Preparation, and Mechanism of Formation, of Alkyl and Phenyl Complexes of Ruthenium(II)

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New alkyl and phenyl complexes $[Ru(CO)_2L_2ClR]$ (L = PMe_2Ph or $PMePh_2$; R = Me, Et, or Ph) have been prepared by reaction of the all-*trans*- or all-*cis*-isomers of $[Ru(CO)_2L_2Cl_2]$ with HgR_2 or $SnMe_4$: the *cis*-isomers of $[Ru(CO)_2L_2Cl_2]$ do not react with these reagents. Mechanisms for the reactions, involving initial dissociation of a carbonyl ligand, are proposed on the basis of information about their stereochemistry and kinetics, and studies of halide-exchange reactions of all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ with bromide and iodide ion. In the case of reactions between $[Ru(CO)(PMe_2Ph)_3Cl_2]$ and HgR_2, in which complexes $[Ru(CO)(PMe_2Ph)_3ClR]$ are formed as intermediates, the transfer of alkyl or phenyl ligand between mercury and ruthenium has been found to be reversible.

ALKYL complexes of ruthenium(II) have been postulated as intermediates in a number of reactions of organic compounds which involve the use of ruthenium compounds as catalysts or reactants. Examples are the hydrogenation,[1-3] isomerization,[2,4] hydration,[5] and dimerization [6] of olefins, and the decarbonylation of aldehydes.[7] Aryl complexes of ruthenium (oxidation state unspecified) have been proposed as intermediates in the reaction of arylmercury compounds with olefins in the presence of $RuCl_3$.[8] The only direct evidence for the presence of alkyl or aryl complexes of ruthenium in

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these systems, however, was the observation by n.m.r. spectroscopy of species believed to contain an ethyl group bonded to ruthenium when olefin hydrogenation catalysts such as $[Ru(PPh_3)_3ClH]$ were treated with C_2H_4 under pressure: these species could not be isolated.[1,2]

We decided to attempt the preparation of alkyl and aryl complexes of ruthenium(II) which might serve as models for the proposed catalytic intermediates. Most of these intermediates are portrayed as species containing simple unidentate ligands such as halide ions and ligands containing group 5 donor atoms, and the aim was to obtain complexes of this general type. Most known alkyl and aryl complexes of ruthenium(II) did not appear to be suitable. Thus, in view of the apparent need in catalytic processes for vacant (or easily vacated) co-ordination sites on the metal, the complexes $[Ru(L\text{–}L)_2ClR]$ and $[Ru(L\text{–}L)_2R_2]$ (R = alkyl or aryl, L–L = bidentate phosphorus ligand) seemed unsuitable because four of the sites are taken up by the firmly held phosphorus ligands.[9] Complexes containing π-cyclopentadienyl [10] and π-benzene [11] ligands were ignored because the aromatic ligand may severely modify the properties of the metal, and various *ortho*-metallation products [12,13] were ruled out because the chelation of the alkyl or aryl group to the metal may drastically affect its behaviour.

One complex described in the literature [14] which did appear suitable as a model was $[Ru(CO)_2(PPh_3)_2IMe]$: the results of our unsuccessful attempts to prepare this complex by the literature method {oxidative addition of MeI to $[Ru(CO)_3(PPh_3)_2]$} have been described elsewhere.[15] We then turned to the possibility of preparing complexes of the general type $[Ru(CO)_2L_2ClR]$ or $[Ru(CO)_2L_2R_2]$ (L = ligand with phosphorus donor atom, R = alkyl or phenyl) by treating complexes $[Ru(CO)_2L_2Cl_2]$ with anionic alkylating and arylating agents. This paper gives the results of these and related reactions, and discusses the mechanism of formation of the complexes which were obtained.

RESULTS AND DISCUSSION

(1) *Preparation of Complexes* $[Ru(CO)_2L_2ClR]$ (R = *Alkyl or Phenyl*).—Our first attempts involved the use of the *cis*-isomers of complexes $[Ru(CO)_2L_2Cl_2]$ [16] (for structures, see Scheme 1). Lupin and Shaw [17] have shown that the Ru–Cl stretching frequencies for chloride ligands *trans* to carbonyl ligands in ruthenium(II) complexes are relatively low (311—266 cm^{-1}), implying that the Ru–Cl bonds are fairly weak. In addition, these complexes are known [16,18] to undergo exchange with bromide or iodide ion X^- to form *cis*-$[Ru(CO)_2L_2X_2]$. Despite this, we were unable to obtain alkyl complexes from the reaction of compounds *cis*-$[Ru(CO)_2L_2Cl_2]$ (L = PMe_2Ph, $PMePh_2$, or PPh_3) with Grignard reagents or lithium alkyls, nor was there any reaction between *cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ and either $HgMe_2$ or $HgPh_2$.

Having discovered convenient routes to the all-*trans*- and all-*cis*-isomers of complexes $[Ru(CO)_2L_2Cl_2]$,[16] we decided to try these as alternative starting materials. The all-*trans*-isomers seemed unpromising, since the Ru–Cl stretching frequencies for ruthenium(II) complexes containing a pair of mutually *trans* chloride ligands are fairly high (347—299 cm^{-1}).[17] Nevertheless, the complex all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ was found to react with $HgMe_2$ in acetone. Removal of the solvent followed by column chromatography yielded a product shown by elemental analysis to be $[Ru(CO)_2(PMe_2Ph)_2ClMe]$. Despite the use of a large excess of $HgMe_2$ there was no evidence for the formation of $[Ru(CO)_2(PMe_2Ph)_2Me_2]$. The crude product was somewhat contaminated with *cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$: the extent of contamination decreased as the excess of $HgMe_2$ used in the preparation was increased.

Details of the i.r. and n.m.r. spectra of $[Ru(CO)_2(PMe_2Ph)_2ClMe]$ (and all other new complexes described in the paper) are given in Table 1. It can be seen that the carbonyl ligands must be mutually *cis* and the PMe_2Ph ligands mutually *trans*, but that the Ru–P bonds do not lie in a plane of symmetry through the

TABLE 1

I.r.[a] and n.m.r.[b] spectra of new complexes

Complex	ν_{C-O}/cm^{-1}	δ/p.p.m.	Assignment
$[Ru(CO)_2(PMe_2Ph)_2ClMe]$	2 025, 1 955	1.64 (t, 6), 1.51 (t, 6)	P*Me*$_2$Ph
		0.33 (t, 3)	Ru*Me*
$[Ru(CO)_2(PMe_2Ph)_2ClEt]$ [c]	2 020, 1 948	2.25 (q, 2) [d]	Ru*CH*$_2$CH$_3$
		1.61 (t, 6), 1.56 (t, 6)	P*Me*$_2$Ph
		0.19 (t, 3) [d]	RuCH$_2$*CH*$_3$
$[Ru(CO)_2(PMe_2Ph)_2ClPh]$	2 035, 1 958	1.48 (t, 6), 1.21 (t, 6)	P*Me*$_2$Ph
$[Ru(CO)_2(PMePh_2)_2ClMe]$ [c]	2 030, 1 960		
$[Ru(CO)_2(PMePh_2)_2ClPh]$	2 035, 1 962	1.69 (t)	P*Me*Ph$_2$
$[Ru(CO)(PMe_2Ph)_3ClPh]$	1 915	1.36 (t, 6), 1.20 (t, 6)	P*Me*$_2$Ph
		1.07 (d, 6)	P*Me*$_2$Ph

[a] In acetone solution. Details are given for the C–O stretching region only. [b] In benzene solution. Resonances due to phenyl protons are not included. Multiplicities and relative areas are given in parentheses after the chemical shift values: d = doublet, t = triplet, and q = quartet. [c] Not isolated in a pure state. [d] Further splitting due to coupling to the phosphorus nuclei can be observed.

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[10] A. Davidson, J. A. McCleverty, and G. Wilkinson, *J. Chem. Soc.*, 1963, 1133.
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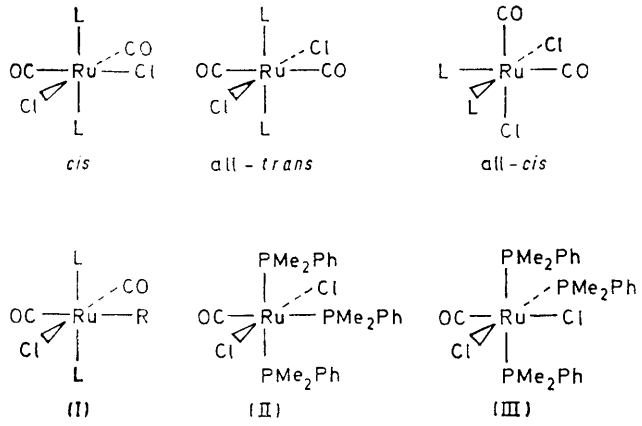
molecule. The structure of the complex must therefore be (I) (see Scheme 1), where L = PMe_2Ph and R = Me, and can be seen to match that of *cis*-[$Ru(CO)_2(PMe_2Ph)_2Cl_2$]—from which it cannot be made—rather than that of the actual starting material, all-*trans*-[$Ru(CO)_2(PMe_2Ph)_2Cl_2$].



SCHEME 1 Structures of complexes [$Ru(CO)_2L_2Cl_2$], [$Ru(CO)_2L_2ClR$], and [$Ru(CO)(PMe_2Ph)_3Cl_2$]

The complex [$Ru(CO)_2(PMe_2Ph)_2ClPh$] was prepared in the same way using $HgPh_2$, and also assigned structure (I) on the basis of its i.r. and n.m.r. spectra. In this reaction, it was not necessary to use a large excess of $HgPh_2$ to avoid contamination of the product by *cis*-[$Ru(CO)_2(PMe_2Ph)_2Cl_2$]; even when excess was used, however, no replacement of the second chloride ligand occurred. Reaction of all-*trans*-[$Ru(CO)_2(PMe_2Ph)_2Cl_2$] with $HgEt_2$ yielded a species which could not be isolated in a pure state, but appears from its i.r. and n.m.r. spectra to be [$Ru(CO)_2(PMe_2Ph)_2ClEt$]. Finally, it was discovered that the complex [$Ru(CO)_2(PMe_2Ph)_2ClMe$] could also be prepared from all-*trans*-[$Ru(CO)_2(PMe_2Ph)_2Cl_2$] and $SnMe_4$.

The related complex all-*trans*-[$Ru(CO)_2(PMePh_2)_2Cl_2$] was found to react with $HgPh_2$ to give [$Ru(CO)_2(PMePh_2)_2ClPh$]. Preparation of the analogous methyl complex, using $HgMe_2$, was complicated by the simultaneous formation of *cis*-[$Ru(CO)_2(PMePh_2)_2Cl_2$]; the desired product was not obtained in a pure state but was characterized by i.r. spectroscopy.

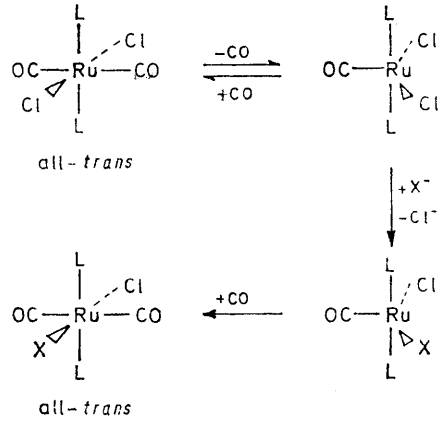
The study was then extended to the reactions of the complexes all-*cis*-[$Ru(CO)_2L_2Cl_2$] (L = PMe_2Ph or $PMePh_2$) with $HgMe_2$ and $HgPh_2$ in acetone solution. Again the products were mono-methyl and -phenyl complexes [$Ru(CO)_2L_2ClR$]; contamination by *cis*-[$Ru(CO)_2L_2Cl_2$] was not a problem with $HgPh_2$ but was serious for the reactions with $HgMe_2$, and again [$Ru(CO)_2(PMePh_2)_2ClMe$] could not be obtained in a pure state. The most surprising feature of these reactions was that the structure of the products was the same [*i.e.* (I)] as that of those obtained using all-*trans*-[$Ru(CO)_2L_2Cl_2$]; comparison of structure (I) with that of the starting materials all-*cis*-[$Ru(CO)_2L_2Cl_2$] reveals that the reactions involve a marked change in stereochemistry.

Major points of mechanistic interest arising from these preparations are: (*a*) the relative reactivity of the three isomers of the complexes [$Ru(CO)_2L_2Cl_2$] towards organo-mercury compounds (in particular the fact that the all-*trans* complexes are so much more reactive than the *cis*); (*b*) the changes in stereochemistry which accompany the reactions; (*c*) the exclusive formation of mono-alkyl and -phenyl complexes.

We felt that a study of the simpler halide exchange reactions of the isomers of [$Ru(CO)_2(PMe_2Ph)_2Cl_2$] with bromide and iodide ion might cast some light on these points.

(2) *Mechanistic Evidence from Halide-exchange Reactions.*—Contrary to initial expectations (see above), we found that all-*trans*-[$Ru(CO)_2(PMe_2Ph)_2Cl_2$] reacts with bromide or iodide ion under much milder conditions than those necessary to convert *cis*-[$Ru(CO)_2(PMe_2Ph)_2Cl_2$] into its bromo- and iodo-analogues.[16,18] This 'unexpected' result is in line with the relative reactivity of the two isomers towards organomercury compounds (but two awkward features, which will be considered later, are that the halide-exchange reactions —unlike those with HgR_2—proceed with *retention* of the all-*trans*-stereochemistry and with replacement of *both* chloride ligands). Clearly, then, the strength of the Ru–Cl bonds is not of primary importance in either type of reaction.

It was noted that the relative reactivity of the *cis*- and all-*trans*-isomers towards halide exchange parallels that for carbonyl-substitution reactions,[16] suggesting that the first step in halide exchange in *trans*-[$Ru(CO)_2(PMe_2Ph)_2Cl_2$] might actually be loss of a carbonyl ligand. If so, one would expect the exchange to be



SCHEME 2 Proposed mechanism for halide exchange in all-*trans*-[$Ru(CO)_2L_2Cl_2$]

inhibited by the presence of free CO in the solution, and this was found to be the case. Initial loss of a carbonyl ligand, as shown in Scheme 2 (L = PMe_2Ph; X = Br or I), presumably allows halide exchange to occur by an S_N2 mechanism; overall retention of stereochemistry is to be expected because uptake of CO in the final step will occur preferentially *trans* to the remaining carbonyl ligand because its *trans*-directing influence is greater

than that of halide ions (see discussion in ref. 16). A second exchange can be effected in the same way.

(3) *Mechanism of Formation of Complexes* $[Ru(CO)_2L_2ClR]$.—It now seemed likely that the reactions of the complexes all-*trans*-$[Ru(CO)_2L_2Cl_2]$ with organomercury compounds would also involve loss of a carbonyl ligand as a first step. Tests for inhibition by CO were carried out on the reactions of all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ with $HgMe_2$ and $HgPh_2$. In both cases the reaction rate was greatly reduced by saturating the solution with CO.

It was decided that a kinetic study should be made of the reactions, and to avoid the complication of variation in CO concentration in the solution during the reactions (and possible loss of a little CO from solution) the study was carried out using solutions saturated with CO under an atmosphere of CO. The inhibition by CO necessitated the use of higher temperatures, and hence a change of solvent from that—acetone—used for most of the preparative work. Unfortunately the inhibition was so severe in the case of the reaction with $HgMe_2$ that, even using a very large excess of $HgMe_2$, the competing rearrangement of all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ to the *cis*-isomer became a major complication. In addition, $[Ru(CO)_2(PMe_2Ph)_2ClMe]$ itself reacts rapidly with CO to form $[Ru(CO)_2(PMe_2Ph)_2Cl(COMe)]$. For these reasons, the study of the reaction with $HgMe_2$ was abandoned.

The reaction, under CO, of all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ with $HgPh_2$, however, yielded only $[Ru(CO)_2(PMe_2Ph)_2ClPh]$ in each of the solvents used. In all cases the concentration of $HgPh_2$ was much greater than that of the ruthenium complex, and could be assumed to remain effectively constant throughout a given run. The reaction was found to be first-order in all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$, and values of the first-order rate constant, k_{obs}, for various different concentrations of $HgPh_2$ are collected in Table 2. From

TABLE 2

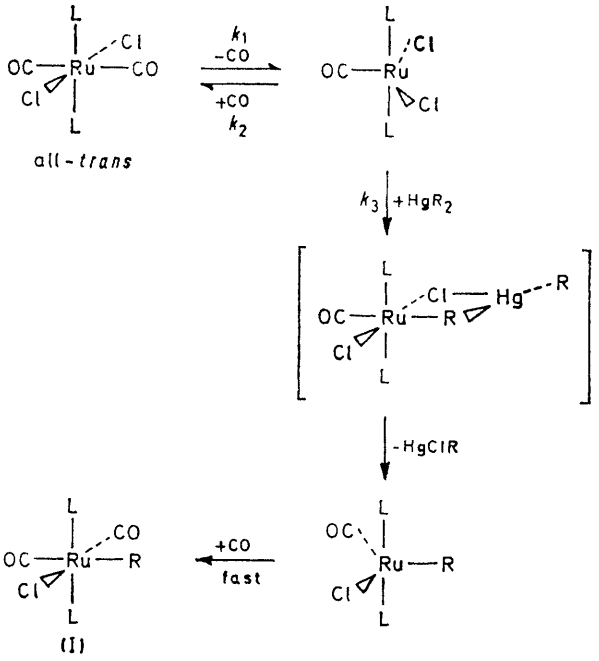
Observed rate constants for the reaction of the all-*trans*- and all-*cis*-isomers of $[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ with $HgPh_2$ [a]

Isomer	Solvent [b]	$[HgPh_2]$/ mol dm^{-3}	$10^4\,k_{obs}$/ s^{-1}
all-*trans* [c]	Nitroethane	0.050	3.07
		0.100	6.09
		0.150	9.36
		0.200	12.80
	Cyclohexanone	0.150	7.93
	Chlorobenzene	0.150	14.28
all-*cis* [d]	Nitroethane	0.050	2.17
		0.100	3.47
		0.200	6.41
	Cyclohexanone	0.100	5.24
	Chlorobenzene	0.100	8.15

[a] Initial concentration of $[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ *ca.* 5×10^{-3} mol dm^{-3}. [b] Dielectric constants at 293 K: nitroethane, 19.7; cyclohexanone, 18.2; chlorobenzene 5.94. [c] At 343.0 K. [d] At 333.0 K.

the data for nitroethane as solvent it can be seen that the reaction is also first-order in $HgPh_2$. Although the three solvents chosen for the study vary widely in dielectric constant, there is little variation in reaction rate.

A mechanism compatible with all the evidence is shown in Scheme 3, where R = Ph and L = PMe_2Ph.



SCHEME 3 Proposed mechanism for reactions between complexes all-*trans*-$[Ru(CO)_2L_2Cl_2]$ and HgR_2

Using the steady-state approximation for the concentration of the intermediates, the rate expression is:

$$\frac{-d[\text{all-}trans]}{dt} = \frac{k_1k_3[\text{all-}trans][HgR_2]}{k_2[CO] + k_3[HgR_2]}$$

This expression fits the observed first-order dependence on the concentration of all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$, and also that on the concentration of $HgPh_2$, provided that $k_2[CO]$ can be assumed to be much larger than $k_3[HgR_2]$ (R = Ph). In view of the dramatic effect of CO on the reaction rate, this seems a reasonable assumption to make.

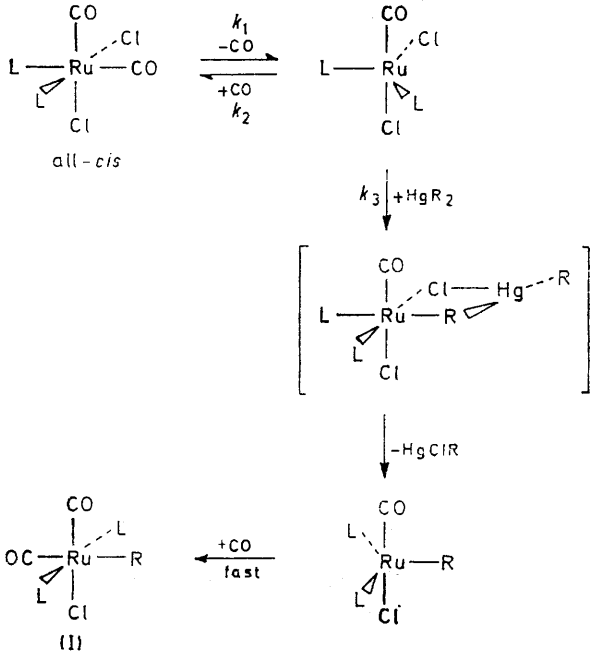
In that it does not involve the formation of ionic species as intermediates, the mechanism in Scheme 3 fits the observed lack of sensitivity of the reaction rate to the dielectric constant of the solvent. It also explains the change in stereochemistry during the reaction: when CO re-enters in the last step it does so *trans* to the phenyl or alkyl ligand since this is now the ligand with the greatest *trans*-effect.[19] This can be compared with the situation for the halide-exchange reactions (see Scheme 2), in which there is no change in stereochemistry.

The reactions of all-*cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ with $HgPh_2$ and $HgMe_2$ show similar kinetic behaviour. Both are inhibited by CO, and a kinetic study of the reaction with $HgPh_2$ under an atmosphere of CO showed it to be first-order in all-*cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$, the

[19] R. Mason and A. D. C. Towl, *J. Chem. Soc.* (*A*), 1970, 1601.

observed rate constant increasing with the concentration of $HgPh_2$ (see Table 2). The mechanism drawn in Scheme 4 (L = PMe_2Ph, R = Ph) fits the kinetic data and explains the unexpected change in stereochemistry during the reaction. Initial loss of the carbonyl ligand *trans* to PMe_2Ph rather than that *trans* to Cl^- is to be expected on the basis both of relative *trans*-effects [18] and of observations on the stereochemistry of carbonyl-substitution reactions of these complexes.[16] In the final step, the carbonyl ligand re-enters *trans* to the phenyl or alkyl ligand because these ligands possess a greater *trans*-effect than PMe_2Ph.[19]

(4) *Reaction between* $[Ru(CO)(PMe_2Ph)_3Cl_2]$ *and* HgR_2 (R = *Alkyl or Phenyl*).—Two isomers of $[Ru(CO)(PMe_2Ph)_3Cl_2]$ [structures (II) and (III) in Scheme 1] are known.[18] Of these, only isomer (II) reacts with



SCHEME 4 Proposed mechanism for reactions between complexes all-*cis*-$[Ru(CO)_2L_2Cl_2]$ and HgR_2

compounds HgR_2. I.r. (in acetone solution) and n.m.r. (in benzene solution) studies of the reaction between (II) and $HgPh_2$ revealed that a new species was formed in the solution, but that this in turn was converted into the unreactive isomer (III) of $[Ru(CO)(PMe_2Ph)_3Cl_2]$. The intermediate, which could not be obtained in a pure state, was identified as $[Ru(CO)(PMe_2Ph)_3ClPh]$ by comparison of its i.r. and n.m.r. spectra with those of a fully characterized sample of this compound prepared from $[Ru(CO)_2(PMe_2Ph)_2ClPh]$ and PMe_2Ph.

It seemed probable that the intermediate was converted into (III) by reaction with HgClPh formed in the first step of the reaction, and this was confirmed by treating the isolated sample of $[Ru(CO)(PMe_2Ph)_3ClPh]$ with HgClPh.

Overall, therefore, the reaction is simply the isomerization of (II) to (III), catalysed by $HgPh_2$ (in the absence of $HgPh_2$, the same conversion requires strong heating [18]). I.r. studies of the reactions of (II) with $HgMe_2$ and $HgEt_2$ indicated that they follow similar paths, with ultimate conversion into (III) *via* intermediate alkyl complexes.

The most important feature of these reactions is that they demonstrate the reversibility of the transfer of the organic ligand between mercury and ruthenium. Reverting to the reactions of complexes $[Ru(CO)_2L_2Cl_2]$, this may help to explain why no dialkyl or diphenyl complexes of ruthenium could be obtained, despite the fact that the remaining chloride ligand in $[Ru(CO)_2(PMe_2Ph)_2ClPh]$ could be replaced by iodide ion under mild conditions {and the earlier observation that both chloride ligands in all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ could be replaced by bromide or iodide}. There must be an appreciable change in the electron density on the metal when the first alkyl or phenyl ligand is introduced, and this may make the equilibrium position in a second exchange very unfavourable.

EXPERIMENTAL

All preparative work was carried out under an atmosphere of dry nitrogen. I.r. spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer, n.m.r. spectra on a Varian A60A 60 MHz spectrometer, using a V-6057 variable-temperature accessory, and analytical data were obtained with a Perkin-Elmer 240 elemental analyser.

Preparation of Complexes.—Details of the preparation of the *cis*-, all-*trans*-, and all-*cis*-isomers of complexes $[Ru(CO)_2L_2Cl_2]$ (L = ligand with phosphorus donor atom) have been given in an earlier paper, as have those for the preparation of isomers (II) and (III) of $[Ru(CO)(PMe_2Ph)_3Cl_2]$.[16] $HgMe_2$ and $HgEt_2$ were prepared as described in the literature.[20] $HgPh_2$ and $SnMe_4$ were obtained from Koch–Light and Emanuel respectively.

Complexes $[Ru(CO)_2L_2ClR]$.—$[Ru(CO)_2(PMe_2Ph)_2ClMe]$. To a solution of all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ (0.10 g) in acetone (15 ml) was added $HgMe_2$ (0.46 g). After 4 h at 313 K, the solvent as removed under reduced pressure. The residue was purified by column chromatography on alumina, using $CHCl_3$ as eluant, and recrystallized from light petroleum (b.p. 313—333 K) at 273 K. Colourless *crystals* were obtained (m.p. 365—368 K, yield 66%) (Found: C, 46.9; H, 5.25. Calc. for $C_{19}H_{25}ClO_2P_2Ru$: C, 47.16; H, 5.21%). Use of all-*cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ in place of the all-*trans*-isomer yielded the same product (reaction time 7 h), but the extent of contamination of the crude product by *cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ was greater, making purification more difficult. In the preparation of $[Ru(CO)_2(PMe_2Ph)_2ClMe]$ from the all-*trans*-isomer, $SnMe_4$ (0.50 g) could be used instead of $HgMe_2$, with a reaction time of 5 h (yield 60%).

$[Ru(CO)_2(PMePh_2)_2ClMe]$. The procedure was the same as that above, using all-*trans*-$[Ru(CO)_2(PMePh_2)_2Cl_2]$ (0.09 g) and a reaction time of 5 h. Even after chromatography and recrystallization, the product was still slightly impure, but was assumed to be $[Ru(CO)_2(PMePh_2)_2ClMe]$ since its i.r. spectrum was similar to that of $[Ru(CO)_2(PMe_2Ph)_2ClMe]$. Similar purification problems were

[20] C. S. Marvel and V. L. Gould, *J. Amer. Chem. Soc.*, 1922, **44**, 153.

encountered in its preparation from all-*cis*-$[Ru(CO)_2(PMePh_2)_2Cl_2]$.

$[Ru(CO)_2(PMe_2Ph)_2ClPh]$. The complex all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ (0.10 g) and $HgPh_2$ (0.07 g) were stirred in acetone (15 ml) at 313 K for 8 h. The product was purified in the same way as the analogous methyl complex, to give colourless *crystals* (m.p. 376—378 K, yield 65%) (Found: C, 52.35; H, 5.05. Calc. for $C_{24}H_{27}ClO_2P_2Ru$: C, 52.80; H, 4.98%). The same product was obtained using all-*cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ in place of the all-*trans*-isomer, the reaction being carried out at 298 K (reaction time 3 h, yield 75%). These methods could also be used to prepare $[Ru(CO)_2(PMePh_2)_2ClPh]$, starting with 0.12 g of all-*trans*- or all-*cis*-$[Ru(CO)_2(PMePh_2)_2Cl_2]$. The product was obtained as colourless *crystals* (m.p. 423—427 K, yields 45 and 65% respectively) (Found: C, 60.95; H, 4.75. Calc. for $C_{34}H_{31}ClO_2P_2Ru$: C, 60.94; H, 4.66%).

$[Ru(CO)_2(PMe_2Ph)_2ClEt]$. To a stirred solution of all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ (0.10 g) in acetone (15 ml) was added $HgEt_2$ (0.50 g). After 2 h at 313 K, the i.r. spectrum of the solution indicated that the desired complex had been formed, but it could not be isolated in a pure state. Further evidence for the formation of $[Ru(CO)_2(PMe_2Ph)_2ClEt]$ was obtained by monitoring the reaction, in benzene solution, by n.m.r. spectroscopy.

$[Ru(CO)(PMe_2Ph)_3ClPh]$. A solution of $[Ru(CO)_2(PMe_2Ph)_2ClPh]$ (0.10 g) and PMe_2Ph (0.03 g) in acetone (25 ml) was heated under reflux for 1 h. Removal of the solvent under reduced pressure left a colourless oil which became crystalline when triturated with light petroleum (b.p. 313—333 K). Recrystallization from light petroleum (b.p. 353—373 K) gave colourless *crystals* (m.p. 403—408 K, yield 77%) (Found: C, 56.95; H, 5.7. Calc. for $C_{31}H_{38}ClOP_3Ru$: C, 56.75; H, 5.84).

Reaction of $[Ru(CO)(PMe_2Ph)_3Cl_2]$ *with* $HgPh_2$. Isomer (II) of $[Ru(CO)(PMe_2Ph)_3Cl_2]$ (0.31 g) and $HgPh_2$ (0.18 g) were heated under reflux in acetone (30 ml). I.r. spectra of the solution indicated that the complex $[Ru(CO)(PMe_2Ph)_3ClPh]$ (identified by comparison with a sample prepared as above) was formed but then reacted further to form isomer (III) of $[Ru(CO)(PMe_2Ph)_3Cl_2]$, which was isolated from the solution and fully characterized. These conclusions were confirmed by a parallel study, by n.m.r. spectroscopy, of the reaction in benzene solution.

I.r. studies of the reactions of $[Ru(CO)(PMe_2Ph)_3Cl_2]$ with $HgMe_2$ (0.35 g) or $HgEt_2$ (0.39 g) showed that they followed a similar course.

Halide-exchange Studies.—Solutions of all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ (0.10 g) in acetone (10 ml) were stirred with LiBr (0.17 g) or NaI (0.30 g) at 313 K. After 16 h the solutions were filtered and the solvent removed under reduced pressure. The products were extracted with benzene and recrystallized from acetone. Analysis and spectroscopic data confirmed that these were the known [18] complexes, all-*trans*-$[Ru(CO)_2(PMe_2Ph)_2X_2]$ (X = Br or I).

Kinetic Studies.—The reactions of all-*trans*- and all-*cis*-$[Ru(CO)_2(PMe_2Ph)_2Cl_2]$ with $HgPh_2$ were monitored by following the disappearance of a C–O stretching band characteristic of the starting material (that at *ca.* 2 000 cm^{-1} for the all-*trans*-isomer, and that at *ca.* 2 075 cm^{-1} for the all-*cis*-isomer). Solvents were purified immediately before use and saturated with CO, and the reactions were performed under a CO pressure of 760 mmHg. Linear plots of log(absorbance) against time were obtained for at least $2\frac{1}{2}$ half-lives, and the values given for the observed rate constant in Table 2 were obtained from a least-mean-squares treatment of absorbance and time data. Values were found to be reproducible to, at worst, 5%.

We thank the S.R.C. for maintenance grants to C. F. J. B. and J. A. D.

[5/1914 *Received*, 21*st October*, 1975]