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NUCLEAR MAGNETIC RESONANCE STUDIES IN COORDINATION CHEMISTRY
V. KINETIC STUDIES OF EXCHANGE REACTIONS INVOLVING 1,5-CYCLOOCTADIENE COMPLEXES OF RHODIUM(I)*

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SUMMARY

NMR studies showed that the signals of the non-equivalent olefinic protons of the diene complexes (diene)RhCl(L) and (diene)IrCl(L) (diene = 1,5-cyclooctadiene, bicyclo[2.2.1]hepta-2,5-diene and L = PR_3, AsR_3 or SbR_3 with R = aryl or substituted aryl or alkyl) broaden and eventually coalesce to one signal when the temperature of the $CDCl_3$ solutions is raised.

Kinetic studies on the monomeric complexes (COD)RhCl(L) (COD = 1,5-cyclooctadiene; L = $AsPh_3$, PPh_3) showed that this coalescence is caused by monomer–monomer reactions. If, however, ligand L is also present, fast ligand exchange reactions are observed. If along with (COD)RhCl(L) the dimer $[(COD)RhCl]_2$ is present, the olefinic signals of both complexes coalesce. For L = $AsPh_3$ the kinetic behaviour is explained by a reaction between an active intermediate "(COD)RhCl($AsPh_3$)" and $[(COD)RhCl]_2$, while for L = PPh_3 reactions occur between (COD)RhCl(PPh_3) and the monomeric species (COD)RhCl formed from the dissociation of the dimer.

Finally, it is shown that addition of Cl^- to (COD)RhCl($AsPh_3$) also results in the coalescence of the olefinic signals. The chloride effect upon (COD)RhCl(PPh_3) is negligible.

INTRODUCTION

Previous kinetic studies—using NMR—of reactions of π-methallyl compounds (π-C_4H_7)PdCl(L) (L = PPh_3[1], $AsPh_3$[2]) with ligand L or with a "dimer" species {*i.e.* $[(\pi\text{-}C_4H_7)PdCl]_2$ or (π-C_4H_7)PdCl} showed that the type of reactions occurring depends very much on the ligand L. In the case of the arsine system reactions with ligand L were the dominant feature, while for the phosphine system intriguing reactions were observed of (π-C_4H_7)PdCl(PPh_3) with $[(\pi\text{-}C_4H_7)PdCl]_2$ and (π-C_4H_7)-PdCl, respectively. In both systems no measurable influence of added Cl^- on the rates was observed.

To obtain information on the possible occurrence of these reactions in other types of complexes we have started a similar study of diene complexes of Rh^I and Ir^I.

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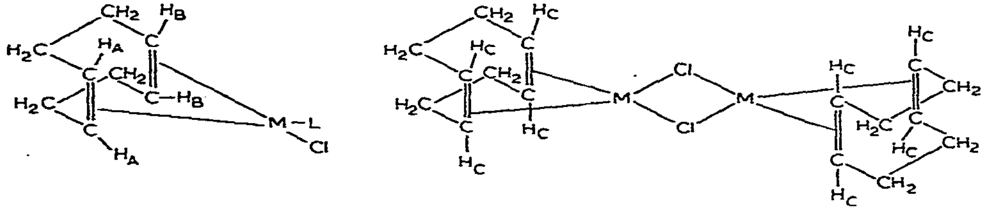
* A preliminary communication on this work has recently been published[14].

In this report we describe the preparation and properties of a number of these diene complexes (of which a few have been reported by other workers[3,4,5]) to demonstrate qualitative similarities in behaviour. The compounds investigated are of the type (diene)MCl(L) and [(diene)MCl]$_2$ (L = Group-V donor ligand; M = Rh^I, Ir^I; diene = 1,5-cyclooctadiene and bicyclo[2.2.1]hepta-2,5-diene)*. Their structures are probably similar to that of the square planar complex [(COD)RhCl]$_2$[6]. The reactions are studied by means of line-width measurements of the olefinic protons H_A, H_B of (diene)MCl(L) and H_C of the dimer [(diene)MCl]$_2$:



Subsequently, we discuss the kinetics and possible mechanisms of reactions of 1,5-cyclooctadiene complexes (COD)RhCl(L)**, in which L = $AsPh_3$ and PPh_3. In a subsequent report the results for the analogous Ir complexes will be presented.

PREPARATION AND PROPERTIES

The complexes (COD)IrCl(PPh_3), (COD)RhCl(PPh_3) and (Nor)RhCl(L) (Nor = bicyclo[2.2.1]hepta-2,5-diene; L = PPh_3, $AsPh_3$, $SbPh_3$) were prepared ac-

TABLE 1

PROPERTIES OF COMPOUNDS

Complex	M.p. (°C)	Conductance in 1,2-$C_2H_4Cl_2$, ($cm^2 \cdot \Omega^{-1} \cdot mole^{-1}$)	Mol. weights in 1,2-$C_2H_4Cl_2$ at 37°	
			Found	Calcd.
(COD)IrCl(PPh_3)	153–156	0.0	578	599
(COD)IrCl($AsPh_3$)	130–140	0.0	630	643
(COD)IrCl{As[p-$(CH_3)_2NC_6H_4]_3$}	>180	0.2	774	772
(COD)IrCl($AsPh_2Me$)	120–122	0.0	529	581
(COD)IrCl[PPh_2(p-BrC_6H_4)]	114–116	0.0	660	678
(COD)IrCl(PEt_2Ph)	110–112	0.2	503	503
(COD)RhCl(PPh_3)	123–125	0.0	508	509
(COD)RhCl($AsPh_3$)	133–136	0.0	502	573
(COD)RhCl($SbPh_3$)	dec.	0.0	511	620
(COD)IrCl(PPh_3)	109–110	0.0	417	860
(COD)IrCl$(AsPh_3)_2$	97–99	0.0	530	948
(COD)IrCl{As[p-$(CH_3)_2NC_6H_4]_3$}$_2$	(220)	0.4	626	1212
(COD)IrCl$(SbPh_3)_2$	172–174	0.1	700	1043

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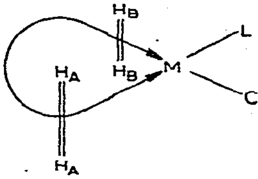
* COD = 1,5-cyclooctadiene; Nor = bicyclo[2.2.1]hepta-2,5-diene (norbornadiene).

** Recently we were informed that NMR work on this type of systems is also being carried by Prof. J. Lewis and coworkers (private communication).

TABLE 2

CHEMICAL SHIFTS OF PROTONS H_A AND H_B OF (diene)MCl(L)
In ppm from TMS (*in* $CDCl_3$) (HA 100).



Complex[a]	Chemical shifts H_A	Chemical shifts H_B	Temp. (°C)	$J(H_A–H_A)$[b]	$J(H_B–H_B)$[b]
$(COD)IrCl(PPh_3)$[c]	5.15	2.73	+20	4.5	3.4
$(COD)IrCl(PPhEt_2)$	4.92	2.88	+20	4.2	3.2
$(COD)IrCl[PPh_2(p\text{-}BrC_6H_4)]$[c]	5.20	2.76	+20	4.6	3.2
$(COD)IrCl(AsPh_3)$	4.92	3.12	−60		
$(COD)IrCl\{As[p\text{-}(CH_3)_2NC_6H_4]_3\}$[c]	4.75	3.20	0		
$(COD)IrCl(AsPh_2Me)$	4.86	3.10	−30		
$(COD)IrCl(SbPh_3)_2$	3.54		+20		
$(COD)RhCl(PPh_3)$	5.52	3.10	0		
$(COD)RhCl(AsPh_3)$	5.25	3.52	0		
$(COD)RhCl(SbPh_3)$	4.20		0		
$(Nor)RhCl(PPh_3)$	5.34	3.00	−20		
$(Nor)RhCl(AsPh_3)$[d]	5.07	3.25	−80		
COD	5.52		+20		
Nor	6.82		+20		

[a] The chemical shift for the olefinic protons of $[(COD)RhCl]_2$ is 4.18 ppm, for $[(COD)IrCl]_2$ it is 4.19 ppm and for $[(Nor)RhCl]_2$ it is 3.96 ppm from TMS (δ). [b] Found by double resonance. [c] Complexes $(COD)IrCl(L)_2$ give a coalesced signal at the weighted mean of H_A and H_B. [d] In the presence of $[(Nor)RhCl]_2$.

cording to procedures described by Winkhaus and Singer[3], Chatt and Venanzi[4] and Bennett and Wilkinson[5], respectively. The other complexes mentioned in the Introduction were prepared in a completely analogous way from the dimers $[(diene)MCl]_2$ and two moles of ligand L. Some properties and the relevant NMR data of these compounds are recorded in Tables 1 and 2. The analytical data are given in Table 3.

Besides these complexes we also isolated five-coordinate complexes $(COD)IrCl(L)_2$ $\{L=PPh_3, AsPh_3, As[p\text{-}(CH_3)_2NC_6H_4]_3\}$ from reaction mixtures of (COD)IrCl(L) and L in ethanol. In the case of $SbPh_3$ the complex $(COD)IrCl(SbPh_3)_2$ is the only one isolated.

Infrared spectra of mulls and of $1,2\text{-}C_2H_4Cl_2$ solutions indicated that owing to the absence of free double bond absorptions, both double bonds are coordinated to the metal. The complexes (diene)MCl(L) are monomeric in $1,2\text{-}C_2H_4Cl_2$, while $(COD)IrCl(L)_2$ is completely dissociated into (COD)IrCl(L) and L, as evidenced by the molecular weight data.

NMR spectra of (diene)MCl(L) showed the non-equivalence of protons H_A and H_B (Table 2, Fig. 1). At appropriate temperatures the signals of H_A and H_B broadened and in most cases coalesced at the weighted mean. The rate of coalescence was low for $L=PPh_3$, higher for $L=AsR_3$ and very high for $L=SbPh_3$.

TABLE 3

ANALYSES OF COMPLEXES (diene)MCl(L) AND (COD)IrCl(L)$_2$

Complex		%C	%H	%Cl	%M (Rh, Ir)	%P/As/Sb/N/Br
(COD)IrCl(PPh$_3$)	Found	52.0	4.6	6.1		4.8
	Calcd.	52.1	4.5	5.9		5.2
(COD)IrCl(AsPh$_3$)	Found	48.2	4.4	5.7	30.4	13.1 ± 1.5
	Calcd.	48.6	4.2	5.5	30.0	11.7
(COD)IrCl{As[p-(CH$_3$)$_2$NC$_6$H$_4$]}	Found	49.5	5.7	4.5	24.9	5.4 (N); 9.0 (P)
	Calcd.	49.6	5.8	4.6	24.9	5.4 (N); 9.7 (P)
(COD)IrCl(AsPh$_2$Me)	Found	43.3	4.4	6.4	33.2	11.1
	Calcd.	43.4	4.3	6.1	33.2	12.9
(COD)IrCl[PPh$_2$(p-BrC$_6$H$_4$)]	Found	44.8	4.0	9.0	27.5	3.7 (P); 10.2 (Br)
	Calcd.	46.1	3.8	5.2	28.5	4.6 (P); 11.8 (Br)
(COD)IrCl(PPhEt$_2$)	Found	40.0	5.2	7.9	40.5	4.6
	Calcd.	43.0	5.4	7.1	38.4	6.2
(COD)IrCl(PPh$_3$)$_2$	Found	61.7	5.0	4.1	22.8	6.8
	Calcd.	61.4	4.9	4.1	22.4	7.2
(COD)IrCl(AsPh$_3$)$_2$	Found	55.7	4.4	3.7	20.3	15.8 ± 1.0
	Calcd.	54.1	4.5	4.0	21.0	14.8
(COD)IrCl(SbPh$_3$)$_2$	Found	50.3	4.0	3.8	20.3	20.4
	Calcd.	50.6	4.0	3.4	18.5	23.4
(COD)IrCl{As[p-(CH$_3$)$_2$NC$_6$H$_4$]$_3$}	Found	55.0	6.0	4.0	16.5	6.9 (N); 12.4 (As)
	Calcd.	55.4	6.4	2.9	15.9	6.9 (N); 12.4 (As)

Conductance measurements of mixtures of (diene)MCl(L) and L showed that ionic compounds [(COD)Ir(L)$_2$]$^+$Cl$^-$ may be formed in suitable solvents such as nitromethane by the reaction:

$$\text{(COD)IrCl(L)} + \text{L} \leftrightarrows [\text{(COD)Ir(L)}_2]^+\text{Cl}^-$$

It was observed that the concentration of the ionic species increases when the temperatures are lowered or on addition of L. The effect was larger for phosphine than for arsine. In the case of Rh no evidence was found for the formation of ionic species by this type of reaction.

EXPERIMENTAL

The elemental analyses were performed by the usual techniques, except for the metals, As and Sb, which were performed by activation analyses. The molecular weights were obtained with a Mechrolab vapour pressure osmometer model 201A and about 10^{-2} M solutions at $+37°$ with 1,2-C$_2$H$_4$Cl$_2$ as solvent. The conductivities were measured with a Philips Philoscope G.M. 4249 using Pt electrodes. The NMR spectra were measured with a Varian Spectrometer (DP 60 and HA 100); CDCl$_3$ was used as solvent. Low temperatures were obtained with the Varian variable dewar inserts. Tetramethylsilane (TMS) was employed as an internal standard. For each kinetic measurement we used either (COD)RhCl(L), or (COD)RhCl(L) and L, or (COD)RhCl(L) and [(COD)RhCl]$_2$ as reaction components. They were weighed in a sample tube and after that the necessary volume of CDCl$_3$ was added.

The rates of the coalescence were usually calculated both in the slow and fast exchange limits[7]. For the $[(COD)RhCl]_2$/(COD)RhCl(L) systems only the slow-exchange limit was used. Since the chemical shift differences are high, we could measure the slow-exchange broadening over sufficiently large temperature ranges (*i.e.* from −20 to +80°).

For the natural line widths of the signals of H_A, H_C and H_B* we used values of 10.5, 10.0 and 10.0 cps (at 100 Mc), respectively. These values are approximately independent of the temperature ranges. This was easily checked for samples of the pure dimer. For the arsine and in particular for the phosphine compound it was observed that the signals H_A and H_B begin to broaden only at high temperatures, *i.e.* above −10 and +70°, respectively. Below these temperatures no significant change in line width was found. In the case of the phosphine system suitable corrections were made for the disappearance of the P coupling, which is caused by PPh_3 exchange.

The accuracy of the activation parameters is estimated to be 10–15% in the activation energy, while the accuracy of the frequency factor A is $10^{\pm 1.5}$. It has not been attempted to increase the precision of these parameters, since they are sufficient for the present purpose of our work, *i.e.* the determination of the reactions taking place.

RESULTS OF THE KINETIC MEASUREMENTS

We will discuss reactions for:

(*A*) mixtures of the monomer (COD)RhCl(L) and L (*i.e.* L/Rh > 1),
(*B*) mixtures of the monomer and the dimer $[(COD)RhCl]_2$ (*i.e.* L/Rh < 1), and
(*C*) solutions of the pure monomer (L/Rh = 1). Finally, in
(*D*) we describe the influence of excess 1,5-cyclooctadiene and Cl^- on the reactions occurring.

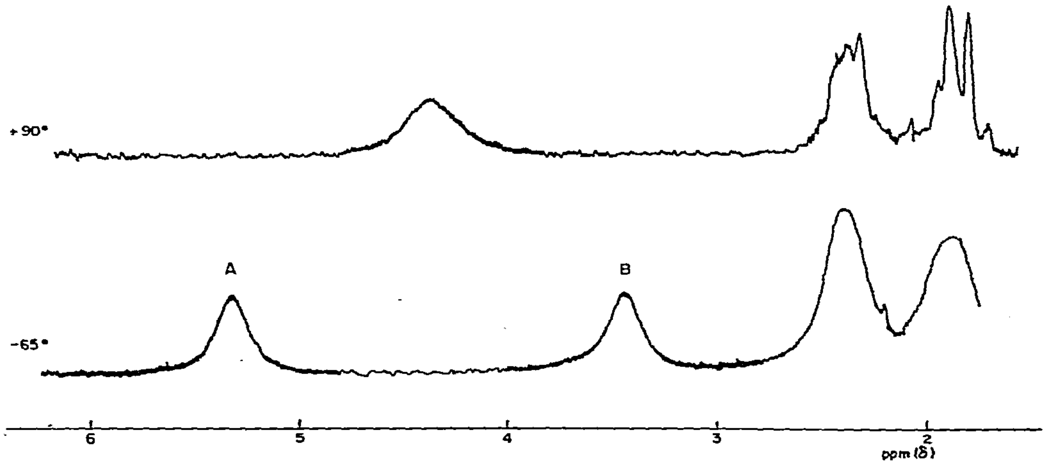


Fig. 1. Temperature dependence of the signals of protons H_A and H_B of $(COD)RhCl(AsPh_3)$ (0.25 mole/l) in $CDCl_3$ in the presence of 0.20 mole/l $AsPh_3$.

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* Protons H_A and H_B do not couple with each other.

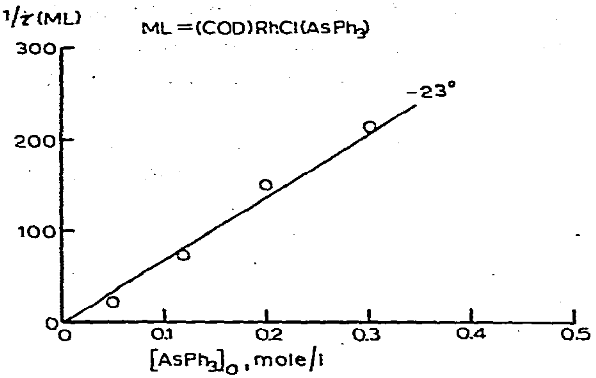
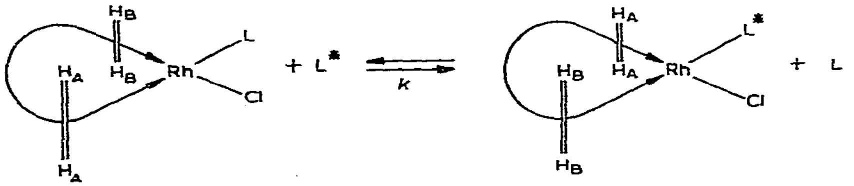


Fig. 2. Dependence of $1/\tau$(ML) (L=AsPh$_3$) on $[L]_0$ for $[ML]_0$=0.20 mole/l.

A. L/Rh > 1

Reactions between (COD)RhCl(L) (=ML) and L (L=AsPh$_3$, PPh$_3$) were studied between −50 and +80° for L=AsPh$_3$ (Fig. 1), and between −60 and 0° for L=PPh$_3$. The reciprocal of the lifetime of protons H_A or H_B $1/\tau_A=1/\tau_B$ [$=1/\tau$(ML)] was found to be proportional to $[L]_0$ (Fig. 2) at constant $[ML]_0$ and independent of $[ML]_0$ at constant $[L]_0$* (Fig. 3). Clearly, there is no significant formation of an ionic species [(COD)RhL$_2$]$^+$Cl$^-$, as also indicated by the absence of conductivity up to high ratios of L/Rh in CHCl$_3$, 1,2-dichloroethane and of a five-coordinate species (COD)RhClL$_2$**, as was found for Ir. The proposed reaction, which is similar to that of the π-allyl–palladium systems[1,2], is:



The reaction constants k are:

$$k = 10^6\, e^{-4000/RT}\ \mathrm{l\cdot mole^{-1}\cdot s^{-1}} \quad \text{for L} = \mathrm{AsPh_3}$$

and

$$k = 10^5\, e^{-4000/RT}\ \mathrm{l\cdot mole^{-1}\cdot s^{-1}} \quad \text{for L} = \mathrm{PPh_3}$$

The reaction presumably proceeds via a five-coordinate intermediate (COD)-RhCl(L)$_2$, in view of the isolation of (COD)IrCl(L)$_2$ from alcohol solutions. The proposed mechanism is drawn more extensively in Fig. 4. Depending on whether the second ligand L (II) or the original ligand L (I) leaves the intermediate (B), complex (A) or complex (C) is formed. In the latter case the diene has to rotate in the plane of the olefinic double bonds through 120° in the intermediate (B). Only when (C) is

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* $[L]_0$ and $[ML]_0$ denote the concentrations based on weighed in quantities.

** Thus $[ML]_0$ and $[L]_0$ are approximately equal to the equilibrium concentrations [ML] and [L], respectively.

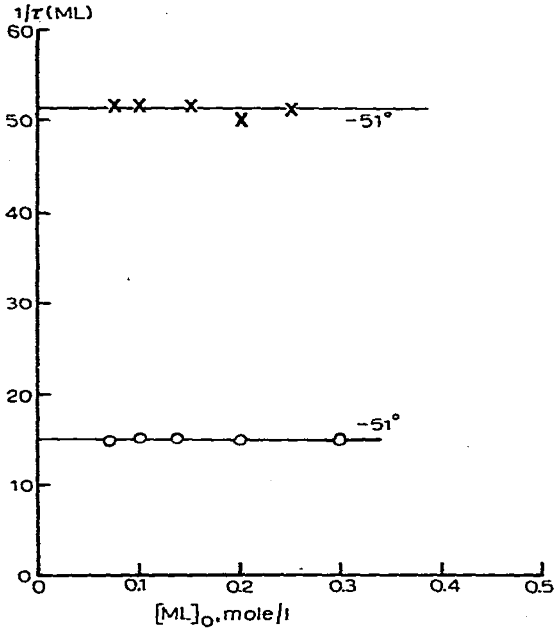

Fig. 3. Dependence of $1/\tau(ML)$ on $[ML]_0$ for $[L]_0=0.20$ mole/l; ○ = (COD)RhCl(PPh$_3$); × = (COD)-RhCl(AsPh$_3$).

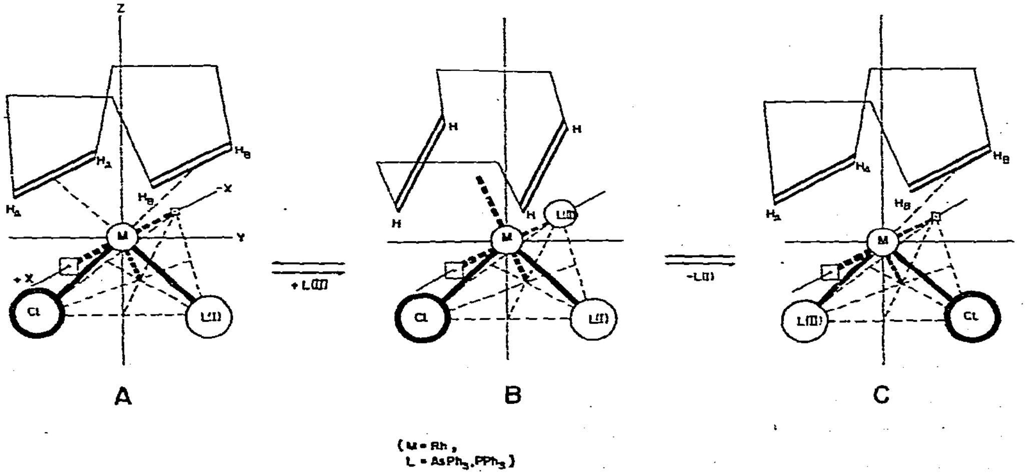

Fig. 4. A possible mechanism for the interchange of protons H_A and H_B.

formed, is line-broadening observed, because of the site exchange of the olefinic protons. In going from (A) to (B) the plane of the olefinic bond has to make a tumbling movement through an angle of 37°, since this plane is perpendicular to the bisectrix of the ClRhL(I) angle in (A) and perpendicular to the line through Rh and the centre of the ClL(I)L(II) triangle in (B).

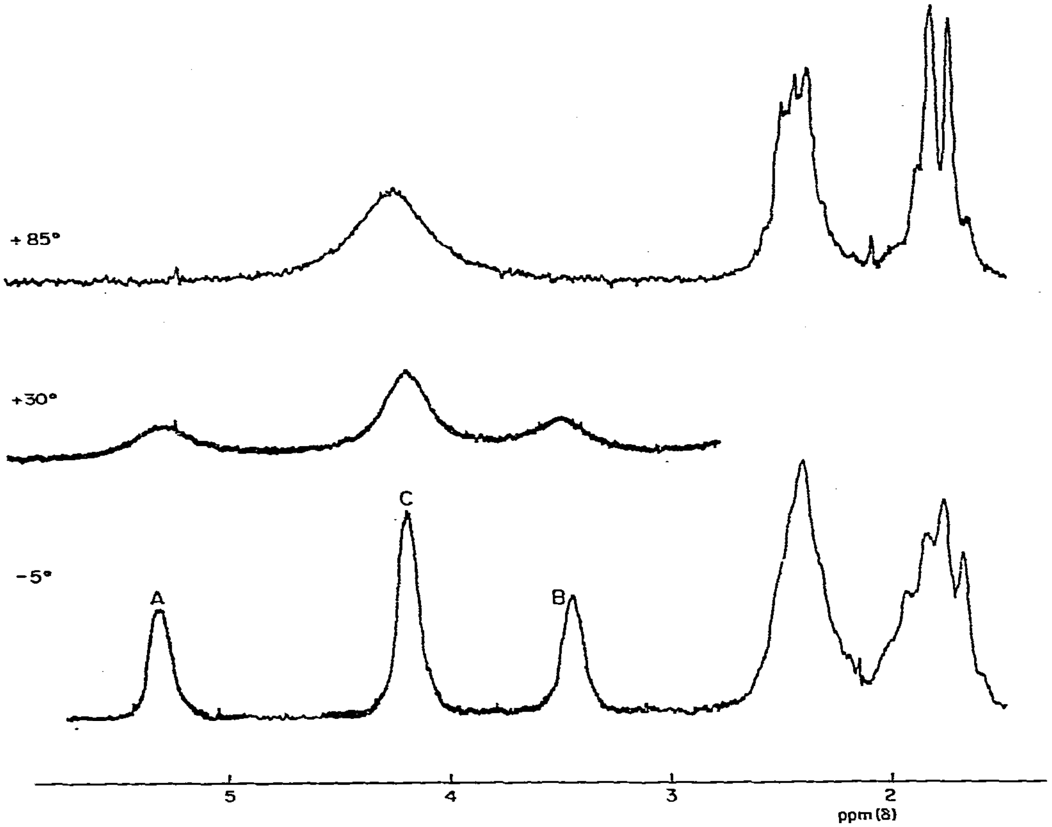

Fig. 5. Temperature dependence of the signals H_A and H_B of (COD)RhCl(AsPh$_3$) (0.20 mole/l) and of H_C of [(COD)RhCl]$_2$ (0.09 mole/l).

B. L/Rh < 1

If both monomer (COD)RhCl(L) (=ML) and dimer [(COD)RhCl]$_2$ (=M$_2$) are present in CDCl$_3$, three signals are observed for protons H_A and H_B of ML and for H_C of M$_2$ (Fig. 5). At elevated temperatures the three signals coalesce, indicating chemical exchange. The kinetics for the AsPh$_3$ and PPh$_3$ systems are different. They will be discussed in the following sections.

1. *L*=*AsPh*$_3$. The line broadening of the signals of H_A, H_B and H_C was studied between −40 and +30° in the slow-exchange limit. The rate $1/\tau(\mathrm{ML})$ of the monomer (COD)RhCl(AsPh$_3$) is independent of the concentrations $[\mathrm{ML}]_0$ and $[\mathrm{M_2}]_0$, while $1/\tau(\mathrm{M_2})$ is proportional to $[\mathrm{ML}]_0$ at constant $[\mathrm{M_2}]_0$ and proportional to $1/[\mathrm{M_2}]_0$ at constant $[\mathrm{ML}]_0$ (Figs. 6, 7)*. The following reaction scheme agrees with these results:

In a rate-determining step an active intermediate "(COD)RhCl(AsPh$_3$)" is formed:

$$\mathrm{(COD)RhCl(AsPh_3)} \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \text{“}\mathrm{(COD)RhCl(AsPh_3)}\text{”} \tag{1}$$

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* The concentrations $[\mathrm{ML}]_0$ and $[\mathrm{M_2}]_0$ based on weighed-in quantities are within the limits of observation equal to the equilibrium concentrations [ML] and [M$_2$], respectively (L = AsPh$_3$, PPh$_3$).

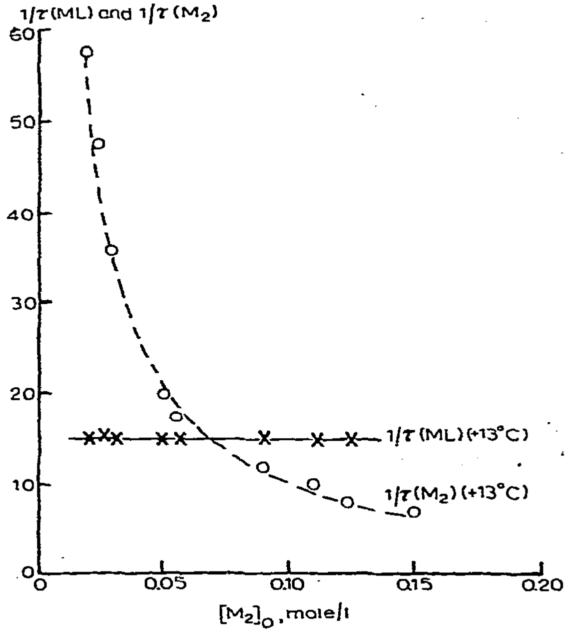

Fig. 6. Dependence of $1/\tau(ML)$ and $1/\tau(M_2)$ on $[M_2]_0$ for $[ML]_0 = 0.20$ mole/l; ML = (COD)RhCl($AsPh_3$), M_2 = [(COD)RhCl$]_2$. The broken line represents a calculated $1/\tau(M_2)$ on $1/[M_2]_0$ dependence.

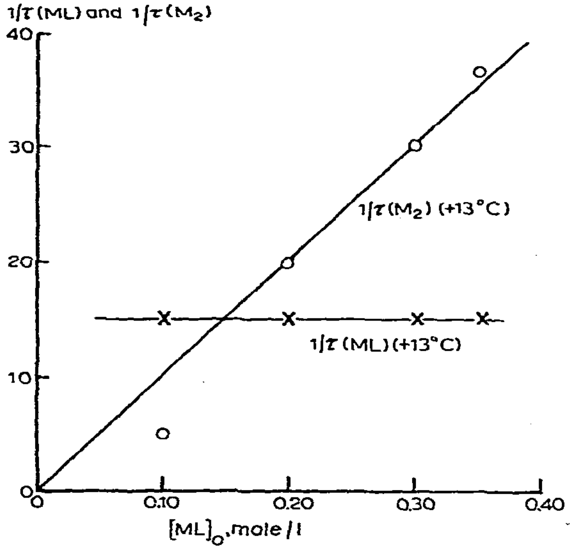

Fig. 7. Dependence of $1/\tau(ML)$ and $1/\tau(M_2)$ on $[ML]_0$ for $[M_2]_0 = 0.05$ mole/l; ML = (COD)RhCl($AsPh_3$); M_2 = [(COD)RhCl$]_2$.

The intermediate further reacts in a fast step with a dimer molecule M_2 with exchange of $AsPh_3$.

$$\underset{\text{“ML”}}{\text{“(COD)Rh}^{\dagger}\text{Cl(AsPh}_3\text{)”}} + \underset{M_2}{\text{(COD)RhCl}_2\text{Rh(COD)}} \underset{k_2}{\rightleftharpoons}$$

$$\underset{M_2}{\text{(COD)Rh}^{\dagger}\text{Cl}_2\text{Rh(COD)}} + \underset{\text{“ML”}}{\text{“(COD)RhCl(ASPh}_3\text{)”}} \qquad (2)$$

For $k_{-1} \ll k_2 \cdot [M_2]$ the rates are:

$$1/\tau(ML) = k_1 \text{ and } 1/\tau(M_2) = \tfrac{1}{2}k_1 \cdot [ML]_0/[M_2]_0{}^{\star}$$

where

$$k_1 = 10^{13}\, e^{-15{,}000/RT}\ \mathrm{s}^{-1}$$

The frequency factor of 10^{13} sec^{-1} is consistent with a reaction in which the monomolecular reaction step (1) is rate-determining.

The nature of the active intermediate “(COD)RhCl(AsPh$_3$)”, which we have to propose in view of the observed concentration dependencies, is as yet unknown. Some possibilities will be mentioned in the discussion.

2. $L = PPh_3$. Line broadening of the signals H_A, H_B and H_C occurs at higher temperatures than for the arsine system, *i.e.* between +20 and +80°. The observed concentration dependencies for $1/\tau(ML)$ and $1/\tau(M_2)$ are:

$$1/\tau(ML) = K' \cdot [M_2]_0^{\frac{1}{2}} \text{ and } 1/\tau(M_2) = k'' \cdot [ML]_0/[M_2]_0^{\frac{1}{2}} \quad \text{(Fig. 8 and 9)}$$

These results can be explained by the following reaction sequence. The dimer M_2 dissociates into two monomeric species:

$$[\text{(COD)RhCl}]_2 \underset{k_3}{\overset{k_{-3}}{\rightleftharpoons}} 2\,\text{(COD)RhCl} \qquad (3)$$

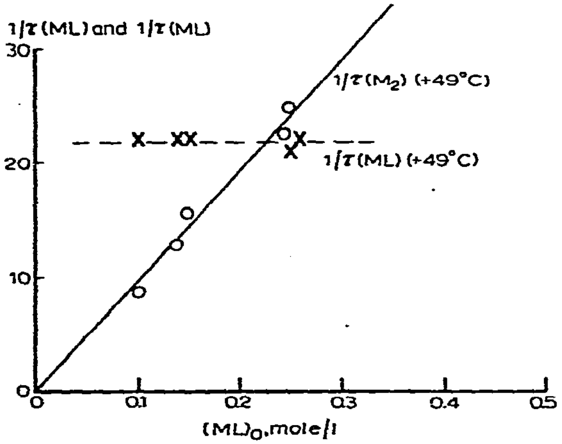

Fig. 8. Dependence of $1/\tau(ML)$ and $1/\tau(M_2)$ on $[ML]_0$ for $[M_2]_0 = 0.075$ mole/l; ML = (COD)RhCl(PPh$_3$) and M_2 = [(COD)RhCl]$_2$.

⋆ The factor $\frac{1}{2}$ arises from the fact that the number of olefinic sites in the dimer is twice that of the monomer ML.

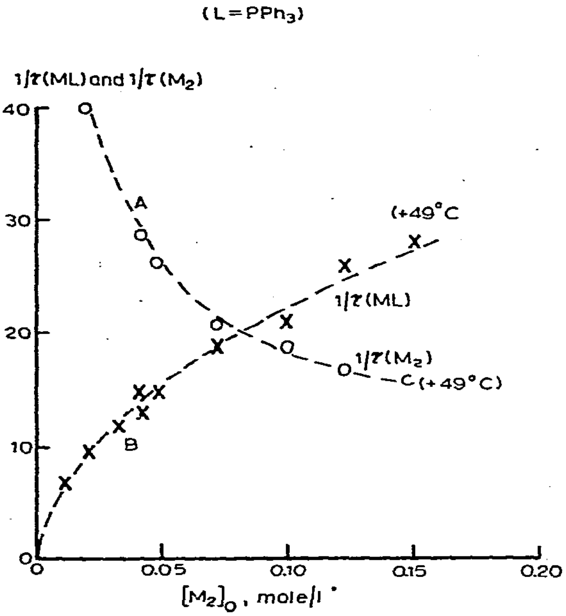

Fig. 9. Dependence of $1/\tau(M_2)$ and $1/\tau(ML)$ on $[M_2]_0$ for $[ML]_0 = 0.20$ mole/l; ML = (COD)RhCl(PPh_3). The broken line A has been calculated for a $1/\tau(M_2)$ on $1/\sqrt{[M_2]_0}$ dependence, while curve B represents the $1/\tau(ML)$ on $\sqrt{[M_2]_0}$ dependence.

The monomeric species (COD)RhCl reacts in the rate-determining step with (COD)RhCl(PPh_3) with exchange of PPh_3:

$$(COD)Rh^{\dagger}Cl + (COD)RhCl(PPh_3) \underset{k_4}{\rightleftharpoons} (COD)Rh^{\dagger}Cl(PPh_3) + (COD)RhCl \qquad (4)$$

For $k_{-3} \cdot [M] \gg k_4 \cdot [ML]$ the rates are:

$$1/\tau(ML) = k_4 \cdot K_3^{\frac{1}{2}} \cdot [M_2]_0^{\frac{1}{2}} \quad \text{(Figs. 8 and 9)}$$

$$1/\tau(M_2) = \tfrac{1}{2} k_4 \cdot K_3^{\frac{1}{2}} \cdot [ML]_0/[M_2]_0^{\frac{1}{2}}, \quad \text{(Figs. 8 and 9)}$$

where

$$k'_{obs} \cong k''_{obs} \cong k_4 \cdot K_3^{\frac{1}{2}} \cong 10^8\, e^{-9600/RT}\ \mathrm{l}^{\frac{1}{2}} \cdot \mathrm{mole}^{-\frac{1}{2}} \cdot \mathrm{s}^{-1}$$

It is possible that (COD)RhCl does not react with the monomer, but with the active monomer "(COD)RhCl(PPh_3)", which, in view of our results on the arsine system, is probably formed, although much less easily. Since we are not able to deduce this from the above concentration dependencies of the rates, we will restrict ourselves to reactions (3) and (4).

We have attempted to devise other reaction models for both the arsine and phosphine systems. However, if, for example, we construct reaction models which involve dissociation of L and subsequently reactions of L with the monomer and the dimer, respectively (analogous to the situation for the π-allylpalladium arsine[1] and 1,5-cyclooctadiene-iridium arsine systems*), the calculated concentration dependencies do not agree with the observed ones.

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* Part VI.

C. L/Rh = 1

The coalescence of the signals of H_A and H_B for solutions of pure (COD)-RhCl(L) was studied for L=AsPh$_3$ between 0 and +40° and for L=PPh$_3$ between +60 and +90°, both in the slow-exchange limit. The rate $1/\tau$(ML) for the arsine case is proportional to $[ML]_0$. A precise determination of the order for L=PPh$_3$, however, was rendered difficult owing to the small exchange contributions to the line width, which could still be measured below the boiling point of the solutions. It is clear, however, that $1/\tau$(ML) for (COD)RhCl(PPh$_3$) also increases with $[ML]_0$.

The reaction responsible for the coalescence of the signals of H_A and H_B may be a direct interaction between two ML molecules. A more attractive proposal, however, seems to us a reaction between a monomer and the reactive monomer species, for example for the arsine system*:

$$(COD)RhCl(AsPh_3) \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \text{“}(COD)RhCl(AsPh_3)\text{”} \qquad (1)$$

which already takes place at −20°. The active monomer then reacts in a rate-determining step with a monomer:

$$\text{“}(COD)RhCl(AsPh_3)\text{”} + (COD)RhCl(AsPh_3) \underset{k_5}{\rightleftharpoons}$$

$$(COD)RhCl(AsPh_3) + \text{“}(COD)RhCl(AsPh_3)\text{”} \qquad (5)$$

Another possibility is a reaction between two active monomer species.

The k_{obs} for L=AsPh$_3$ is $10^9\ e^{-10{,}500/RT}$ l·mole^{-1}·s^{-1} and $10^8\ e^{-12{,}000/RT}$ l·mole^{-1}·s^{-1} for L=PPh$_3$ (calculated from $1/\tau(ML) = k_{obs}\cdot[ML]_0$).

D. Influence of 1,5*-cyclooctadiene and* Cl^- *on the rates*

In order to obtain more information about the above systems and in particular about the nature of the intermediate “(COD)RhCl(AsPh$_3$)” we studied the influence of 1,5-cyclooctadiene or Cl^- addition (in the form of benzylhexadecyldimethylammonium chloride) to solutions of ML proper and to mixtures of ML and M_2 (L=AsPh$_3$, PPh$_3$) in CDCl$_3$ from about room temperature to about 60°.

For the phosphine system no measurable effect was observed on the rates upon addition of the diene** or Cl^-. In the case of the arsine system free diene had no influence on the rates, but Cl^- caused a fast coalescence of the H_A and H_B signals of ML, and of H_A, H_B and H_C signals for mixtures of ML and M_2. Although quantitative measurements were not possible, it was clear that the rates of coalescence increased with the Cl^- concentration. The results may be interpreted in the following way:

If only (COD)RhCl(AsPh$_3$) and Cl^- are present, there is obviously a chloride

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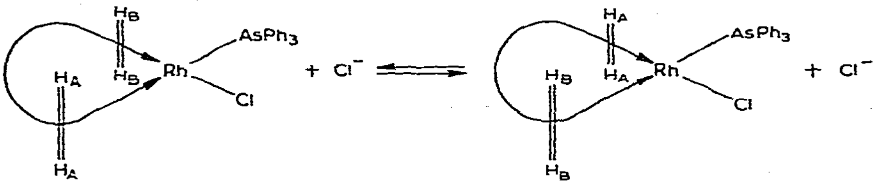
* Since the equilibration between ML and the activated intermediate “ML” must be assumed to explain the kinetic data for AsPh$_3$/Rh < 1, it may well be that the experimentally observed second-order rate constant for the exchange reaction of (COD)RhCl(AsPh$_3$) with AsPh$_3$ (*i.e.* L/Rh > 1) is actually equal to $k_b \cdot K_1$ according to the scheme:

$$ML \underset{k_1}{\rightleftharpoons} \text{“}ML\text{”} \quad \text{and} \quad \text{“}ML\text{”} + L \underset{k_b}{\rightleftharpoons} \text{“}ML\text{”} + L$$

** It is of interest to observe that [(COD)RhCl]$_2$ does not react with COD while norbornadiene exchanges with [NorRhCl]$_2$[9].

exchange reaction, which is accompanied by a *cis–trans* isomerization as for the arsine exchange reaction:



It was observed qualitatively that this Cl^- exchange reaction is slower than the analogous $AsPh_3$ exchange reaction.

If dimer is present besides $(COD)RhCl(AsPh_3)$ and Cl^- the situation is less clear. However, since the dimer peaks coalesce with the monomer peaks, which shows that dimer is converted into monomer and *vice versa*, there must, besides exchange of Cl^-, also be exchange of ligand $AsPh_3$. The following tentative reaction schemes may explain the results:

$$\begin{tikzcd}
(COD)RhCl(AsPh_3)+Cl^- \arrow[r, leftrightarrows] & {[(COD)RhCl_2(AsPh_3)]^-} \arrow[r, leftrightarrows] \arrow[d, shift left] & (COD)RhCl(AsPh_3)+Cl^- \\
\frac{1}{2}[(COD)RhCl]_2+Cl^- \arrow[r, leftrightarrows] & {[(COD)RhCl_2]^-+AsPh_3} \arrow[u, shift left] &
\end{tikzcd}$$

Besides these reactions the dimer reacts of course with $AsPh_3$:

$$[(COD)RhCl]_2+2\,AsPh_3 \rightleftarrows 2\,(COD)RhCl(AsPh_3)$$

We cannot exclude the direct reaction of $[(COD)RhCl]_2$ with the anionic intermediate $[(COD)RhCl_2(AsPh_3)]^-$ with exchange of $AsPh_3$, which seems reasonable also in view of our recently acquired knowledge on monomer–dimer reactions[2]. The anionic species may with one of its Cl atoms attack one of the Rh atoms of the dimer. Clearly more investigations are needed here.

Whatever the mechanism of the chloride exchange reaction, it is clear that the Cl^- exchange reaction is very much faster for $(COD)RhCl(AsPh_3)$ than for $(COD)RhCl(PPh_3)$. The ligand exchange reaction of $(COD)RhCl(AsPh_3)$ with $AsPh_3$ is also faster than the reaction between $(COD)RhCl(PPh_3)$ with PPh_3, but only about five times as fast.

DISCUSSION

To explain the kinetic differences between the arsine and the phosphine system for $L/Rh < 1$, the nature of the active intermediate "$(COD)RhCl(AsPh_3)$" is of main interest in our opinion. In this connection attention should be directed to the observations that the chloride exchange reaction is much faster for $(COD)RhCl(AsPh_3)$ than for $(COD)RhCl(PPh_3)$ and that the ligand exchange reaction of $AsPh_3$ with the arsine complex is faster than the reaction of PPh_3 with $(COD)RhCl(PPh_3)$. These differences may be qualitatively understood from the following reasoning.

In the exchange reactions between $(COD)RhCl(L)$ and L or Cl^- a five-coordinate species is assumed to be involved. This assumption seems well substantiated by a large number of experimental data for square planar complexes with a d^8 configuration[10,11]. Five-coordination is favoured in complexes with ligands having poorer σ-donor and better π-acceptor properties[12]; thus the ligands in the series $PPh_3 < AsPh_3 < SbPh_3$ will increasingly stabilize five-coordination. One will thus expect a lower activation energy for the formation of $[(COD)RhCl_2AsPh_3]^-$ than for $[(COD)RhCl_2PPh_3]^-$. Furthermore, since PPh_3 is the strongest electron donor, the positive charge on the Rh atom will be higher in $(COD)RhCl(AsPh_3)$. The attack by Cl^- on the rhodium will therefore be easier for the arsine complex because of the higher positive charge.

These two factors will contribute to the faster formation of the five-coordinate intermediate for the arsine complex. Since the potential energy curve is symmetrical the exchange will be easier for Cl^- with $(COD)RhCl(AsPh_3)$ than with $(COD)RhCl(PPh_3)$.

Comparison of the relative rates of exchange between $(COD)RhCl(AsPh_3)$ and $AsPh_3$ and between $(COD)RhCl(PPh_3)$ with PPh_3 is more difficult. On the one hand the arsine complex favours the formation of the five-coordinate intermediate more than does the phosphine complex, whereas the phosphine is more nucleophilic than arsine.

From the results we conclude that the stabilization of the five-coordinate intermediate is the most important factor, since the arsine exchange reaction is the fastest. In agreement herewith we have found that the relative difference between the rates of exchange for the arsine complex with $AsPh_3$ and for the phosphine complex with PPh_3 is much smaller than between Cl^- with $(COD)RhCl(AsPh_3)$ and $(COD)RhCl(PPh_3)$ with Cl^-.

We suggest therefore that the reactive intermediate "$(COD)RhCl(AsPh_3)$", which we inferred from the kinetic behaviour for $L/Rh < 1$, is a five-coordinate species with *e.g.* $CDCl_3$ as the fifth ligand. The structure of this intermediate $(COD)RhCl(AsPh_3)(CDCl_3)$* is then expected to be very similar to—for example—$(COD)IrCl(SbPh_3)_2$ and is from the above reasoning expected to be formed more easily for $L = AsPh_3$ than for $L = PPh_3$.

In the arsine case the intermediate "$(COD)RhCl(AsPh_3)$" reacts in a fast step with the dimer $[(COD)RhCl]_2$ to form a "monomer–dimer" intermediate association complex M_3L. If the $Rh-AsPh_3$ bond is sufficiently weak** in M_3L, the $AsPh_3$ may jump from the original Rh atom to another one of the M_3L intermediate. In the case of $(COD)RhCl(PPh_3)$ no monomer–dimer reactions are observed, may be because an active species "$(COD)RhCl(PPh_3)$" is formed with much more difficulty. It is of interest to mention that for mixtures of $(\pi\text{-}C_4H_7)PdCl(PPh_3)$ and $[(\pi\text{-}C_4H_7)PdCl]_2$[2] and of $(Nor)RhCl(PPh_3)$ with $[(Nor)RhCl]_2$[13] below room temperature monomer–dimer reactions were observed, but *without* chemical exchange of PPh_3. In these cases the reactions between monomer and dimer are rate-determining. Thus, although species "$(\pi\text{-}C_4H_7)PdCl(PPh_3)$" and "$(Nor)RhCl(PPh_3)$" may be formed and react with the dimer in a rate-determining step, the M–P bonds are clearly much

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* Solvent effect studies are being carried out to ascertain this point.

** In the case of $(\pi\text{-}C_4H_7)PdCl(AsPh_3)$[2] and also of $(COD)IrCl(AsPh_3)$[8] in the presence of the dimer, the metal–As bond is clearly so weak that dissociation occurs of $AsPh_3$, which is not the case for Rh–As. For both systems (Pd and Ir) fast reactions were found between $AsPh_3$ with the monomer and dimer, respectively. For the Pd–As case, however, precise measurements showed also small contributions of monomer–dimer reactions.

stronger than the M–As bonds, so that PPh_3 remains bonded in M_3L to the same metal atom.

The bonding situation for all three PPh_3 complexes $(COD)RhCl(PPh_3)$, $(Nor)RhCl(PPh_3)$[13] and $(\pi\text{-}C_4H_7)PdCl(PPh_3)$[2] is further quite similar, since for all of them between +20 and +80° reactions occurred between ML and M (formed from dissociation of the dimers) with chemical exchange of PPh_3 [reactions (3) and (4)]. Clearly, the intermediate M_2L provides for the strongly bonded PPh_3 ligand a low-energy pathway to transfer from one metal to another. An obvious reason seems a shorter M–M distance in M_2L than in M_3L.

The active intermediate "ML" may also play a role in the reactions between two molecules of ML and even in ligand exchange reaction of ML with L, as was indicated before. More investigations are needed here.

One could imagine also other structures for the active intermediate "ML", for example:

(*a*) The formation of a contact or solvent-separated ion pair $[(COD)Rh(AsPh_3)]^+Cl^-$. This type of species seems, however, unlikely, since we would expect it to form more easily for the phosphine complex. Furthermore, even a great excess of L ($AsPh_3$, PPh_3) in very polar solvents did not produce any ionic conducting species.

(*b*) Dissociation of the diene. This seems even more unlikely, since added diene did not exchange with coordinated diene, as would then be expected.

(*c*) Partial dissociation of the diene, *i.e.* the diene remains attached to the metal atom with one double bond only. This may be a possibility. For the time being and in anticipation of the results of experiments concerning the solvent effect, we prefere the square pyramidal configuration*.

CONCLUDING REMARKS

We have shown that the type of kinetics observed for the isostructural systems discussed depends very much on the strength of the metal–ligand bond and very probably also on the effective positive charge on the metal atom and its capacity to increase its coordination number.

Furthermore, we have found that the monomer–dimer type of reactions, until recently unknown, occurs much more generally than was expected.

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* It is expected that in solution the two coordination sites above and below the plane of the square planar complex $(COD)RhCl(AsPh_3)$ are occupied by two weakly coordinating solvent molecules ($CDCl_3$). A refinement of the above mechanism of reaction (1) would then be that the five-coordinate active species $(COD)RhCl(AsPh_3)(CDCl_3)$ is formed by the loss of one of the two solvent molecules:

$$(COD)RhCl(AsPh_3)_2(CDCl_3)_2 \underset{k_1}{\rightleftharpoons} (COD)RhCl(AsPh_3)(CDCl_3)$$

Note added in proof: It has now been observed that $AsPh_3$ may dissociate from Rh in CD_2Cl_2 (Part VIII) (analogous to $(COD)IrCl(AsPh_3)$ in $CDCl_3$ (Part VI), but not in $CDCl_3$, as found here. It may therefore well be that in $CDCl_3$ the activated species is a solvent-caged monomer $(COD)RhCl\|AsPh_3(CDCl_3)$. In the better coordinating solvent CD_2Cl_2 the $AsPh_3$ ligand dissociates to a small extent, which does not occur in $CDCl_3$.

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