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NMR STUDIES OF π-METHALLYLPALLADIUM COMPOUNDS

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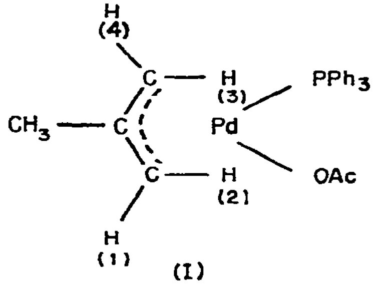
SUMMARY

The preparation and properties are reported of π-methallylpalladium acetate L (L = triphenylphosphine and triphenylarsine). The temperature-dependent NMR spectrum of the adduct of triphenylphosphine shows that the protons *cis* to the phosphine in the π-methallyl group easily isomerize, whereas the other two protons do not exchange in the NMR time-scale below 50°. The process is monomolecular and is assumed to proceed via the well-known π–σ rearrangement. The relative ease of the rearrangement gives some insight into the nature of π–σ reactions in general. At higher temperatures a left-right interchange occurs in the phosphine complex, which is the only reaction observed in the arsine adduct. It is shown that anion exchange does not necessarily lead to left-right interchange of the square-planar complex. It is observed that even before changes in the allyl group occur, anion exchange, in NMR terms, can be extremely fast. Several examples are given of anion exchange in Pd^{II} with retention of configuration.

RESULTS

The proton NMR spectrum of $(\pi\text{-}C_4H_7)Pd(OAc)(PPh_3)$ at several temperatures is given in Fig. 1. The peak assignments have been made by analogy with those of other asymmetric π-allylic systems[1-4]. The protons are numbered as follows:



(I)

The relevant values of the chemical shifts and the coupling constants are for the protons (1) to (4): 4.97, 4.21, 2.51 and 2.84 ppm [$J(P\text{-}H_{(1)}) = 7$ Hz, $J(H_{(1)}\text{-}H_{(4)}) = 2.5$ Hz, $J(P\text{-}H_{(2)}) = 9.5$ Hz]. The methyl peak of the methallyl group occurs at 2.01 ppm

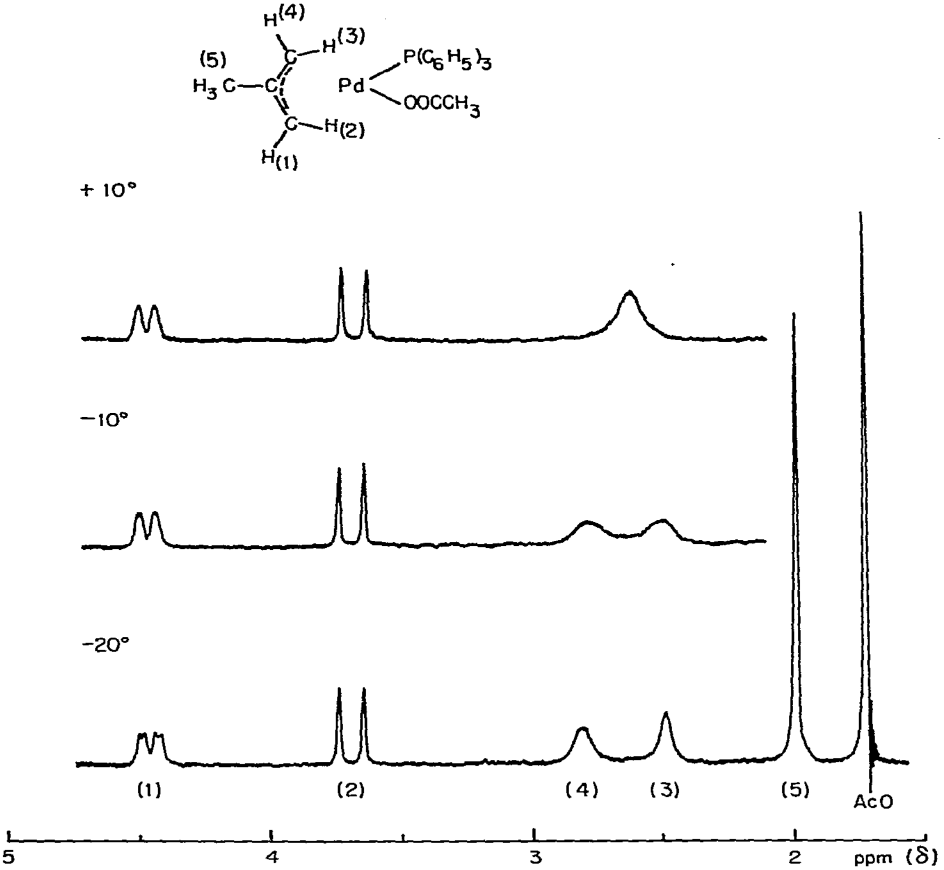


Fig. 1. Proton NMR spectra of (π-C_4H_7)Pd(OAc)(PPh_3) at several temperatures in CD_2Cl_2. Concentration 0.48 mole·l^{-1}.

downfield from TMS and that of the acetate at 1.75 ppm.

At about −30° the interchange of protons (3) and (4) starts in the NMR time scale. The temperature of collapse of this first process is about 0°. Variation in concentration between 0.1 and 0.5 mole · l^{-1} indicated the process to be monomolecular in CD_2Cl_2. The signals of protons (1) and (2) remain sharp below 45°, except for the small coupling $J(H_{(1)}$–$H_{(4)})$, which disappears already between −30° and −25°. The reaction rate of the first process is not influenced by the addition of π-methallylpalladium acetate dimer (0.05–0.20 mole · l^{-1}).

At 50° the broadening of signals (1) and (2) begins, together with that of the sharp [(3),(4)] signal.

When establishing the influence of various soluble metal acetates (both donors and acceptors) we failed to find reagents capable of affecting the reactions of the allyl group in the NMR time scale. Phenylmercury acetate leads to a coalescence of the two acetate absorptions at −40° (chemical shift difference 20 Hz).

Fig. 2 shows some spectra of mixtures of (π-C_4H_7)Pd(X)(PPh_3) (with X = Cl

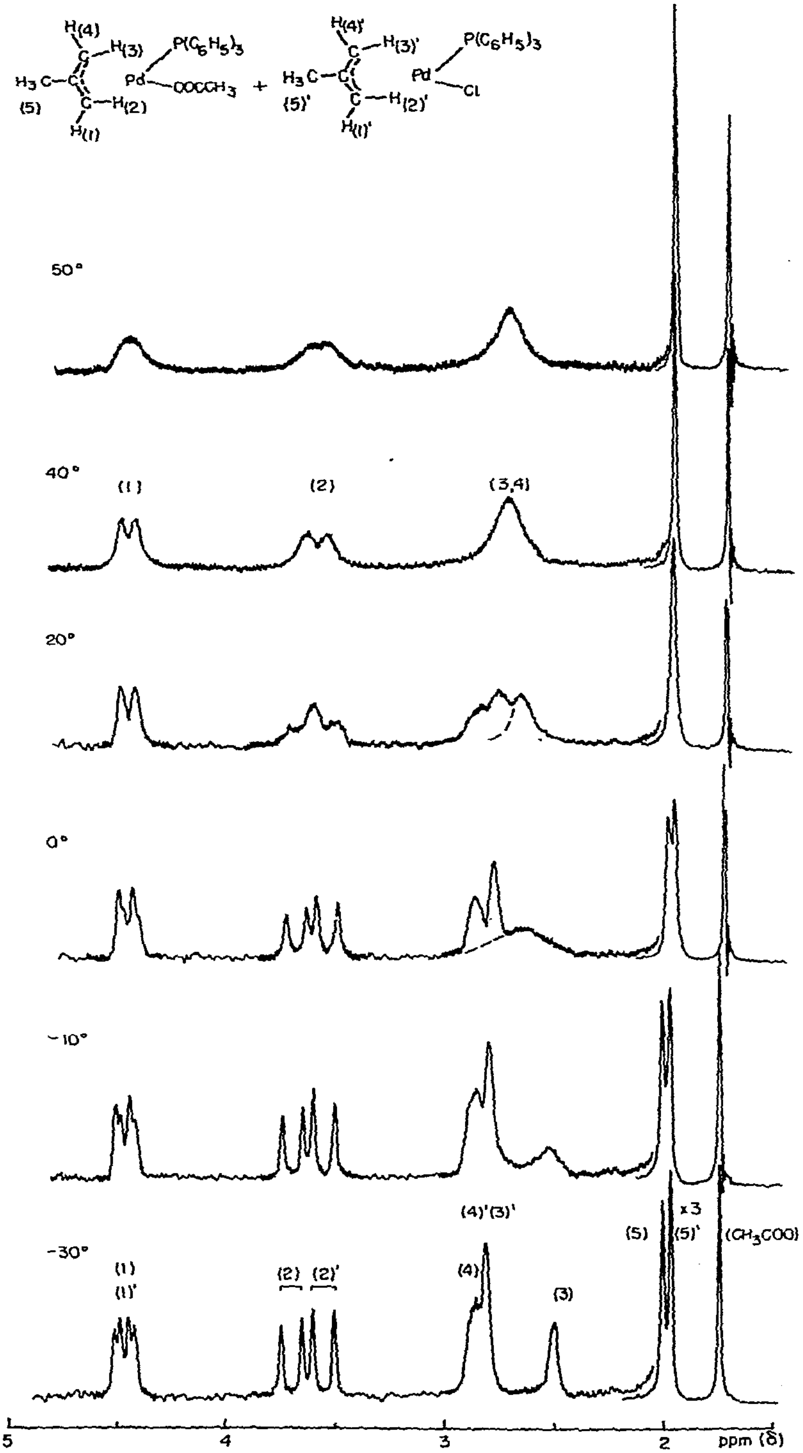


Fig. 2. Spectra of $(\pi\text{-}C_4H_7)PdCl(PPh_3)$ and $(\pi\text{-}C_4H_7)Pd(OAc)(PPh_3)$. Both concentrations 0.30 mole·l^{-1}.

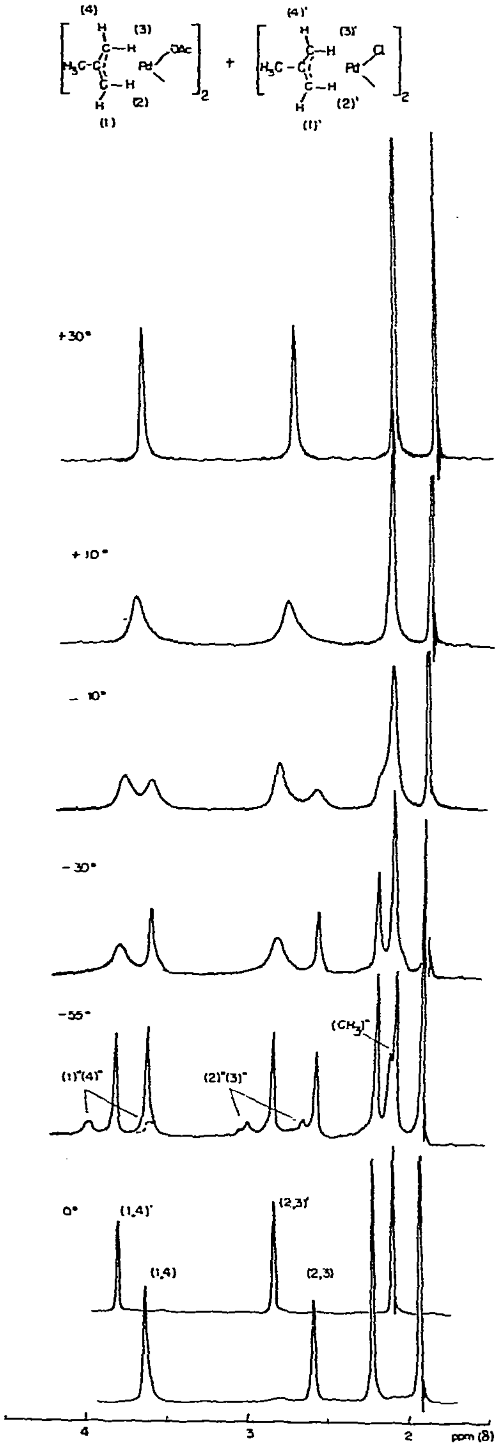


Fig. 3. NMR spectra of the dimers $[(\pi\text{-}C_4H_7)PdCl]_2$ and $[(\pi\text{-}C_4H_7)Pd(OAc)]_2$.

and OAc). It can be seen that the isomerization rate of (3) and (4) of the acetate complex is not influenced by the chloride complex added. The spectrum is just a summation of the spectra of the two compounds below 0°. From the methyl peaks at about 2 ppm it is seen that anion exchange begins at about 0°. The broadening of the other signals is also ascribed to this anion exchange. In those cases where the chemical shift differences are small [protons (1)' and (1) of chloride and acetate, and the two methyl peaks] we soon observe a sharp signal (1), indicating that no rearrangements occur in the allyl group. At 40° protons (2)' and (2) also coalesce and a phosphorus coupling is observed again.

With triphenylphosphine added the usual[5] reactions are observed, but the (3),(4)-exchange is not influenced.

Another example of anion exchange is depicted in Fig. 3, where the NMR spectra of the mixtures of acetate and chloride dimers are recorded. As the chemical shifts of the methallyl groups differ in the two dimers we can observe the exchange of the anions, which appears to be very fast. Some new signals are present, which are assigned to the mixed dimer $[(\pi\text{-}C_4H_7)Pd]_2(OAc)(Cl)$. The exchange between the mixed dimer and the chloride dimer is markedly faster than that between the mixed dimer and acetate dimer.

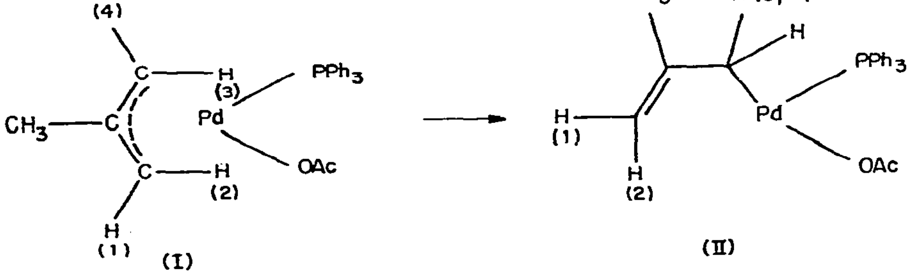
The spectra of $(\pi\text{-}C_4H_7)Pd(OAc)(AsPh_3)$ are recorded in Fig. 4. As usual[4], upon raising the temperature all the signals (1)–(4) broaden.

DISCUSSION

The π–σ reaction in allylpalladium compounds

The rearrangements taking place in allylic transition-metal compounds have been extensively studied in our laboratory[4–7]. It was found that in phosphine adducts of π-methallylpalladium chloride exchange of protons (3) and (4) occurs, which is catalysed by dimeric Pd^{II} and Rh^{I} compounds[5,7]. Although the kinetics were thoroughly studied, no mechanisms were put forward for these unusual reactions. Therefore it seemed worth while to study similar compounds containing anions that could also be observed in the NMR spectrum in order to estimate the role of the anion. The first systems investigated were those containing acetate anions. The compound $[(\pi\text{-}C_3H_5)Pd(OAc)]_2$ is known in the literature[8] and a crystal structure has been reported[9].

The intramolecular rearrangement in $(\pi\text{-}C_4H_7)Pd(OAc)(PPh_3)$ leading to coalescence of protons (3) and (4) is not observed in the corresponding chloride complex. Schematically the process (Fig. 1) can be visualized as:



(I) (II)

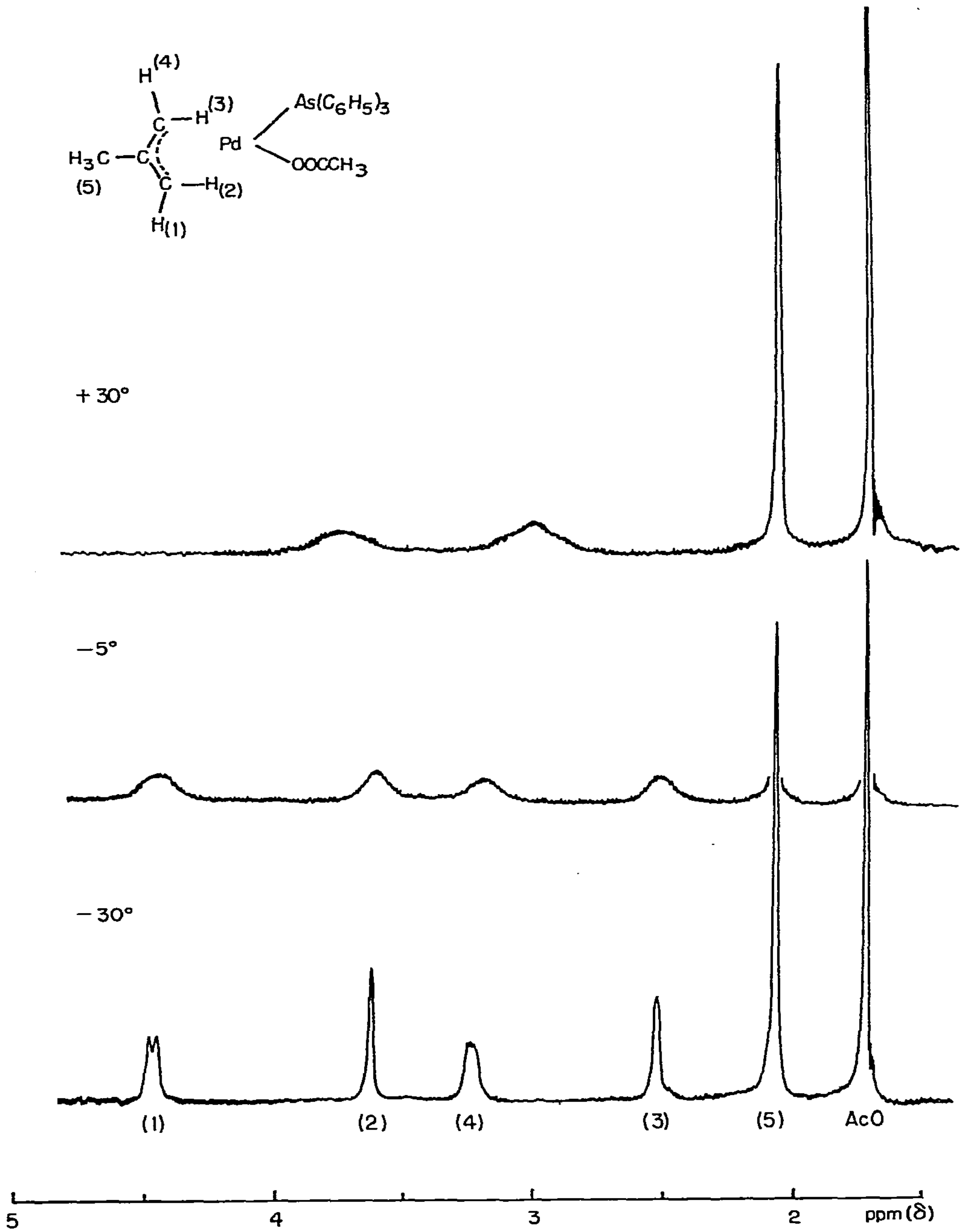
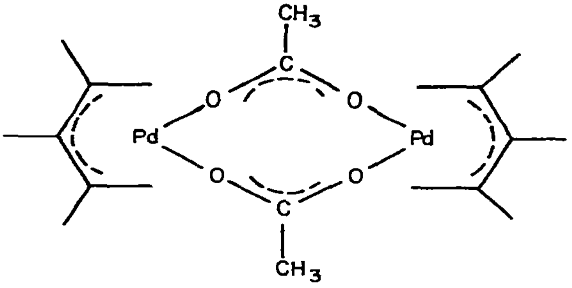


Fig. 4. NMR spectra of (π-C_4H_7)Pd(OAc)($AsPh_3$) in CD_2Cl_2. Concentration 0.30 mole·l^{-1}.

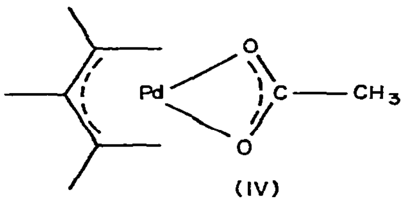
The acetate complex differs in two respects from the chloride complex: (1) the acetate anion may act as a bidentate, and (2) its electronic properties may be different. Both differences may account for the anomalous behaviour of the acetate compound.

The bidentate character of the acetate ion is of limited importance. The distance between the two oxygen atoms in an acetate group (2.2 Å) is much smaller than the distance required for complex formation between a palladium ion and two *cis*-ligands with oxygen atoms as donor atoms (3.0 Å). As a result, (π-C_3H_5)Pd(OAc) is dimeric[9] with the schematic structure (III),



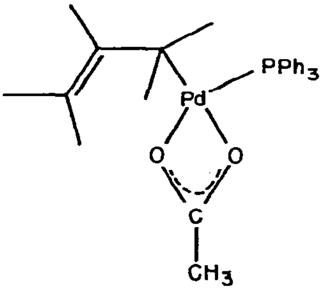
(III)

and not monomeric (IV).



(IV)

According to molecular-weight determinations (π-C_4H_7)Pd(OAc)(PPh_3) is monomeric. The stabilization of the σ-intermediate (V) as caused by a bidentate acetate ion must be small, although a definite influence may be present:



(V)

It is supposed here that the character of the metal–anion bond plays an important role in the π–σ reaction. From the crystal structure of (π-C_4H_7)PdCl(PPh_3) it is known[10] that the allyl group is asymmetric; the asymmetry, however, does not necessarily lead to a bonding picture differing from the symmetric π-allyl group[4], as is suggested by Powell *et al.*[11]. The asymmetry in allylpalladium complexes is often referred to as a *trans*-effect. Strictly speaking, *trans-effect*[12] only denotes the ability of ligands to labilize the metal–ligand bond *trans* to it towards substitution. Although no substitution occurs during a π–σ rearrangement, the term *trans*-effect seems to be very useful (*vide infra*). A static *trans*-effect as observed from X-ray studies is also found in allylpalladium complexes[10], which can be compared with the findings for substituted chloroplatinum compounds[21].

Bonding in π-allyl-metal compounds with special reference to π–σ rearrangements

A bonding scheme for π-allyl compounds has been given by Vrieze and Cossee[4]. The present approach differs from theirs, but the result is essentially the same. The half-sandwich model given previously[4] is particularly useful when studying the π-rotation (or left–right interchange) with simultaneous ligand-exchange. The present scheme gives a simple argument for the tilted structure of π-allyl compounds and it can be used when discussing the π–σ reaction.

As the symmetry in π-allyl–metal complexes is rather low, considerable mixing of orbitals will occur[4]. We will first build up the symmetric complex (with one plane of symmetry) and then introduce two different ligands. Starting from the Hückel-orbitals for the π-allyl anion, denoted ψ_1, ψ_2 and ψ_3 (increasing energy) and the divalent Pd-ion requiring square-planar coordination, the following simplified scheme is obtained. The lowest-lying totally symmetric filled ψ_1 will combine with the empty Pd(5*s*) orbital and a combination of Pd($5p_x$ and $5p_y$). As the xy-plane is not a plane of symmetry, several other orbitals (such as $5p_z$) may also contribute. In order to obtain a maximum overlap no particular restrictions for the steric arrangement of the compound are present, except that the carbon *p*-orbitals are directed parallel to the coordination square.

Energy considerations[4] lead to the conclusion that the most important contribution to the bonding comes from the interaction of the (formally) filled ψ_2 orbital of the allyl anion and the $d_{(x^2-y^2)}$ orbital. The most favourable configuration is drawn in Fig. 5a; it has the two carbon atoms in the plane of the metal ion and the two ligands A and B, the allyl anion thus acting as a bidentate ligand. The allyl plane is perpendicular to the xy-plane. The next step is the construction of a configuration suitable for back-donation from filled metal orbitals to the empty ψ_3. The latter orbital has a nodal plane perpendicular to the allyl plane intersecting the two carbon–carbon bonds (Fig. 5b). Obviously, maximum overlap of ψ_3 and Pd-p_z and a combination Pd($d_{xz}+d_{yz}$) is obtained when the allyl-nodal plane coincides with the metal–nodal plane (xy) determined by Pd, A and B. This is illustrated in Fig. 5b, where the two terminal carbon atoms are placed below the xy-plane.

However, this configuration gives a considerable decrease in overlap of the most important bonding combination (Fig. 5a). This is easily resolved by a tilt of the allyl plane in such a way that the *p*-orbitals of the terminal carbon atoms give a good overlap with $d_{(x^2-y^2)}$ and that the nodal (xy) plane still approximately intersects the two nodes of the ψ_3 function. The back-bonding interaction cannot be prevented from being diminished. A similar or even larger advantage of the bent structure is that the distance from the central carbon atom to the metal ion in Fig. 5c is smaller than the corresponding distance in Fig. 5a, whereas the ψ_2 interaction is maintained. Hence, starting from a, the tilting enlarges the interaction of ψ_1 with the empty metal orbitals. In practice the dihedral angle of the allyl plane and the M–A–B plane turns out to be[13] of the order of 120°.

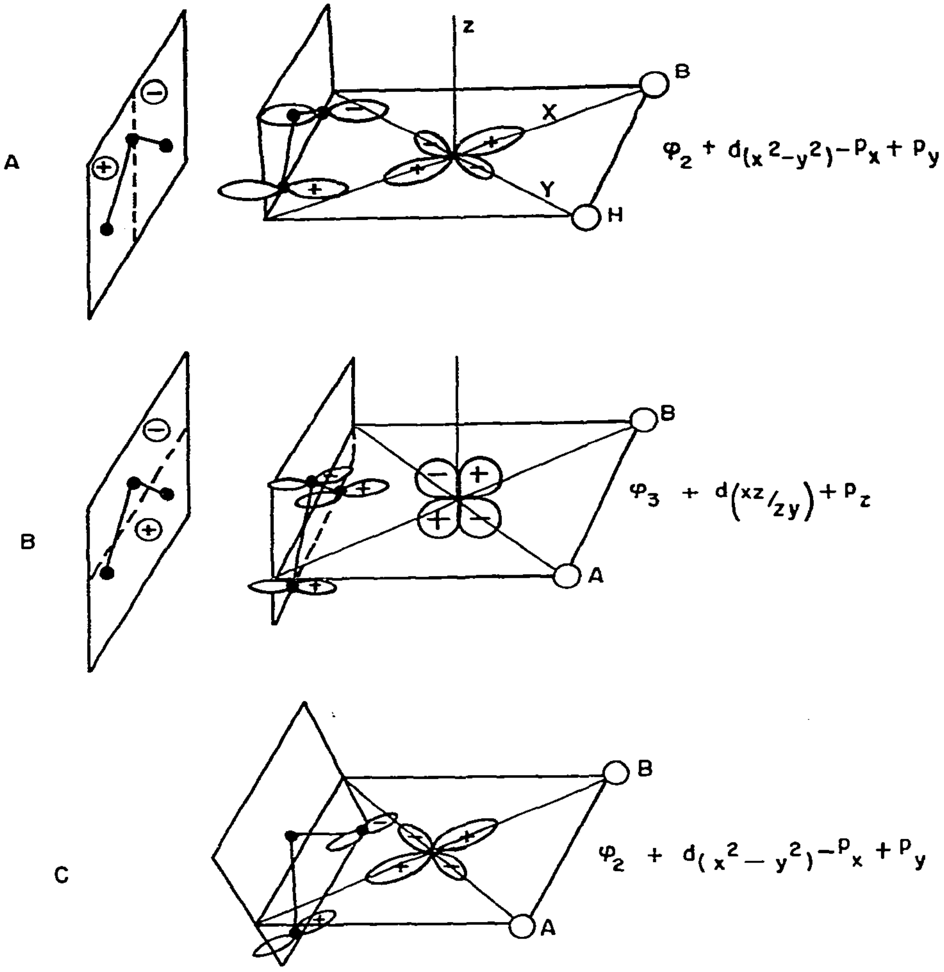


Fig. 5. The allyl group in a square-planar d_8 system.

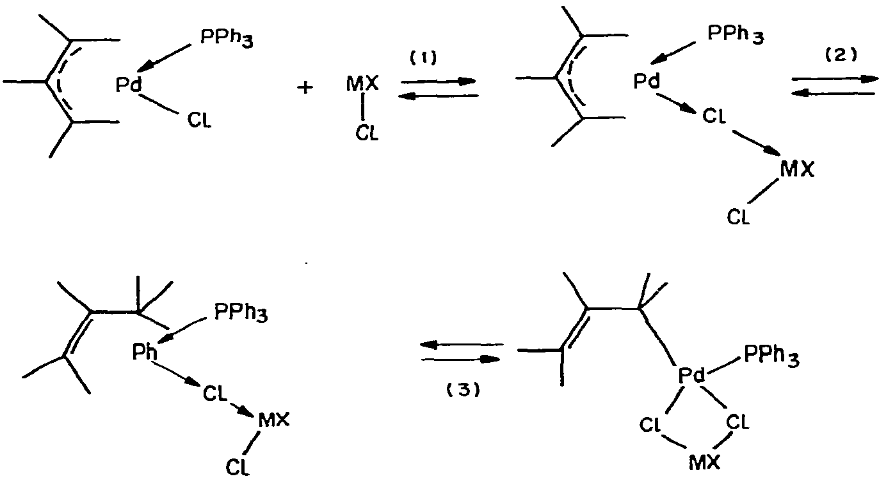
Bonding in asymmetric allyl–metal compounds

When A and B are different ligands (*e.g.* Cl^- and PPh_3) the allyl group is asymmetric, as appears from both structural data[10] and NMR parameters. The effect in the ground state can be accounted for in MO terms by assuming that Pd(p) orbitals are involved, and that π-back-donation plays a role[12]. In our simplified picture a phosphine ligand in the B-position and a chloride ion in the A-position give a relatively small contribution of p_x (compared with p_y) in the bonding orbital simply denoted ψ_2. The electron density of the highest filled ligand orbital ψ_2 will therefore be slightly higher on the carbon atom *trans* to the ligand with the *smallest trans*-effect. The effect on ψ_1 is assumed to be smaller, since ψ_1 has a lower energy. In the extreme case the highest occupied allyl orbital is a σ-bond to the metal (ψ_2) and the ψ_1 orbital is converted into the π-orbital *trans* to the phosphine. It is now clear why in a complex with $B = OAc^-$ and $A = PPh_3$ an intramolecular π–σ reaction is observed at an attainable temperature and not when $B = Cl^-$. The difference in *trans*-effect is larger for the former combination, and if a π–σ reaction occurs, it should be found for the acetates at lower temperatures.

It should be borne in mind, however, that the molecule is a very short time in the σ-allyl form. The bonding is only weakly influenced, but the effect is just large enough to allow a π–σ reaction interchanging (3) and (4) to occur at a temperature about 100° lower than that of the π–σ reaction at the other end of the molecule interchanging (1) and (2). The dimeric chloride also shows a monomolecular π–σ reaction at 90°, which can be observed using double resonance[15]. The *trans*-effects of amines and chloride ions[14] are about the same and therefore no π–σ reactions are expected below 90°, which is indeed observed[15]. In complexes containing arsines[17] or amines[18] ligand exchange mechanisms dominate.

π–σ reactions initiated by acceptor molecules

Adopting the above view on π–σ rearrangements a reasonable mechanism for the monomer–dimer reactions observed in allylpalladium–phosphine systems[5] can be suggested. When the donating capacity of the chloride ion is reduced by an acceptor molecule [*e.g.* the dimer $(\pi\text{-}C_3H_5PdCl)_2$ or the dissociated dimers $\pi\text{-}C_3H_5\text{-}PdCl$ or (diene)$RhCl$[7]] the differences in *trans*-effects (PPh_3 and Cl^-) increase, giving a situation comparable with the acetate monomer. The following steps are considered:



The importance of the last step is as yet unknown, but as in the case of the acetate complex, we suppose that both the electronic effect [step (2)] and the bidentate effect [step (3)] play a role in the π–σ reaction.

Anion exchange reactions

In the systems studied here two routes of studying anion exchange* can be

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* Recently[20] exchange reactions of allylpalladium thiocyanate and halide dimers have been reported. This is a type (1) system where the exchanging anion itself is not observed in the spectrum.

distinguished:

(1). RM–OAc+R'M–Cl

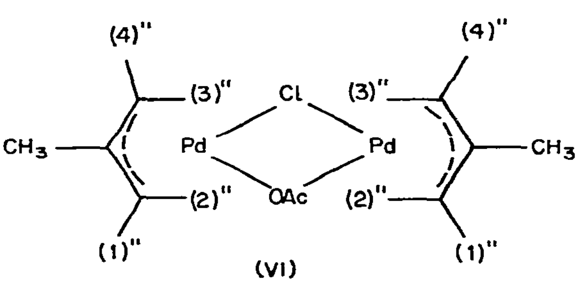
(2). RM–OAc+QM–OAc

In case (1) only one anion is observed in the NMR spectrum and this signal remains unchanged when the OAc passes to another RM group. However, two R-signals occur and transfer of an anion (or an R-group) gives rise to broadening and coalescence of the two R-peaks. Instead of OAc^- we may take of course any anion other than Cl^-. In case (2) two different anion peaks are observed and here we can study anion (or R, Q) exchange on the anion signals themselves, where the R and Q signals are unaffected, unless (R)spin–(anion)spin coupling occurs.

An example of case (1) is presented in Fig. 2, giving the spectra of mixtures of $(\pi\text{-}C_4H_7)Pd(OAc)(PPh_3)$ and $(\pi\text{-}C_4H_7)PdCl(PPh_3)$. Several interesting features can be observed in the spectra, but attention will be paid here to the main points. Evidently, the π–σ reaction of the acetate is not influenced by the addition of the chloride monomer, although at about 0° the anion exchange becomes visible in the NMR spectrum. In this medium the exchange is presumably a concerted process involving a double anion bridge. The conclusion here is that the formation of a double anion bridge between two monomers does not catalyse the π–σ reaction. This supports the conclusion of the previous section in that it is the bridge formation of monomeric chlorides with electron-*withdrawing* dimers (or half-dimers) that stimulates the π–σ reaction, while the formation of a double anion bridge is less important, especially when the attacking molecule is not electron-withdrawing.

Comparison of Fig. 1 and Fig. 2 leads to the conclusion that the left–right interchange (π-rotation[4]) occurs at slightly lower temperatures. A detailed concentration study is necessary. The qualitative observations are in accordance with the proposed[5,7] mechanism for concentration-dependent π-rotation accompanied by anion exchange.

Another example of case (1) is the anion exchange between two dimers $[(\pi\text{-}C_4H_7)PdCl]_2$ and $[(\pi\text{-}C_4H_7)PdOAc]_2$. Marked dissociation of dimers[5] occurs in contrast to phosphine complex monomers. This dissociation, and the formation of mixed dimers $(\pi\text{-}C_4H_7)PdOAcClPd(\pi\text{-}C_4H_7)$ favour a fast anion exchange. In Fig. 3 the numbers refer to the protons in the acetate, the primed numbers to the protons in the chloride and the double-primed numbers to the protons in the mixed dimer (VI):



(VI)

The compound is asymmetric and the *syn*-protons (1)" and (4)" have different chemical shifts (as for the *anti*-protons). On the basis of the *trans*-effect the protons (3)" and (4)" would be expected to occur at higher field than the protons (2)" and (1)", respectively.

At about $-55°$ at least three compounds are observed in the NMR spectrum*. In a 1/1 mixture of Cl–OAc the percentage of mixed dimer amounts to about twenty.

At $-30°$ the signals of the mixed dimer and the chloride dimer coalesce. At higher temperatures ($-20°$) the exchange of acetate dimer can be observed in the NMR spectrum. Finally, at $+30°$ the average signals of the dimers are obtained. A fast anion exchange is observed, whereas a π–σ reaction is absent at this temperature, as is to be expected. It is tentatively concluded that chloride ion exchange is faster than acetate ion exchange. We assume that in monomer/dimer mixtures of chlorides also anion exchange will occur, (which unfortunately cannot be observed with chlorine NMR measurements) even before any change in the proton spectrum is detected. Anion transfers appear to be much faster than ligand exchange. The stereochemistry of ligands and chloride ions and the bond strenghts may explain this difference. The chloride ion can be attacked from any direction by a metal ion, whereas the phosphine has only one coordination site, which is already bonded to a metal atom.

Anion exchange in Pd^{II} complexes with retention of configuration

It is well-known[12] that ligand exchange processes in palladium(II) complexes are very fast and without retention of configuration. In platinum(II) complexes exchange is much slower and the configuration is retained. We suggest that the latter rule should read that exchange with retention of configuration occurs at lower temperature than exchange with loss of configuration. Several examples are found indicating that the same rule holds for Pd^{II} and Rh^{I} complexes as far as anion exchange is concerned (*cf.* ligand exchange in ref. 4). Comparison with the "classic" substitution in Pt^{II}, however, is difficult, since *cis*- and *trans*-forms have different energies and this energy gap is larger in Pt^{II} compounds.

The advantage of the study of substitution processes with NMR is that although the *cis/trans* isomers may be energetically identical, it can be deduced whether substitution occurs with retention or loss of configuration. The criterion applied here to palladium complexes is therefore more reliable than the one found in studies of substitution in platinum complexes with retention of configuration where the possible isomers have different energies.

The first example of anion exchange with retention of configuration has already been shown in Fig. 2. The X-exchange in $(\pi\text{-}C_4H_7)PdX(PPh_3)$ ($X=Cl^-$ and OAc^-) is visible at 0° and evidently no left–right interchange at a rate of 3 sec^{-1} occurs below 40°.

The second example is a type (2) anion exchange, RM–OAc+QM–OAc, where RM is the monomeric phosphine complex and QM is the dimer. In this spectrum (Fig. 6) we observe two C_4H_7 absorptions as well as two acetate CH_3 absorptions. In this case a broadening of the acetate peaks occurs, but the R- and Q-signals remain sharp. Evidently, the anion exchange with retention of configuration starts 50° below the exchange of protons (1) and (4), and of protons (2) and (3) of the monomer.

At 10° the acetate signals coalesce. For the sake of completeness it may be mentioned that phosphine exchange from monomer to dimer can be observed in the NMR time scale at about 70° (not shown).

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* Details of several carboxylate–palladium spectra will be published separately.

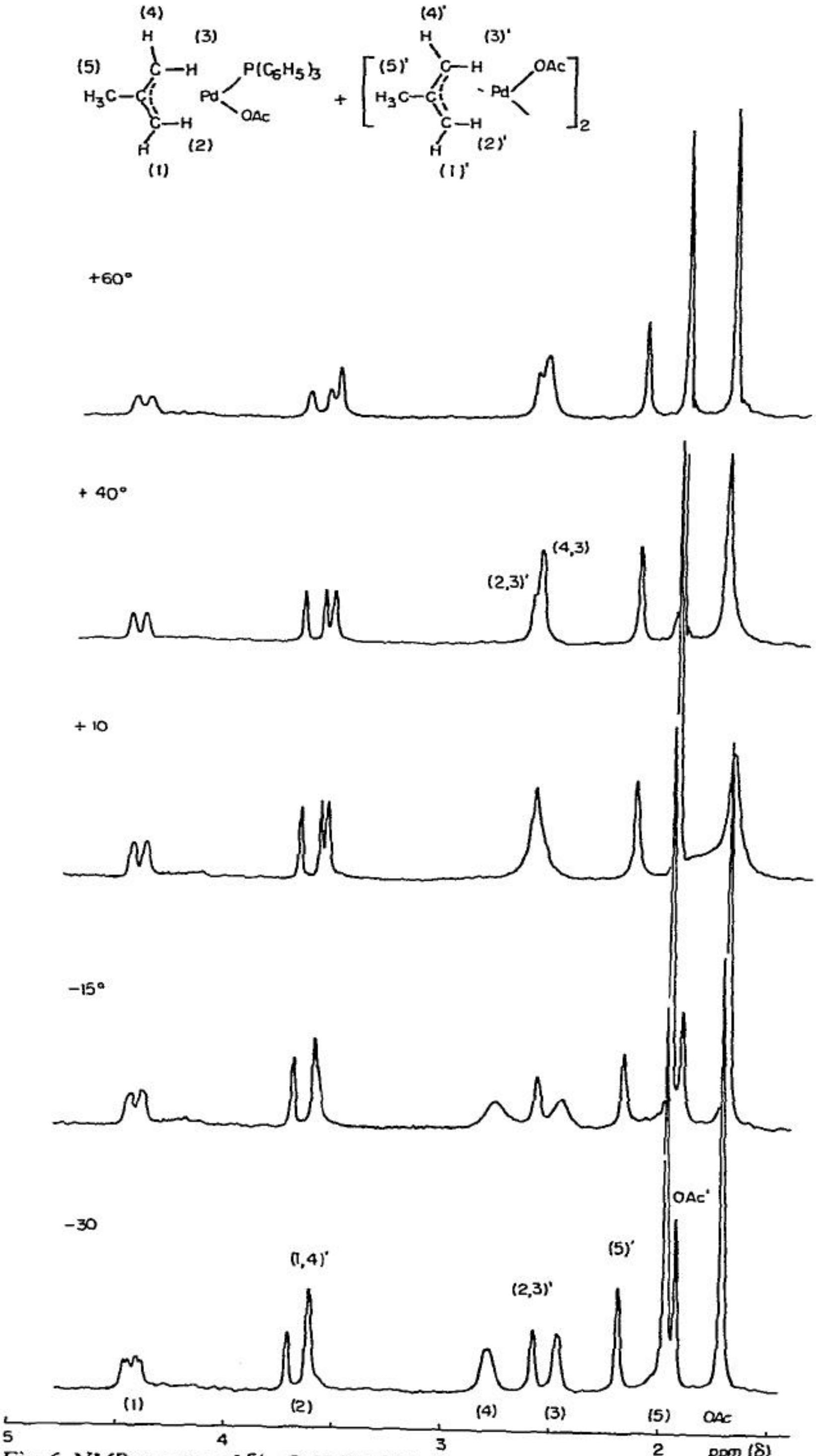
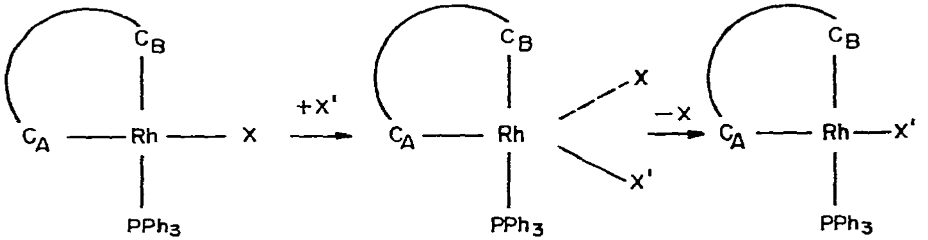


Fig. 6. NMR spectra of $[(\pi\text{-}C_4H_7)Pd(OAc)]_2$ and $(\pi\text{-}C_4H_7)Pd(OAc)(PPh_3)$ in CD_2Cl_2. Concentrations 0.03 and 0.24 mole·l^{-1}, respectively.

Anion exchange in (π-C_4H_7)Pd(OAc)(PPh_3) and PhHgOAc (type 2) is extremely fast in 10/1 solution in CD_2Cl_2. The acetate signals are in slow exchange at −80°, intermediate at −60°, and in fast exchange in NMR terms at −40° (chemical shift difference 18 Hz). In contrast to the reaction of similar compounds with mercury dichloride[19] no mercury–phosphine adducts are formed when phenylmercury chloride is used.

Finally, an example of rhodium(I) is mentioned. In the type (2) system consisting of (COD)Rh(OAc)(PPh_3) and [(COD)Rh(OAc)$]_2$ the acetate exchange with retention of configuration of the monomer is faster than the observed left-right interchange of the olefinic groups (COD = 1,5-cyclooctadiene).

The mechanism of the substitution presumably involves a trigonal bipyramidal structure[12]:



Ligand exchange of monomer with free ligand on the other hand is usually a process without retention of configuration[4,5]. It should be noted that a possible retention of configuration can only be found when a nuclear coupling caused by the ligand on the organic moiety occurs: disappearance of the coupling without A–B interchange indicates exchange with retention of configuration, and simultaneous disappearance of the coupling and A–B exchange broadening indicates the opposite. When such a coupling is not present the only exchange that can be observed (on the allyl group or the diene) is an exchange without retention of configuration (A–B interchange).

(π-C_4H_7)Pd(OAc)($AsPh_3$)

The NMR spectrum of the arsine monomer is shown in Fig. 4. A simultaneous broadening of all four signals (1–4) is observed. This behaviour has been found for all arsine systems[4] and is attributed to dissociation of the monomer, followed by fast ligand exchange.

EXPERIMENTAL

The NMR spectra were recorded in CD_2Cl_2 with a Varian spectrometer HA 100; low temperatures were obtained with Varian variable-temperature dewar inserts. TMS (tetramethylsilane) was used as an internal standard.

Molecular weights were determined with a Mechrolab Osmometer Model 301 A in dichloroethane.

The complex [(π-C_4H_7)Pd(OAc)$]_2$ was prepared from the corresponding chloride and silver acetate in acetone[8]. Triphenylphosphine and triphenylarsine were carefully purified by recrystallization from ethanol under oxygen-free nitrogen. The monomers were prepared from the calculated amounts of dimer and ligand in chloroform. Excess pentane was added. Upon cooling overnight yellow crystals were obtained. The compounds were stored under nitrogen at −20°.

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