Coordination Chemistry Reviews
Elsevier Publishing Company, Amsterdam
Printed in the Netherlands.

HYDRIDO-COMPLEXES OF RHODIUM(III) WITH TERTIARY PHOSPHINES

A. SACCO, R. UGO AND A. MOLES

Istituto di Chimica Generale e Inorganica, Università di Bari (Italy)

Although some hydrido-complexes of rhodium(III), such as $[RhHX_2(AsPh_2Me)_3]$ and $[RhHCl\,en_2][BPh_4]$, are known[1,2], analogous complexes with tertiary phosphines have not hitherto been described[3]*. In contrast to the behaviour of the iridium complexes of formula $[IrX_3(PR_3)_3]$, which readily give hydrido-complexes[4] of the type $[IrH_nX_{3-n}(PR_3)_3]$, the corresponding complexes of rhodium give, by treatment with alcohols and KOH, only carbonyl-derivatives[5] of formula $[RhX(CO)(PR_3)_2]$.

However, earlier[6] we found that the rhodium(III) halides give, by treating with ethyldiphenylphosphine in ethanol under mild conditions, hydrido-complexes of formula $[RhHX_2(PEtPh_2)_3]$, where X = Cl, Br, I.

Some time later, other authors[7] described mononuclear complexes of the type $[RhCl_3(MR_3)_3]$ and binuclear halo-brigded complexes of the type $[Rh_2Cl_6(MR_3)_3]$ and $[Rh_2Cl_6(MR_3)_4]$ as products of the reaction between rhodium trichloride and a number of tertiary phosphines and arsines in hot alcoholic solution; their attempts to replace chlorine by hydrogen were unsuccessful.

The disagreement between the results of such studies and those obtained in our previous work prompted a re-examination of the products of the reaction between rhodium(III) halides and tertiary phosphines. We found that the type of compound obtained varies considerably, according to both the particular phosphine involved and the experimental conditions.

Reactions between rhodium halides and ethyldiphenylphosphine

Addition of the phosphine to a hot alcoholic solution of rhodium trihalide trihydrate under nitrogen gave a yellow crystalline precipitate of formula $[RhHX_2(PEtPh_2)_3]$ (X = Cl, Br, I). These complexes show a sharp infrared band at about 2100 cm^{-1} (α-form, see Table I) due to the metal–hydrogen stretching vibration. The corresponding deuterido-complexes, obtained in hot deuterated ethanol, have

---

* Recently, the formation of a solvated hydrido-complex of the type $RhH_2Cl(S)(Ph_3P)_2$ has been reported, see ref. 3.

TABLE I

STRETCHING FREQUENCIES (cm^{-1})

Compound	*hydrido*	*deuterido*	*carbonyl*
$RhHCl_2(PEtPh_2)_3$ α	2120	1515	
$RhHCl_2(PEtPh_2)_3$ β	1982		
$RhHBr_2(PEtPh_2)_3$ α	2110	1510	
$RhHBr_2(PEtPh_2)_3$ β	1964		
$RhHI_2(PEtPh_2)_3$ α	2100	1502	
$RhHI_2(PEtPh_2)_3$ β	1960		
$RhHCl_2(PPh_3)_3$ α	2220		
$RhHCl_2(PPh_3)_3$ β	2120	1510	
$RhH_2Cl(PPh_3)_3$	2012–2082		
$RhHCl_2(PEt_2Ph)_3$	2115		
$RhCl(CO)(PEtPh_2)_2$			1960
$RhBr(CO)(PEtPh_2)_2$			1962
$RhI(CO)(PEtPh_2)_2$			1965
$RhCl_3(CO)(PEtPh_2)_2$			2107

a sharp band at about 1510 cm^{-1} (ratio of hydride to deuteride stretching frequencies = 1.39–1.40).

The same hydrido-complexes were obtained from rhodium trihalide and the tertiary phosphine in boiling *t*-butanol and acetone; this behaviour, unlike that of the reaction between iridium halides and tertiary phosphines[8], ruled out the solvent as source of the hydrogen giving rise to the metal–hydrogen bond. Treatment of the rhodium halides with the phosphine in a number of solvents, with a molar ratio phosphine : rhodium ranging from 2:1 to 5:1, gave, beside the hydrido-complex, phosphine oxide and hydrogen halide with a molar ratio of 1:1 as products of the reaction, which occurs according to the following equation:

$$RhX_3 \cdot 3H_2O + 4PEtPh_2 = [RhHX_2(PEtPh_2)_3] + OPEtPh_2 + HX + 2H_2O$$

The reducing agent is therefore the phosphine itself and the source of hydride in the metal complex is water; this is also proven by the fact that the same hydrido-complexes were obtained in boiling water, without organic solvents. On treating alcoholic solutions of rhodium trihalides with the same phosphine and hypophosphorous acid at room temperature under nitrogen, hydrido-complexes showing elemental analysis identical to that of the above-mentioned complexes but exhibiting different Rh–H vibrations were obtained (β-form; see Table I). The β-form changes to the α-form in boiling ethanol, in which both are insoluble.

Rhodium(III) complexes of formula $RhX_3(PEtPh_2)_3$ were obtained by reacting hydrated rhodium trihalides and phosphine in ethanol or methoxyethanol at temperatures below 25°. On treating these compounds with phosphine (molar ratio phosphine : rhodium complex of 1.3:1) in boiling ethanol the hydrido-complexes in the α-forms were obtained; on treating with hypophosphorous acid in ethanol at room temperature the β-forms were obtained.

Reactions between rhodium trichloride and triphenylphosphine

On treating the rhodium halide with the phosphine (molar ratio phosphine: rhodium of 4.5:1) in boiling acetone under nitrogen a yellow crystalline precipitate of formula $[\mathrm{RhHCl_2(PPh_3)_3}]$ was obtained. This compound, which shows a Rh–H vibration at 2220 $\mathrm{cm^{-1}}$, easily loses hydrogen chloride in boiling ethanol giving the red–purple crystalline compound of formula $\mathrm{RhCl(PPh_3)_3}$, also obtained directly by interaction of ethanolic solutions of rhodium trichloride with an excess of triphenylphosphine[3]. On treating $\mathrm{RhCl(PPh_3)_3}$ with hydrogen chloride in benzene a stereoisomer of the above-mentioned hydrido-complex was obtained, showing a Rh–H vibration at 2120 $\mathrm{cm^{-1}}$ (the corresponding deuteride has a Rh–H vibration at 1510 $\mathrm{cm^{-1}}$). This latter hydride in ethanol at room temperature loses hydrogen chloride more easily than the former.

On treating $\mathrm{RhCl(PPh_3)_3}$ with hydrogen in benzene at room temperature and atmospheric pressure a dihydrido-complex, of formula $\mathrm{RhH_2Cl(PPh_3)_3}$, showing Rh–H vibrations at 2012 and 2082 $\mathrm{cm^{-1}}$, was obtained. This compound readily loses hydrogen in solution, giving the starting complex.

Reactions between rhodium trichloride and diethylphenylphosphine

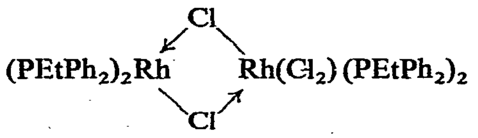
Addition of this phosphine to a hot alcoholic solution of rhodium trichloride gave the already described complex of formula[7] $\mathrm{RhCl_3(PEt_2Ph)_3}$. By refluxing the reaction mixture for eight days, a hydrido-complex of formula $\mathrm{RhHCl_2(PEt_2Ph)_3}$ ($\nu_{\mathrm{Rh-H}} = 2115\ \mathrm{cm^{-1}}$) was obtained in very poor yield. The yield was improved (about 10%) operating under an atmosphere of hydrogen.

Reactions of the hydridodihalotris(ethyldiphenylphosphine)rhodium(III) complexes

On treating these complexes (both α- and β-form) with mercury dihalides in hot ethanol, red crystalline compounds of formula $\mathrm{Rh(HgX)X_2(PEtPh_2)_3}$ were obtained; from these, by treating with the phosphine in ethanol, the β-forms of the starting hydrido-complexes were obtained.

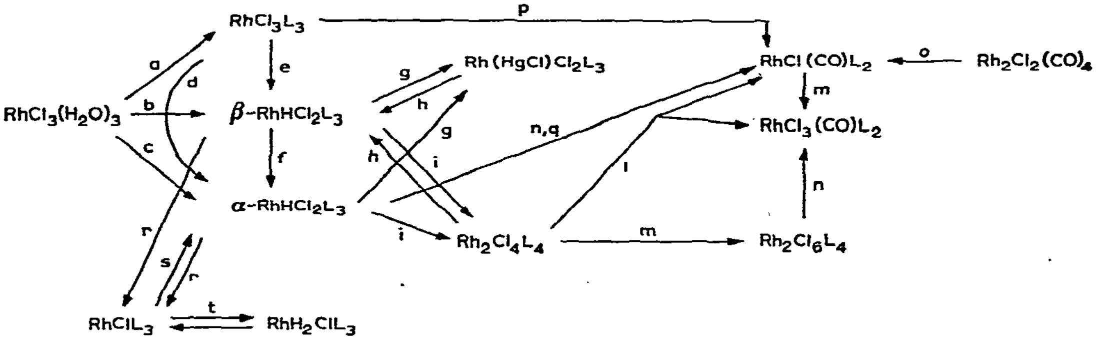
Both the α- and the β-forms of the hydrido-complexes are very sparingly soluble in benzene under nitrogen; however, in presence of air they slowly dissolve giving a yellow solution from which, by adding hexane, a compound of formula $\mathrm{RhCl_2(PEtPh_2)_2}$ was obtained.

This compound is diamagnetic and we assign to it a halo-bridged binuclear structure of the type



with a monovalent tetracoordinated rhodium atom and a trivalent hexacoordinated rhodium atom. This structure is supported by the fact that on treating the compound with carbon monoxide in benzene at room temperature and atmospheric pressure the carbonyl compounds $\mathrm{RhCl(CO)(PEtPh_2)_2}$ and $\mathrm{RhCl_3(CO)(PEtPh_2)_2}$ were obtained. Both carbonyls were also prepared by independent ways (see Table II). Addition of the phosphine to the halo-bridged compound in cold ethanol under nitrogen gave the β-$\mathrm{[RhHCl_2(PEtPh_2)_3]}$, and addition of chlorine in benzene gave a halo-bridged compound of rhodium(III), of formula $\mathrm{Rh_2Cl_6(PEtPh_2)_4}$, analogous to the corresponding complexes described by Chatt[7].

TABLE II



$\mathrm{L = PEtPh_2}$

a) plus L in methoxyethanol at 15–20°; b) plus L and $\mathrm{H_3PO_2}$ in EtOH; c) plus L in boiling solvents; d) plus L in boiling 95% EtOH; e) plus $\mathrm{H_3PO_2}$ in EtOH; f) in boiling EtOH; g) plus $\mathrm{HgCl_2}$ in EtOH; h) plus L in EtOH; i) by dissolution in benzene in presence of air; l) plus CO in $\mathrm{C_6H_6}$; m) plus $\mathrm{Cl_2}$ in $\mathrm{C_6H_6}$; n) plus CO in boiling EtOH; o) plus L in $\mathrm{C_6H_6}$; p) plus CO in EtOH or plus HCl in boiling 80% EtOH; q) in boiling 80% EtOH; r) plus L and aniline in EtOH at 50°; s) plus HCl in $\mathrm{C_6H_6}$; t) plus $\mathrm{H_2}$ in $\mathrm{C_6H_6}$.

The hydridodihalotris(ethyldiphenylphosphine) rhodium(III) complexes show considerable thermal stability (decomp. ~ 210°) and, in contrast to the behaviour of the corresponding triphenylphosphine complexes are rather stable under nitrogen atmosphere, even in chlorinated solvents. However, on treatment with aniline in ethanol they lose hydrogen chloride giving rhodium(I) complexes of formula $\mathrm{RhX(PEtPh_2)_3}$. Addition of HCl to a benzene solution of $\mathrm{RhCl(PEtPh_2)_3}$ gave the α-$\mathrm{[RhHCl_2(PEtPh_2)_3]}$.

Discussion

The reaction between rhodium trihalides and tertiary phosphines occurs according to the following three steps:

$$\mathrm{RhX_3} \xrightarrow{+\mathrm{L}} \underset{(\mathrm{I})}{\mathrm{RhX_3L_3}} \xrightarrow{+[\mathrm{H^-}]-\mathrm{Cl^-}} \underset{(\mathrm{II})}{\mathrm{RhHX_2L_3}} \underset{+\mathrm{HX}}{\overset{-\mathrm{HX}}{\rightleftarrows}} \underset{(\mathrm{III})}{\mathrm{RhXL_3}}$$

With the more basic phosphines, like the trialkylphosphines, the reaction stops at the first step, in agreement with the results obtained by Chatt[7]. With the less basic phosphines, like triphenylphosphine, the reaction goes readily till the third step, in agreement with the results reported by Young. The last step is easily reversible and depends strongly on the nature of the solvent. Our results suggest that the stability of the hydrido-complexes of rhodium(III) is very sensitive to small changes in the σ-donor and π-acceptor properties of the ligand, as it occurs in the series: triphenyl-, ethyldiphenyl- and diethylphenyl-phosphine.

The stable hydrido-complexes obtained by us were too insoluble in benzene for dipole-moment measurements; on the basis of the stronger trans-effect of the phosphine compared with that of the halide, we tentatively assign to the α-forms an octahedral configuration in which the halide is in trans-position to the hydride, and to the β-forms a configuration in which the phosphine is trans to the hydride.

Acknowledgement

We gratefully acknowledge the support of the Italian Council for Research (Consiglio Nazionale delle Ricerche, Roma).

REFERENCES

1 J. Lewis, R. S. Nyholm and G. K. N. Reddy, *Chem. Ind. (London)*, (1960) 1386.
2 R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, (1963) 3594.
3 J. F. Young, J. A. Osborn, F. H. Jardine and G. Wilkinson, *Chem. Commun.*, (1965) 131.
4 L. Vaska and J. W. Di Luzio, *J. Am. Chem. Soc.*, 83 (1961) 756; L. Malatesta, *Advances in the Chemistry of the Coordination compounds*, Ed. Kirschner, Macmillan, New York, 1961, p. 475.
5 J. Chatt and B. L. Shaw, *Chem. Ind. (London)*, (1960) 931; (1961) 290.
6 A. Sacco and R. Ugo, *Chim. Ind. (Milan)*, 45 (1963) 1096.
7 J. Chatt, N. P. Johnson and B. L. Shaw, *J. Chem. Soc.*, (1964) 2508.
8 L. Vaska and J. W. Di Luzio, *J. Am. Chem. Soc.*, 84 (1962) 4989.