an intermediate and decarbonylates the 2-methoxyethanol, giving a ruthenium-carbonyl complex.



Dicarbonyl Complexes.—Two series of isomeric dicarbonyl complexes of formula $[\text{RuCl}_2(\text{CO})_2(\text{MR}_3)_2]$ ($\text{M} = \text{P}, \text{As}$) were obtained, a *cis*-form with the configuration (VII) and a less stable *trans*-form with the configuration (VIII).

The *cis*-dicarbonyl complexes were prepared by three methods.

(1) By prolonged (20 hour) treatment of ruthenium trichloride trihydrate with carbon monoxide in boiling 2-methoxyethanol, giving a pale yellow solution which, when treated with the appropriate tertiary phosphine or arsine, gave good yields of the *cis*-dicarbonyl complexes $[\text{RuCl}_2(\text{CO})_2(\text{MR}_3)_2]$. (2) By treatment with carbon monoxide of the chloro-bridged salt $[\text{Ru}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6]\text{Cl}$ in ethanol at 75°/50 atm. for 16 hour. (3) By boiling the chloro-bridged salt $[\text{Ru}_2\text{Cl}_3(\text{PEt}_2\text{Ph})_6]\text{Cl}$ with potassium hydroxide (2 mol. per ruthenium atom) in allyl alcohol, when a mixture of ethane, ethylene, and propylene was evolved in the approximate ratio of 1 : 2 : 2 by volume. The resultant solution on acidification evolved no gases [cf. the behaviour in ethanol, when hydrogen is evolved (as described above)]. From the solution, the *cis*-dicarbonyl complex $[\text{RuCl}_2(\text{CO})_2(\text{PEt}_2\text{Ph})_2]$ was isolated in 25–30% yield. We hope to elucidate the mechanism of this complex reaction by further study; presumably, the ethylene was produced in the decarbonylation reaction and the propylene in a hydrogen-transfer reaction analogous to that occurring between allyl alcohol and ruthenium trichloride.¹⁰ The ethane could have been formed by a decarbonylation coupled with a hydrogen-transfer reaction.

These *cis*-dichlorodicarbonyl complexes are extremely stable thermally, and are also chemically inert. Thus they do not give hydrido-carbonyl complexes on boiling with alcohols in the presence of base, and metathesis of chlorine by bromine, by treatment with lithium bromide, is very slow in boiling acetone, and even in boiling 2-methoxyethanol (b. p. 124°) takes several hours for completion.

The yellow *trans*-dicarbonyl complexes $[\text{RuCl}_2(\text{CO})_2(\text{PR}_3)_2]$ of configuration (VIII) (low or zero dipole moments) were prepared by treating ruthenium trichloride trihydrate with carbon monoxide in boiling ethanol for 5 hour, and adding the tertiary phosphine (2 mol.) to the resultant red solution. These *trans*-dicarbonyl complexes, on heating to 160°, rapidly isomerised to the *cis*-isomers with configuration (VII). They also isomerised

⁹ Halpern, Harrod, and James, *J. Amer. Chem. Soc.*, 1961, **83**, 753.

¹⁰ Nicholson and Shaw, *Proc. Chem. Soc.*, 1963, 282.

in solution above 80°, and recrystallisation of *trans*-[RuCl₂(CO)₂(PEt₂Ph)₂] from boiling 2-methoxyethanol gave the *cis*-isomer.

The *cis*-isomers, in spite of their quite large dipole moments (>4.4 D), are much more stable than the *trans*-isomers, from which they are formed by thermal isomerisation. Carbon monoxide is a very strongly double-bonding ligand and prefers not to be in a *trans*-position to another carbon monoxide; a position *trans* to a tertiary phosphine is acceptable since the latter is a much better σ-donor than it is a π-acceptor. Complexes containing both a tertiary phosphine (or arsine) and carbon monoxide as uncharged ligands are often more stable than those containing either all of one or all of the other. Thus, *cis*-[RuCl₂(CO)₂(PEt₂Ph)₂] is more stable than either [RuCl₂(CO)₄] or [RuCl₂(PEt₂Ph)₄]. Also, [Ni(CO)₂(PPh₃)₂] is more stable than [Ni(CO)₄] or [Ni(PPh₃)₄], and [CoH(CO)₃PPh₃] is more stable than [CoH(CO)₄], or [CoH(PPh₃)₄] which is unknown.

The colours, melting points, and frequencies of the carbonyl-stretching vibration (in Nujol mull and in benzene solution) of the new ruthenium complexes are shown in Table I.

Several of these complexes were briefly described in two preliminary publications,¹ and similar complexes with triphenylphosphine and triphenylarsine as ligands have since been briefly described by Vaska.^{4,11}

TABLE I.
Colours, melting points, and carbonyl-stretching frequencies of some ruthenium complexes.

| Complex | Confign. | Colour | M. p. | ν(C≡O) † (cm. ⁻¹) | |
|---|----------|-------------|------------|-------------------------------|------------|
| | | | | Nujol | Benzene |
| <i>cis</i> -[RuCl ₂ (AsMe ₂ Ph) ₄] | | Orange | 179—190° * | — | — |
| <i>trans</i> -[RuCl ₂ (AsMe ₂ Ph) ₄] | | Red | 156—160 | — | — |
| [RuCl ₃ (PEt ₂ Ph) ₃] | (I) | Red-brown | 178—184 * | — | — |
| [RuCl ₃ (AsEt ₂ Ph) ₃] | (I) | Red-brown | 173—176 * | — | — |
| [RuCl ₂ (CO)(PEt ₂ Ph) ₃] | (III) | White | 232—250 * | 1942 | 1932 |
| [RuBr ₂ (CO)(PEt ₂ Ph) ₃] | (III) | Pale yellow | 209—220 * | 1948, 1916 | 1946 |
| [RuI ₂ (CO)(PEt ₂ Ph) ₃] | (III) | Yellow | 190—198 * | 1943 | 1934 |
| <i>cis</i> -[RuCl ₂ (CO) ₂ (PEt ₂ Ph) ₂] | (VII) | White | 105—107.5 | 2042, 1977 | 2033, 1969 |
| <i>cis</i> -[RuCl ₂ (CO) ₂ (PEt ₂ Ph) ₂] | (VII) | White | 144—146 | 2037, 1980 | 2048, 1975 |
| <i>cis</i> -[RuCl ₂ (CO) ₂ (AsEt ₂ Ph) ₂] | (VII) | White | 142—145 | 2053, 1981 | — |
| <i>cis</i> -[RuBr ₂ (CO) ₂ (PEt ₂ Ph) ₂] | (VII) | White | 121.5—123 | 2030, 1964 | 2044, 1978 |
| <i>cis</i> -[RuI ₂ (CO) ₂ (PEt ₂ Ph) ₂] | (VII) | White | 157—159 | 2035, 1964 | 2040, 1977 |
| <i>trans</i> -[RuCl ₂ (CO) ₂ (PEt ₂ Ph) ₂] | (VII) | Yellow | 111—114 | 1988 | 1990 |
| <i>trans</i> -[RuCl ₂ (CO) ₂ (PEt ₂ Ph) ₂] ... | (VIII) | Yellow | 127—149 * | 1999 | 1997 |
| [RuHCl(CO)(PEt ₂ Ph) ₃] | (II) | White | 99—101 | 1910 | 1910 |
| [RuHBr(CO)(PEt ₂ Ph) ₃] | (II) | White | 110—113 | 1915 | 1914 |
| [RuHI(CO)(PEt ₂ Ph) ₃] | (II) | White | 141—144 * | 1929 | 1920 |

* With decomposition. † All bands due to ν(C≡O) were very strong.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus, and are corrected. Operations involving tertiary phosphines or arsines were carried out in an atmosphere of nitrogen.

Tri-μ-chlorohexakis(diethylphenylphosphine)diruthenium(II) Chloride.—An improved method of preparation. Diethylphenylphosphine (13.71 g.) was added to a solution of ruthenium trichloride trihydrate (3.5 g.) in 2-methoxyethanol (120 c.c.), and the mixture was heated under reflux for one hr. On cooling, the product separated as needles (8.60 g., 97%).

cis- and trans-Dichlorotetrakis(dimethylphenylarsine)ruthenium(II), [RuCl₂(AsMe₂Ph)₄].—Ruthenium trichloride trihydrate (1.5 g.) was dissolved in methanol (50 c.c.) and dimethylphenylarsine (5.41 g.) was added under nitrogen. The solution was then boiled for 17 hr. and cooled, when orange crystals separated. These, when recrystallised from ethanol, gave *cis-dichlorotetrakis(dimethylphenylarsine)ruthenium(II)* as prisms (2.09 g.) (Found: C, 42.6; H, 4.95%; M, ebullioscopic in 0.54% benzene solution, 858. C₃₂H₄₄As₄Cl₂Ru requires C, 42.7; H, 4.9%; M, 900). The methanolic mother-liquors from this preparation, on standing for

¹¹ Vaska and Diluzio, *J. Amer. Chem. Soc.*, 1962, **83**, 1262.

several days, deposited red crystals (1.36 g.), which after recrystallisation from methylene chloride–light petroleum (b. p. 40–60°) gave the *trans-isomer* as needles (Found: C, 42.9; H, 5.0%).

Trichlorotris(diethylphenylphosphine)ruthenium(III), $[\text{RuCl}_3(\text{PEt}_2\text{Ph})_3]$.—A solution of ruthenium trichloride trihydrate (2.00 g.) in ethanol (70 c.c.) was shaken under carbon monoxide at 1 atm./20° for 11 days to give a blood-red solution. Diethylphenylphosphine (4.05 g.) was then added to the solution, and on cooling to 0° a deep brown solid was deposited; recrystallisation from ethanol gave the product as *needles* (1.72 g.) (Found: C, 51.05; H, 6.4%; *M*, ebullioscopic in 0.62% benzene solution, 773; in 1.27% solution, 772. $\text{C}_{30}\text{H}_{45}\text{Cl}_3\text{P}_3\text{Ru}$ requires C, 51.05; H, 6.4%; *M*, 706). Evaporation of the mother-liquors gave an orange solid which, on recrystallisation from ethanol, gave needles (0.34 g.). Infrared spectroscopy showed this to be identical with a sample of *trans*-dichloro(dicarbonyl)bis(diethylphenylphosphine)-ruthenium(II) (see below).

Trichlorotris(diethylphenylarsine)ruthenium(III), $[\text{RuCl}_3(\text{AsEt}_2\text{Ph})_3]$.—A solution of ruthenium trichloride trihydrate (1.42 g.) in 2-methoxyethanol (25 c.c.) was heated under reflux for 1 hr. and diethylphenylarsine (4.35 g.) was then added. On cooling, the solution deposited a red solid which, on recrystallisation from light petroleum (b. p. 80–100°), gave the product as *needles* (0.20 g.) (Found: C, 43.5; H, 5.55. $\text{C}_{30}\text{H}_{45}\text{As}_3\text{Cl}_3\text{Ru}$ requires C, 43.0; H, 5.4%).

Monocarbonyl Complexes of Ruthenium(II).—*Dichloro(carbonyl)tris(diethylphenylphosphine)ruthenium(II)*, $[\text{RuCl}_2(\text{CO})(\text{PEt}_2\text{Ph})_3]$. (a) From tri-*μ*-chlorohexakis(diethylphenylphosphine)diruthenium(II) chloride and ethanol. Aqueous potassium hydroxide (1*N*; 2 c.c.) was added to a suspension of the chloride (0.66 g.) in boiling ethanol (20 c.c.), and the resulting orange solution was boiled for 45 min. On adding concentrated hydrochloric acid (0.2 c.c.) to the solution, there was a vigorous effervescence and, on cooling, a white solid separated; recrystallisation from ethanol gave the product as *needles* (0.59 g.) (Found: C, 53.35; H, 6.6%; *M*, ebullioscopic in 4.92% benzene solution, 748. $\text{C}_{31}\text{H}_{45}\text{Cl}_2\text{OP}_3\text{Ru}$ requires C, 53.3; H, 6.5%; *M*, 698).

(b) From ruthenium trichloride trihydrate and carbon monoxide. A solution of ruthenium trichloride trihydrate (2.0 g.) in 2-methoxyethanol (50 c.c.) was shaken in an atmosphere of carbon monoxide for 11 days, and diethylphenylphosphine (3.92 g.) was then added. The product crystallised from the solution as *needles* (1.53 g.) (Found: C, 53.3; H, 6.6%).

(c) From ruthenium trichloride trihydrate and ethylene. A solution of ruthenium trichloride trihydrate (0.87 g.) in 2-methoxyethanol (25 c.c.) was heated under reflux in an atmosphere of ethylene for 16 hr., and diethylphenylphosphine (1.49 g.) was then added. The solution was diluted with water, and the resultant precipitate crystallised from ethanol to give the required product (0.26 g.), shown to be identical with a pure sample, by means of its infrared spectrum.

(d) From tri-*μ*-chloro(carbonyl)tris(diethylphenylphosphine)diruthenium(II) chloride and carbon monoxide. A suspension of this salt (0.50 g.) in ethanol (25 c.c.) was shaken under carbon monoxide for 3 months at 20°, and the solvent was then removed under reduced pressure. Recrystallisation of the residue from methanol gave the required product (0.14 g.), shown to be identical with a sample as prepared above, by means of its infrared spectrum.

(e) From the hydrido-chloride. A solution of hydridochloro(carbonyl)tris(diethylphenylphosphine)ruthenium(II) (0.11 g.) in methanol (2 c.c.) was treated with concentrated hydrochloric acid (0.05 c.c.). Hydrogen was evolved rapidly and a white crystalline precipitate (0.099 g.) formed. This was shown to be identical with an authentic sample of dichloro(carbonyl)tris(diethylphenylphosphine)ruthenium(II), by means of its infrared spectrum.

Dibromo(carbonyl)tris(diethylphenylphosphine)ruthenium(II), $[\text{RuBr}_2(\text{CO})(\text{PEt}_2\text{Ph})_3]$. Tri-*μ*-chlorohexakis(diethylphenylphosphine)diruthenium(II) chloride (1.0 g.) and lithium bromide (2 g.) were dissolved in 2-methoxyethanol (25 c.c.), and the resultant solution was boiled for 3½ hr. After cooling, water was added and the resultant pale yellow precipitate was recrystallised from ethanol to give the product as *needles* (0.55 g.) (Found: C, 47.6; H, 5.8. $\text{C}_{31}\text{H}_{45}\text{Br}_2\text{OP}_3\text{Ru}$ requires C, 47.3; H, 5.8%).

Di-iodo(carbonyl)tris(diethylphenylphosphine)ruthenium(II), $[\text{RuI}_2(\text{CO})(\text{PEt}_2\text{Ph})_3]$. Hydrido-iodo(carbonyl)tris(diethylphenylphosphine)ruthenium (0.4 g.; see below) was dissolved in ethanol (30 c.c.), and potassium iodide (0.1 g.) and dilute sulphuric acid (0.2 c.c.) were then added. Hydrogen was evolved and a yellow solid precipitated. The resultant suspension was heated under reflux for 3 min., and then cooled, and the precipitated solid was recrystallised

from benzene-methanol to give the product as *plates* (0.37 g.) (Found: C, 42.25; H, 5.2. $C_{31}H_{45}I_2OP_3Ru$ requires C, 42.25; H, 5.15%).

cis-Dicarbonyl Complexes of Ruthenium(II).—*cis-Dichloro(dicarbonyl)bis(triethylphosphine)ruthenium(II)*, $[RuCl_2(CO)_2(PEt_3)_2]$. A solution of ruthenium trichloride trihydrate (1.06 g.) and triethylphosphine (1.88 g.) in allyl alcohol (40 c.c.) was heated under reflux for 3 hr. Aqueous potassium hydroxide solution (1N; 12.5 c.c.) was then added, and boiling was continued for a further 2½ hr. Concentrated hydrochloric acid (2 c.c.) was added to the reaction mixture, and the solvent was removed under reduced pressure. Recrystallisation of the benzene-soluble portion of the residue from methanol gave the product as *plates* (0.83 g.) (Found: C, 36.35; H, 6.85. $C_{14}H_{30}Cl_2O_2P_2Ru$ requires C, 36.2; H, 6.5%).

cis-Dichloro(dicarbonyl)bis(diethylphenylphosphine)ruthenium(II), $[RuCl_2(CO)_2(PEt_2Ph)_2]$. (a) Aqueous potassium hydroxide solution (5N; 1.2 c.c.) was added to a solution of tri- μ -chlorohexakis(diethylphenylphosphine)diruthenium(II) chloride (2.0 g.) in boiling allyl alcohol (25 c.c.), and the reaction mixture was boiled for 2 hr. After the addition of concentrated hydrochloric acid (1.2 c.c.), the solvent was removed under reduced pressure. Crystallisation of the benzene-soluble portion of the residue from light petroleum (b. p. 80–100°) gave the product as *needles* (0.42 g.) (Found: C, 47.15; H, 5.4; Cl, 12.25. $C_{22}H_{30}Cl_2O_2P_2Ru$ requires C, 47.15; H, 5.4; Cl, 12.65%).

(b) Carbon monoxide was bubbled through a boiling solution of ruthenium trichloride trihydrate (2.0 g.) in 2-methoxyethanol (25 c.c.) for 20 hr. Diethylphenylphosphine (2.20 g.) was then added to the boiling solution, which was then cooled and diluted with water. The resultant white precipitate was recrystallised from light petroleum (b. p. 80–100°) to give the required product (2.68 g.).

(c) A suspension of tri- μ -chlorohexakis(diethylphenylphosphine)diruthenium(II) chloride (1.00 g.) in ethanol (25 c.c.) was shaken under carbon monoxide at 75°/50 atm., for 16 hr. On cooling, the required product (0.48 g.) crystallised.

cis-Dichloro(dicarbonyl)bis(diethylphenylarsine)ruthenium(II), $[RuCl_2(CO)_2(AsEt_2Ph)_2]$. This was obtained in a similar way to the above [method (b)] by bubbling carbon monoxide through a boiling solution of ruthenium trichloride trihydrate (2.08 g.) in 2-methoxyethanol (25 c.c.) for 8 hr., and then adding diethylphenylarsine (4.33 g.). The product was obtained as *prisms* (2.77 g.) from light petroleum (b. p. 80–100°) (Found: C, 41.0; H, 4.85. $C_{22}H_{30}As_2Cl_2O_2Ru$ requires C, 40.75; H, 4.65%).

trans-Dicarbonyl Complexes of Ruthenium(II).—*trans-Dichloro(dicarbonyl)bis(triethylphosphine)ruthenium(II)*, $[RuCl_2(CO)_2(PEt_3)_2]$. Carbon monoxide was bubbled through a boiling solution of ruthenium trichloride trihydrate (2.80 g.) in ethanol (50 c.c.) for 5½ hr. Triethylphosphine (4.74 g.) was added to the resultant bright red solution which, on cooling, deposited a yellow solid; recrystallisation from light petroleum (b. p. 80–100°) gave the product as *prisms* (1.55 g.) (Found: C, 35.9; H, 6.5%).

trans-Dichloro(dicarbonyl)bis(diethylphenylphosphine)ruthenium(II), $[RuCl_2(CO)_2(PEt_2Ph)_2]$. This compound was prepared in a similar way to the above, by bubbling carbon monoxide through a boiling solution of ruthenium trichloride trihydrate (2.30 g.) in 2-methoxyethanol (50 c.c.) for 1½ hr., and then adding diethylphenylphosphine (5.67 g.). The product was obtained as *needles* (3.35 g.) from ethanol (Found: C, 47.3; H, 5.5%).

Isomerisation of trans-Dichloro(dicarbonyl)bis(diethylphenylphosphine)ruthenium(II) to the cis-Isomer.—The *trans*-isomer (0.82 g.) was heated to 160° under 1 atm. of nitrogen for 2 min. The resultant pale orange liquid was recrystallised from ethanol to give *needles* (0.46 g.) identical with a sample of the *cis*-isomer.

Metathesis.—(a) *cis-Dibromo(dicarbonyl)bis(diethylphenylphosphine)ruthenium(II)* from the *dichloro-compound*. A solution of the dichloro-compound (0.4 g.) and lithium bromide (1.0 g.) in 2-methoxyethanol (25 c.c.) was boiled for 5 hr. The solution was then cooled, water added, and the resultant white precipitate recrystallised from light petroleum (b. p. 60–80°) to give the *cis-dibromo-compound* as *prisms* (0.32 g.) (Found: C, 41.2; H, 4.65. $C_{22}H_{30}Br_2O_2P_2Ru$ requires C, 40.7; H, 4.65%). (b) *cis-Di-iodo(dicarbonyl)bis(diethylphenylphosphine)ruthenium(II)* from the *dichloro-compound*. A solution of the dichloro-compound (0.4 g.) and sodium iodide (1.0 g.) in 2-methoxyethanol (25 c.c.) was boiled for 5 hr. After cooling, water was added and the products were isolated with ether. The *cis-Di-iodo-compound* was obtained as *prisms* (0.25 g.) from methanol (Found: C, 35.8; H, 4.2; I, 34.9. $C_{22}H_{30}I_2P_2Ru$ requires C, 35.55; H, 4.05; I, 34.15%).

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Hydridocarbonyl Complexes of Ruthenium(II).—*Hydridochloro(carbonyl)tris(diethylphenylphosphine)ruthenium(II)*, $[\text{RuHCl}(\text{CO})(\text{PEt}_2\text{Ph})_3]$. (a) Tri- μ -chlorohexakis(diethylphenylphosphine)diruthenium(II) chloride (0.67 g.) was dissolved in boiling ethanol (25 c.c.) aqueous potassium hydroxide solution (1N; 2 c.c.) was added, and the resultant solution was boiled for $3\frac{1}{4}$ hr. The solvent was removed under reduced pressure, and the ether-soluble portion of the residue was recrystallised from methanol to give the product as *needles* (0.21 g.) (Found: C, 56.0; H, 6.95. $\text{C}_{31}\text{H}_{46}\text{ClO}_3\text{P}_3\text{Ru}$ requires C, 56.05; H, 7.0%).

(b) A solution of dichloro(carbonyl)tris(diethylphenylphosphine)ruthenium(II) (0.698 g.) in ethanol (20 c.c.) was treated with aqueous potassium hydroxide solution (1N; 2 c.c.) and heated under reflux for 1 hr. The solvent was removed under reduced pressure, and the ether-soluble portion of the residue was recrystallised from methanol to give the product (0.46 g.), m. p. 98—100°.

Hydridobromo(carbonyl)tris(diethylphenylphosphine)ruthenium(II), $[\text{RuHBr}(\text{CO})(\text{PEt}_2\text{Ph})_3]$. A solution of tri- μ -chlorohexakis(diethylphenylphosphine)diruthenium(II) chloride (1.0 g.) and lithium bromide (2.5 g.) in 2-diethylaminoethanol (25 c.c.) was boiled under nitrogen for $1\frac{1}{8}$ hr. The brown reaction mixture was cooled, water was added, and the product isolated with benzene. Recrystallisation from methanol gave the product as *prisms* (0.68 g.) (Found: C, 52.5; H, 6.6. $\text{C}_{31}\text{H}_{46}\text{BrO}_3\text{P}_3\text{Ru}$ requires C, 52.55; H, 6.55%).

Hydridoiodo(carbonyl)tris(diethylphenylphosphine)ruthenium(II), $[\text{RuHI}(\text{CO})(\text{PEt}_2\text{Ph})_3]$. A solution of tri- μ -chlorohexakis(diethylphenylphosphine)diruthenium(II) chloride (0.5 g.) and sodium iodide (1.5 g.) in 2-diethylaminoethanol (25 c.c.) was heated under reflux for $1\frac{1}{2}$ hr. Water was added to the cold brown solution and the product isolated with benzene. The product was obtained as *prisms* (0.20 g.) from methanol (Found: C, 49.3; H, 6.3. $\text{C}_{31}\text{H}_{46}\text{IO}_3\text{P}_3\text{Ru}$ requires C, 49.3; H, 6.15%).

TABLE 2.

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

| $10^3\omega$ | $\Delta\varepsilon/\omega$ | $10^2\Delta n/\omega$ | $-\Delta v/\omega$ | τ^P | ε^P | o^P | μ (D) |
|--|----------------------------|-----------------------|--------------------|----------|-----------------|--------|-----------|
| <i>trans</i> - $[\text{RuCl}_2(\text{AsMe}_2\text{Ph})_4]$ | | | | | | | |
| 1.549 | 0.668 | — | — | — | — | — | — |
| 2.731 | 0.678 | — | — | — | — | — | — |
| 11.26 | — | 11.26 | — | — | — | — | — |
| 24.14 | — | 11.37 | — | — | — | — | — |
| 4.104 | — | — | 0.536 | — | — | — | — |
| 6.639 | — | — | 0.527 | 279 | 252 | 27 | 1.15 |
| <i>cis</i> - $[\text{RuCl}_2(\text{AsMe}_2\text{Ph})_4]$ | | | | | | | |
| 2.955 | 7.822 | — | — | — | — | — | — |
| 3.433 | 7.759 | — | — | — | — | — | — |
| | | | (0.53) | 1486 * | (252) | 1234 * | 7.75 * |
| $[\text{RuCl}_3(\text{PEt}_2\text{Ph})_3]$ | | | | | | | |
| 3.703 | 7.878 | — | — | — | — | — | — |
| 5.624 | 7.811 | — | — | — | — | — | — |
| | | | (0.46) | 1188 * | (188) | 972 * | 6.9 * |
| $[\text{RuCl}_2(\text{CO})(\text{PEt}_2\text{Ph})_3]$ | | | | | | | |
| 2.295 | 9.200 | — | — | — | — | — | — |
| 3.097 | 9.221 | — | — | — | — | — | — |
| 3.841 | 9.253 | — | — | — | — | — | — |
| 5.535 | 9.213 | — | — | — | — | — | — |
| 11.76 | — | 11.09 | — | — | — | — | — |
| 14.19 | — | 11.67 | — | — | — | — | — |
| 4.384 | — | — | 0.433 | — | — | — | — |
| 5.320 | — | — | 0.470 | 1358 | 186.5 | 1144 | 7.5 |
| $[\text{RuBr}_2(\text{CO})(\text{PEt}_2\text{Ph})_3]$ | | | | | | | |
| 3.825 | 9.164 | — | — | — | — | — | — |
| 6.556 | 9.220 | — | — | — | — | — | — |
| 18.03 | — | 11.78 | — | — | — | — | — |
| 18.60 | — | 11.80 | — | — | — | — | — |
| 5.536 | — | — | 0.450 | — | — | — | — |
| 9.043 | — | — | 0.468 | 1525 | 212 | 1282 | 7.9 |

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TABLE 2. (Continued.)

| $10^3\omega$ | $\Delta\varepsilon/\omega$ | $10^2\Delta n/\omega$ | $-\Delta v/\omega$ | τ^P | ε^P | o^P | μ (D) |
|---|----------------------------|-----------------------|--------------------|----------|-----------------|-------|-----------|
| [RuI ₂ (CO)(PEt ₂ Ph) ₃] | | | | | | | |
| 2·908 | 9·077 | — | — | — | — | — | — |
| 3·524 | 9·066 | — | — | — | — | — | — |
| 16·07 | — | 12·15 | — | — | — | — | — |
| 25·00 | — | 12·42 | — | — | — | — | — |
| 3·011 | — | — | 0·545 | — | — | — | — |
| 5·199 | — | — | 0·540 | 1665 | 218 | 1415 | 8·3 |
| <i>trans</i> -[RuCl ₂ (CO) ₂ (PEt ₃) ₂] | | | | | | | |
| 3·999 | 0·420 | — | — | — | — | — | — |
| 6·678 | 0·432 | — | — | — | — | — | — |
| 35·50 | — | 5·62 | — | — | — | — | — |
| 38·78 | — | 5·60 | — | — | — | — | — |
| 8·003 | — | — | 0·427 | — | — | — | — |
| 8·822 | — | — | 0·440 | 136 | 112 | 7 | 0·6 |
| <i>cis</i> -[RuCl ₂ (CO) ₂ (PEt ₃) ₂] | | | | | | | |
| 2·440 | 4·934 | — | — | — | — | — | — |
| 2·559 | 4·825 | — | — | — | — | — | — |
| | | | (0·43) | 526 * | (112) | 397 * | 4·4 * |
| <i>trans</i> -[RuCl ₂ (CO) ₂ (PEt ₂ Ph) ₂] | | | | | | | |
| 4·525 | 0·653 | — | — | — | — | — | — |
| 7·490 | 0·655 | — | — | — | — | — | — |
| | | | (0·43) | 188 * | (142) | 25 * | 1·1 * |
| <i>cis</i> -[RuCl ₂ (CO) ₂ (PEt ₂ Ph) ₂] | | | | | | | |
| 3·464 | 4·274 | — | — | — | — | — | — |
| 5·802 | 4·284 | — | — | — | — | — | — |
| | | | (0·43) | 571 * | (142) | 408 * | 4·45 * |
| <i>cis</i> -[RuCl ₂ (CO) ₂ (AsEt ₂ Ph) ₂] | | | | | | | |
| 5·001 | 3·157 | — | — | — | — | — | — |
| 5·026 | 3·197 | — | — | — | — | — | — |
| 25·61 | — | 9·73 | — | — | — | — | — |
| 40·64 | — | 9·70 | — | — | — | — | — |
| 6·679 | — | — | 0·539 | — | — | — | — |
| 8·098 | — | — | 0·529 | 506 | 152 | 331 | 4·0 |
| <i>cis</i> -[RuBr ₂ (CO) ₂ (PEt ₂ Ph) ₂] | | | | | | | |
| 4·705 | 4·151 | — | — | — | — | — | — |
| 4·735 | 4·169 | — | — | — | — | — | — |
| | | | (0·46) | 642 * | (148) | 472 * | 4·8 * |
| <i>cis</i> -[RuI ₂ (CO) ₂ (PEt ₂ Ph) ₂] | | | | | | | |
| 3·789 | 4·047 | — | — | — | — | — | — |
| 5·204 | 4·023 | — | — | — | — | — | — |
| | | | (0·54) | 698 * | (158) | 517 * | 5·05 * |
| [RuHCl(CO)(PEt ₂ Ph) ₃] | | | | | | | |
| 2·465 | 2·034 | — | — | — | — | — | — |
| 5·573 | 2·055 | — | — | — | — | — | — |
| 24·34 | — | 10·64 | — | — | — | — | — |
| 29·99 | — | 10·07 | — | — | — | — | — |
| 5·958 | — | — | 0·352 | — | — | — | — |
| 7·283 | — | — | 0·368 | 411 | 192 | 190 | 3·05 |
| [RuHBr(CO)(PEt ₂ Ph) ₃] | | | | | | | |
| 7·583 | 2·190 | — | — | — | — | — | — |
| 8·338 | 2·193 | — | — | — | — | — | — |
| 25·05 | — | 10·65 | — | — | — | — | — |
| 30·55 | — | 11·08 | — | — | — | — | — |
| 5·112 | — | — | 0·397 | — | — | — | — |
| 9·510 | — | — | 0·413 | 449 | 198 | 221 | 3·3 |
| [RuHI(CO)(PEt ₂ Ph) ₃] | | | | | | | |
| 2·218 | 2·660 | — | — | — | — | — | — |
| 3·120 | 2·590 | — | — | — | — | — | — |
| | | | (0·47) | 526 * | (200) | 296 * | 3·8 * |

* Calculated from estimated values of densities and refractivities, shown in parentheses.¹²

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Notes.

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Collection and Identification of Gases.—The gases evolved in the reactions with alcohols were first collected over water in a gas burette, and then dried and transferred to another gas burette containing mercury. Gas chromatography was carried out at 0° on a silica-gel column containing diethyl succinate as the liquid phase.

Determination of Dipole Moments.—These (see Table 2) were determined as described previously.¹² The margin of error is less than ± 0.1 D for moments greater than 4D. Atom polarisation was assumed to be 15% of the electron polarisation.

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¹² Chatt and Shaw, *J.*, 1959, 705, 4020.
