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Synthesis and Reactions of Binuclear Rhodium(III) Tertiary Phosphine Chloride Complexes

E. B. McASLAN and T. A. STEPHENSON*

Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ, U.K.

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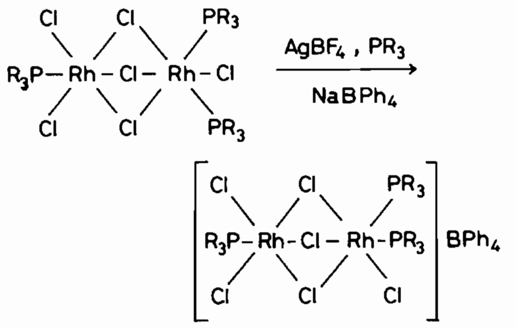
Although the binuclear rhodium(III) complexes $[Rh_2Cl_6(PR_3)_n]$ (n = 3, 4) were first reported 20 years ago [1], little is known about either their mode of formation or possible interconversion reactions (*cf.* studies on related chloride-bridged diruthenium(II) complexes [2]). We have reinvestigated the preparation of these materials using, in particular, variable temperature $^{31}P-\{^{1}H\}$ NMR spectroscopy to examine both the isolated products and the species present in the mother liquor and our preliminary results are given in this communication.

Earlier studies have shown that $[Rh_2Cl_6(PR_3)_3]$ (I) can be obtained by reaction of $RhCl_3 \cdot 3H_2O$ and PR_3 (1; 1.5 molar ratios) in boiling ethanol for short periods, whereas with a 1:2 molar ratio, $[Rh_2Cl_6(PR_3)_4]$ (II) was isolated [1]. The latter can also be synthesized by reaction of *mer*-$[RhCl_3(PR_3)_3]$ with $RhCl_3 \cdot 3H_2O$ (2:1 molar ratio) in hot ethanol [1], by photolysis of $[RhCl_3CO(PPr^n_3)_2]$ in benzene [3], or by exposure of $CHCl_3$/ethanol solutions of *mer*-$[RhCl_3(PR_3)_3]$ to air for several days [4]. X-ray structures of $[Rh_2Cl_6(PBu^n_3)_3]$ [5] and $[Rh_2Cl_6(PBu^n_3)_4]$ [6] (made as in ref. [1]) support these structural assignments based initially [7] on $^{31}P-\{^{1}H\}$ NMR spectral evidence. Interestingly, attempts to repeat the preparation of $[Rh_2Cl_6(PBu^n_3)_4]$ (II) using the $RhCl_3 \cdot 3H_2O$, PBu^n_3 (1:2 molar ratio) method gave a mixture of (II), (I) and *mer*-$[RhCl_3(PBu^n_3)_3]$ [7].

We have found that compound (I) can be prepared either by treatment of $[Bu^n_4N]_3[Rh_2Cl_9]$ [8] with $Ag[BF_4]$ and PEt_2Ph (1:4:4 molar ratio) in boiling ethanol (28% yield) or in high yield (>60%) by reaction of equimolar amounts of *mer*-$[RhCl_3(PR_3)_3]$ (PR_3 = PMe_2Ph, PEt_2Ph) with $RhCl_3 \cdot 3H_2O$ in the same solvent. Treatment of the mother liquor of the latter reaction with $Na[BPh_4]$ then gave small amounts (10–15%) of the new cationic complexes $[(PR_3)_2ClRhCl_3RhCl(PR_3)_2]BPh_4$ (III). A higher yield route to (III) is by reaction of (I) with equimolar amounts of $Ag[BF_4]$ and PR_3 in ethanol, followed by addition of $[BPh_4]^-$ (eqn. 1).



(1)

Note that treatment of (I) with PR_3 alone at 223 K gives first (II) (^{31}P NMR evidence) and then *mer*-$[RhCl_3(PR_3)_3]$ as the temperature is raised (eqn. 2):

$$\underset{\textbf{I}}{[Rh_2Cl_6(PR_3)_3]} \xrightarrow{PR_3} \underset{\textbf{II}}{[Rh_2Cl_6(PR_3)_4]} \xrightarrow{2PR_3} mer\text{-}[RhCl_3(PR_3)_3] \qquad (2)$$

The $^{31}P-\{^{1}H\}$ nmr spectra of the cations consist of a broad doublet at ambient temperature but on cooling to 223 K, the ABX pattern expected for structure (III) is observed (*e.g.* for PR_3 = PEt_2Ph, $^{31}P-\{^{1}H\}$ nmr in $CDCl_3$ at 298 K, δ 38.8 ppm (br. dt), $^{1}J_{RhP}$ 117.2 Hz; at 223 K, ABX δ_A, 42.9 ppm $^{1}J_{RhP_A}$ = 117.9 Hz; δ_B, 36.7 ppm, $^{1}J_{RhP_B}$ = 116.5 Hz, $^{2}J_{P_AP_B}$ = 20.1 Hz). These changes in spectra are concentration independent, reversible with temperature and occur with retention of Rh–P coupling. A similar intramolecular scrambling process is observed for the $[Rh_2Cl_5\{(PPh_2O)_2H\}_2]^-$ anion [9] and the $[Ir_2H_5L_4]^+$ cations (L_2 = $2PPh_3$ [10], $Ph_2P(CH_2)_3PPh_2$ [11]). Rotation of one end of the molecule with respect to the other around the three fold axis, rather than facile terminal/bridge ligand interchange via double and/or single bridged intermediates, is proposed to explain the temperature dependent nmr spectra of these hydride species. The insensitivity of the scrambling process in (III) to change of solvent is consistent with a rotation rather than a cleavage pathway.

A study of the reaction between various molar ratios of $RhCl_3 \cdot 3H_2O$ and PEt_2Ph in hot ethanol (Table I) indicates that at 1:4 molar ratios, only *mer*-$[RhCl_3(PEt_2Ph)_3]$ is isolated; 1.3 gives the *mer*-monomer and the cation (III) whereas at 1:2 molar ratios some $[Rh_2Cl_6(PEt_2Ph)_3]$ is precipitated and $[Rh_2Cl_5(PEt_2Ph)_4]^+$ is trapped out with $[BPh_4]^-$. We have not succeeded in isolating any of the double chloride bridged $[Rh_2Cl_6(PEt_2Ph)_4]$ (II) from these reactions.

However, examination of the $^{31}P-\{^{1}H\}$ NMR

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*Author to whom correspondence should be addressed.

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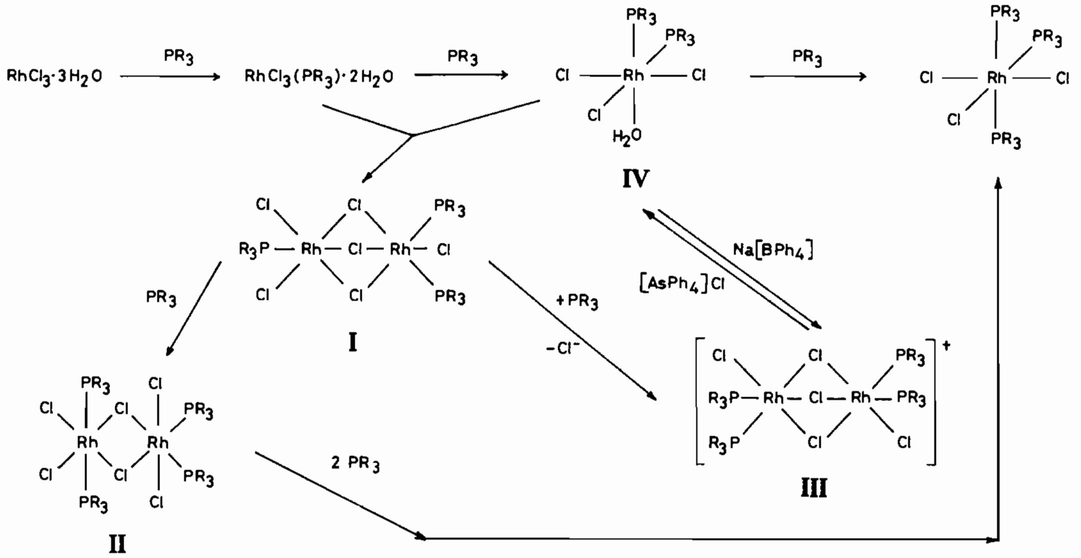
TABLE I. Percentage Yield of Products Isolated from the Reaction of $RhCl_3 \cdot 3H_2O$ with Various Molar Ratios of PEt_2Ph.[a]

Rh: PEt_2Ph	1:1	2:3	1:2	2:5	1:3	2:7	1:4
$[Rh_2Cl_6(PEt_2Ph)_3]$ (I)	46	88	11	0	0	0	0
$[Rh_2Cl_5(PEt_2Ph)_4]BPh_4$ (III)	0	6	73	75	58	10	0
mer-$[RhCl_3(PEt_2Ph)_3]$	0	0	0	6	22	67	76

[a] Reaction in refluxing ethanol for one hour.



Scheme I. Possible mechanism of formation and interconversion of the various species.

spectra of the mother liquor of the $RhCl_3 \cdot 3H_2O$/PEt_2Ph/ethanol reaction (1:2 molar ratio), after precipitation of $[Rh_2Cl_6(PEt_2Ph)_3]$ (I), shows that there are two major species in solution. Both of these show broad doublets at ambient temperature and ABX patterns at low temperature. One of these patterns corresponds to the triple chloride bridged cation $[Rh_2Cl_5(PEt_2Ph)_4]^+$ (III) and an X-ray analysis [12] of the compound isolated from the mother liquor in the absence of added $[BPh_4]^-$ shows that the other signals are due to the aquated monomer $[RhCl_3(PEt_2Ph)_2H_2O]$ (IV). The presence of magnetically inequivalent PEt_2Ph groups in (IV) is responsible for the ABX pattern at low temperature (*i.e.* $^{31}P-\{^1H\}$ NMR spectra of (IV) in ethanol at 298 K, δ 29.7 ppm (br dt), $^1J_{RhP}$ 117.2 Hz; at 223 K, ABX δ_a 34.7 ppm, $^1J_{RhP_A}$ 122.1 Hz; δ_B 24.3 ppm, $^1J_{RhP_B}$ 114.7 Hz, $^2J_{P_AP_B}$ 26.9 Hz). Facile dissociation of the water ligand on raising the temperature presumably generates a five coordinate intermediate in which rapid intramolecular exchange of PEt_2Ph groups can occur, (*cf.* $[RuCl_2(PPh_3)_3]$ and related species [2]).

Compounds (III) and (IV) are also the major species in the mother liquors of the reactions of $RhCl_3 \cdot 3H_2O$ with both *mer*-$[RhCl_3(PEt_2Ph)_3]$ and PEt_2Ph (various molar ratios). The $^{31}P-\{^1H\}$ nmr spectra of the various mother liquors also show evidence for a third minor species in solution. This complex does not exhibit fluxional behaviour, (broad doublet at δ 34.2 ppm, $^1J_{RhP}$ 120.6 Hz at 298–223 K), and could be another isomer of either (IV) (or II) with magnetically equivalent PEt_2Ph groups.

The high yield of $[Rh_2Cl_6(PR_3)_3]$ as a single isomer from these various reactions, together with the observation of the solvated monomer strongly suggests that, as in the analogous ruthenium system [2], intermolecular coupling of species such as $[RhCl_3(PR_3)_2H_2O]$ and $[RhCl_3(PR_3)(H_2O)_2]$ are involved in its formation (see Scheme I). Further studies on attempted isolation of other possible intermediates and extension to analogous iridium complexes are now in progress.

Acknowledgements

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