Reactions Involving Transition Metals. Part X.[1] Reactions of the Complexes α- and β-[L_3RhHX_2] (L = Tertiary Phosphine or Arsine, X = Cl or Br)

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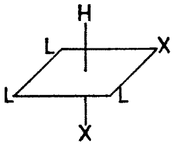
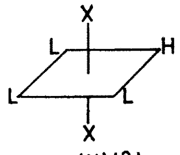
The reactions of the complexes α- and β-[L_nRhHX_2] (n = 2 or 3; L = tertiary phosphine or arsine; X = Cl or Br) with acidic, basic, oxidising, and reducing reagents have been investigated. The α-isomers are inert to acids (except nitric acid) but are rapidly dehydrohalogenated by bases. With weak bases, equilibria are established, the positions of which show that stability to dehydrohalogenation increases in the series L = $Ph_2RP < PhR_2P < R_3P$, R = Et < Me (n = 3) and L = $Ph_3P < Ph_3As < Ph_3Sb$ (n = 2). The β-isomers react similarly with bases and give trihalogeno-complexes with hydrogen halides. With sulphur dioxide both isomers are reduced and form the SO_2 complexes [L_3RhXSO_2]·HX (X = Cl or Br). Both isomers also react with nitric acid to give [$L_2RhX_2NO_3$].

IN THE preceding paper [1] it was shown, on the basis of i.r. and n.m.r. studies, that the isomeric rhodium complexes α- and β-L_3RhHX_2 (L = tertiary phosphine or arsine; X = Cl or Br) have the geometrical configurations (I) and (II) respectively, like the corresponding iridium complexes,[2,3] and that the β-form isomerises spontaneously to the thermodynamically more stable α-form probably by a dissociative mechanism. The reactivity of the hydrido-ligand in the iridium complexes is known to depend on the nature of the ligand in the *trans*-position,[2] and it was of interest to determine whether similar differ-



(I),(α)



(II),(β)

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[1] Part IX, C. E. Betts, R. N. Haszeldine, and R. V. Parish, preceding paper.

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ences in behaviour occur for rhodium. Accordingly, the reactions of the α- and β-isomers with some acids, bases, oxidants, and reductants have been investigated.

RESULTS AND DISCUSSION

(a) *Reactions with Acids.*—The complexes β-[$(Ph_2MeE)_3RhHCl_2$]($E = P$ or As) react with hydrogen chloride to give [$(Ph_2MeE)_3RhCl_3$] and hydrogen. The corresponding bromo-complex ($E = P$), on treatment with hydrogen bromide, also yields hydrogen but the solid product isolated gave an n.m.r. spectrum containing several sets of signals. Presumably, halogen exchange with the solvent (dichloromethane) occurred, giving mixed trihalogeno-complexes. The same results were obtained at 0 °C with stoicheiometric quantities of reagents. Similar effects were noted previously in the attempted recrystallisation of bromo-complexes from dichloromethane,[1] and other examples have been mentioned.[4] It is also relevant that we were unable to prepare the complex [$(Ph_2MeP)_3RhBr_3$].

The complexes α-[$(Ph_2MeP)_3RhHX_2$] ($X = Cl$ or Br) are completely unaffected by an excess of the corresponding hydrogen halide, as would be expected from their easy preparation by reaction (1).

$$[L_3RhCl] + HCl \longrightarrow \alpha\text{-}[L_3RhHCl_2] \qquad (1)$$

The reactivity of the hydride thus depends on the nature of the ligand *trans* to it. If this ligand has low *trans*-influence, the hydride reacts slowly or not at all with acids (α-isomer, *trans*-halide). When the *trans*-influence is increased, as in the β-isomer (*trans*-phosphine or -arsine), the M–H bond is weakened by reducing donation to the metal from the formal H^- ligand, and reaction occurs readily. The bond weakening is also shown in the lower Rh–H stretching frequencies and n.m.r. coupling constants displayed by the β-isomers. These trends are thus similar to those of the corresponding iridium(III) complexes.[2]

TABLE 1

Percentage of α-[L_3RhHCl_2] in the equilibrium mixtures α-[L_3RhHCl_2] + base $\rightleftharpoons$ [L_3RhCl] + base·HCl (total Rh concentration, 0.056M for dichloromethane solutions at room temperature).

L/Base (pK_a)	*o*-Chloroaniline (2.43)	Aniline (4.63)	*s*-Collidine (7.43)	Morpholine (8.33)	Triethylamine (11.21)
Bu_3P	100	100	90	20	0
$Oct^n{}_3P$	100	95	85	0	0
Et_3P	100	95	80	10	0
$PhBu^n{}_2P$	100	95	70	10	0
$PhMe_2P$	100	95	70	5	0
$PhEt_2P$	95	90	50	0	0
Ph_3Sb [a]	90	60	40	0	0
Ph_2MeAs	100	80	40	15	0
Ph_2MeP	90	80	30	5	0
Ph_3As [a]	90	50	25	0	0
Ph_2EtP	70	50	15	0	0
Ph_3P [a]	0	0	0	0	0
$Ph_2(C_6H_{11})P$ [a]	0	0	0	0	0
$(C_6H_{11})_3P$ [a]	0	0	0	0	0
Ph_2MeAs [b]	95	80	30	0	0
Ph_2MeP [b]	90	50	25	5	0

[a] Rhodium(III) present as [L_2RhHCl_2]. [b] For α-[L_3RhHBr_2] in CH_2Br_2.

Apart from some isomerisation of the β-form, neither of the isomers of [$(Ph_2MeP)_3RhHCl_2$] showed any reaction with acetic, sulphuric, fluoroboric, or perchloric acids. With nitric acid, both isomers react to give the product [$(Ph_2MeP)_2RhCl_2NO_3$] which is also obtained from the trichloro-complex. This product is discussed in detail below [section (f)].

(b) *Reactions with Bases.*—The complexes α-[L_3RhHCl_2] react with strong bases (*e.g.* triethylamine) with complete loss of hydrogen halide, forming the rhodium(I) complexes [L_3RhCl]. With stoicheiometric quantities of weaker bases, an equilibrium is set up [equation (2)] the position of which depends on the strength of the base and on the ease of dehydrochlorination of the complex. The position of the equilibrium has been measured for a series

$$[L_3RhHCl_2] + B \rightleftharpoons [L_3RhCl] + B{\cdot}HCl \qquad (2)$$

of complexes using a variety of bases. The complexes were usually generated *in situ* by the addition of hydrogen chloride to a solution of the complex [L_3RhCl]. It has been shown [1] that this procedure gives exclusively the α-isomers except in the case of bulky ligands such as Ph_3E ($E = P$, As, or Sb), $Ph_2(C_6H_{11})P$, and $(C_6H_{11})_3P$, which give complexes of stoicheiometry [L_2RhHCl_2]. The equilibrium position was measured by the intensity of the Rh–H stretching band in the i.r. spectrum at *ca.* 2 100 cm^{-1}. Equilibrium was attained more slowly for the tertiary arsine complexes than for those of the tertiary phosphines. The results obtained, expressed as the percentage of rhodium(III) remaining at equilibrium, are given in Table 1. Within the limits of the technique (*ca.* ±10%) similar series are found with each base.

The stability of the complexes α-[L_3RhHCl_2] to reductive elimination of hydrogen chloride increases in the order $L = Ph_2RP < PhR_2P < R_3P$ and $R = Et < Me$. This corresponds to the order of increasing basicity of L

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[4] F. J. Jardine, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 1574.

and represents the decreasing formal promotion energy ($4d_{z^2}$ to $5p_z$) of the metal. A similar order was found for the equilibrium (3).[5] A recent publication has shown that, with very bulky ligands, steric effects may also be important;[6] in the series investigated here, steric and electronic effects run in parallel. The apparent decrease in stability from chloro- to bromo-complexes is contrary to the trend found in other systems.[5,7] However, this discrepancy may be due to the different solvents used for the two halides.

$$[L_2Ir(CO)Cl] + PhCO_2H \rightleftharpoons [L_2Ir(CO)Cl(PhCO_2)H] \quad (3)$$

It has recently been shown[8] that the five-co-ordinate sterically hindered complex $[(Bu^tPr^n{}_2P)_2RhHCl_2]$ is stable to strong bases (*e.g.* pyridine or 2,6-dimethylpyridine), but all our five-co-ordinate phosphine complexes, $[L_2RhHCl_2]$, undergo complete loss of hydrogen chloride with even the weakest base. The triphenyl-arsine and -stibine complexes are considerably more stable, paralleling the behaviour with hydrogen as addend.[9] Although these ligands have low basicity towards a proton,[10] it is likely that donation to a ' soft ' metal atom, such as rhodium, increases with increasing polarisability, $Ph_3P < Ph_3As < Ph_3Sb$.

The complex β-$[(Ph_2MeP)_3RhHCl_2]$ did not react with aniline but underwent complete loss of hydrogen chloride with morpholine. The latter reaction was slower than for the α-isomer (about three times) and was unaffected by the presence of the free phosphine or by the absence of light. It thus seems that this isomer undergoes slow dehydrochlorination directly, without isomerising. The relative reactivities of the isomers with base are thus the reverse of those with acids, as might be expected.

These results explain the formation of carbonyl complexes when the complexes $[L_3RhX_3]$ are treated with an alcoholic base.[11] As with the corresponding iridium complexes,[2] the first stage would be the formation of a hydrido-complex and an aldehyde. Probably the β-isomer is formed initially which either reacts directly or, more likely under the reaction conditions used, isomerises and then reacts with the base to give the rhodium(I) complex $[L_3RhCl]$ which is well-known to abstract carbon monoxide from organic carbonyl compounds.

$$[L_3RhCl_3] + RCH_2OH + OH^- \longrightarrow [L_3RhHCl_2] + RCHO + H_2O + Cl^-$$

$$[L_3RhHCl_2] + OH^- \longrightarrow [L_3RhCl] + H_2O + Cl^-$$

$$[L_3RhCl] + RCHO \longrightarrow [L_2Rh(CO)Cl] + RH + L$$

The complex *trans*-$[(dppe)_2RhHCl]BPh_4$ is unaffected by any of the bases, even triethylamine which dehydrochlorinates all the complexes $[L_3RhHCl_2]$. On electronic grounds alone, the chelate complex would not be expected to be especially resistant to reduction. It seems likely that the reduction of the complexes $[L_3RhHCl_2]$ occurs by *cis*-elimination, which is not possible for the chelate complex.

(c) *Reaction with Halogens.*—Both isomers α- and β-$[(Ph_2MeP)_3RhHCl_2]$ react readily with an excess of chlorine to give $[(Ph_2MeP)_3RhCl_3]$ and, presumably, hydrogen chloride. Reaction also occurs with bromine, but tractable products were not obtained (see above).

(d) *Reactions with Oxygen.*—Solutions of the hydrido-complexes are very sensitive to air or oxygen and careful degassing of solvents is necessary to obtain, for instance, good n.m.r. spectra. Although the complexes α- and β-$[(Ph_2MeP)_3RhHCl_2]$ are only sparingly soluble in benzene, considerable quantities dissolve in the presence of oxygen, giving dark-coloured solutions. Similar behaviour is reported for the corresponding ethyldiphenylphosphine complexes, and a complex formulated as $[(Ph_2EtP)_2Rh^I(Cl)_2Rh^{III}Cl_2(PEtPh_2)_2]$ was obtained.[12] Addition of hexane to oxidised solutions of the Ph_2MeP complexes gave yellow solids of various compositions and molecular weights, not corresponding to any obvious formulation. The n.m.r. spectra of the solutions were complex and irreproducible, indicating the presence of several species. When oxygen was passed through a fresh solution a rapid initial reaction occurred (*ca.* 2 min), in which the high- and low-field patterns of the starting material were destroyed. This was followed by a complex series of slower reactions which depended on the concentrations of oxygen and of the complex. It was not possible to identify any of the products.

(e) *Reactions with Sulphur Dioxide.*—Reductive-elimination of hydrogen chloride from the hydrido-complexes occurs with a base and it was of interest to establish whether reduction could also be accomplished by sulphur dioxide and whether complexes containing this potential ligand would be formed.

The complexes α-$[L_3RhHX_2]$ ($L = Ph_2MeP$, Ph_2MeAs; $X = Cl$, Br) and β-$[(Ph_2MeP)_3RhHCl_2]$, suspended in refluxing ethanol, react slowly with sulphur dioxide to give products of apparent constitution $[L_3RhX_2(SO_2)]$. When sulphur dioxide is passed through solutions of the complexes $[L_3RhCl]$, yellow solids of composition $[L_3RhCl(SO_2)]$ are obtained for $L = Ph_2MeP$ and Ph_2MeAs, and a brown solid, $[L_2RhCl(SO_2)]$, for $L = Ph_3P$. The last reaction has been reported also by Levison and Robinson.[13] The complex $[(dppe)_2RhHCl]BPh_4$ is reduced by sulphur dioxide to $[(dppe)_2Rh]BPh_4$, but no further reaction occurs.

The i.r. and n.m.r. spectra * of corresponding com-

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* I.r. and n.m.r. spectra data are deposited as a Supplementary Publication; No. SUP 21468 (3 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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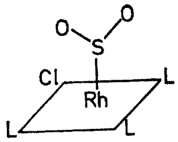
plexes $[L_3RhCl(SO_2)]$ and '$L_3RhCl_2SO_2$' are virtually identical, which suggests that the oxidation state of the rhodium is the same in both series. No evidence of paramagnetism was found. It seems probable that the first stage of the reaction of the complexes $[L_3RhHCl_2]$ is a reductive elimination of hydrogen chloride to form $[L_3RhCl]$. This complex then reacts further with sulphur dioxide to form $[L_3RhCl(SO_2)]$ which incorporates a molecule of hydrogen chloride as it crystallises. This is supported by the observation that the Ph_2MeAs complex reacts much more slowly than the Ph_2MeP complex, which parallels their behaviour with bases. The reductive-elimination step is reversible, as the passage of nitrogen through a solution of the complex $[(Ph_2MeP)_3RhCl(SO_2)]\cdot HCl$ gives the α-hydrido-complex. The complex $[(Ph_2MeP)_3RhCl(SO_2)]$ is unaffected under these conditions.

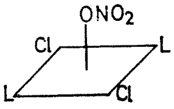
The n.m.r. spectra of the complexes show two sets of signals for the ligand-methyl groups, in intensity ratio 1:2, the more intense signal being to lower field. For the phosphine complexes this signal is a triplet, the other a doublet. The spectra are very similar to those of $[(Ph_2MeP)_3RhCl]$ and α- and β-$[(Ph_2MeE)_3RhHCl_2]$ ($E =$ P or As),[1] and are consistent with a structure in which the neutral ligands lie in one plane, two necessarily being mutually *trans*. Sulphur dioxide may act either as a Lewis acid or as a Lewis base. In these complexes the former mode of co-ordination seems likely, *i.e.* $L_3ClRh \rightarrow SO_2$, as suggested for the complexes $[(Ph_3P)_2M(CO)Cl(SO_2)]$ ($M =$ Rh or Ir).[14] This is supported by the similarity in the i.r. absorptions of the sulphur dioxide. The frequencies for the complexes described here are slightly lower than for the carbonyl compounds,[15] consistent with the greater basicity expected for $[L_3RhCl]$ than for $[L_2Rh(CO)Cl]$. The structure of the complexes $[L_3RhCl(SO_2)]$ is presumably similar to that found[14,16] for $[(Ph_3P)_2M(CO)Cl(SO_2)]$, with non-planar $M\text{-}SO_2$ units (III). The mode of incorporation of the hydrogen halide in $[L_3RhX(SO_2)]\cdot HX$ is not known.



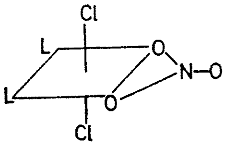
(III)

(f) *Nitrato-Complexes.*—The complexes α- and β-$[L_3RhHCl_2]$ and $[L_3RhCl_3]$ ($L = Ph_2MeP$ or Ph_2MeAs) react with nitric acid or, more slowly, with sodium nitrate solution to give monomeric products of composition $[L_2RhCl_2(NO_3)]$. Similar bromo-derivatives can also be obtained. These complexes give non-conducting solutions in dichloroethane. Co-ordination of the nitrate group is also indicated by the i.r. spectra (see Supplementary Publication), although it is not possible to distinguish between unidentate and bidentate bonding. The chloro-complexes show single Rh–Cl stretching modes at 350—364 cm^{-1}, assigned by comparison with the bromo-complexes. The occurrence of only one such mode suggests that the two chloride ligands may be mutually *trans*, although the frequency is rather higher than expected. Two further bands in the low-frequency region are tentatively assigned as Rh–O stretching modes; the frequencies are similar to those reported by other workers with a range of metals.[17,18] The difficulties in assigning the mode of bonding of a nitrato-group have been discussed by Bullock and Parrett,[18] and it seems that a simple correlation with the number of M–O stretching modes cannot be made with confidence.

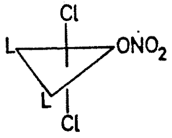
The n.m.r. spectra of the complexes $[(Ph_2MeAs)_2RhX_2(NO_3)]$ ($X =$ Cl or Br) show single resonances for the ligand-methyl groups, demonstrating the equivalence of these ligands. The phosphine complexes also give single patterns, consisting of a widely spaced doublet (*ca.* 15 Hz) with a complicated pattern between the two branches. This is characteristic of a system in which the P–P coupling, *via* the metal atom, is relatively weak,[19] and contrasts with the situation often found in metal complexes in which P–P coupling is either very weak (*cis*) or is strong (*trans*). Intermediate coupling between mutually *cis*-ligands has been observed for *fac*-$[\{Me(MeO)_2P\}_3W(CO)_3]$[20] and $[(Ph_2MeP)_2Pd(S_2CO)]$.[21] In the latter case weakening of the P–P coupling by dissociative ligand exchange was observed. A similar effect may be occurring in the nitrato-complexes. Alternatively, the intermediate coupling could arise from an unusual stereochemistry or co-ordination number. The most likely structures, in the light of the available evidence, are (IV)—(VI); (V) is similar to that found recently[7] for the complex $[(Bu^tPr^n{}_2P)_2RhHCl_2]$.



(IV)



(V)



(VI)

EXPERIMENTAL

Experimental methods and instrumental techniques are described in the preceding paper.[1] Typical methods for each type of reaction are described below. Analytical data are presented in Table 2.

Reaction of β-$[(Ph_2MeAs)_3RhHCl_2]$ *with* HCl.—The complex (0.71 g, 0.78 mmol) was added to a dichloromethane solution of hydrogen chloride (0.054M; 35 ml). The solvent was removed under reduced pressure and the residue, after recrystallisation from benzene–hexane, was identified as $[(Ph_2MeAs)_3RhCl_3]$ by i.r. spectroscopy, melting point, and

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analysis. In a separate experiment with β-[$(Ph_2MeP)_3RhHCl_2$], the gas evolved was identified as hydrogen by mass spectrometry.

Reactions of α-[L_3RhHX_2] *with Bases*.—The complexes were usually obtained by treating [{$(C_8H_{14})_2RhCl$}$_2$] (0.145 mmol) in dichloromethane with the ligand (0.84 mmol) and then with hydrogen chloride. The resulting solution was evaporated to dryness under nitrogen, the residue redissolved, and the solution re-evaporated in order to remove any excess of hydrogen chloride. The residue was dissolved in dichloromethane and the volume adjusted to 5 ml. The intensity of the Rh–H stretching band at *ca.* 2 100 cm^{-1} in the i.r. spectrum was measured. The base (0.28 mmol) was added and, after equilibration, the spectrum was remeasured. With 2,4,6-trimethylpyridine the amine hydrochloride absorption interfered, and a solution of the hydrochloride was used as reference. The concentrations of the hydrido-complexes were determined by calibration of the i.r. cells with solutions of known concentration. Equilibrium was obtained for the complexes α-[$(Ph_2MeE)_3RhHX_2$] after 15 min (E = P, X = Cl), 30 min (E = As, X = Cl), 2 h (E = P, X = Br), or 12 h (E = As, X = Br). Dibromomethane was used throughout with bromo-complexes, to eliminate halogen exchange.

TABLE 2

Analytical data

	Decomp. pt. (t/°C)	Found				Calc.			
		%C	%H	%S/N	M [a]	%C	%H	%S/N	M
[$(Ph_2MeP)_3RhCl(SO_2)$]·HCl [b]	155—158	56.1	4.5	3.5	665	55.8	4.7	3.7	838
[$(Ph_2MeP)_3RhBr(SO_2)$]·HBr	171	53.8	4.8		588	50.5	4.2		927
[$(Ph_2MeAs)_3RhCl(SO_2)$]·HCl	169—171	48.5	4.0		972	48.8	4.1		970
[$(Ph_2MeAs)_3RhBr(SO_2)$]·HBr	171—177	44.5	3.7		1 059	44.2	3.7		1 058
[$(Ph_3P)_2RhCl(SO_2)$]		59.4	4.4		725	59.5	4.2		726
[$(Ph_2MeP)_3RhCl(SO_2)$] [c]	155—158	58.0	4.6		544	58.2	4.9		802
[$(PhEt_2P)_3RhCl(SO_2)$]	167—171	51.2	6.2		700	51.5	6.0		700
[$(Ph_2MeP)_2RhCl_2(NO_3)$]	198—201	49.1	4.4	2.5		49.1	4.1	2.2	
[$(Ph_2MeP)_2RhBr_2(NO_3)$]	200—202	43.1	3.6	2.2	725	43.1	3.7	1.9	724
[$(Ph_2MeAs)_2RhCl_2(NO_3)$]	181—183	43.0	3.7	2.1	724	43.1	3.6	1.9	724
[$(Ph_2MeAs)_2RhBr_2(NO_3)$]	189	38.7	3.4	1.8	816	38.4	3.2	1.7	813

[a] Mechrolab osmometer in benzene or dichloromethane, at 37 °C. [b] Cl = 8.1 (8.5)%. [c] Cl = 4.5 (4.4)%.

Reaction of α-[$(Ph_2MeP)_3RhHCl_2$] *with* Cl_2.—Chlorine was bubbled through a solution of the complex (0.85 g) in dichloromethane (25 ml) for 5 min. The solvent was removed under reduced pressure and the residue recrystallised from benzene–hexane. The i.r. spectrum and melting point of the product were identical to those of [$(Ph_2MeP)_3RhCl_3$]; yield 0.84 g, 95%.

Reaction of α-[$(Ph_2MeP)_3RhHCl_2$] *with* SO_2.—Sulphur dioxide was passed for 30 min through a suspension of the complex (0.51 g) in refluxing ethanol (20 ml). The resulting bright yellow *solid* was filtered off and washed with hexane; yield 0.50 g, 91%.

Reaction of [$(Ph_2MeP)_3RhCl$] *with* SO_2.—A suspension of [$(C_8H_{14})_2RhCl$]$_2$ (0.27 g) in benzene (15 ml) was treated with Ph_2MeP (0.87 g) and sulphur dioxide was passed through the resulting red solution, which immediately became yellow. Addition of hexane gave yellow *crystals* which were filtered off and washed with hexane.

Reaction of α-[$(Ph_2MeAs)_3RhHBr_2$] *with* HNO_3.—Concentrated nitric acid (3 ml) was added to a suspension of the complex (0.87 g) in ethanol (10 ml) and the mixture was shaken for 7 days. The resulting orange *solid* was filtered off and washed with dibromomethane; yield 0.71 g, 98%.

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