1142. *Some Halido- and Hydrido-alkyl and -aryl Complexes of Ruthenium*(II) *and Osmium*(II).*

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The preparation, properties, and structure of some complex alkyl and aryl derivatives of ruthenium(II) and osmium(II) are described. They are of the types *cis*-[MR_2(diphosphine)$_2$], and *cis*- and *trans*-[MXR(diphosphine)$_2$] (M = Ru or Os; X = Cl, Br, I, SCN, or H; R = alkyl or aryl; diphosphine = $Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2$, $Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2$, or $Ph_2P{\cdot}CH_2{\cdot}PPh_2$). These compounds provide the first examples of compounds having both a hydrogen atom and an organic group attached to the same transition metal by σ-bonds. Nuclear magnetic resonance and infrared data are discussed.

A NUMBER of stable hydrido- and related σ-bonded organo-complexes derived from transition metals and stabilized by tertiary phosphines are now known,[1-3] but no alkyl or aryl derivative of ruthenium and osmium has been described, except briefly by us.[4] Now we present their detailed preparation and properties. They are the series of octahedral complexes of ruthenium(II) and osmium(II) stabilized by the diphosphines, $R_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PR_2$ (R = Me or Ph) and $Ph_2P{\cdot}CH_2{\cdot}PPh_2$, and the diarsine, *o*-$C_6H_4(AsMe_2)_2$, as listed in Tables 1 and 2. They provide the first examples of transition-metal compounds having both hydrogen and a σ-bonded organic group attached to the metal atom.

A discussion of the function of the tertiary phosphine and similar ligands of high ligand-field strength in stabilizing hydrido- and related organo-complexes will be found in refs. 1 and 2, mainly with reference to the planar four-co-ordinated complexes, *trans*-[$PtR_2(PR'_3)_2$] and analogous compounds of Pd, Ni, Co, and Fe. Their stabilities decrease rapidly in the order of metals Pt > Pd > Ni > Co > Fe. The paramagnetic iron(II) complexes [$FeR_2(PR'_3)_2$] and the halides [$FeX_2(PR'_3)_2$] are very unstable; indeed only one organoiron compound (with R = C_6Cl_5 and PR'_3 = PEt_2Ph) was sufficiently stable to be obtained pure.

In order to extend the range of organo-complexes to the other metals of the iron group, we used as starting materials, *cis*- and *trans*-[MX_2(diphosphine)$_2$] [M = Ru or Os; X = halogen; diphosphine = $R_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PR_2$ (R = Me or Ph) or $Ph_2P{\cdot}CH_2{\cdot}PPh_2$].[5] It was expected that the low-spin d^6-electronic configuration of the bivalent octahedral metals would enhance the stability of the alkyl and aryl derivatives, as would the use of chelate ditertiary phosphines as ligands, and indeed we have derived alkyl and aryl complexes of unexpectedly high thermal stability, some decomposing only at >350°.

Halido-alkyl and -aryl Complexes.—Preparation. The compounds listed in Table 1 were obtained by the reaction of alkyl- and aryl-lithium compounds, and of neat trialkyl aluminiums on the dihalido-complexes, *cis*- and *trans*-[MX_2(diphosphine)$_2$]. These octahedral dihalido-complexes are less reactive towards such reagents than the corresponding planar complexes, *e.g.*, [$PtX_2(PR'_3)_2$],[2,6] and no organic derivative was obtained from them by using Grignard reagents, except low yields of inseparable mixtures isolated from reactions with arylmagnesium bromides.

The *cis*-dihalido-complexes are more reactive than the *trans*-isomers, and the reagents used tended to complement each other so that the methods of preparation are best classified

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[1] Chatt, *Proc. Chem. Soc.*, 1962, 318; and references therein.
[2] Chatt and Shaw, *J.*, 1961, 285; and references therein.
[3] Calvin and Coates, *J.*, 1960, 2008.
[4] Chatt and Hayter, *Proc. Chem. Soc.*, 1959, 153.
[5] Chatt and Hayter, *J.*, 1961, 896.
[6] Chatt and Shaw, *J.*, 1959, 705, 4020.

according to the reagents. No general method was evolved. All preparations were made under nitrogen.

(*a*) Alkyl-lithium reagent. A solution of methyl-lithium in ether reacted readily with *cis*-$[MCl_2(diphosphine)_2]$, to give good yields of the corresponding *cis*-dimethyl compounds. The *cis*-isomers also resulted from treating *cis*-$[RuClMe\{Ph_2P\cdot(CH_2)_n\cdot PPh_2\}_2]$ ($n = 1$ or 2) with an equivalent of methyl-lithium. Attempts to prepare the corresponding *trans*-dimethyl isomers all failed, owing either to lack of reaction as with *trans*-$[MCl_2\{Ph_2P\cdot(CH_2)_n\cdot PPh_2\}_2]$, or to extensive decomposition on working up the mixture, as with *trans*-$[RuCl_2(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)_2]$ and *trans*-$[MClMe(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)_2]$.

TABLE 1.

Alkyl and aryl complexes.

Compound	M. p. (decomp.) *in vacuo*	Colour	Dipole moments (D)
cis-$[RuMe_2(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)_2]$	270—300° †	Colourless	4·35 *
trans-$[RuClMe(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)_2]$	314—316·5	Pale yellow	3·7
$[RuIMe(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)_2]$	292·5—300	Pale yellow	—
cis-$[RuMe_2(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)_2]$	250—256	Yellow	3·45 *
cis-$[RuClMe(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)_2]$	312—315	Pale yellow	6·95
$[Ru(SCN)Me(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)_2]$	281—282 ‡	Pale yellow	—
trans-$[RuClMe(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)_2]$	333·5—336·5	Pale yellow	4·9 *
$[RuBrMe(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)_2]$	311—312·5	Pale orange	—
trans-$[RuBrMe(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)_2]$	366—369	Lemon yellow	5·2 *
cis-$[RuIMe(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)_2],\frac{1}{2}C_6H_6$	328—331	Orange	7·8 *
$[RuIMe(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)_2]$	398—402	Pale yellow	—
trans-$[RuClEt(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)_2]$	329—331·5	Lemon yellow	4·7 *
$[RuIEt(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)_2]$	397—402	Lemon yellow	—
trans-$[RuClPr^n(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)_2]$	332—335	Yellow	4·85 *
$[RuBrPr^n(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)_2]$	362—365	Pale yellow	—
cis-$[RuMe_2(Ph_2P\cdot CH_2\cdot PPh_2)_2],C_6H_6$	246—247	Lemon yellow	4·4 *
α-$[RuClMe(Ph_2P\cdot CH_2\cdot PPh_2)_2]$	289—294	Yellow	—
β-$[RuClMe(Ph_2P\cdot CH_2\cdot PPh_2)_2]$	225—227 ‡	Pale yellow	—
trans-$[RuClEt(Ph_2P\cdot CH_2\cdot PPh_2)_2],\frac{1}{2}C_6H_6$	289—290	Light orange	5·3 *
$[RuClMe\{o\text{-}C_6H_4(AsMe_2)_2\}_2]$	>350 ‡	Pale yellow	—
trans-$[RuClPh(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)_2]$	295	Colourless	1·75 * §
$[RuIPh(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)_2]$	302	Yellow	—
trans-$[RuCl\ p\text{-tolyl}(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)_2]$	247—256	Pale yellow	2·45 * §
$[RuBr\ p\text{-tolyl}(Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2)_2]$	254—260	Pale yellow	—
$[RuPh_2(Ph_2P\cdot CH_2\cdot PPh_2)_2]$	177—178	Pale yellow	
$[OsMe_2(Ph_2P\cdot CH_2\cdot PPh_2)_2]$	253—255·5	Pale yellow	—
cis-$[OsClMe(Ph_2P\cdot CH_2\cdot PPh_2)_2]$	193·5—198	Orange	6·6 *
trans-$[OsClMe(Ph_2P\cdot CH_2\cdot PPh_2)_2],\frac{1}{2}C_6H_6$	281·5—291·5	Pale yellow	5·5 *
trans-$[OsClEt(Ph_2P\cdot CH_2\cdot PPh_2)_2],\frac{1}{2}C_6H_6$	294·5—297·5	Golden yellow	4·95 *
cis-$[OsPh_2(Ph_2P\cdot CH_2\cdot PPh_2)_2],\frac{1}{2}C_6H_6$	237—238	Pale yellow	6·1
cis-$[OsClMe(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)_2],\frac{1}{2}C_6H_6$	295—296 ‡	Pale yellow	6·6 *
$[OsClEt(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)_2]$	310—314	Pale yellow	

* Dipole moments calculated from estimated refractivities and densities. † Sublimes at 120° *in vacuo*. ‡ M. p.s determined in air. § The cause of these low moments is not obvious and owing to circumstances outside our control we could not check these values.

This parallels the failure to obtain *trans*-$[PtMe_2(PR_3)_2]$ easily, and may be attributed to the difficulty of placing the two alkyl groups which have a very high *trans*-effect in mutually *trans*-positions.[6]

Ethyl-lithium did not react with either the *cis*- or *trans*-dichlorido-complexes.

(*b*) Trialkylaluminium reagent. The alkyl aluminiums, $(AlR_3)_2$ (R = Me, Et, and Pr^n) in absence of solvent and near their boiling points reacted with both *cis*- and *trans*-$[MX_2(diphosphine)_2]$ to form highly coloured (dark red or black) oils. After 5 minutes' reaction the mixture was cooled and the oil washed with light petroleum to remove surplus alkylaluminium. Hydrolysis with ethanol caused vigorous evolution of gas with the precipitation of the monoalkyl complex $[MClR(diphosphine)_2]$ and aluminium hydroxide.

This reaction never gave the dialkyl complexes, and in some cases there was isomerization without alkylation.[5]

$$trans\text{-}[RuCl_2(R'_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PR'_2)_2] + (AlR_3)_2 \longrightarrow cis\text{-}[RuCl_2(R_2'P{\cdot}CH_2{\cdot}CH_2{\cdot}PR'_2)_2](R' = \text{Me or Et})$$

The failure to obtain dialkyls may have been due to some special feature of the oily intermediate, *e.g.*, a structure such as $[MR(\text{diphosphine})_2][AlCl_2R_2]$ which prevented the addition of more than one alkyl group to the metal atom, or to the removal of the second alkyl group by the ethanol under the vigorous conditions of the hydrolysis.

The alkylations usually occurred with inversion of configuration as follows:

$$trans\text{-}[MCl_2\{Ph_2P{\cdot}(CH_2)_nPPh_2\}_2] + (AlMe_3)_2 \longrightarrow cis\text{-}[MClMe\{Ph_2P{\cdot}(CH_2)_n{\cdot}PPh_2\}_2]\ (n = 1 \text{ or } 2)$$
$$cis\text{-}[MCl_2(Ph_2P{\cdot}CH_2{\cdot}PPh_2)_2] + (AlMe_3)_2 \longrightarrow trans\text{-}[MClMe(Ph_2P{\cdot}CH_2{\cdot}PPh_2)_2]$$
$$cis\text{- or } trans\text{-}[MCl_2(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2] + (AlR_3)_2 \longrightarrow trans\text{-}[MClR(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]\ (R + \text{Et or Pr}^n)$$

The chloridoalkyl derivatives containing the phosphines ($Ph_2P{\cdot}[CH_2]{\cdot}_nPPh_2$ ($n = 1$ and 2) were best purified by chromatography, although there was always some loss on the column; the dimethyls and *trans*-$[RuClMe(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2]$ decomposed rapidly on attempted chromatography, and were purified by crystallization or sublimation.

(*c*) Aryl-lithium reagent. Both *cis*- and *trans*-$[RuCl_2(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2]$ react with phenyl-lithium and with *p*-tolyl-lithium to give *trans*-$[RuClR(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2]$ (R = Ph or *p*-tolyl). Attempts to convert this product into the diaryl complexes by further reaction with aryl-lithium were unsuccessful. Reaction occurred but attempted isolation of the product without hydrolysis yielded no crystals, and after hydrolysis with ethanol the original chloridoaryl complex was recovered.

Diphenyl derivatives, *cis*-$[MPh_2(Ph_2P{\cdot}CH_2{\cdot}PPh_2)_2]$ (M = Ru and Os) were obtained by reaction of phenyl-lithium with the corresponding *cis*-dichlorido-complex. The corresponding *trans*-dichlorido-complexes did not react.

Numerous attempts to prepare alkyl and aryl derivatives of ruthenium and osmium containing the ligand $Et_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PEt_2$ failed. Reaction usually occurred, but the products decomposed during purification.

Bromides, iodides, and thiocyanates were obtained by metathesis from the chlorides and by the action of hydrogen halide on the hydridoalkyl complexes (Table 2).

The aryl complexes of iron(II), cobalt(II), and nickel(II), stabilized by tertiary phosphines, are stable only when the aryl group contains an *ortho*-substituent. It is supposed that the main function of this substituent is to protect the metal atom from nucleophilic attack by other reagents, and also to stabilize the planar configuration with its larger ligand-field stabilization energy relative to the tetrahedral configuration of ligands.[2,7]

In the ruthenium and osmium complexes described here, an *ortho*-substituent would be expected to introduce such steric strain into the molecule as to cause high instability. Attempts to prepare *trans*-$[RuCl(o\text{-tolyl})(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2]$ gave a low yield of a pale yellow substance which had approximately the correct analysis but progressively decomposed on attempted purification or on storage under nitrogen and it proved impossible to prepare any stable *ortho*-substituted aryl complexes in this series.

Properties. The reactivities and stabilities of the organo-derivatives (Table 1) depend both on the organic groups attached to the metal and on the diphosphine. The dimethyl- and halido-aryl compounds have greater reactivity than the halidoalkyl compounds, and the derivatives containing the aliphatic diphosphine are more reactive than their aromatic analogues. Thus the most reactive compounds are the dimethyl- and halido-aryl complexes, containing the ligand $Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2$; these decompose slowly in air and immediately in contact with alcohol or water. The most stable are the halidoalkyl compounds containing the ligands $Ph_2P{\cdot}[CH_2]_n{\cdot}PPh_2$ ($n = 1$ and 2). They approach the

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[7] Owston and Rowe, *J.*, **1963**, **3411.**

platinous alkyls, *cis*-$[PtR_2(PR'_3)_2]$ (R = alkyl),[6] in their high resistance to hydrolysis and aerial oxidation. The greater stability of the complexes derived from the aromatic diphosphines is probably due partly to steric factors, the metal atom and susceptible organo-group being well shielded from attacking reagents, and partly to electronic deactivation by the phenyl groups. Despite the sensitivity of many of the organo-complexes to oxidation and hydrolysis, most of them are stable thermally and do not decompose in a vacuum below their melting points, which lie in the range 250—400°.

Reactions. Only a few elementary reactions have been examined.

(*a*) Metathetical replacement of chlorine. Chloride ion was readily replaced by bromide, iodide, and thiocyanate in the chlorides listed in Table 1, where the chloride ion is always in *trans*-position to phosphorus or carbon, both of which have high *trans*-effects. Reaction occurred most readily in the least sterically-hindered *trans*-$[RuClMe(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2]$ where reaction with iodide ion was fast and quantitative at room temperature, as it was with *cis*-$[MCl_2(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2]$. This contrasts markedly with the rate of reaction of *trans*-$[MCl_2(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2]$ (M = Os or Ru) where chloride ion is in *trans*-position to another chloride ion (of low *trans*-effect) and several days' reaction in boiling solvents is required for the replacement of both chloride ions by iodide ions.[5]

(*b*) Cleavage. Alkyl and aryl groups were cleaved from the metal by reaction with hydrogen chloride in ether or with the halogens. These reactions usually occurred with retention of configuration, except in reaction (3) below, where retention would have given *cis*-$[RuCl_2(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]$ which is unknown.[5]

$$\textit{trans}\text{-}[RuClR(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2]\ (R = Me\ \text{or}\ Ph) + HCl \longrightarrow \textit{trans}\text{-}[RuCl_2(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2] \quad . \quad (1)$$

$$\textit{cis}\text{-}[RuMe_2(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2] + 2HCl/2Cl_2 \longrightarrow \textit{cis}\text{-}[RuCl_2(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2] + 2CH_4/2MeCl \quad . \quad (2)$$

$$\textit{cis}\text{-}[RuClMe(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2] + Cl_2 \longrightarrow \textit{trans}\text{-}[RuCl_2(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2] + MeCl \quad . \quad . \quad . \quad (3)$$

Hydrido-alkyls and -aryls.—Preparation. The chlorido-alkyl or -aryl complexes (Table 1) are readily reduced by lithium aluminium hydride to hydrido-alkyl or -aryl complexes (Table 2).

TABLE 2.

Hydrido-alkyl and -aryl complexes.

Compound	M. p. (decomp. *in vacuo*)	Dipole moment (D)	ν(M–H)	τ(M–H) *
cis-$[RuHMe(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]$	247—251·5°	3·25	1884 * cm.$^{-1}$	18·9
trans-$[RuHMe(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]$	290·5—293	2·95 †	1868 *	18·4
cis-$[RuHEt(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]$	289—294	3·25	1873 *	—
cis-$[RuHPr^n(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2],C_6H_6$ ...	278—280	3·15	1867 *	—
trans-$[RuHPh(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2]$	159—161	3·90 †	1757 ‡	23·3
$[RuH(p\text{-tolyl})(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2]$	146—153	—	1766 ‡	—
$[OsHMe(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2],C_6H_6$	145—155	—	1948 *	—
$[OsHEt(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2],\frac{1}{2}C_6H_6$	311·5—314·5	—	1941 ‡	—

* In benzene. † Dipole moments calculated from estimated refractivities and densities. ‡ In Nujol mull.

These hydrido-alkyl and -aryl complexes form colourless (ruthenium) or pale yellow (osmium) crystals, which decompose slowly in air. Their infrared spectra show strong bands due to metal–hydrogen stretching vibrations in the region 1750—1950 cm.$^{-1}$ (Table 2).[9] This assignment was confirmed in the case of *cis*-$[RuHMe(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]$ from the infrared spectrum of the corresponding deuteride prepared by reduction of the *cis*-chlorido-methyl compound with lithium aluminium deuteride [ν(Ru–H), 1902; ν(Ru–D) 1375; δ(Ru–D) 545 cm.$^{-1}$ in hexachlorobutadiene mulls; δ(Ru–H) was obscured by ligand absorbtions].

Nuclear Magnetic Resonance Spectra.—The presence of metal–hydrogen bonds was confirmed by the observation of absorption bands in the high-field region of their nuclear magnetic resonance spectra (Table 2).

trans-[$RuHPh(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2$] absorbs at τ 23·3, the band being a quintet with intensities in the approximate ratios 1 : 4 : 6 : 4 : 1. This pattern indicates a *trans*-configuration and is due to the coupling of the hydrogen to four equivalent phosphorus atoms (J_{HP} = 23·5 c./sec.). Similar absorption bands have previously been observed in the spectra of *trans*-[$RuHX(Et_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PEt_2)_2$] (X = Cl, Br, or I) in the range τ 31·8—29·3.[8] It is noteworthy that the spectrum of *trans*-[$RuClPh(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2$] (in $CDCl_3$) shows complex absorption, due to the phenyl group, centred at τ 3·30. The ratio between the protons of the phosphine ligand and the protons of the phenyl group was found to be 6·9 (calc. 6·4). The phenyl absorption is shifted to higher field relative to other organic aromatic protons, owing probably to greater electron screening caused by mesomeric electron drift from the metal.

The complex, *cis*-[$RuHMe(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2$], absorbs at τ 18·9, the band being in the form of a double quartet. This is consistent with a *cis*-configuration, with J_{HP} (*trans*) = 76 c./sec. and J_{HP} (*cis*) = 19 c./sec. The large difference between the two types of hydrogen–phosphorus coupling constants has also been observed for similar iridium(III) hydrido-complexes stabilized by tertiary phosphines.[10]

trans-[$RuHMe(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2$] has a complex absorption band centred at τ ~18·4. Owing to the weakness of the absorption, it has not been possible to obtain any further information about the geometry of the complex. However, the pattern is certainly not that of a simple quintet, as expected for a *trans*-configuration. It is possible that the coupling between the ruthenium-hydrogen and the *trans*-methyl group is sufficiently large to account for the complexity of the spectrum.

The τ values (18·9—23·3) of the above hydrido-organo-complexes are considerably lower than those of the corresponding hydrido-halido-complexes (29·3—31·8).[8] This is paralleled by the dihydrido-complex,[11] *trans*-[$FeH_2\{o\text{-}C_6H_4(PEt_2)_2\}_2$] ($\tau$ 23·1), and the corresponding hydrido-chlorido-complex (τ 40·5).[8] In each case the replacement of a group of exceptionally high ligand-field strength and *trans*-effect (Me, Ph, or H) [12] by a halogen of very low ligand-field strength and moderate *trans*-effect has considerably increased the chemical shift of the proton resonance, although the increase does not have any exact correlation with either of these (cf. the τ values in ref. 13).

Reactions. The hydrido-alkyl complexes react readily with aqueous or ethereal hydrogen halides to give *trans*-halido-alkyl complexes and hydrogen. Alkyl groups are not cleaved even in the presence of an excess of acid, but they are cleaved by a second mole of halogen:

$$cis\text{- or } trans\text{-}[RuHRL_2] + HX \longrightarrow trans\text{-}[RuXRL_2] + H_2$$

$$cis\text{-}[RuHEtL_2] + I_2 \longrightarrow trans\text{-}[RuIEtL_2] + HI$$

$$cis\text{-}[RuHEtL_2] + 2Cl_2 \longrightarrow trans\text{-}[RuCl_2L_2] + EtCl + HCl$$

$$(L = Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2).$$

Infrared Spectra.—Recent work on the infrared spectra of the alkyl complexes of platinum(II), palladium(II), and gold (I) has shown that bands assignable to the metal–carbon stretching, ν(M–C) (450—600 cm.$^{-1}$) and to the deformation modes of vibration of alkyl groups σ-bonded to the metal are observed, especially the symmetrical deformation mode of methyl groups, δ(Me, s) (1170—1230 cm.$^{-1}$).[14,15] Dr. D. M. Adams has examined the spectra of the compounds as listed in Table 3.

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[8] Chatt and Hayter, *J.*, 1961, 2605.

[9] Chatt, Duncanson, and Shaw, *Chem. and Ind.*, 1958, 859.

[10] Shaw and Sheppard, personal communication.

[11] Chatt, Hart, and Rosevear, *J.*, 1961, 5504.

[12] Chatt and Hayter, *J.*, 1961, 772.

[13] Chatt and Shaw, *J.*, 1962, 5075.

[14] Calvin, Coates, and Dixon, *Chem. and Ind.*, 1959, 1628.

[15] Adams, Chatt, and Shaw, *J.*, 1960, 2047.

TABLE 3.

Methyl vibrations in the compounds [$RuXMeL_2$]
(X = anionic ligand, $L = Me_2P\cdot CH_2\cdot CH_2\cdot PMe_2$).

Compound	δ(Me, s) (cm.$^{-1}$)	ν(Ru–C) (cm.$^{-1}$)
trans($RuClMeL_2$	1200m	483vw
trans-[$RuIMeL_2$]	1195s	465vw
trans-[$Ru(SCN)MeL_2$]	1199w	—
cis-[$RuMe_2L_2$]	1185w 1157m	—

Bands due to ν(Ru–C) vibrations are expected near 500 cm.$^{-1}$, but only very weak absorption was observed (Table 3) and the assignment must be regarded as very tentative. In the halido-alkyl complexes, both ν(Ru–C) and δ(Me, s) are lower in the iodide than in the chloride, as was found in the corresponding alkyl complexes of platinum(II). The alkyl complexes stabilized by diphosphines, $Ph_2P\cdot[CH_2]_n\cdot PPh_2$ ($n = 1$ or 2), do not show any absorption which may be attributed to the presence of an alkyl group, apart from a weak band at 1326 cm.$^{-1}$ for [$RuHR(Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2)_2$] (R = Et or Pr^n). Other instances are known of this unaccountable absence of methyl deformation vibrations.[14,16]

EXPERIMENTAL

Microanalyses and molecular-weight measurements are by the Analytical Department of the Akers Research Laboratories and by Schwarzkopf Laboratories, Woodside, N.Y. Unless otherwise indicated, the molecular weights were determined with a Mechrolab osmometer. The infrared spectra were measured on a Grubb-Parsons G.S. 2A spectrometer. The nuclear magnetic resonance spectra were measured on Varian Associates HR-60 and A-60 instruments, with tetramethylsilane as internal reference.

M. p.s were determined in capillary tubes under a vacuum or on a Kofler hot stage where vacuum is not specified. Spence " H " grade alumina was used for chromatography. The alkylaluminiums were handled in a nitrogen-filled glove-box and other preparations were carried out in a stream of nitrogen. The organometallic complexes, once prepared, were sufficiently stable to be handled in air. Representative members of the complexes were found to be non-electrolytes in nitrobenzene solution at 20°.

Preparations Involving Methyl-lithium.—cis-*Dimethyldi-*(1,2-*bisdimethylphosphinoethane*)-*ruthenium*(II). *cis*-Dichloridodi-(1,2-bisdimethylphosphinoethane)ruthenium(II) (0·50 g.) was suspended in benzene and treated with methyl-lithium in ether (2·2 equiv., 8·3 ml.). The complex dissolved in 2 days at room temperature and a precipitate of lithium chloride was formed. After filtration, solvent was removed at 12 mm. and the residue, on sublimation in a vacuum at 160°, gave the pure *complex* (33% yield) (Found: C, 39·0; H, 8·9. $C_{14}H_{38}P_4Ru$ requires C, 39·0; H, 8·9%).

The following complexes were similarly prepared, but were purified by crystallisation:

cis-*Dimethyldi-*(1,2-*bisdiphenylphosphinomethane*)*ruthenium*(II) was prepared in 32% yield from *cis*-[$RuCl_2(Ph_2P\cdot CH_2\cdot PPh_2)_2$] and crystallized from benzene containing 20% of light petroleum as a benzene monosolvate (Found: C, 71·1; H, 5·8. $C_{58}H_{56}P_4Ru$ requires C, 71·2; H, 5·8%).

cis-*Dimethyldi-*(1,2-*bisdiphenylphosphinoethane*)*ruthenium*(II) was prepared from the corresponding *cis*-chloridomethyl complex and obtained from light petroleum containing 20% of benzene in 25% yield (Found: C, 69·9; H, 5·7. $C_{54}H_{54}P_4Ru$ requires C, 69·9; H, 5·9%).

cis-*Dimethyldi-*(1,2-*bisdiphenylphosphinomethane*)*osmium*(II) was obtained from *cis*-[$OsCl_2(Ph_2P\cdot CH_2\cdot PPh_2)_2$] and crystallized from benzene in 10% yield (Found: C, 63·8; H, 5·2. $C_{52}H_{50}OsP_4$ requires C, 63·15; H, 5·1%).

Preparations Involving Alkylaluminiums.—cis-*Chloridomethyldi-*(1,2-*bisdiphenylphosphinoethane*)*ruthenium*(II). *trans*-Dichloridodi-(1,2-bisdiphenylphosphinoethane)ruthenium(II) (0·50 g.) was warmed with trimethylaluminium (1·5 ml.) to about 80°, giving a dark red visous oil, which did not change colour below the b. p. of trimethylaluminium. After about 5 minutes' heating,

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[16] Adams, unpublished observations.

the mixture was cooled and the oil washed by decantation with light petroleum. More light petroleum (20 ml.) was then added and next ethanol, cautiously, dropwise, giving a vigorous reaction with effervescence and precipitation of a yellow solid. When the oil was completely decomposed, solvent was removed at 12 mm. and the residue crystallized from benzene, to give the pure *complex* in 70% yield [Found: C, 67·1; H, 5·35; Cl, 3·6; P, 13·1; Ru, 10·4%; *M* (C_6H_6): 917 (1·7% solution). $C_{53}H_{51}ClP_4Ru$ requires C, 67·1; H, 5·4; Cl, 3·8; P, 13·1; Ru, 10·65%; *M*, 948].

The following compounds were similarly prepared:

trans-*Chloridomethyldi*(1,2-*bisdimethylphosphinoethane*)*ruthenium*(II) was prepared from the *cis*-dichlorido-complex and crystallized from light petroleum in 33% yield (Found: C, 34·8; H, 7·8. $C_{13}H_{35}ClP_4Ru$ requires C, 34·55; H, 7·8%).

α-*Chloridomethyldi*-(1,2-*bisdiphenylphosphinomethane*)*ruthenium*(II) was prepared from the *trans*-dichlorido-complex and purified by elution from alumina with 1 : 4 ether–benzene. Crystallization from benzene gave the pure *complex* in 25% yield (Found: C, 66·3; H, 5·3. $C_{51}H_{47}ClP_4Ru$ requires C, 66·55; H, 5·1%).

β-*Chloridomethyldi*(1,2-*bisdiphenylphosphinomethane*)*ruthenium*(II) was obtained from the *cis*-dichlorido-complex and crystallized from ethyl acetate and then 1 : 1 light petroleum–benzene (60% yield). Drying in a vacuum at 100° for 16 hr. removed benzene of solvation (Found: C, 66·7; H, 5·4. $C_{51}H_{47}ClP_4$ Ru requires C, 66·55; H, 5·15%).

Chloridomethyldi-(o-*phenylenebisdimethylarsine*)*ruthenium*(II) was obtained from the *trans*-dichlorido-complex and crystallized from benzene in 45% yield (Found: C, 35·2; H, 4·9. $C_{21}H_{35}As_4ClRu$ requires C, 34·85; H, 4·9%).

trans-*Chloridoethyldi*-(1,2-*bisdiphenylphosphinoethane*)*ruthenium*(II) was prepared from the *trans*-dichlorido-complex and purified by elution from alumina with 1 : 4 ether–benzene. Crystallization from benzene containing 30% of light petroleum afforded the pure complex in 40% yield (Found: C, 67·2; H, 5·6. $C_{54}H_{53}ClP_4Ru$ requires C, 67·4; H, 5·55%). This compound was also prepared by the reaction between hydrogen chloride in ether and *cis*-hydridoethyldi-(1,2-bisdiphenylphosphinoethane)ruthenium(II).

trans-*Chloridoethyldi*-(1,2-*bisdiphenylphosphinomethane*)*ruthenium*(II) was obtained from either the *cis*- or the *trans*-dichlorido-complex and purified by elution from alumina with 1 : 9 ether–benzene. Crystallization from 1 : 1 light petroleum–benzene gave the pure compound in 30% yield. This compound crystallizes with half a molecule of benzene, which was not removed after 16 hr. *in vacuo* at 100° (Found: C, 68·0; H, 5·5. $C_{55}H_{52}ClP_4Ru$ requires C, 67·9; H, 5·4%).

trans-*Chlorido-n-propyldi*-(1,2-*bisdiphenylphosphinoethane*)*ruthenium*(II) was prepared from the *trans*-dichlorido-complex and purified as above, being obtained in 60% yield [Found: C, 67·8; H, 5·5%; *M* (ebullioscopically in benzene) 768 (1·12% solution), 815 (1·9%). $C_{55}H_{55}ClP_4Ru$ requires C, 67·65; H, 5·7%; *M*, 976·5]. This compound was also prepared by the action of hydrogen chloride in ether on *cis*-hydrido-n-propyldi(1,2-bisdiphenylphosphinoethane)ruthenium(II).

cis-*Chloridomethyldi*-(1,2-*bisdiphenylphosphinomethane*)*osmium*(II) was prepared from the *trans*-dichlorido-complex and crystallized from methylcyclohexane in 27% yield (Found: C, 60·8; H, 4·8. $C_{51}H_{47}ClOsP_4$ requires C, 60·7; H, 4·7%).

trans-*Chloridomethyldi*-(1,2-*bisdiphenylphosphinomethane*)*osmium*(II) was obtained from the *cis*-dichlorido-complex and crystallized from 1 : 1 light petroleum–benzene as a hemisolvate in 75% yield (Found: C, 61·8; H, 5·0. $C_{54}H_{50}ClOsP_4$ requires C, 61·8; H, 4·8%). Drying *in vacuo* at 100° for 24 hr. gave the unsolvated compound (Found: C, 61·0; H, 4·65. $C_{51}H_{47}ClOsP_4$ requires C, 60·7; H, 4·7%).

cis-*Chloridomethyldi*-(1,2-*bisdiphenylphosphinoethane*)*osmium*(II) was obtained from the *trans*-dichlorido-compound and crystallized from 1 : 1 light petroleum–benzene as a hemisolvate (Found: C, 62·75; H, 5·2. $C_{53}H_{51}ClOsP_4$ requires C, 62·5; H, 5·1%).

trans-*Chloridoethyldi*-(1,2-*bisdiphenylphosphinomethane*)*osmium*(II) was obtained from either the *cis*- or the *trans*-dichlorido-complex in 75 or 21% yield, respectively. It crystallized from 1 : 1 light petroleum–benzene as a hemisolvate (Found: C, 62·3; H, 5·0 $C_{55}H_{52}ClOsP_4$ requires C, 62·2; H, 4·9%).

Chloridoethyldi-(1,2-*bisdiphenylphosphinoethane*)*osmium*(II) was obtained from the *trans*-dichlorido-complex in 45% yield and crystallized from ethyl acetate (Found: C, 61·4; H, 5·0. $C_{52}H_{49}ClOsP_4$ requires C, 61·7; H, 5·1%).

Preparations Involving Aryl-lithium.—trans-*Chloridophenyldi-*(1,2-*bisdimethylphosphinoethane*)*ruthenium*(II). *cis*-Dichloridodi-(1,2-bisdimethylphosphinoethane)ruthenium(II) (0·50 g.) was suspended in benzene (20 ml.) and treated with a solution of phenyl-lithium (2·2 equiv. in ether, 11·5 ml.). The complex dissolved during 3 hours' shaking at room temperature, to give an orange solution and a precipitate of lithium chloride. A few drops of ethanol were added to discharge the orange colour and give a clear yellow solution. Solvent was removed at 12 mm. and the benzene-soluble portion of the residue was crystallized from acetone and then sublimed *in vacuo* at 200° to give the pure *complex* in 40% yield [Found: C, 41·8; H, 7·3; Cl, 7·2%; *M* (C_6H_6): 542 (1·3% solution). $C_{18}H_{37}ClP_4Ru$ requires C, 42·1; H, 7·3; Cl, 6·9%; *M*, 514]. This compound was prepared similarly from the *trans*-dichlorido-complex in 50% yield.

The following complexes were similarly prepared:

trans-*Chlorido-*p-*tolyldi-*(1,2-*bisdimethylphosphinoethane*)*ruthenium*(II) was obtained in 30% yield by vacuum-sublimation at 170° (Found: C, 42·9; H, 7·3; $C_{19}H_{39}ClP_4Ru$ requires C, 43·2; H, 7·45%).

*Bromido-*p-*tolyldi-*(1,2-*bisdimethylphosphinoethane*)*ruthenium*(II) was obtained in 15% yield by sublimation *in vacuo* at 200° (Found: C, 39·9; H, 6·8. $C_{19}H_{39}BrP_4Ru$ requires C, 39·9; H, 6·9%). Similar attempts to prepare *trans*-chlorido-*o*-tolyldi-(1,2-bisdimethylphosphinoethane)ruthenium(II) afforded an off-white solid, subliming at 200° *in vacuo* as pale yellow crystals (69%), m. p. 160—200° (decomp.) (in a vacuum). This product darkened rapidly on storage in a sealed ampoule under nitrogen (Found: C, 41·7; H, 7·4%).

Iodidophenyldi-(1,2-*bisdimethylphosphinoethane*)*ruthenium*(II). The *trans*-chloridophenyl complex (0·20 g.) in acetone (5 ml.) was treated with lithium iodide (0·2 g.) in acetone. A white precipitate was gradually formed and, after 10 minutes' refluxing, the solution was filtered and evaporated. The residue was crystallized from 1 : 1 light petroleum–benzene and then sublimed in a vacuum at 200° (25% yield) (Found: C, 35·5; H, 6·1. $C_{18}H_{37}IP_4Ru$ requires C, 35·7; H, 6·2%).

Diphenyldi-(1,2-*bisdiphenylphosphinomethane*)*ruthenium*(II). *cis*-[$RuCl_2(Ph_2P{\cdot}CH_2{\cdot}PPh_2)_2$] was suspended in benzene and treated with four equivalents of phenyl-lithium in ether. After 24 hours' storage with occasional shaking, the complex dissolved to give a dark orange solution. Just sufficient ethanol was then added to give a clear yellow solution, the solvent removed at 12 mm., and the product extracted in benzene. Crystallization from 1 : 1 light petroleum–benzene afforded the pure *complex* in 35% yield (Found: C, 73·0; H, 5·4. $C_{62}H_{54}P_4Ru$ requires C, 72·7; H, 5·3%).

cis-*Diphenyldi-*(1,2-*bisdiphenylphosphinomethane*)*osmium*(II) was similarly prepared and crystallized from benzene–light petroleum in 60% yield as a hemisolvate (Found: C, 67·7; H, 5·1. $C_{65}H_{57}OsP_4$ requires C, 67·75; H, 5·0).

Metathetical Replacement Reactions.—*Iodidomethyldi-*(1,2-*bisdimethylphosphinoethane*)*ruthenium*(II). *trans*-Chloridomethyldi-(1,2-bisdimethylphosphinoethane)ruthenium(II) (0·10 g.) in acetone (3 ml.) was treated with sodium iodide (1 equiv.) in acetone (10 ml.). An immediate white precipitate was formed and, after 5 minutes' warming on a steam-bath, the solution was filtered. Dilution of the filtrate with light petroleum (30 ml.) gave the pure *complex* in 40% yield (Found: C, 28·5; H, 6·4; $C_{13}H_{35}IP_4Ru$ requires C, 28·7; H, 6·5%).

Bromidomethyldi-(1,2-*bisdiphenylphosphinoethane*)*ruthenium*(II) was prepared by refluxing the *cis*-chloridomethyl complex with lithium bromide (20 times excess) in tetrahydrofuran solution for 16 hr. A white precipitate was formed and, after filtration, the solvent was removed at 12 mm. and the water-insoluble residue dissolved in chloroform and chromatographed on alumina. Elution with benzene gave the pure *complex* (60% yield) (Found: C, 64·4; H, 5·4. $C_{53}H_{51}BrP_4Ru$ requires C, 64·1; H, 5·2%). Crystallization from ethyl acetate gave orange crystals, m. p. 307—309·5° (decomp.) (*in vacuo*), containing a half molecule of solvent (Found: C, 63·3; H, 5·0. $C_{55}H_{55}BrOP_4Ru$ requires C, 63·7; H, 5·35%). Solvation was confirmed from the strong band at 1737 cm.$^{-1}$ due to ν(C=O) of the ester, in the infrared spectrum (Nujol mull) of the compound.

cis-*Iodidomethyldi*(1,2-*bisdiphenylphosphinoethane*)*ruthenium*(II) was similarly prepared and purified, being obtained from 1 : 1 light petroleum–benzene (50% yield). Drying in a vacuum at 100° for 16 hr. did not remove a half molecule of benzene of solvation (Found: C, 62·9; 62·7; H, 5·1; 5·1; I, 12·2. $C_{55}H_{54}IP_4Ru$ requires C, 62·3; H, 5·0; I, 11·8%).

Thiocyanatomethyldi-(1,2-*bisdiphenylphosphinoethane*)*ruthenium*(II) was similarly prepared and purified, being obtained from benzene in 70% yield (Found: C, 66·8; H, 5·4; N, 2·05.

$C_{54}H_{51}NP_4RuS$ requires C, 66·8; H, 5·3; N, 1·45%). The infrared spectrum (Nujol mull) of this compound contains a strong band at 2107 cm.$^{-1}$ due to ν(C≡N).

Reaction of Hydrogen Halide on the Hydridoalkyl Complexes.—trans-*Chloridomethyldi*-(1,2-*bisdiphenylphosphinoethane*)*ruthenium*(II). *cis*-Hydridomethyldi-(1,2-bisdiphenylphosphinoethane)ruthenium(II) (0·20 g.) in benzene (3 ml.) was treated with a solution of hydrogen chloride (1 equiv.) in ether (1·34 ml.). Hydrogen was evolved and the solution changed from colourless to yellow. After 10 min., the solution was chromatographed on alumina, elution with 1 : 4 ether–benzene yielding the pure *complex*, which crystallized from benzene in 50% yield [Found: C, 67·0; H, 5·3; Cl, 3·7%; *M* (CH_2Br_2), 993 (0·50% solution). $C_{53}H_{51}ClP_4Ru$ requires C, 67·1; H, 5·4; Cl, 3·8%; *M*, 948].

The following compounds were similarly prepared and purified:

trans-*Bromidomethyldi*-(1,2-*bisdiphenylphosphinoethane*)*ruthenium*(II) in 45% yield (Found: C, 64·4; H, 5·2. $C_{53}H_{51}BrP_4Ru$ requires C, 64·1; H, 5·2%).

Iodidomethyldi-(1,2-*bisdiphenylphosphinoethane*)*ruthenium*(II) in 55% yield (Found: C, 61·55; H, 5·2. $C_{53}H_{51}IP_4Ru$ requires C, 61·2; H, 4·9%). This compound was also prepared by a metathetical replacement reaction from the *trans*-chloridomethyl complex in 60% yield, and its identity was confirmed by its m. p. and mixed m. p. with an authentic specimen.

trans-*Iodidoethyldi*(1,2-*bisdiphenylphosphinoethane*)*ruthenium*(II) in 35% yield (Found: C, 61·9; H, 5·2; I, 12·2. $C_{54}H_{53}IP_4Ru$ requires C, 61·5; H, 5·1; I, 12·0%).

TABLE 4.

Dipole moments.

$10^3\omega$	$\Delta\varepsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$	$_TP$	$_EP$	$_OP$	μ (D)
cis-$[RuMe_2(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2]$							
3·757	5·329						
5·087	5·301						
4·420			0·339	536	(129)	388 *	4·35
cis-$[RuMe_2(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]$							
2·421	1·907						
3·937	1·888		(0·32)	560 *	(275)	245 *	3·45
cis-$[RuMe_2(Ph_2P{\cdot}CH_2{\cdot}PPh_2)_2],C_6H_6$							
2·035	2·479						
4·700	2·473		(0·32)	697 *	(265)	392 *	4·4 *
trans-$[RuClMe(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2]$							
2·418	3·711						
4·140	3·710						
4·123			0·315				
5·222			0·364				
67·74		8·56					
68·73		9·11		424	129	276	3·7
cis-$[RuClMe(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]$							
1·433	5·998						
1·533	6·008		(0·35)	1305 *	(275)	989 *	6·95 *
trans-$[RuClMe(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]$							
1·378	3·260						
2·130	3·208		(0·35)	803 *	(275)	487 *	4·9 *
trans-$[RuBrMe(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]$							
2·522	3·495						
3·272	3·434		(0·37)	878 *	(278)	558 *	5·2 *
cis-$[RuIMe(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2],\frac{1}{2}C_6H_6$							
0·833	6·484						
1·004	6·481		(0·38)	1564 *	(283)	1239 *	7·8 *
trans-$[RuClEt(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]$							
2·210	3·011						
2·632	3·326						
4·173	3·232						
3·287			0·395				
5·491			0·401	793	(279)	472 *	4·8 *

TABLE 4. (*Continued.*)

$10^3\omega$	$\Delta\varepsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$	${}_{T}P$	${}_{E}P$	${}_{O}P$	μ (D)
trans-$[RuClPr^n(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]$							
2·103	3·154						
2·196	3·152		(0·35)	812 *	(283)	486 *	4·85 *
trans-$[RuClEt(Ph_2P{\cdot}CH_2{\cdot}PPh_2)_2],\frac{1}{2}C_6H_6$							
1·633	3·534						
1·738	3·647						
2·559	3·453		(0·35)	881 *	(270)	570 *	5·3 *
cis-$[OsClMe(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2],\frac{1}{2}C_6H_6$							
1·719	4·645						
2·088	4·632		(0·35)	1197 *	(269)	888 *	6·6 *
cis-$[OsClMe(Ph_2P{\cdot}CH_2{\cdot}PPh_2)_2]$							
1·467	4·978						
2·074	5·057		(0·35)	1194 *	(260)	895 *	6·6 *
trans-$[OsClMe(Ph_2P{\cdot}CH_2{\cdot}PPh_2)_2],\frac{1}{2}C_6H_6$							
1·078	3·397						
1·258	3·369		(0·35)	917 *	(260)	619 *	5·5 *
trans-$[OsClEt(Ph_2P{\cdot}CH_2{\cdot}PPh_2)_2],\frac{1}{2}C_6H_6$							
2·110	2·778						
2·721	2·743		(0·35)	805 *	(264)	501 *	4·95 *
trans-$[RuClPh(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2]$							
3·329	1·157						
6·259	1·129		(0·35)	233 *	(148)	62 *	1·75 *
trans-$[RuCl(p\text{-tolyl})(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2]$							
3·563	1·745						
4·987	1·756		(0·35)	299 *	(153)	124 *	2·45 *
cis-$[OsPh_2P{\cdot}CH_2{\cdot}PPh_2)_2],\frac{1}{2}C_6H_6$							
2·923	4·313						
3·198	4·378						
6·157			0·406				
8·729		16·53					
10·32		16·65		1177	357·5	766	6·1
cis-$[RuHMe(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]$							
4·938	1·940						
5·212	1·909						
15·60		15·39					
17·04		15·51					
2·707			0·480				
4·863			0·391	525	270	215	3·2
trans-$[RuHMe(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2],C_6H_6$							
3·779	1·318						
4·794	1·313		(0·32)	490 *	(270)	180 *	2·95
cis-$[RuHEt(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2]$							
3·525	1·718						
4·785	1·690						
4·392			0·296				
4·421			0·317	530	(275)	214 *	3·25
cis-$[RuHPr^n(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2],C_6H_6$							
2·804	1·744						
3·545	1·722						
13·66		14·18					
17·34		14·34					
3·911			0·307				
4·757			0·273	593	337	205	3·15
trans-$[RuHPh(Me_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PMe_2)_2]$							
3·664							
4·068	3·984		(0·32)	477 *	(143)	312 *	3·90 *

* Calc. by using estimated values of densities and refractivities; estimated values are in parentheses.[6]

Bromido-n-propyldi-(1,2-*bisdiphenylphosphinoethane*)*ruthenium*(II) in 30% yield (Found: C, 64·4; H, 5·3. $C_{55}H_{55}BrP_4Ru$ requires C, 64·7; H, 5·4%).

Preparation of Hydrido-alkyl and -aryl Complexes.—cis-*Hydridomethyldi*(1,2-*bisdiphenylphosphinoethane*)*ruthenium*(II). *cis*-Chloridomethyldi-(1,2-bisdiphenylphosphinoethane)ruthenium(II) (0·30 g.) in tetrahydrofuran (20 ml.) was reduced with lithium aluminium hydride in tetrahydrofuran, the colour fading to very pale yellow on refluxing. After 15 min., ethanol was added to destroy the excess of metal hydride, and solvent was removed at 12 mm. The benzene-soluble portion of the white solid residue was crystallized from 1 : 4 light petroleum–benzene, to give the pure *complex* in 65% yield [Found: C, 70·0, 69·2; H, 5·7, 5·35; P, 13·8; Ru, 9·8; O, 0·4%; Cl, 0·0; *M* (ebullioscopically in benzene), 1043 (0·90% solution), 1095 (1·16%). $C_{53}H_{52}P_4Ru$ requires C, 69·65; H, 5·7; P, 13·6; Ru, 11·1%; *M*, 914].

The following complexes were similarly prepared:

trans-*Hydridomethyldi-*(1,2-*bisdiphenylphosphinoethane*)*ruthenium*(II) in 50% yield by reduction of the *trans*-chloridomethyl complex and subsequent crystallization as above. Prolonged heating in a vacuum at 80° causes decomposition, as does exposure to light [Found: C, 68·9; H, 5·6; P, 13·4; Ru, 9·5; O, 0·4%; Cl, 0·0; *M* (C_6H_6), 768 (0·63% solution), 788 (0·86%). $C_{53}H_{52}P_4Ru$ requires C, 69·65; H, 5·7; P, 13·6; Ru, 11·1%; *M*, 914].

cis-*Hydridoethyldi-*(1,2-*bisdiphenylphosphinoethane*)*ruthenium*(II) was obtained from 1 : 4 light petroleum–benzene (65% yield), as a monosolvate (Found: C, 71·55; H, 5·9. $C_{60}H_{60}P_4Ru$ requires C, 71·6; H, 6·0%). Heating it in a vacuum at 80° for 90 min. gave the unsolvated complex (Found: C, 69·8; H, 5·9. $C_{54}H_{54}P_4Ru$ requires C, 69·9; H, 5·9%).

cis-*Hydrido-n-propyldi-*(1,2-*bisdiphenylphosphinoethane*)*ruthenium*(II) crystallized as above in 70% yield. This compound crystallized with a molecule of benzene, which was not removed after 13 hr. at 60° in a vacuum (Found: C, 72·0; H, 6·1. $C_{61}H_{62}P_4Ru$ requires C, 71·8; H, 6·1%).

Hydridomethyldi-(1,2-*bisdiphenylphosphinoethane*)*osmium*(II) was prepared from the *cis*-chloridomethyl complex and crystallized from 1 : 1 light petroleum–benzene as a monosolvate (35% yield) (Found: C, 65·15; H, 5·6. $C_{59}H_{58}OsP_4$ requires C, 65·5; H, 5·4%).

Hydridoethyldi-(1,2-*bisdiphenylphosphinomethane*)*osmium*(II) was obtained as in the preceding case as a hemisolvate (55% yield) (Found: C, 64·1; H, 5·0. $C_{55}H_{53}OsP_4$ requires C, 64·2; H, 5·3%).

trans-*Hydridophenyldi-*(1,2-*bisdimethylphosphinoethane*)*ruthenium*(II). *trans*-Chloridophenyldi-(1,2-bisdimethylphosphinoethane)ruthenium(II) (0·44 g.) in tetrahydrofuran (10 ml.) was treated with an excess of lithium aluminium hydride in tetrahydrofuran, to give a colourless solution. After 5 minutes' refluxing, the solvent was evaporated in a stream of nitrogen, leaving an oily solid. Extraction by boiling light petroleum (3 × 25 ml.) gave a white solid, which, on crystallization from light petroleum gave the pure *complex* in 35% yield [Found: C, 45·55; H, 7·9; P, 25·7; Ru, 21·6%; *M* (C_6H_6), 484 (0·53% solution). $C_{18}H_{38}P_4Ru$ requires C, 45·1; H, 8·0; P, 25·85; Ru, 21·2%; *M*, 480].

*Hydrido-*p-*tolydi-*(1,2-*bisdimethylphosphinoethane*)*ruthenium*(II) was similarly obtained in 30% yield (Found: C, 46·5; H, 8·1. $C_{19}H_{40}P_4Ru$ requires C, 46·2; H, 8·2%).

Dipole Moments.—These were determined (see Table 4) as described in ref. 6 where the symbols are explained.

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