

NUCLEAR MAGNETIC RESONANCE STUDIES IN COORDINATION CHEMISTRY

VII. KINETIC STUDIES OF EXCHANGE REACTIONS INVOLVING BICYCLO[2.2.1]HEPTA-2,5-DIENE COMPLEXES OF RHODIUM(I)

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SUMMARY

NMR studies of the coalescence of the signals of the inequivalent olefinic protons of the monomer (Nor)RhCl(PPh₃) (Nor = bicyclo[2.2.1]hepta-2,5-diene) have indicated the occurrence of monomer–monomer reactions. In the presence of free triphenylphosphine a fast ligand-exchange reaction was observed with the monomer. When, however, besides the monomer the dimeric [(Nor)RhCl]₂ was present, below +20° monomer–dimer reactions took place without exchange of PPh₃. Above +20° phosphine-exchange reactions occurred between (Nor)RhCl(PPh₃) and (Nor)RhCl, the latter being formed by dissociation of the dimer. Addition of Cl⁻ to solutions of the monomer, and to mixtures of monomer and dimer, resulted in halide-exchange reactions, while addition of free norbornadiene had no observable effect.

With the triphenylarsine system we could only study reactions of the monomer (Nor)RhCl(AsPh₃) in the presence of dimer. The arsine system is different from the phosphine one in that reactions were found of dissociated AsPh₃ with the arsine compound and the dimer, respectively.

The results for these systems are compared with those for the 1,5-cyclooctadiene systems of Rh^I and Ir^I and the π -allylpalladium systems.

I. INTRODUCTION

Previous reports in this series¹ concerned NMR studies of the influence of the ligand L on reactions of π -methallylpalladium compounds (π -C₄H₇)PdCl(L) (L = AsPh₃ (Parts I and II); PPh₃ (Part III), P(n-C₄H₉)₃ etc. (Part IV)) and of isoelectronic complexes (COD)MCl(L) (COD = 1,5-cyclooctadiene; L = AsPh₃, PPh₃; M = Rh^I (Part V), Ir^I (Part VI)). It was observed that reactions may occur between these monomeric complexes and species such as: ligands L, the monomer itself, the parent dimer compounds *e.g.* [(π -C₄H₇)PdCl]₂ and [(COD)MCl]₂, species (π -C₄H₇)PdCl and (COD)MCl, which are formed by dissociation of the dimers, and, finally, halide ions (Cl⁻) and dienes.

The reactions in the phosphine systems were very similar. Particularly in the presence of dimer we found that, owing to the high metal–phosphorus bond strength, the amount of dissociated PPh₃ was very small, so that ligand-exchange reactions

were not observed. The triphenylarsine systems, however, differed very much in this respect, because the metal-arsine bond strength is rather susceptible to the influence of the other groups present in the compound. Dissociation of triphenylarsine was observed for the π -metallyl compound (π -C₄H₇)PdCl(AsPh₃) and for (COD)IrCl(AsPh₃), but not for (COD)RhCl(AsPh₃).

In the two preceding reports we compared the behaviour of the compounds (COD)RhCl(L) (Part V) and (COD)IrCl(L) (Part VI). In this report we present a study of the reactions of (Nor)RhCl(L), where Nor = bicyclo[2.2.1]hepta-2,5-diene and L = AsPh₃ or PPh₃. The results are compared with those of the 1,5-cyclooctadiene compounds (COD)RhCl(L). The effect of the diene is discussed.

II. EXPERIMENTAL

In previous reports^{1a,b} we described the preparation and some of the properties of the monomers (Nor)RhCl(L) (L = AsPh₃, PPh₃) and the dimer [(Nor)RhCl]₂.

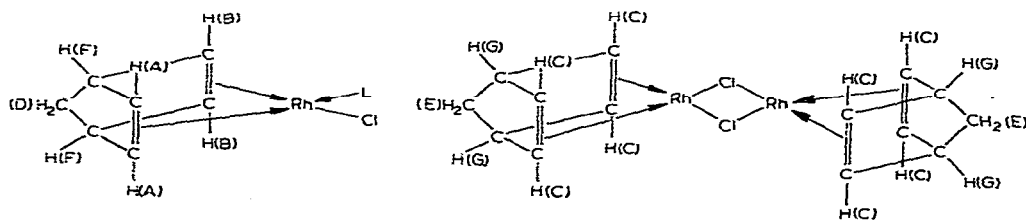
The NMR spectra were measured with a Varian Spectrometer (HA 100 and DP 60), CDCl₃ being used as solvent and tetramethylsilane (TMS) as internal standard. For mixtures of the monomer (Nor)RhCl(PPh₃) and PPh₃ the concentrations were between 0.1 and 0.4 and 0.005 mole/l, respectively. For mixtures of monomer and dimer, the concentrations were between 0.1 and 0.4 and between 0.05 and 0.3 mole/l, respectively.

The conductivities were measured with a Philips Philoscope G.M. 4249 using platinum electrodes. Dichloromethane and nitromethane were employed as solvents.

III. KINETIC ANALYSIS

The reactions of (Nor)RhCl(PPh₃) with PPh₃ were measured for the slow exchange limit³ from the widths of the signals of the olefinic protons H(A) and H(B), and for the fast exchange limit³ from the width of the coalesced signal.

The pseudo first-order reaction rates $1/\tau$ (τ is the life time of the protons concerned³) for mixtures of the monomer (Nor)RhCl(PPh₃) and the dimer [(Nor)RhCl]₂ were calculated in the slow exchange limit from the signals of the protons H(A) and H(B) of the monomer and further of the methylene protons H(D) and H(E) of monomer and dimer, respectively.



In the case of L = AsPh₃ measurements were carried out only on the H(A) and H(B) signals of (Nor)RhCl(AsPh₃), and not on those of H(D) and H(E) owing to the small difference in chemical shift. In no case could we compute the rates on the H(C) signal of the dimer, owing to overlap with the absorptions of the H(F) and H(G) protons.

Double resonance experiments showed that the H(A) and H(B) protons do not couple with each other. Both H(A) and H(B) couple with the neighbouring H(F) protons ($J(\text{H(A)}-\text{H(F)}) = 1.5$ cps; $J(\text{H(B)}-\text{H(F)}) = 1.8$ cps). For the phosphine compound we also observed a coupling with the rhodium nucleus and the phosphorus nucleus ($J(\text{Rh-H(A,B)}) = 2.0$ cps; $J(\text{P-H(A)}) = 1.5$ cps and $J(\text{P-H(B)}) = 2.2$ cps). The methylene CH_2 signals H(D) and H(E) of monomer and dimer, respectively, appeared as triplets ($J(\text{H(D)}-\text{H(F)}) = 1.6$ cps (for $\text{L} = \text{AsPh}_3$ and PPh_3) and $J(\text{H(E)}-\text{H(G)}) = 1.6$ cps) owing to coupling with the two H(F) and H(G) protons, respectively.

The contribution to the linewidth due to exchange for the absorptions of H(A) and H(B) was obtained by subtracting the linewidth in the absence of exchange (~ 10 cps and ~ 7 cps for the phosphine and arsine compound, respectively) from the actual linewidth. In the case of phosphine exchange a suitable correction was made for the coalescence of the P-doublets. Previously it was shown that this method of obtaining the exchange contributions to the linewidths is reasonable for this type of compounds, because the coupling constants are small compared with the difference in chemical shift*.

The rates of exchange, measured on the triplets of protons H(D) and H(E), were calculated from the component linewidths. These estimated by use of a line shape analysis of three overlapping Lorentz curves which, as shown before, yielded good results^{1c}. A natural linewidth of 1.8–2.0 cps (*i.e.* in the absence of exchange) was subtracted from the component linewidths.

The results show that the above methods of approximation are very useful to obtain data on the kinetic behaviour. The error in the activation energies is estimated to be 2 kcal/mole.

IV. RESULTS OF THE KINETIC MEASUREMENTS

In sections A, B and C we will discuss the kinetic results for mixtures of the monomer $(\text{Nor})\text{RhCl}(\text{PPh}_3)$ ($\text{L/Rh} > 1$), for mixtures of $(\text{Nor})\text{RhCl}(\text{L})$ ($\text{L} = \text{PPh}_3$, AsPh_3) and the dimer ($\text{L/Rh} < 1$), and for solutions of the monomer ($\text{L} = \text{PPh}_3$) alone ($\text{L/Rh} = 1$), respectively. Section D deals with the influence of added chloride ions and norbornadiene.

The chemical shifts of the monomer and dimer complexes are given below.

TABLE I

CHEMICAL SHIFTS OF NORBORNADIENE PROTONS OF $(\text{Nor})\text{RhCl}(\text{L})$ AND $[(\text{Nor})\text{RhCl}]_2$ ppm from TMS; in CDCl_3 solution

Compound	T(°C)	$\delta\text{H(A)}$	$\delta\text{H(B)}$	$\delta\text{H(D)}$	$\delta\text{H(F)}$
$(\text{Nor})\text{RhCl}(\text{PPh}_3)$	-60°	5.34	3.00	1.39	3.77
$(\text{Nor})\text{RhCl}(\text{AsPh}_3)^a$	-60°	5.03	3.25	1.33	3.83
			$\delta\text{H(C)}$	$\delta\text{H(E)}$	$\delta\text{H(G)}$
$[(\text{Nor})\text{RhCl}]_2$	-60°	3.96		1.21	3.96

^a Measured in the presence of the dimer.

* For further comments on this approximation see ref. 1e, f.

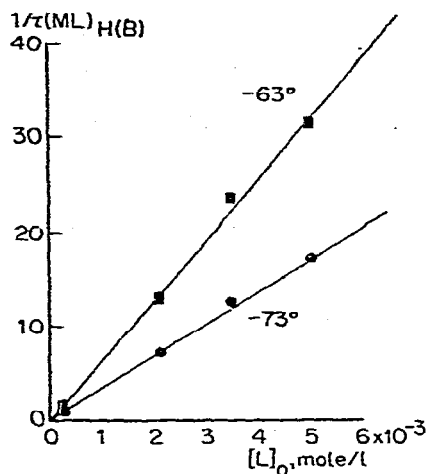


Fig. 1. Dependence of $1/\tau(\text{ML})_{\text{H(B)}}$ for $\text{L} = \text{PPh}_3$ on $[\text{L}]_0$ for $[\text{ML}]_0 = 0.30$ mole/l [$\text{ML} = (\text{Nor-C}_7\text{H}_8)\text{RhCl}(\text{PPh}_3)$].

A. $L/\text{Rh} > 1$

The signals of the H(A) and H(B) protons of $(\text{Nor})\text{RhCl}(\text{PPh}_3)$ (in CDCl_3 at -20°) appeared at 5.34 and 3.00 ppm from TMS, respectively. When a very small

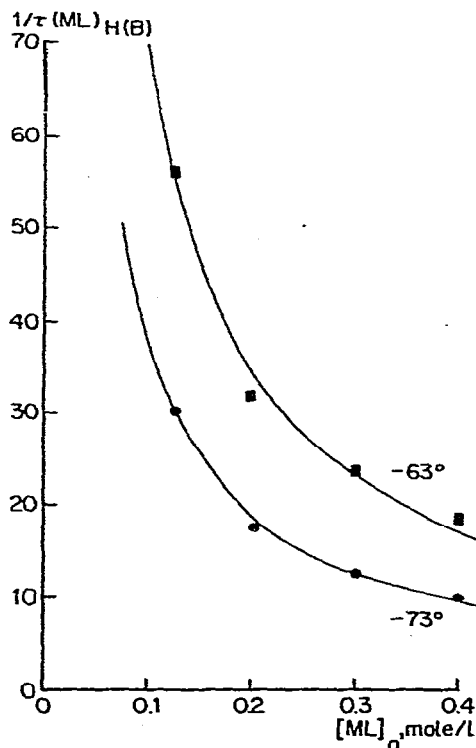
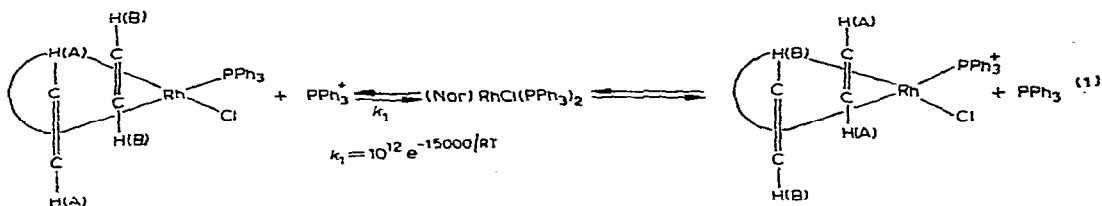


Fig. 2. Dependence of $1/\tau(\text{ML})_{\text{H(B)}}$ for $\text{L} = \text{PPh}_3$ on $[\text{ML}]_0$ for $[\text{L}]_0 = 0.0035$ mole/l [$\text{ML} = (\text{Nor})\text{RhCl}(\text{PPh}_3)$].

amount of PPh_3 was added they immediately collapsed to one signal. The reaction rate $1/\tau(\text{ML})_{\text{H(B)}}$ was measured as a function of the weighed-in amounts of ligand ($[\text{L}]_0$) and monomer ($[\text{ML}]_0$), respectively, between -75° and -40° . Figure 1 shows that $1/\tau(\text{ML})_{\text{H(B)}} (= 1/\tau(\text{ML})_{\text{H(A)}})$ is proportional to $[\text{L}]_0$ for constant $[\text{ML}]_0$, while it decreases with increasing $[\text{ML}]_0$ for constant $[\text{L}]_0$ (Fig. 2).

Since the ionic conductivity in CH_2Cl_2 for mixtures of $(\text{Nor})\text{RhCl}(\text{L})$ ($\text{L} = \text{PPh}_3, \text{AsPh}_3$) and L in the ratio 1 : 5 between -80° to $+30^\circ$ is virtually nil, we suggest a ligand-exchange reaction via a five coordinated intermediate $(\text{Nor})\text{RhCl}(\text{PPh}_3)_2$;



The strong decrease of $1/\tau(\text{ML})_{\text{H(B)}}$ with $[\text{ML}]_0$ (Fig. 2) at low temperatures ($\sim -60^\circ$) indicates that a fairly large amount of the weighed-in amount of PPh_3 is converted by monomer into $(\text{Nor})\text{RhCl}(\text{PPh}_3)_2$. The proportionality to $[\text{L}]_0$ (Fig. 1) confirms that few ionic species are present, since, if a large amount of ionic species is

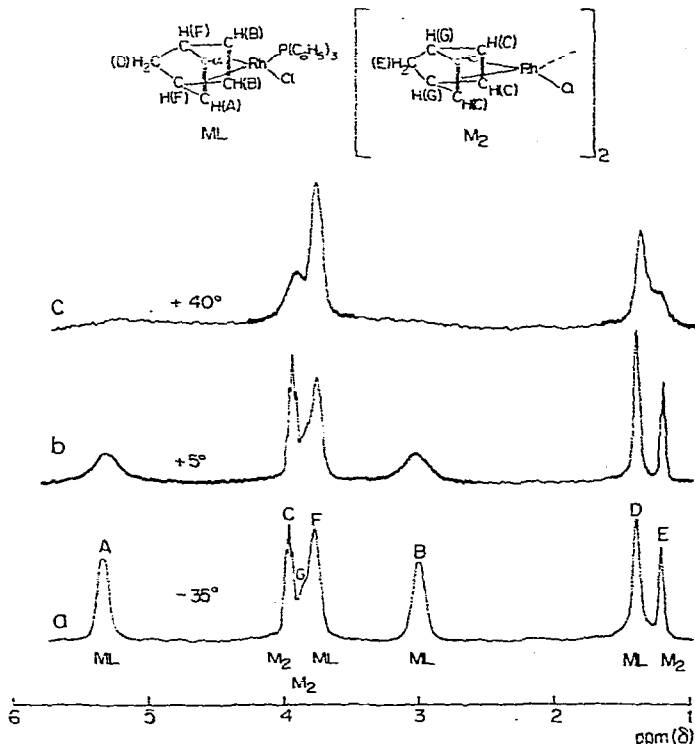


Fig. 3. Temperature dependence of the absorptions of $(\text{Nor})\text{RhCl}(\text{PPh}_3)$ (0.40 mole/l) and $[(\text{Nor})\text{RhCl}]_2$ (0.10 mole/l). a, No exchange occurs; b, Signals H(A) and H(B) coalesce, while the dimer signals and the methylene H(D) signal of ML remain sharp; c, The dimer signals broaden too.

formed and a small amount of five-coordinated species, the rate becomes proportional to $[L]_0^2$ (Ref. 1c).

The interchange of H(A) and H(B) may be explained by a rotation of the diene group in the plane of olefinic bonds in the intermediate $(\text{Nor})\text{RhCl}(\text{PPh}_3)_2$, which is similar to that proposed earlier for $(\text{COD})\text{MCl}(\text{L})$ ($\text{M} = \text{Rh}^{1e}, \text{Ir}^{1f}$).

No rate measurements could be carried out for $(\text{Nor})\text{RhCl}(\text{AsPh}_3)$, because, even in the absence of free AsPh_3 , the H(A) and H(B) signals collapsed, except at very low temperatures.

B. $L/\text{Rh} < 1$

We will first discuss the phosphine system and then the arsine system.

$L = \text{PPh}_3$. (a) *Temperatures between -20 and $+30^\circ$.* Figures 3a and 3b show that in this temperature region the absorptions of H(A) and H(B) broaden, but that those of the methylene protons H(D) do not. Furthermore, the dimer signals remain sharp, which clearly indicates that there is no exchange of PPh_3 between monomer and dimer. This behaviour is completely similar to that of the π -methallylpalladium complex $(\pi\text{-C}_4\text{H}_7)\text{PdCl}(\text{PPh}_3)$ in the presence of $[(\pi\text{-C}_4\text{H}_7)\text{PdCl}]_2$ in the same temperature range^{1c}. The rate observed, which is independent of $[\text{ML}]_0$ (see Fig. 4 and 5),

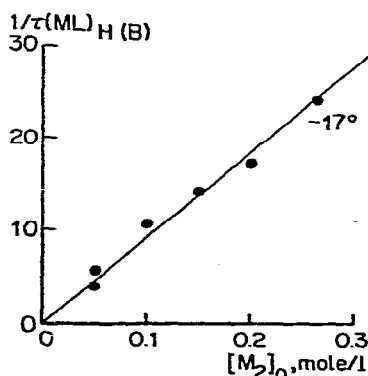


Fig. 4. Dependence of $1/\tau(\text{ML})_{\text{H(B)}}$ on $[\text{M}_2]_0$ for $[\text{ML}]_0 = 0.20$ mole/l ($\text{ML} = (\text{Nor})\text{RhCl}(\text{PPh}_3)$, $\text{M}_2 = [(\text{Nor})\text{RhCl}]_2$).

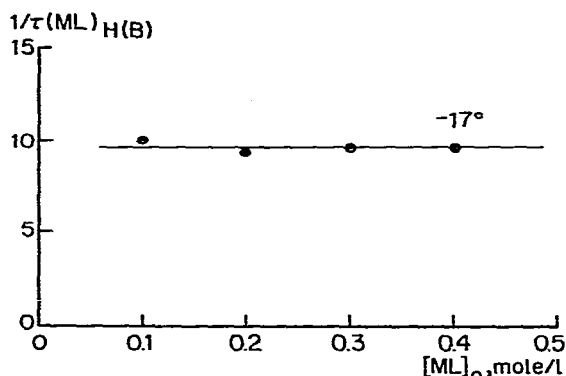


Fig. 5. Dependence of $1/\tau(\text{ML})_{\text{H(B)}}$ on $[\text{ML}]_0$ for $[\text{M}_2]_0 = 0.10$ mole/l ($\text{ML} = (\text{Nor})\text{RhCl}(\text{PPh}_3)$, $\text{M}_2 = [(\text{Nor})\text{RhCl}]_2$).

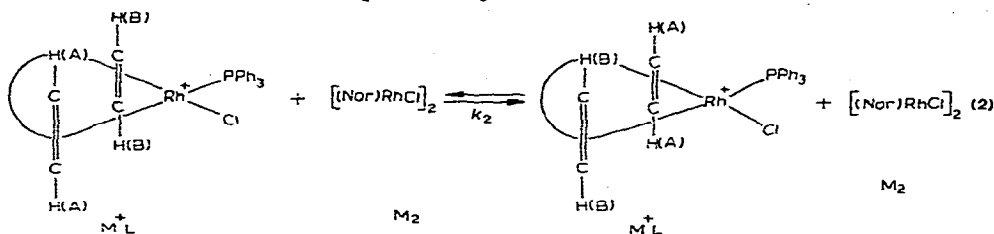
is:

$$1/\tau(\text{ML})_{\text{H(B)}} = \frac{d[\text{ML}]}{dt} \quad ([\text{ML}] = k'[\text{M}_2]_0^*)$$

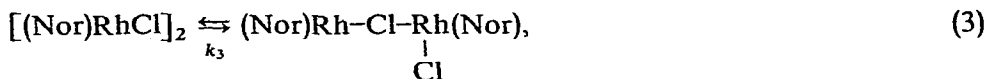
where $k' = 10^8 e^{-8600/RT}$.

* If it is found that the weighed-in amounts $[\text{M}_2]_0$ and $[\text{ML}]_0$ are about equal to the equilibrium concentrations $[\text{M}_2]$ and $[\text{ML}]$, respectively.

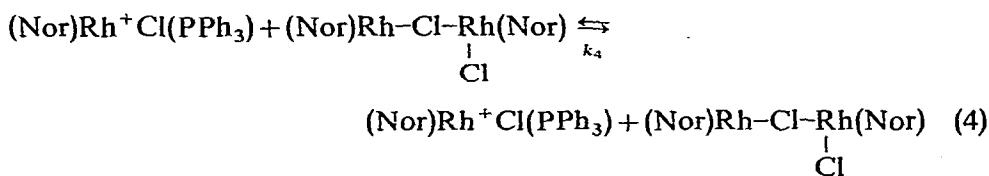
This result can be explained by a monomer-dimer reaction:



There may be a pre-equilibrium as proposed for the Pd system^{1c}:



followed by the rate-determining step:



which may involve an attack of the terminal chlorine atom of the dimer on ML. For reactions (3) and (4) the rate is:

$$1/\tau(\text{ML})_{\text{H(B)}} = k_4 K_3 [\text{M}_2].$$

In reactions (2) and (4) there is no exchange of PPh₃.

(b) *Temperatures between +30 and +80°.* In this temperature range the dimer signals, too, broaden at the same time as the methylene H(D) absorption of the monomer, which coalesced with the methylene H(E) signal of the dimer (Fig. 3c). This

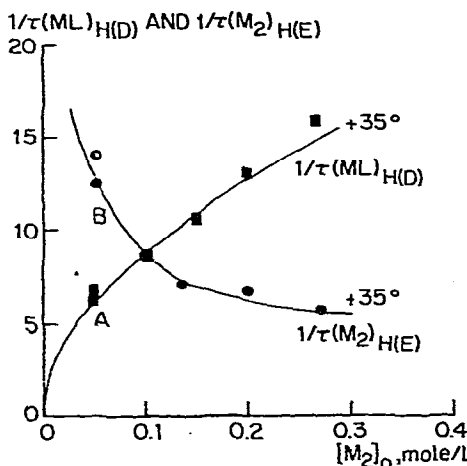


Fig. 6. Dependence of $1/\tau(\text{ML})_{\text{H(D)}}$ and $1/\tau(\text{M}_2)_{\text{H(E)}}$ on $[\text{M}_2]_0$ for $[\text{ML}]_0 = 0.20$ mole/l. ($\text{ML} = (\text{Nor})\text{RhCl}(\text{PPh}_3)$, $\text{M}_2 = [(\text{Nor})\text{RhCl}]_2$). Curve A represents a calculated $1/\tau(\text{ML})$ on $[\text{M}_2]_0^{\frac{1}{2}}$ dependence, while curve B represents a calculated $1/\tau(\text{M}_2)$ on $[\text{M}_2]^{-\frac{1}{2}}$ dependence.

coalescence indicates that there is rapid interconversion of monomer into dimer via exchange of PPh_3 .

Measurements of the concentration dependence yielded:

$$1/\tau(\text{ML})_{\text{H(D)}} = k'' [\text{M}_2]_0^{\frac{1}{2}}, \text{ which is independent of } [\text{ML}]_0 \text{ (Figs. 6 and 7)}$$

and

$$1/\tau(\text{M}_2)_{\text{H(E)}} = k'' [\text{ML}]_0 / [\text{M}_2]_0^{\frac{1}{2}}, \text{ (Figs. 6 and 7)}$$

where $k'' = 10^{16} e^{-21000/RT} \text{ l}^{\frac{1}{2}} \cdot \text{mole}^{-\frac{1}{2}} \cdot \text{sec}^{-1}$.

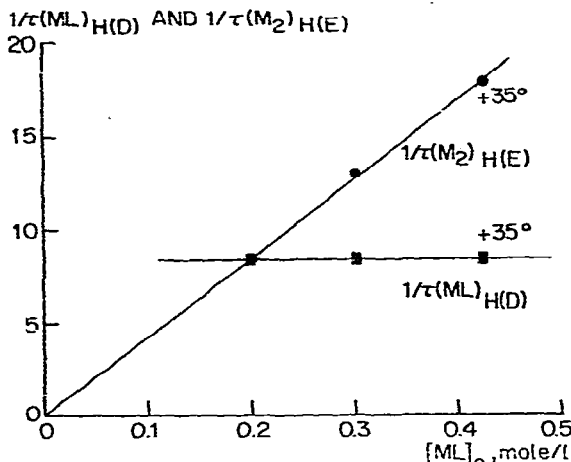
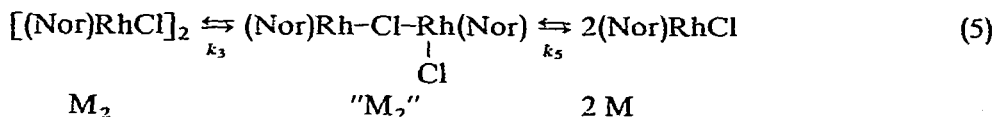
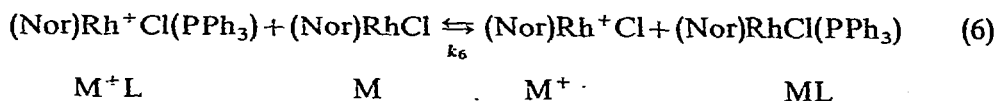


Fig. 7. Dependence of $1/\tau(\text{ML})_{\text{H(D)}}$ and $1/\tau(\text{M}_2)_{\text{H(E)}}$ on $[\text{ML}]_0$ for $[\text{M}_2]_0 = 0.10 \text{ mole/l}$ ($\text{ML} = (\text{Nor})\text{RhCl}(\text{PPh}_3)$, $\text{M}_2 = [(\text{Nor})\text{RhCl}]_2$).

These dependencies are similar to those for $(\text{COD})\text{RhCl}(\text{PPh}_3)^{1e}$ and $(\pi\text{-C}_4\text{H}_7)\text{-PdCl}(\text{PPh}_3)^{1c}$ in the presence of the parent dimer compounds for the same temperature range. The proposed reaction scheme, which is analogous to the one suggested before¹, is:



and, subsequently, a rate-determining exchange step:



The following rate equations were derived:

$$1/\tau(\text{ML})_{\text{H(D)}} = k_6(K_3 \cdot K_5)^{\frac{1}{2}} [\text{M}_2]^{\frac{1}{2}}$$

and

$$1/\tau(\text{M}_2)_{\text{H(E)}} = \frac{1}{2} k_6(K_3 \cdot K_5)^{\frac{1}{2}} [\text{ML}] / [\text{M}_2]^{\frac{1}{2}}.$$

$L = \text{AsPh}_3$. The reactions for mixtures of the monomer $(\text{Nor})\text{RhCl}(\text{AsPh}_3)$ and the dimer could only be studied from the widths of the signals H(A) and H(B) of

the monomer between -80° and -60° . In this temperature region the signals of the dimer and the methylene protons H(D) did not change in linewidth, whereas at higher temperatures they did broaden with coalescence of the methylene signals H(D) and H(E) of monomer and dimer, respectively (Fig. 8; although the spectral changes are very similar to those in Fig. 3 the situation is very different, as is shown below).

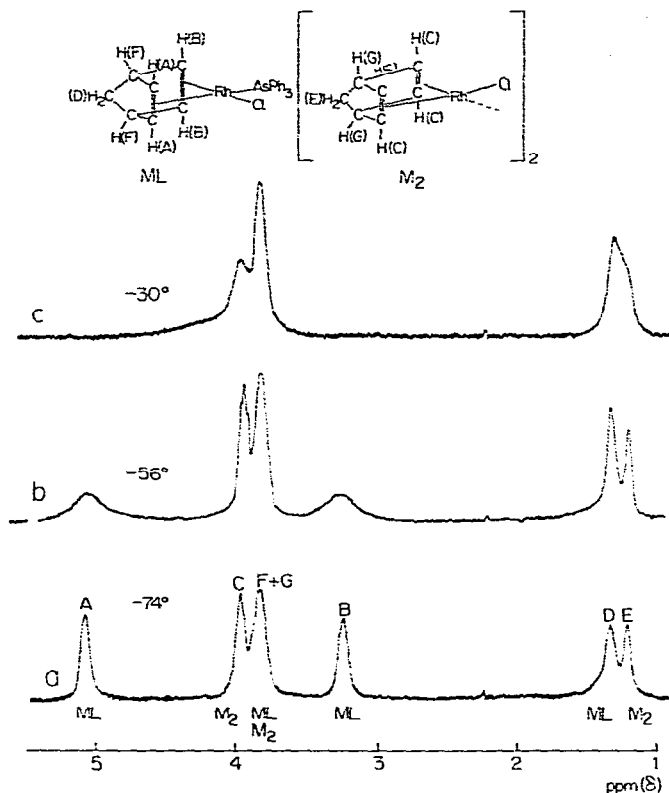


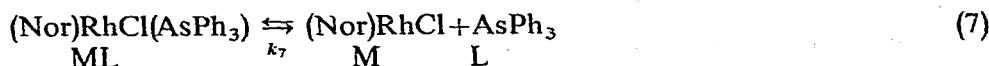
Fig. 8. Temperature dependence of the absorptions of a mixture of $(\text{Nor})\text{RhCl}(\text{AsPh}_3)$ (0.20 mole/l) and $[(\text{Nor})\text{RhCl}]_2$ (0.05 mole/l). a, No exchange occurs; b, Signals H(A) and H(B) of the arsine compound coalesce while the other signals remain sharp; c, The other signals broaden too.

The measurements showed that:

$$1/\tau(\text{ML})_{\text{H(D)}} = k''' [\text{ML}]_0 / [\text{M}_2]_0^{\frac{1}{2}} \quad (\text{Fig. 9 and 10}).$$

(As mentioned in the Kinetic analysis the reactions of the dimer could not be measured). The reaction scheme is similar to the one proposed for $(\text{COD})\text{IrCl}(\text{AsPh}_3)$ in the presence of $[(\text{COD})\text{IrCl}]_2^{1f*}$:

Dissociation of the monomer:



* A reaction scheme based on Cl^- exchange or monomer-dimer type reactions cannot explain the observed concentration dependencies.

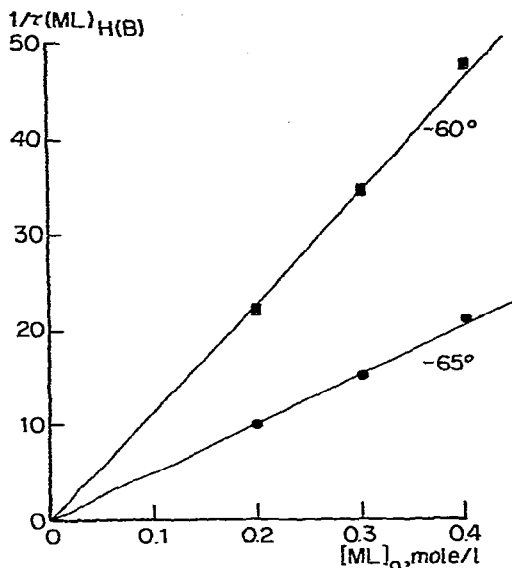


Fig. 9. Dependence of $1/\tau(\text{ML})_{\text{H(B)}}$ on $[\text{ML}]_0$ for $[\text{M}_2]_0 = 0.10$ mole/l ($\text{ML} = (\text{Nor})\text{RhCl}(\text{AsPh}_3)$, $\text{M}_2 = [(\text{Nor})\text{RhCl}]_2$).

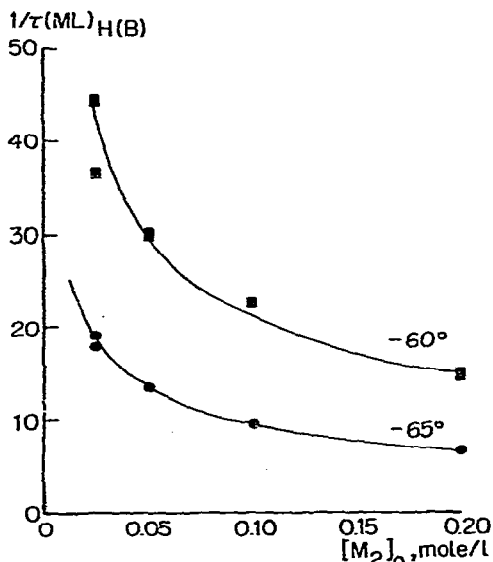
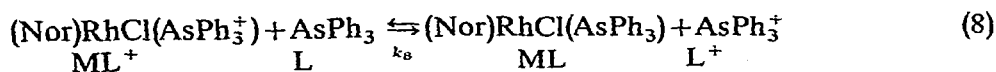


Fig. 10. Dependence of $1/\tau(\text{ML})_{\text{H(B)}}$ on $[\text{M}_2]_0$ for $[\text{ML}]_0 = 0.20$ mole/l ($\text{ML} = (\text{Nor})\text{RhCl}(\text{AsPh}_3)$, $\text{M}_2 = [(\text{Nor})\text{RhCl}]_2$). The curves represent calculated $1/\tau(\text{ML})$ on $[\text{M}_2]_0^{\pm}$ dependencies.

The dissociated AsPh_3 reacts with monomer:



The dissociated AsPh_3 may also react with the dimer, but only at temperatures higher than -60° :



This reaction probably proceeds via two steps in the same way as was discussed. Finally, the dimer may dissociate:



The observed concentration dependence can be explained if one assumes that reaction (8) is the rate-determining step, in which case:

$$1/\tau(\text{ML}) = k_8(K_7/K_{10}^{\frac{1}{2}})[\text{ML}]/[\text{M}_2]^{\frac{1}{2}},$$

where $k_8(K_7/K_{10}^{\frac{1}{2}}) = 10^{17} e^{-16000/RT} \text{ l}^{\frac{1}{2}} \cdot \text{mole}^{-\frac{1}{2}} \cdot \text{sec}^{-1}$

C. $L/Rh = 1$

Rate measurements for solutions of the monomer $(\text{Nor})\text{RhCl}(\text{PPh}_3)$ alone in CDCl_3 , which were carried out between $+10^\circ$ and $+50^\circ$ in the slow exchange limit of the H(A) and H(B) signals, showed that $1/\tau(\text{ML})_{\text{H(B)}}$ is proportional to the monomer concentration $[\text{ML}]_0$ (Fig. 11).

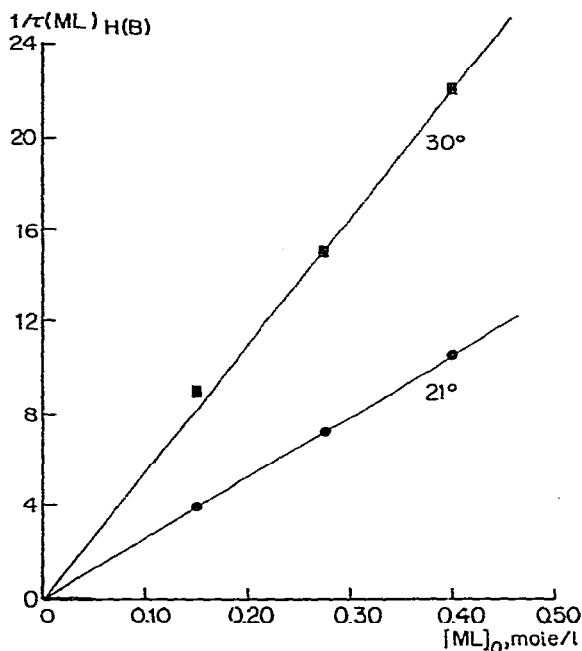
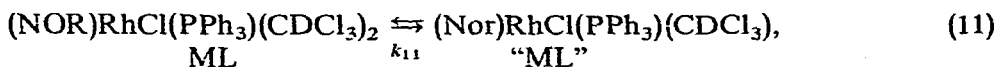


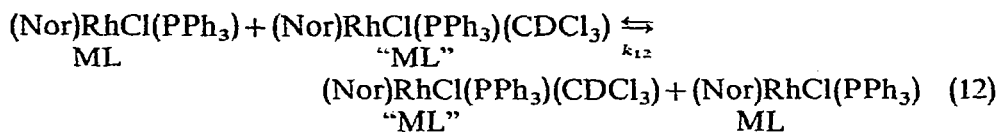
Fig. 11. Dependence of $1/\tau(\text{ML})_{\text{H(B)}}$ on $[\text{ML}]_0$, in the absence of dimer or ligand $[\text{ML} = (\text{Nor})\text{RhCl}(\text{PPh}_3)]$.

The proposed reaction scheme, which is similar to that of $(\text{COD})\text{RhCl}(\text{AsPh}_3)^{1e}$, may involve a direct reaction of two monomer molecules, with or without exchange of PPh_3 , or a reaction between an "activated" monomer molecule and the monomer itself*:

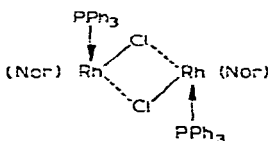
* For a discussion on the "activated" monomer type of species see ref. 1e and Part VIII (in press).



which reaction involves the loss of one of the two solvent molecules which in solution may be weakly coordinated to the rhodium atom. The activated molecule "ML" further reacts in a rate-determining step:



Another possibility involves the reaction of two activated monomers. Whatever the mechanism may be, it seems likely that the intermediate is binuclear, for example:



The observed reaction constant $k_{obs.}$ is $10^{12} e^{-15000/RT} \text{ l. mole}^{-1} \cdot \text{sec}^{-1}$ (calculated from $1/\tau(\text{ML}) = k_{obs.} [\text{ML}]_0$).

D. Influence of added norbornadiene and Cl^-

Addition of norbornadiene to solutions of $(\text{Nor})\text{RhCl}(\text{PPh}_3)$ in CDCl_3 did not noticeably influence the rates; no exchange of norbornadiene was observed*.

When Cl^- ions were added in the form of benzylhexadecyldimethylammonium chloride to solutions of $(\text{Nor})\text{RhCl}(\text{PPh}_3)$ or to solutions of the monomer and the dimer, the rate of coalescence of the H(A) and H(B) signals increased, which is undoubtedly due to halide-exchange reactions. The halide ions did not cause the ligand to dissociate as was found for $(\text{COD})\text{RhCl}(\text{AsPh}_3)^{1e}$. This was concluded from the observation that the dimer signals remained sharp.

It is noteworthy that addition of Cl^- to $(\text{COD})\text{RhCl}(\text{PPh}_3)$, $(\text{COD})\text{IrCl}(\text{PPh}_3)$ and $(\pi\text{-C}_4\text{H}_7)\text{PdCl}(\text{PPh}_3)$ had no observable effect.

V. DISCUSSION

Comparing the behaviour of $(\text{Nor})\text{RhCl}(\text{PPh}_3)$ with that of $(\text{COD})\text{RhCl}(\text{PPh}_3)^{1e}$, we find that the norbornadiene complex forms five-coordinated species more readily than the 1,5-cyclooctadiene complex. This is confirmed by the ligand-exchange reaction (1), in which the five-coordinated complex $(\text{Nor})\text{RhCl}(\text{PPh}_3)_2$ is formed, while $(\text{COD})\text{RhCl}(\text{PPh}_3)_2^{**}$ —if existent at all—is produced only in negligible amounts***. Consistent with the stabilization of five-coordination for the norbornadiene complex is the increase in rate when going from the 1,5-cyclooctadiene to

* Diene-exchange reactions were observed for norbornadiene with $[(\text{Nor})\text{RhCl}]_2^+$, but not for 1,5-cyclooctadiene with $[(\text{COD})\text{RhCl}]_2$ (Ref. 1e).

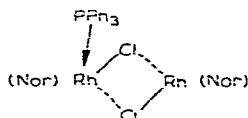
** $(\text{COD})\text{IrCl}(\text{PPh}_3)_2$ on the other hand is readily formed^{1c}.

*** Comparison of the rates of both systems shows that the PPh_3 exchange reaction proceeds much faster for the norbornadiene than for the cyclooctadiene system.

the norbornadiene rhodium complex in the reactions with Cl^- ions and with a dimer molecule (reactions (2) or (3) and (4)). The symmetrical potential energy curves for these reactions suggest that stabilization of the five-coordinated intermediate* will bring about a decrease in activation energy relative to a synchronous process and that, therefore, these reactions will proceed faster than for the 1,5-cyclooctadiene compound.

It is not very clear why five-coordination is more favoured by coordinated norbornadiene than by coordinated cyclooctadiene. A factor may be that norbornadiene, in line with the results from Westland's⁸ work, accepts more readily electrons from the metal atom (by π -back-bonding) than 1,5-cyclooctadiene. This would agree with the fact that the observed tendency for $(\text{COD})\text{RhCl}(\text{AsPh}_3)$ to dissociate AsPh_3 is only very small** (measured in the presence of dimer ^{1e}), while AsPh_3 dissociates from $(\text{Nor})\text{RhCl}(\text{AsPh}_3)$ in the presence of $[(\text{Nor})\text{RhCl}]_2$. In the latter reaction the smaller strength of the $\text{Rh}-\text{AsPh}_3$ bond would be caused by loss in π -bonding, because norbornadiene competes more successfully for the π -electrons of the metal atom than 1,5-cyclooctadiene.

When we consider reactions (3), (5) and (6), which are observed for mixtures of $(\text{Nor})\text{RhCl}(\text{PPh}_3)$ and $[(\text{Nor})\text{RhCl}]_2$ at temperatures higher than $+20^\circ$, it is of interest to note that this type of reactions has also been observed for mixtures of $(\text{COD})\text{RhCl}(\text{PPh}_3)$ and $[(\text{COD})\text{RhCl}]_2$ ^{1e} and of $(\pi\text{-C}_4\text{H}_7)\text{PdCl}(\text{PPh}_3)$ and $[(\pi\text{-C}_4\text{H}_7)\text{PdCl}]_2$ ^{1c}. The reaction constant $k_{\text{obs.}} = [k_6(K_3 \cdot K_5)^{\frac{1}{2}}]$ of $10^{16} e^{-21000/RT} \text{ l}^{\frac{1}{2}} \cdot \text{mole}^{-\frac{1}{2}} \cdot \text{sec}^{-1}$ for the norbornadiene system is quite different from the $k_{\text{obs.}}$ for the cyclooctadiene system ($10^8 e^{-9600/RT} \text{ l}^{\frac{1}{2}} \cdot \text{mole}^{-\frac{1}{2}} \cdot \text{sec}^{-1}$), but very similar to that for the π -methylallyl palladium phosphine system ($10^{14} e^{-20500/RT} \text{ l}^{\frac{1}{2}} \cdot \text{mole}^{-\frac{1}{2}} \cdot \text{sec}^{-1}$). The proposed reaction intermediate of reaction (6) has a binuclear structure:



This intermediate, by virtue of the closeness of the two rhodium atoms, may offer a low energy path for exchange of PPh_3 from the rhodium on the left-hand side to the metal atom on the right-hand side. In view of the discussions above we would expect this binuclear intermediate, in which one of the rhodium atoms is five-coordinated, to be formed more easily for norbornadiene than for cyclooctadiene. It is, however, impossible to make a quantitative comparison between the two systems, since nothing is known about the equilibrium $\text{M}_2 \rightleftharpoons 2 \text{M}$ for $[(\text{Nor})\text{RhCl}]_2$ and $[(\text{COD})\text{RhCl}]_2$.

Similarly, we will not attempt to compare the ligand exchange reactions for the systems which involve $(\text{Nor})\text{RhCl}(\text{AsPh}_3)$ and $(\text{COD})\text{IrCl}(\text{AsPh}_3)$, because nothing is known about the equilibrium constants of the pre-equilibria (*e.g.* reactions (7) and (10)).

In subsequent studies we will try to obtain more information about the intimate reaction mechanism of the reactions discussed in this and previous reports and to investigate the dissociation equilibria of the dimer compounds (M_2) alone.

* The existence of five-coordinated intermediates has been well substantiated for reactions of square planar complexes with a d^8 -configuration^{5,6,7}.

** This tendency is larger in CD_2Cl_2 solution (Part VIII, in press).

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