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NMR Coalescence Effects Resulting from Stereochemical Non-rigidity and Halide Exchange in Octahedral Rhodium(III) and Iridium(III) Tertiary Phosphine Complexes

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Abstract

The PMe_2Ph ligands in the aquo-cations *mer*-$[MCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ rapidly exchange on the NMR time-scale giving coalescence in the ^1H and ^{31}P NMR spectra. Dissociation of the H_2O ligand which is *trans* to PMe_2Ph leads to a five-coordinate intermediate. This intermediate (M = Rh) is believed to be involved in the rapid reaction of $[RhCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ with *mer*-$[RhCl_3(PMe_2Ph)_3]$ by a chloride transfer mechanism leading to total exchange of the PMe_2Ph ligands.

Introduction

Low-spin octahedral d^6-transition metal complexes are generally substitutionally inert and this has enabled cobalt(III) complexes to be used extensively in structural and mechanistic studies. Rhodium(III) and iridium(III) (especially the latter) are also commonly inert, although the use made of rhodium in catalysis frequently depends upon the lability of octahedral rhodium(III) compounds. The combination of a strong *trans*-labilising ligand *trans* to a weakly coordinating ligand might favour substitutional lability and this combination appears to be present (H_2O *trans* to PMe_2Ph) in the cations *mer*-$[MCl_2(H_2O)(PMe_2Ph)_3]^+$ (M = Rh or Ir), (1) and (2) respectively [1–3].

Results and Discussion

The chloride ligand which is *trans*- to PMe_2Ph in *mer*-$[RhCl_3(PMe_2Ph)_3]$, compound (3), is particularly labile, much more labile than the two chloride ligands *trans* to each other. Thus treatment of *mer*-$[RhCl_3(PMe_2Ph)_3]$, compound (3), with $AgClO_4$ (1 mol per mol Rh) in wet acetone gives AgCl and a yellow solution from which *mer*-$[RhCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$, compound (1), may be isolated as orange needles. The iridium compound (2) is prepared similarly but in the presence of acetonitrile *mer*-$[MCl_2(MeCN)(PMe_2Ph)_3][ClO_4]$ (M = Rh or Ir) are obtained. The ^1H NMR (methyl) spectrum for cation (1) in CD_2Cl_2 was earlier misinterpreted as containing a triplet (*trans* PMe_2Ph ligands with virtual coupling) which overlies a doublet (unique PMe_2Ph) at around δ 1.6 [3]. We have now shown that the Me-signal is a simple quartet (δ 1.68; apparent J 2.9 Hz) at 20 °C which results from coalescence of a triplet (δ 1.78) and a doublet (δ 1.32) which are clearly resolved at −60 °C. The coalescence temperature is approximately −35 °C. The observed quartet at 20 °C confirms that spin–spin correlation, including virtual coupling, is retained within the $Rh(PMe_2Ph)_3$ group of atoms. $^{31}P\{^1H\}$ NMR spectra for cation (1) (Fig. 1) confirm that rapid phosphine exchange is occurring without any phosphine dissociation ($^{103}Rh-^{31}P$ coupling is observed above coalescence giving the observed doublet). Furthermore separate ^1H NMR signals for coordinated H_2O (δ 4.56) and free water (δ 2.73) were observed at −60 °C for solutions of compound (1) and these also coalesce at about −30 °C, so that phosphine exchange and water exchange have comparable rates. Similar coalescence behaviour also occurs for *mer*-$[IrCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$, compound (2), although the coalescence temperature is higher (25 °C; ^1H NMR methyl signals). Rhodium compounds are expected to be more labile or undergo intramolecular changes more rapidly than iridium compounds and this is what is observed, but it is still remarkable that coalescence for compound (2) occurs so readily.

We propose a mechanism involving H_2O dissociation (Scheme 1). Rapid reversible equilibrium between compounds (1) and the square pyramidal compound (4) alone would lead to an exchange of free with coordinated water faster than phosphine exchange. However, since these exchange rates are observed to be comparable, either compound (4) undergoes very rapid pseudo-rotation via the

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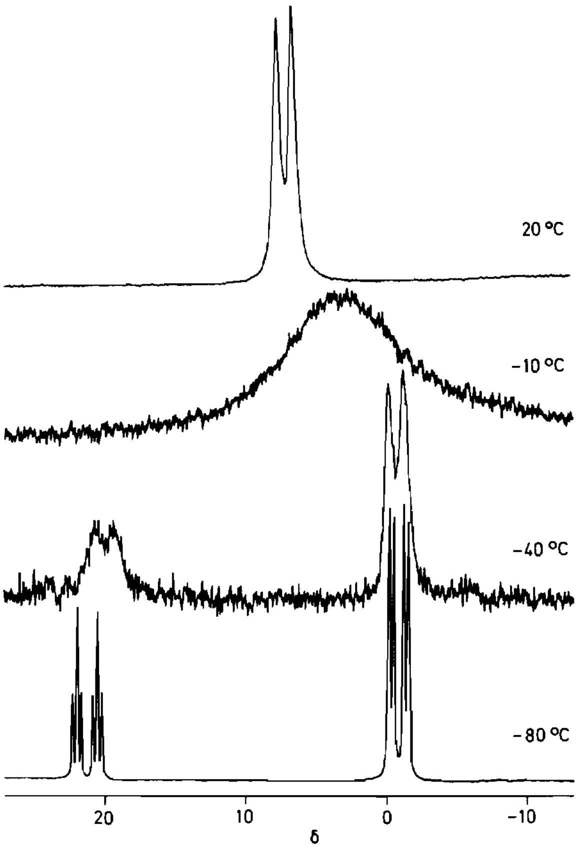
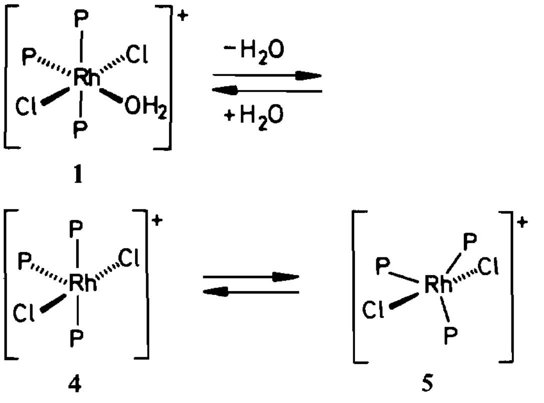


Fig. 1. $^{31}P\{^1H\}$NMR spectra of *mer*-[$RhCl_2(H_2O)(PMe_2$-$Ph)_3$][ClO_4], compound (**1**), in CH_2Cl_2 (δ with respect to 80% H_3PO_4).



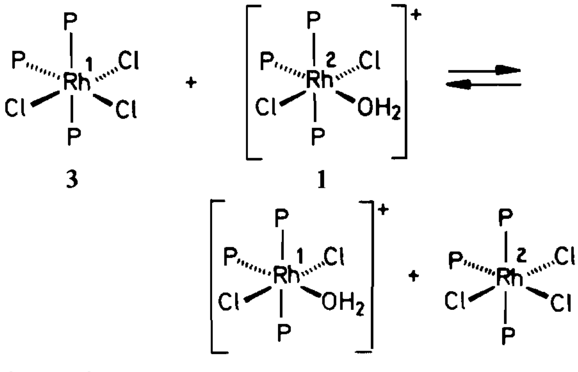
Scheme 1.

trigonal bipyramidal cation (5) or the dissociation of water leads to (5) directly. Solutions of (1) in dichloromethane are orange at room temperature, becoming paler on cooling and darker orange on warming so that the five-coordinate intermediate may have a significant concentration at higher temperatures and we are attempting to isolate and establish the geometry of this species. The five-coordinate d^6-complexes [$MCl_2(PPh_3)_3$] (M = Ru or O_5) have been shown to have square-pyramidal geometry in solution at low temperature, but undergo rapid pseudo-rotation at higher temperatures in a similar fashion to that we propose for the cationic complex (4) [4].

Ligands more strongly coordinated than H_2O, anionic ligands in particular, do not dissociate rapidly enough to give NMR coalescence. The complexes *mer*-[$MCl_3(PMe_2Ph)_3$] (M = Rh or Ir) are non-dynamic, and, whereas *mer*-[$RhCl_2(MeCN)$-$(PMe_2Ph)_3$][ClO_4] is fluxional (T_c ~ 0 °C; ^1H NMR), the iridium analogue shows no NMR line-broadening even at 55 °C. The compounds *mer*-[$MCl_2L(PMe_2Ph)_3$][ClO_4] (L = CO or py) are rigid.

The compound *mer*-[$RhCl_3(PMe_2Ph)_3$], compound (3), shows no spontaneous phosphine exchange giving sharp separated ^1H and ^{31}P NMR signals for the different PMe_2Ph ligands up to well above room temperature. However, interestingly we have found that compound (**1**) catalyses exchange in compound (3) so that rates high enough for coalescence can be obtained. Thus a $CDCl_3$ solution containing roughly equal amounts of (1) and (3) shows separate ^1H NMR signals for each at –55 °C. Up to about 0 °C compound (1) shows its expected fluxional behaviour but at higher temperatures the PMe_2Ph signals for (3) also broaden and coalesce with those for compound (1) so that at 58 °C a single broad signal is observed (Fig. 2). The changes in spectra are reversed on lowering the temperature.

The exchange of the rhodium atoms Rh^1 and Rh^2 requires that chloride ligand transfer between the metal atoms. The mechanism we propose for this intermolecular exchange (Scheme 2) involves the intermediate chloro-bridged species (6) formed by the association of compounds (3) and (4). Exchange of Rh^1 and Rh^2 must be sufficiently rapid that, together with the process shown in Scheme 1, there is complete PMe_2Ph exchange. We predict that Lewis acids other than (1) should catalyse PMe_2Ph exchange in compound (3). No Rh–P cleavage is involved.



Scheme 2.

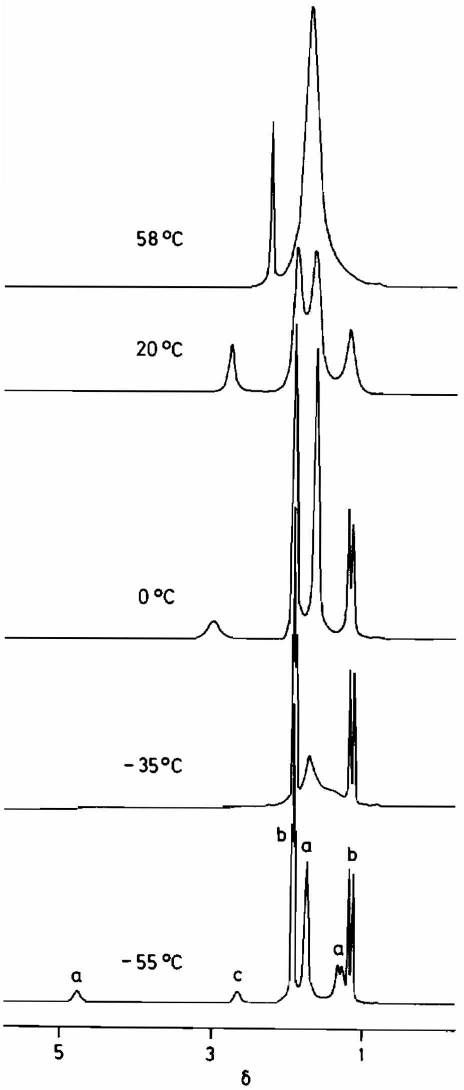
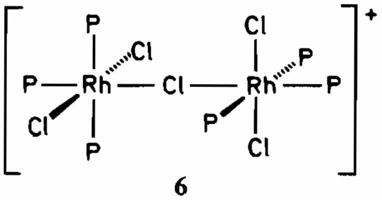


Fig. 2. ^{1}H NMR spectra of a mixture of $[RhCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$ (marked a) and $[RhCl_3(PMe_2Ph)_3]$ (marked b) in $CDCl_3$ containing some water (marked c).



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We have also observed that the exchange of the halide ligands between *mer*-$[RhCl_3(PMe_2Ph)_3]$ and *mer*-$[RhI_3(PMe_2Ph)_3]$ occurs specifically for the halide ligands *trans* to PMe_2Ph. The initial products of exchange are *mer*-$[RhCl_2I(PMe_2Ph)_3]$ and *mer*-$[RhClI_2(PMe_2Ph)_3]$ in which the unique halide ligands are *trans* to PMe_2Ph. This exchange is catalysed by $[RhCl_2(H_2O)(PMe_2Ph)_3][ClO_4]$, compound (**1**), consistent with our proposed mechanism. We have not been able to observe the intermediate (**6**) but have isolated related species such as *mer,-mer*-$[(PMe_2Ph)_3Cl_2Ir(\mu\text{-}CN)IrCl_2(PMe_2Ph)_3][ClO_4]$ by reaction of compound (**2**) with *mer*-$[IrCl_2(CN)(PMe_2Ph)_3$ in which the cyanide is *trans* to PMe_2Ph. The cyanide ligand bridges more readily than chloride.

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