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^{31}P and ^{13}C NMR investigation of the system tetracarbonyldi-μ-chlorodirhodium(I)–tertiary phosphine

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Abstract

^{13}C and ^{31}P{^{1}H} NMR data at low temperature prompted us to characterize *cis*-[Rh(CO)$_2$(PR$_3$)Cl] (**3**) (**3a**, PR$_3$ = PPh$_3$; **3b**, PR$_3$ = PMe$_2$Ph), as surprisingly stable products of the reaction between [{Rh(CO)$_2$(μ-Cl)}$_2$] (**1**) and tertiary phosphines in toluene (P : Rh = 1). Every attempt to isolate solid **3a** led to the *cis*- and *trans*- halide-bridged dimers [{Rh(CO)(PPh$_3$)(μ-Cl)}$_2$] (**5a**) and **6a** which are formed from **3a** by slow decarbonylation, a process which is greatly accelerated by the evaporation of the solvent under vacuum.

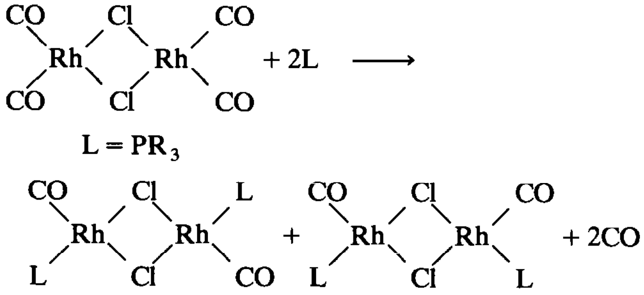
The analogous reaction of **1** with dimethylphenylphosphine follows a similar pathway; in this case, however, low temperature NMR spectra allowed us to characterize the pentacoordinated dinuclear species [{Rh(CO)$_2$(PMe$_2$Ph)(μ-Cl)}$_2$] (**2b**) as the unstable intermediate of the bridge-splitting process.

The reaction of **3** with a second equivalent of phosphine (P : Rh = 2) leads, at room temperature, to the well known product *trans*-[Rh(CO)(PR$_3$)$_2$Cl] (**8**) accompanied by evolution of CO; however our data show that when the reaction is performed at 200 K, decarbonylation is prevented and spectroscopic evidence of trigonal bipyramidal pentacoordinate [Rh(CO)$_2$(PR$_3$)$_2$Cl] (**7**), stable only at low temperature, can be obtained.

1. Introduction

The reaction of the tetracarbonyldi-μ-chlorodirhodium(I) complex, [{Rh(CO)$_2$(μ-Cl)}$_2$], with various amounts of tertiary phosphines has been studied intensively [1–2] and there are confusing interpretations in the literature concerning the mechanism and the intermediates involved [3]. The many different phosphines which have been used as ligands reflect the interest in halo(carbonyl)(phosphine)rhodium complexes as homogeneous catalysts, mainly in the hydrogenation and hydroformylation of alkenes [4].

Complex **1** reacts with primary amines, enimines and tricyclohexylphosphinoxide to undergo the bridge-splitting reactions to give the *cis*-dicarbonyl derivatives, *cis*-[Rh(CO)$_2$LCl] [5]. On this basis, the reactions of **1** with tertiary phosphines were first interpreted as bridge-splitting reactions, leading to *trans*-[Rh(CO)$_2$(PR$_3$)Cl] through the unstable intermediate *cis*-[Rh(CO)$_2$(PR$_3$)Cl] [6]. It was later shown that the product of the reaction between **1** and tertiary phosphines L in various solvents (L : Rh = 1) is a mixture of *cis* and *trans* nuclear halide-bridged complexes {Rh(CO)L(μ-Cl)}$_2$] [7]:



Even though the formulation of the products was unambiguously established by oxygen elemental analysis and by the molecular weight determination, the reaction pathway and the possible intermediates of the reaction were still unclear, the interpretations being supported only by the carbonyl stretching frequencies measured at room temperature. In particular it remained a question as to whether bridge splitting and concomitant intermediate formation of *cis*-halo(di-

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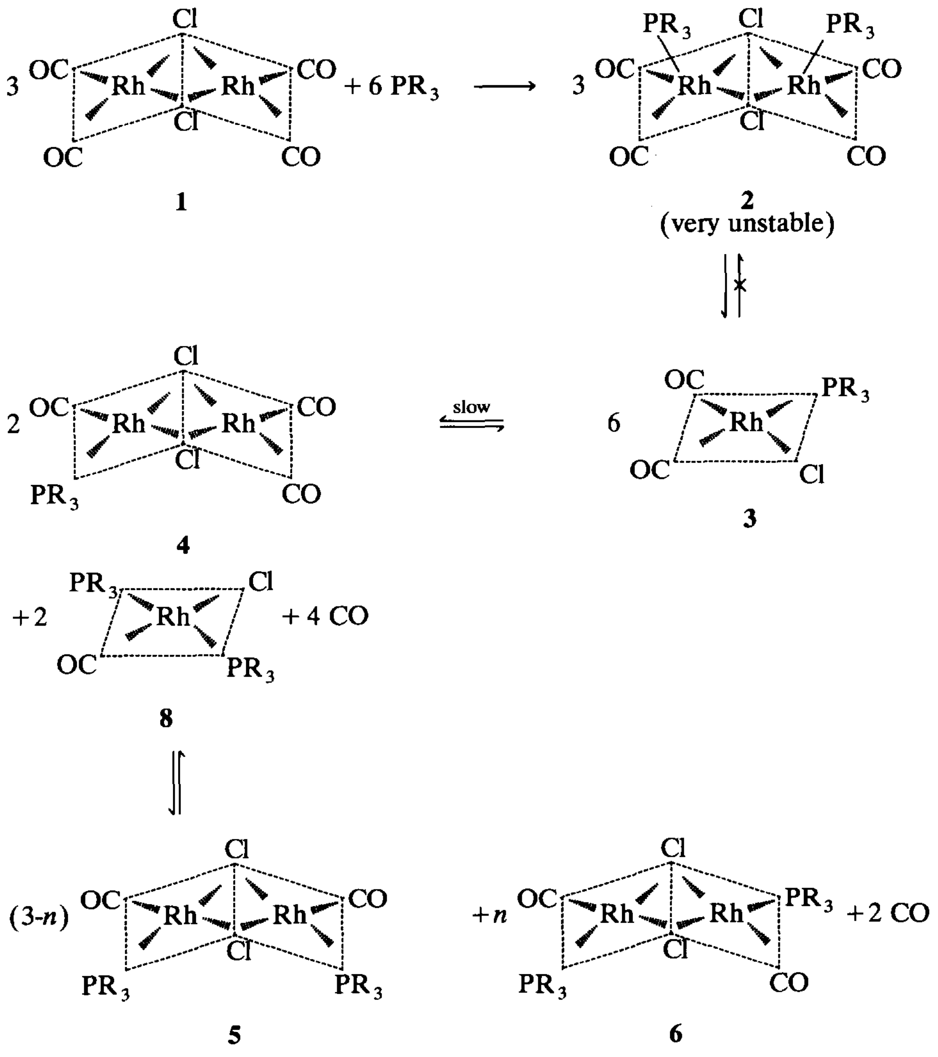
carbonyl)(phosphines)rhodium was significant compared with substitution routes in which the dinuclear structure was maintained [3,7a]. Rollman [8] postulated a bridge-splitting process leading to *cis*-[Rh(CO)$_2$-(PPh$_3$)Cl] in the reaction of **1** with PPh$_3$ (P : Rh = 1 : 1) in CH_2Cl_2 under a stream of CO. This hypothesis is mainly supported by the two strong IR absorptions (2093 and 2009 cm^{-1}) in the carbonyl stretching region; however very similar frequencies have been attributed to dinuclear structures [7a,9,10]. Thus in the absence of NMR characterization the occurrence of bridge-splitting in **1** by tertiary phosphine as well as the existence of *cis*-[Rh(CO)$_2$LCl] (L = tertiary phosphine) was far from proven. The possibility of ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR studies at variable temperatures encouraged us to investigate the intermediates involved in the reaction pathways leading to **5**, **6** and **8** from [{Rh(CO)$_2$(μ-Cl)}$_2$] and tertiary phosphine.

2. Results

2.1. Reaction of 1 with one equivalent of PPh$_3$ (P : Ph = 1)

The ^{31}P {^{1}H} NMR spectrum of a toluene solution of **1** and PPh$_3$ (PPh$_3$: Rh = 1) (mixed at 200 K) shows at 235 K a sharp doublet at 25.3 ppm and a broad resonance centred at 32 ppm. The NMR sample was removed from the spectrometer and brought to room temperature. It was then immediately returned to the NMR probe at 235 K. The broad resonance had disappeared and the spectrum showed only the sharp doublet at 25.3 ppm; the spectrum of this solution broadened into a single large resonance at 300 K, indicating



a, PR$_3$ = PPh$_3$; b, PR$_3$ = PMe$_2$Ph

Scheme 1.

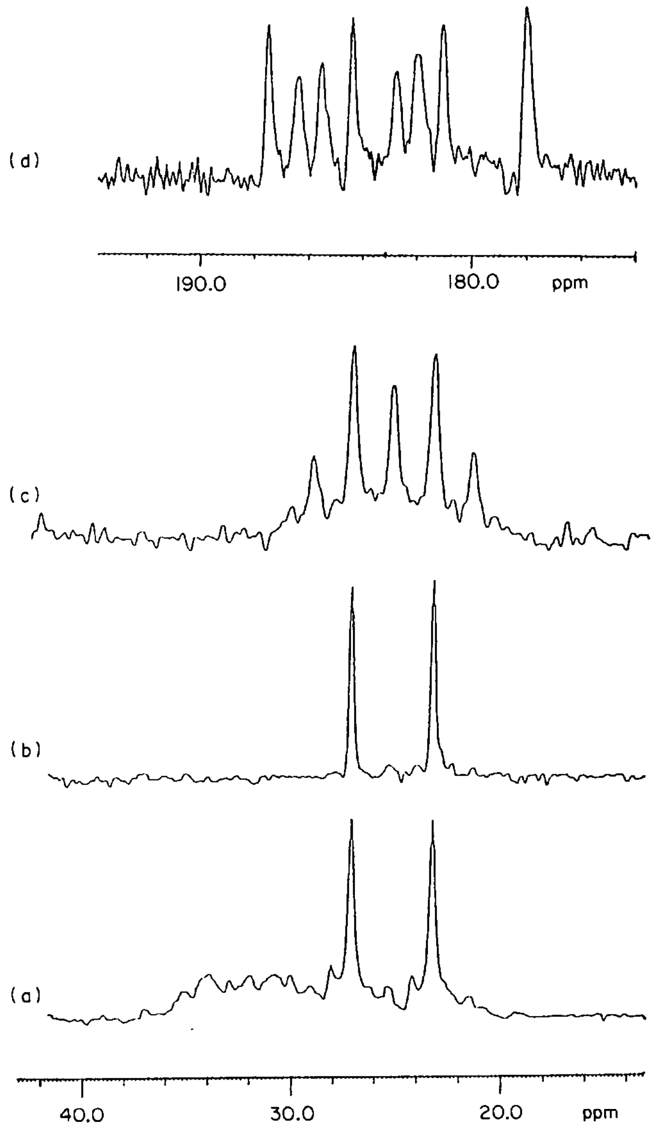
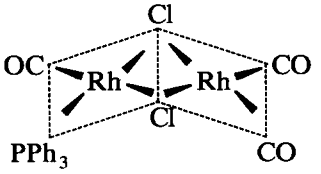


Fig. 1. (a) ^{31}P {^{1}H} NMR spectrum in toluene of **1** and PPh_3 (PPh_3 : Rh = 1) at 235 K; (b) ^{31}P {^{1}H} NMR spectrum in toluene of the same sample warmed at 300 K and immediately returned to 235 K; (c) ^{31}P {^{1}H} NMR spectrum in toluene at 235 K of the same sample ^{13}CO enriched at room temperature (~ 40%). (d) ^{13}C {^{1}H} NMR spectrum in toluene at 235 K of *cis*-[Rh(^{13}CO)$_2$(PPh_3)Co].

that fast exchange of phosphines takes place at this temperature. The very unstable species, formed only at low temperature, which gives rise to the broad resonance centred at 32 ppm, was assigned, by analogy with the reaction with PMe_2Ph (*vide infra*), to **2a** (Scheme 1). The sharp doublet at 25.3 ppm (^{1}J(RhP) = 127.3 Hz) must be attributed to *cis*-[Rh(CO)$_2$(PPh_3)Cl] (**3a**), formed from **1** by a bridge-splitting reaction. This complex, quite surprisingly in view of the lack of any previous NMR spectroscopic characterization, is stable for hours in toluene at room temperature and is also formed quantitatively if a phosphine is slowly added to toluene solutions of **1** at room temperature. The proposed structure of **3a** is supported by the NMR spectroscopic data of a sample saturated with ^{13}CO at room temperature (carbonyl *trans* to C *ca.* 40% enriched *). The ^{31}P {^{1}H} NMR spectrum of this sample shows the doublet at 25.3 ppm and also a triplet centred at the same frequency, which is due to the isotopomer *cis*-[Rh(CO)(^{13}CO)(PPh_3)Cl] (^{2}J(CP*trans*) ≈ ^{1}J(RhP)). The ^{13}C{^{1}H} NMR spectrum of the same sample shows at 235 K a doublet (^{2}J(CP) = 124 Hz) of doublets (^{1}J(RhC) = 60 Hz) at 182.1 ppm.

The ^{13}C {^{1}H} NMR spectrum of **3a** in toluene obtained from [{Rh(^{13}CO)$_2$(μ-Cl)}$_2$] (> 90% ^{13}CO enriched) and PPh_3 at 235 K shows a doublet (^{1}J(RhC) = 60.3 Hz) of doublets (^{2}J(CP) = 123.4 Hz) at 182.0 ppm for the carbonyl *trans* to the phosphine and a doublet (^{1}J(RhC) = 71.4 Hz) of doublets (^{2}J(CP) = 16.3 Hz) at 183.3 ppm for the carbonyl *cis* to the phosphine (C–C coupling less than line width) (Fig. 1). The IR spectrum of **3a** in toluene shows at room temperature and at 235 K two strong absorptions at 2087 and 2009 cm^{-1}; the molecular weight of freshly prepared solutions of **3a**, determined osmometrically in toluene at 297 K, is 435.

Complex **3a** is indefinitely stable in toluene at 235 K in the capped NMR tube, but changes slowly at room temperature. The ^{31}P {^{1}H} NMR spectrum of a toluene solution left for two hours at 300 K shows two more doublets, together with the resonance of **3a** at 25.3 ppm. One doublet at 28.2 ppm (^{1}J(RhP) = 127.0 Hz) corresponds to that of an authentic sample of the well-known *trans*-[Rh(CO)(PPh_3)$_2$Cl] (**8a**). The other, centred at 44.7 ppm (^{1}J(RhP) = 175.5 Hz) is in our opinion attributable to the dinuclear monosubstituted species, **4a**; though we cannot prove it.



4a

The assignment is consistent with the relatively large value of ^{1}J(RhP) and is supported by the requirement of the formation of **8a** (complex with PPh_3 : Rh = 2) for a ratio of PPh_3 : Rh < 1. Moreover, when the reaction between **1** and PPh_3 is performed with a PPh_3 : Rh ratio equal to 0.5, the *cis*-[Rh(CO)$_2$(PPh_3)Cl] initially formed slowly generates **4a** as the only new product detectable by ^{31}P NMR spectroscopy. Complex **4a** is also the only product detected when **3a** is left at room

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* Owing to the large *trans*-effect of the phosphine, the *trans*-carbonyl is preferentially exchanged.

temperature for 1 h in the presence of 1 equivalent of $[\{Rh(CO)_2(\mu\text{-}Cl)\}_2]$.

The formation of the dinuclear monosubstituted phosphine, **4a**, in an octane solution of **1** and PPh_3 (PPh_3 : Rh = 0.4) has also been proposed by Poilblanc [8a] on the basis of an IR spectrum with new absorptions at 2088 and 2020 cm^{-1} in the carbonyl stretching region. The $^{31}P\{^1H\}$ NMR spectrum of **4a** is very similar to that obtained for the dinuclear *cis* and *trans* species **5a** and **6a** in chloroform (*vide infra*), but **4a** is much more soluble.

After 24 h or more at room temperature the reaction mixture slowly precipitates a yellow-orange powder. This powder is insoluble in toluene, but soluble in $CDCl_3$; the $^{31}P\{^1H\}$ NMR spectrum of the resulting solution at 235 K shows two doublets of approximately equal intensity at 45.9 ppm ($^1J(RhP) = 175.8$ Hz) and 44.7 ppm ($^1J(RhP) = 176.9$ Hz), attributed to the *cis* and *trans* dimers, **5a** and **6a**. The same $^{31}P\{^1H\}$ NMR spectrum is obtained by dissolving the moderately soluble mixture of **5a** and **6a** in chloroform. The IR spectra of the two samples are the same; they both have a very strong absorption at 1983 cm^{-1}, attributed by Stephenson to **6a**, and two weak absorptions at 2090 and 2021 cm^{-1} (Nujol mulls) attributed to **5a**. Upon heating the mixture of complexes under reflux for a few seconds in benzene under nitrogen, the absorptions above 2000 cm^{-1} disappear, and only the very strong band at 1983 cm^{-1} is observed. This was attributed to the irreversible transformation of **5a** into the thermodynamically more stable **6a** [7a]. However, we observed that the $^{31}P\{^1H\}$ NMR spectrum in chloroform at 235 K of the refluxed heated material again shows the two doublets of approximately equal intensity at 44.7 and 45.9 ppm.

The relative intensities of these resonances change with the temperature. At 273 K the equilibrium is shifted toward the doublet at 44.7 ppm (intensity ratio 1.7 : 1) (*trans*-isomer), whereas at 320 K the two doublets collapse to a doublet (Rh–P coupling retained) at 45.0 ppm. These results suggest that the equilibrium shifts towards **6a** at room temperature and that at 320 K the interconversion, fast on the NMR timescale, does not imply breaking of Rh–P bonds.

We interpret the IR spectrum of the *cis* and *trans* mixture at room temperature as overlapping unresolved absorptions at 1983 cm^{-1} both in Nujol and in chloroform. The weak IR bands observed at 2090 and 2021 cm^{-1}, and attributed by Stephenson to **5a**, are due to contamination of the products by small amounts of **4a** which shows very strong absorptions at 2088 and 2020 cm^{-1} in octane according to Poilblanc [9a]. After heating under reflux complete transformation of **4a** and **8a** to **5a** and **6a** should cause the disappearance of the absorptions above 2000 cm^{-1} in the IR spectrum. The splitting of the two weak bands above 2000 cm^{-1} (69 cm^{-1}) in the mixture obtained by Stephenson's procedure is consistent with a structure of **4a** with two *cis* carbonyls on the same metal, whereas the *cis*-dimer **5a**, with the two carbonyls on adjacent rhodium atoms, should show a much lower splitting (10 cm^{-1}) [11].

In order to test the hypothesis that the bridge-splitting process in benzene too is the first step of the reaction between **1** and PPh_3, the reaction has been

TABLE 1. Selected NMR spectroscopic data

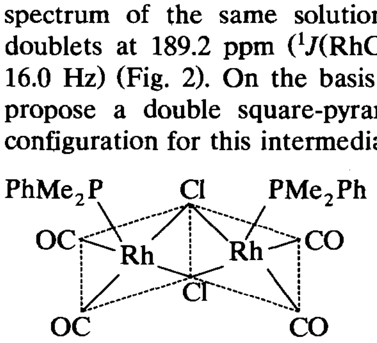
Complex	Temp K	^{31}P		^{13}C [a]			
		δ [b]	$^1J(RhP)$ [c]	δ [b]	$^1J(RhC)$ [c]	$^2J(CP)$ [c]	$^2J(CC)$ [c]
2a	200	32 ppm (broad)					
2b	200	7.8(d)	90.7	189.2(dd)	72.3	16.0	
3a	235	25.3(d)	127.3	*trans* to P 182.0(dd)	60.3	123.4	
				cis to P 183.3(dd)	71.4	16.3	
3b	200	−1.0(d)	119.3	*trans* to P 183.4(ddd)	56.8	122.6	5.1
				cis to P 184.2(ddd)	71.9	18.8	5.1
4a	235	44.7(d)	175.5				
4b	235	18.2(d)	164.5	179.3(d)	75.9		
				184.5(dd)	83.4	20.4	
5a [d]	235	44.7(d)	176.9				
5b	235	17.7(d)	168.7				
6a [d]	235	45.9(d)	175.8				
7a [e]	200	36.0(d)	89.5				
7a [e,f]	200	36.2(d)	89.5				
7b	200	12.4(d)	88.0				
8a	235	28.2(d)	127.0				
8b	235	−1.4(d)	116.8				

Unless otherwise specified the spectral data were obtained in toluene. [a] Obtained from $[\{Rh(^{13}CO)_2(\mu\text{-}Cl)\}_2] > 90\%$ enriched. [b] Multiplicity is in parenthesis. [c] Coupling constants in Hz. [d] Obtained in $CDCl_3$. [e] Under 1 atm of CO. [f] Obtained in CD_2Cl_2.

performed in this solvent at room temperature and the ^{31}P {^{1}H} NMR spectrum of the solution recorded at 250 K after addition of toluene-d_8 (*ca.* 60%). Even though the evolution of carbon monoxide during the addition of PPh_3 to the benzene solution of **1** was evident the ^{31}P{^{1}H} NMR spectrum at 250 K shows the residual presence in solution of the *cis*-dicarbonyl, **3a**, the *trans*-halocarbonylbis(triphenylphosphine), **8a**, and the dinuclear monosubstituted product, **4a**. The *cis* and *trans* dimers, **5a** and **6a**, are slowly formed from this solution if it is left at room temperature or when the benzene solution is evaporated to dryness, but mononuclear *cis* **3a** is quantitatively reformed by passing CO into the reaction mixture at any time. The system is very sensitive to the CO partial pressure; during the evaporation of the solvent under reduced pressure, carbon monoxide is removed from the mixture and the equilibria are shifted towards **5a** and **6a**. Our suggestions are summarized in Scheme 1 and the significant NMR parameters collected in Table 1.

2.2. Reaction of 1 with one equivalent of $PMe_2Ph(P:Rh = 1)$

The ^{31}P{^{1}H} NMR spectrum of a solution of **1** and PMe_2Ph(P : Rh = 1) in toluene mixed in the NMR tube at 200 K and recorded at the same temperature shows a sharp doublet centred at 7.9 ppm (^1J(RhP) = 90.7 Hz). The relatively low value of the coupling constant suggests that this resonance is due to a phosphorus donor atom of a pentacoordinate rhodium(I) derivative. In order to gain more information on the nature of this species, we performed the same reaction with [{Rh(^{13}CO)$_2$(μ-Cl)}$_2$] (> 90% ^{13}CO enriched). The ^{31}P {^{1}H} NMR spectrum of the enriched sample in toluene at 200 K, shows a doublet of triplets centred at 7.6 ppm (^1J(RhP) = 90 Hz; ^2J(CP) = 15.8 Hz). The spin system (AXY_2) is consistent with a phosphorus coupled to a rhodium and to two magnetically equivalent ^{13}CO molecules. Also consistent with this, the ^{13}C {^{1}H} NMR spectrum of the same solution shows a doublet of doublets at 189.2 ppm (^1J(RhC) = 72.3 Hz; ^2J(CP) = 16.0 Hz) (Fig. 2). On the basis of the NMR data we propose a double square-pyramidal pentacoordinate configuration for this intermediate.



2b

Trigonal bipyramidal structures, however, cannot be excluded. To our knowledge this complex is the first reported example of an unsplit adduct of the rhodium halocarbonyl dimers. The corresponding reaction of **1** with triphenylphosphine leads, as mentioned, to a material with a broad resonance at 32 ppm in the ^{31}P {^{1}H} NMR spectrum, whose fine structure could not be resolved.

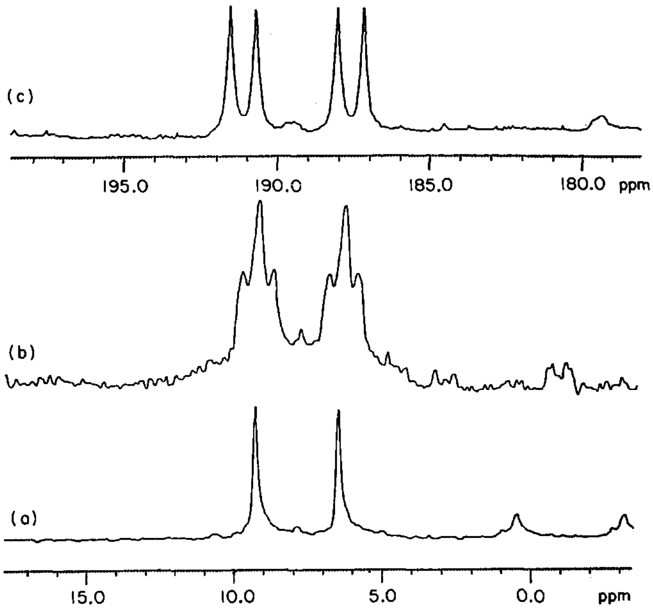


Fig. 2. (a) ^{31}P {^{1}H} NMR spectrum in toluene at 200 K of [{Rh(CO)$_2$(PMe$_2$Ph)(μ-Cl)}$_2$]; (b) ^{31}P {^{1}H} NMR spectrum in toluene at 200 K of [{Rh(^{13}CO)$_2$(PMe$_2$Ph)(μ-Cl)}$_2$]; (c) ^{13}C {^{1}H} NMR spectrum in toluene at 200 K of [{Rh(^{13}CO)$_2$(PMe$_2$Ph)(μ-Cl)}$_2$].

Complex **2b** (slowly at 240 K, but immediately at room temperature) is irreversibly converted into the square planar *cis*-[Rh(CO)$_2$(PMe$_2$Ph)Cl] (**3b**) whose ^{31}P {^{1}H} NMR spectrum in toluene at 200 K shows a doublet centred at −1.0 ppm (^1J(RhP) = 119.3 Hz). The IR spectra of the toluene solution of **3b** at 235 K and at room temperature has two bands for the symmetric and asymmetric carbonyl stretches at 2089 and at 2002 cm^{-1}.

The ^{13}C{^{1}H} NMR spectrum of **3b**, obtained from [Rh(^{13}CO)$_2$(μ-Cl)]$_2$ > 90% enriched and PMe_2Ph, shows two doublets of doublets of doublets, the former centred at 184.2 ppm (^1J(RhC) = 71.9 Hz; ^2J(CP) = 18.8 Hz; ^2J(CC) = 5.1 Hz) the latter centred at 183.4 ppm (^2J(RhC) = 56.8 Hz; ^2J(CP) = 122.6 Hz; ^2J(CC) = 5.1 Hz). The data are consistent with the presence of two magnetically different carbonyls, *trans* to a chloride and to a phosphine in a rhodium (I) square-planar configuration, respectively.

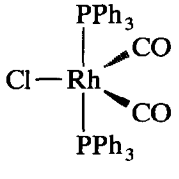
At room temperature **3b** slowly forms **4b** and **8b**, but no NMR evidence of the formation of the *cis* or *trans* dinuclear **5b** and **6b** was obtained. The ^{31}P {^{1}H} NMR spectrum at 235 K of **5b**, obtained as described by Poilblanc adding the dimethylphenylphosphine to

[{Rh(CO)(C_2H_4)(μ-Cl)}$_2$] (P : Rh = 1), shows a doublet at 17.7 ppm (^1J(RhP) = 168.7 Hz). The *cis* configuration of this derivative was demonstrated by X-ray structure analysis [11].

The ^{31}P {^{1}H} NMR spectrum of a mixture of **1** and PMe_2Ph in toluene (P : Rh = 1) after 3 h at room temperature and monitored at 235 K shows a doublet at 18.2 ppm (^1J(RhP) = 164.5 Hz), assigned to **4b**, a doublet at −1.4 ppm (^1J(RhP) = 116.8 Hz) assigned to **8b**, and the residual presence of **3b** (intensity ratio *ca.* 1 : 1 : 1). ^{31}P {^{1}H} NMR spectra of **1** and PMe_2Ph (P : Rh = 0.5) after 3 h mixed in toluene at room temperature and monitored at 235 K, show that **4b** is by far the predominant species. The IR spectrum of the toluene solution at room temperature then shows strong absorptions at 2089, 2021 and 1995 cm^{-1}, attributed to **4b**. The analogous [{Rh(^{13}CO)$_2$(μ-Cl)}$_2$] (> 90% ^{13}CO enriched) and PMe_2Ph (P : Rh = 0.5), after 3 h at room temperature and monitored at 235 K, shows in the ^{31}P {^{1}H} NMR spectrum a doublet (^1J(RhP) = 164.5 Hz) of doublets (^2J(CP) = 20.3 Hz) centred at 18.3 ppm. The ^{13}C {^{1}H} NMR spectrum of the same sample at 235 K shows a doublet (^1J(RhC) = 83.4 Hz) of doublets (^2J(CP) = 20.4 Hz) at 184.5 ppm, and a doublet (^1J(RhC) = 75.9 Hz) at 179.3 ppm ((dd) : (d) intensity ratio about 0.5), consistent with the dinuclear monosubstituted formulation of **4b** (the two adjacent carbonyls are not magnetically distinguishable).

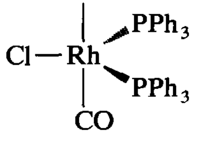
2.3. Reaction of 1 with two equivalents of PR_3 (P : Rh = 2)

As previously mentioned, the addition of a second equivalent of PR_3 to a toluene solution of **3** at room temperature quantitatively leads to decarbonylation and formation of **8**. However, if the phosphine is added slowly at 200 K, the evolution of carbon monoxide does not take place. The ^{31}P {^{1}H} NMR spectrum of the toluene solution of **3a** and PPh_3 (P : Rh = 2) at 200 K shows a doublet at 35.4 ppm (^1J(RhP) = 92.7 Hz). The low value of the coupling constant and the absence of CO evolution strongly suggest a five-coordinate dicarbonyl structure for this intermediate. The doublet could be attributed to a trigonal bipyrimidal structure with two equivalent phosphines.



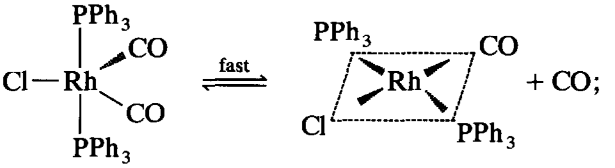
7a

or



7'a

Upon raising the temperature of the sample to 250 K, evolution of CO is clearly visible, but it can be stopped immediately by lowering the temperature of the NMR tube. The spectrum recorded when the CO evolution is complete (less than a minute at room temperature) corresponds, as expected, to that of the *trans*-[Rh(PPh_3)$_2$(CO)Cl] (**8a**). All the intermediate spectra at 200 K show sharp doublets with δ and *J* averaged between those of the pentacoordinate **7a** and those of the square planar **8a** (δ = 28.2 ppm; ^1J(RhP) = 127.0 Hz). This result is explained by a fast equilibrium in solution between **7a** and **8a**, shifted towards **7a** at 200 K. The irreversible evolution of carbon monoxide and the poor solubility of the square-planar complex shift the equilibrium towards **8a** at room temperature.



7a **8a**

(1)

This equilibrium is consistent with the configuration **7a**, the only trigonal bipyramidal isomer able to activate direct carbon monoxide exchange with the square-planar *trans* configuration of **8a** (entering, leaving and *trans*-directing ligand equatorial *cis* ligands axial [12]). This fast equilibrium could be of relevance for the intepretation of the mechanistic role played by **8a** as catalyst in hydroformulation, hydrogenation and especially carbonylation and decarbonylation reactions [13].

Sanger reported that dichloromethane solutions of **8a** under 1 atm of CO led to [Rh(CO)$_2$(PPh_3)$_2$Cl] [14]. The δ and ^1J(RhP) values for this pentacoordinate species at 223 K are 31.1 ppm and 116 Hz, respectively, between those of **7a** and **8a**. According to our interpretation, mixtures of the two complexes in fast equilibrium in the NMR time scale are responsible for the intermediate values of δ and *J*.

Fast carbon monoxide exchange takes place without breakage of the Rh–P bonds; this explains the sharp doublets in the ^{31}P {^{1}H} NMR spectra as well as the otherwise unexpected lack of Rh–C and C–P spin–spin couplings in the ^{13}C NMR spectrum of **7a** (^{13}CO enriched) at low temperature reported by Sanger [14]. Only small changes in δ and ^1J(RhP) were observed in the ^{31}P {^{1}H} NMR spectrum of **7a** when **3a** and PPh_3 were mixed at 200 K in toluene under 1 atm of CO (δ = 36.0 ppm; ^1J(RhP) = 89.5 Hz at 200 K). Very similar NMR parameters were obtained in CD_2Cl_2 (Table 1).

The analogous reaction of **2b** with PMe_2Ph is similar. The pentacoordinate [Rh(PMe_2Ph)$_2$(CO)$_2$Cl] (**7b**) in toluene at 200 K shows a rather broad doublet (line width 10 Hz) at 12.4 ppm (^1J(RhP) = 88 Hz). The line width could be accounted for by carbonyl-exchange with a time constant at 200 K comparable with the NMR time scale.

3. Discussion

The addition of phosphine to **1** causes the formation of unstable pentacoordinate adducts **2** which, at room temperature, rapidly undergo the irreversible bridge-splitting leading to relatively stable *cis* **3**. The NMR and IR spectra, and the molecular weights unambiguously prove the mononuclear *cis*-dicarbonyl structure of **3**.

These species confirm the proposal of Poilblanc and Rollmann [8,9] concerning the equilibrium between dinuclear and mononuclear species, in contrast with Stephenson's suggestion [7a] of a substitution route in which the dinuclear structure is maintained. Thus, by analogy with reactions of nitrogen donors and tricyclo-exylphosphinoxide [5], the products of the reactions between **1** and phosphines in toluene at room temperature, are the *cis* mononuclear compounds **3**. The formation of the dinuclear halide-bridged species, **5** and **6**, from **3** is probably connected with the lability of the carbonyl *trans* to phosphorus and with the poor solubility of the dinuclear complexes. The dissociation of the carbonyls from *cis*-[Rh(CO)$_2$(PR$_3$)Cl] leads to coordinatively unsaturated fragments which recombine to give the halide-bridge species. Their precipitation forces the equilibria towards the formation of dimer and prevents the isolation of **3**.

The complex **3a** is relatively stable at room temperature, especially under CO. The addition of a second equivalent of phosphine to **3** at 200 K causes the formation of pentacoordinate species containing two phosphines, two carbonyls and one chloride. Sanger reported that this kind of complex could be obtained from CO (1 atm) and *cis*-[Rh(CO)(PPh$_3$)$_2$X] (X = Cl, Br, or I), [14]. We could not confirm this but the preparation is quantitative and straightforward by addition of 1 equivalent of phosphine to solutions of **3** at 200 K.

The NMR spectra and the fast exchange of carbon monoxide between **7** and **8** suggest a structure with the chloride and the two carbonyls in the equatorial plane. The same configuration has been found for the analogous iridium complex [IrCl(CO)$_2$(PPh$_3$)$_2$] in the solid state [16] and should on theoretical grounds be thermodynamically more stable. For an 18-electron [ML$_5$], the HOMOs (e′ non-bonding orbitals of the metal) are high in energy and are potentially strong π-back-donors. Therefore, π-acceptor ligands should preferentially occupy the equatorial positions, since the e′ orbitals have maximum density in the equatorial plane [17]. However, the existence in solution of fast equilibria between different geometric isomers cannot be excluded *a priori*. Intramolecular interchange of the ligands (Berry pseudorotation) within the coordination sphere could provide pathways for the mutual fast interconversion of the pentacoordinate species [18]. The existence of fast equilibria, frozen on the NMR time scale at very low temperature, between pentacoordinate configurations of different thermodynamic stability has been shown to occur for dicarbonylhydridobis(triphenylphosphine)rhodium [19].

In conclusion a definitive configuration of the pentacoordinate **7** cannot be obtained with the results reported in this paper. Further investigations are being undertaken in our laboratory to elucidate it.

4. Experimental details

4.1. General conditions and physical measurements

All reactions, unless otherwise specified, were carried out under dry, high purity nitrogen. ^{31}P and ^{13}C NMR spectra were measured at 32.442 and 20.15 MHz using a Bruker WP-80 SY spectrometer. The chemical shifts are referenced to Me$_4$Si for ^{13}C and external H$_3$PO$_4$ 85% for ^{31}P (high frequency is taken as being positive, IUPAC, 1976). IR spectra were obtained with a Perkin-Elmer 783 spectrophotometer. The temperature of the cell compartment could be controlled by a stream of dry nitrogen.

The molecular weight was determined on a Mechrolab Osmometer at 297 K; to a toluene solution of **1** (10^{-2} M) cooled at 200 K, the stoichiometric amount of PPh$_3$ (PPh$_3$: Rh = 1) was added dropwise. The sample was gently shaken and brought to room temperature immediately before determination of the molecular weight.

4.2. Reagents

The complex [{Rh(CO)$_2$(μ-Cl)]$_2$] and the tertiary phosphines were commercial products, used as received.

4.3. Rhodium(I) complexes

[Rh(CO)(PR$_3$)$_2$Cl] (**8**), *cis*-[{Rh(CO)(PR$_3$)(μ-Cl)}$_2$] (**5**) and *trans*-[{Rh(CO)(PR$_3$)(μ-Cl)}$_2$] (**6**) were prepared according to reported procedures [3].

[Rh(^{13}CO)$_2$(μ-Cl)]$_2$, > 90% enriched, was obtained by direct exchange of the commercial rhodium complex with 98% ^{13}CO [20] using standard Schlenk techniques (^{13}CO 98% isotopic purity obtained from Cambridge Isotope Laboratories). In order to increase the percentage of this isotopomer the enrichment was repeated three times, each time leaving the benzene solution of **1** under 1 atm of ^{13}CO 98% for a week.

Attempts to isolate *cis*-[Rh(CO)$_2$(PR$_3$)Cl] (**3**) and [Rh(CO)$_2$(PR$_3$)$_2$Cl] (**7**), from both toluene and dichloromethane failed even at low temperature under 1 atm of CO. Mixtures of products were obtained in the attempts to isolate the asymmetrically substituted complexes **4**.

4.4. NMR experiments

The reactions between **1** and PPh$_3$ (PPh$_3$: Rh = 1) were typically performed by cooling 2 ml of the toluene solution of **1** (*ca.* 20 mg) in a 10 mm NMR tube to 200 K under N$_2$; the stoichiometric amount of phosphine was dissolved in *ca.* 0.5 ml of deuterated toluene and slowly added to the complex by a syringe through a serum cap.

The toluene solutions of **3** obtained by this procedure were used as starting material for the preparation of **7**. In that case the sample was cooled to 200 K; the second equivalent of tertiary phosphine (PR$_3$: Rh = 2) was again added dropwise by syringe. The samples, rapidly shaken, were immediately transferred to the NMR probe maintained at the desired temperature.

The same procedure was followed for the experiments under CO. In this case the solution of **3** in toluene in the NMR tube at 200 K was saturated with carbon monoxide (1 atm) introduced *via* a needle. The CO stream was maintained during the addition of the second equivalent of phosphine.

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