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NUCLEAR MAGNETIC RESONANCE STUDIES IN COORDINATION CHEMISTRY
IV. REACTIONS OF π-ALLYLPALLADIUM COMPLEXES AS INFLUENCED BY VARIOUS PHOSPHORUS LIGANDS

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SUMMARY

It is shown that in π-allylpalladium complexes, *e.g.* $(\pi\text{-}C_4H_7)PdClL$ (L = $AsPh_3$, PPh_3) and substituted π-methallyl compounds, so-called "π–σ" reactions may occur, *i.e.* reversible interconversions from the π-allyl to a short-lived σ-allyl form with interchange of the *syn*- and *anti*-protons. These interchanges are caused either by reactions of the monomeric complex with excess free ligand L or by reactions of the complex with dimeric π-allylpalladium chloride compounds. In the case of these dimer-dependent "π–σ" reactions it was found that at low temperatures *syn*- and *anti*-protons interchange on one side of the allyl group, whereas at higher temperatures interchange occurs on both sides of the allyl group of the monomer. The interchange on one side was studied in particular for various phosphine compounds. It proved to be first order in the monomer and first order in the dimer complex for L = $P(n\text{-}C_4H_9)_3$.

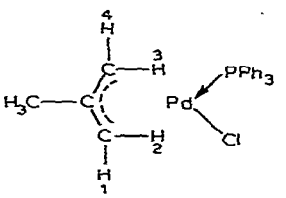
Additional information about "π–σ" reactions in general was further obtained for dimethyl-substituted π-methallylpalladium compounds.

Also included are the results of NMR measurements on the formation and ligand exchange reactions of ionic complexes $[(\pi\text{-}C_4H_7)Pd(PR_3)_2]^+Cl^-$ for various phosphines.

I. INTRODUCTION

In the first report[1] of this series we discussed the qualitative behaviour of the π-allyl group in compounds $(\pi\text{-}C_3H_4R)PdClL$ (L = group V donor ligand; R = H, CH_3), which were studied with NMR as a function of the type of ligand L, the ligand L-to-metal ratio and the temperature (in $CDCl_3$ solution). Subsequent linewidth studies furnished more quantitative kinetic data on the reactions of π-methallyl complexes for L = $AsPh_3$[2] and PPh_3[3]. These two systems proved to differ widely in kinetic behaviour, which was mainly ascribed to the Pd–P bond being far more stable than the Pd–As bond[3].

Intriguing reactions which were noted in these systems are the bimolecular* "π–σ" reactions, which involve the interchange of *syn*- and *anti*-protons of the allyl group in $(\pi\text{-}C_4H_7)PdClL$ via a σ-allyl intermediate and which are caused by reactions of $(\pi\text{-}C_4H_7)PdClL$ with L ($L=AsPh_3$[2], PPh_3[3]) or of $(\pi\text{-}C_4H_7)PdCl(PPh_3)$ with $[(\pi\text{-}C_4H_7)PdCl]_2$[3]. In the case of the reactions of $(\pi\text{-}C_4H_7)PdCl(PPh_3)$ with $[(\pi\text{-}C_4H_7)PdCl]_2$ at low temperature ($< 20°$) the *syn*- and *anti*-protons on one side of the allyl group interchange their positions (interchange between sites 3 and 4 of the phosphine complex). At higher temperatures there is an interchange of *syn*- and *anti*-protons on both sides of the allyl group. The interchange between 3 and 4 could not be studied quantitatively for $L=PPh_3$, owing to the small difference in chemical shift



between these two signals[3]. Instead we have studied complexes of other phosphines where we have a much larger chemical shift between the signals of 3 and 4.

Another interesting phenomenon is the formation of ionic compounds $[(\pi\text{-}C_4H_7)Pd(PR_3)_2]^+Cl^-$ from $(\pi\text{-}C_4H_7)PdCl(PR_3)$ and PR_3, which was observed both with NMR in $CDCl_3$ solution[3] and with conductance studies in CH_2Cl_2[3], and aqueous acetone[8]. The formation of the ionic complex proved to be favoured by strong electron-donating ligands such as PR_3 and much less so by $AsPh_3$ and $SbPh_3$[2,3,8].

In view of the important role which both the "π–σ" reactions and the formation of the ionic compounds play in the kinetics of in particular the Pd–PPh_3 system[3], it was of interest to obtain more information about both phenomena. The present report gives details of NMR studies into π-methallylpalladium complexes of phosphines other than PPh_3 together with pertinent information on "π–σ" reactions for dimethyl-substituted π-methallylpalladium compounds of PPh_3 and $AsPh_3$.

II. EXPERIMENTAL

The π-methallylpalladium dimer $[(\pi\text{-}C_4H_7)PdCl]_2$ has been prepared according to standard methods[1]. The compounds $\{\pi\text{-}[1,1,2\text{-}(CH_3)_3C_3H_2]PdCl\}_2$ and $\{\pi\text{-}[1\text{-}syn,2,3\text{-}syn\text{-}(CH_3)_3C_3H_2]PdCl\}_2$ were obtained by a method of Volger[14]. Triphenylphosphine and tri-n-butylphosphine, both of commercial grade, were purified by recrystallization and distillation, respectively. The ligand $P(OCH_2)_3C\text{–}CH_3$[15] was prepared from $CH_3\text{–}C(CH_2OH)_3$ and PCl_3, while Et_2PhP, Me_2PhP and $MePh_2P$ were obtained from the appropriate Grignards and Cl_2PhP and $ClPh_2P$, respectively.

The NMR spectra were recorded on a Varian spectrometer (Ha 100 and DP

* Monomolecular "π–σ" reactions have been found for $Zr(\pi\text{-}C_3H_5)_4$, $Th(\pi\text{-}C_3H_5)_4$[4,5] etc. and $L_2Cl_2Rh\text{-}(\pi\text{-}C_4H_7)$[6,7], while ligand-dependent "π–σ" reactions were observed for π-allyl complexes of Ni and Pd[7,8–13], and Pt[18]. In almost all cases intermediates of the σ-allyl type were assumed.

60) using $CDCl_3$ as solvent. Low temperatures were obtained with Varian variable dewar inserts. Tetramethylsilane (TMS) was used as an internal reference.

Kinetic measurements by means of NMR were made of the interchange of protons between sites 3 and 4 (*cis* to PR_3) for the compounds $(\pi\text{-}C_4H_7)PdCl(PR_3)$ in the presence of $[(\pi\text{-}C_4H_7)PdCl]_2$. The reaction rates were obtained in the slow exchange limit from the linewidth of the signal of the proton in site 3 (see Table 1), from which values for the lifetime τ_i ($i=3$) were calculated*. In the case of PPh_2Me signal 4 was used for the calculation of τ_i ($i=4$; $\tau_3=\tau_4$), because signal 3 overlaps with the ligand absorptions. A suitable correction was made for the natural linewidth and in the case of PPh_2Me also for the long-range coupling on signal 4, which became smaller with higher reaction rates**.

II. "π–σ" REACTIONS

In section *A* we will discuss "π–σ" reactions in complexes $(\pi\text{-}C_4H_7)PdCl(PR_3)$, and in section *B* substituted π-methallyl complexes.

A. π-Methallylpalladium compounds

In the previous report we presented data on "π–σ" reactions caused by interactions of $(\pi\text{-}C_4H_7)PdCl(PPh_3)$ (=ML) and $[(\pi\text{-}C_4H_7)PdCl]_2$ (=M_2). The results can be summed up as follows***:

Below $-20°$ the only observable movement of the allyl groups was the interchange of protons in sites 3 and 4 of ML. This reaction occurred in the presence of M_2, but no quantitative data could be obtained owing to the small chemical shift between signals 3 and 4. There was no exchange of PPh_3 between ML and M_2, since the dimer peaks did not change in linewidth.

Between -20 and $+80°$ several reactions took place, namely†:

$$M_2 \underset{k_1}{\leftrightarrows} M^+//M^+ \underset{k_3}{\leftrightarrows} 2\,M^+$$

$(-20°-+80°)$ $M^+//M^+ + ML \leftrightarrows M^+//M^+ + ML$

(no exchange of PPh_3: signals 1, 2, 3 and 4 of ML collapse to one signal)

$(+20°-+80°)$ $M^+ + ML \leftrightarrows M^+L + M$

(chemical exchange)

Since these reactions are highly interesting and rather unusual, we also studied the interchange between sites 3 and 4 proper for other phosphine compounds.

The NMR spectra of $(\pi\text{-}C_4H_7)PdClL$ (in $CDCl_3$) [L=PPh_3, PPh_2Me, $PPhMe_2$, $PPhEt_2$, $P(n\text{-}C_4H_9)_3$ and $P(OCH_2)_3CCH_3$] at about $-40°$ consist of two doublets (proton in site 1), due to coupling of this proton with the P-nucleus (spin $\frac{1}{2}$)

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* For the methods of calculation of τ_i see refs. 2–4 and 16 and refs. quoted therein.

** In general it is observed[2,3] that the long-range coupling between the protons in sites 1 and 4 becomes smaller and eventually goes to zero for higher reaction rates both for L=PPh_3 and $AsPh_3$.

*** The mechanism proposed by Powell and Shaw in scheme 2 of ref. 19, which was based on qualitative data, is not right, as was shown by our quantitative kinetic data of this paper and of ref. 3.

† For an extensive treatment of these reactions see ref. 3.

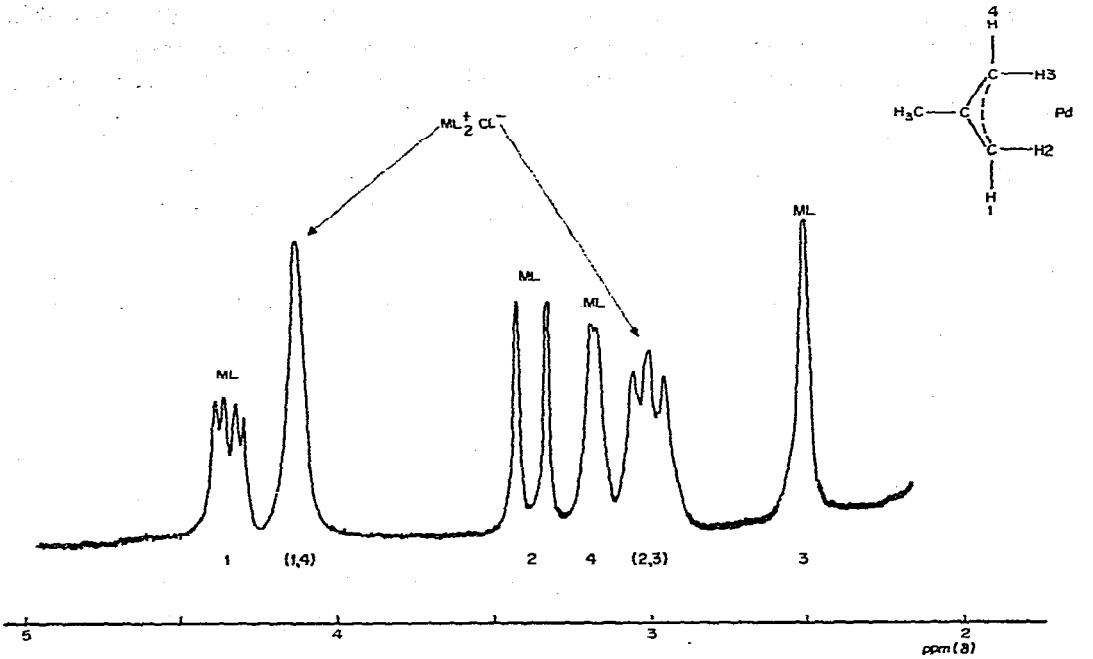


Fig. 1. The allylic part of the NMR spectrum of a mixture of $(\pi\text{-}C_4H_7)PdCl[P(n\text{-}C_4H_9)_3]$ (=ML) and $\{(\pi\text{-}C_4H_7)Pd[P(n\text{-}C_4H_9)_3]_2\}^+Cl^-$ (=$ML_2^+Cl^-$), which is formed from ML and L (in $CDCl_3$).

and a smaller long-range coupling with the proton in 4, a doublet (P-coupling) of the proton in site 2, a doublet (proton in site 4, due to the long-range coupling) with 1, and a singlet (proton in 3), respectively (see Table 1)*. As an example the NMR spectrum of $(\pi\text{-}C_4H_7)PdCl[P(n\text{-}C_4H_9)_3]$ is given in Fig. 1.

Clearly the bonding in these compounds must be very similar, since the chemical shifts differ little (Table 1). The only differences are:

(*a*) the difference in chemical shift between signals 3 and 4 for $L=PPh_3$, which is small in comparison with the other compounds;

(*b*) the large values for the P-coupling on signals 1 and 2 for the $P(OCH_2)_3CCH_3$ compound;

(*c*) the relatively low field chemical shift values (δ from TMS) for the signals 3 and 4 of the $P(OCH_2)_3CCH_3$ compound as compared with the others.

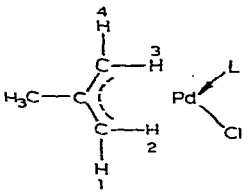
A feature common to all the complexes is the constant value of 2.9 c/s for the long-range coupling constant between protons in sites 1 and 4.

At temperatures higher than $-40°$ the signals 3 and 4 of $(\pi\text{-}C_4H_7)PdCl(PR_3)$ coalesce, for all phosphines considered, in the presence of dimer. The temperature range studied for this coalescence lies between -40 and $0°$. No change in linewidth is observed in this temperature region for the absorptions 1 and 2 of the monomer (*i.e.* PR_3 does not exchange perceptibly) or for any other signal of monomer (CH_3)

* It is assumed that PR_3 *is trans* to the protons which absorb at the lowest magnetic field. This seems reasonable in view of the larger Pd–C bond distance *trans* to PPh_3 in the structure of $(\pi\text{-}C_4H_7)PdCl(PPh_3)$[17].

TABLE 1

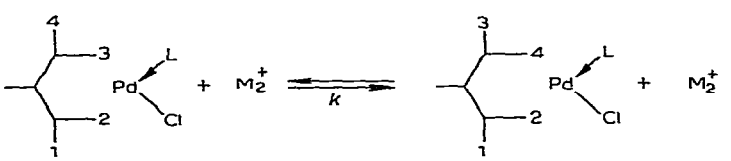
CHEMICAL SHIFTS OF THE PROTONS IN SITES 1 TO 4 IN ppm FROM TMS (δ) OF THE COMPOUNDS (π-C_4H_7)PdClL



L	Temp. (°C)	Proton absorptions of the allyl protons (δ) 1	2	3	4
		Two doublets	Doublet	Singlet	Doublet
PPh_3	−40	4.50 J[P−H(1)] = 6.5 c/s J[H(1)−H(4)] = 2.9 c/s	3.62 J[P−H(2)] = 9.8 c/s	2.80	2.89 J[H(1)−H(4)] = 2.9 c/s
PPh_2Me	−40	4.48 J[P−H(1)] = 6.5 c/s J[H(1)−H(4)] = 2.9 c/s	3.49 J[P−H(2)] = 10.0 c/s	2.61	3.10 J[H(1)−H(4)] = 2.9 c/s
$PPhMe_2$	−40	4.42 J[P−H(1)] = 6.5 c/s J[H(1)−H(4)] = 2.8 c/s	3.43 J[P−H(2)] = 10.0 c/s	2.60	3.17 J[H(1)−H(4)] = 2.8 c/s
$PPhEt_2$	−45	4.46 J[P−H(1)] = 6.5 c/s J[H(1)−H(4)] = 2.8 c/s	3.47 J[P−H(2)] = 10.0 c/s	2.57	3.16 J[H(1)−H(4)] = 2.8 c/s
$P(n\text{-}C_4H_9)_3$	−40	4.36 J[P−H(1)] = 6.0 c/s J[H(1)−H(4)] = 2.9 c/s	3.40 J[P−H(2)] = 9.8 c/s	2.48	3.16 J[H(1)−H(4)] = 2.9 c/s
$P(OCH_2)_3CCH_3$	−59	4.53 J[P−H(1)] = 11.3 c/s J[H(1)−H(4)] = 2.9 c/s	3.53 J[P−H(2)] = 16.5 c/s	2.78	3.82 J[H(1)−H(4)] = 2.9 c/s

and dimer. The absence of broadening on the CH_3 peak of (π-C_4H_7)PdCl(PPh_3) (=ML) and on the peaks of $[(\pi\text{-}C_4H_7)PdCl]_2$ (=ML_2) shows that there is no exchange of PPh_3 between monomer and dimer. However, in all cases it was qualitatively found that the rates of interchange between 3 and 4 increased with the dimer concentration. When we measured this process quantitatively for L = $P(n\text{-}C_4H_9)_3$, the rate $1/\tau_3$ (ML) proved to be proportional to $[M_2]$ ([ML] was kept constant) and independent of [ML], when $[M_2]$ was kept constant: thus $1/\tau_3(ML) = k \cdot [M_2]$ (Fig. 2).

A simple reaction model compatible with the kinetic results is:



In the reaction the intermediate may be a short-lived association complex M_3L, but after the association the original complexes are formed back; no exchange of PPh_3 has occurred, only interchange of 3 and 4.

In Table 2 the activation parameters have been recorded for various phos-

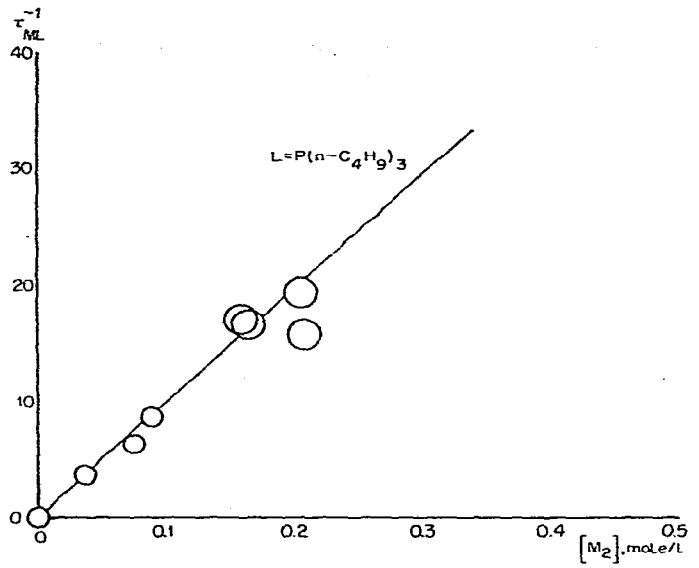
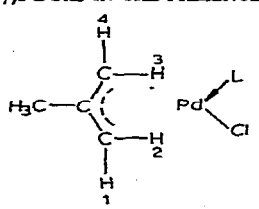


Fig. 2. The dependence of $1/\tau_3$(ML) on $[M_2]$ for [ML] varying between 0.30 and 0.50 mole/l. ML = $(\pi\text{-}C_4H_7)PdCl[P(n\text{-}C_4H_9)_3]$ and $M_2 = [(\pi\text{-}C_4H_7)PdCl]_2$.

phines. No straightforward correlation exists between the activation energies and the qualitatively known electron donor capacities of PR_3. The frequency factors are about 10^{10}, which is lower than those of the reactions of ML and M//M ($\sim 10^{15}$),

TABLE 2

ARRHENIUS PARAMETERS FOR THE INTERCHANGE PROCESS OF PROTONS IN SITES 3 AND 4 IN THE COMPLEXES $(\pi\text{-}C_4H_7)PdClL$ IN THE PRESENCE OF $[(\pi\text{-}C_4H_7)PdCl]_2$



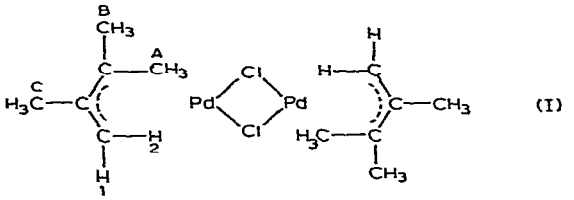
L[a]	Activation energy E (kcal/mole)	Frequency factor A ($l \cdot mole^{-1} \cdot sec^{-1}$)
PPh_3[b]		
PPh_2Me	10.7	$\sim 10^{10}$
$PPhMe_2$	7.8	$\sim 10^{10}$
$PPhEt_2$	13.8	$\sim 10^{12}$
$P(n\text{-}C_4H_9)_3$	9.6	$\sim 10^{8}$
$P(OCH_2)_3CCH_3$[c]	~10	

[a] The rates were measured on proton in site 3, except for $L = PPhMe_2$, where the band of 4 was used. In all cases dimer was present. [b] Could not be measured as signals 3 and 4 are too close to each other. [c] Could not be determined precisely.

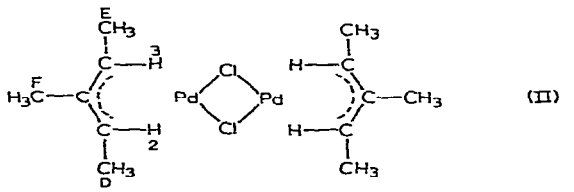
mentioned above, where there is coalescence of the signals 1, 2, 3 and 4* of the methallyl group in ML. In this last reaction again no exchange of PPh_3 between ML and M_2 is observed (see also ref. 3).

B. Dimethyl-substituted π-methallylpalladium compounds

In order to investigate if more information about "π–σ" reactions could be obtained from reactions involving substituted π-methallylpalladium compounds, we carried out NMR measurements on reaction mixtures of ligands L ($AsPh_3$, PPh_3) with the complexes $\{\pi\text{-}[1,1,2\text{-}(CH_3)_3C_3H_2]PdCl\}_2$ (I) and $\{\pi\text{-}[1\text{-}syn,2,3\text{-}syn\text{-}(CH_3)_3\text{-}C_3H_2]PdCl\}_2$ (II), respectively, for both L/Pd > 1 and L/Pd < 1.



(I)



(II)

The NMR spectrum of (I) consists of two peaks at 3.72 and 3.17 ppm (δ from TMS) due to protons in sites 1 and 2, respectively, and three signals at 2.06, 1.37 and 1.23 ppm, respectively, originating from the CH_3 groups C, B and A (in $CDCl_3$ at $-30°$).

The complex (II) was prepared in one isomeric form, *i.e.* with groups D and E *syn* to F. A quartet was observed at 3.52 ppm $\{J[CH_3\text{–}H(2,3)] = 6.4$ c/s$\}$, the methyl signal F at 2.03 ppm and a methyl doublet of two equivalent methyl groups D and E at 1.25 ppm $\{J[CH_3\text{–}H(2,3)] = 6.4$ c/s; in $CDCl_3$ at $+23°\}$.

Addition of L ($AsPh_3$, PPh_3) to (I) yielded the compounds $\pi\text{-}[1,1,2\text{-}(CH_3)_3\text{-}C_3H_2]PdClL$ with L always *trans* to the dimethyl-substituted carbon atom, undoubtedly for steric reasons. The chemical shifts are shown in Table 3**.

A rise of temperature and/or increase of the concentration of free ligand L gave for both compounds a coalescence of signals 1 and 2 at L/Pd > 1, while no perceptible broadening was observed on the A and B signals even at $+80°$. The same coalescence was found at L/Pd < 1, probably owing to reactions with dissociated ligand and/or dimer. It can therefore be concluded that protons in sites 1 and 2, which are *cis* to L, interchange their positions probably via a σ-allyl intermediate, while in the time scale of the NMR experiment no interchange of A and B, which are *trans* to L, is found.

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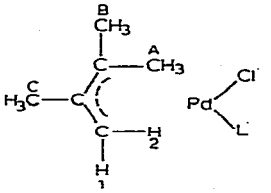
* Absorptions 1 and 2 broaden, owing to interchange in ML, but not owing to PPh_3 exchange between ML and M_2, since the dimer signals do not change in linewidth. There is also no PPh_3 exchange between two ML's, the rates $1/\tau$ (ML) being independent of $[ML]^3$.

** *Note added in proof*: Concentration dependence (of ligand) studies for this compound have recently been reported by Powell and Shaw[19]. Their results agree with ours.

TABLE 3

CHEMICAL SHIFTS OF THE ALLYLIC PROTONS AND METHYL PROTONS FOR L = PPh_3 [COMPLEX (III), 23°] AND $AsPh_3$ [COMPLEX (IV), −30°]



L	Chemical shifts (δ) of protons in sites 1	2	Chemical shifts of the CH_3 groups A	B	C
PPh_3	doublet	doublet	doublet	doublet	singlet
	2.87	2.72	1.81	1.47	1.86
	J[H(1)–H(2)] = 2.3 c/s		J(P–CH_3) = 10.0 c/s	J(P–CH_3) = 5.6 c/s	
$AsPh_3$[a]	doublet	doublet	singlet	singlet	singlet
	3.15	2.99	1.82	1.49	1.96
	J[H(1)–H(2)] = ~2 c/s				

[a] At +70° the shifts are 3.20, 2.95, 1.71, 1.42 and 1.92 ppm, respectively.

Reactions of one mole of ligand L (L = $AsPh_3$, PPh_3) per mole of Pd with the dimeric complex (II) at −80°* in $CDCl_3$ yielded the compounds π-[1-*syn*,2,3-*syn*-$(CH_3)_3C_3H_2$]PdClL, in which the π-allyl group, as indicated by the NMR spectra, is bonded to Pd in roughly the same (asymmetric) way as the allyl group in (π-C_4H_7)-PdCl(PPh_3)[17]. The chemical shifts are shown in Table 4.

When the temperature was raised to about +10° the signals of protons in sites 2 and 3 and also the signals of the methyl groups D and E coalesced at their weighted mean, respectively, for both L = $AsPh_3$ and PPh_3 if L/Pd ≧ 1. In the case of PPh_3 no P-coupling was observed on the collapsed signals, indicating ligand exchange. This process, which is reversible, is clearly fully analogous to the similar interchanges of protons between sites 1 and 4 and also between 2 and 3, respectively, for (π-C_4H_7)-PdClL[2,3], in which the π-allyl group remains π-bonded (rotation of π-allyl group in its own plane) to the metal during the ligand (L) exchange reaction. When we kept the temperature for the solutions of these dimethyl-substituted complexes below +10° (small excess of free ligand L present) no significant isomerization occurred. At higher temperatures and/or higher L/Pd ratio such isomerizations, which are dependent on [L], did take place.

Isomerizations via a σ-allyl intermediate do occur, however, at as low a temperature as −30° in the monomeric complexes, if dimer is present in solution (*i.e.* L/Pd < 1), clearly because of "monomer–dimer" interactions of the type discussed above for (π-C_4H_7)PdCl(PPh_3). This holds not only for L = PPh_3 but also for L = $AsPh_3$. As an example Fig. 3a shows the spectrum of π-[1-*syn*,2,3-*syn*-$(CH_3)_3$-C_3H_2]PdCl($AsPh_3$) (VI) in the presence of the dimeric compound in $CDCl_3$ solution at −60° (see also Table 4). No isomerizations took place at this temperature. Upon

* If ligand L is added at room temperature to the dimer solution extensive isomerization occurs of the *syn* and *anti* groups of the monomeric complex.

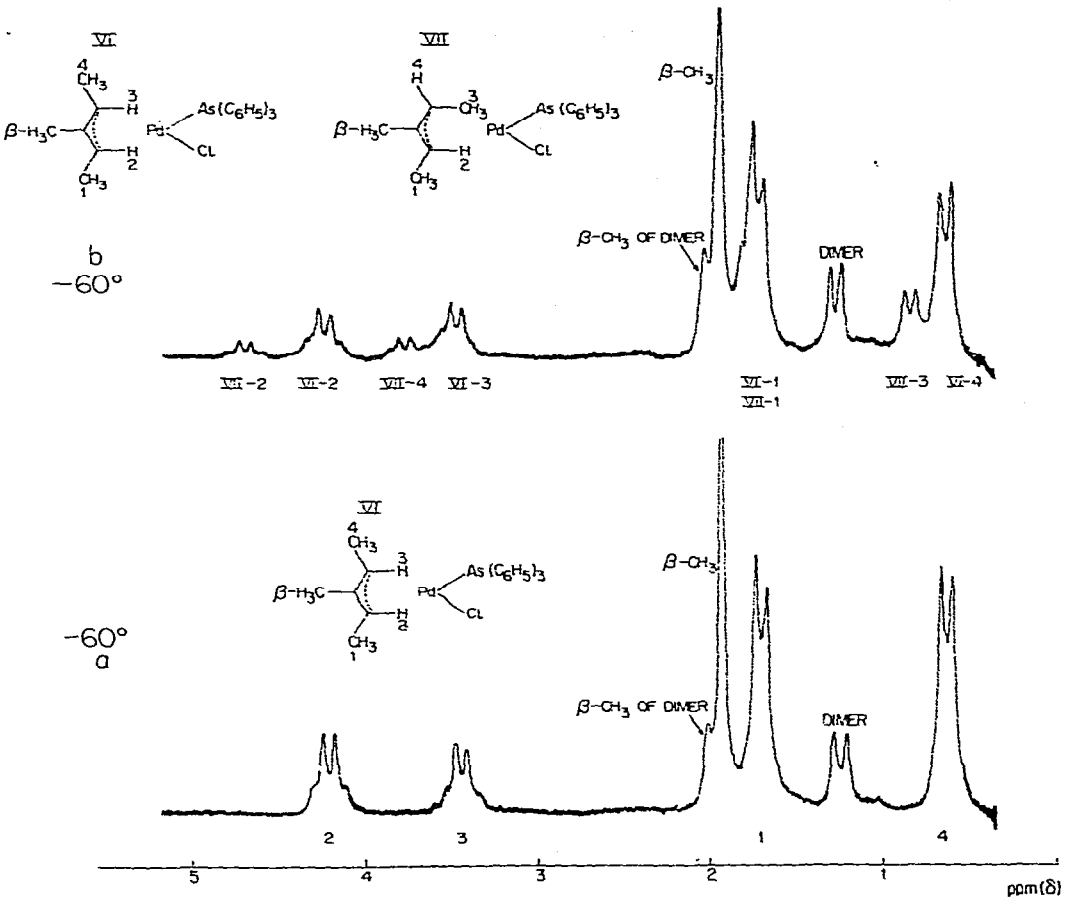


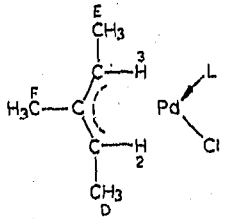
Fig. 3. (a) The NMR spectrum of π-[1-*syn*,2,3-*syn*-$(CH_3)_3C_3H_2$] PdCl($AsPh_3$) at −60° in the presence of dimer in $CDCl_3$. (b) The NMR spectrum of the same mixture at −60° after having been at a temperature of 0°. One new compound is formed, namely (VII) (The intensity of protons (2,3) of the dimer is too small to be visible).

raising the temperature, we see (Fig. 3b) besides the signals of these two compounds also those of only one new complex, which is most probably the compound π-[1-*anti*,2,3-*syn*-$(CH_3)_3C_3H_2$] PdCl($AsPh_3$) (VII). Compound (VII)* is formed from (VI) by interchange of the CH_3 and H groups *cis* to $AsPh_3$. From double resonance experiments it was deduced that the *anti*-CH_3 group of (VII) (*cis* to $AsPh_3$) absorbs at 0.82 ppm (doublet), while the *syn*-proton (*cis* to $AsPh_3$) absorbs at 3.76 ppm (quartet). The *syn*-CH_3 group of (VII) (*trans* to $AsPh_3$) is observed at 1.76 ppm, which is at about the same magnetic field as the analogous *syn*-CH_3 group in (VI) (Fig. 3b). The *anti*-proton of (VII) is found at 4.67 ppm, while the analogous *anti*-proton in (VI) is found at 4.20 ppm (Fig. 3b). This difference is probably due to the different angle which the π-allyl plane makes with the PdCl($AsPh_3$) plane in complex (VII) as com-

* The equilibrium concentration of (VII) is lower than that of (VI), since the situation with a CH_3 group *anti* to β-CH_3 (Fig. 3b) is sterically less favourable.

TABLE 4

CHEMICAL SHIFTS OF THE ALLYLIC PROTONS AND METHYL PROTONS FOR L=PPh_3 [COMPLEX (V), −50°] AND $AsPh_3$ [COMPLEX (VI), −65°]



L	Chemical shifts of groups in the sites				
	2	3	D	E	F
PPh_3	multiplet 4.25 $J[P-H(2)]=9.0$ c/s $J[CH_3-H(2)]=7.0$ c/s	quartet 3.35 $J[CH_3-H(3)]=7.0$ c/s No P-coupling[a]	triplet 1.75 $J(P-CH_3)=8.0$ c/s $J[H(2)-CH_3]=7.0$ c/s	triplet 0.50 $J(P-CH_3)=7.0$ c/s $J[H(3)-CH_3]=7.0$ c/s	singlet 1.86
$AsPh_3$	quartet 4.20 $J[CH_3-H(2)]=6.2$ c/s	quartet 3.45 $J[CH_3-H(3)]$ 6.4 c/s	doublet 1.71 $J[H(2)-CH_3]=6.2$ c/s	doublet 0.63 $J[H(3)-CH_3]=6.4$ c/s	singlet 1.93

[a] In general it is observed that protons only couple with the P nucleus, when they are *trans* to PR_3, while CH_3 groups both *cis* and *trans* to PR_3 couple with P in all the compounds studied.

pared to (VI), owing to the bulkiness of the *anti*-CH_3 group in complex (VII). It seems unlikely that the difference in chemical shifts of the groups *trans* to $AsPh_3$ in (VI) and (VII) should be caused by an isomerization of CH_3 and H *trans* to $AsPh_3$. In that case we would expect the CH_3 groups (*trans* to $AsPh_3$) *syn* and *anti* to β-CH_3 to absorb at different magnetic fields, and not at about the same field of 3.70 ppm*.

A similar behaviour was noted for the case of PPh_3, where, in the presence of dimer, isomerization occurs in the allyl group of the monomer. One new triplet is formed at 0.76 ppm, and one broad multiplet near 4.70 ppm, owing to the formation of an *anti*-CH_3 group and a *syn*-proton (*cis* to PPh_3). The *syn*-CH_3 group *trans* to PPh_3 again absorbs at the same magnetic field as the analogous *syn*-CH_3 group in the non-isomerized compound, while the *anti*-proton *trans* to PPh_3 is not clearly observed owing to its low intensity.

Summarizing, we conclude that for both $L=AsPh_3$ and $L=PPh_3$ isomerization can occur of the methyl group and proton *cis* to L in the compounds π-[1-*syn*,2,3-*syn*-$(CH_3)_3C_3H_2$] PdClL and probably not *trans* to L. We have to assume further that no dissociation of ligand L takes place, since otherwise we would expect the formation of three new isomers *i.e.* a complex with one *syn*-CH_3 group *cis* to L, a complex with a *syn*-CH_3 group *trans* to L, and one with two *syn*-CH_3 groups.

The isomerization** process of these substituted π-allyl compounds is thus exactly analogous to that for $(\pi\text{-}C_4H_7)PdCl(PR_3)$ in the presence of dimer (below $-20°$); however, it is important to note that it can also occur for $L=AsPh_3$.

IV. REACTIONS OF $(\pi\text{-}C_4H_7)PdCl(PR_3)$ WITH EXCESS PR_3

Previously, in the discussion of the kinetic study of the system $[(\pi\text{-}C_4H_7)\text{-}PdCl]_2 + PPh_3$ $(1 < PPh_3/Pd < 1.1)$, we proposed the reaction scheme*** shown on the top of the next page.

Besides the relatively fast bimolecular ligand-exchange reaction (1a) of ML with L ($L=PPh_3$), an ionic product was formed very slowly (15–30 minutes), probably via the five-coordinate intermediate $(\pi\text{-}C_4H_7)PdL_2Cl$ from $(\pi\text{-}C_4H_7)PdLCl$ and L.

Conductance studies with aqueous acetone as solvent by Shaw *et al.*[8] indicated that the formation of ionic species $[(\pi\text{-}C_4H_7)PdL_2]^+Cl^-$ $(= ML_2^+Cl^-)$ is increasingly favoured in the order $SbPh_3 \sim AsPh_3 < PPh_3 < PEt_3 \sim PEt_2Ph \sim PPhMe_2$, which is also approximately the order of increasing electron donor capacity.

NMR studies on systems containing $[(\pi\text{-}C_4H_7)PdCl]_2$ and a ligand L $(L/Pd > 1)$ showed that for $L=PPhMe_2$, $PPhEt_2$ and $P(n\text{-}C_4H_9)_3$ (at about $-40°$ in $CDCl_3$), besides the signals for $(\pi\text{-}C_4H_7)PdLCl$, also signals occurred of the protons in sites (1,4) and (2,3) of the symmetrically bonded π-methallyl group of the ionic compound at about 4.2 and 3.3 ppm from TMS, respectively (Table 5). The latter high field absorption is split into a triplet $\{J[P\text{–}H(2,3)] = 5.0$ c/s$\}$ owing to coupling

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* A model complex where CH_3 groups *trans* to $AsPh_3$ occur both *syn* and *anti* to β-CH_3 is of course π-[1,1,2-$(CH_3)_3C_3H_2$] PdCl($AsPh_3$). In this case the chemical shifts of the two CH_3 groups are 1.82 and 1.49 ppm, *i.e.* a difference of about 0.3 ppm.

** As the CH_3 group is bulky, the isomerization clearly has to go via a σ-allyl intermediate and not by a CH_2 "rotation mechanism"[5].

*** Studied by considering the rates of interchange of the two *syn*-protons and the two *anti*-protons, respectively[3].

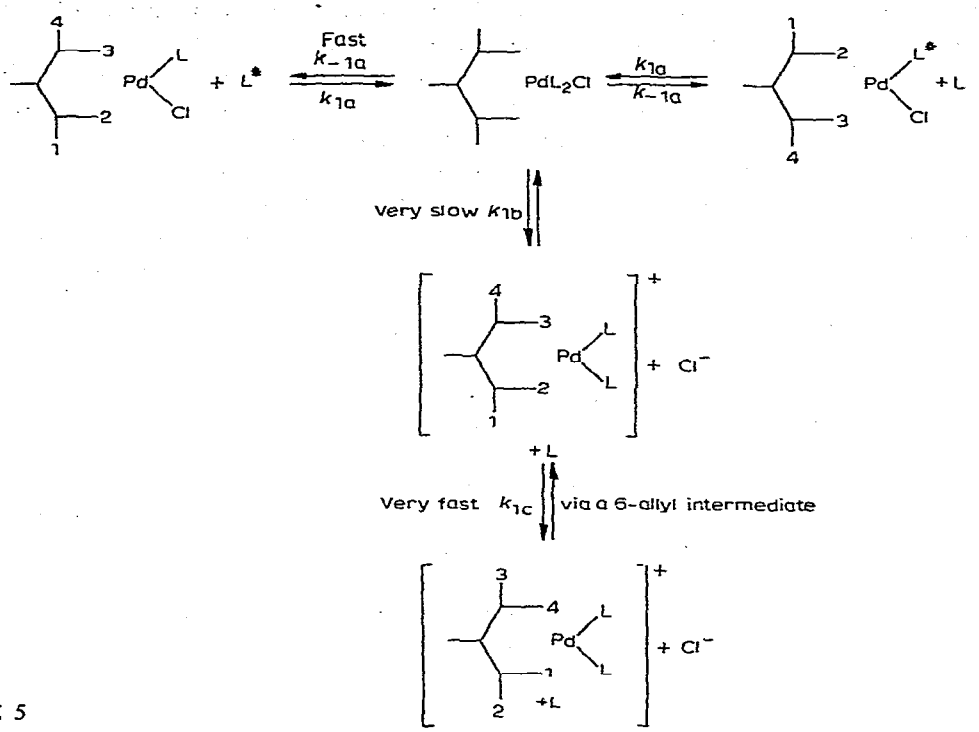
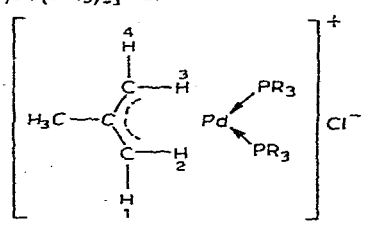


TABLE 5

CHEMICAL SHIFTS OF PROTONS IN SITES (1,4) AND (2,3) IN ppm FROM TMS (δ) OF THE COMPOUNDS $[\pi\text{-}C_4H_7Pd(PR_3)_2]^+Cl^-$



L	Temp. (°C)	Proton absorptions of (1,4)	(2,3)
PPh_3	−40	singlet 3.68	
PPh_2Me	−40	singlet 3.70	
$PPhMe_2$	−35	singlet 4.22	triplet 3.37; J[P–H(2,3)] = 5.0 c/s
$PPhEt_2$	−50	singlet 4.26	triplet[a] 3.30; J[P–H(2,3)] ≅ 5 c/s
$P(n\text{-}C_4H_9)_3$	−35	singlet 4.12	triplet 3.00; J[P–H(2,3)] = 5.0 c/s

[a] The triplet components are of about equal intensity for $PPhEt_2$ owing to virtual coupling. This is unusual, since virtual coupling is much more common when the PR_3 are *trans* to each other than *cis*, as is the case here.

with two equivalent P-nculei (see Fig. 1). For $L=PPh_2Me$ and PPh_3, however, the protons in sites (1,4) and (2,3) of the ionic species absorbed at the same magnetic field*, without showing P-coupling. Obviously, these two ligands enter into a fast exchange process even at low temperature (−50°) [see reaction (1c) of the scheme above]. This reaction (1c) presumably proceeds via a short-lived four-coordinate ionic σ-allyl intermediate:

$$[(\pi\text{-}C_4H_7)Pd(PR_3)_2]^+Cl^- + PR_3 \underset{\pm k_{1c}}{\Longleftrightarrow} [(\sigma\text{-}C_4H_7)Pd(PR_3)_3]^+Cl^-$$
short-lived intermediate

This exchange process is thus fast for bulky ligands such as PPh_3 and PPh_2Me and slow for less bulky ones such as $PPhMe_2$, $PPhEt_2$ and $P(n\text{-}C_4H_9)_3$. Even when the L/Pd ratio is about 4 the reaction (1c) for the last three ligands remains relatively slow.

An increase in temperature gave in all cases a broadening and finally coalescence of the signals of $(\pi\text{-}C_4H_7)PdCl(PR_3)$ and $[(\pi\text{-}C_4H_7)Pd(PR_3)_2]^+Cl^-$. This behaviour can be accounted for by reactions of the type (1a) and (1b) shown in the reaction scheme above for the PPh_3 system[3].

V. DISCUSSION

It is clear that combination of the results of this and previous work[1,2,3] has led to a greatly improved understanding of the reactions occurring in the PPh_3 and $AsPh_3$ systems.

When only the monomer $(\pi\text{-}C_4H_7)PdClL$ and excess ligand L ($L=AsPh_3$[2], PPh_3[3]) are present in solution, we find that for a small excess of L bimolecular ligand exchange reactions take place, whereby the allyl group remains π-bonded to Pd in its rotational movement during the reaction. At the same time an ionic complex is formed of the type $[(\pi\text{-}C_4H_7)PdL_2]^+Cl^-$ (almost nonexistent for $L=AsPh_3$[2]) which itself can give rise to ligand exchange reactions with free ligand L [reaction (1c)]. This exchange reaction was found to be fast for bulky phosphine ligands and slow for less bulky ones; steric factors therefore seem of importance.

At higher temperatures and/or higher L/Pd ratio ligand-dependent "π–σ" reactions are observed, which were studied quantitatively only for $L=AsPh_3$ (first order in $AsPh_3$). Similar "π–σ" reactions also take place in substituted π-methallyl compounds.

For mixtures of $(\pi\text{-}C_4H_7)PdClL$ (=ML) and $[(\pi\text{-}C_4H_7)PdCl]_2$ (=M_2) we observed for $L=PPh_3$ "π–σ" reactions between ML and M_2. At low temperatures (−40°–0°) these reactions involved an interchange of *syn*- and *anti*-protons on one side of the allyl group of ML. This interchange, which was quantitatively studied for $L=P(n\text{-}C_4H_9)_3$, is caused by an interaction of ML with M_2.

$$M^+L + M_2 \leftrightarrows M^+L + M_2$$

(no exchange of PPh_3; interchange of 3 and 4).

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* The ionic complex $[(\pi\text{-}C_4H_7)Pd(PPh_3)_2]^+Cl^-$ has been isolated by Shaw *et al.* (private communication). They showed that a freshly made solution of this complex in $CDCl_3$ gave two absorptions with P-coupling on the high-field one, in exact analogy with the other PR_3 compounds in Table 5. However, the two absorptions coalesce on standing (after ½ h). This is due to slow partial dissociation of the ionic species $ML_2^+Cl^-$ in ML and L. The free ligand L so formed can then react fast with ML [reaction (1a)] and with $ML_2^+Cl^-$ [reaction (1c)]. It is thus clear that the step (1b) is very slow compared with the other ones.

At higher temperatures *syn*- and *anti*-protons on both sides of the allyl group of ML interchange because of a reaction with M_2, again without exchange of PPh_3. The higher frequency factor of this reaction indicated the presence of a preequilibrium[3]. At still higher temperatures chemical exchange reactions between ML and M_2 were also observed[3].

The study of these "monomer–dimer" reactions in the case of phosphine π-methallyl compounds is possible because of the large stability of the Pd–P bond, keeping the concentration of free PR_3 from the dissociation of ML very low. For L = $AsPh_3$ the "monomer–dimer" reactions clearly also take place, as is evidenced by the isomerization of the *syn* and *anti* groups in the complex π-[1-*syn*,2,3-*syn*-$(CH_3)_3C_3H_2$]PdCl($AsPh_3$) in the presence of dimer, in complete analogy with the PPh_3 case. No such reactions could, however, be detected* for (π-C_4H_7)PdCl($AsPh_3$) in the presence of dimer with the aid of linewidth measurements, because the reactions with free $AsPh_3$ dissociated from ML are much faster.

Furthermore, the question on which side of the allyl group of the complex (π-C_4H_7)PdClL and of π-[1-*syn*,2,3-*syn*-$(CH_3)_3C_3H_2$]PdClL isomerization via a σ-allyl intermediate occurs clearly depends very much on the position of the ligand L; *i.e.*, the Pd–C bond of the π-allyl–Pd linkage *trans* to L is preferentially broken (whereby isomerization occurs at the carbon atom *cis* to L**) owing to the weakening effect of the ligand L opposite to it (*trans* effect). This effect is not clearly reflected in the activation energies for various phosphines (Table 2), no doubt because the reaction is not monomolecular, but involves interaction of ML with M_2. The activation energies will then comprise a part due to the attack of M_2 on ML and a part due to the "π–σ" movement.

Although these results have afforded more insight into the monomer–dimer reactions in particular, which evidently occur also for L = $AsPh_3$, as becomes observable for substituted π-methallyl complexes, the question of the molecular mechanism of these reactions still remains unanswered. In previous work[3] we suggested as a possibility an attack of the dimer with its chlorine atom on the monomer; evidently more research is needed to clarify this point.

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* Although a small but definite influence of $[M_2]$ on $1/\tau_2$(ML) has in fact been observed for the (π-C_4H_7)-Pd–$AsPh_3$ system (see ref. 2).

** For models of "π–σ" reactions see refs. 2, 3, 7.

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