Reactions Involving Transition Metals. Part IX.[1] The Structure and Isomerism of Some Dihalogenohydridotris(ligand)rhodium(III) Complexes

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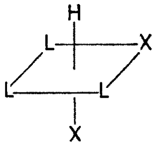
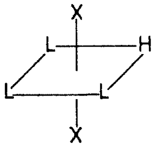
The isomers α- and β-[L_3RhHX_2] (L = tertiary phosphine or arsine, X = Cl or Br) are shown to have the same structures as the corresponding iridium complexes, *i.e.* a *mer*-configuration for the neutral ligands and hydride *trans* to halogen (α-form) or to the neutral ligand (β-form). The isomerisation β → α is enhanced by heat and light, but is inhibited in the presence of the free neutral ligand, indicating a dissociative mechanism. The bulky ligands $Ph_n(C_6H_{11})_{3-n}P$ (*n* = 0—3) and Ph_3As give products of variable stoicheiometry but only two neutral ligands appear to be co-ordinated to the metal.

HYDRIDO-COMPLEXES of iridium(III) of the type [L_3IrHX_2] (L = tertiary phosphine or arsine; X = Cl, Br, or I) are well characterised, and may be obtained by the interaction of the complexes [L_3IrX_3] with a base (*e.g.* KOH) in an alcohol (*e.g.* EtOH). Two isomeric forms have been isolated which have been assigned the structures [(I) α-form] and [(II) β-form] on the basis of i.r. and n.m.r. studies.[2,3] By contrast, the corresponding complexes of rhodium are less well-defined. Although in one case (L = Ph_2MeAs) the action of alcoholic potassium hydroxide leads to a hydrido-complex,[4] in other cases carbonyl complexes are formed.[5] For relatively weakly basic tertiary phosphines (*e.g.* Ph_3P or Ph_2EtP) the direct reaction of an excess of the ligand with an alcoholic solution of a rhodium halide gives the complexes [L_3RhHX_2];[6] more basic ligands (such as $PhMe_2P$ or Et_3P) yield only the trihalogeno-complexes [L_3RhX_3].[7] For these ligands hydrido-complexes may be obtained by the use of reducing agents (*e.g.* HPO_2[8] or Zn–HCl[4]), and two isomers have been reported,[6] denoted α and β on the basis of the values of the Rh–H stretching frequencies, by analogy with the corresponding iridium complexes. The α-form shows the higher frequency and Sacco *et al.*[6] have tentatively suggested that the hydride is *trans* to chloride (I) in this isomer and *trans* to a phosphine [*i.e.* (II) or (III)] in the β-isomer. Complexes of the type [L_2RhHX_2] (L = Ph_3P, Ph_3As, or Ph_3Sb) have also been obtained, by the oxidative addition of hydrogen chloride to the complexes [L_3RhX].[9,10] Although these complexes were difficult to obtain pure, they seem definitely to contain only two neutral ligands per rhodium atom, in contrast to the two reported[6] forms of [$(Ph_3P)_3RhHCl_2$]. Complexes of formula [L_2RhHCl_2] (L = $Bu^tPr^n_2P$, Bu^t_2MeP, Bu^t_2EtP, or $Bu^t_2Pr^nP$) have recently been obtained by reaction of the ligand and rhodium trichloride.[11]



(I)



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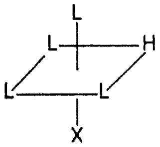

(III)

This investigation was undertaken in order to resolve this anomaly and to characterise these complexes more fully. Solutions of the complexes were found to be very sensitive to oxygen, but once this was realised it was possible to obtain reproducible diagnostic data. The complexes α- and β-[L_3RhHX_2] are found to be similar to the corresponding iridium complexes, but with triphenylphosphine and some other similar ligands bis-ligand complexes are formed. After the completion of our work, similar results were reported by Intille.[12]

RESULTS

Preparation.—The interaction of the trihydrate of rhodium trichloride or tribromide in hot ethanol with dimethylphenylphosphine or methyldiphenylarsine gave only the complexes *mer*-[L_3RhX_3]. With methyldiphenylphosphine, rhodium trichloride gave mixtures of the complexes *mer*-[$(Ph_2MeP)_3RhCl_3$] and α-[$(Ph_2MeP)_3RhHCl_2$]. No complexes could be isolated from this phosphine and rhodium tribromide, and the hydridodichloro- and trichloro-complexes gave intractable mixtures when treated with lithium bromide. The complexes α-[$(Ph_2MeP)_3RhHX_2$] (X = Cl or Br) were obtained by the addition of phosphinic acid to the refluxing ethanolic solutions, and the corresponding arsine complexes were obtained similarly. When this reaction was conducted at room temperature, the β-isomers were formed. The presence of additional water seems to be necessary to facilitate the reduction since in its absence the Ph_2MeAs–$RhBr_3$–HPO_2 system gave only the tribromo-complex.

Solutions presumed to contain the complexes [L_3RhCl] were prepared by treating the complex [$(C_8H_{14})_2RhCl$] or [$(C_2H_4)_2RhCl$] with the stoicheiometric amount of the ligand.[13] The addition of hydrogen chloride to these purple-red solutions gave an immediate colour change to yellow and the i.r. and n.m.r. spectra (see below) showed the presence of the complexes α-[L_3RhHX_2]. The addition of hydrogen bromide to a solution of [$(Ph_2MeP)_3RhCl$] gave a

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complex mixture of species (as shown by the n.m.r. spectra) even when stoicheiometric amounts were used at low temperature). Usually these solutions were used for further investigation without isolation of the complexes (see following paper [14]), but for L = $PhMe_2P$ and Et_3P attempts were made to obtain the solid complexes, without success. Removal of the solvent at room temperature gave sticky yellow solids which tenaciously retained variable amounts of solvent. Crystalline solids could be obtained by precipitation with hexane at low temperatures, but these decomposed on warming (at −60 °C for L = Et_3P and *ca.* −30 °C for L = $PhMe_2P$). Attempts to prepare these complexes at room temperature by reduction of the trihalide complexes failed.

The addition of hydrogen chloride to ' L_3RhCl ' solutions with L = $Ph_n(C_6H_{11})_{3-n}P$ (n = 0—3) or Ph_3As gave an immediate change in colour, but products of definite stoicheiometry could not be obtained. Yellow solids of various compositions were obtained, the analytical data depending on the initial concentration of the ligand employed. These solutions appeared to contain the hydrochlorides of the ligands in addition to the complexes. The original purple-red colour was instantly regenerated by the addition of any base or, more slowly, by the passage of nitrogen through, or reduction in pressure over, a solution of the triphenylphosphine complex.

N.m.r. Spectra (*Table* 1).—(i) *Low-field region.* For all the methyl-phosphine and -arsine complexes the low-field spectra (τ 8—9) are typical of the *mer*-configuration, *viz.* two sets of signals of relative intensity 1:2, the more intense set being to lower field.[3,15] For the phosphine complexes the typical coupling patterns are also found, the higher-field signal being a doublet (J_{P-H}, 10—16 Hz), while the lower-field set is an apparent triplet [^2J(P-H) + ^4J(P-H) = 7—8 Hz] owing to ' virtual coupling ' of the methyl protons with both the mutually *trans* phosphorus atoms. For the complex α-[$(PhMe_2P)_3RhHCl_2$] two such triplets are observed, indicating the lack of a plane of symmetry through the *trans*-phosphines.[3]

(ii) *High-field region.* All the hydrido-complexes give signals in the region τ 20—26. The isolated α-isomers and the solutions obtained by adding hydrogen chloride to the ligand/olefin-complex mixtures all give very similar spectra consisting of an overlapping pair of double triplets, with all coupling constants in the range 9—22 Hz. Thus, the hydride ligand must be *cis* to all three phosphines, two of which are equivalent, and coupling occurs with this pair (triplets), with the unique phosphine (doublets) and with the rhodium (doublets; ^{103}Rh, 100%, $I = \frac{1}{2}$). It is not possible to identify the rhodium–hydrogen and unique phosphorus–hydrogen coupling constants, but tentative assignments have been made.* The arsine complexes show only a simple doublet with coupling to rhodium.

The hydride-signals of the two β-isomers occur at lower field than for the corresponding α-isomers. For the phosphine complex a pair of double triplets is again seen, but the separation is much greater (206 Hz), indicating that the hydride is *trans* to the unique phosphine. This appears to be the largest such coupling constant reported for a complex of a Group VIII metal.

The spectra of the triphenyl-phosphine and -arsine complexes are similar to those previously reported.[9,10] The triphenylphosphine complex shows a well-resolved doublet of triplets the shape and pattern of which are independent of the total quantity of the phosphine present in the solution. It thus appears that only two phosphine molecules are coordinated. The coupling constant [^2J(P-H) ≈ 20 Hz] is slightly larger than that found previously,[10] and is also larger than that for the triplets of the α- and β-isomers, but is in the range normally associated with a hydride *cis* to two equivalent phosphines.

The spectra of solutions containing complexes of the cyclohexyl phosphines, $Ph_n(C_6H_{11})_{3-n}P$ (n = 0, 1, or 2), are very broad (50—300 Hz centred at *ca.* τ 26.3) but independent of the ligand concentration when three or more molar equivalents of the ligand are present. The signals are narrower at −75 °C, but no fine structure is resolved. At lower concentrations, there are indications of a second set of signals, appearing as a pair of doublets, *ca.* 4 p.p.m. upfield of the more intense resonances.

Infrared Spectra. *—(i) Rh–H *stretching modes.* The hydrido-complexes all show bands in the region 1 960—2 150 cm^{-1} which may be assigned to Rh–H stretching modes. For the α-isomers these bands lie in a relatively narrow range (2 060—2 130 cm^{-1}), while the two β-isomers give lower values (1 992—1 993 cm^{-1}). These values are consistent with structures in which the hydride is *trans* to halogen or to phosphine or arsine, respectively, as suggested earlier [6] and required by the n.m.r. spectra. Reasonable agreement with previous reports is found, making allowance for the variety of media used. The spectra of the triphenyl-phosphine and -arsine complexes are similar to those reported by Wilkinson [9,10] and to Sacco's ' β-$(Ph_3P)_3RhHCl_2$ '.

(ii) *Rh-Cl stretching modes.** The rhodium–chlorine stretching modes of the chloro-complexes were identified by comparison with the corresponding bromo-complexes. The spectra of the complexes [L_3RhCl_3] show three bands, in agreement with previous reports,[15] and confirm the *mer*-configuration indicated by the n.m.r. spectra. The complexes α-[L_3RhHCl_2] (L = Ph_2MeP or Ph_2MeAs) show two Rh–Cl stretching modes at 270 and 284—288 cm^{-1}, which must represent chloride *trans* to L and to hydride. The *trans*-influence of hydride is normally considered to be greater than that of phosphine or arsine ligands [see ref. 16 for a summary of data for iridium(III) compounds], but the higher-frequency bands are similar in position to that of *trans*-[$(dppe)_2RhHCl$]BPh_4 (dppe = 1,2-bisdiphenylphosphinoethane) and are tentatively assigned to chloride *trans* to hydride. The complexes β-[L_3RhHCl_2] (L = Ph_2MeP, Ph_2MeAs) have bands at higher frequency still (*ca.* 320 cm^{-1}), characteristic of chloride *trans* to chloride.

Isomerisation.—The isomerisation of the complexes β-[L_3RhHCl_2] (L = Ph_2MeP or Ph_2MeAs) to the α-form proceeds readily in solution and is accelerated by heat. Under normal conditions of temperature and illumination the phosphine complex isomerises completely in 1 h in dichloromethane solution, whereas the arsine complex requires *ca.* 12 h. These reactions were followed by i.r. and n.m.r. spectroscopy. The isomerisation of the phosphine complex is considerably retarded by keeping the solution in the dark

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* See Supplementary Publication No. SUP 21469 (5 pp.); for details of Scheme see Notice to Authors No. 7, *J.C.S. Dalton*, **1974**, Index issue (items less than 10 pp. are supplied as full-size copies).

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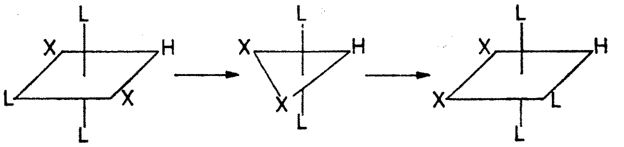
and is completely inhibited by the addition of an excess of the phosphine.

DISCUSSION

The observations of previous workers [6-10] have been confirmed and extended. Two forms of the complexes $[L_3RhHX_2]$ can be obtained. The β-isomers are formed by the action of ethanolic phosphinic acid on the complexes $[L_3RhX_3]$ in the cold. On warming the α-isomers are obtained, presumably by isomerisation. The complexes $[L_3RhX_3]$ of the more basic ligands appear to be resistant to reduction by an excess of the ligand, as reported previously,[6] and the most satisfactory route to the α-isomers is by the oxidative addition of hydrogen chloride to the complexes $[L_3RhCl]$. Intille [12] reports that, for $L = Me_3P$, Me_2PhP, or Et_3P, oxidative addition gives initially the β-form. We did not observe this; the difference in reaction media may be significant. However, the α-complexes of these more basic ligands are surprisingly difficult to isolate, although more stable in solution than many of the complexes which can be obtained in crystalline form.[14]

The i.r. and n.m.r. data show unambiguously that the α-isomers have configuration (I) and the β-isomers have configuration (II). Structurally, the rhodium complexes are precisely similar to the corresponding iridium complexes.[2,3] The downfield shift and reduction in coupling constants for hydride *trans* to a phosphine rather than to a halide is similar to that found in other systems. The Rh–H coupling constant is also reduced when phosphine ligands are replaced by arsines.

The isomerisation (β ⟶ α) proceeds more readily than for the corresponding iridium complexes and, like the latter,[17] is accelerated by light. The reaction is inhibited by the addition of the free ligand, which suggests a dissociative mechanism. This presumably involves loss of the ligand *trans* to the hydride and formation of a trigonal bipyramidal intermediate or transition state. The corresponding iridium complexes are known to undergo ready replacement of this ligand,[18] by a mechanism involving initial attack by the solvent, but no isomerisation is observed suggesting greater steric rigidity for the intermediate. In the rhodium case there is no definite evidence that the ligand which dissociates is that *trans* to the hydride. It is possible that one of the other neutral ligands is lost, as appears to happen for the dihydrido-complex $[(Ph_2MeP)_3RhH_2Cl]$.[13] If dissociation of this type occurred, a rearrangement of the trigonal bipyramidal intermediate would be required.



Another possible mechanism, involving reductive elimination of hydrogen halide, is apparently supported by our observation that only the α-isomers are formed in solutions of $[L_3RhX]$, but does not account for the observed inhibition by the ligand.

$$\beta\text{-}[L_3RhHX_2] \xrightarrow{-HX} \text{‘}L_3RhX\text{’} \xrightarrow{HX} \alpha\text{-}[L_3RhHX_2]$$

The least-stable complexes obtained were those of the ligands $Ph_n(C_6H_{11})_{3-n}P$ ($n = 0$—3) and Ph_3As, for which satisfactory analytical data could not be obtained. Similar results have been found by other workers for the triphenyl ligands,[9,10] although two forms of a complex with analyses consistent with formulation as $[(Ph_3P)_3RhHCl_2]$ have been reported by Sacco.[6] The n.m.r. spectra of the triphenylphosphine complex clearly indicate that only two phosphine ligands are co-ordinated, even when an excess of ligand is present. Products of composition $[(Ph_3P)_3RhHCl_2]$ could be obtained by using the appropriate quantity of the phosphine, but there is no evidence to suggest that this is a definite compound. The i.r. and n.m.r. spectra of products in the composition range $(Ph_3P)_{2.0-3.7}RhHCl_2$ were identical. Resolved n.m.r. spectra could not be obtained with the cyclohexylphosphines, but the additional signals observed with a deficiency of these ligands suggest the presence of a species containing only one co-ordinated phosphine. It therefore seems reasonable to suggest that the major species observed in these cases are also bis-phosphine complexes. The analytical data are also closer to those required by this formulation, although no hydrido-complex with tricyclohexylphosphine could be isolated. Since the basicities of the cyclohexylphosphines are not greatly different from those of, for example, the corresponding ethylphosphines, the co-ordination of only two ligands must be a steric effect. Similar trends have been found for the complexes $[L_nReNCl_2]$, where $n = 2$ for $L = Ph_3P$, $n = 2$ or 3 for $L = Ph_2EtP$, Ph_2Pr^iP, and $n = 3$ for less bulky ligands.[19] Similarly, the complexes of phosphines containing t-butyl groups have stoicheiometry L_2RhHCl_2.[11] A difference in co-ordination number and presumably in electron density on the metal, between the complexes of the cyclohexyl phosphines and those of the other alkyl phosphines, might explain the great differences in the stabilities of the complexes to loss of hydrogen chloride.[14] The structures of the bis-phosphine complexes may be similar to the square-pyramidal configuration reported recently [11] for $[(Bu^tPr^n{}_2P)_2RhHCl_2]$, although the higher Rh–H stretching frequencies and lower hydride chemical-shift values suggest a different structure, possibly closer to a trigonal bipyramidal form analogous to that found for the silyl complex $[(Ph_3P)_2RhH(SiCl_3)Cl]\cdot 0.3HSiCl_3$.[20]

EXPERIMENTAL

All reactions were carried out under nitrogen and all solvents were degassed and saturated with nitrogen immediately before use. I.r. and n.m.r. spectra were obtained using Perkin-Elmer 621 and Varian HA100 spectrometers.

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Analytical and molecular weight data are presented in the Table.

Analytical data

	Decomp. pt. (t/°C)	Found (%)		Calc. (%)	
		C	H	C	H
$[(Ph_2MeP)_3RhCl_3]$	159	57.8	4.9	57.8	4.8
$[(Ph_2MeAs)_3RhCl_3]$	191—195	50.0	4.2	49.7	4.1
$[(Ph_2MeAs)_3RhBr_3]$	216—219	45.7	3.8	43.5	3.7
$[(PhMe_2P)_3RhCl_3]$	218—221	46.9	5.2	46.2	5.2
$[(PhMe_2P)_3RhBr_3]$	231—235	38.1	4.7	37.9	5.1
$[(Ph_3P)_2RhHCl_2]$		60.5 [a]	4.7 [a]	61.9	4.5
$[(Ph_3As)_2RhHCl_2]$		52.9 [a]	4.3 [a]	54.8	3.9
$[(Ph_2C_6H_{11}P)_2RhHCl_2]$		58.9 [a]	6.6 [a]	60.2	6.8
α-$[(Ph_2MeP)_3RhHCl_2]$	167—170	60.4	5.2	60.4	5.5
β-$[(Ph_2MeP)_3RhHCl_2]$	158—161	60.1	5.2	60.4	5.5
α$[(Ph_2MeP)_3RhHBr_2]$	183—187	53.9	4.9	54.1	4.6
α-$[(Ph_2MeAs)_3RhHCl_2]$	172—175	51.4	4.4	51.4	4.3
β-$[(Ph_2MeAs)_3RhHCl_2]$	158—161	51.4	4.3	51.4	4.3
α-$[(Ph_2MeAs)_3RhHBr_2]$	160—165	46.6	4.2	46.8	4.0

[a] Representative data.

The complexes $[\{(C_2H_4)_2RhCl\}_2]$, $[\{(C_8H_{14})_2RhCl\}_2]$, $[(Ph_3P)_3RhCl]$, and $[(dppe)_2RhHX]BPh_4$ (X = Cl or Br) were prepared by literature methods.[21-24] Reactions of $RhCl_3{\cdot}3H_2O$ with Ph_2MeP, Ph_2MeAs, or $PhMe_2P$ and of $RhBr_3{\cdot}3H_2O$ with Ph_2MeAs or $PhMe_2P$ were carried out as described previously.[6] A similar reaction of $RhBr_3{\cdot}3H_2O$ with Ph_2MeP gave only amorphous brown solids the i.r. spectra of which showed absorption at 2 100 cm^{-1} {*i.e.* α-$[(Ph_2MeP)_3RhHBr_2]$}.

Complexes α-$[L_3RhHX_2]$.—These complexes were prepared by methods of which the following are typical.

(a) Hydrobromic acid (48%; 10 ml), phosphinic acid (2 ml), and methyldiphenylphosphine (6.1 g) were added to a solution of rhodium tribromide trihydrate (2.1 g) in ethanol (150 ml), and the mixture was refluxed for 3 h. The resulting yellow-orange *solid* was filtered off, washed with hexane, and recrystallised from dibromomethane–hexane; yield, 3.3 g (62%). (Note: with dichloromethane, halogen exchange may occur.)

(b) Methyldiphenylphosphine (0.78 g) was added to a solution of the complex $[\{(C_2H_4)_2RhCl\}_2]$ (0.25 g) in dichloromethane (15 ml). Ethylene was evolved and a deep red solution formed which became yellow when hydrogen chloride was passed through it. The addition of hexane gave pale yellow *crystals* which were filtered off and washed with hexane; yield, 0.81 g (85%).

Similar products were obtained for L = Ph_2MeAs and X = Cl or Br. Products of variable composition were obtained by method (b) for L = $Ph_n(C_6H_{11})_{3-n}P$, Ph_3As and X = Cl. The complexes with L = Ph_2EtP, $PhMe_2P$, $PhEt_2P$, $PhBu_2P$, Et_3P, Bu^n_3P, or Oct^n_3P and X = Cl were obtained in solution by method (b) but were not isolated.

β-*Dichlorohydridotris(methyldiphenylphosphine)rhodium*(III).—The complex $[(Ph_2MeP)_3RhCl_3]$ (0.46 g), suspended in ethanol (15 ml), was treated with phosphinic acid (2 ml) and water (2 ml). The mixture was shaken for 2 h and the resulting yellow *solid* was filtered off and washed with ethanol; yield, 0.41 g (93%).

The *complex* β-$[(Ph_2MeAs)RhHCl_2]$ was obtained similarly, shaking being continued, in the dark, for 1 week (yield, 87%).

The authors are grateful to Mr. C. Evans for the n.m.r. spectra and to the S.R.C. for financial support (C. E. B.).

[4/2318 *Received, 7th November*, 1974]

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