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NUCLEAR MAGNETIC RESONANCE STUDIES IN COORDINATION CHEMISTRY
III. KINETIC STUDIES OF REACTIONS OCCURRING IN THE SYSTEM $[(\pi\text{-}C_4H_7)PdCl]_2$ + TRIPHENYLPHOSPHINE

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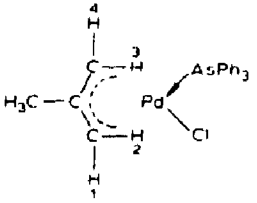
1. INTRODUCTION

In Part I[1] of this series we studied, by means of NMR, the temperature-dependent behaviour of the π-allyl group in systems containing reaction mixtures of the dimeric complex $[(\pi\text{-}C_4H_7)PdCl]_2$ and a ligand L (L = PPh_3, $AsPh_3$, $SbPh_3$ etc.) in $CDCl_3$ in order to obtain information on the influence of the ligands L on the character of the metal–allyl bond. It was found that the allyl group of the monomeric complexes $(\pi\text{-}C_4H_7)PdCl(L)$, which is immediately formed by the reaction of the dimer and the ligand L, can perform movements at the metal atom. One of the movements, which is observed as an interchange of protons between sites 1 and 4 (and hence also between 2 and 3) is a rotation of the π-methallyl group in its own plane, as proposed for the triphenylarsine system[2,3]:



Another movement, by which, on the one hand, protons in sites 1 and 2 and, on the other, protons in sites 3 and 4 become magnetically equivalent, involves the formation of a short-lived σ-allyl intermediate**, as proposed by us[1,4,5] and others[6–12]. This so-called π–σ reaction may be either monomolecular as for $L_2Cl_2Rh(\pi\text{-}C_4H_7)$[4,5], or bimolecular, as in the triphenylarsine system[2,3].

In Part II[3] a detailed quantitative study has been reported of the reactions in the triphenylarsine system. From the rates at which protons in sites 2 and 3 (or in 1 and 4) became magnetically equivalent (rotational movement) it was deduced that when dimer is present three reactions occur: a dissociation of the monomer according to eqn. (1), and the reactions between the dissociated $AsPh_3^*$ and the monomer and the dimer, eqns. (2) and (3) respectively.

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** Information about the σ-allyl intermediate has been obtained, not only from NMR but also from infrared[10] and optical activity measurements[9].

$$(\pi\text{-}C_4H_7)PdCl(AsPh_3^*) \rightleftarrows (\pi\text{-}C_4H_7)PdCl + AsPh_3^*\,, \tag{1}$$

$$(\pi\text{-}C_4H_7)PdCl(AsPh_3) + AsPh_3^* \rightleftarrows (\pi\text{-}C_4H_7)PdCl(AsPh_3^*) + AsPh_3 \tag{2}$$

$$[(\pi\text{-}C_4H_7)PdCl]_2 + 2\,AsPh_3^* \rightleftarrows 2\,(\pi\text{-}C_4H_7)PdCl(AsPh_3^*) \tag{3}$$

When an excess of $AsPh_3$ is used (*i.e.* when no dimer is present), then, when the excess is small, only reaction (2) is observed, while at a larger Ph_3As/Pd ratio a ligand exchange reaction (4) takes place, which proceeds via a short-lived σ-allyl intermediate*:

$$(\pi\text{-}C_4H_7)PdCl(AsPh_3) + AsPh_3 \rightleftarrows (\sigma\text{-}C_4H_7)PdCl(AsPh_3)_2 \tag{4}$$

At a high Ph_3As/Pd ratio (≈ 3), and at very low temperature, reaction (5) becomes noticeable, which involves the formation of an ionic species:

$$(\pi\text{-}C_4H_7)PdCl(AsPh_3) + AsPh_3^* \rightleftarrows [(\pi\text{-}C_4H_7)Pd(AsPh_3)_2]^+Cl^- \tag{5}$$

In this paper we will discuss the kinetic study of the triphenylphosphine system. Although the qualitative temperature dependence of the NMR spectra of the $AsPh_3$ and PPh_3 systems is roughly analogous[1], the kinetics are quite different, which is probably due to the fact that dissociation of the Pd–P bond is very difficult as compared with that of the Pd–As bond.

II. EXPERIMENTAL

The dimer $[(\pi\text{-}C_4H_7)PdCl]_2$ was obtained according to well known methods[13] and recrystallized several times from chloroform. Triphenylphosphine (from commercial sources) was very carefully purified by repeated recrystallizations from ethanol under oxygen-free nitrogen. As the solid phosphorus ligand slowly oxidizes on standing, recrystallization is necessary after a few months.

The NMR spectra were measured with a Varian Spectrometer (DP 60 or HA 100); $CDCl_3$ was used as solvent. Low temperatures were obtained with the Varian variable dewar inserts. TMS (tetramethylsilane) was employed as an internal standard. The solutions were degassed before use, to prevent oxidation of free phosphine, if present.

For each measurement we used the dimer and triphenylphosphine as reaction components. They were weighed in a sample tube and after that the necessary volume of $CDCl_3$ was added.

The rates of exchange for $PPh_3/Pd > 1$ (see Fig. 1 and the kinetic analysis) were calculated in the slow exchange limit[14] from the width of components A and B of doublet 2, and in the fast exchange limit[14] from the width of the collapsed signal (2, 3). For $PPh_3/Pd < 1$ the rates could be calculated for comparatively low temperatures from the width of components A and B of doublet 2, and for higher temperatures from the dimer signals and the methyl signals of monomer and dimer (see Fig. 2). In the case of appreciable overlap of components A and B of doublet 2 the component line width *e.g.* of component A was estimated by using a line shape analysis of two

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* For a discussion of the activation parameters and the molecular mechanism, see refs. 2 and 3.

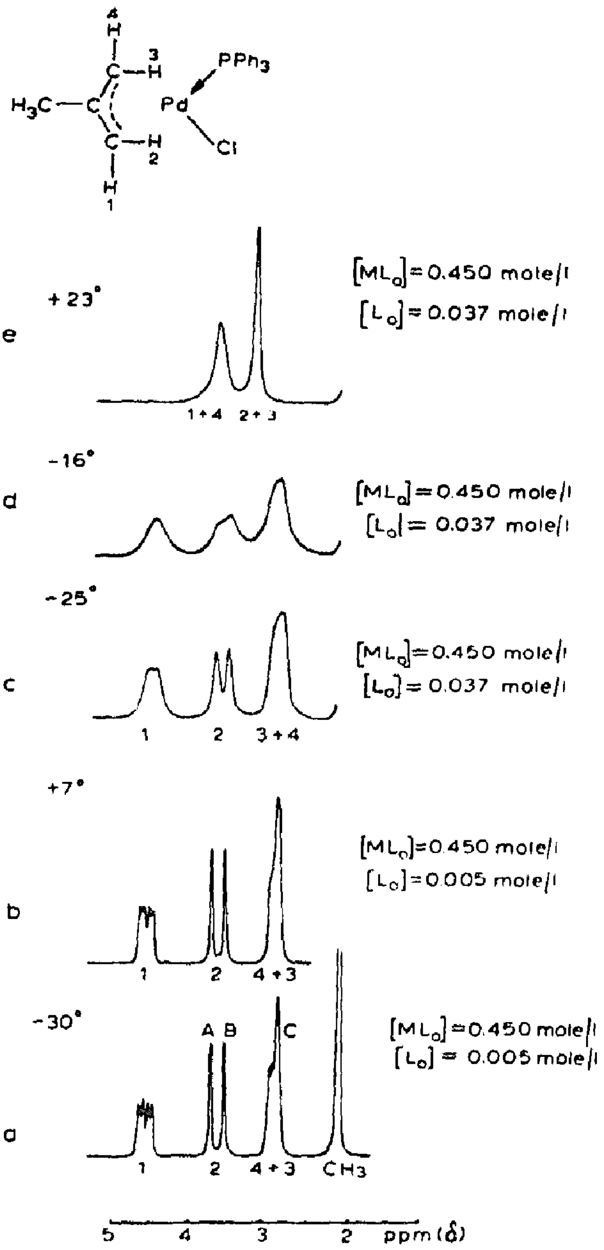

Fig. 1. The temperature dependence of the allylic proton signals of $(\pi\text{-}C_4H_7)PdCl(PPh_3)$ ($\equiv ML_0$) as a function of $[PPh_3]$ ($\equiv [L_0]$) and T. Figs. 1b–1e show the coalescence of protons in sites 1 and 4 and, also, of protons in 2 and 3.

overlapping Lorentz curves, which gave excellent results*.

The conductivities were measured with a Philips Philoscope G.M. 4249 using Pt electrodes. The solvents employed were CH_2Cl_2 and $CHCl_3$.

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* The observed line widths were corrected—with respect to the widths in the absence of exchange—by a value of 1.5 to 2.5 cps, dependent on the temperature.

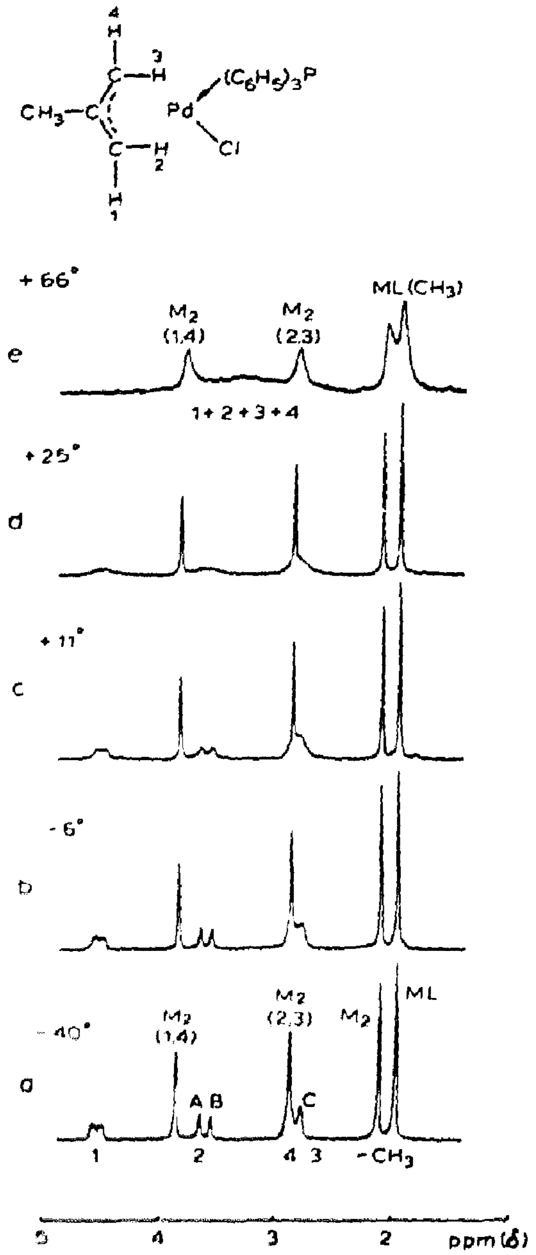


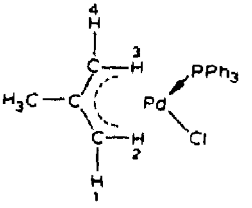
Fig. 2. The temperature dependence of the allylic proton signals of (π-C_4H_7)PdCl(PPh_3) (= ML) and dimer [(π-C_4H_7)PdCl]$_2$ (= M_2) ([ML] = 0.25 mole/l, [M_2] = 0.10 mole/l) in $CDCl_3$ as a function of *T*. Fig. 2b shows the coalescence of signals 3 and 4, Figs. 2c–2d the coalescence of signals 1, 2, 3 and 4 of ML, Fig. 2e the collapse of the CH_3 signals of ML and M_2.

III. KINETIC ANALYSIS

A. $PPh_3/Pd > 1$

In this case no dimer is present in solution. The spectrum of the monomer (π-C_4H_7)PdCl(PPh_3) (at −30°, Fig. 1a) consists of a doublet at 4.50 ppm (δ) (J_{P-1} =

6.8 cps; each component of the doublet shows a small long-range coupling between protons in sites 1 and 4*, $J_{1-4}=2.9$ cps), a doublet at 3.60 ppm ($J_{P-2}=9.8$ cps), a singlet at 2.78 ppm and a doublet at 2.89 ppm ($J_{1-4}=2.9$ cps), which have been assigned to protons in sites 1, 2, 3 and 4 respectively (Fig. 1a). The CH_3 signal occurs at 1.96 ppm from TMS.



At temperatures between −25 and +23°, with a small excess of PPh_3 (Figures 1b–e), a phosphine exchange reaction is observed, which results in the coalescence of absorptions 2 and 3 on the one hand, and of 1 and 4 on the other, to two signals (1, 4) and (2, 3) at 3.19 and 3.66 ppm respectively, *i.e.* at the weighted means of the original peaks. It is important to note that the P-coupling has disappeared, which is an indication of phosphine exchange.

It was found that the easiest way to study this interchange between 1 and 4 and between 2 and 3 is by measuring the width of components A and B of doublet 2 (at 3.62 ppm) in the slow exchange case, and the width of the collapsed signal (2, 3) (Fig. 1e) at 3.19 ppm in the fast exchange limit. Assigning to the two components of doublet 2 and to singlet 3 the symbols A, B and C respectively (Fig. 1a), the protons in, for example, A may jump to B (spin reversal of P nucleus of spin $\frac{1}{2}$) or to C (interchange between 2 and 3). This is a three-site problem, which deserves special attention because it may give rise to complications in the interpretation of the spectra. In Appendix I the correct treatment for the most general case is given. This complete analysis leads to the conclusion that two constants occur in the relation between the experimental quantity $\Delta\nu_{\frac{1}{2}}$ ex(line width) and the rate values $1/\tau$, namely:

in the slow exchange limit:	in the fast exchange limit:
$\Delta\nu_{\frac{1}{2}}\text{ex}(A)^{**} = P/\tau$	$\Delta\nu_{\frac{1}{2}}\text{ex}(2,3)^{**} = R\tau$

The constants P and R are fairly complicated functions of two parameters, a/z and b/z (see Appendix I). The parameter a/z represents the fraction of the total number of events which gives rise to spin reversal due to phosphine exchange without rotation of the π-allyl group in its own plane. The parameter b/z represents the fraction of events which is accompanied by a rotation of the π-allyl group in its own plane. Both parameters a/z and b/z depend on the reaction mechanism involved.

At this stage a precise mechanism is not known, so that conclusions about velocities cannot be drawn immediately. The order of the ligand exchange reaction, however, can be obtained as usual from the log $\Delta\nu_{\frac{1}{2}}$ex *versus* $1/T$ plots as a function of the concentrations, since P and R are only proportionality constants. After the

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* The long-range coupling was observed independently also by Ramey and Statton[8]. This coupling disappears at higher reaction rates.

** $\Delta\nu_{\frac{1}{2}}$ex(A) and $\Delta\nu_{\frac{1}{2}}$ex(2, 3) are the contributions to the line widths of signal (A) (in the slow exchange) and of the collapsed signal (2, 3) (fast exchange) due to exchange.

determination of the reaction order a reasonable reaction mechanism can be adopted; next, values of a/z and b/z can be calculated and, finally, the $1/\tau$ values (see Appendix I and discussion).

B. $PPh_3/Pd < 1$

If, besides monomer (π-C_4H_7)PdCl(PPh_3) (=ML) also dimer [(π-C_4H_7)-PdCl]$_2$ (=M_2) is present in $CDCl_3$, the NMR spectrum consists of the monomer signals of protons in sites 1, 2, 3 and 4 (see section A) and of the dimer signals (1, 4) at 3.85 ppm and (2, 3) at 2.86 ppm (δ). At higher field the methyl signals of monomer and dimer appear at 1.96 and 2.12 ppm respectively (Fig. 2a) (at −40°).

At higher temperatures the signals 3 and 4 coalesce to one peak at 2.84 ppm, while no perceptible broadening is observed on the doublets of 1 and 2 of ML. The reaction rate for this process cannot be determined because of the closeness of the signals 3 and 4. It seems very likely, however, that the rate will increase with increasing dimer concentration, as also found for other phosphines such as P(n-C_4H_9)$_3$ and PEt_2Ph[17] etc. Neither the dimer signals nor the monomer CH_3 signal broaden in this temperature region.

Between −20 and +25° the ML signals 1 and 2 also broaden and finally coalesce with 3 and 4 to one broad band. Again, neither the dimer signals nor the CH_3 signals of ML and M_2 change in line width (Fig. 2b–2d). Thus up to +25° there is no exchange of M or L between M_2 and ML.

The Bloch equations including exchange for sites A, B and C of ML become, when $\tau_{AB}^{-1} = \tau_{BA}^{-1} = 0$ (since there is no PPh_3 exchange):

$$\frac{d}{dt} G_A + \alpha_A \cdot G_A = -i \cdot \gamma \cdot H_1 \cdot M_0 \cdot p_A - \tau_{AC}^{-1} \cdot G_A \qquad + \tau_{CA}^{-1} \cdot G_C$$

$$\frac{d}{dt} G_B + \alpha_B \cdot G_B = -i \cdot \gamma \cdot H_1 \cdot M_0 \cdot p_B \qquad - \tau_{BC}^{-1} \cdot G_B \qquad + \tau_{CB}^{-1} \cdot G_C$$

$$\frac{d}{dt} G_C + \alpha_C \cdot G_C = -i \cdot \gamma \cdot H_1 \cdot M_0 \cdot p_C + \tau_{AC}^{-1} \cdot G_A + \tau_{BC}^{-1} \cdot G_B - (\tau_{CA}^{-1} + \tau_{CB}^{-1}) \cdot G_C$$

In the slow passage approximation we find for the slow exchange case:

$$1/T_2(A) = 1/T_2^*(A) + \tau_{AC}^{-1}$$

$$1/T_2(B) = 1/T_2^*(B) + \tau_{BC}^{-1}$$

$$1/T_2(C) = 1/T_2^*(C) + \tau_C^{-1}$$

As $\tau_{AC}^{-1} + \tau_{BC}^{-1} = \tau_{CA}^{-1} + \tau_{CB}^{-1} = \tau_C^{-1}$, the rates are $\tau_{AC}^{-1} = \tau_{BC}^{-1} = \frac{1}{2}\tau_C^{-1}$ and $\tau_{AC}^{-1} = \pi \cdot \Delta\nu_{\frac{1}{2}}\text{ex}$ (A or B).

Between +25 and +80° all the dimer signals broaden, and so does the CH_3 signal of the monomer (Fig. 2e). In this case there is a chemical exchange between M_2 and ML. The rates can be calculated from the CH_3 peak of ML (at 1.96 ppm) and either the dimer signals (2, 3) or (1, 4), or the CH_3 peak.

In the slow exchange limit the width of the methyl peak is:

$$1/T_2(CH_3)_{ML} = 1/T_2^*(CH_3)_{ML} + \tau^{-1}(CH_3)_{ML}$$

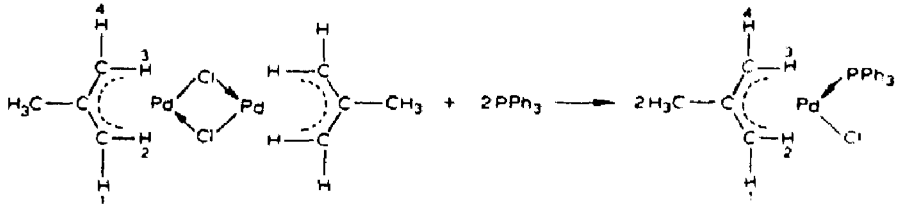
while for the dimer:

$$1/T_2(\mathrm{CH_3})_{\mathrm{M_2}} = 1/T_2^*(\mathrm{CH_3})_{\mathrm{M_2}} + \tau^{-1}(\mathrm{CH_3})_{\mathrm{M_2}}$$

The monomer signals 1, 2, 3 and 4 coalesce to one very broad flat band and this band cannot therefore be used for the measurement of rates (Fig. 2e) in this temperature region.

IV. RESULTS

Addition of PPh_3 to the dimer $[(\pi\text{-}C_4H_7)PdCl]_2$ yields $(\pi\text{-}C_4H_7)PdCl(PPh_3)$:



If more than two moles of PPh_3 are added, the presence of an ionic species $[(\pi\text{-}C_4H_7)Pd(PPh_3)_2]^+Cl^-$ becomes noticeable, as originally observed by Shaw and co-workers[18] from conductivity measurements on aqueous acetone solutions. The ionic species is formed by the slow reaction:

$$(\pi\text{-}C_4H_7)PdCl(PPh_3) + PPh_3 \leftrightarrows [(\pi\text{-}C_4H_7)Pd(PPh_3)_2]^+Cl^-$$

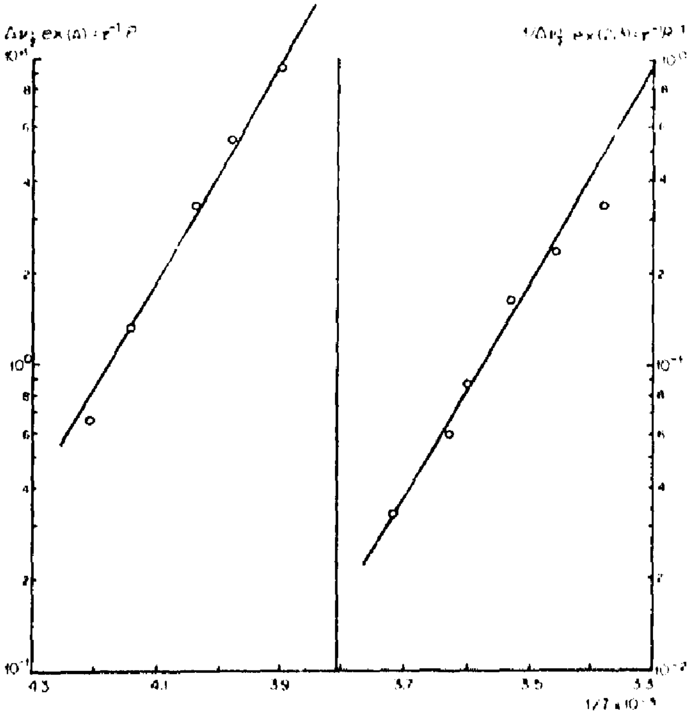


Fig. 3. The temperature dependence of log $\Delta\nu_{\frac{1}{2}}$ex(A) and of log $1/\Delta\nu_{\frac{1}{2}}$ex(2, 3) for $[ML_0] = 0.45$ mole/l and $[L_0] = 0.021$ mole/l.

This equilibrium, which for the $AsPh_3$ case lies far on the left and has no appreciable influence on the kinetics[2,3], is here very important.

In the following sections we will discuss various reactions involving the monomer $(\pi\text{-}C_4H_7)PdCl(PPh_3)$ (=ML), ionic species $[(\pi\text{-}C_4H_7)Pd(PPh_3)_2]^+Cl^-$ ($=ML_2^+Cl^-$), dimer $[(\pi\text{-}C_4H_7)PdCl]_2$ ($=M_2$) and PPh_3 (=L), for $PPh_3/Pd > 1$ and $PPh_3/Pd < 1$ respectively.

A. $PPh_3/Pd > 1$

1. *$1 < PPh_3/Pd < 1.1$ and temperatures between −30 and +20°.* Between −30 and +20° the absorptions 1 and 4 and, also, 2 and 3 coalesce to the weighted mean of the original peaks with the simultaneous disappearance of the P-coupling (Fig. 1b–1e). In Fig. 3 are shown the values of $\log \Delta\nu_{\frac{1}{2}}\mathrm{ex}(A)$ for the slow exchange case and of $\log[1/\Delta\nu_{\frac{1}{2}}\mathrm{ex}(2,3)]$ for the fast exchange case as a function of $1/T$ for one concentration of $[ML_0]$ and $[L_0]$*. To obtain the order of the reaction the values of $[ML_0]$ were varied between 0.20 and 0.50 mole/l, while $[L_0]$ was varied between 0.005 and 0.050 mole/l**. Fig. 4 shows (from the fast exchange regions of the experiments), that $1/\Delta\nu_{\frac{1}{2}}\mathrm{ex}$ (2, 3) is second-order in $[L_0]$ for $[ML_0]$ is constant. If $[L_0]$ is kept constant, however, $1/\Delta\nu_{\frac{1}{2}}\mathrm{ex}(2,3)$ decreases with increasing $[ML_0]$ (Fig. 5)***.

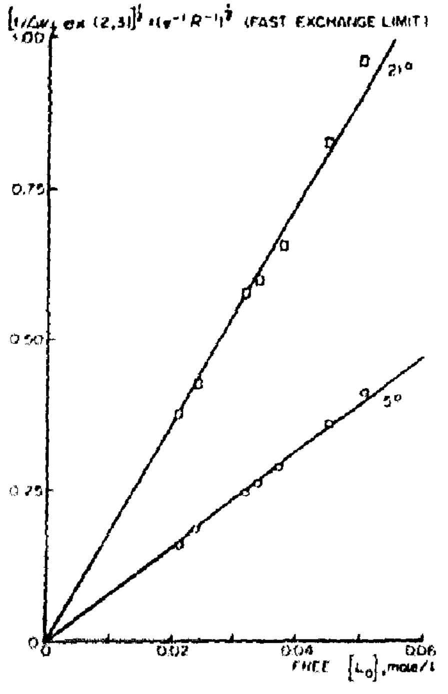


Fig. 4. The dependence of $[1/\Delta\nu_{\frac{1}{2}}\mathrm{ex}(2,3)]^{\frac{1}{2}}$ on $[L_0]$ for $[ML_0] = 0.45$ mole/l.

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* Starting concentrations of ML and L, *i.e.* the weighed-in amounts.

** At higher concentrations of L_0 the reaction is too fast to be followed by NMR.

*** The same dependences are obtained from the slow exchange limit region.

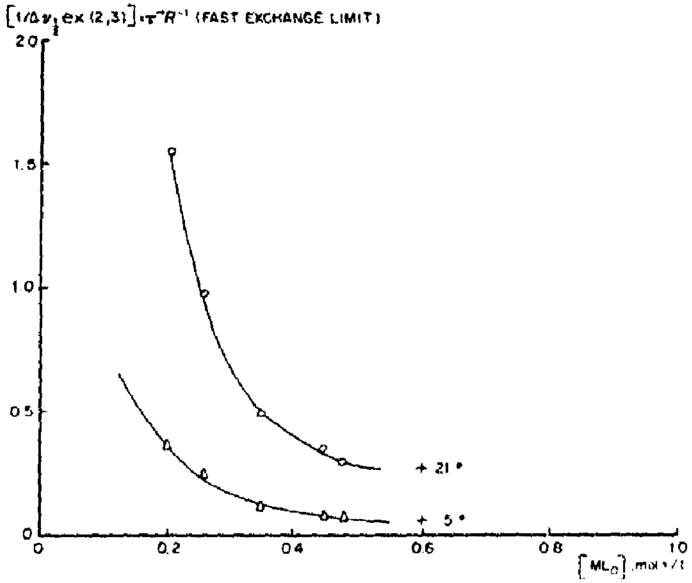

Fig. 5. The dependence of $[1/\Delta\nu_{\frac{1}{2}}\mathrm{ex}(2,3)]$ on $[ML_0]$ for $[L_0] = 0.0375$ mole/l.

The concentration dependences can be understood if we include the reaction*:

$$ML + L \leftrightarrows ML_2^+ + Cl^-$$

besides a bimolecular ligand exchange reaction:

$$ML + L^* \leftrightarrows ML^* + L$$

We can combine these two reactions into the following reaction scheme:

$$\begin{tikzcd}
ML + L^* \arrow[r, shift left, leftarrow, "k_{-1a}"] \arrow[r, shift right, "k_{1a}"'] & ML_2 \arrow[r, shift left, "k_{1a}"] \arrow[r, shift right, leftarrow, "k_{-1a}"'] \arrow[d, shift right, "k_{1b}"'] & ML^* + L \\
& ML_2^+ + Cl^- \arrow[u, shift right] &
\end{tikzcd}$$

We further assume that the ionic species is formed from a short-lived intermediate species $(\pi\text{-}C_4H_7)PdCl(PPh_3)_2$, in which the Pd is five-coordinate, via the side reaction (1b). It was observed by Shaw and Powell** and by us that $k_{1b} \lll k_{1a}\cdot[L]$, the time needed for (1b) to reach equilibrium being 15–30 minutes***.

If, moreover, $k_{-1a} \gg k_{1a}\cdot[L]$, the reaction rate becomes:

$$1/\tau(ML) \cong k_{1a}\cdot[L]$$

The equilibrium concentration of L will be determined by the equilibrium constant:

$$K = \frac{[ML_2^+]\cdot[Cl^-]}{[ML]\cdot[L]} = \frac{([L_0]-[L])^2}{([ML_0]-[L_0]+[L])\cdot[L]}$$

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* If no ionic species were formed, $1/\Delta\nu_{\frac{1}{2}}\mathrm{ex}(2,3)$ or $\Delta\nu_{\frac{1}{2}}\mathrm{ex}(A)$ would be independent of $[ML_0]$ for $[L_0]$ is constant.

** B. L. Shaw and J. Powell, private communication.

*** In each measurement we waited 30 minutes to be certain to work under conditions of equilibrium.

where the starting concentrations of ML (= $[\mathrm{ML}_0]$) and of [L] (= $[\mathrm{L}_0]$) are:

$$[\mathrm{ML}_0] = [\mathrm{ML}] + [\mathrm{ML}_2^+] = [\mathrm{ML}] + [\mathrm{L}_0] - [\mathrm{L}] \quad \text{and}$$

$$[\mathrm{L}_0] \quad = [\mathrm{L}] + [\mathrm{ML}_2^+]$$

It was deduced from conductance measurements (see next section) that between −30 and +20° the constant K varies roughly between 2 and 0.5. It can be shown by solving the above equation of K for [L] that for K between about 0.1 and 10, and for $[\mathrm{ML}_0]$ and $[\mathrm{L}_0]$ between 0.1 and 0.5 mole/l and between 0.01 and 0.06 mole/l respectively, the equilibrium concentration of L can be approximated to*:

$$[\mathrm{L}] = \frac{[\mathrm{L}_0]^2}{K\cdot[\mathrm{ML}_0]}$$

The rate $1/\tau(\mathrm{ML})$ becomes:

$$1/\tau(\mathrm{ML}) = k_{1a}\cdot[\mathrm{L}] = k_{1a}\cdot[\mathrm{L}_0]^2/K\cdot[\mathrm{ML}_0]$$

If $[\mathrm{ML}_0]$ is kept constant, then $1/\tau(\mathrm{ML})$ and, hence, $1/\Delta\nu_{\frac{1}{2}}\mathrm{ex}(2,3)$ [or $\Delta\nu_{\frac{1}{2}}\mathrm{ex}(\mathrm{A})$] also, are proportional to $[\mathrm{L}_0]^2$ (Fig. 4). For $[\mathrm{L}_0]$ is constant, $1/\tau(\mathrm{ML})$ and, hence, $1/\Delta\nu_{\frac{1}{2}}\mathrm{ex}(2,3)$ also, are proportional to $1/[\mathrm{ML}_0]$ (Fig. 5). The reverse of $1/\tau(\mathrm{ML})$ is:

$$\tau^{+1}(\mathrm{ML}) = K\cdot[\mathrm{ML}_0]/k_{1a}\cdot[\mathrm{L}_0]^2$$

In Fig. 6 is shown the dependence of $\Delta\nu_{\frac{1}{2}}\mathrm{ex}(2,3)$ on $[\mathrm{ML}_0]$ for $[\mathrm{L}_0]$ is constant. The line in Fig. 6 does not pass through zero, which is probably due to the inaccuracy in

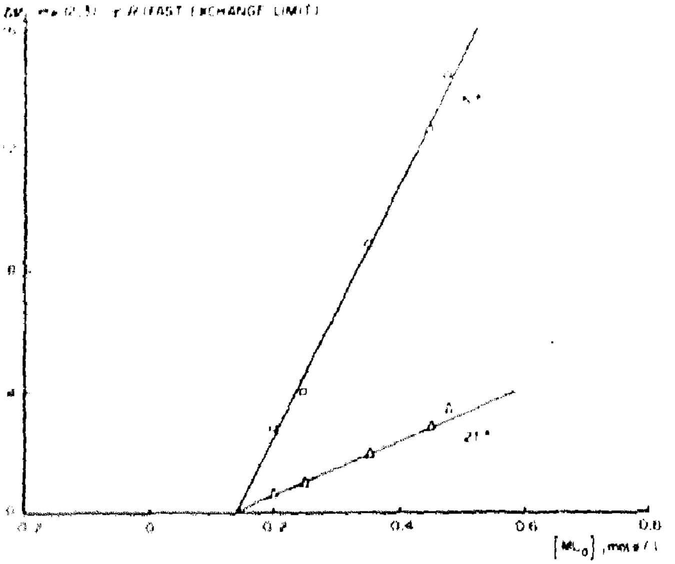

Fig. 6. The dependence of $[\Delta\nu_{\frac{1}{2}}\mathrm{ex}(2,3)]$ on $[\mathrm{ML}_0]$ for $[\mathrm{L}_0] = 0.0375$ mole/l.

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* This was checked by numerical calculations using the non-approximated formula for [L], and substituting various values for K, $[\mathrm{ML}_0]$ and $[\mathrm{L}_0]$.

the rate measurements for small concentrations of $[\mathrm{ML_0}]$ and in the estimation of the natural linewidths (*i.e.* the linewidth in the absence of exchange).

2. *$PPh_3/Pd > 1$ and temperatures between −100 and +40°.* The presence of ionic species $\mathrm{ML_2^+Cl^-}$, which cannot be observed for very low concentrations of free $\mathrm{PPh_3}$, begins to become noticeable at high L/Pd ratios as a single absorption at 3.68 ppm (at about the shift of doublet 2) besides the signals of ML already present. The absorptions of the *syn*-protons and *anti*-protons 1, 2, 3 and 4 of $\mathrm{ML_2^+Cl^-}$ appear even at −80° as one signal, which is due to a fast exchange reaction of $\mathrm{ML_2^+Cl^-}$ with L (π–σ reaction)*:

$$\mathrm{ML_2^+Cl^-} + \mathrm{L} \underset{k_{1c}}{\overset{k_{1c}}{\rightleftharpoons}} \mathrm{ML_2^+Cl^-} + \mathrm{L} \quad \text{(via a } \sigma\text{-allyl intermediate)}$$

With increasing $\mathrm{PPh_3/Pd}$ ratio (≈ 2) the four absorptions of 1, 2, 3 and 4 of ML also coalesce to one signal at 3.43 ppm, which is the weighted mean; the ionic species $\mathrm{ML_2^+Cl^-}$ is still visible separately (at 20°) as one signal at 3.68 ppm, which grows in intensity with increasing $\mathrm{PPh_3/Pd}$ ratio. At higher temperatures the two signals coalesce and the collapsed signal moves to higher field, up to 3.43 ppm. It is clear that the equilibrium:

$$\mathrm{ML} + \mathrm{L} \rightleftharpoons \mathrm{ML_2^+} + \mathrm{Cl^-}$$

moves to the right with decreasing temperature and increasing L/Pd ratio.

These conclusions, reached on the basis of NMR data, were fully confirmed by conductivity measurements in $\mathrm{CH_2Cl_2}$, which is sufficiently close to $\mathrm{CDCl_3}$ in properties to permit comparison. Conductivities of mixtures of ML and L in the ratios 2 to 3 as a function of temperature (Fig. 7) showed that the amount of ionic species increases with increasing $\mathrm{PPh_3/Pd}$ ratio and decreasing temperature. In Fig. 7 these conductivity curves are compared with the temperature-dependent conductivity curve of a well-defined uni-univalent electrolyte, *viz.* $[\mathrm{(DP)_2Rh}]^+\mathrm{Cl^-}$ [DP = 1,2-bis(diphenylphosphino)ethane].

From this comparison we can estimate the concentrations of $\mathrm{ML_2^+Cl^-}$ at each temperature. Thus we can calculate the equilibrium constant $K = [\mathrm{ML_2^+}]\cdot[\mathrm{Cl^-}]/[\mathrm{ML}]\cdot[\mathrm{L}]$.

The equilibrium constant K is roughly 2.0 to 0.5 in the temperature region of −30 to +20°.

Though these values are, naturally, not very accurate, they are nevertheless important, as we now know the influence of the above equilibrium reaction on the equilibrium concentration of [L] provided that the conclusions drawn for $\mathrm{CH_2Cl_2}$ as solvent also hold for $\mathrm{CDCl_3}$, in which we measure the kinetics.

3. *$PPh_3/Pd > 1$ and temperatures higher than +40°.* A reaction between ML and L which involves the formation of a σ-methallyl intermediate complex is observed

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* In this connection it is of interest to mention that also in the case of $\mathrm{PPh_2Me}$, for $1 < \mathrm{PPh_2Me/Pd} < 2$ the allylic protons 1, 2, 3 and 4 of $[(\pi\text{-}\mathrm{C_4H_7})\mathrm{Pd(PPh_2Me)_2}]^+\mathrm{Cl^-}$ absorb at one magnetic field; on the signal no P-splitting is present[17]. In contrast, we found that phosphines with more alkyl substituents [*e.g.* $\mathrm{P(n\text{-}C_4H_9)_3}$, $\mathrm{PPhEt_2}$, $\mathrm{PPhMe_2}$] give two signals: one single peak for protons in site (1, 4) and one triplet for (2, 3) (due to coupling with two equivalent P-nuclei). NMR measured as a function of L/Pd indicated that the three latter compounds are more stable both thermodynamically and kinetically (*i.e.* with respect to $\mathrm{PPh_3}$ exchange).

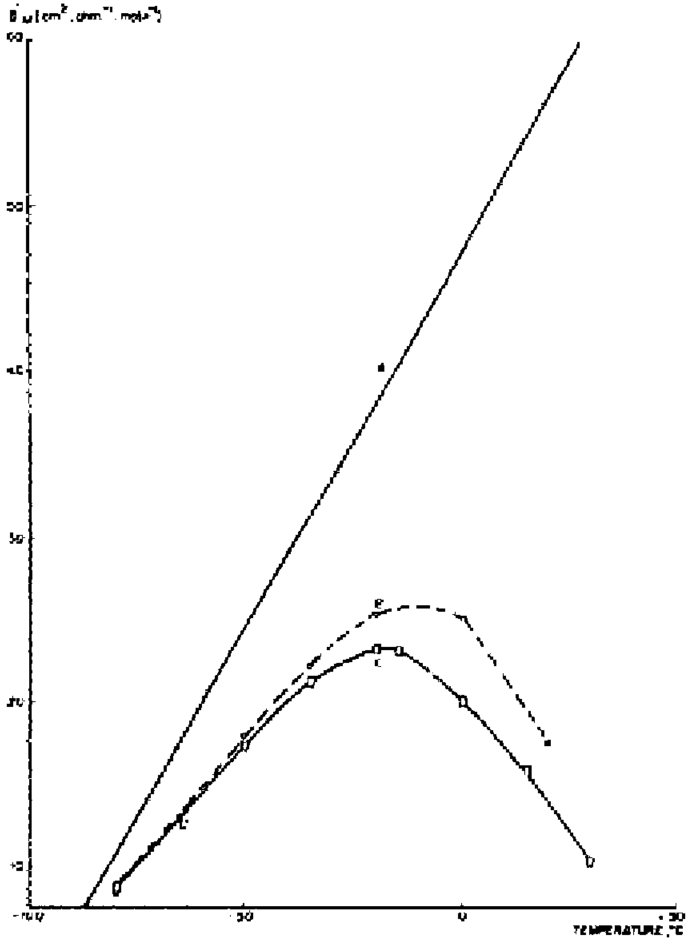

Fig. 7. The conductivities as a function of the temperature for: A. $[(Ph_2PCH_2CH_2PPh_2)_2Rh]^+Cl^-$; B. A mixture of ML and L so that L/Pd = 3; C. A mixture of ML and L so that L/Pd = 2.

as the collapse of the four signals 1, 2, 3 and 4 of ML. We have not measured this reaction because of overlap of bands. Cotton and co-workers[10], who studied this process with infrared as well, found for large PPh_3/Pd ratios absorptions at stretching frequencies, which are typical for C=C bonds, indicating σ-allyl-bonded groups in the intermediate of the reaction.

B. $PPh_3/Pd \leq 1$

1. *Temperatures below −20°.* There is only a collapse of signals 3 and 4 of ML. This process could not be studied for the PPh_3 case because of the small chemical shift difference (Fig. 2). The rate of this π–σ reaction, however, was found to be first-order in the dimer concentration $[M_2]$ for $L = P(n\text{-}C_4H_9)_3$[17].

2. *Temperatures between −20 and +20°.* The absorptions of protons in sites 1 and 2 of ML also broaden, but the dimer signals and the CH_3 signals of ML and M_2 do not (Fig. 2b–2d). The exact nature of the movements of the methallyl group of ML is not known in this case. However, as we observed, a collapse to one broad band of the

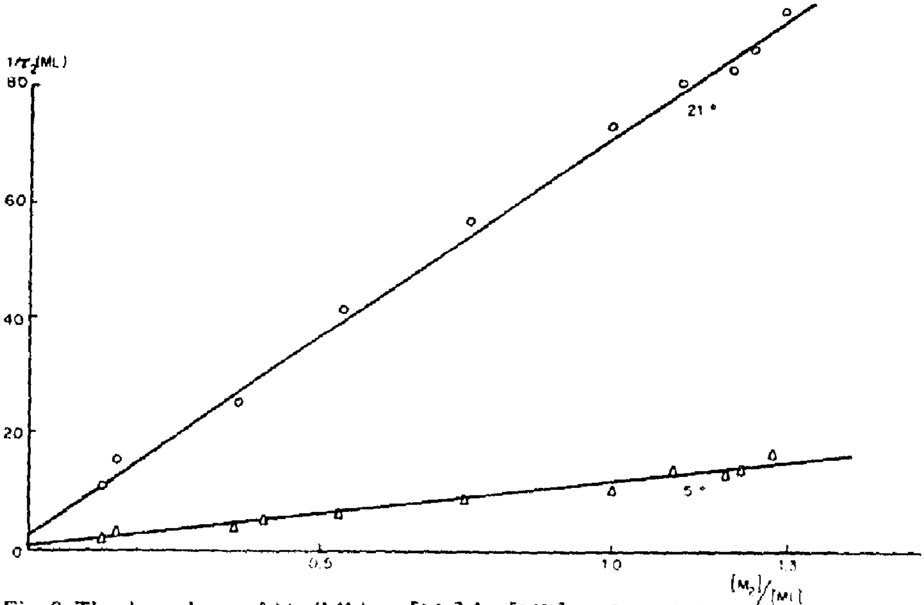

Fig. 8. The dependence of $1/\tau_2(ML)$ on $[M_2]$ for $[ML] = 0.20$ mole/l.

signals 1, 2, 3 and 4, the movements very likely are a combination of a π–σ reaction and a rotational type of movement of the allyl group in its own plane.

From a concentration dependence study it was found that the rate of intramolecular exchange of the allyl group of ML, as measured on doublet 2 in the slow exchange limit, is proportional to $[M_2]$ ($[ML]$ = constant) and independent of $[ML]$* ($[M_2]$ = constant) (see Figs. 8 and 9). The dimer species is thus involved in a reaction with ML, but after the "association" the dimer is "formed" back without exchange of M or L having taken place.

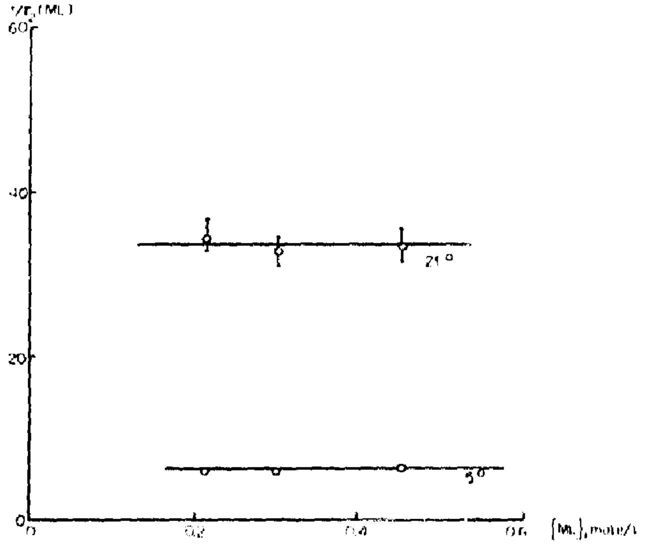

Fig. 9. The dependence of $1/\tau_2(ML)$ on $[ML]$ for $[M_2] = 0.075$ mole/l.

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* The starting concentrations $[M_2]_0$ and $[ML]_0$ are equal to the equilibrium concentrations $[M_2]$ and $[ML]$ respectively.

The rates are:

$1/\tau_{2,3}(M_2) = 0$

$1/\tau_2(ML) = k \cdot [M_2] \qquad k \approx 10^{15} e^{-17500/R \cdot T}\ \text{l} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$

A possible reaction model is:

$$M_2 \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} M//M$$

$$M//M + M^*L \underset{k_2}{\rightleftarrows} M//M + M^*L$$

In this case, when assuming the pre-equilibrium to rationalize the high frequency factor of k, the rates are (see Appendix):

$1/\tau_2(ML) \ = k_2 \cdot K_1 \cdot [M_2] = k \cdot [M_2]$

$1/\tau_{2,3}(M_2) = 0$ (as no chemical exchange occurs)

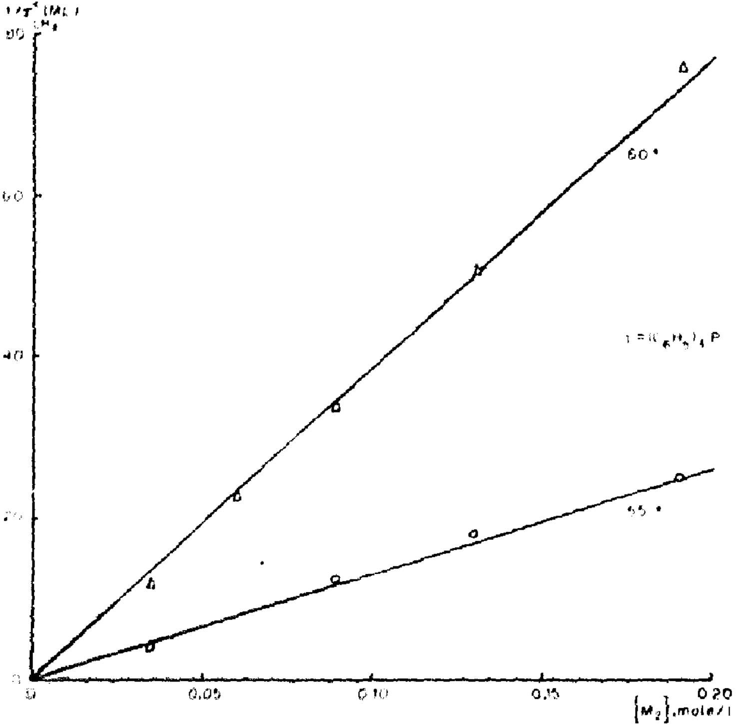

Fig. 10. The dependence of $1/\tau^2(CH_3)_{ML}$ on $[M_2]$ for $[ML] = 0.20$ mole/l.

provided that $k_{-1} \gg k_2 \cdot [ML]$ and $k_{+1} \ll k_{-1}$.

The species M//M may be a dimer with one chloride bridge broken, or a so-called "solvent-caged monomer"*.

3. *Temperatures between +20 and +80°.* In this temperature region the dimer

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* Solvent-caged monomers have been proposed for $Al_2(CH_3)_6$ in kinetic studies, using NMR, of CH_3 group exchanges by Williams and Brown[19].

signals broaden and so do the CH_3 signals of M_2 and ML, owing to a chemical exchange of M (or L) between M_2 and ML (Fig. 2e).

Rate studies showed that:

$$1/\tau(CH_3)_{ML} = k'\cdot[M_2]^{\frac{1}{2}}\,* \quad \text{(Fig. 10)}$$

$$1/\tau(CH_3)_{M_2} = k''\cdot[ML]/[M_2]^{\frac{1}{2}} \quad \text{(Fig. 11 and 12)}$$

$$k' \approx k'' \approx 10^{14}\,e^{-20500/R\cdot T}\ l^{\frac{1}{2}}\cdot mole^{-\frac{1}{2}}\cdot sec^{-1}$$

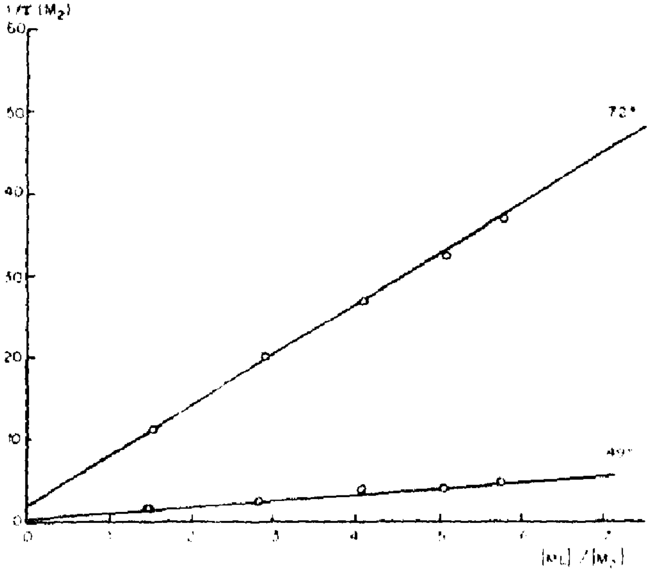

Fig. 11. The dependence of $1/\tau(M_2)$ on [ML] for $[M_2] = 0.075$ mole/l.

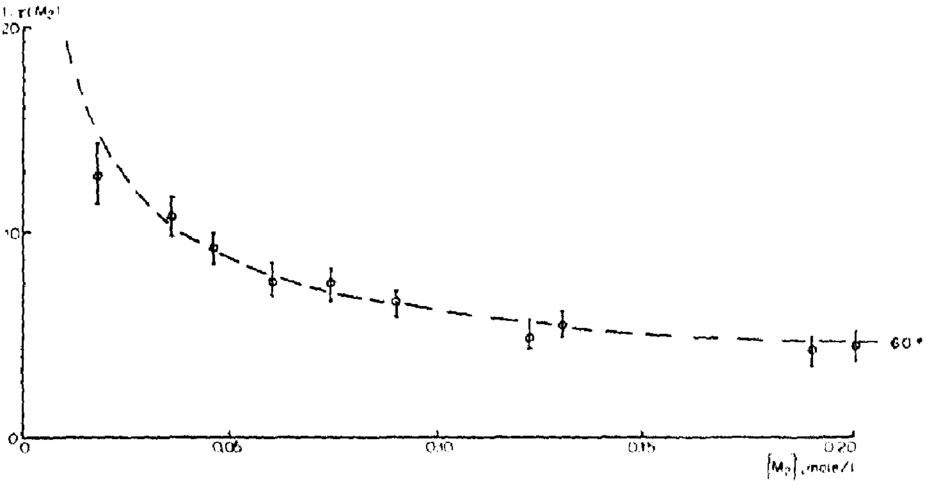

Fig. 12. The dependence of $1/\tau(M_2)$ on $[M_2]$ for $[ML] = 0.20$ mole/l. The broken line has been calculated on the basis of the $1/\tau(M_2) \sim [M_2]^{-\frac{1}{2}}$ dependence.

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* $1/\tau(CH_3)_{ML}$ is independent of [ML], as was shown by measurements for $[M_2] = 0.10$ mole/l, while [ML] was varied between 0.14 and 0.40 mole/l.

These concentration dependences can be rationalized, consistently with the reaction model in the previous section, if it is assumed that the species M//M dissociates into a small amount of two monomer species M. The reaction model is:

$$M_2 \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} M//M \underset{k_3}{\overset{k_{-3}}{\rightleftharpoons}} 2\,M^*$$

$$M^* + ML \underset{k_4}{\rightleftharpoons} M + M^*L$$

Provided that $k_{-3}\cdot[M^*] \gg k_{+4}\cdot[ML]$ and $k_{-1}\cdot k_{-3}\cdot[M^*] \gg k_{+1}\cdot(k_{-3}\cdot[M^*]+k_{+3})$, the rates are (see Appendix II):

$$1/\tau(CH_3)_{ML} = k_4\cdot(K_1\cdot K_3)^{\frac{1}{2}}\cdot[M_2]^{\frac{1}{2}} = k'\cdot[M_2]^{\frac{1}{2}}$$

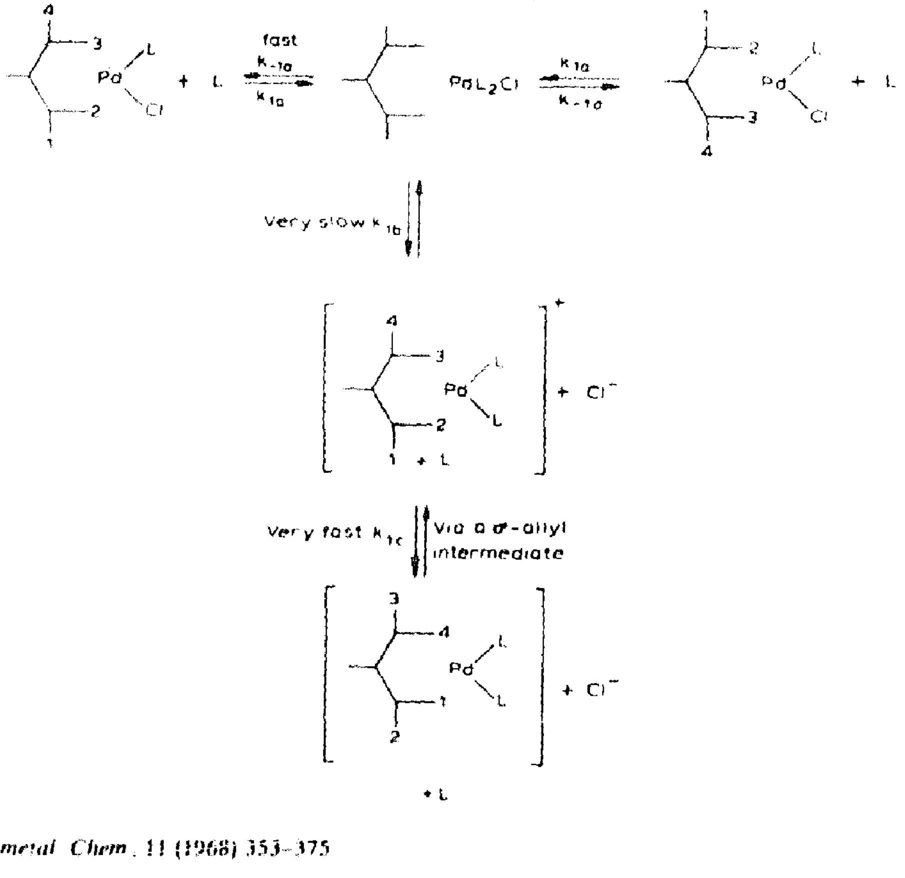
$$1/\tau(CH_3)_{M_2} = \tfrac{1}{2}\,k_4\cdot(K_1\cdot K_3)^{\frac{1}{2}}\cdot[ML]/[M_2]^{\frac{1}{2}} = k''\cdot[ML]/[M_2]^{\frac{1}{2}}$$

(N.B. The factor $\frac{1}{2}$ results from the fact that only one half of M_2 arrives in ML.)

We have tried to derive other reaction models, but none of them gave the experimental concentration dependences.

V. DISCUSSION

The results obtained from the kinetic measurements in $CDCl_3$ solution are summarized below. The first part of the discussion will be concerned with the reactions for $PPh_3/Pd > 1$, the second with those for $PPh_3/Pd < 1$.



$PPh_3/Pd > 1$

The reactions occurring for $1 < PPh_3/Pd < 1.1$ at temperatures below +20° are shown in the scheme* on the previous page.

The horizontal reaction represents the coalescence of the signals of protons in sites 1 and 4 and also of protons in 2 and 3. (The methallyl group remains π-bonded to Pd; no π–σ reaction.) This bimolecular reaction between $(\pi\text{-}C_4H_7)PdCl(PPh_3)$ and PPh_3 manifested itself as pseudosecond order in PPh_3**. This phenomenon was caused by the equilibrium involving the slow formation of the ionic species:

$$ML + L \underset{k_{1a}}{\rightleftharpoons} ML_2 \underset{k_{1b}}{\rightleftharpoons} ML_2^+ + Cl^-$$

Because of the particular range of values for $K(0.5–2)$ and the concentrations used for $[ML_0]$ and $[L_0]$, the equilibrium concentration of $[L]$ is approximately proportional to $[L_0]^2/K\cdot[ML_0]$.

It is reasonable to assume that the mechanism of the fast ligand exchange reaction:

$$(\pi\text{-}C_4H_7)PdCl(PPh_3) + PPh_3^* \rightleftharpoons (\pi\text{-}C_4H_7)PdCl(PPh_3^*) + PPh_3$$

is similar to that proposed for the reaction of $(\pi\text{-}C_4H_7)PdCl(AsPh_3)$ with free $AsPh_3$[2,3]. The PPh_3 ligand attacks the complex $(\pi\text{-}C_4H_7)PdCl(PPh_3)$ (A) along the negative X-axis, which is sterically the most favourable path (Fig. 13: see also ref. 3, Fig. 1). In the resulting short-lived five-coordinate intermediate $(\pi\text{-}C_4H_7)PdCl(PPh_3)_2$ (B), which has pseudotrigonal symmetry, the π-methallyl group may rotate in its own plane. Depending on whether the original ligand or the second ligand leaves (B), a new complex (C) or the original complex (A) is formed (Fig. 13). In this mechanism the number of interchanges of protons between sites 1 and 4 (or between 2 and 3) is equal to the number of PPh_3 exchanges, so that $a/z = 0$ and $b/z = 1$*** (as deduced easily from Fig. 13). If we introduce these values for a/z and b/z into P and R (see kinetic analysis

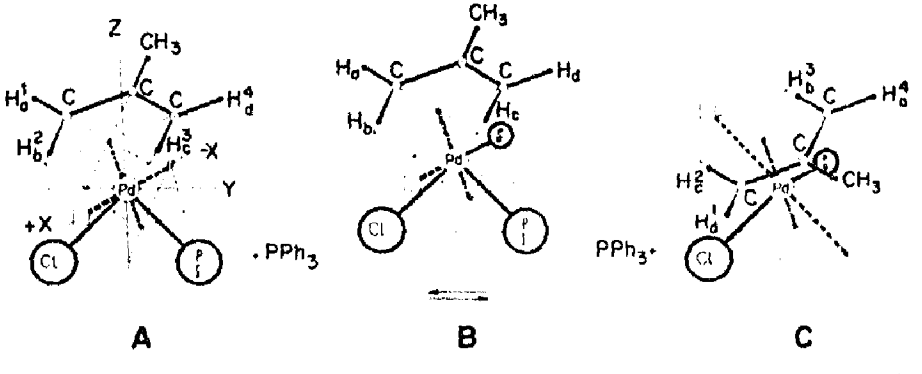


Fig. 13. Interconversion of the *syn*-protons (in sites 1 and 4) and of the *anti*-protons (in sites 2 and 3) via a five-coordinate π-allyl form (either activated complex or intermediate) in the bimolecular reaction of $(\pi\text{-}C_4H_7)PdClPPh_3$ with PPh_3. (The attack of the PPh_3 molecule is along the negative X-axis.)

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* For convenience, in this scheme we have numbered not the sites, as we usually do, but the protons.

** *i.e.* in the starting concentration $[L_0]$ of PPh_3.

*** If we substitute these values of a/z and b/z into P and R of Fig. 3, we find that the resulting $1/\tau$ values for the slow and the fast exchange cases lie on one line, as should be.

and Appendix I) and calculate $1/\tau$ we find:

$$k = 10^{12} e^{-14000/R \cdot T}$$

where $k = k_{1a}/K$.

Comparison with the $AsPh_3$ system for L/Pd > 1 shows that the only difference lies in the amount of ionic species formed. In the case of $AsPh_3$ the K value (for the equilibrium $ML + L \rightleftarrows ML_2^+ + Cl^-$) is smaller than 0.05, so that $1/\tau(ML)$ ($L = AsPh_3$) for the ligand exchange reaction:

$$ML + L^* \rightleftarrows ML^* + L$$

is first-order in $[L_0]$ since $[L] \approx [L_0]$, as was checked by numerical calculations for the concentration ranges of $[ML_0]$ and $[L_0]$ used in the $AsPh_3$ system[3].

Reaction (1b) is very slow compared with the others, since it takes 15–30 minutes to reach equilibrium. Reaction (1c), which is a ligand exchange reaction of $ML_2^+Cl^-$ with L, and of which the order could not be determined, is again fast, as is indicated by the complete coalescence of the absorptions due to protons in site (1,4) and (2,3) of the symmetrical complex*. The movement of the allyl group in reaction (1c) is a π–σ one; it takes place even at −80° in the ionic complex $ML_2^+Cl^-$, while at that temperature no π–σ reaction takes place in ML.

At temperatures higher than +20° and/or at higher L/Pd ratios we observed ligand-dependent π–σ reactions for ML as evidenced by the complete coalescence of signals 1, 2, 3 and 4. No kinetic studies were carried out.

$PPh_3/Pd < 1$

When dimer is present the situation is completely different, since the amount of free PPh_3, which can only originate from dissociation of ML, is virtually nil. Thus we observed the following reactions, which are different from those found for the $AsPh_3$ case (see Introduction).

Below −20° the only observable movement of the allyl group of ML is the intramolecular interchange of protons in sites 3 and 4, *cis* to PPh_3, via a short-lived σ-allyl intermediate, undoubtedly due to a reaction with the dimer M_2.

Between −20° and +80° several reactions occur:

$$M_2 \underset{k_1}{\rightleftarrows} M^*//M^* \underset{k_3}{\rightleftarrows} 2\,M^*$$

$(-20° \text{ to } +80°)\ M^*//M^* + ML \underset{k_2}{\rightleftarrows} M^*//M^* + ML$; no chemical exchange; signals 1, 2, 3 and 4 of ML collapse.

$(+20° \text{ to } +80°)\ M^* + ML \underset{k_4}{\rightleftarrows} M^*L + M$; chemical exchange.

The formation of a reactive intermediate M // M is only proposed to rationalize the observed high frequency factors in the $1/\tau$ formulas. If it exists it probably is a

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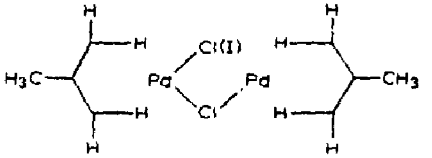
* These signals are separate when a fresh solution is made of the original complex, as was shown by Shaw and co-workers (private communication). After 30 minutes standing these separate signals coalesce. This is due to the slow partial dissociation of $ML_2^+Cl^-$ into ML and L and to the subsequent fast exchange reactions of the dissociated L with ML [reaction (1a)] and $ML_2^+Cl^-$ [reaction (1c)] respectively.

dimer with one chloride bridge broken:



No mechanisms are put forward for these very unusual reactions, in which especially the π–σ movements of the allyl group, caused by interactions with the dimer, are an interesting feature, since they occur at much lower temperatures than in ligand (L)-dependent π–σ reactions ($>20°$).

It may be that the attack of the non-bridging Cl atom of both M//M and (π-C_4H_7)PdCl along the positive X-axis on the complex (π-C_4H_7)PdCl(PPh_3)(Fig. 13, A) is the driving force. We hope to be able to give a more detailed discussion in the future.

An important result which can be deduced from the kinetic data is that PPh_3 is bonded much more strongly to Pd than $AsPh_3$ and that, as a result, when dimer is present, the amount of free PPh_3 is very small. Therefore reactions are found which were not observed for the $AsPh_3$ system, since in the latter the dissociation of ligand from Pd is less difficult and the concentration of free $AsPh_3$ larger.

It is relevant to remark that there are now strong indications that for the $AsPh_3$ system similar reactions may occur to those for the PPh_3 case. They are, however, much slower than the ligand ($AsPh_3$) exchange reactions.

APPENDIX I

In this appendix the complete derivation is given for the relation between $1/\tau$ and the line width in the slow and the fast exchange limit for the special three-site problem (peaks A, B and C of Fig. 1), which was qualitatively discussed in the kinetic analysis.

The Bloch equations for the three-site system, including exchange, are, in standard notation[15]:

$$\frac{\mathrm{d}}{\mathrm{d}t}G_{\mathrm{A}}+\alpha_{\mathrm{A}}\cdot G_{\mathrm{A}}=-i\cdot\gamma\cdot H_1\cdot M_0\cdot p_{\mathrm{A}}-(\tau_{\mathrm{AB}}^{-1}+\tau_{\mathrm{AC}}^{-1})\cdot G_{\mathrm{A}}+\tau_{\mathrm{BA}}^{-1}\cdot G_{\mathrm{B}}+\tau_{\mathrm{CA}}^{-1}\cdot G_{\mathrm{C}} \qquad (1a)$$

$$\frac{\mathrm{d}}{\mathrm{d}t}G_{\mathrm{B}}+\alpha_{\mathrm{B}}\cdot G_{\mathrm{B}}=-i\cdot\gamma\cdot H_1\cdot M_0\cdot p_{\mathrm{B}}+\tau_{\mathrm{AB}}^{-1}\cdot G_{\mathrm{A}}-(\tau_{\mathrm{BA}}^{-1}+\tau_{\mathrm{BC}}^{-1})\cdot G_{\mathrm{B}}+\tau_{\mathrm{CB}}^{-1}\cdot G_{\mathrm{C}} \qquad (1b)$$

$$\frac{\mathrm{d}}{\mathrm{d}t}G_{\mathrm{C}}+\alpha_{\mathrm{C}}\cdot G_{\mathrm{C}}=-i\cdot\gamma\cdot H_1\cdot M_0\cdot p_{\mathrm{C}}+\tau_{\mathrm{AC}}^{-1}\cdot G_{\mathrm{A}}+\tau_{\mathrm{BC}}^{-1}\cdot G_{\mathrm{B}}-(\tau_{\mathrm{CA}}^{-1}+\tau_{\mathrm{CB}}^{-1})\cdot G_{\mathrm{C}} \qquad (1c)$$

α_{X} $= 1/T_2^*(\mathrm{X})+2\pi\cdot i\cdot(\nu_{\mathrm{X}}-\nu)$
ν_{X} is the chemical shift (cps) of signal X (X = A, B, C)
τ_{YY}^{-1} is the number of times a proton jumps from site X to site Y (X, Y = A, B, C)
p_{X} is the fraction of protons in site X. The fractions p_{A}, p_{B} and p_{C} are $\frac{1}{4}$, $\frac{1}{4}$ and $\frac{1}{2}$ respectively.

The three-site problem discussed here is of a rather special type, as the number of jumps from A to B or *vice versa* (*i.e.* spin reversals, due to PPh_3 exchange) may in principle be much larger (or smaller) than the number of A→C (or C→A) jumps. If we assume that an arbitrary number of z protons are present in site A, there must be z and $2z$ protons in B and C respectively. If a of the z protons jump from site A to B and a fraction b/z from A to C, it will be clear, from symmetry arguments, that, also, a fraction a/z jumps from B to A and a fraction b/z from B to C. From detailed balancing at chemical equilibrium it follows that then a fraction $b/2z$ has to jump back from C to B and, also, a fraction $b/2z$ from C to A.

We define a time τ so that:

$$\tau_{AB}^{-1} = \tau_{BA}^{-1} = (a/z)\cdot\tau^{-1} \tag{2a}$$

$$\tau_{AC}^{-1} = \tau_{BC}^{-1} = (b/z)\cdot\tau^{-1} \tag{2b}$$

$$\tau_{CA}^{-1} = \tau_{CB}^{-1} = (b/2z)\cdot\tau^{-1} \tag{2c}$$

It now follows from equation (2a)–(2c), that*:

$$\tau_A^{-1} = \tau_{AB}^{-1} + \tau_{AC}^{-1} = \{(a+b)/z\}\cdot\tau^{-1} \tag{3a}$$

$$\tau_B^{-1} = \tau_{BA}^{-1} + \tau_{BC}^{-1} = \{(a+b)/z\}\cdot\tau^{-1} \tag{3b}$$

$$\tau_C^{-1} = \tau_{CA}^{-1} + \tau_{CB}^{-1} = (b/z)\cdot\tau^{-1} \tag{3c}$$

Writing equations (1a)–(1c) in the slow passage approximation and substituting (2a)–(3c) yields:

$$\{\alpha_A\cdot\tau + (a+b)/z\}\cdot G_A - (a/z)\cdot G_B \qquad - (b/2z)\cdot G_C = -i\cdot\gamma\cdot H_1\cdot M_0\cdot p_A\cdot\tau \tag{4a}$$

$$-(a/z)\cdot G_A + [\alpha_B\cdot\tau + (a+b)/z]\cdot G_B - (b/2z)\cdot G_C = -i\cdot\gamma\cdot H_1\cdot M_0\cdot p_B\cdot\tau \tag{4b}$$

$$-(b/z)\cdot G_A - (b/z)\cdot G_B + \qquad [\alpha_C\cdot\tau + (b/z)]\cdot G_C = -i\cdot\gamma\cdot H_1\cdot M_0\cdot p_C\cdot\tau \tag{4c}$$

In the limit of slow exchange the width of signals A, B and C is given by:

$$1/T_2(A) = 1/T_2^*(A) + \{(a+b)/z\}\cdot\tau^{-1} = 1/T_2^*(A) + \pi\cdot P\cdot\tau^{-1} \tag{5a}$$

$$1/T_2(B) = 1/T_2^*(B) + \{(a+b)/z\}\cdot\tau^{-1} = 1/T_2^*(B) + \pi\cdot P\cdot\tau^{-1} \tag{5b}$$

$$1/T_2(C) = 1/T_2^*(C) + (b/z)\cdot\tau^{-1}. \tag{5c}$$

where $(a+b)/z = \pi\cdot P$ and $\pi\cdot P\cdot\tau^{-1} = \pi\cdot\Delta\nu_{\frac{1}{2}}\mathrm{ex}$** of signal A. (5d)

$1/T_2^*(X)$ is the natural line width of X in the absence of exchange. In the limit of fast exchange the determinant Δ determines the line shape for the case in which τ is so small that terms containing τ^2 can be neglected (not where these terms are multiplied by factors $\alpha_A\cdot\alpha_B$ which may be large):

$$\Delta = \frac{2a\cdot b + b^2}{2z^2}\cdot[\tau\cdot(\alpha_A+\alpha_B+2\alpha_C) + \tau^2\cdot\{\alpha_A\cdot\alpha_B\cdot(b/z) + \alpha_A\cdot\alpha_C\cdot(a+b)/z + \alpha_B\cdot\alpha_C\cdot(a+b)/z\}] \tag{6}$$

---

* For the usual three-site (or more) problem τ is defined as the mean time between reorientations or site changes[16], and $\tau_j = \tau/\sum_i p_i = \tau/(1-p_j)$. The rates τ_A^{-1}, τ_B^{-1} and τ_C^{-1} are then $\frac{3}{4}\tau^{-1}$, $\frac{3}{4}\tau^{-1}$ and $\frac{1}{2}\tau^{-1}$ respectively, instead of the more general formulas (3a)–(3c).

** $\Delta\nu_{\frac{1}{2}}\mathrm{ex}$ is the contribution to the line width owing to exchange (cps).

When the exchange is very fast the second term may be neglected. The line width of the collapsed signal (2,3) is then determined by the first term:

$$1/T_2 = \tfrac{1}{4}[T_2^{*-1}(\mathrm{A}) + T_2^{*-1}(\mathrm{B}) + 2\,T_2^{*-1}(\mathrm{C})]$$

while the signal is centred at:

$$\omega = \tfrac{1}{4}(\omega_{0\mathrm{A}} + \omega_{0\mathrm{B}} + 2\,\omega_{0\mathrm{C}})$$

which is observed experimentally.

If the exchange is less fast, the second term also contributes to the line width. Neglecting products $T_2^{*-1}(\mathrm{X})\cdot T_2^{*-1}(\mathrm{Y})$ (X, Y = A, B, C), the real part of the second term divided by $4(2a\cdot b+b^2)\cdot\tau/2z^2$ is:

$$\{2z^2/(8a\cdot b+4b^2)\}\cdot\tau\cdot[-(b/z)\cdot(\omega_{0\mathrm{A}}-\omega)\cdot(\omega_{0\mathrm{B}}-\omega)$$
$$-[(a+b)/z]\cdot(\omega_{0\mathrm{A}}-\omega)\cdot(\omega_{0\mathrm{C}}-\omega)-[(a+b)/z]\cdot(\omega_{0\mathrm{B}}-\omega)\cdot(\omega_{0\mathrm{C}}-\omega)]$$

Substitution of the chemical shifts $\nu_{0\mathrm{A}}$* (= 364.5 cps), $\nu_{0\mathrm{B}}$ (= 354 cps), $\nu_{0\mathrm{C}}$ (= 278 cps) and the shift ν(= 319 cps) of the collapsed signal (2, 3) (at 100 Mc) into this expression gives the correction in the transverse relaxation time T_2:

$$1/T_2 = 1/T_2^* + [2z^2/(2a\cdot b+b^2)]\cdot\pi^2\cdot\tau\cdot[-1615\,b/z+3320(a+b)/z] =$$
$$= 1/T_2^* + \pi R\cdot\tau\,, \quad (7a)$$

where $R \;= [2z^2/(2a\cdot b+b^2)]\cdot\pi[-1615\,b/z+3320(a+b)/z]$
and $\pi\cdot R\cdot\tau = \pi\cdot\Delta\nu_{\frac{1}{2}}\mathrm{ex}$ of the collapsed signal (2, 3). (7b)

APPENDIX II

Consider the following reaction scheme:

$$\mathrm{A} \underset{k_{+1}}{\overset{k_{-1}}{\rightleftharpoons}} \mathrm{B}^*$$

$$\mathrm{B}^* + \mathrm{C} \underset{k_{+2}}{\rightleftharpoons} \mathrm{B} + \mathrm{C}^*$$

Given is that A and C are observed by NMR, while B* is an intermediate, which may or may not be observed. The kinetics for this system can be obtained by regarding it as a formal three-site problem, analogous to the example given in Appendix II of ref. 1. It can then be shown, by using Bloch equations including exchange, that if A and B* are in the fast exchange limit, while C is in the slow exchange limit with the collapsed signal** of A and B*, the contribution to the line width of the collapsed signal of A and B due to slow exchange with C is:

$$k_{+1}\cdot k_{+2}\cdot[\mathrm{C}]/k_{-1}$$

The contribution to the line width of signal C owing to slow exchange with the collapsed signal (A, B) is:

$$k_{+1}\cdot k_{+2}\cdot[\mathrm{A}]/k_{-1}$$

---

* $\nu = \omega/2\,\pi$.

** For the sake of convenience one NMR signal is assigned to each species A, B, C etc. If in reality two or more signals belong to one species this will not change the results, but will only lead to trivial complications.

If, on the other hand, the signals B and C are in the fast exchange limit, while signal A does not overlap with the collapsed signal (B, C) the line broadening of A due to slow exchange with (B, C) is:

$$k_{+1}$$

while the line broadening of the collapsed signal (B, C) is:

$$k_{+1}\cdot[\mathrm{A}]/[\mathrm{C}]$$

Expansion of the above reaction scheme to:

$$\mathrm{A} \underset{k_{+1}}{\overset{k_{-1}}{\rightleftharpoons}} \mathrm{B} \underset{k_{+3}}{\overset{k_{-3}}{\rightleftharpoons}} 2\mathrm{D}^*$$

$$\mathrm{D}^* + \mathrm{E} \underset{k_4}{\rightleftharpoons} \mathrm{D} + \mathrm{E}^*$$

yields the following results. If A, B and D are in the fast exchange limit (B and D being intermediates), while E is in the slow exchange limit with the collapsed signal (A, B, D), it can be shown that for $k_{-3}\cdot[\mathrm{D}^*] \gg k_4\cdot[\mathrm{E}]$ and $k_{-1}\cdot k_{-3}\cdot[\mathrm{D}^*] \gg k_{+1}\cdot(k_{-3}\cdot[\mathrm{D}^*] + k_{+3})$ the line broadening of the collapsed signal (A, B, D) owing to slow exchange with E is:

$$(k_1\cdot k_3)^{\frac{1}{2}}\cdot k_4\cdot[\mathrm{E}]/(k_{-1}\cdot k_{-3})^{\frac{1}{2}}\cdot[\mathrm{A}]$$

while the line broadening of signal E is given by*:

$$(k_1\cdot k_3)^{\frac{1}{2}}\cdot k_4\cdot[\mathrm{A}]^{\frac{1}{2}}/(k_{-1}\cdot k_{-3})^{\frac{1}{2}}$$

SUMMARY

Kinetic studies, using NMR, of the rates of interchange (temperature $< +20°$) between the *syn*-protons and between the *anti*-protons of the π-allyl group in the complex $(\pi\text{-C}_4\text{H}_7)\text{PdCl}(\text{PPh}_3)$ showed that when this monomeric complex and free PPh_3 are present in CDCl_3, a bimolecular reaction occurs of the monomer with one molecule of PPh_3. For this reaction a one-step mechanism via a five-coordinate intermediate $(\pi\text{-C}_4\text{H}_7)\text{PdCl}(\text{PPh}_3)_2$ is proposed. From NMR and conductivity measurements it was deduced that, in addition, an ionic complex, $[(\pi\text{-C}_4\text{H}_7)\text{Pd}(\text{PPh}_3)_2]^+\text{Cl}^-$, is slowly formed.

At temperatures higher than +20° all four *syn*- and *anti*-protons become magnetically equivalent via the formation of a σ-allyl intermediate. Quantitative studies of this reaction were not possible.

Studies of reaction mixtures of $(\pi\text{-C}_4\text{H}_7)\text{PdCl}(\text{PPh}_3)$ and $[(\pi\text{-C}_4\text{H}_7)\text{PdCl}]_2$ showed that dissociation of PPh_3 in the first complex does not occur, in contrast to the behaviour of the AsPh_3 system; instead, reactions were found which between −40 and +20° involve the interaction of the phosphine complex with a dimer species, and between +20 and +80° a reaction of the phosphine complex with a species $(\pi\text{-C}_4\text{H}_7)\text{PdCl}$ (from dissociation of the dimer) with exchange of $(\pi\text{-C}_4\text{H}_7)\text{PdCl}$ (or PPh_3).

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* In our case E = ML and A = M_2

The kinetic parameters and the molecular mechanism of the various reactions are discussed and compared with the results for the triphenylarsine system.

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