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NUCLEAR MAGNETIC RESONANCE STUDIES IN COORDINATION CHEMISTRY

X*. THE REACTIONS OF (π-METHALLYL)PALLADIUM CHLORIDE CONTAINING VARIOUS PHOSPHINES WITH 1,5-CYCLOOCTADIENE–RHODIUM CHLORIDE DIMER

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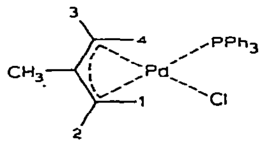
SUMMARY

Movement of the π-methallyl group in (π-methallyl)palladium chloride phosphines can be catalysed by other dimers besides the parent palladium dimer. In the present study this is demonstrated with 1,5-cyclooctadiene–rhodium chloride dimer, for compounds with various phosphine ligands. It was found that the mobility increases as the donor capacity of the ligand decreases, *viz.* $P(C_2H_5)_2(C_6H_5) < P(C_2H_5)(C_6H_5)_2 < P(C_6H_5)_3 < P(C_6H_4Cl)_3$. The *cis–trans* isomerization (also called π-rotation) was taken as the measure of this mobility, since in some cases the π–σ reaction (isomerization of the two protons *cis* to the phosphine via a σ-intermediate) could not be studied because of accidental signal overlap.

INTRODUCTION

In Parts I–IV[1] of this series the reactions taking place in systems of (π-allyl)-palladium chlorides (I) were reported. From the NMR proton signals 1, 2, 3 and 4 of the allyl (or methallyl) group two reactions were distinguished, *viz.* an interchange of protons 3 and 4 in the *cis*-position with respect to the ligand, and an interchange of the *syn*-protons 2 and 3 and simultaneously the *anti*-protons 1 and 4. The interchange of protons 3 and 4 evidently proceeds via a σ-intermediate (II) since the protons 1 and 2 maintain their orientation towards the methyl group. This π–σ reaction was observed in mixtures of the monomer (I) (with tri-n-butylphosphine) and the parent dimer compound (III). At higher temperatures, often after a sharpening of the collapsed



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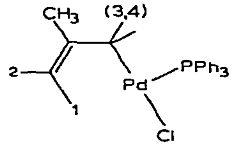

II

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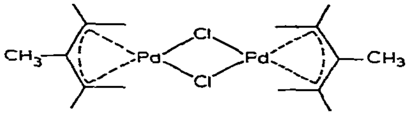
* For part IX see ref. 5.

signal (3, 4), another reaction sets in, which causes a broadening of the signals 1, 2 and (3, 4). This broadening was attributed to a π-rotation reaction, involving a left-right interchange of 1 and 2 with 4 and 3, respectively, similar to the reaction which takes place in systems comprising a monomer with a free ligand. In dimer–monomer mixtures with arsines (Part II) the observed reactions were indeed found to be due to free arsine formed by dissociation of the monomer. With the phosphine systems, however, it was concluded from the concentration dependences that reactions were taking place directly between monomer and dimer. At low temperatures both the π–σ reaction and the π-rotation were found to occur, and no exchange of phosphine between monomer and dimer was observed within the NMR time-scale.



(III)

Nothing is known about the intimate reaction mechanism apart from the concentration dependences, but it seemed plausible that an association of dimer (or dissociated dimer) with monomer takes place via metal–chloride bridges and that during the association the allyl group proceeds with its reaction without phosphine exchange from monomer metal to dimer metal, as can be deduced from the fact that the signals of the dimer do not broaden.

The aim of the present study has been to show the generality of monomer–dimer reactions by taking monomers and dimers with different metal ions. For this purpose $[(COD)RhCl]_2$ was chosen as dimer (COD = 1,5-cyclooctadiene) and various (π-methallyl)palladium chloride phosphine complexes as monomer. The phosphine ligands studied were: $P(C_6H_4Cl)_3$, $P(C_6H_5)_3$, $P(C_2H_5)(C_6H_5)_2$ and $P(C_2H_5)_2(C_6H_5)$, and for some of these, the reactions with the parent palladium dimer, as well as with $[(COD)RhCl]_2$, had to be investigated, in so far as they had not been reported previously (Parts I–IV).

It was assumed that the differences found for the various ligands would provide information about the nature of the rate-determining step of the process and also, in conjunction with the general aspects of monomer–dimer reactions, about the structure of the association intermediate.

EXPERIMENTAL

$[(COD)RhCl]_2$ was prepared from $RhCl_3(H_2O)_3$ and 1,5-cyclooctadiene in ethanol as described by Chatt and Venanzi[2]. $[(\pi\text{-methallyl})PdCl]_2$ was obtained according to the method of Fischer[3]. The monomers were obtained by treating the dimer with the calculated amount of phosphine in chloroform or dichloromethane, the product being separated by addition of pentane.

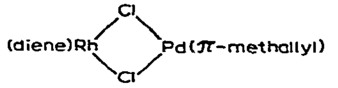
The NMR spectra were recorded on a Varian HA-100 Spectrometer using the Varian Variable Temperature Insert. The components were weighed in a sample tube, after which the necessary volume of solvent was added. CD_2Cl_2 and $CDCl_3$ were used as solvents and tetramethylsilane was employed as internal standard reference. The rates of the reactions were calculated on the basis of measurements in the slow exchange limit.

RESULTS

In a mixture of rhodium dimer and palladium monomer small amounts of rhodium monomer and palladium dimer may form according to the equation:

$$2\,(\pi\text{-methallyl})\text{PdCl(phosphine)} + [(\text{diene})\text{RhCl}]_2 \rightleftarrows [(\pi\text{-methallyl})\text{PdCl}]_2 + 2\,(\text{diene})\text{RhCl(phosphine)} \qquad (1)$$

This equation, it should be emphasized, indicates only the species formed, and does not afford any information about the reaction mechanism, which may, for instance, involve dissociation. A careful study of the NMR spectra of dimer mixtures indicated that mixed dimers of the type:



did not occur, although many other systems do give such complex dimers, as will be reported in a subsequent paper[4]. The equilibrium (1) lies far to the left, but nevertheless the formation of palladium dimer was found to cause many difficulties. In most cases the reactions of palladium monomer with its parent dimer are much faster than the reaction of the palladium monomer with the rhodium dimer. Therefore the reactions caused by palladium dimer had to be taken into account.

As pointed out in the Introduction, two reactions without ligand exchange occur in allyl monomer–dimer systems (*i.e.* the dimer signals do not broaden), *viz.* the π–σ reaction [interchange of protons 3 and 4 (II)] and the left–right interchange or π-rotation. The first reaction that is observed as the temperature is increased is the exchange of protons 3 and 4. This is seen in the broadening of the signals of 3 and 4, but there is no broadening of signals 1 and 2. Subsequently, however, when the π-rotation starts, signals 1 and 2 do broaden, while the broadening of 3 and 4 increases. The final extent of the broadening of 3 and 4 [or the collapsed (3, 4) signal] is found to be a summation of the broadening of proton 1 (or 2) as a result of π-rotation and the

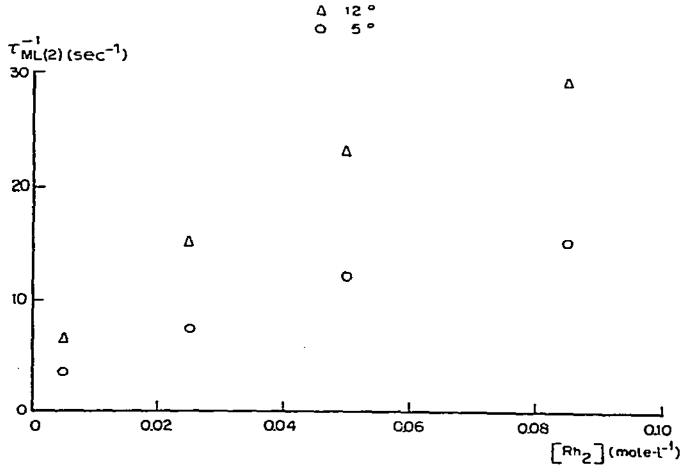


Fig. 1. Dependence of $\tau^{-1}_{ML(2)}$ (π-rotation) on the actual rhodium concentration in $CDCl_3$. ML = (π-methallyl)-$PdCl[P(C_6H_4Cl)_3]$ and [ML] = 0.225 mole·l^{-1}. Temperatures 5 and 12°.

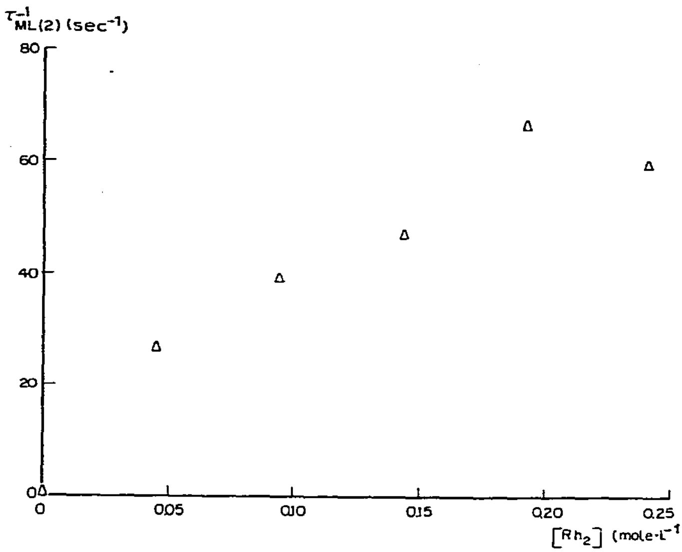


Fig. 2. Dependence of $\tau^{-1}_{ML(2)}$ on the actual rhodium concentration in $CDCl_3$. ML=(π-methallyl)PdCl-[$P(C_6H_5)_3$] and [ML]=0.20 mole·l^{-1}. Temperature 30°.

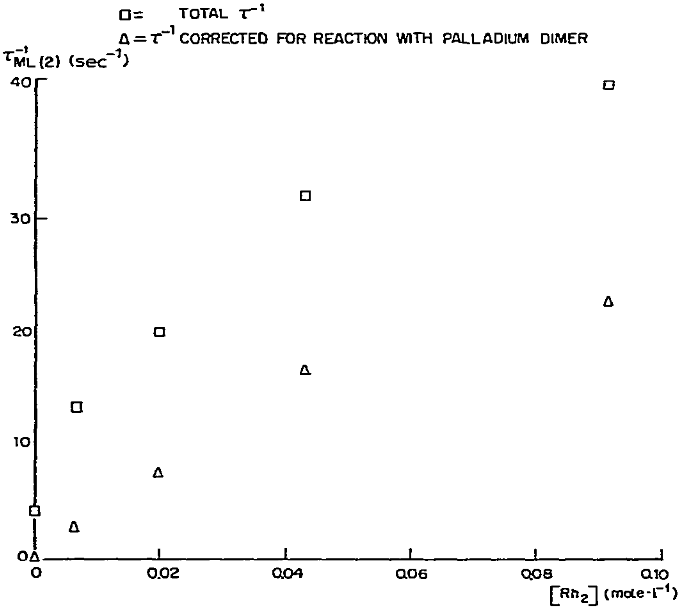


Fig. 3. Dependence of $\tau^{-1}_{ML(2)}$ on the actual rhodium dimer concentration in $CDCl_3$. ML=(π-methallyl)-PdCl[$P(C_2H_5)(C_6H_5)_2$] and [ML]=0.45 mole·l^{-1}. Temperature 50°.

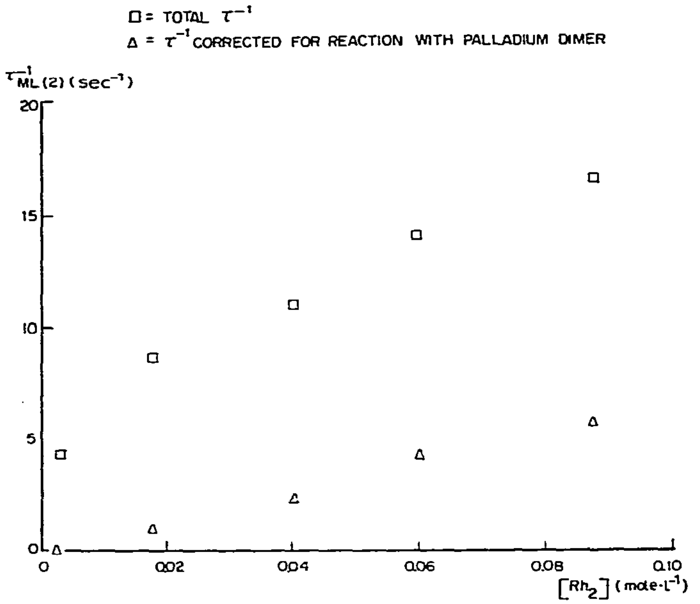


Fig. 4. Dependence of $\tau_{ML(2)}^{-1}$ on the actual rhodium dimer concentration in $CDCl_3$. ML = (π-methallyl)-PdCl[$P(C_2H_5)_2(C_6H_5)$] and [ML] = 0.50 mole·l^{-1}. Temperature 60°.

broadening due to the π–σ reaction (the rate of which can be calculated from the data obtained at the lower temperatures), thus proving that the second reaction is indeed the π-rotation. In this paper we concentrate on the broadening of signal 2, *i.e.* the π-rotation reaction.

In Figs. 1–4 we have plotted the observed rates *vs.* the corrected (*i.e.* actual) rhodium dimer concentrations in $CDCl_3$. It follows from eqn. (1) that the weighed-in amounts are not equal to the actual concentrations. The latter were calculated from equilibrium constants obtained by integration of NMR spectra for solutions of the dimers and monomers. The equilibrium constants for three of the phosphine systems are given in Table 1. Dissociation of the (chlorophenyl)phosphine complex is negligible. The observed π-rotation rates for the (π-methallyl)palladium chloride phosphines must be split into:

(*a*). a reaction due to the traces of palladium dimer formed and
(*b*). the reaction being studied, caused by rhodium dimer.

It was found that the rhodium monomer was not able to bring about a similar

TABLE 1

EQUILIBRIUM CONSTANTS K_1 FOR THE REACTION

$2\,(\pi\text{-}C_4H_7)PdCl(L) + [(COD)RhCl]_2 \rightleftarrows [(\pi\text{-}C_4H_7)PdCl]_2 + 2\,(COD)RhCl(L)$

L	K_1
$P(C_6H_5)_3$	5.5×10^{-5}
$P(C_6H_5)_2(C_2H_5)$	1.6×10^{-4}
$P(C_6H_5)(C_2H_5)_2$	3.8×10^{-4}

reaction in this time and temperature region. The concentrations of palladium dimer were calculated from the eqns.:

$$\frac{[Pd_2]\cdot[RhL]^2}{[PdL]^2\cdot[Rh_2]} = K_1 \tag{2a}$$

$$\left.\begin{aligned}[Rh_2] &= [Rh_2]_{\text{weighed-in}} - [Pd_2]\\ [PdL] &= [PdL]_{\text{weighed-in}} - [RhL]\\ [RhL] &= 2[Pd_2]\end{aligned}\right\} \tag{2b}$$

where M_2 stands for the dimers and ML for the monomers. In addition, reaction rates for these monomers not studied previously with palladium dimer were measured in the region of interest.

From the palladium dimer concentration and the rate of the reaction caused by palladium dimer we calculated the correction needed in the mixtures of palladium monomer and rhodium dimer in order to obtain the rates of the reaction of palladium monomer with rhodium dimer only.

From Figs. 1–4 it will be seen that in the case of the chloro-substituted phenylphosphine (Fig. 1) the correction is negligible and that in the case of triphenylphosphine (Fig. 2) it is very small. Then, however, it increases rapidly and in the case of the diethylphenylphosphine (Fig. 4) it is even larger than the rate due to the rhodium dimer reaction. As may be expected from eqn. (2a, b), the concentrations and hence the rates are also dependent on the weighed-in amounts of the monomer, but for the sake of simplicity, only the dependence on the rhodium dimer is reported.

When similar experiments were carried out in CD_2Cl_2, the same kinetics were found and the rates were usually 1.5–2 times as high as in $CDCl_3$.

DISCUSSION

General features

The first conclusion to be drawn is that the reactions observed[1] in solutions of (π-methallyl)PdCl(phosphine) and [(π-methallyl)PdCl]$_2$ also occur when the latter reactant is replaced by [(COD)RhCl]$_2$. In general the rates with palladium dimer are larger than the rates of reactions with rhodium dimer, and the observations stress the dynamic character of the π-methallyl group in the palladium compounds. Apparently a large number of compounds are able to catalyse the isomerization of the π-methallyl complexes.

The concentration dependences indicate that the dissociated rhodium dimer is the active species, except in the case of (π-methallyl)PdCl[$P(C_2H_5)_2(C_6H_5)$] and rhodium dimer, where a linear dependence on the dimer concentration is found, as was also found for PdL–Pd_2 systems. In this latter case, however, the uncertainty about the rate of the reaction with rhodium dimer is rather large, since the linebroadening observed for the (π-methallyl)palladium monomer is to a large extent due to (admittedly small) amounts of palladium dimer present in the solution.

The influence of the ligand and a possible mechanism

The effect of changes in the phosphines on the charge distribution of the complex is very small. However, it is known that kinetic data are very sensitive to small changes in the molecule[1]. In Fig. 5 are depicted the rates of the π-rotation as caused by rhodium dimer in palladium compounds with various phosphines. It will be seen that the rate (broadening of signal 2) increases considerably as the donor capacity of the ligand decreases. We now discuss a possible mechanism for left–right interchange in reactions with dimers in the light of whether it is consistent with this observed dependence on ligand properties.

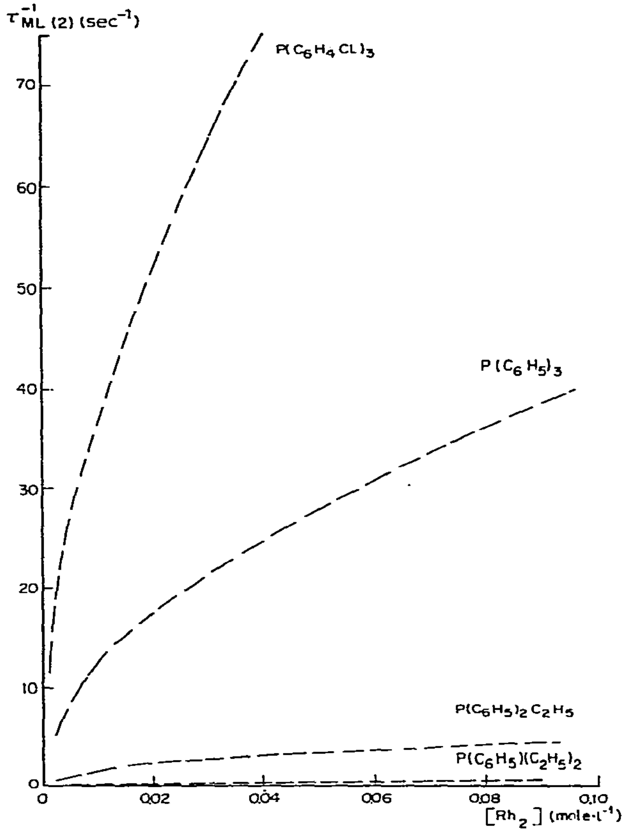


Fig. 5. The influence of the ligand on $\tau_{ML(2)}^{-1}$ at actual Rh_2 concentrations in $CDCl_3$ at 30°.

A mechanism for the interconversion of the *syn*-protons (at sites 1 and 4) and of the *anti*-protons (at sites 2 and 3) via a five-coordinate form with simultaneous exchange of ligand L has been put forward in Part II of this series[1]. The proposed intermediate is shown here in Fig. 6.

A qualitative molecular orbital picture, given in Part I[1], suggests that a rotation of the allyl group with respect to the L–L–Cl plane would take much less energy than a monomolecular *cis–trans* isomerization in a square-planar four-coordinate complex, and hence it was assumed that the *cis–trans* isomerization in mixtures of monomers and dimers also proceeds via a similar intermediate (Part III[1]). To judge by the chemical behaviour, however, both the dimer and dissociated dimer parts are weak acceptors rather than donors. The interactions with dimers therefore cannot be directly compared with the reactions of the group-V donor ligands. In fact the first step

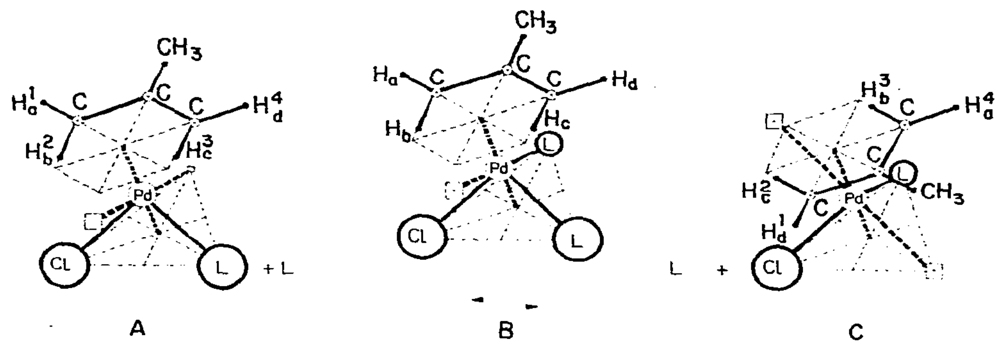
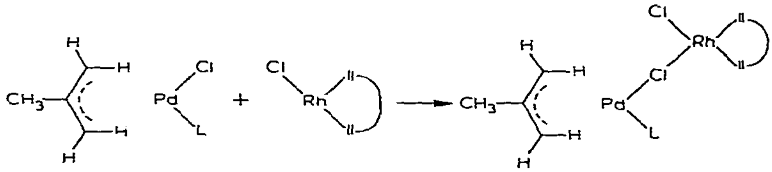


Fig. 6. The five-coordinate form assumed to be involved in the ligand exchange and left–right interchange of the allyl group. Numbers refer to sites, a, b, c and d to protons.

in the (monomer)–(dissociated dimer) reaction is presumably the formation of a single chloro-bridge:



in which the monomer acts as donor and the rhodium ion as acceptor. This is then followed by the formation of a double bridge, which leads to the situation shown in Fig. 7. The equilibrium concentration of this species is very small since no indication of its existence is found in the NMR spectrum (one would expect to observe either the intermediate itself or a change in the chemical shifts of the monomer and dimer upon mixing two solutions containing the respective reagents). This thus suggests that dimerization of (COD)RhCl with (COD)RhCl takes place in preference to association of Pd-monomer with (COD)RhCl, *i.e.* molecules with equal bonding characteristics combine.

But how would the ligand affect the two-step association of Pd–L and (COD)-RhCl? It is assumed that the influence of the substitution of different ligands on the effective charge of the chloride ion is smaller than the influence on the palladium. The formation of the monochloro bridge is therefore expected to be only slightly affected by the substitution. At the same time a decrease in the donor strength of the ligand will give a relatively more positive palladium atom and as a result the association involving a double bridge (Fig. 7) will become more important. Furthermore, the rotation of the allyl group is energetically easier when the three ligands Cl/2, Cl/2 and L are of comparable strength, which, considering that in general L is a stronger ligand than Cl, is most likely to be found when L is weak. In this respect the proposed mechanism seems to accord well with the observed reaction rates (Fig. 5).

In view of the above one might expect a correlation between the observed π-rotation and the rate of chloride-ion exchange ($\mathrm{PdL{-}Rh_2}$), but this is not essential. In the first place the intermediate (Fig. 7) may be asymmetric with respect to the $\mathrm{Pd}\genfrac{}{}{0pt}{}{\diagup\mathrm{Cl}\diagdown}{\diagdown\mathrm{Cl}\diagup}\mathrm{Rh}$ unit; in the second place chloride-ion exchange can also occur via other

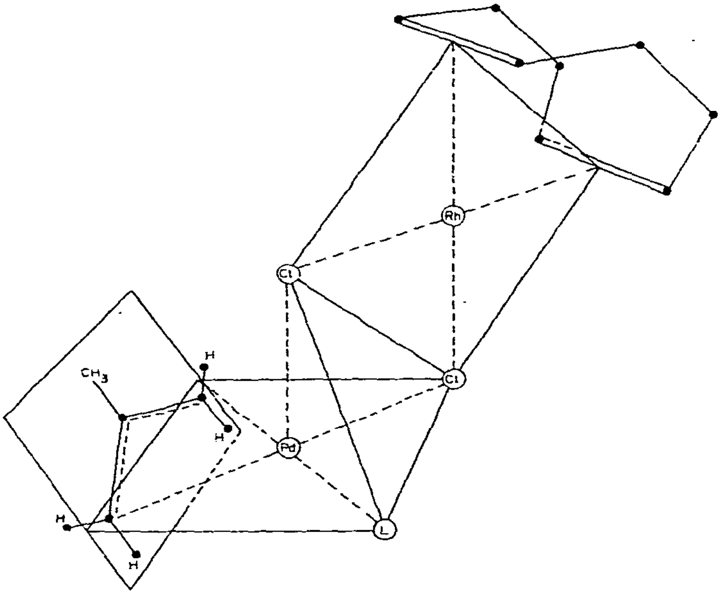


Fig. 7. Proposed intermediate for monomer–dimer association in which a left–right interchange may occur.

reactions that do not lead to π-rotation; and in the third place chloride-ion exchange via the intermediate of Fig. 7 can occur without involving left–right interchange.

Finally, it should be stressed once more that the above discussion only applies to the π-rotation occurring in monomer-dimer solutions and not to the π–σ reaction occurring in the same solutions.

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