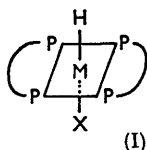


511. *Hydrido-complexes of Ruthenium(II) and Osmium(II).*

By J. CHATT and R. G. HAYTER.

A series of hydrido-complexes of the types *trans*-[MHX(chelate)₂] (I) (M = Ru, Os; X = Cl, Br, I, H, SCN, CN, NO₂; chelate = a chelating ditertiary phosphine) has been prepared and shown to have considerable thermal stability, especially when the diphosphine contains aromatic groups. The unique hydrogen atom shows a large chemical shift in the nuclear magnetic resonance spectrum and causes an absorption band (ν_{M-H}) (M = Ru, Os) in the infrared spectrum in the region 1600—2050 cm.⁻¹. The dipole moments (X ≠ H) are of the order 5 D. The effect of X on ν_{M-H} is discussed and a possible correlation with kinetic data suggested.

AFTER the discovery of planar hydrido-complexes of platinum(II)¹ stabilised by tertiary phosphines, and possibly of the unstable analogous compounds of palladium(II)¹ and nickel(II),² we set out to prepare similar octahedral complexes and here we describe the preparation and properties of ruthenium and osmium hydrido-complexes of the general types *trans*-[MHX(diphosphine)₂] (I).³



M = Ru, Os.

X = Cl, Br, I, H, SCN, CN, or NO₂.

P-P = C₂H₄(PR₂)₂ (R = Me, Et, Ph),
CH₂(PPh₂)₂, or o-C₆H₄(PEt₂)₂.

(I)

The ruthenium and osmium compounds are similar in properties, those of osmium being slightly more stable thermally but more rapidly oxidised by air.

Hydrido-Complexes of Ruthenium(II).—The complex hydrido-halides of ruthenium(II), which are all of *trans*-configuration, were prepared by reduction of the dihalogeno-complexes,⁴ *cis*-[RuX₂(diphosphine)₂] (X = Cl, Br, or I), with lithium aluminium hydride in ether or tetrahydrofuran, followed by treatment with ethanol to destroy any residual

¹ Chatt, Duncanson, and Shaw, *Proc. Chem. Soc.*, 1957, 343.

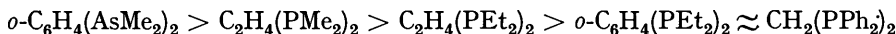
² Green, Street, and Wilkinson, *Z. Naturforsch.*, 1959, 14b, 738.

³ For preliminary communications see: Chatt and Hayter, *Proc. Chem. Soc.*, 1959, 153; Chatt, Hart, and Hayter, *Nature*, 1960, 187, 55.

⁴ Chatt and Hayter, *J.*, 1961, 896.

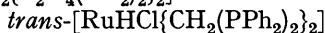
tetrahydride, dihydride, or AlH_4^- complexes which had been produced. The *trans*-dihalides were not reduced by this reagent.

The hydrido-halides are colourless or pale yellow crystalline solids, often melting without decomposition in a vacuum, and thermally stable to about 300° . The solid hydrides decompose slowly in contact with moist air, the rate of decomposition decreasing roughly in order of ligands:

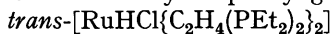


The complex $[\text{RuHCl}\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2]$ was too unstable to be crystallised or fully characterised; *trans*- $[\text{RuHCl}\{\text{CH}_2(\text{PPh}_2)_2\}_2]$ darkens slowly in air over a period of days. The hydrides are soluble in most organic solvents, those with the aliphatic ligands being very soluble even in light petroleum. The complex *trans*- $[\text{RuHCl}\{\text{C}_2\text{H}_4(\text{PMe}_2)_2\}_2]$ is also soluble in dilute aqueous ammonia and was recovered in good yield on rapid neutralisation with dilute hydrochloric acid. An excess of acid gave hydrogen and *cis*- $[\text{RuCl}_2\{\text{C}_2\text{H}_4(\text{PMe}_2)_2\}_2]$. Treatment of *trans*- $[\text{RuHCl}\{o\text{-C}_6\text{H}_4(\text{PEt}_2)_2\}_2]$ with an equivalent of hydrogen chloride in ether gave a mixture of *trans*- (25%) and *cis*-dichloro-complex (75%).

The chloride ion in *trans*- $[\text{RuHCl}\{\text{C}_2\text{H}_4(\text{PR}_2)_2\}_2]$ ($\text{R} = \text{Me}, \text{Et}$) is labile, as it is in *trans*- $[\text{PtHCl}(\text{PR}_3)_2]$,⁵ and it can be replaced by iodide, thiocyanate, cyanide, or nitrite anions, on treatment with the corresponding alkali-metal salt, as well as by hydrogen on treatment with lithium aluminium hydride. This lability contrasts with the inertness of the chloride ion in *trans*- $[\text{RuCl}_2\{\text{C}_2\text{H}_4(\text{PR}_2)_2\}_2]$. The chloride ion in



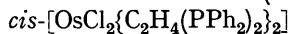
is inert, probably owing to steric hindrance by the phenyl groups.



was recovered unchanged after attempts at alkylation with diazomethane or with ethylene at $80^\circ/40$ atm. The hydrido-complexes obtained are listed in Table 1, together with certain physical properties. It was not possible to obtain *trans*- $[\text{RuHCl}\{\text{C}_2\text{H}_4(\text{PPh}_2)_2\}_2]$ because the corresponding *cis*-dichloro-complex⁴ is not available for reduction.

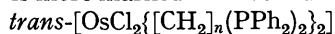
The two complex ruthenium dihydrides in Table 2 were prepared by reduction of the corresponding hydrido-halide, *trans*- $[\text{RuHX}(\text{diphosphine})_2]$, or *cis*-dihalide with lithium aluminium hydride, the use of hydroxylic solvents being avoided. They are paler, more soluble and more rapidly oxidised by air than the corresponding hydrido-halides.

Hydrido-complexes of Osmium(II).—The complex hydrido-halides and dihydrides of osmium were prepared similarly to those of ruthenium (see Table 1). Since



is available *trans*- $[\text{OsHCl}\{\text{C}_2\text{H}_4(\text{PPh}_2)_2\}_2]$, C_6H_6 was obtained, although the corresponding ruthenium compound is unknown.

The chloro-complexes of ruthenium(II) with the ligands $[\text{CH}_2]_n(\text{PPh}_2)_2$ ($n = 1$ or 2) tend to solvate; this tendency is more marked with osmium. Thus,



crystallises as a solvate with chloroform, which is retained in a vacuum at 80° , while *trans*- $[\text{OsHCl}\{[\text{CH}_2]_n(\text{PPh}_2)_2\}_2]$ crystallises with a tightly-held molecule of benzene. In the hydrido-chloride ($n = 1$), the benzene is not removed by crystallisation from ethyl acetate and has the unusual property of suppressing the band due to the Os-H stretching vibration in the infrared spectrum. This benzene is about 50% removed by evacuation at 100° for 48 hr. and the infrared spectrum (Nujol mull) then shows a weak $\nu_{\text{Os-H}}$ band at 2077 cm^{-1} . If this compound is prepared in the absence of benzene, it crystallises solvated from ethyl acetate and its infrared spectrum then shows strong bands due to $\nu_{\text{Os-H}}$ (2074 cm^{-1}) and $\nu_{\text{C=O}}$ (1735 cm^{-1}). Models show that the benzene molecule is a suitable size to fit in the cavity above the hydridic hydrogen. This is unlikely to suppress the Os-H stretching vibration completely, but probably makes it inactive in the infrared region.

⁵ Basolo, Chatt, Gray, Pearson, and Shaw, *J.*, 1961, 2207.

The complex $trans\text{-}[\text{RuHCl}\{\text{CH}_2(\text{PPh}_2)_2\}_2]$ was similarly solvated with $\frac{1}{2}\text{C}_6\text{H}_6$ or 1.5EtOAc, but the solvent was not so tightly held and $\nu_{\text{Ru-H}}$ was still observed.

Structure.—The *trans*-octahedral structure of the hydrido-chlorides and dihydrides of ruthenium and osmium was established by dipole moment and nuclear magnetic resonance

TABLE I. *Tertiary phosphine and arsine hydrido-complexes of ruthenium(II) and osmium(II)*.

Compound	M. p. (vacuum)	Colour *	Dipole moment (D)	$\nu_{\text{Ru-H}}$ (cm.^{-1}) ‡	Chemical shift (p.p.m., H_2O standard)
I <i>trans</i> - $[\text{RuHCl}\{\text{C}_2\text{H}_4(\text{PEt}_2)_2\}_2]$	174.5—176°	—	4.9 ^e	1938	+27.1 ^e
II <i>trans</i> - $[\text{RuHBr}\{\text{C}_2\text{H}_4(\text{PEt}_2)_2\}_2]$	188—190 †	Yellow	5.65 ^e	1945	+26.3 ^e
III <i>trans</i> - $[\text{RuHI}\{\text{C}_2\text{H}_4(\text{PEt}_2)_2\}_2]$	212—224 †	Yellow	5.8	1948	+24.6 ^e
IV <i>trans</i> - $[\text{RuH}(\text{SCN})\{\text{C}_2\text{H}_4(\text{PEt}_2)_2\}_2]$	245—249 †	—	—	1919	—
V <i>trans</i> - $[\text{RuH}(\text{CN})\{\text{C}_2\text{H}_4(\text{PEt}_2)_2\}_2]^a$	—	—	—	1803	—
VI <i>trans</i> - $[\text{RuH}_2\{\text{C}_2\text{H}_4(\text{PEt}_2)_2\}_2]$	147—153	—	2.1 ^e	1615 ^f	—
VII <i>trans</i> - $[\text{RuHCl}\{\text{C}_2\text{H}_4(\text{PMe}_2)_2\}_2]$	217—221	—	4.8 ^e	1891	—
VIII <i>trans</i> - $[\text{RuHBr}\{\text{C}_2\text{H}_4(\text{PMe}_2)_2\}_2]$	215—220 † ^d	Yellow	—	1895	—
IX <i>trans</i> - $[\text{RuHI}\{\text{C}_2\text{H}_4(\text{PMe}_2)_2\}_2]$	322 †	Yellow	—	1898	—
X <i>trans</i> - $[\text{RuH}(\text{SCN})\{\text{C}_2\text{H}_4(\text{PMe}_2)_2\}_2]$	240 †	—	—	1870 ^b	—
XI <i>trans</i> - $[\text{RuH}(\text{CN})\{\text{C}_2\text{H}_4(\text{PMe}_2)_2\}_2]$	230 †	Yellow	—	1754 ^b	—
XII <i>trans</i> - $[\text{RuH}(\text{NO}_2)\{\text{C}_2\text{H}_4(\text{PMe}_2)_2\}_2]$	240 †	Yellow	—	1858 ^b	—
XIII <i>trans</i> - $[\text{RuHCl}\{o\text{-C}_6\text{H}_4(\text{PEt}_2)_2\}_2]$	250—256 †	Yellow	4.45 ^e	1978 ^b (br)	—
XIV <i>trans</i> - $[\text{RuHI}\{o\text{-C}_6\text{H}_4(\text{PEt}_2)_2\}_2]$	278—283 †	Brown	—	1976 ^b (br)	—
XV <i>trans</i> - $[\text{RuH}_2\{o\text{-C}_6\text{H}_4(\text{PEt}_2)_2\}_2]$	276.5—278.5 †	Yellow	1.2 ^e	1617 ^b	—
XVI <i>trans</i> - $[\text{RuHCl}\{\text{CH}_2(\text{PPh}_2)_2\}_2, \frac{1}{2}\text{C}_6\text{H}_6]$	283—284.5 †	Yellow	4.95 ^e	1978 ^f	—
XVII <i>trans</i> - $[\text{RuHCl}\{o\text{-C}_6\text{H}_4(\text{AsMe}_2)_2\}_2]^a$	190 † ^d	—	—	1804	—
XVIII <i>trans</i> - $[\text{OsHCl}\{\text{C}_2\text{H}_4(\text{PEt}_2)_2\}_2]$	170.5—171.5	—	4.6 ^e	2039	+31.3
XIX <i>trans</i> - $[\text{OsHI}\{\text{C}_2\text{H}_4(\text{PEt}_2)_2\}_2]$	224—231	Yellow	—	2051	+26.1
XX <i>trans</i> - $[\text{OsH}(\text{SCN})\{\text{C}_2\text{H}_4(\text{PEt}_2)_2\}_2]$	200 †	—	—	2009	—
XXI <i>trans</i> - $[\text{OsH}_2\{\text{C}_2\text{H}_4(\text{PEt}_2)_2\}_2]$	150—155	—	—	1721 ^f	—
XXII <i>trans</i> - $[\text{OsHCl}\{\text{C}_2\text{H}_4(\text{PMe}_2)_2\}_2]$	190—205 †	—	5.05 ^e	2014 ^f	—
XXIII <i>trans</i> - $[\text{OsHCl}\{\text{C}_2\text{H}_4(\text{PPh}_2)_2\}_2, \text{C}_6\text{H}_6]$	313.5—318 †	Yellow	—	2046 ^f	—
XXIV <i>trans</i> - $[\text{OsHCl}\{\text{CH}_2(\text{PPh}_2)_2\}_2, \text{C}_6\text{H}_6]$	294.5—298.5 †	Yellow	3.85	2045 ^b	—
XXV <i>trans</i> - $[\text{OsH}_2\{o\text{-C}_6\text{H}_4(\text{PEt}_2)_2\}_2]$	293—297	Lemon	—	1720 ^b	—

* Colourless unless stated. † With decomp. ‡ n-Hexane solutions unless marked.

^a Not pure. ^b Benzene solution. ^c Chloroform solution. ^d In air. ^e Calc. from estimated values of densities and refractivities. ^f Nujol mull.

measurements. The moments of the hydrido-chlorides are in the range 3.8—5.0 D, similar to that of $trans\text{-}[\text{PtHCl}(\text{PEt}_2)_2]$ (4.2 D).

The chemical shifts of the unique protons in the complex hydrides (see Table I) are large, even for transition-metal hydrides. The proton resonance consists of five equally spaced bands with intensities roughly in the ratios 1 : 4 : 6 : 4 : 1, although, in some cases, only the three more intense centre bands were visible. This pattern confirms the *trans*-configuration, being consistent with the coupling of the hydrogen nucleus to four equivalent phosphorus nuclei, each of spin $\frac{1}{2}$.

If these large chemical shifts were due entirely to diamagnetic shielding, the hydridic hydrogen would appear to be associated with about twice as many electrons as the hydrogen in water, whose chemical shift relative to the unshielded proton is +27 p.p.m. The hydridic hydrogen should thus be negatively charged but the dipole moments indicate that it carries a slight positive charge; evidently diamagnetic shielding is not the main cause of the large shifts, and it seems likely that some other effect, such as paramagnetic circulation on the metal atom, is mainly responsible.⁶

Infrared Spectra.—The infrared spectra of the complex hydrido-halides show strong metal-hydrogen stretching bands ($\nu_{\text{M-H}}$) in the region 1800—2050 cm.^{-1} (see Table). This assignment was confirmed from the infrared spectrum (hexachlorobutadiene mull) of

⁶ Bishop, Down, Emtage, Richards, and Wilkinson, *J.*, 1959, 2484.

trans-[RuDCl(C₂H₄(PEt₂)₂)₂] (prepared from *cis*-[RuCl₂{C₂H₄(PEt₂)₂}₂] and LiAlD₄) which showed a weakened $\nu_{\text{Ru-H}}$ band at 1954 cm.⁻¹, as well as a new partially obscured band at 1410 cm.⁻¹ ($\nu_{\text{Ru-D}}$) [isotopic shift factor (1.92)⁻¹]. Another new band was observed in the spectrum of the deuteride at 516 cm.⁻¹, and was tentatively assigned to $\delta_{\text{R-D}}$. The corresponding region in the spectrum of the hydride was obscured by strong absorption. $\nu_{\text{M-H}}$ is about 100 cm.⁻¹ higher in an osmium compound than in the corresponding ruthenium compound.

The frequencies, $\nu_{\text{M-H}}$, in the compounds *trans*-[MHX{C₂H₄(PR₂)₂}₂] (M = Ru, Os; R = Me, Et) are of interest because they depend markedly on the anionic ligand X and can be correlated with certain kinetic data, as they can in the analogous series of platinous complexes *trans*-[PtHX(PEt₃)₂]. In the platinum series the sequence of decreasing $\nu_{\text{Pt-H}}$ is X = NO₃ > Cl > Br > I > NO₂ > SCN > CN.⁷ This is closely similar to the sequence of decreasing reactivity of the group X in [Pt dien X]⁺ in reaction with pyridine where the order is NO₃ > Cl > Br > I > SCN > NO₂ > CN⁸ and to the *trans*-effect series as established by Russian workers.^{9,7}

Such extensive data are not available in the ruthenium and osmium series of complexes but signs of a similar relationship can be found. The sequence of $\nu_{\text{M-H}}$ (M = Ru, Os) in complexes of C₂H₄(PR₂)₂ (R = Me, Et) (see Table 1) is I > Br > Cl > SCN > NO₂ > CN > H. The complexes of the *o*-phenylenediphosphine give broad bands whose positions are not as well defined. This sequence shows a gross similarity to that of the platinous compounds, *viz.*, halide > (SCN, NO₂) > CN, but is different in detail, notably in the reversed sequence of the halides. Kinetic data on the displacement of X from ruthenium(II) and osmium(II) complexes are not available, but in the displacement of X by water from the cobalt(III) complexes [Co(NH₃)₅X]⁺, which are isoelectronic in the valency shell, the order of decreasing reactivity of X is I > Br > Cl > SCN > NO₂,¹⁰ in which the reversed order of halogens also appears. No *trans*-effect series has been established for ruthenium(II) or osmium(II) complexes, but we know qualitatively that the hydride ion has a high *trans*-effect (p. 2606), as in the platinous series,⁵ and so should occur near CN in the *trans*-effect series. It is observed near CN in the $\nu_{\text{Ru-H}}$ series, and if the value of $\nu_{\text{Ru-H}}$ is a reliable guide it has an even greater *trans*-effect than CN, hitherto considered to have the greatest *trans*-effect of anionic ligands.

Thus it appears that a similar relationship between $\nu_{\text{M-H}}$, lability, and *trans*-effect of the anionic ligands, X, may exist in both octahedral and square-planar complexes. There are slight differences in the detailed sequence of the ligands X when they are arranged in order of the magnitudes of the above effects, depending mainly on the metal in the complex. These differences are probably related to differences in the π -bonding capacities of the metals, as suggested by Basolo, Gray, and Pearson⁸ in discussing the kinetic series. The "platinum sequence" would be characteristic of the stronger dative π -bonding metals and the "ruthenium-osmium sequence" of moderately dative π -bonding metals. The same distinction may also apply to square-planar *versus* octahedral complexes in general, because in square-planar complexes with the vacant *p_z*-orbital, dative π -bonding is enhanced by *dp*-hybridisation.¹¹

The chelating ligand also influences $\nu_{\text{M-H}}$ in the hydrido-halide complexes. Thus in the series *trans*-[RuHCl(chelate)₂] $\nu_{\text{M-H}}$ falls from 1978 to 1804 cm.⁻¹ in a sequence which appears to be roughly that of decreasing electronegativity and double-bonding capacity of the ligands, *viz.*, *o*-C₆H₄(PEt₂)₂ \approx CH₂(PPh₂)₂ > C₂H₄(PEt₂)₂ > C₂H₄(PMe₂)₂ > *o*-C₆H₄(AsMe₂)₂.

⁷ Chatt, Duncanson, and Shaw, *Chem. and Ind.*, 1958, 859.

⁸ Basolo, Gray, and Pearson, *J. Amer. Chem. Soc.*, 1960, **82**, 4200.

⁹ See Hel'man, *Izvest. Sekt. Platiny drug. blagovod. Metal., Inst. obshchei neorg. Khim.*, 1954, **28**, 88.

¹⁰ See Basolo and Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, 1958, p. 122.

¹¹ Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, **332**.

EXPERIMENTAL

Microanalyses were by the Microanalytical Department of these Laboratories. M. p.s were determined on a Kofler hot stage, unless otherwise stated. The complex hydrides were manipulated in an atmosphere of dry nitrogen. Light petroleum was the fraction of b. p. 60—80°. For the dihalogeno-complexes used in the following preparations see ref. 4.

Preparation of Hydrido-complexes of Ruthenium(II) and Osmium(II).—(i) *Hydrido-halides. cis-Dichlorodi-}{1,2-bis(diethylphosphino)ethane}ruthenium* (0.20 g.) was dissolved in dry tetrahydrofuran (10 ml.) and treated with an excess of lithium aluminium hydride in tetrahydrofuran under nitrogen. The original yellow solution rapidly became colourless and, after 5 minutes' refluxing, ethanol was slowly added until effervescence ceased. Solvent was then removed at 12 mm. and the benzene-soluble portion of the white residue crystallised from light petroleum, yielding pure *trans-hydridochlorodi-}{1,2-bis(diethylphosphino)ethane}ruthenium*(II) (I) (0.13 g., 61%) as needles, decomp. 310° in a vacuum (Found: C, 43.6; H, 9.0; Cl, 2.1%; *M*, ebullioscopically in benzene, 570. $C_{20}H_{49}ClP_4Ru$ requires C, 43.7; H, 9.0; Cl, 6.45% *M*, 550). This compound has a magnetic susceptibility in the solid state of -0.45×10^{-6} c.g.s. units.

The following compounds were similarly prepared from the corresponding *cis*-dihalogeno-complexes:

trans-Hydridobromodi-}{1,2-bis(diethylphosphino)ethane}ruthenium(II) (II) (50% yield), tablets from light petroleum (Found: C, 39.9; H, 8.3. $C_{20}H_{49}BrP_4Ru$ requires C, 40.4; H, 8.3%).

trans-Hydridoiododi-}{1,2-bis(diethylphosphino)ethane}ruthenium(II) (III) (55% yield), feathery plates from light petroleum (Found: C, 37.5; H, 7.7%; *M*, ebullioscopically in benzene, 622. $C_{20}H_{49}IP_4Ru$ requires C, 37.45; H, 7.7%; *M*, 641.5), magnetic susceptibility -1.0×10^{-6} c.g.s. units in the solid state.

trans-Hydridochlorodi-}{1,2-bis(dimethylphosphino)ethane}ruthenium(II) (VII) (35% yield), needles from light petroleum (Found: C, 33.1; H, 7.3. $C_{12}H_{33}ClP_4Ru$ requires C, 32.9; H, 7.6%), sublimes unchanged in a vacuum at 120° and decomposes at $\sim 300^\circ$.

trans-Hydridobromodi-}{1,2-bis(dimethylphosphino)ethane}ruthenium(II) (VIII) (32%), needles from light petroleum (Found: C, 29.7; H, 6.9. $C_{12}H_{33}BrP_4Ru$ requires C, 29.9; H, 6.9%), sublimes at $< 280^\circ$.

trans-Hydridoiododi-}{1,2-bis(dimethylphosphino)ethane}ruthenium(II) (IX) (55%), needles (Found: C, 27.3; H, 6.2; I, 24.3. $C_{12}H_{33}IP_4Ru$ requires C, 27.2; H, 6.3; I, 24.0%).

trans-Hydridochlorodi-}{o-phenylenebis(diethylphosphino)ethane}ruthenium(II) (XIII) (75%), prisms from 2:1 benzene–light petroleum (Found: C, 51.8; H, 7.6%; *M*, ebullioscopically in 1.2% benzene solution, 674; in 1.57% solution, 650. $C_{28}H_{49}ClP_4Ru$ requires C, 52.05; H, 7.6%; *M*, 646).

trans-Hydridoiododi-}{o-phenylenebis(diethylphosphino)ethane}ruthenium(II) (XIV) (70%), from 2:1 benzene–light petroleum (Found: C, 45.5; H, 6.7. $C_{28}H_{49}IP_4Ru$ requires C, 45.6; H, 6.7%).

trans-Hydridochlorodi-}{1,2-bis(diphenylphosphino)ethane}ruthenium(II) (XVI) (75%), prisms from 2:1 benzene–light petroleum, crystallising with 0.5 mol. of benzene, which is not removed in a vacuum at 100° in 48 hr. (Found: C, 67.5; H, 5.4. $C_{53}H_{48}ClP_4Ru$ requires C, 67.3; H, 5.1%). Subsequent crystallisation from ethyl acetate yielded yellow needles, m. p. 287.5—289° (decomp.; in a vacuum) (Found: C, 64.8; H, 5.4. $C_{50}H_{45}ClP_4Ru \cdot 1.5CH_3 \cdot CO_2C_2H_5$ requires C, 64.8; H, 5.5%). The infrared spectrum (Nujol mull) showed a strong band at 1735 cm^{-1} due to $\nu_{C=O}$ of the ester.

trans-Hydridochlorodi-}{1,2-bis(diethylphosphino)ethane}osmium(II) (XVIII) (47%), needles (from light petroleum), decomp. ca. 315° in a vacuum (Found: C, 37.95; H, 7.7. $C_{20}H_{49}ClOsP_4$ requires C, 37.6; H, 7.7%).

trans-Hydridoiododi-}{1,2-bis(diethylphosphino)ethane}osmium(II) (XIX) (45%), needles from light petroleum (Found: C, 32.8; H, 6.8. $C_{20}H_{49}IOsP_4$ requires C, 32.9; H, 6.8%). This compound was also prepared from the hydrido-chloride by treatment with lithium iodide in acetone and was identified by its infrared spectrum.

trans-Hydridochlorodi-}{1,2-bis(dimethylphosphino)ethane}osmium(II) (XXII) (21%), sublimed in a vacuum at 180° (Found: C, 27.1; H, 6.3. $C_{12}H_{33}ClOsP_4$ requires C, 27.35; H, 6.3%).

trans-Hydridochlorodi-}{1,2-bis(diphenylphosphino)ethane}osmium(II) (XXIII) (40%), plates

(from 5 : 1 benzene–light petroleum), solvated with a molecule of benzene (Found: C, 63·1; H, 5·2. $C_{58}H_{55}ClOsP_4$ requires C, 63·2; H, 5·0%).

trans-Hydrido-chlorodi-{1,2-bis(*di*phenylphosphino)ethane}osmium(II) (XXIV) (85%), needles (from 1 : 1 benzene–light petroleum), solvated with a molecule of benzene [Found: C, 62·3; H, 4·9%; *M*, ebullioscopic in benzene, 1157 (0·24% solution), 1108 (0·65%). $C_{56}H_{51}ClOsP_4$ requires C, 62·6; H, 4·8%; *M*, 1074]. Recrystallisation from ethyl acetate gave lemon-yellow needles, m. p. 294–296° (decomp.; in a vacuum), unchanged in infrared spectrum and analysis (Found: C, 62·3; H, 4·9%). Approximately half the solvated benzene was removed *in vacuo* at 100° in 48 hr. (Found: C, 61·2; H, 5·0. $C_{55}H_{48}ClOsP_4$ requires C, 61·55; H, 4·7%).

This compound was also prepared in the absence of benzene, ethyl acetate being used as solvent for crystallisation, and was obtained as yellow needles, m. p. 291–294° (decomp.; in a vacuum) (Found: C, 60·3; H, 4·8. $C_{50}H_{45}ClOsP_4$ requires C, 60·3; H, 4·6. $C_{50}H_{45}ClOsP_4 \cdot \frac{1}{2}CH_3 \cdot CO_2C_2H_5$ requires C, 60·1; H, 4·75%). The infrared spectrum (Nujol mull) shows the presence of ν_{Os-H} (2074 cm^{-1}), as well as bands due to ethyl acetate at 1735, 1235, and 1048 cm^{-1} .

(ii) *Metathetical replacement reactions.* (a) *trans-Hydrido-chlorodi*-{1,2-bis(*di*ethylphosphino)ethane}ruthenium(II) (0·10 g.) was dissolved in acetone (5 ml.) and treated with a solution of potassium thiocyanate (0·20 gm.) in acetone (5 ml.) under nitrogen. An immediate white precipitate appeared and, after 5 minutes' warming on a steam-bath, the solution was filtered and the solvent removed at 12 mm. The benzene-soluble portion of the white solid residue was crystallised from light petroleum, yielding pure *trans-hydridothiocyanatodi*-{1,2-bis(*di*ethylphosphino)ethane}ruthenium(II) (IV) as needles (0·03 g., 31%) (Found: C, 43·5; H, 8·35; N, 2·5. $C_{21}H_{45}NP_4RuS$ requires C, 44·0; H, 8·6; N, 2·45%), ν_{max} (in hexane) 2090s cm^{-1} (C≡N).

Similarly prepared were the following:

trans-Hydridothiocyanatodi-{1,2-bis(*di*methylphosphino)ethane}ruthenium(II) (X), prisms (from 1 : 1 benzene–light petroleum) (50%) (Found: C, 33·7; H, 7·45. $C_{13}H_{33}NP_4RuS$ requires C, 33·9; H, 7·2%), ν_{max} (in Nujol) 2098s cm^{-1} (C≡N).

trans-Hydridothiocyanatodi-{1,2-bis(*di*ethylphosphino)ethane}osmium(II) (XX), needles (22%) (from light petroleum) (Found: C, 38·4; H, 7·5; N, 2·3. $C_{21}H_{49}NOSP_4$ requires C, 38·1; H, 7·5; N, 2·1%), ν_{max} (in hexane) 2101 cm^{-1} .

(b) *trans-Hydrido-cyanodi*-{1,2-bis(*di*methylphosphino)ethane}ruthenium(II) (XI) was obtained when *trans*-[$RuHCl\{C_2H_4(PMe_2)_2\}_2$] (0·15 g.) in acetone (10 ml.) was refluxed with potassium cyanide (0·2 g.) in water (3 ml.) under nitrogen for 15 min.; the acetone layer then decanted and evaporated and the benzene-soluble residue crystallised from 1 : 1 benzene–light petroleum (20% yield; needles) (Found: C, 35·2; H, 7·8; N, 2·8. $C_{13}H_{33}NP_4Ru$ requires C, 36·45; H, 7·8; N, 3·3%; ν_{max} (Nujol mull) 2062vs cm^{-1}).

A similar attempt to prepare *trans*-[$RuH(CN)\{C_2H_4(PEt_2)_2\}_2$] (V) in dry acetone was only partially successful, the infrared spectrum (Nujol mull) of the product showing bands due to unchanged hydrido-chloride (1948 cm^{-1}) and to hydrido-cyanide (2069 and 1807 cm^{-1}).

Similarly prepared was *trans-hydridonitrodi*-{1,2-bis(*di*methylphosphino)ethane}ruthenium(II) (XII) needles (50%) (from 3 : 7 benzene–light petroleum) (Found: C, 32·2; H, 7·3; N, 3·4. $C_{12}H_{33}NO_2P_4Ru$ requires C, 32·1; H, 7·4; N, 3·1%), ν_{max} (Nujol mull) 1300s, 1258s, and 803s cm^{-1} (NO_2).

(iii) *Dihydrides.* *trans-Hydrido-chlorodi*-{1,2-bis(*di*ethylphosphino)ethane}ruthenium(II) (0·20 g.) in dry tetrahydrofuran (10 ml.) was treated with an excess of lithium aluminium hydride in tetrahydrofuran. The pale yellow solution immediately became colourless. After 5 min., the solution was filtered and evaporated in a stream of nitrogen, leaving a mixture of colourless solid and oil. The solid was extracted into light petroleum and crystallisation afforded pure *trans-dihydrido*-{1,2-bis(*di*ethylphosphino)ethane}ruthenium(II) (VI) as prisms (52 mg., 27%). This distils at about 160° and decomposes at 280° in an evacuated tube (Found: C, 46·4; H, 9·7. $C_{20}H_{50}P_4Ru$ requires C, 46·6; H, 9·8%).

trans-Dihydrido-{1,2-bis(*di*ethylphosphino)ethane}osmium(II) (XXI) was similarly prepared in 50% yield (prisms from light petroleum). A good analysis was not obtained, further crystallisation or distillation resulting in a slightly poorer analysis (Found: C, 40·9; H, 8·5. Calc. for $C_{20}H_{50}OsP_4$: C, 39·7; H, 8·3%). The infrared spectrum (Nujol mull) of the product is identical with that of *trans*-[$RuH_2\{C_2H_4(PEt_2)_2\}_2$], apart from the metal–hydrogen stretching bands.

Analogously prepared from the corresponding *cis*-dichloro-complexes were *trans*-dihydrido-*o*-phenylenebis(diethylphosphine)-ruthenium(II) (XV), prisms (50%) (from benzene) (Found: C, 54.9; H, 8.2. $C_{28}H_{50}P_4Ru$ requires C, 55.0; H, 8.2%), and -osmium(II) (XXV), prisms (70%) (from benzene) (Found: C, 48.2; H, 7.25. $C_{28}H_{50}OsP_4$ requires C, 48.0; H, 7.2%).

Physical Measurements.—The dipole moments were determined as described in ref. 12 and are recorded in Table 2. The moments of all the dihydrido-complexes were low, indicating a *trans*-configuration, but because of their great sensitivity to air and moisture exact moments were not determined.

TABLE 2. *Dipole moments.*

Compound	$10^3\omega$	$\Delta\epsilon/\omega$	$10^2\Delta n/\omega$	$-\Delta v/\omega$	τP	ϵP	oP	Dipole moment (D)
I	3.293	5.242						
	7.038	5.260						
	5.269			0.323				
	7.824			0.358	676	(165)	487 *	4.9 *
	7.208	6.145		(0.37)	826 *	(149)	655 *	5.65 *
II	3.401	6.150						
III	6.270	6.152						
	19.32		7.90					
	28.96		8.71					
	4.281			0.297				
	5.400			0.370	889	173	691	5.8
VII	3.523	6.228						
	5.026	6.145		(0.35)	614 *	(124)	471 *	4.8 *
XVI	1.406	3.284		(0.35)	804 *	(261)	504 *	4.95 *
XIII	5.483	3.709						
	5.692	3.689		(0.35)	604 *	(176)	401 *	4.45 *
XVIII	1.764	3.743						
	2.724	3.766		(0.35)	604 *	(145)	437 *	4.6 *
XII	1.496	5.294						
	3.209	5.253		(0.35)	649 *	(108)	524 *	5.05 *
XXIV	1.804	2.157						
	2.977	2.109						
	21.80		14.39					
	27.48		14.56					
	4.043			0.519	632	285	304	3.85

Estimated values are in parentheses. * Calc. from estimated values of densities and refractivities.

The magnetic resonance of the hydrogen nuclei was obtained at 40 Mc with a Varian Associates 4300B spectrometer, flux stabilisation and sample spinning being used. The chemical shifts were measured against cyclohexane as an internal standard on a scale defined so that the value for cyclohexane itself is +3.9. This scale for non-polar solvents approximates to one based on water as zero in aqueous solution. Addition of 4.66 to each chemical shift converts it to the τ scale.

The infrared spectra were recorded on a Grubb-Parsons G.S.2A spectrometer.

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¹² Chatt and Shaw, *J.*, 1959, 705.