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Invited Review

The System μ-Dichlorotetracarbonyldirhodium–Tertiary Phosphines

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1. Introduction

Rhodium(I) carbonyl–phosphine complexes have been long involved in studies of catalytic hydrogenation, hydroformylation, carbonylation, and decarbonylation reactions.[1] The search for useful precursors for these reactions has been mainly focused on the versatile complex *trans*-$[RhCl(CO)(PPh_3)_2]$ and its analogs.[2–5] This compound may be prepared by reaction of excess of PPh_3 on $[RhCl(CO)_2]_2$ which involves both chloride-bridge splitting and displacement of carbon monoxide. When reacting with such ligands L as primary amines, enimines, and tricyclohexylphosphine oxide (see further), $[RhCl(CO)_2]_2$ undergoes only the reaction of bridge-splitting to give the *cis*-dicarbonyl derivatives, *cis*-$[RhCl(CO)_2L]$.[6–8]

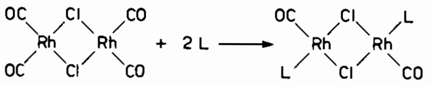
Based on the present knowledge of bonding and electronic properties of Rh^I complexes as related to their reactivity, we deemed it worthwhile to examine the system originating from the reaction of carbon monoxide on $[RhCl(CO)_2]_2$ in the presence of tertiary phosphines as a possible catalytic system. In particular, on the basis of the above mentioned bridge-splitting reactions, we would have expected that a more or less stable product of type *cis*-$[RhCl(CO)_2(PR_3)]$[9] would be formed for a Rh/phosphine molar ratio = 1. The catalytic effectiveness of such a system was predictably related to (*i*) the dicarbonyl configuration which would labilize a CO group and (*ii*) the ability to undergo oxidative addition of small molecules. As a matter of fact, it has recently been found that *cis*-$[RhCl(CO)_2(PPh_3)]$, produced *in situ* on addition of cyclohexenyl hydroperoxide to *trans*-$[RhCl(CO)(PPh_3)]_2$, is a powerful catalyst of hydroformylation and isomerization of olefins.[10] However, as far as the nature of species present in the system is concerned, matters appear to be much more complicated than expected.[9–13]

In view of the complexity of the system and of the conflicting interpretations which have arosen as regards formation of stable products and reaction intermediates, we deemed it necessary to summarize the present "state of the art" for this intriguing topic, while focusing on some still open questions.

2. The Reaction of $[RhCl(CO)_2]_2$ with Tertiary Phosphines

A. Reaction Products

The reaction of $[RhCl(CO)_2]_2$ (**I**) with tertiary phosphines L (L/Rh molar ratio = 1) in various solvents gives the stable dimeric halide-bridged complex *trans*-$[RhCl(CO)L]_2$ (**II**):[11,12]

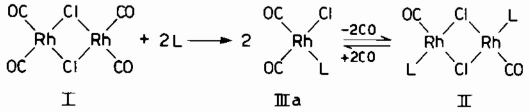


I II

(L= triphenylphosphine)

(1)

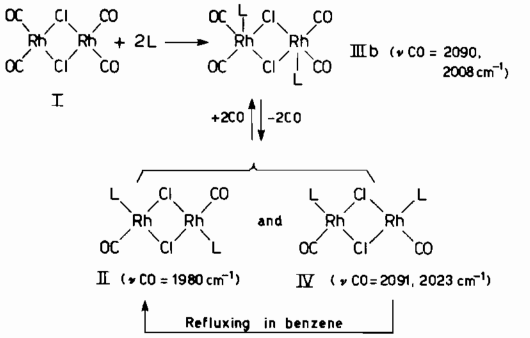
II had been originally formulated as a monomeric dicarbonyl species.[9] Dicarbonyl species may be present in the system as reaction intermediates.[11,12] Thus, although the dimeric formulation for **II** is established, there is still much debate on the possible intermediates and on the mechanism of formation. It was inferred from i.r. evidence[11,13] that process (1) involved prior halide bridge cleavage in **I** followed by loss of carbon monoxide from the resulting labile *cis*-dicarbonyl monomeric species (**IIIa**) to give eventually **II**:



(2)

The first stage in reaction (2), *i.e.*, the formation of **IIIa**, is substantially identical with the reaction of **I** with amines,[6] enimines,[7] or phosphine oxides[8] (L′), which gives *cis*-dicarbonyl complexes, *cis*-[RhCl(CO)$_2$L′]. Unlike **IIIa** these are stable toward loss of carbon monoxide probably owing to the higher π-acceptor and lower σ-donating abilities of tertiary phosphines which would destabilize the *cis*-dicarbonyl configuration. The intermediate **IIIa** could only be detected in solution by its i.r. spectrum in the carbonyl stretching region (2090 and 2005 cm^{-1} in benzene). On attempted isolation, it is converted into the dimeric **II**. This reaction sequence can be reversed upon treatment of a solution of **II** with carbon monoxide.

The i.r. spectrum of **II** shows a strong CO stretching band at 1980 cm^{-1} (B$_u$ for C$_{2h}$ symmetry), together with two very weak bands at 2091 and 2023 cm^{-1} (Nujol).[12] Upon refluxing **II** in benzene, these weak absorptions disappear. On carbonylation of **II** in solution in benzene, toluene, and chloroform, two strong bands are present in the i.r. spectrum (2090 and 2008 cm^{-1} in benzene). From this solution complex **II** contaminated by the compound with weak bands at 2091 and 2023 cm^{-1} is recovered on removal of solvent. These findings have led to an alternative interpretation of process (2):

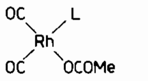


(3)

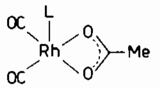
In this sequence, **IIIb** is an alternative formulation for the labile intermediate **IIIa** in process (2), arising from *trans*-addition of L to **I**. In no stage does chloride-bridge splitting occur, indicating a different mechanistic behavior of tertiary phosphines relative to other Lewis bases.[6–8]

Owing to the low stability of the intermediate (**IIIa** or **IIIb**), a choice between the two formulations is only a matter of speculation. A compelling choice can only be made either on theoretical grounds or on an unequivocal experimental finding, which is still to be achieved.

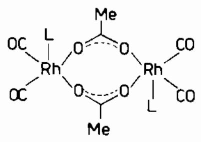
In support of formulation **IIIb** it has been observed that carbonylation of the acetato-bridged *trans*-[Rh(MeCOO)(CO)L]$_2$ resulting from metathetical reaction of **II** with acetate ion gives an orange solution whose i.r. spectrum is indicative of symmetrical acetate coordination,[14] as expected for **IIIb** and not unidentate coordination as expected for **IIIa**. However, this argument is open to question since it is not granted at all that carbonylation of the *acetato-bridged trans*-[Rh(MeCOO)(CO)L]$_2$ should necessarily produce a monomeric species analogous to **IIIa** with a *unidentate* acetate, *i.e.*:



Either a monomeric five-coordinate species with bidentate acetate,



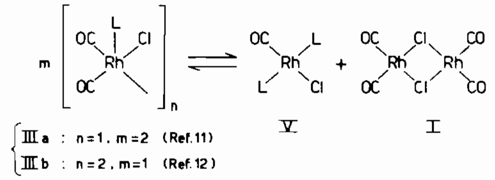
or a dimeric acetato-bridged species,



might as well be produced on carbonylation of *trans*-[Rh(MeCOO)(CO)L]$_2$.

IV is the suggested formulation for the other complex isolated with **II**.

If the carbonylation of **II** is carried out on a methanol suspension or concentrated dichloromethane solution,[12] a precipitate of *trans*-[RhCl(CO)L$_2$] (**V**) is obtained and [RhCl(CO)$_2$]$_2$ can be isolated from the solution, indicating that the following equilibrium exists in solution:

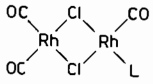


(4)

In other words, *trans*-[RhCl(CO)L$_2$] is much less soluble than **III** in methanol and its precipitation will shift the equilibrium to the right-hand side of eq. (4).

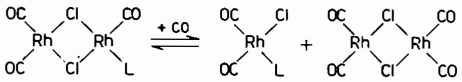
B. Study of the Rh/CO/L System in Solution

The complexity of the system concerned here manifests itself in a comprehensive study of the reaction at various L/Rh molar ratios and CO concentrations in solution (L = PMe$_3$, PMe$_2$Ph, PPh$_3$, P(NMe$_2$)$_3$).[11] When L/Rh = 1/2 only the tricarbonyl–monosubsti-



VI

tuted dimer **VI** is formed. Carbonylation of **VI** leads to a mixture of [RhCl(CO)$_2$]$_2$ and **IIIa**:

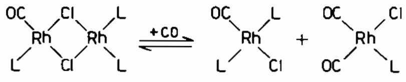


VI **IIIa** **I**

(5)

When L/Rh = 1, the reaction product **II** undergoes carbonylation to **IIIa** (see eq. 2) or **IIIb** (see eq. 3).

When L/Rh = 3/2, the dimeric monocarbonyl–trisubstituted species **VII** is produced which on carbonylation gives a mixture of *trans*-[RhCl(CO)L$_2$] and **IIIa** :



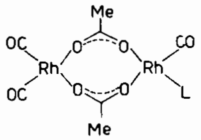
VII **V** **IIIa**

(6)

Of all these species, only **II**, **V**, and **VI** are sufficiently stable to be isolated in the solid state.

The fact that the nature of products obtained changes with changing L/Rh molar ratio is an indication that these reactions are thermodynamically rather than kinetically controlled.

Complex **VI** is one of a few examples of monosubstituted tricarbonyl dinuclear rhodium derivatives known so far. A similar, more stable species is the carboxylato-bridged complex **VIII**,



VIII

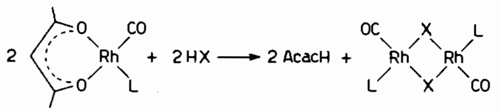
which is prepared by the reaction of [Rh(MeCOO)(CO)$_2$]$_2$ with one mol of L (L = PPh$_3$).[13] **VIII** is carbonylated to the starting [Rh(MeCOO)(CO)$_2$]$_2$ in solution at 1 atm of CO.

The dimeric *trans*-dicarbonyl configuration for **II** (L = PMe$_3$) was confirmed by the absence of a second order structure in the ^{1}H nmr spectrum.[11]

C. Reactions of *trans*-[RhX(CO)(PPh$_3$)]$_2$

(i) Halide substitution

trans-[RhCl(CO)(PPh$_3$)]$_2$ undergoes metathetical reactions on treatment with the appropriate lithium salt (LiX) in acetone or with silver acetate in benzene to give the chloride-substitution products *trans*-[RhX(CO)(PPh$_3$)]$_2$ (X = Br, I, SCN, MeCOO).[12] Infrared evidence indicates that in the thiocyanato complex a bridging SCN group is present (ν_{CN} = 2135 cm^{-1}).[15] In the acetato-complex, the separation of 133 cm^{-1} between the asymmetric and symmetric carboxylate stretching frequencies is indicative of bridging acetate groups.[14] Complexes of type *trans*-[RhX(CO)L]$_2$ (X = Cl, Br; L = PPh$_3$, AsPh$_3$) can also be obtained by reaction of the parent [Rh(Acac)(CO)L] in diethyl ether with the appropriate hydrogen halide in methanol:[16]



(7)

(ii) Bridge-splitting reactions

The halide bridge in *trans*-[RhX(CO)(PPh$_3$)]$_2$ can be easily split by a number of Lewis bases (L) in benzene at r.t. with formation of the monomeric disubstituted "mixed" derivatives, *trans*-[RhX(CO)(PPh$_3$)L] (X = Cl, L = AsPh$_3$, py, *p*-toluidine, Me$_2$S).[12] Further mixed complexes of type *trans*-[RhX(CO)LL′] (X = Cl, Br; L = PPh$_3$, L′ = AsPh$_3$, SbPh$_3$, P(OPh)$_3$; L = AsPh$_3$, L′ = SbPh$_3$, P(OPh)$_3$) were prepared in an analogous way.[16] The nitrogen- and sulphur-containing complexes decompose slowly in solution or air-exposure of the solids. These mixed compounds also undergo metathetical halide substitution.

The mixed tertiary phosphine derivatives, *trans*-[RhCl(CO)(PPh$_3$)L] (L = PMePh$_2$, PCy$_3$) are similarly obtained by reaction of **II** with L in acetone and addition of ether. However, ^{1}H nmr studies indicate that the following disproportionation equilibrium exists in solution:[12]

$$\underset{\mathbf{IX}}{2[\mathrm{RhCl(CO)(PPh_3)L}]} \rightleftharpoons [\mathrm{RhCl(CO)(PPh_3)_2}] + [\mathrm{RhCl(CO)L_2}] \quad (8)$$

This equilibrium lies well over to the left-hand side but isolation of the mixed **IX** actually depends on its solubility relative to [RhCl(CO)(PPh$_3$)$_2$]. In fact, when L is a more alkylated ligand such as PMe$_2$Ph, Me$_2$SO *etc.*, preferential precipitation of the latter will occur.

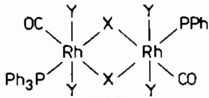
The reaction of **II** with SbPh$_3$ appears to be much more complicated, the following equilibria being established in solution:[12]

$$\textit{trans}\text{-}[\mathrm{RhCl(CO)(PPh_3)(SbPh_3)}] + \mathrm{SbPh_3} \rightleftharpoons \underset{\mathbf{X}}{[\mathrm{RhCl(CO)(PPh_3)(SbPh_3)_2}]} \rightleftharpoons \quad (9)$$
$$1/3\ \textit{trans}\text{-}[\mathrm{RhCl(CO)(PPh_3)_2}] + \underset{\mathbf{XI}}{2/3\ [\mathrm{RhCl(CO)(SbPh_3)_3}]} + 1/3\ \mathrm{PPh_3}$$

The occurrence of five-coordinate species **X** and **XI** is a further manifestation of the tendency of antimony donor ligands to stabilize five-coordination in d^8 metal complexes.[17,18]

(iii) Oxidative additions

With halogen or hydrogen chloride. Complex **II** undergoes oxidative addition with halogens (Y_2) or hydrogen chloride in chlorinated solvent to give products which have been formulated as:[11,12]

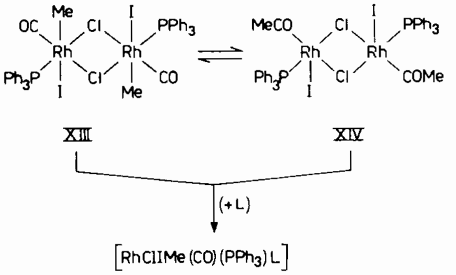


XII

XII ($XY_2 = Cl_3$, Br_3) can also be obtained by reaction of [Rh(acac)(CO)(PPh_3)] with chlorine or bromine in CCl_4.[19] Addition of hydrogen chloride to **II** gives the trichloro-adduct **XII** (X = Y = Cl), indicating that the likely intermediate for this reaction, *viz.*, the hydrido–dichloro-adduct [$RhHCl_2(CO)(PPh_3)]_2$, is too unstable to be isolated. Examples of cleavage of a transition metal–hydride bond by acids with evolution of molecular hydrogen such as this are quite common.[20,21] [RhCl(CO)(PPh_3)($AsPh_3$)] also undergoes oxidative addition reactions, to give [RhClXY (CO)(PPh_3)($AsPh_3$)] ($XY = Cl_2$, I_2).[12]

With methyl iodide. The oxidative addition of methyl iodide to **II** is more complicated than that of halogens as the expected oxidative addition product, *viz.*, a methyl–rhodium(III) σ-bonded species undergoes further rearrangement to an acetyl–rhodium complex.

The final reaction product has an i.r. spectrum exhibiting both acetyl carbonyl and terminal metal carbonyl stretching absorptions (1710 and 2065 cm^{-1}, respectively). If the reaction is carried out for a prolonged time, the acetyl carbonyl band increases in intensity at the expense of the terminal carbonyl band,[12] suggesting that the product isolated is a mixture of isomeric methyl–carbonyl– and acetyl–rhodium(III) species, **XIII** and **XIV**. If a chloroform or dichloromethane solution of this isomeric mixture is treated with an excess of PPh_3, $AsPh_3$, or $SbPh_3$ (L) and pentane is added immediately, the resulting precipitate is a pure methyl–rhodium(III) carbonyl species **XV** formed by splitting of the chloride bridge by L:



XIII XIV (10)

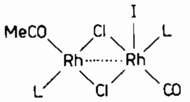
[RhClIMe(CO)(PPh$_3$)L]

XV

The formation of pure **XV** starting from a solution containing predominantly the acetyl–rhodium species **XIV** in equilibrium with **XIII** may be related to the greater reactivity of **XIII** towards Lewis bases. The lower solubility of the resultant monomeric alkyl complex relative to the acyl isomer must also be responsible. The compounds **XV** on light exposure slowly isomerize to the acetyls [RhClI(MeCO)(PPh_3)L].

XV (L = $AsPh_3$) can also be obtained from the reaction of [RhCl(CO)(PPh_3)($AsPh_3$)] with methyl iodide but the product is again in equilibrium with its acetyl isomer.

Alternatively, it has been reported that addition of methyl iodide to **II** (L = PMe_3, PPh_3) gives a compound which analyses as [$Rh_2Cl_2I(CO)(COMe)L_2$]·xMeI (x = 0.2–0.3) and on i.r. evidence appears to contain both acetyl and terminal carbonyl groups.[11] The following structure (**XVI**) was proposed on the basis of ^1H nmr spectra:

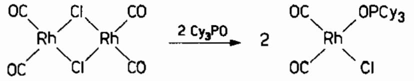


XVI

However, this formulation is hardly consistent with the above mentioned reaction (10). This question is still open.

3. Stable *cis*-dicarbonyl Species

In pursuing the search for novel *cis*-dicarbonyl rhodium(I) species as potentially versatile substrates, we have prepared *cis*-[RhCl(CO)$_2$(Cy$_3$PO)] (**XVII**; Cy$_3$PO = tricyclohexylphosphine oxide) from the reaction of [RhCl(CO)$_2$]$_2$ with Cy$_3$PO (Rh/Cy$_3$PO molar ratio = 1) in dichloromethane [ν(CO) at 2078 and 1998 cm^{-1} in CS_2]:[8]



XVII

XVII is stable toward loss of carbon monoxide, resembling its *cis*-dicarbonyl-amine analogs.[6,7] Cy$_3$PO is less effective in labilizing the CO group *trans* to it than tertiary phosphines and arsines since formation of the expected decarbonylation product, [RhCl(CO)(OPCy$_3$)]$_2$, was not observed under our experimental conditions.

The structure of **XVII** has been confirmed by an X-ray structure determination.[8] The overall coordination geometry about the rhodium atom is closely square-planar with the two carbonyl ligands arranged

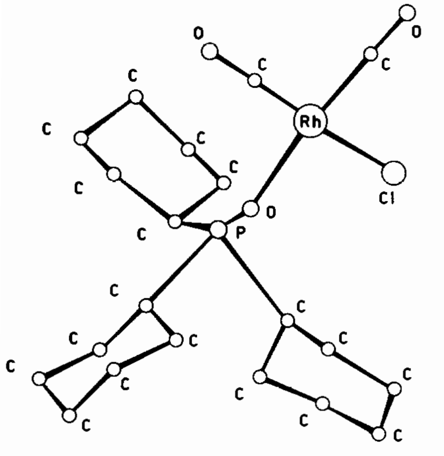


Figure 1. A perspective view of *cis*-$[RhCl(CO)_2(Cy_3PO)]$.

in a *cis* configuration as predicted on the basis of the i.r. spectrum (Figure 1).

4. Conclusions

The dimer $[RhCl(CO)_2]_2$ reacts with nitrogen or oxygen donor ligands L to give halide-bridge splitting monomeric products of type *cis*-$[RhCl(CO)_2L]$. When L is a tertiary phosphine the final products are halide-bridged dimers of type $[RhCl(CO)L]_2$. *Cis*-dicarbonyl complexes may be formed as labile intermediates, some of which display good catalytic activity. Oxidative addition of halogens or alkyl halides on to $[RhCl(CO)L]_2$ produces dimeric adducts of Rh^{III}, the nature of which is actually a subject of some controversy.

5. References

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