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THE NATURE OF THE SYSTEM $(\pi\text{-}C_4H_7PdCl)_2$–ELECTRON DONOR FROM ^1H, ^{13}C AND ^{31}P NMR SPECTROSCOPIC AND ELECTRODIALYSIS STUDIES

II. $(\pi\text{-}C_4H_7PdCl)_2$–TRIPHENYLPHOSPHINE

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SUMMARY

A study has been made of the reactions between $(\pi\text{-}C_4H_7PdCl)_2[=M_2]$ and $PPh_3[=L]$ in a $CDCl_3$ solution. In the presence of excess M_2, the complex $C_4H_7Pd\text{-}Cl\cdot PPh_3$ was obtained, the initial formation of the complex being readily observed in both the ^1H and ^{13}C NMR spectra. At temperatures above 40°, the signals of both complexes became averaged in the ^{13}C NMR spectra. In the presence of excess phosphine (up to the ratio $PPh_3/Pd=2$), exchange reactions involving free and complexed PPh_3 took place. The kinetics of the system has been studied using ^{31}P NMR spectra. The intermediates formed were shown to be ML_2 and ML_3 which decompose to give ML and L and also dissociate into ions. The nature of the ions present was established by electrodialysis studies of the system $(^{14}C_4H_7Pd^{36}Cl)_2 + PPh_3$. It was found that low temperatures and concentrations gave predominantly Cl^- and $C_4H_7Pd\cdot L_2^+$ ions, whilst high temperatures and concentrations led to the formation of $C_4H_7^-$ and $PdCl\cdot L_3^+$ ions.

The data on electrical conductivity and electrodialysis have been compared qualitatively with the ^{13}C NMR spectra.

INTRODUCTION

In part I of this series[1], it was shown that the interaction of $(\pi\text{-}C_3H_5PdCl)_2$ and $(\pi\text{-}C_4H_7PdCl)_2[=M_2]$ with electron donating ligands (L) such as triphenylphosphine (PPh_3) and dimethylsulfoxide (DMSO) results in a significant change in the ^{13}C NMR spectrum of the respective complexes involving an upfield shift of C_1 absorption signals and a downfield shift of C_2 and, particularly, C_3 absorption signals. Under the same conditions, the ^1H NMR spectrum indicates an averaging in the shielding of the *syn* and *anti* protons in the allyl group as the concentration of the ligand is increased. Most authors[4–7] consider that this effect arises from a rapid $\pi \rightleftharpoons \sigma$ equilibrium transition which leads to the magnetic equivalence of the protons due to rotation about the C–C bond in the short lived σ-allylic state.

According to another point of view[3], this equivalence of *syn* and *anti* protons

is attained as a result of their restricted rotation about the C–C bond without disturbing the symmetry of the allyl group. Although this point of view is inconsistent with the asymmetry of the crotylpalladium chloride–triphenylphosphine[1] and methallylpalladium chloride–triphenylphosphine[2] complexes, it is possible to study this effect directly by ^{13}C NMR spectroscopy as this particular method gives an indication of the state of the carbon skeleton in the allyl group.

This second interpretation suggests that the changes occurring in the allyl group are of a purely intramolecular character, while the first interpretation suggests that they are associated with complex-ligand exchange. To clarify this problem an attempt has been made to study the processes taking place in the system $C_4H_7PdCl \cdot PPh_3$ by ^{31}P NMR spectroscopy.

Since variations in the NMR spectra of allylpalladium compounds are accompanied by a change in their electrical conductivity[5], the dependence of the electrical conductivity on the concentration of the added ligand has been studied in some detail over a wide temperature range.

To determine the nature of ions responsible for the electrical conductivity, electrodialysis studies have been made using a complex in which both the allyl group and the halogen have been labelled, *i.e.* $(\pi\text{-}^{14}C_4H_7 \cdot Pd^{36}Cl)_2$.

EXPERIMENTAL

^{13}C NMR spectra were recorded on a Brucker HX-90 spectrometer at a frequency of 22.63 MHz using rotating 10 mm ampoules. Signals due to free induction were integrated on a Fabri-Tek "1074" computer following the application of the measuring frequency as a powerful 2 μs impulse; the normal NMR spectrum was obtained after Fourier transformation of the integrated signal. In order to obtain a reasonable signal/noise ratio, the transformation was made after the application of up to 8000 impulses where broad-band decoupling of spectra occurred and 16000–32000 impulses in the case of undecoupled spectra. The accuracy of the shift measurements is limited by the number of computer channels; with a sweep width of 5000 Hz ($\Delta T = 100$ μs) and 2048 point splittings, the shift may be measured accurately to ± 2.5 Hz. The resolution of the instrument is limited by this value. The interval between impulses was 0.2 s which is not enough for complete relaxation of all the ^{13}C nuclei, and hence the intensity and width of some of the lines were slightly distorted. The use of greater time interval between impulses, however, seemed unreasonable for it would considerably prolong the duration of the experiment (from several hours to several weeks), especially in the case of experiments carried out without spin–spin decoupling. ^1H and ^{31}P NMR spectra were recorded at 90 and 36.43 MHz respectively. Solutions of bis(π-crotylpalladium chloride) in deuterochloroform were used in all cases, the required amount of Ph_3P being added directly into the ampoule. An internal, ^{19}F (C_6F_6), lock was utilized. TMS was used as an internal reference for all ^1H and ^{13}C NMR measurements, all shifts being with respect to this standard.

The electrical conductivity of the solutions was measured on a constant current megameter using a cell equipped with co-planar platinum electrodes. The electrodialysis of the complex $^{14}C_4H_7Pd^{36}Cl$ was undertaken in a three-cell dialyser; after applying the current, samples were removed from all the cells at definite time intervals.

The radioactivity of the samples was measured on a Beckman LS-250 liquid scintillation spectrometer.

Bis(π-crotylpalladium chloride) (π-$^{14}C_4H_7Pd^{36}Cl)_2$ was prepared by the reaction of palladium chloride with crotyl chloride-^{14}C in a 50% acetic acid solution[10]. Crotyl chloride-^{14}C was obtained by treating butadiene-^{14}C with acetic acid in the presence of Cu_2Cl_2. The ^{36}Cl isotope was introduced into the complex by exchange. To accomplish this, (π-$^{14}C_4H_7PdCl)_2$ was dissolved in acetone and heated for several hours over a $Na^{36}Cl$ precipitate. The resulting double-labelled complex was separated from $Na^{36}Cl$ by repeated recrystallization. The crystals obtained were washed with alcohol and ether and dried *in vacuo*.

RESULTS

The ^{13}C NMR spectrum of $(\pi\text{-}C_4H_7PdCl)_2$ depicted in Fig. 1a contains four

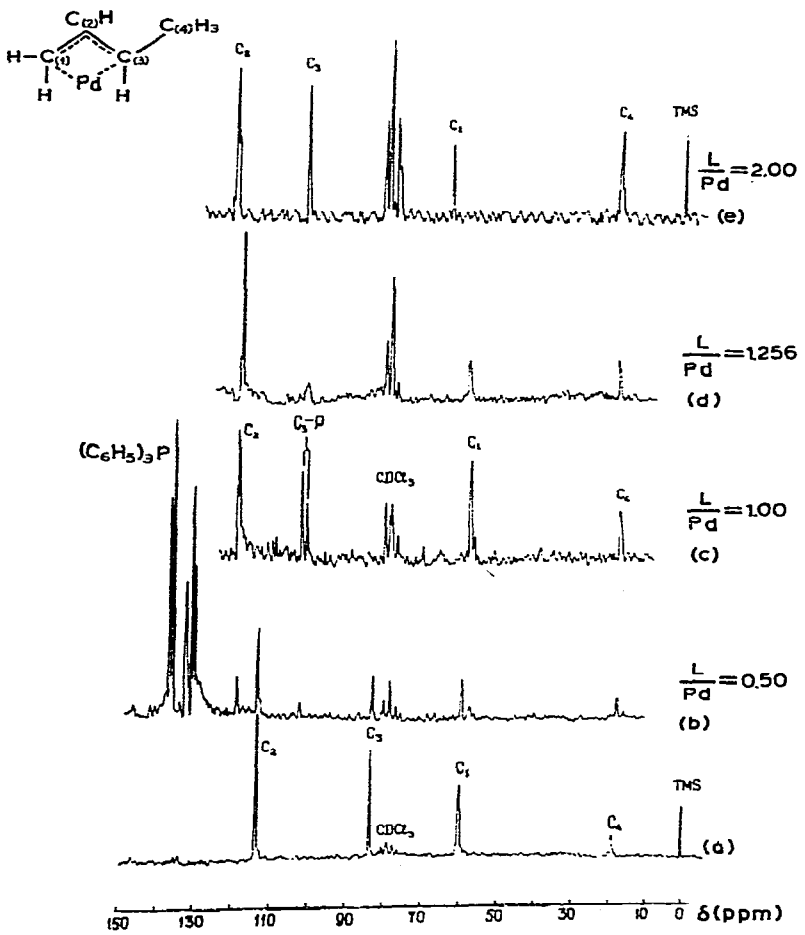


Fig. 1. The ^{13}C NMR spectrum of a crotylpalladium chloride complex with added triphenylphosphine in $CDCl_3$ solution. $[(C_4H_7PdCl)_2] = 0.75$ mol/l.

single lines corresponding to the C_1, C_2, C_3 and C_4 nuclei at 59, 111, 81 and 18 ppm respectively (the assignment of the lines was made using spectra obtained without spin–spin decoupling of the ^{13}C–H group).

When PPh_3 is added, new absorption signals appear and a corresponding decrease in the intensity of the signal of the initial complex occurs (Fig. 1b). When the ratio $PPh_3/Pd=1$ (Fig. 1c), the lines of the initial complex have completely disappeared and the only spectrum observed is that of the new complex which possesses three singlets at 54, 118 and 16 ppm, a doublet at 99 ppm and a multiplet corresponding to the phenyl nuclei of the PPh_3 ligand at 140 ppm. A further increase in the phosphine concentration leads to the widening of the doublet at 99 ppm and to a disappearance of its coupling; at the ratio $PPh_3/Pd=2$, the spectrum consists of four narrow singlets at 50, 100, 118 and 15 ppm, respectively.

Heating the solution of the complex with a PPh_3/Pd ratio of 1 causes the doublet at 99 ppm to widen and at 35° this transforms into a singlet the chemical shifts of all the lines remaining practically unchanged.

The ^1H NMR spectrum of $(\pi\text{-}C_4H_7PdCl)_2$ shown in Fig. 2a consists of four

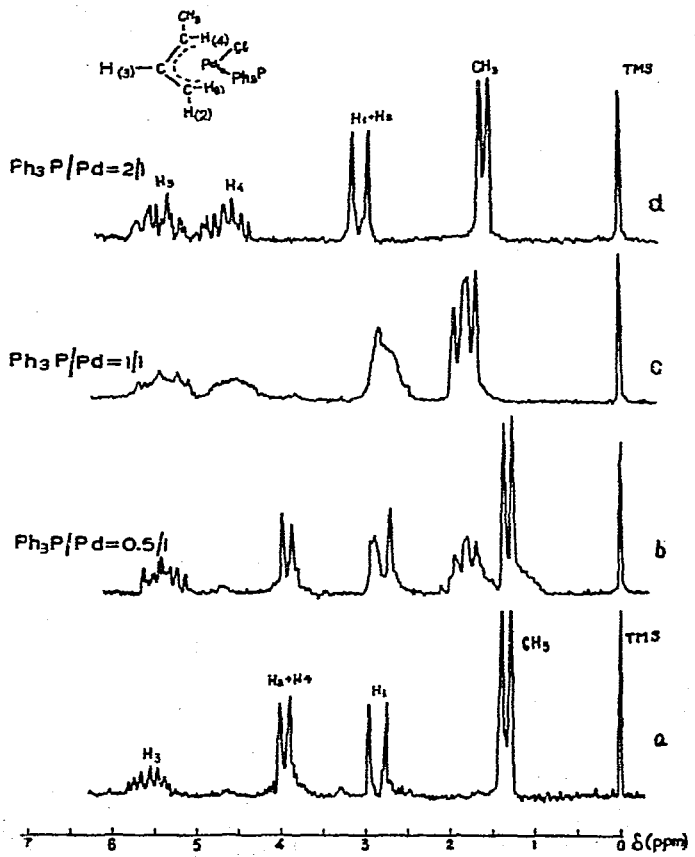


Fig. 2. The ^1H NMR spectrum of a crotylpalladium chloride complex with added triphenylphosphine in $CDCl_3$ solution. $[C_4H_7PdCl)_2]=0.25$ mol/l.

groups of lines: the CH_3 doublet at 1.4 ppm, the H_1 doublet at 2.9 ppm, the H_2+H_4 doublet at 4.0 ppm and the H_3 multiplet at 5.6 ppm, the intensity ratio of the lines being 3/1/2/1.

The addition of PPh_3 results in the appearance of new lines and a decrease in the intensity of the initial complex, as occurred in the ^{13}C spectra (Fig. 2b).

At a ratio $PPh_3/Pd=1$, the signal of the initial complex disappears, the resulting spectrum being that of the new compound (Fig. 2c) which consists of a quartet at 2.0 ppm (corresponding to a triplet at 60 MHz), a wide absorption line and multiplets at 5.5 and 4.9 ppm.

Further addition of phosphine leads initially to a broadening of the quartet at 2.0 ppm and of other lines, then to their narrowing and shifting and, finally, at a ratio $PPh_3/Pd=2$ the spectrum consists of four groups of narrow lines: doublets at 1.7 ppm and 3.2 ppm and multiplets at 5.0 and 5.5 ppm, respectively, the intensity ratio of lines being 3/2/1/1 (Fig. 2d). With $PPh_3/Pd=1$, a variation in the temperature and absolute concentration leads to a change in the line widths, and from the change in the line width of a signal in the quartet at 1.7 ppm as the concentration of the complex was changed it was concluded that the rate of exchange of a proton between two non-equivalent positions is proportional to the concentration of the complex raised to the power 0.5 (Fig. 3).

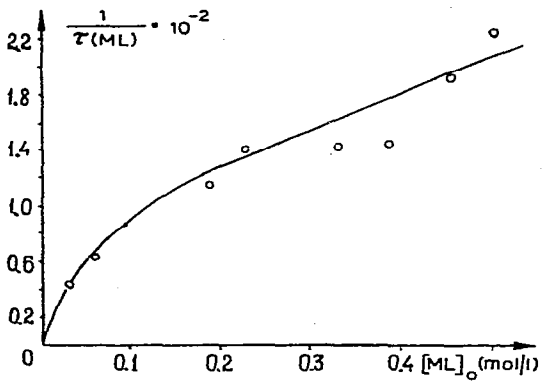


Fig. 3. The exchange rate in relation to the complex concentration; t 20°, $CDCl_3$ solution.

On cooling the solution of the complex of ratio $PPh_3/Pd=1$ to $-60°$, splitting of the methyl group absorption region occurs. The chemical shifts of the H_1 and H_2 protons are very similar, thus the constants $J(H_1–H_3)=J(H_2–H_3)=9$ Hz and $J(H_1–H_2)=0$. The line intensity ratio of the quartet at 2.0 ppm does not change, however, on cooling, and the quartet splitting in the spectra obtained at 60 and 90 MHz proved to have the same value (9Hz).

The ^{31}P NMR spectrum of triphenylphosphine in $CDCl_3$ solution exhibits a poorly resolved absorption region with the signal shifted downfield by 6.0 ppm relative to H_3PO_4.

On addition of PPh_3 to the solution of $(\pi\text{-}C_4H_7PdCl)_2$, the phosphine absorption signals in the ^{31}P NMR spectrum appear as a wide single line at a lower field relative to the signal of free PPh_3. At $PPh_3/Pd=1$, this shift reaches its greatest

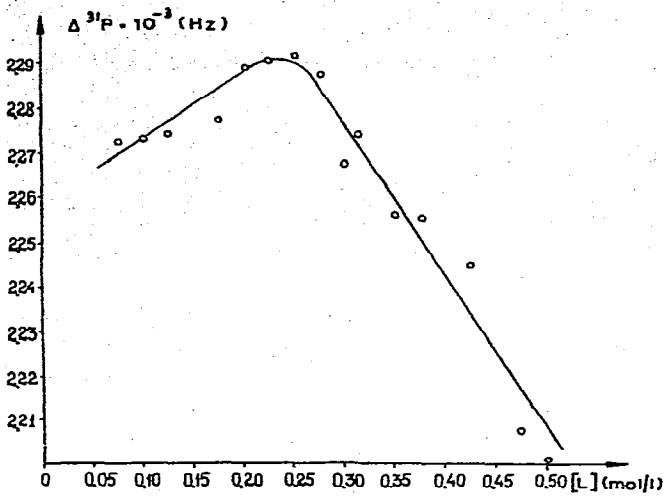


Fig. 4. The ^{31}P chemical shift in relation to the PPh_3 concentration in the system $(C_4H_7PdCl)_2 + PPh_3$ in $CDCl_3$ solution $[(C_4H_7PdCl)_2] = 0.25$ mol/l.

value (30 ppm) and any further increase in the ratio only results in a decrease in the magnitude of the shift (Fig. 4).

Increasing the ratio of PPh_3/Pd in fact leads to the gradual irreversible decomposition of the complex to give mainly dicrotyls and inorganic compounds of the type $(PPh_3)_3 \cdot PdCl$. The reaction rate however increases as the concentration of the complex and the temperature is increased, thus suggesting that the decomposition processes possess a radical character.

The electrical conductivity of solutions containing $(\pi\text{-}C_4H_7PdCl)_2$ and PPh_3 appears to depend on the concentration of the ligand and complex, the actual dependence being quite complicated. On varying the concentration of PPh_3 at constant $[(\pi\text{-}C_4H_7PdCl)_2]$, the electrical conductivity increases as the third power of the concentration of the added ligand. (Fig. 6). At a ratio $PPh_3/Pd = 1$ (Fig. 5) and at 0°, the electrical conductivity passes through a maximum. At $PPh_3/Pd = 2$, the electrical conductivity exhibits two maxima, one at 15° and the other at 50°. When the ratio PPh_3/Pd is kept constant at a value of 2, the electrical conductivity depends on the absolute concentration of the complex (Fig. 5d, e, f).

In order to characterize the type of ions present under different conditions, electrodialysis studies have been undertaken on the complex $(\pi\text{-}^{14}C_4H_7Pd^{36}Cl)_2$ in the presence of PPh_3.

Two sets of experiments were conducted for which the following conditions were chosen:

(I) $PPh_3/Pd = 2$; $[Pd] = 0.05$ mol/l; $t = 20°$ (Fig. 5d)
(II) $PPh_3/Pd = 2$; $[Pd] = 0.2$ mol/l: $t = 50°$ (Fig. 5f)

With conditions of type (I), ^{14}C moved almost exclusively towards the cathode and ^{36}Cl towards the anode; Pd was found in the cathode compartment (mostly as a metallic powder deposited on the electrode). In the second set of experiments, by contrast, ^{14}C was found in the anode compartment while ^{36}Cl and Pd occurred in the cathode compartment.

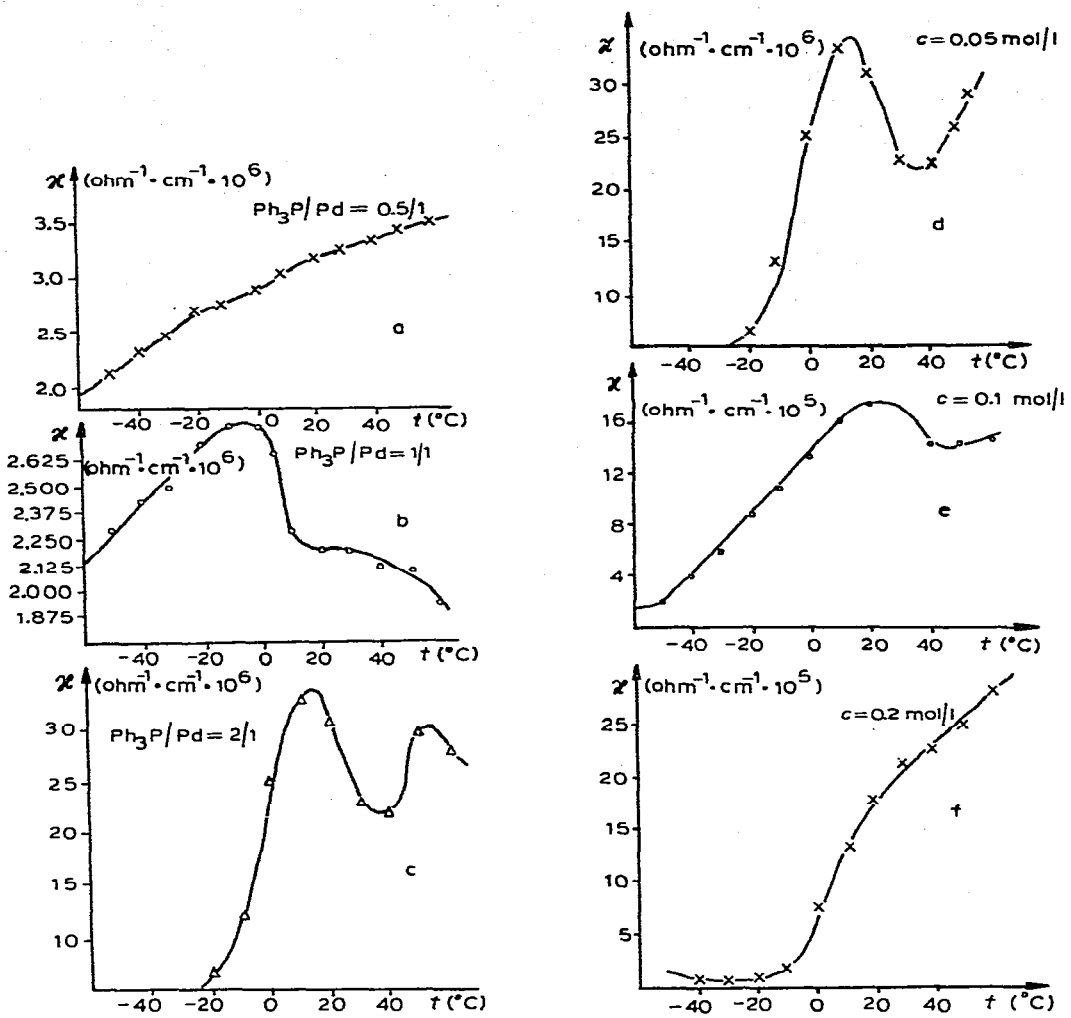


Fig. 5. The electrical conductivity of the system $(C_4H_7PdCl)_2 + PPh_3$ in $CHCl_3$ solution in relation to the temperature; a, b, c: $[(C_4H_7PdCl)_2] = 0.1$ mol/l, d, e, f: $L/Pd = 2$.

DISCUSSION

As the ratio PPh_3/Pd is changed, three different regions can clearly be distinguished. These regions are $PPh_3/Pd < 1$; $PPh_3/Pd = 1$ and $PPh_3/Pd > 1$, all of which differ in their kinetic and chemical behaviour. For this reason, they have been treated separately in the following discussion.

1. $PPh_3/Pd < 1$

The ^1H (Fig. 2b) and ^{13}C (Fig. 1b) NMR spectra exhibit two absorption lines: one corresponding to the initial material $(\pi\text{-}C_4H_7PdCl)_2$ $[=M_2]$ and the other to $C_4H_7PdCl \cdot PPh_3$ $(=ML)$. No exchange occurs between ML and M_2; this takes place only through the agency of reactions (1)–(3) (see below).

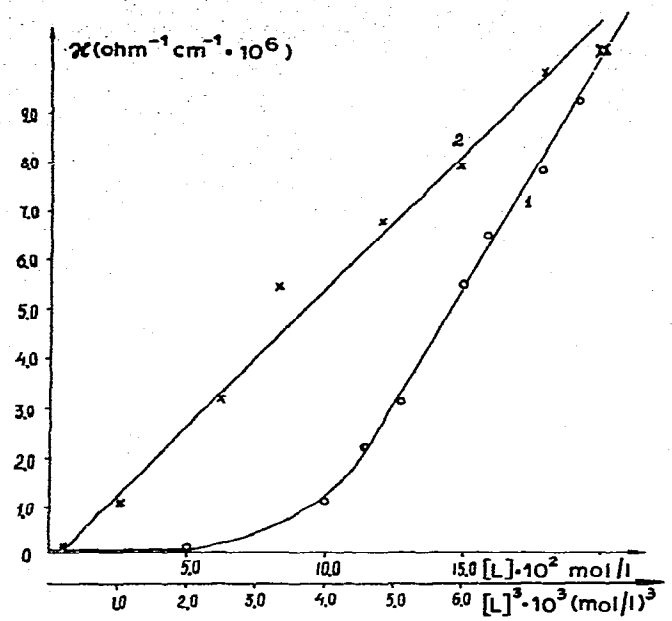


Fig. 6. The electrical conductivity in relation to the triphenylphosphine concentration in $CHCl_3$ solution $[(C_4H_7PdCl)_2] = 0.05$ mol/l.

On heating, the signals due to the allyl carbons of ML broaden and $J(C_3\text{–}P)$ disappears while the signals attributed to M_2 remain narrow. On further heating (up to 306 K and above), broadening of the M_2 signals occurs followed by the collapse of the signals attributable to the CH_3 group present in both M_2 and ML which are replaced by a singlet. This suggests that an equilibrium is rapidly established in solution between M_2 and M as depicted by the equations below:

$$M_2 \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} 2M^* \tag{1}$$

$$M + L \underset{k_{-2}}{\overset{k_{+2}}{\rightleftharpoons}} ML \tag{2}$$

$$ML + L \underset{k_{-3}}{\overset{k_{+3}}{\rightleftharpoons}} ML_2 \tag{3}$$

$$M^* + ML \underset{k_{-4}}{\overset{k_{+4}}{\rightleftharpoons}} M^*L + M \tag{4}$$

Reaction (4) is only significant at elevated temperatures when an exchange occurs between the monomers produced and ML with reaction (1) probably being significant also.

In the concentration range $0.05 \rightarrow 0.025$ mol·l^{-1} at room temperature $[M_2] \gg [L]$, and hence free phosphine formed by reaction (2) is more likely to react with M produced by reaction (1) rather than with ML (by reaction (3) .

Then $[L_0]=[ML]+[L]$ or $[ML_0]\simeq[ML]+[L]$.

The shift of the averaged phosphine signal in the ^{31}P NMR spectrum arising from rapid exchange obeys the condition:

$$\frac{\Delta L}{\Delta ML}=\frac{[ML]}{[L]} \tag{5}$$

where $\Delta L=\delta_{exp}-\delta_L$ and $\Delta ML=\delta(ML)-\delta_{exp}$.

When $[ML]\gg[M_2]$, the magnitude of the equilibrium constant for reaction (4) may be calculated if it is assumed that $[M]\approx[L]$ and $[ML]\simeq[ML]_0$. Then

$$K_2=\frac{[ML]_0}{[L]_0^2} \tag{6}$$

and from equations (5) and (6)

$$K_2=\frac{\Delta L^2}{\Delta ML^2}\cdot\frac{1}{[ML]_0}$$

From the data in Fig. 4, it is possible to calculate, therefore, that $K_2\approx10^4\ l\cdot mol^{-1}$.

2. *$PPh_3/Pd=1$*

From the relevant ^1H and ^{13}C NMR spectra, it is obvious that triphenyl phosphine reacts with π-crotylpalladium chloride to give a stable compound of formula $C_4H_7PdCl\cdot PPh_3$ (as deduced from the signal intensities in the ^1H NMR spectrum) with the phosphine ligand acting as an electron donor (the signal being shifted downfield by 30 ppm compared to pure PPh_3).

The magnitude of the chemical shifts indicates that the H_1 and H_2 protons are situated at nearly the same distance from the Pd atom and that the angle between them is such that $J(H_1\text{–}H_2)=0$, *i.e.* that the angle is approximately 120°. The proton signals corresponding to H_1 and especially H_2 are shifted upfield in comparison to their position in the π-allylic complex while the H_4 and CH_3-group signals are shifted downfield.

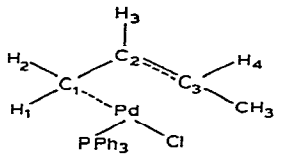
A similar phenomenon is observed in the ^{13}C NMR spectrum: the C_1 signals are shifted downfield while those corresponding to C_3 are shifted upfield. As M_2 is converted into ML, the signals corresponding to H_3 and C_2 remain unchanged.

The above data agree well with the proposed structure of ML in which the electron density distribution differs from the π-allylic structure initially present and which is similar to π, σ-structure deduced from X-ray evidence[8] ^1H NMR[11] and ^{13}C NMR spectra[1].

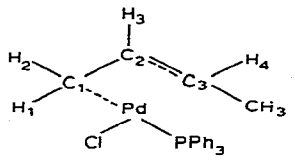
That the absorption signal corresponding to the CH_3-group protons at 60 and 90 MHz is strongly split indicates that this signal must be induced by spin–spin coupling, the only possible coupling of this kind in this instance being due to the phosphorus atom. From the magnitude of the relative spin–spin coupling constants of the phosphorus nucleus with various protons and carbon atoms, *i.e.* $J(C_3\text{–}P)=24$ Hz, $J(C_2\text{–}P)$, $J(C_1\text{–}P)<1$ Hz, $J(H_3\text{–}P)\simeq1\text{–}2$ Hz, $J(H_4\text{–}P)<1$ Hz and $J(CH_3\text{–}P)=8$ Hz, it follows that in this instance interaction between the phosphine ligand and the allyl group occurs through a C_3 carbon atom, (usually $J(C_\alpha\text{–}P)>J(C_\beta\text{–}P)$ and $J(H_\alpha\text{–}P)>J(H_\beta\text{–}P)$)[13].

Since the observed constant $J(CH_3–P)$ for the interaction between the methyl group protons and the phosphorus nucleus has a magnitude of 8 Hz, it is not unreasonable to assume that the methyl group is *syn* relative to the palladium atom as in the complex methallylpalladium chloride-triphenylphosphine[5]. In this position the methyl group is more strongly shielded by the palladium atom which explains the upfield shift of the methyl-group carbon signal in the ^{13}C spectra.

Unfortunately, ^{13}C NMR spectroscopy is not an absolute method for deciding whether the phosphine ligand is either *cis* or *trans* relative to the corresponding atoms of the allyl function and the usual representation[8] of ML is that with the maximum electron density in the *trans* position (II) relative to the ligand, although it would be easier to explain the splitting off of the CH_3-group protons and C_3 carbon by assuming the *cis* position (I) where the phosphine molecule is able to interact directly with these groups rather than through a Pd atom.



(II)



(I)

The absorption line width in the ^1H NMR spectra changes as the absolute concentration of ML in solution at room temperature changes.

From the change in the absorption line width for the methylene group it was found that the exchange rate constant varies as the square-root of the concentration of the complex (Fig. 3).

All the observed changes in the various parameters of the NMR spectra with temperature and concentration are obviously of an intermolecular nature and may be attributed to abstraction and addition reactions involving the phosphine ligand such as those expressed in equations (1) and (2) above.

It is known[5] that reaction (2) lies to the right and that the concentrations of [M] and [L] are correspondingly small; for the same reason $[M_2]$ is also small, and hence a rise in temperature or a decrease in the absolute concentration of ML in solution leads to a slight shifting of (2) to the left and (1) to the right. In all cases, however, most of the complex remains in the ML form. Line broadening and disappearance of spin–spin coupling in the NMR spectra may be attributed to rapid phosphine ligand exchange[12].

The dependence of the exchange rate constant upon the square-root of the concentration of the complex (Fig. 3) can be readily explained if account is taken of the fact that free phosphine arising from reaction (2) also reacts with the complex according to reaction (3) above.

From this it follows therefore that:

$$\frac{1}{\tau(ML)} = -\frac{d[ML]}{[ML]d\tau} = -k_{+2}\frac{[M][L]}{[ML]} + k_{-2} + k_{+3}[L] - k_{-3}\frac{[ML_2]}{[ML]}$$

But $k_{+2}[M][L]/[ML] = k_{-2}$ and therefore $[L] = K_2^{-\frac{1}{2}}[ML]_0^{\frac{1}{2}}$ where K_2 is the equilibrium constant for reaction (2), provided that $[M] \approx [L]$ and $[ML] = [ML]_0$.

Hence $\tau(ML)^{-1} = k_{+3}K_2^{-\frac{1}{2}}[ML]_0^{\frac{1}{2}} - k_{-3}[ML_2]/[ML]$. This equation will only agree with the experimental results if $\tau(ML)^{-1} \propto [ML]_0^{\frac{1}{2}}$ *i.e.* if $k_{+3}K_2^{-\frac{1}{2}}[ML]_0^{\frac{1}{2}} \gg k_{-3}[ML_2]/[ML]$ which is not unreasonable as $[ML_2]/[ML] \ll 1$ since [L] is small.

Hence $\tau(ML)^{-1} \simeq k_{+3}K_2^{-\frac{1}{2}}[ML]_0^{\frac{1}{2}}$.

If $\tau(ML)^{-1}$ is plotted graphically as a function of $[ML]_0^{\frac{1}{2}}$ it is possible to obtain a value for $k_{+3}K_2^{-\frac{1}{2}}$ from the slope. In this way a value of $k_{+3}K_2^{-\frac{1}{2}} = 2.7 \times 10^2$ was obtained, and therefore $k_{+3} = 2.7 \times 10^4$ l·mol^{-1}·s^{-1}.

3. *L/Pd* > 1

The addition of PPh_3 to $C_4H_7PdCl \cdot PPh_3$ results in a broadening of the C_3 absorption lines in the ^{13}C NMR spectrum; on further addition of PPh_3, the C_3–P coupling disappears, the C_1 signal shifts downfield by 5.0 ppm and the C_3 signal moves upfield by 0.9 ppm (when the ratio $PPh_3/Pd = 2$) all these shifts being relative to their positions in ML.

At $PPh_3/Pd > 1$, the phosphine signal shifts upfield as the phosphine concentration increases, the line width remaining unchanged and equal to that of ML *i.e.*, 50 Hz. Analysis of the kinetic data showed that in the range $L/Pd \leqslant 1.2$ this shift could be explained quite well in terms of reaction (3). The constancy of the line width and the absence of an absorption signal corresponding to free phosphine indicate that reaction (3) proceeds at a high rate on the NMR time scale ($\tau < 10^{-3}$ s).

On cooling, the ^{31}P signal shifts downfield and at 0° the signal broadens and finally splits into several lines at −10°, the shift being equal to the ML shift.

At 20°, in the presence of a high L/Pd ratio, the dependence of the collapsed signal shift on the phosphine concentration is no longer capable of explanation in terms of reaction (3). Under the same experimental conditions, signals corresponding to H_1 and H_2 protons and the CH_3 group in the ^1H NMR spectra begin to broaden and collapse until at $PPh_3/Pd = 1.2$ all the lines become narrow and the H–P coupling disappears. When the ratio $PPh_3/Pd = 2$, the absorption signal corresponding to the CH_2 group shifts downfield by 0.23 ppm while that of the CH_3 group moves upfield by 0.12 ppm relative to that of ML. Further increase in the ratio does not essentially change the nature of the spectrum which may be attributed to the exchange rate being too great to be followed by NMR spectroscopy.

Cooling the solution in $CHCl_3$ when the ratio $PPh_3/Pd = 2$ gives the opposite effect. In this case the absorption signal of the CH_2 group shifts upfield while those of the CH_3 and CH groups move downfield, the lines again broadening and splitting.

Whilst disappearance of H–P coupling may be explained in terms of a rapid phosphine exchange, the averaging of the signals of the H_1 and H_2 protons may be due to their rotation about a single C–C bond in the σ-allylic species (no such rotation occurs in π-allylic M_2 or in π, σ-ML). The simultaneous disappearance of the ^1H and ^{31}P splittings at the point where the system apparently no longer depends on reaction (3) suggests that the proton equivalence results from the addition of one more phosphine molecule per palladium atom.

Variations in the NMR spectra are accompanied by changes in the electrical conductivity of the system. Though no direct relationship between the electrical conductivity of the system and, for example, the exchange rate of the methyl protons apparently exists, the electrical conductivity is usually greatest when the exchange rate is greatest.

The considerable influence of temperature upon the variation of the electrical conductivity in this system may be due to the formation of ions in the various solutions arising from the varying reactions occurring in the system[12].

At moderate temperatures and moderate concentrations of the complex, electrodialysis studies indicate that the allyl group of the complex passes into the cathode compartment. In addition to the allyl group, palladium also passes into the cathode compartment of the cell being deposited on the electrode as a metallic powder. Since the chloride ion passes almost exclusively into the anode compartment, the only possible reaction occurring in this case is:

$$RPdCl \rightleftharpoons RPd^+ + Cl^- \tag{7}$$

At high concentrations of the complex and at high temperatures the direction of the reaction changes: the allyl group now passes into the anode compartment while the chloride ion and palladium pass into the cathode compartment. The most likely reaction in this case is

$$RPdCl \rightleftharpoons R^- + PdCl^+ \tag{8}$$

It has been shown[5b] that in the presence of excess phosphine reaction (7) occurs at low temperatures to give the stable ion $[ML_2]^+Cl^-$.

The observed shift in the phosphine signal in the ^{31}P spectrum as the temperature decreases probably results from an increase in the contribution of the ions $[C_4H_7Pd(PPh_3)_2]^+Cl^-$ to the averaged signal.

The dependence of the conductivity on the absolute concentration and on the ligand concentration to the power of approximately 2.8 may be explained by the formation of ionic particles involving cleavage of the Pd–C bond via the formation of ML_3.

$$ML_2 + L \underset{k_{-9}}{\overset{k_{+9}}{\rightleftharpoons}} ML_3 \tag{9}$$

$$ML_3 \underset{k_{-10}}{\overset{k_{+10}}{\rightleftharpoons}} R^- + PdXL_3^+ \tag{10}$$

A solution containing ML and free ligand will therefore initially undergo phosphine exchange through reaction (3) and even at a ratio of $PPh_3/Pd = 1.7$ the free ligand will be at its equilibrium concentration in the system. The ligand can also react with ML_2 via reaction (9) to yield the allylic complex ML_3 which, in turn, dissociates into the ions $[C_4H_7]^-$ and $[PdL_3X]^+$.

The formation of ML_3 which should be short lived and of a σ-allylic nature should give rise to an NMR spectrum in which the signals of the protons α to the palladium atom would appear in a high field, while those of the carbon atoms and remaining protons would appear in a lower field in comparison to the signals of the corresponding π,σ-complexes.

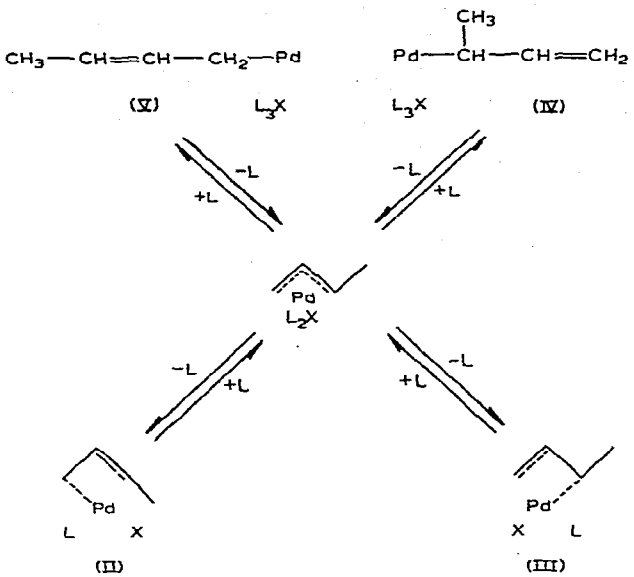
With the crotyl group, the decomposition of ML_2 into ML and L via reaction (3) should lead to the formation of two isomers (Scheme 1).

The favoured isomer would be (II) while the thermodynamically less favourable isomer would have strong Pd–C_3 interaction resulting in C_1 being much more olefinic than its counterpart in isomer (II).

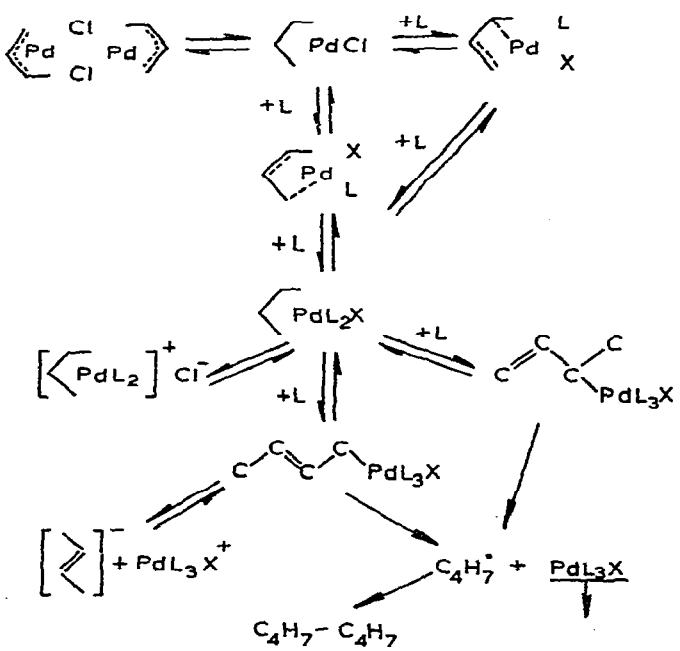
Similarly, the addition of L to ML_2 may give both the crotyl and α-methyl-

allylic complexes in which both the protons of the CH_2 group and the whole ligand may rotate about the σ-bond. By analogy with metal crotyls (C_4H_7MgCl, $B(C_4H_7)_3$), it is reasonable to assume that (V) is the more stable form.

SCHEME 1



SCHEME 2



Since an increase in the temperature results in an upfield shift of the C_3 signals and a downfield shift of C_1 signals, it appears that the proportions of (III) and (IV) in the solution increase as the temperature increases.

CONCLUSIONS

Investigations of the interaction between $(\pi\text{-}C_4H_7PdCl)_2$ and PPh_3 over a wide temperature and concentration range have shown that rapid reactions take place involving various covalent and ionic species in which the allyl group is bonded to the palladium atom through a π- or σ-bond. The resulting signal in the NMR spectra is dependent on the ratio of these species in the system.

When PPh_3 is present in large excess, irreversible reactions become significant in the system resulting in the decomposition of the complex.

The reactions occurring in the system may be depicted by Scheme 2.

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