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Halide Redistribution Reactions of Rhodium(III) and Iridium(III) Complexes of the Type *mer*-$[MX_3(PMe_2Ph)_3]$ (X = Cl or I)

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Abstract

Halide exchange between *mer*-$[RhCl_3L_3]$ and *mer*-$[RhI_3L_3]$ (L = PMe_2Ph) in chloroform at room temperature gives an equilibrium mixture of these two compounds and one specific isomer each (*trans, mer*) of $[RhCl_2IL_3]$ and $[RhClI_2L_3]$ such that there is an approximately equal quantity of each species in solution after several hours. This exchange is catalysed by the aqua-complex $[RhCl_2(H_2O)L_3][ClO_4]$ or by $[(Ph_3P)_2N]Cl$ {[PPN]Cl}. The mechanism of exchange catalysed by the aqua-complex involves halide transfer via intermediates of the type $[L_3X_2Rh{-}X{-}RhX_2L_3]^+$ (X = Cl or I). Transfer is very rapid, rapid enough to give total ^1H NMR coalescence of PMe_2Ph signals in mixtures of $[RhCl_3L_3]$ and $[RhCl_2(H_2O)L_3][ClO_4]$. A further uncatalysed halide exchange occurs slowly to give a mixture of $[RhCl_3L_3]$, $[RhI_3L_3]$, and both possible isomers (*trans,mer* and *cis,mer*) of the two mixed halide complexes. The composition of the equilibrium mixture indicates a six-fold preference for chloride over iodide in the labile site *trans* to PMe_2Ph. Possible mechanisms for this slow process are discussed. With iridium only the first process occurs at measurable rates.

Introduction

Halide redistribution reactions have not been studied as extensively for transition-metal compounds as for main-group ones [1]. For rhodium and iridium, behaviour depends strongly upon oxidation state and it is well-known that square-planar d^8-compounds of rhodium(I) and iridium(I) are substitutionally labile and ligand transfer reactions rapid [2]. In contrast octahedral d^6-compounds of rhodium(III) and iridium(III) might be expected to be inert. Indeed $[Rh(H_2O)_6]^{3+}$ and $[Ir(H_2O)_6]^{3+}$ are among the most inert aqua-complexes [3, 4]. Substitution lability can be modified enormously by the ligands present. For example, we have shown that the aqua-ligands in $[RhCl_2(H_2O)L_3]^+$ and $[IrCl_2(H_2O)L_3]^+$ (L = PMe_2Ph here and elsewhere in this paper) are many orders of magnitude more labile than in the hexa-aqua ions and ^1H and ^{31}P NMR coalescence occurs as a consequence [5, 6]. Halide-transfer between $[IrCl(CO)L_2]$ and $[RhCl_3(CO)L_2]$ to give $[IrCl_3(CO)L_2]$ and $[RhCl(CO)L_2]$ seems to depend upon there being coordinative unsaturation in one reagent to allow the formation of the double chloro-bridged species $[Cl(CO)L_2Rh(\mu\text{-}Cl)_2IrCl(CO)L_2]$. Both halides are transferred simultaneously by an inner-sphere electron-transfer process [7]. Halide redistribution reactions of coordinatively saturated rhodium(III) compounds seem only to have been studied for $[RhCl_3(SMe_2)_3]$ and $[RhBr_3(SMe_2)_3]$ which give mixed halo-species by a mechanism that was not established [8].

In this paper we describe the reaction of $[RhCl_3L_3]$ and $[RhI_3L_3]$ to give mixed halo-analogues and a few results on the corresponding iridium system.

Results

Halide exchange is apparent within minutes of preparing a solution of *mer*-$[RhCl_3L_3]$ and *mer*-$[RhI_3L_3]$ (L = PMe_2Ph) (each initially at 0.1 mol dm^{-3}) in $CDCl_3$ at room temperature. The exchange was followed by ^1H NMR spectroscopy and by $^{31}P\{^1H\}$ NMR spectroscopy (see Tables I and II for characterising data). The concentrations of reagents and products change over one month to give the ^1H spectrum in Fig. 1 as equilibrium is approached. The species present and their mole fractions after 34 days (816 h) are given in Fig. 2. We assume that these are close to their equilibrium values.

The assignments of the spectrum are as given in Table I and Fig. 1. Each compound gives a spectrum totally characteristic of the *mer*-configuration; no evidence for *fac*-isomers was obtained. Thus each *mer*-isomer gives a virtual triplet for the methyl groups of the mutually *trans* pair of PMe_2Ph ligands and a doublet for PMe_2Ph *trans* to halide. *Trans,mer*-isomers are formed initially and *cis,mer* ones subsequently. Since each *cis,mer*-isomer contains diastereotopic methyl groups for the mutually *trans* PMe_2Ph ligands each gives two virtual triplets and a doublet in the methyl region of the ^1H NMR spectrum.

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TABLE I. ^{1}H (methyl) NMR Data[a] for Complexes of General Type *mer*-$[MX_3L_3]$

Complex[b]	Doublets		Triplets	
	δ	^2J(PH) (Hz)	δ	$\lvert^2J(PH) + {}^4J(PH)\rvert$ (Hz)[c]
mer-$[IrCl_3L_3]$	1.24	11.1	1.89	8.7
mer-$[IrI_3L_3]$	1.66	10.4	2.53	8.0
trans,mer-$[IrCII_2L_3]$	1.77	10.4	2.16	8.2
trans,mer-$[IrCl_2IL_3]$	1.18	10.8	2.19	8.4
mer-$[RhCl_3L_3]$[d]	1.21	11.4	1.97	8.4
mer-$[RhI_3L_3]$[d]	1.61	10.2	2.56	7.4
trans,mer-$[RhCII_2L_3]$	1.71	10.5	2.22	7.6
cis,mer-$[RhCII_2L_3]$	1.34	10.8	2.20	7.6
			2.53	7.6
trans,mer-$[RhCl_2IL_3]$[d]	1.15	11.4	2.24	8.0
cis,mer-$[RhCl_2IL_3]$	1.43	11.1	1.98	8.9
			2.18	7.8

[a]Spectra recorded at room temperature in $CDCl_3$ at 200 MHz (Ir) or 400 MHz (Rh). [b]L = PMe_2Ph. [c]Separation of outer lines of triplet. [d]Data here correspond quite closely to those reported earlier [11].

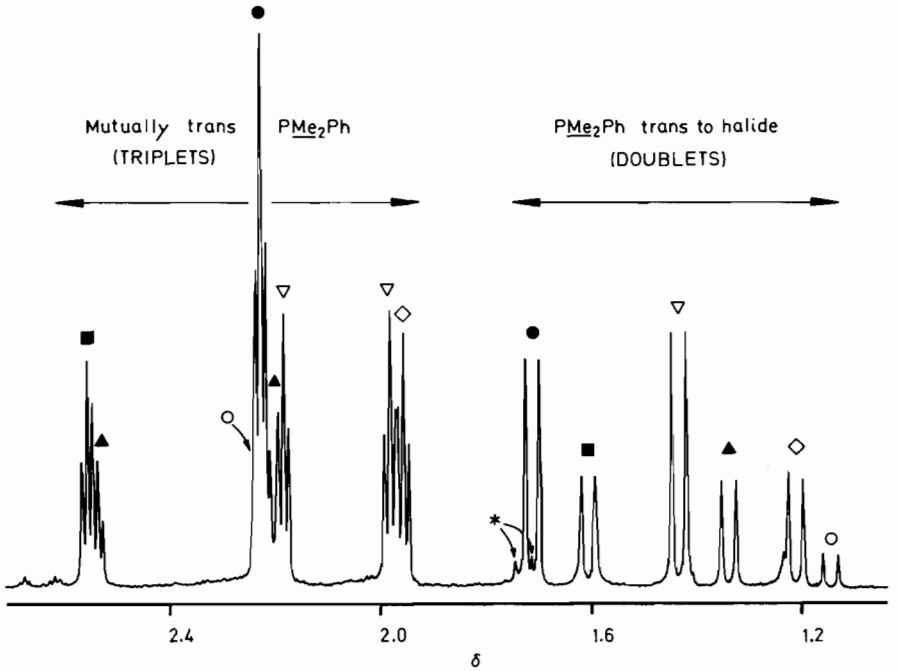


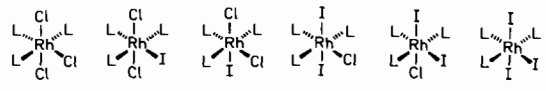
Fig. 1. ^{1}H NMR spectrum of a solution formed from *mer*-$[RhCl_3L_3]$ and *mer*-$[RhI_3L_3]$ (L = PMe_2Ph) each initially at approximately equal concentration in $CDCl_3$ recorded after 34 days at room temperature. The signals are assigned as follows: ◇, *mer*-$[RhCl_3L_3]$; ○, *trans,mer*-$[RhCl_2IL_3]$; ▽, *cis,mer*-$[RhCl_2IL_3]$; ●, *trans,mer*-$[RhCII_2L_3]$; ▲, *cis,mer*-$[RhCII_2L_3]$; ■, *mer*-$[RhI_3L_3]$. Peaks marked * are assigned to $OPMe_2Ph$ formed slowly over 34 days.

It is clear from Figs. 1 and 2 that there is a clear preference for chloride over iodide for the halide site *trans* to PMe_2Ph in the mixed halo-compounds. The observed mole fractions are very different from those calculated on the basis of a completely statistical distribution, but much closer to those when a six-fold preference for chloride *versus* iodide *trans* to PMe_2Ph is included. The approach to the equilibrium mixture occurs in two distinct stages (Fig. 3). The initial exchange products are $[RhCl_2IL_3]$ and $[RhCII_2L_3]$, each formed specifically as the *trans, mer*-isomers. The *cis,mer*-isomers are only formed much later as a result of the slow second stage of the exchange reaction. Concentrations change rapidly over two to three hours in the first stage to give a solution containing essentially equal concentrations

TABLE II. $^{31}P\{^1H\}$ NMR Data for Complexes of General Type *mer*-$[MX_3L_3]$

Complex[a]	$\delta(P^A)$[b,c]	$J(RhP^A)$ (Hz)	$\delta(P^B)$[b,c]	$J(RhP^B)$ (Hz)	$J(P^AP^B)$ (Hz)
mer-$[IrCl_3L_3]$	−190.4		−181.4		16.9
mer-$[IrI_3L_3]$	−205.1		−211.5		16.1
trans,mer-$[IrClI_2L_3]$	−200.7		−198.2		16.2
trans,mer-$[IrCl_2IL_3]$	−192.8		−191.9		16.3
mer-$[RhCl_3L_3]$	−137.0	112.6	−146.6	84.5	25.2
mer-$[RhI_3L_3]$	−152.5	107.4	−170.5	83.5	23.3
trans,mer-$[RhClI_2L_3]$	−144.0	110.1	−160.4	82.9	25.5
cis,mer-$[RhClI_2L_3]$	−147.9	107.7	−160.3	84.0	23.0
trans,mer-$[RhCl_2IL_3]$	−144.7	109.1	−154.8	84.6	22.9
cis,mer-$[RhCl_2IL_3]$	−140.1	110.3	−151.4	83.7	25.6

[a] L = PMe_2Ph; in $CDCl_3$. [b] P^A = unique PMe_2Ph; P^B = mutually *trans* pair of PMe_2Ph ligands. [c] Spectra recorded at 80.962 MHz with chemical shifts referenced to $P(OMe)_3$ in C_6D_6.



	mer	trans,mer	cis,mer	trans,mer	cis,mer	mer
(A)	12.5	12.5	25.0	12.5	25.0	12.5
(B)	12.5	2.9	34.6	28.1	9.4	12.5
(C)	12.9	3.8	30.5	27.1	12.6	13.1

Fig. 2. Species present in an equilibrium mixture formed from *mer*-$[RhCl_3L_3]$ and *mer*-$[RhI_3L_3]$ in $CDCl_3$ at room temperature. Mole fractions calculated on the basis of a completely statistical distribution of halide (A) and those calculated the same except for a 6-fold preference for Cl compared with I for the position *trans* to PMe_2Ph (B) are compared with the observed mole fractions (C).

of the two starting materials and equal but slightly lower concentrations of the two products; see equilibrium (1) and Fig. 3. Extrapolation of the curves up to 2 h to beyond 2 h would seem to lead to an equilibrium mixture containing approximately equal concentrations of $[RhCl_3L_3]$, $[RhI_3L_3]$, *trans,mer*-$[RhCl_2IL_3]$, and *trans,mer*-$[RhClI_2L_3]$. That is, K_1 for equilibrium (1) = *ca.* 1.0 and there is no

mer + mer ⇌ trans,mer + trans,mer (1)

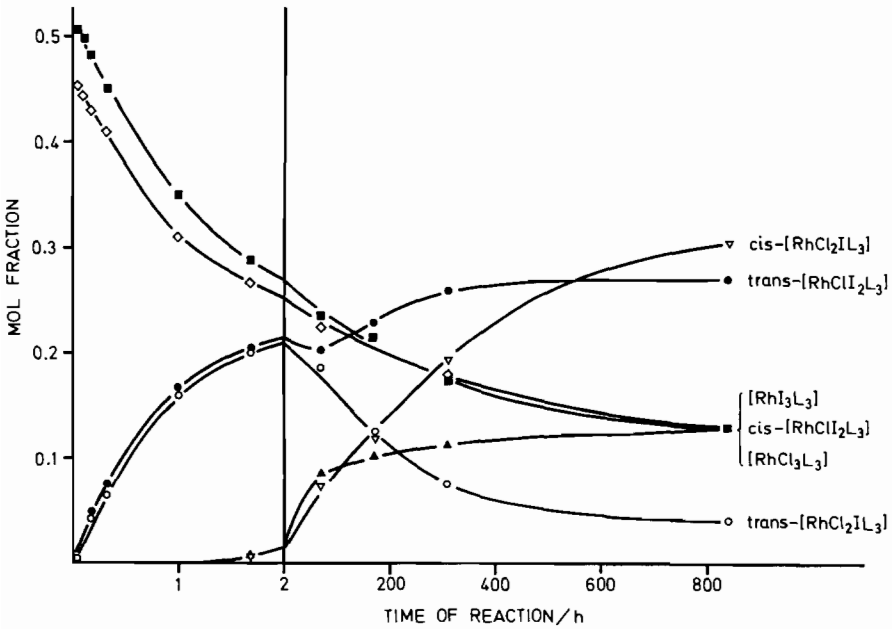
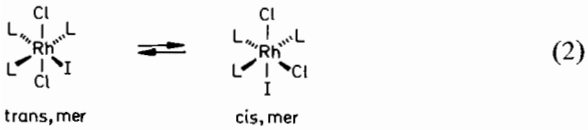
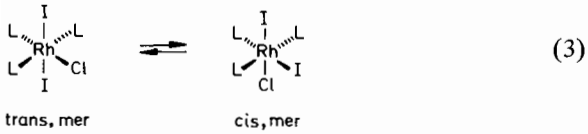


Fig. 3. Plot of mole fractions of Rh complexes against time for an initial solution containing approximately equal concentrations of *mer*-$[RhCl_3L_3]$ and *mer*-$[RhI_3L_3]$ in $CDCl_3$. The symbols used for the different species are the same as in Fig. 1.

preference for hetero- *versus* homo-halide complexes. However, this equilibrium is not fully reached due to the onset of the second stage of the exchange. After 2 h the other two isomers of the mixed halides (*cis,mer*) are just detectable and their concentrations increase slowly over many days and equilibrium is only approached after about 1 month at room temperature. Assuming that equilibria (2) and (3) have



(2)



(3)

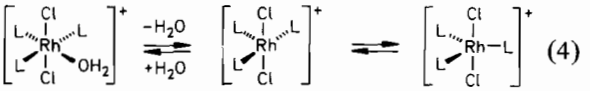
been reached at this time, room-temperature values for K_2 and K_3 for these equilibria are 8.0 and 0.33 respectively. As stated above there is a marked preference for chloride *trans* to PMe_2Ph.

The first stage of the exchange, equilibrium (1), is different mechanistically from the second one which leads to all the species in Fig. 2. We considered that the first stage might involve the dissociation of halide ion *trans* to PMe_2Ph. This was known to be the most labile substitutionally since treatment of *mer*-$[RhCl_3L_3]$ with $AgClO_4$ in wet organic solvent (methanol or acetone) gives *trans,mer*-$[RhCl_2(H_2O)L_3][ClO_4]$ but further chloride replacement does not occur even if an excess of $AgClO_4$ is used. We therefore examined the effect of catalytic quantities (2 mol% of total Rh) of the aqua-complex to a mixture of *mer*-$[RhCl_3L_3]$ and *mer*-$[RhI_3L_3]$ in $CDCl_3$. The exchange in equilibrium (1) is completed much faster and the rate is higher the more aqua-complex added. The rate of the second stage of the exchange to give *cis,mer*-isomers is largely unaffected by the addition of catalyst. Likewise addition of $[N(PPh_3)_2]Cl$ led to catalysed attainment of the equilibrium (1) but not of subsequent exchange.

Finally we have shown that *mer*-$[IrCl_3L_3]$ and *mer*-$[IrI_3L_3]$ exchange at room temperature by an equilibrium analogous to (1) to give the *trans,mer* isomers of $[IrCl_2IL_3]$ and $[IrClI_2L_3]$ but there was no evidence for the formation of the *cis,mer* isomers even after 12 months at room temperature. The first exchange is much slower than for rhodium and the *trans,mer* mixed halo-compounds are only apparent after 24 h at room temperature and equilibrium is only reached after 28 days. Equal concentrations of the four components are present after this time. We have not examined the catalysis of exchange in the iridium case.

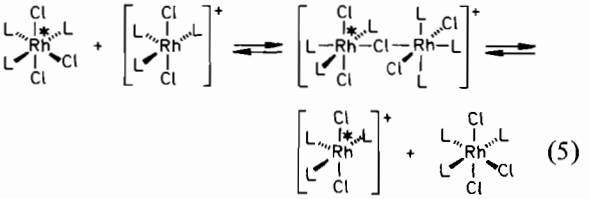
Discussion

The mechanism of equilibrium (1) is different from that of (2) and (3). Halide transfer between $[RhCl_3L_3]$ and $[RhCl_2(H_2O)L_3]ClO_4$ occurs rapidly [5]. Thus low temperature ^1H NMR spectra (−55 °C) of a mixture of these complexes in $CDCl_3$ show separate signals for each complex and separate signals for coordinated water and for some free water in solution. Up to 0 °C the coalescence of separate signals for L in the aqua-complex takes place together with that of free and coordinated water signals [6]. This is due to a rate-determining loss of H_2O and rapid stereochemical non-rigidity of the coordinatively unsaturated cation $[RhCl_2L_3]^+$, see equilibrium (4). At temperatures between 0 and



(4)

58 °C there is coalescence of the PMe_2Ph signals for $[RhCl_3L_3]$ and $[RhCl_2(H_2O)L_3]ClO_4$ and a combination of equilibria (4) and (5) were used to explain this. We believe that equilibria of type (5)



(5)

are responsible for the initial rapid exchange between $[RhCl_3L_3]$ and $[RhI_3L_3]$ catalysed by $[RhCl_2(H_2O)L_3]ClO_4$. Only the halide ligands *trans* to the strongly *trans*-labilizing ligand PMe_2Ph are involved in this stage of the exchange. In the absence of added catalyst it is likely that loss of halide *trans* to PMe_2Ph would give $[RhCl_2L_3]^+$ which would initiate a chain reaction involving equilibria of type (5).

The mechanism of the very slow processes, equilibria (2) and (3), is less clear. It cannot involve $[RhCl_2L_3]^+$ (or related halo-species) since the rate is unaffected by the presence of introduced aqua-cations. However, if solutions are left in air during this slow exchange ^1H NMR spectra show that a little $PhMe_2PO$ is formed but not if air is excluded. This suggests that there may be a route involving phosphine dissociation to give the unsaturated species $[RhCl_3L_2]$ (or related halo-species) which lead to halo-bridged intermediates and halide transfer. Further evidence for phosphine dissociation comes from the scrambling of phosphine ligands between $[RhCl_3(PMe_2Ph)_3]$ and $[RhCl_3(PEt_2Ph)_3]$

which occurs over the time of the second but not the first stage of halide scrambling. Of course, these phosphine exchange reactions may be irrelevant to equilibria (2) and (3) and we cannot rule out that these occur entirely intramolecularly via trigonal twists leading to trigonal prismatic intermediates. Reactions were carried out in the dark to avoid photochemical reactions of this type which are known to give *fac*-isomers [9] which were not detected under the conditions we used.

Experimental

The complexes *mer*-$[RhCl_3L_3]$ [10], *mer*-$[RhI_3L_3]$ [11], *mer*-$[RhCl_3(PEt_2Ph)_3]$ [10], *trans, mer*-$[RhCl_2(H_2O)L_3]ClO_4$ [6], *mer*-$[IrCl_3L_3]$ [12], and *mer*-$[IrI_3L_3]$ [12] were prepared by methods in the literature. NMR spectra were recorded on Varian XL200 and VXR 400 spectrometers.

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