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A COMPREHENSIVE STUDY OF THE SYSTEMS μ-DICHLOROTETRACARBONYLDIRHODIUM–PHOSPHINES AND EVIDENCE OF OXIDATIVE ADDITION INVOLVING NEW DINUCLEAR COMPLEXES*

J. GALLAY, D. DE MONTAUZON and R. POILBLANC

Laboratoire d'Étude et d'Application des Complexes Métalliques, U.E.R. de Chimie Inorganique de l'Université Paul Sabatier, Laboratoire Associé au C.N.R.S. no. 160. 38, rue des 36 ponts, 31-Toulouse (France)

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SUMMARY

An infrared study has established that the $[Rh(CO)_2Cl]_2$–phosphine (L) systems are composed of two series of complexes, mononuclear complexes X_n of formula $RhCl(CO)_{3-n}L_n$ ($n=1, 2, 3$) and dinuclear complexes Y_m of formula $Rh_2Cl_2(CO)_{4-m}L_m$ ($m=0, 1, 2, 3, 4$). The new compounds Y_2 and Y_3 are sufficiently stable to allow elemental analysis but for the compounds X_1 and Y_1 proof of their structures has been obtained by chemical methods and by mass spectrometric investigations. Preliminary PMR studies indicate that quite fast and complex exchanges occur in the system. Reactions of Cl_2, HCl and CH_3I molecules on dinuclear complexes are examples of oxidative additions to two coordinative metal centers.

INTRODUCTION

With organometallic carbonyl compounds, substitution reactions involving carbon monoxide and different ligands invariably lead to the formation of complex mixtures of derivatives. In addition, the composition of these mixtures may be considerably influenced by factors such as the relative concentration of the ligand to metal, the nature of the solvent, the temperature etc. In this paper it is shown that the composition of mixtures obtained by the reaction of phosphines and μ-dichlorotetracarbonyldirhodium $[Rh(CO)_2Cl]_2$ is very dependent on factors of this kind and for this reason it has been found more convenient to consider these mixtures as "systems" made up of three basic components, *i.e.* RhCl, carbon monoxide and phosphine. Thus, the term Rh/CO/L "system" will be used to designate various mixtures studied in the following text.

Among the most important derivatives found in any given "system" are square-planar complexes of type $RhCl(CO)(PPh_3)_2$ and $RhCl(PPh_3)_3$, the catalytic properties of which have been comprehensively studied and found to afford many related derivatives with other phosphines[1,2,3,4]. According to Wilkinson[5], RhCl-

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* A short preliminary communication, published while the present paper was in proof, is to be found in: *C.R. Acad. Sci. Ser. C*, 273 (1971) 988.

$(PPh_3)_3$ exists in solution as the square-planar derivative $RhCl(PPh_3)_2(S)$ where S depicts a solvent molecule. From these solutions the dinuclear complex $[RhCl(PPh_3)_2]_2$ may be isolated, whose related pentafluorophenylphosphine derivative has already been reported[6].

More recently Belluco *et al.*[7] have reported and studied oxidative additions involving derivatives of the type $RhCl(CO)_2L$ where $L = PPh_3$. Such dicarbonyl complexes are well known with L as a Lewis base containing a trivalent nitrogen atom as part of its structure. However, as we have already pointed out[8] the complex isolated by Belluco *et al.* in the solid state most probably has a dinuclear structure*.

In order to study the Rh/CO/L "system" in a comprehensive manner, the following different phosphine ligands have been used: triphenylphosphine, dimethylphenylphosphine and tris(dimethylamino)phosphine. These ligands were chosen because of the facilities they provide, either during the isolation of the derivatives, or in elemental analyses, or alternatively during nuclear magnetic resonance studies.

RESULTS AND DISCUSSION

1. *Synthesis of dinuclear complexes of the general formula* $Rh_2(CO)_{4-n}L_nCl_2$ *with* $n = 2, 3$

As reported recently[8], carbon monoxide evolution has been observed during the attempted isolation of the products from the reaction of phosphines with μ-dichlorotetracarbonyldirhodium, when mild vacuum conditions were employed. Such conditions appear favourable, therefore, for the spontaneous decarbonylation of the "system", and for this reason they were used with considerable success in the first two cases to be discussed below and also in a third case which will be discussed later (see paragraph 3).

With triphenylphosphine as a ligand, present in the ratio L/Rh = 1, in addition to the evolution of gases under the above conditions the precipitation of a yellow solid was also observed. A similar product was also obtained when an attempt was made to isolate the complexes formed during the reaction of a phosphine on μ-dichlorotetracarbonyldirhodium, using a similar L/Rh ratio, by concentrating the solution under vacuum and salting out. The solid derivative thus obtained is apparently similar to that isolated by Belluco *et al.*[7] and described by them as the monosubstituted mononuclear derivative *trans*-$RhCl(CO)_2(PPh_3)$. Additional confirmation of the identity of these two similar products was provided by the observation of a single absorption C–O stretching band in the infrared spectrum at 1980 cm^{-1} with the derivative obtained in our studies. The proximity of calculated percentages for the mononuclear and dinuclear derivatives—$RhCl(CO)_2(PPh_3)$ (C, 52.57; H, 3.28; Cl, 7.78; P, 7.01%) and $Rh_2(CO)_2(PPh_3)_2Cl_2$ (C, 53.21; H, 3.50; Cl, 8.28; P, 7.23%)—makes it rather difficult to distinguish between these two structures on solely analytical grounds. Although our best analytical results for carbon, hydrogen, phosphorus and chlorine were almost identical to the values predicted for the dimeric structure, it should be pointed out that some samples were obtained which on analysis gave results similar to those reported by Belluco *et al.*, for carbon, hydrogen and chlorine

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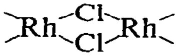
* Recent reinvestigations by these authors[7] agree with our point of view, and we thank them for their personal communciation.

and which agreed with a mononuclear structure. The dinuclear structure of the complex has, in fact, been confirmed by molecular weight determinations in benzene solution using osmotic pressure measurements from which molecular weight values of 860 ± 40 (calculated mol.wt. 857) were obtained.

A similar dinuclear structure is obtained when trimethylphosphine is used as a ligand. In this particular case the "dinuclear" derivative $Rh_2(CO)_2(PMe_3)_2Cl_2$ (C, 19.79; H, 3.71; Cl, 14.64; P, 12.78%) is different, at least from an analytical point of view, from the possible mononuclear derivative $RhCl(CO)_2(PMe_3)$ (C, 22.18; H, 3.32; Cl, 13.12; P, 11.46%). Once more, however, complete confirmation was achieved through molecular weight measurements of 480 ± 10, the dinuclear structure requiring a calculated value equal to 485.

The dinuclear structure of these two complexes must be attributed to the presence of Cl bridges such as exist in the structure of the unsubstituted chlorocarbonyl. The existence of a single C–O stretching band in the infrared spectra of both these compounds suggests a *trans* configuration for the CO groups. Indeed in the case of μ-dichlorotetracarbonyldirhodium $[Rh(CO)_2Cl]_2$ the interaction constants between CO groups acting through a



bridge are not zero[9]. This suggests that derivatives containing the same basic framework should be analyzed, from a vibrational viewpoint, not in terms of independent RhCl, (CO) and (PPh_3) units, but in terms of the whole molecule. For *cis*-$Rh_2(CO)_2L_2Cl_2$, with C_{2v} symmetry, two infrared active bands (A_1 and B_1) are expected, while for the *trans*-$Rh_2(CO)_2L_2Cl_2$ derivative, with C_{2h} symmetry, an infrared active band (B_u) and a Raman active band (A_g) should be observed.

The decarbonylation process in the Rh/CO/L "system" also occurs at other L/Rh ratios; with L/Rh = 3/2, and under forcing conditions (see experimental section), carbon monoxide evolution again occurs and the $Rh_2(CO)(PPh_3)_3Cl_2$ derivative may be isolated. Unfortunately, however, the process cannot be extended to related derivatives for the conditions for decarbonylation would have to be too drastic and only decomposition products are formed.

With triphenylphosphine at L/Rh = 3/2, the derivative obtained is only slightly soluble, but despite this fact the approximate molecular weight values obtained by osmometry in benzene are compatible with a dinuclear structure. In this particular case, such a structure is a logical consequence of the use of a 3/2 ratio and is also implied by the results of elemental analysis. Again, an observed stretching frequency for the CO bond in the infrared spectrum identical with that for the dinuclear disubstituted derivative, under the same conditions, is not an argument in disfavour of such a structure. Indeed in the monocarbonyl derivative $Rh_2(CO)(PPh_3)_3Cl_2$, this frequency (1980 cm^{-1}) is characteristic of the C–O bond strength, whereas in the dicarbonyl derivative, $Rh_2(CO)_2(PPh_3)_2Cl_2$, it only represents a C–O (B_u) extension mode: in this latter instance the frequency corresponding to the average bond strength constant would probably occur at a higher value[10].

2. *A spectrographic study of the Rh/CO/L "system" as a function of the variation in the L/Rh ratio*

Study of the reaction mixtures clearly indicates that the composition of such mixtures is not solely attributable to the dinuclear complexes of the type discussed above, the carbonyl and well-known square-planar derivatives $RhCl(CO)L_2$. In addition, the extreme sensitivity of the system to the CO pressure can be easily shown. If a $10^{-3}M$ solution of $[Rh(CO)_2Cl]_2$ and PMe_3 maintained under CO atmosphere is cooled, the formation of red crystals may be observed. If the same solution (before cooling) is held under a slight vacuum, as occurs during pipetting, blue crystals are formed, although the red colour of the first crystallization product may be restored if carbon monoxide is bubbled through the solution before recooling. It therefore appears as if the "system" is capable of exhibiting absorbtion and desorption properties towards carbon monoxide, and quite clearly this behaviour together with the associated variation in solution composition ultimately leads to the interesting crystallisation phenomena noted above.

Because of the CO pressure effect, in order to study the Rh/CO/L "system" at different L/Rh ratios, a device which allowed the direct circulation of the reaction mixture into the observation cell for infrared spectral measurements had to be used, while a constant pressure of CO in contact with the solution was maintained. This, and other operations, was achieved through the use of the apparatus described in the experimental section.

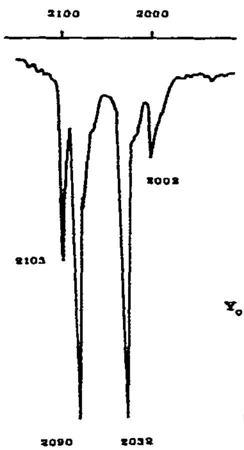
In the first series of experiments, a $10^{-4}M$ solution of the chlorocarbonyl in n-octane was treated with trimethylphosphine at L/Rh ratios of 0.40, 0.65, 1.25, 1.50 and 2 respectively. By direct observation of the infrared spectrum it is possible to follow the gradual changes in composition of the mixture of derivatives, until finally when no further change in the observed spectrum occurs it may be assumed that the mixture has attained thermodynamic equilibrium under the experimental conditions, *i.e.* with a fixed initial L/Rh ratio and with the CO concentration corresponding to its solubility in octane.

In most cases such equilibrium conditions were attained within the time interval necessary for the first spectrographic recording (*i.e.* within about one minute after mixing the reagents), thus indicating that the kinetics were rapid. In addition, it has already been noted above that by the re-introduction of CO into the system it should be possible to upset the equilibrium conditions and reverse the chemical reaction, and this fact when taken in conjunction with the attainment of saturated conditions involving CO and the solution in the experimental system suggests that in this particular study the equilibria involving the Rh/CO/L "system" are near to reversibility.

For each particular ratio of L/Rh several spectra were recorded at equal time intervals (5 minutes) and the various L/Rh ratios adjusted to accord with the data obtained. The following figures illustrate typical results obtained during the course of this study.

Spectrum 1: This depicts the spectrum of the tetracarbonyl complex over the range 2150 to 1900 cm^{-1}, and illustrates the positions and relative intensities of the C–O stretching bands: 2103 s, 2088 vs, 2032 vs, 2002 m.

Spectrum 2: The introduction of ligand L at an L/Rh ratio of 0.40 expands the above spectrum to that of a five-band system. From the discussion below it will be seen that it is reasonable to assume that these bands are derived from the parent carbonyl and from two distinct complexes, X_1 and Y_1. It is assumed that complex X_1 is characterized by CO stretching bands at 2092 vs and 2000 vs respectively, and



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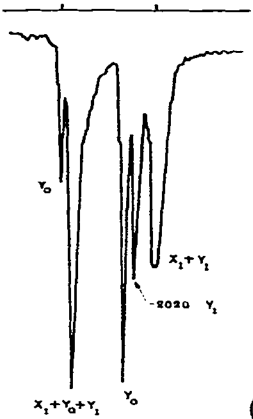

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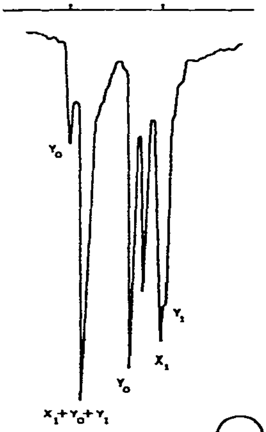
that complex Y_1 has the following absorption frequencies: 2088 vs, 2020 vs, 1995 vs.

Spectra 3–4–5: These spectra may be obtained under similar experimental conditions to those of spectrum 2 (in particular the same L/Rh ratio), but in addition observing the respective concentrations of the components of the system after successive 5 min intervals. It will be seen that the principal changes in the spectra may be attributed to an increase in the concentration of complex Y_1 and a decrease in that of Y_0 and X_1. The system reaches equilibrium within 20 minutes or so.



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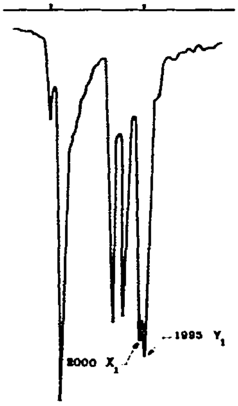

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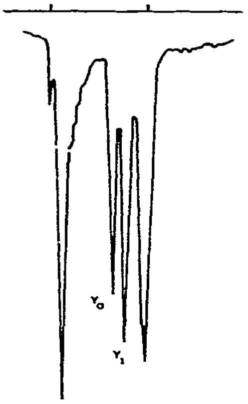

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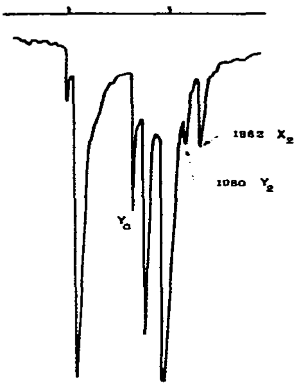
During the establishment of the equilibrium the two bands which were observed at 2000 and 1995 cm^{-1} in spectrum 2, merged into one band and the related intensity variations of the bands at 2020 and 1995 cm^{-1} clearly demonstrate the correctness of their proposed assignment to a single derivative called Y_1.

Spectra 6–7: Spectrum 6 is observed as soon as the L/Rh ratio is adjusted to a value of 0.65, and after 20 minutes or so, spectrum 7 is obtained. Since the concentrations of the individual components in the system remain virtually unchanged during this interval of time, it may be assumed that equilibrium is attained in the



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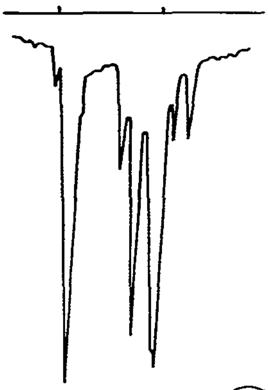

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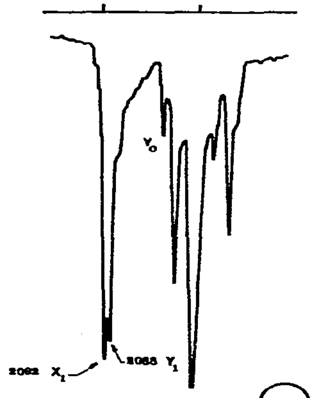
system during the time necessary for the first observation, *i.e.* instantaneously. Both spectra 6 and 7, with an L/Rh ratio of 0.65, differ from the observed spectra at L/Rh = 0.40 because of the appearance of characteristic bands relating to the dinuclear $[Rh(CO)PMe_3Cl]_2$ and mononuclear $RhCl(CO)(PMe_3)_2$ derivatives. For reasons which will be explained later, these two derivatives will be called Y_2 and X_2 respectively.

In general, the presence of carbonyl in small quantities and the formation of derivatives with an L/Rh ratio greater than one (Y_2 and X_2) in a system in which the initial value of this ratio is approximately 0.5, or at least in all cases less than one, is quite significant. It, in fact, implies that the L/Rh ratio should be at least less than one in the two compounds formed (X_1 and Y_1).

Spectrum 8: On increasing the value of the L/Rh ratio to 1.25, virtually complete disappearance of carbonyl Y_0 is observed. Under these circumstances the disappearance of the absorption band at 2090 cm^{-1} corresponding to this compound upsets the apparent simplicity of the high frequency band and leads to the formation of a more complex spectral structure composed of bands at 2088 and 2092 cm^{-1}.

Spectrum 9: Increasing the L/Rh ratio still further to 1.50, leads to a decrease



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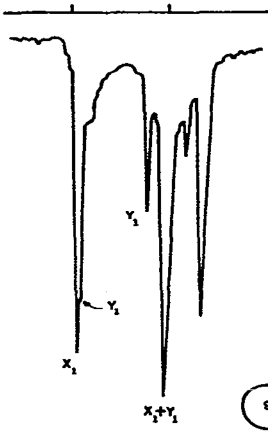

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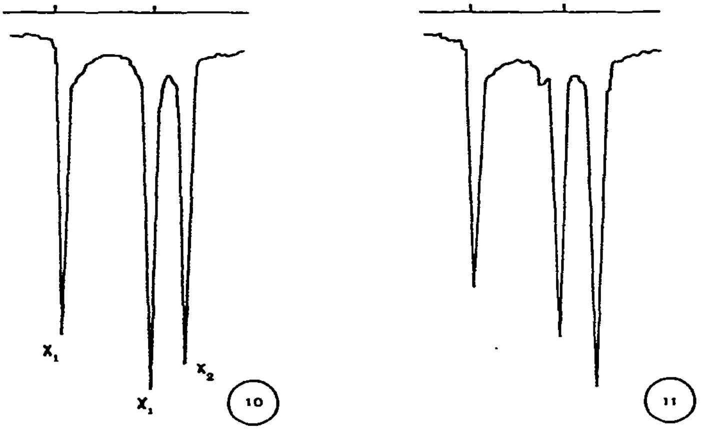
in intensity of the band at 2088 cm^{-1} in comparison with that of the 2092 cm^{-1} band. At the same time a decrease in the intensity of the band at 2020 cm^{-1} also occurs, and these features of the spectrum support the assignment of the band at 2088 cm^{-1} to the Y_1 derivative. At lower frequency values, an increase in the intensity of the band at about 2000 cm^{-1} is not related to any variation in the concentration of the constituent absorbing at 1995 cm^{-1} but to that absorbing at 2000 cm^{-1}. The variations in the bands at 2092 and 2000 cm^{-1} are therefore related and justify the assignment of these two bands to a single X_1 derivative.



Spectra 10–11: These spectra are those observed when the L/Rh ratio is equal to 2; they confirm that compounds X_1 and X_2 are the only derivatives present.

It should be noted that spectrum 10 does not correspond to an equilibrium state, and that spectrum 11 shows the change in composition of the mixture towards an increasing amount of the X_2 derivative.

In conclusion, therefore, it may be stated that as the L/Rh ratio in the Rh/CO/L "system" increases up to 2, the existence of derivatives labelled X_1, X_2 and Y_0, Y_1, Y_2 respectively has been observed. The natures of the complexes X_2, Y_0 and Y_2 are known, but those of the complexes X_1 and Y_1 remain to be characterized.

Similar results to those described above have also been observed with other ligands, especially with dimethylphenylphosphine and tris(dimethylamino)phosphine. The same general pattern as with trimethylphosphine has been observed. However, in

TABLE 1

THE VARIATION OF THE CO STRETCHING FREQUENCIES IN RELATION TO THE NATURE OF THE LIGAND

L	*Y₁*			*Y₂*	*Y₃*	*X₁*		*X₂*
PMe_3	2088 vs	2020 vs	1995 s	1979 vs		2092 vs	2000 vs	1962 vs
PMe_2Ph	2088 vs	2022 vs	2000 s	1980 vs		2092 vs	2003 vs	1964 vs
PPh_3	2089 vs	2020 vs	2000 s	1980 vs	1980 vs	2090 vs	2005 vs	1959 vs
TdP	2088 vs	2021 vs	1995 s	1978 vs		2088 vs	2005 vs	1960 vs

these latter cases, most derivatives precipitated as soon as their concentration in solution increased to between 10^{-3} and 10^{-4} mole/litre according to the individual species. It should be borne in mind that the spectra of the mixtures may provide somewhat misleading information in some cases on the relative rates of the various processes occurring in the system in that the spectra are related to concentrations and the latter may, in fact, be related by differences in the solubilities of the various species.

Spectrographic data for the various derivatives are reported in Table 1, where the nomenclature used with $L = PMe_3$ (Y_1, ...) is capable of extension to other ligands, thus obviously allowing the definition of other "types" of complexes.

3. *A study of the Rh/CO/L "system" as a function of the carbon monoxide concentration in solution*

As already noted above, the type and variety of complexes present in the system is very sensitive to small variations in the CO pressure. A similar state of affairs has also been implied in Wilkinson's observation regarding the carbonylation of the complexes $RhCl(PPh_3)_3$ (X_3, L/Rh = 3) and $[RhCl(PPh_3)_2]_2$ (Y_4, L/Rh = 2). In the presence of carbon monoxide the Y_4 derivative is converted into the X_2 derivative, and we have further noted that the latter complex when in contact with carbon monoxide at a constant temperature of 60° is slowly converted to a mixture of complexes: Y_0, Y_1, Y_2, X_1 and X_2. Thus, starting from the dinuclear form (Y_4), carbonylation first leads to the formation of the mononuclear X_2 derivative, and then to the further reorganisation of the system towards a mixture of complexes with a smaller L/Rh ratio.

With L/Rh ratios of 3/2 and 1 in the system, the reverse reaction (decarbonylation) may be observed. This reaction leads to the formation of the derivatives Y_3 and Y_2 respectively, starting from an initial system consisting of a mixture containing a significant quantity of the derivatives X_1 and X_2.

On the other hand, starting from the dinuclear complexes $Rh_2Cl_2(CO)(PPh_3)_3$ (Y_3) and $Rh_2Cl_2(CO)_2(PPh_3)_2$ (Y_2) the bubbling of carbon monoxide through the system leads initially to the formation of mixtures consisting mainly of X_2 and X_1 derivatives in the first case and X_1 alone in the second case. In fact, with the latter compound (X_1) at an L/Rh ratio of 1, and at a temperature of 60° and a pressure of inert gas equal to atmospheric pressure, it is possible to achieve the evolution of one equivalent of carbon monoxide per gram atom of Rh simply by decreasing the pressure in the system by a few centimetres of Hg. Under these circumstances only Y_2 is formed. If the mixture is cooled down, however, and the pressure increased to 1 atmosphere, absorption of one equivalent of carbon monoxide occurs and X_1 is reformed. This suggests that the following equilibrium exists between X_1 and Y_2 *i.e.* the compound $Rh_2Cl_2(CO)_2L_2$:

$$Rh_2Cl_2(CO)_2L_2 + 2\,CO \rightleftarrows xX_1$$

Secondly, it should be noted that when carbon monoxide is bubbled through solutions of Y_2 and Y_3 an increase in the concentration of species with smaller values of the ratio L/Rh is observed. This type of behaviour is not peculiar to rhodium derivatives as it frequently occurs in carbonyl metal chemistry in general; in this case, however, it is relatively unimportant. On the other hand, the fact that the X_1 derivative is a carbonylation product of Y_2 is most significant.

When L/Rh$=\frac{1}{2}$, decarbonylation of mixtures containing Y_0, Y_1 and X_1 complexes occurs, and using experimental conditions of the kind discussed below (Experimental section), leads to the formation of the Y_1 derivative only. Conversely, the carbonylation of Y_1 leads to the formation of a mixture of carbonyl and the X_1 derivative initially (and to the gradual formation of the unsubstituted carbonyl as the final product).

It is therefore possible, in general, to summarize our observations by the following equations:

$$Rh_2Cl_2(CO)L_3 \overset{+CO}{\rightleftharpoons} RhCl(CO)L_2 + X_1$$

$$Rh_2Cl_2(CO)_2L_2 \overset{+2\,CO}{\rightleftharpoons} x\,X_1$$

$$Y_1 \overset{+CO}{\rightleftharpoons} X_1 + Rh_2Cl_2(CO)_4$$

It should be remembered that only the Y_1 derivative is formed when L/Rh$=\frac{1}{2}$.

4. *The characterization of the derivatives Y_1 and X_1, and mass spectrometric investigations*

The results of the preceding study may be accounted for if we assign the dinuclear structure $Rh_2Cl_2(CO)_3L$ to Y_1 and the mononuclear structure $RhCl(CO)_2L$ to X_1.

All Y_1-type derivatives have little stability, even in an inert medium, and in such cases the accuracy of elemental analyses is somewhat suspect. For this reason all the trimethylphosphine and triethylphosphine derivatives have been studied by means of mass spectrometry[20].

The occurrence of parent ion peaks at mass numbers 436(438) and 478(480) respectively provide strong evidence in favour of the proposed formulae for both compounds, and this is further supported by the observation of $Rh_2Cl_2(CO)_2L$, $Rh_2Cl_2(CO)L$ and Rh_2Cl_2L fragments in the spectra*. On the spectra that we obtained from mixtures containing the $Rh_2Cl_2(CO)_4$ carbonyl it was difficult to distinguish other Y_1 fragmentation ions from carbonyl ones, but the Rh_2Cl_2 mass peak intensity can only be explained if it is assumed to result partly from ions formed by the loss of one CO ligand and partly by the loss of one L ligand from the derivative Y_1.

Finally, a further argument in favour of the proposed formula for the Y_1 complex is provided by the observation of three bands in the CO stretching frequencies region of the IR spectrum (see Fig. 1).

Because of their instability, X_1 derivatives could not be separated from solution and elemental analyses and mass spectroscopic analyses could not be performed. In this case, however, the carbonylation and decarbonylation reactions described above probably provide sufficient evidence in favour of the proposed formula. In addition, the observation of two CO stretching bands in the IR spectrum of these derivatives

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* This type of fragmentation involving the loss of CO groups is similar to that observed with non-substituted carbonyls. In the latter case, only the "Rh_2Cl_2 core" of the complex eventually remained after successive fragmentations.

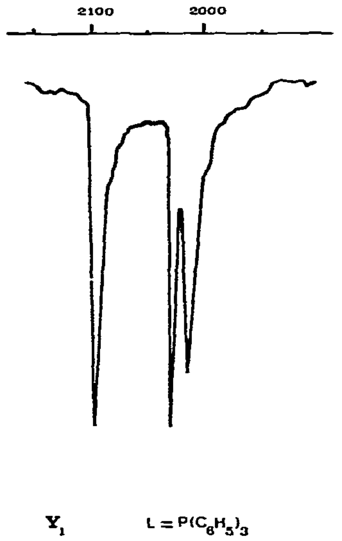

Fig. 1. IR spectrum of $Y_1(PPh_3)$.

suggests that the complexes possess a *cis* configuration similar to that observed by Hieber[11] in the *p*-toluidine compounds.

It therefore appears that the Rh/CO/L "system" is composed of two series of complexes, a mononuclear series X_n with the general formula $RhCl(CO)_{3-n}L_n$ ($n=1$, 2, 3) and a dinuclear series Y_m with the general formula $Rh_2Cl_2(CO)_{4-m}L_m$ ($m=0$, 1, 2, 3, 4). Highly substituted derivatives can be obtained with high L/Rh ratios and for this reason it appears theoretically possible to skip from one series to another by changing the carbon monoxide pressure in equilibrium with the solutions. However when $n=2$, decarbonylation becomes difficult, and conversely, there appears to be no evidence for the existence of a Y_0 carbonylation product.

In the following, the symbols $X_n(L)$ and $Y_m(L)$ will sometimes be used to define the derivatives X_n or Y_m respectively obtained with a given ligand L.

5. *A preliminary PMR study of the Rh/CO/L "system"*

An attempt has been made to obtain additional characterization of X_n and Y_m derivatives by the use of PMR spectroscopy. This has only been partially successful because of the existence of exchange phenomena, which become too significant.

RhCl(CO)L₂ derivatives; L=PMe₃

Ligand exchange has already been studied with $RhCl(CO)(PPh_3)_2$ derivatives, where it appears to proceed by a rapid S_N2 mechanism[12]. Deeming and Shaw[13] have pointed out that exchange involving the complex $RhCl(CO)(PMe_2Ph)_2$ gives rise to proton resonance spectra which vary with the concentration of the free ligand. the proton spectrum consists either of a "virtually coupled" triplet split by Rh–H coupling, or of a doublet preceded by a singlet intermediate stage, depending on whether slow or fast exchange reactions are occurring. This type of situation may be observed on addition of dimethylphenylphosphine to the solution, and the observations are in agreement with theoretical suggestions made by Fackler *et al.*[14].

The same phenomenon was observed in this study and has been used as the basis of a variable-temperature study using trimethylphosphine as the ligand. With an average concentration of ligand the initial spectrum consists of a doublet, but lowering the temperature leads to the coalescence of the signal to a singlet. Only with a low concentration of ligand ($\ll 10^{-1}$ M of ligand per mole of complex) is the formation of a triplet observed, with the characteristics described above.

Since the coupling constant is related to the weighted average of the coupling constants for coordinated or uncoordinated phosphine under fast exchange conditions[13], it is possible to make some deductions regarding the following observations.

The addition of a large excess of phosphine to a solution of the complex $RhCl(CO)(PMe_3)_2$ leads to the precipitation of a highly unstable white product. The latter when separated by centrifugation and dried under nitrogen atmosphere, followed by dissolution in a saturated hydrocarbon, exhibits an IR spectrum characteristic of the initial derivative, but its characteristic odour indicates that it obviously contains considerable quantities of free phosphine. The value of the average coupling constant for these solutions immediately gives the ratio between the complex $X_2(PMe_3)$ and the dissolved free phosphine as very nearly equal to unity suggesting that the formula of the precipitate is $RhCl(CO)(PMe_3)_3$ and that this pentacoordinated species is probably a transition state of the exchange reaction*[,15].

Dinuclear derivatives Y_3 and Y_2

Conclusive data regarding the two dinuclear derivatives $Rh_2Cl_2(CO)_2(PPh_3)_2$ and $Rh_2Cl_2(CO)(PPh_3)_3$, could not be obtained because of their low solubilities in solution. In contrast, however, the derivative $Rh_2Cl_2(CO)_2(PMe_3)_2$ exhibits a simple PMR spectrum consisting of a doublet split by Rh–H coupling (in CH_2Cl_2 $\delta = -2.13$ ppm; $J(P-H) = 10.7$ Hz; $J(Rh-H) = 1.3$ Hz). The absence of a second-order structure is indicative of relatively small $J(P-P)$ coupling and is compatible with the proposed *trans* structure (see above) in which the two phosphorus atoms are linked with two different but equivalent rhodium atoms.

Solutions containing X_1 and Y_1 derivatives

Since it proved impossible to study the complexes X_1 and Y_1 separately in a pure state, they were analysed as mixtures with various L/Rh ratios. Figure 2 shows the results obtained with dimethylphenylphosphine when L/Rh = 0.5 and 1.25 respectively. As shown earlier by IR spectroscopy, at these ratios the system consists essentially of a mixture of X_1 and Y_1 complexes and Y_2 and X_2 derivatives. By analysing at the ratios mentioned above, we obtained confirmation of the variation of the ratio of the concentrations of these derivatives. It is, however, significant that the PMR spectrum shows only one doublet split by Rh–H coupling whereas the mixture certainly contains more than one complex (X_1 and Y_1, and possibly even Y_2). Only at the higher ratio were small quantities of the disubstituted derivative observed in the PMR spectrum. At lower temperatures coalescence of the signal appeared, thus proving once again that an exchange phenomenon occurs. Unfortunately, even at

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* The stabilisation of this intermediate in solution through a mass-effect will probably have to be taken into account in the interpretation of the fast exchange spectra observed in the presence of a high concentration of ligand.

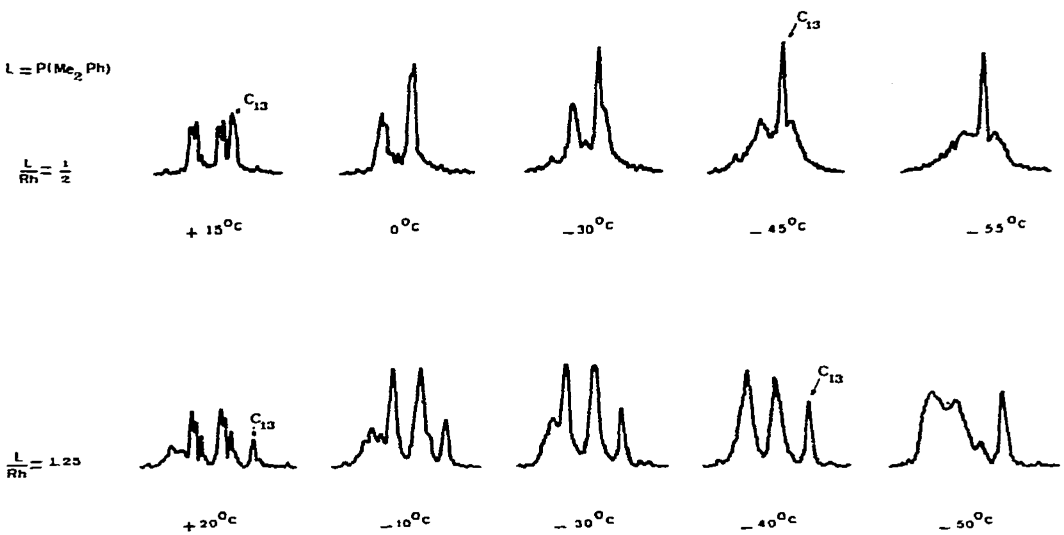

Fig. 2. Variable-temperature PMR spectra of the $[Rh(CO)_2Cl]_2$– phosphine "system", with different L/Rh ratios (L = PMe_2Ph).

–80° this exchange proved to be too rapid to allow further study of this phenomenon.

It appears, in general, that just as the system may be characterized thermodynamically in terms of a sequence of readily reversible reactions, it is characterized by a PMR spectrum which indicates the occurrence of fast exchange phenomena.

6. *Oxidative addition reactions involving dinuclear compounds*

The dinuclear nature of the new derivatives Y_1, Y_2 and Y_3 having been demonstrated, an attempt has been made to determine whether the latter present oxidative addition possibilities similar to those of the known derivatives of Y_4 (with $L = PPh_3$[5] and $L = P(C_6F_5)_3$[6]). Some preliminary results obtained with trimethylphosphine and triphenylphosphine Y_2 derivatives are described here and are outlined in greater detail in Table 2.

Chlorine addition

Chlorine addition to the derivative $Rh_2Cl_2(CO)_2(PMe_3)_2$ is apparently effected in two stages, but the red intermediate complex formed in the first stage could not be isolated or characterised. The final derivative, which possessed the stoichiometric formula $RhCl_3(CO)(PMe_3)$ (I), exhibits a strong band in its IR spectrum at 2120 cm^{-1}, which may possibly be connected with conversion of Rh^I to Rh^{III}. The stoichiometry of the complex corresponds either with a pentacoordinated structure or with a bridged dimeric structure. Since the starting material possesses a stable dinuclear structure (*vide infra*) it seems more probable that the latter structure is more favoured*.

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* In an attempt to verify this suggestion the possible *trans*-configuration of the CO groups of the compound has been studied by Raman spectroscopy but without any conclusive results. Molecular weight measurements by conventional methods are precluded by the low solubility of the compound.

The complex $Rh_2Cl_2(CO)_2(PPh_3)_2$ also reacts in a similar fashion with chlorine and affords a derivative of stoichiometric formula $RhCl_3(CO)(PPh_3)$ (II) with a structure probably similar to that of the trimethylphosphine derivative. It is, however, notable that this latter chlorine derivative possesses an IR spectrum with similar characteristics to those of the complex of supposed formula $RhCl_3(CO)_2(PPh_3)$ (III) obtained by Belluco *et al.*[7] from the allegedly dicarbonyl complex $RhCl(CO)_2(PPh_3)$. Both complexes (II) and (III) are rather similar analytically, and furthermore it must be admitted that some of our analytical results were not too far removed from those for complex (III). This ambiguity obviously disappears when the related trimethylphosphine complexes are considered.

Similarly, the results of bromine and iodine addition on complex $Y_2(PPh_3)$ could be studied spectrographically. The CO stretching frequencies observed in these cases (bromine, 2105 cm^{-1}; iodine, 2094 cm^{-1}) are identical to those existing in the spectra of the related derivatives of the supposed complex $RhCl(CO)_2(PPh_3)$; once more the existence of bridged dinuclear complexes is suggested.

Hydrogen chloride addition

The addition of dry hydrogen chloride to $Y_2(PPh_3)$, which is relatively insoluble in methylene chloride at room temperature, leads to the dissolution of the suspended compound in this solvent. From such a solution it was possible to isolate derivative (II), thus indicating that the oxidative addition which occurs in this case must involve both metal atoms of the bridged dinuclear complex.

Methyl iodide addition

The addition of methyl iodide to the supposed derivative $RhCl(CO)_2(PPh_3)$ has already been discussed, and apparently leads to formation of the mononuclear derivative $RhClI(CO)(COCH_3)(PPh_3)$ (IV). In view of the earlier confusion regarding this topic, it is appropriate to reconsider the reaction in general and to briefly examine whether the supposed complex (IV) is dinuclear and results from an oxidative addition to two metal centers. For the reasons discussed above, we have preferred to study the derivative $Y_2(PMe_3)$. Addition of methyl iodide to this derivative results in a compound of stoichiometric formula $Rh_2Cl_2I(CO)(COCH_3)(PMe_3)_2 \cdot x\,CH_3I$ (V) in which the presence of carbonyl and acetyl groups is confirmed by the presence of stretching frequencies at 2070 and 1687 cm^{-1} in the IR spectrum. The retention of the CH_3I group is in keeping with the analytical results (when $x=0.30$ or so) and explained the apparent lack of reproducibility in the analyses of this compound as being due to a variation in the value of x. Elemental analysis data also exclude a mononuclear formula $RhClI(CO)(COCH_3)(PMe_3)$ for derivative (V). The existence of this compound as a hexacoordinated derivative, and that it belongs to the type of complexes $RhClI(CO)(COCH_3)_2$ synthesized by Heck[15], is also excluded. Although the latter complexes also exhibit CO vibration spectra virtually identical with that of derivative (V), the compounds are completely different as far as their respective analytical requirements are concerned.

The structure of compound (V) has been determined by PMR spectroscopy. The resulting spectrum at 60 MHz exhibits a single peak ($\delta = -3.60$ ppm) which has been assigned to the acetyl group, and a triplet ($\delta = -2.38$ ppm) attributed to coordinated phosphines. It is significant that the ratio of the two signals (of very nearly 6) immediately favours the proposed dinuclear formula. As the separation between the two extreme peaks of the triplet (21 Hz) could not be assigned to J(P–H) coupling, the derivative was studied further at 100 MHz frequency (see Fig. 3).

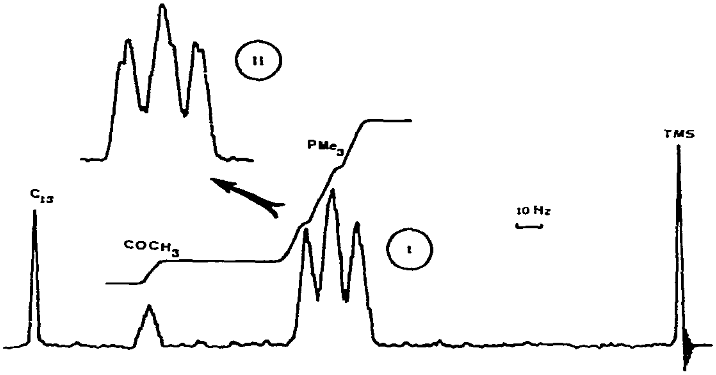
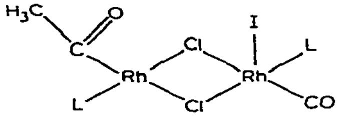


Fig. 3. PMR spectra of Y_2CH_3I observed at 60 MHz frequency (I) and at 100 MHz frequency (II).

At this frequency, the separation increases to 28 Hz as would be expected if the triplet results from the superposition of two doublets coupling at or near 10 Hz. From this it follows that derivative (V) must contain two phosphine ligands (per acetyl group) but in *different magnetic environments.*

Thus, despite the fact that the low solubility of this derivative precludes the measurement of molecular weight, it is still possible to suggest the following basic structure for the compound:



(V)

Since derivative (V) is simply and readily produced from Y_2, it is suggested that the latter also possesses a structure very nearly that of the chlorocarbonyl.

The existence of empty coordination sites in the structure which would also be available to a methyl iodide molecule, would further explain the presence of this residue in our analyses. A similar conclusion may be drawn regarding the structure of the derivative $Y_2(PPh_3)$. Such coordination for methyl iodide has already been postulated in the complex $RhClI(Me)(PPh_3)_2(MeI)^{16}$.

The above formula obviously implies the existence of two divalent rhodium atoms. This proposition is not incompatible with the diamagnetism of this compound as demonstrated by the observation of non-perturbed PMR spectra. Indeed, many Rh^{II} complexes are known to be diamagnetic probably as a consequence of metal–metal interaction. With the compounds discussed here such interaction between the rhodium atoms, which is known to occur with the Y_0 complex, is probably enhanced by the basicity of the complexing ligands.

Finally, in order to explain the action of methyl iodide on bis(trimethylphosphine carbonyl μ-chlororhodium), it may be assumed that, at least initially, oxidative addition occurs on two metal centers, followed presumably by insertion as the second

TABLE 2

COMPARATIVE TABLE OF ANALYTICAL DATA

Compounds	*IR* (cm^{-1})	*Analysis: found (calcd.)*				
		C	*H*	*Cl*	*I*	*P*
$Rh_2Cl_6(CO)_2(PPh_3)_2$	2112 vs	45.32 (45.66)	3.23 (3.00)	21.49 (21.30)		6.35 (6.21)
$Rh_2Cl_2I(CO)(COCH_3)(PPh_3)_2 \cdot 0.20\ CH_3I$	2068 vs, 1717 vs[a]	45.60 (45.32)	3.12 (3.18)	6.80 (6.85)	14.81 (14.66)	5.94 (5.98)
$Rh_2Cl_6(CO)_2(PMe_3)_2$	2120 vs	15.82 (15.31)	2.99 (2.87)	34.12 (33.98)		9.71 (9.89)
$Rh_2Cl_2I(CO)(COCH_3)(PMe_3)_2 \cdot 0.30\ CH_3I$	2070 vs, 1687 vs[a]	16.80 (16.66)	3.34 (3.27)	10.64 (10.56)	24.42 (24.54)	8.84 (9.22)
$RhCl_3(CO)_2(PPh_3)$[b]	2111 vs	(45.60)	(2.90)	(20.20)		(5.89)
$RhCl_3(CO)_2(PMe_3)$		(17.59)	(2.64)	(31.23)		(9.09)
$RhClI(CO)(COCH_3)(PPh_3)$[b]	2065 vs, 1710 vs	(42.10)	(3.00)	(5.90)	(21.20)	(5.16)
$RhClI(CO)(COCH_3)(PMe_3)$		(17.35)	(2.89)	(8.55)	(30.60)	(7.47)
$RhClI(CO)(COCH_3)(PPh_3)_2$		(54.29)	(3.82)	(4.10)	(14.90)	(7.19)
$RhClI(CO)(COCH_3)(PMe_3)_2$		(21.99)	(4.27)	(7.23)	(25.86)	(12.63)
$RhClI(CO)(COCH_3)(PBu_3)_2$[c]	2070 vs, 1670 vs					

[a] In CH_2Cl_2. [b] See ref. 7 for comparative data. [c] See ref. 17 for comparative data.

step. Oxidative addition on two metal centers is relatively unknown*, but might play an important part in the activation of small molecules.

EXPERIMENTAL

The ligand $P(CH_3)_3$ was synthesized according to methods already described[16].

Pure hydrated rhodium chloride was purchased from "Comptoir des métaux précieux". Infrared spectra were recorded on a Perkin–Elmer model 225 instrument using hexadecane solutions and NMR spectra were recorded on Varian A60 and HA 100 instruments respectively. Molecular weights were measured by using a Mechrolab vapour pressure osmometer. Elemental analyses (C, H, Cl, I, P) were undertaken at the C.N.R.S. microanalysis laboratory. Raman spectra were obtained with a CODERG PH1 spectrometer equipped with a Spectra Physics He–Ne Laser. The mass spectra were recorded on an AEI MS902 instrument.

All reactions were carried out at room temperature under nitrogen atmosphere unless otherwise stated.

Apparatus for spectrographic investigations of reaction mixtures

The apparatus, shown in Fig. 4, is composed of a thermostatted reactor connected with a gas circulation circuit, a reaction mixture circulation circuit connected with a spectrographic observation cell, and a Bunte burette. Circulation and dispersion of the gaseous phase through the sintered glass disc of the reactor allowed almost

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* To date, the only other case reported appears to be that concerning the formation of the derivative $Rh_2Cl_2H_4(PPh_3)_4$ as studied by Wilkinson[5].

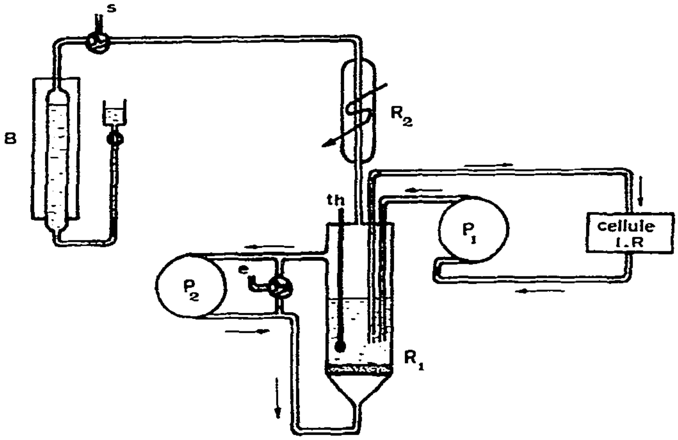

Fig. 4. Apparatus for the spectrographic investigation of reaction mixtures. B. Bunte burette; R_1, thermostatted reactor; R_2, condenser: P_1, pump for the circulation of solutions: P_2, pump for the circulation of gases; th, thermometer; cellule I.R., IR cell: e and s, entry and exit of gas.

instantaneous equilibrium between carbon monoxide in the gaseous phase and in solution.

As an example, the synthesis of triphenylphosphine tricarbonyl μ-dichlorodirhodium is described. The introduction of 10^{-4} *M* $Rh_2(CO)_4Cl_2$ and 10^{-4} *M* PPh_3 into 25 ml of n-octane at room temperature leads to the formation of a mixture of X_1, Y_1 and Y_0 complexes in solution. Inert gas circulation using pump P_2 allows carbon monoxide to pass into the gaseous phase and leads to an increase in the Y_1 concentration at the expense of that of X_1 and Y_0; a similar result is obtained by increasing the temperature. It is important to note that in order to obtain the Y_1 derivative in quantitative yield, carbon monoxide must not be circulated in a closed circuit (even at a low partial pressure) and that it must only be used in conjunction with an inert gas in an open circuit entering the system at "e" and leaving at "s".

Synthesis of individual compounds

μ-dichlorotetracarbonyldirhodium $[Rh(CO)_2Cl]_2$

μ-dichlorotetracarbonyldirhodium has been obtained from hydrated rhodium trichloride using the method of Wilkinson[19].

$$2\,RhCl_3\cdot 3\,H_2O + 6\,CO \rightarrow Rh_2Cl_2(CO)_4 + 2\,COCl_2 + 3\,H_2O$$

However through the use of the following operation conditions it is possible to reduce the time necessary for the reaction from the normal requirement of at least one day to approximately one hour. 1 to 5 grams of hydrated rhodium was intimately mixed with an equal amount of Fontainebleau sand (quality 300 μ) in a tube, the temperature of which was raised to 80° and through which a flow of carbon monoxide was maintained. After 8 to 10 minutes the condensation of steam ended, the latter was removed by heating with a Bunsen burner, and the reactor temperature was then raised to 140° (by successive stages, each stage increasing the temperature by 10° and lasting for half an hour), and finally kept at 140° for 3 hours. An average yield of

70% was obtained by constantly reusing the same sand. The infrared spectrum exhibits the following CO stretching frequencies: 2103 s, 2088 vs, 2032 vs, 2002 m.

Bis(triphenylphosphine carbonyl μ-chlororhodium) $[Rh(CO)(PPh_3)Cl]_2$

10 ml of a toluene solution containing $5 \cdot 10^{-4}$ mole of $Rh_2(CO)_4Cl_2$ and 10^{-3} mole of triphenylphosphine were placed in a Schlenck tube. The tube was then maintained at reduced pressure (150 mmHg) for one to two hours. During this period decarbonylation of the reaction mixture occurs, the latter consisting mainly of the dinuclear monosubstituted derivative Y_1 together with some mononuclear derivative X_1 and free ligand, and a yellow solid precipitates. This solid was removed, dried and washed several times with hexane. (Found: C, 53.34; H, 3.70; Cl, 8.29; P, 7.20. $C_{19}H_{15}ClOPRh$ calcd.: C, 53.21; H, 3.50; Cl, 8.28; P, 7.23%.)

This elemental analysis corresponds to the formula $(RhH_{15}C_{19}OPCl)_n$, and indicating the presence of the CO ligand, the formula becomes $[RhCl(CO)(PPh_3)]_n$. Since the rhodium atom is most certainly tetracoordinated in a +1 oxidation state it is probable that n in this formula is equal to 2, a suggestion which has been verified by molecular weight measurements carried out osmometrically using benzene as a solvent (Found: mol.wt., 860±40, calcd.: 857).

Bis(trimethylphosphine carbonyl μ-chlororhodium) $[Rh(CO)(PMe_3)Cl]_2$

The procedure used in this case was very similar to that employed for the triphenylphosphine derivative with the same L/Rh ratio. Trimethylphosphine reacts rapidly with chlorocarbonyl to again give a mixture essentially containing mononuclear monosubstituted and dinuclear derivatives X_1 and Y_1 respectively. Although the removal of the ligand does not occur under the vacuum conditions employed it is essential not to use a solvent of too high a volatility (for example pentane). Decarbonylation is favoured by the presence of the solvent so that it is essential that the reduction in the volume of the latter due to its high volatility should not impede the progress of the decarbonylation reaction. (Found: C, 19.82; H, 3.70; Cl, 14.62; P, 12.53. $C_4H_9ClOPRh$ calcd.: C, 19.79; H, 3.71; Cl, 14.64; P, 12.78%.)

Bis(dimethylphenylphosphine carbonyl μ-chlororhodium) $[Rh(CO)(PMe_2Ph)Cl]_2$

This complex was synthesized using the same conditions as those described above. Its availability in the pure state was, however, impeded by the difficulty in removing the possible excess of ligand present and by the physical state of the product which was formed as a viscous unstable liquid.

Bis[tris(dimethylamino)phosphine carbonyl μ-chlororhodium] $\{Rh(CO)[P(NMe_2)_3]Cl\}_2$

This complex, which was synthesised in a manner similar to that described above, is formed as a pale yellow solid. It has, however, little stability even in the solid state, and no attempt was made to obtain reproducible analytical results.

Tris(triphenylphosphine) monocarbonyl μ-dichlororhodium $Rh_2(CO)(PPh_3)_3Cl_2$

This derivative may be obtained from reaction mixtures with L/Rh ratio 3/2, but the method involves a difficult decarbonylation. In fact this derivative could only be prepared by the evaporation at 40° in vacuo under dry conditions, of solutions containing the reaction mixture in a solvent consisting of 50/50 toluene and methylene chloride. The operation had to be repeated several times in order to obtain complete decarbonylation. (Found: C, 60.38; H, 4.35; P, 8.77; Cl, 6.53. $C_{55}H_{45}Cl_2OP_3Rh_2$ calcd.: C, 60.50; H, 4.13; P, 8.52; Cl, 6.51%.)

Chlorine addition to $Rh_2Cl_2(CO)_2L_2$ *(*$L=PMe_3$, PPh_3*)*

Dry chlorine was bubbled for a few minutes through a millimolar suspension of Y_2 in about 50 ml of CH_2Cl_2. The solid particles completely dissolved and an orange yellow solution was formed. This solution was concentrated and pentane added when the derivative $Rh_2Cl_6(CO)_2L_2$ was precipitated. After drying, the latter existed as an orange yellow powder (see analysis in Table 2).

Action of dry hydrogen chloride on $Y_2(PPh_3)$

Hydrogen chloride was bubbled through Y_2 suspended in CH_2Cl_2 for 5 minutes until the solid particles dissolved and an orange yellow solution was formed. This solution was concentrated and pentane added. The orange yellow solid which precipitated was first filtered and then dried in vacuo (for analysis see Table 2).

Reaction of methyl iodide with $Y_2(L)$ *(*$L=PMe_3$, PPh_3*)*

One millimole of Y_2 and an excess of CH_3I were mixed in a Schlenk tube. After two hours in the dark, the solid dissolved and a red brown solution was formed. The latter was dried in vacuo and the residue dissolved by methylene chloride. The addition of pentane led to the salting out of $Rh_2Cl_2I(CO)(COCH_3)L_2$, which on drying appeared as a brown powder (for analysis see Table 2).

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