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# LOW-TEMPERATURE NMR STUDIES OF DIMERIC PALLADIUM SALTS

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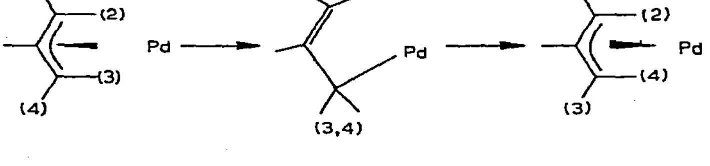
## SUMMARY

The preparation and properties of a number of allylic palladium carboxylates and chlorides are reported. The NMR spectra show that the allyl signals of both the carboxylate and the chloride dimers split at low temperatures (−80° to 40°) in solution, behaviour which is attributed to the freezing out of the transition between several isomers. The temperature dependence of the spectra of the complexes containing dicarboxylates confirms the mechanism proposed previously. In spite of the long distance the chemical shifts of the two allyl groups at both ends of the $PdCl_2Pd$ unit of the dimeric chlorides are influenced by their relative orientation, as is apparent from the NMR spectra. The explanation of the spectral behaviour is based on the assumption that in many allyl complexes the structure known from the solid is not the only one and sometimes not even the most stable one in solution.

## INTRODUCTION

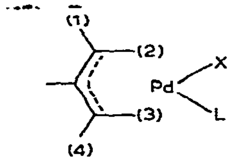
The 1,2,3-*hapto*-allyl metal group, also denoted as π-allyl metal, has in recent years been the subject of extensive studies[1]. In particular, the allyl complexes of the Group VIII metals have attracted much attention because of their use as catalysts in many types of reactions: dimerization[2], polymerization[3] and insertion reactions with CO and $SO_2$[4]. In addition to the studies of the catalytic properties of the above compounds, a large number of papers have been published on the NMR spectra of, in particular, the more stable compounds of iron and palladium. Generally speaking the cobalt and nickel compounds are more active as catalysts, but they are consequently less stable. The palladium complexes appeared to be very interesting because the allyl group and other ligands show rearrangement and exchange reactions at such rates that they can be followed in the NMR spectrum as line broadenings.

The first kind of reaction found is the π–σ–π rearrangement involving interchange of of *syn-* and *anti*-protons.



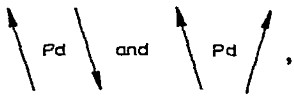
The proof of the detailed mechanism has been given recently[5]. This mechanism for (3, 4) interchange requires a reattachment of the palladium at the other side of the olefin group, which means that the palladium atom ends up at the other side of the allyl plane.

The second reaction[6], called π-rotation, can only be observed with the NMR technique in asymmetric complexes, *e.g.* of the type



In this complex the hydrogens 1, 2, 3 and 4 exhibit different chemical shifts. If an interchange of X and L occurs, the protons 1 and 2 will also exchange their chemical positions with 4 and 3, respectively. This interchange of X and L can take place during an exchange of X or L with excess X or L in a five-coordinate species. Association with other X donors may lead to the same phenomenon. It has been found that an exchange reaction need not necessarily lead to left-right interchange of the allyl group[7]. This means that exchange may occur with retention of configuration.

A third type of reaction is found in systems containing more than one isomer, due to the presence of two allyl groups in one molecule. An example[8] is the compound diallylpalladium, which has an NMR spectrum consisting of two $AM_2X_2$ patterns in the ratio 3/1. This arises from an equilibrium mixture of the two forms



where the arrows stand for the allyl groups. The mechanism of the exchange between the two forms is explained as a π–σ–π rearrangement.

In this paper attention will be paid to compounds containing at least two palladium atoms per molecule, and showing similar isomerism due to the "arrow" nature of the allyl group. The low-temperature behaviour of allylpalladium acetates has been reported in short communications by Powell[9] and, together with some dicarboxylate data, by us[10]. In these molecules two allyl groups bonded to different metal atoms have chemical shifts depending on their relative orientation. This effect has also been found now, although less pronounced, in the palladium compounds containing bridging chloride ions.

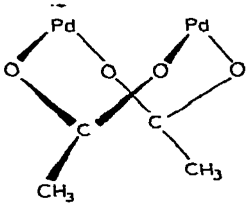
## RESULTS AND DISCUSSION

### *Carboxylates*

The NMR spectra of the dimeric allylpalladium acetates show interesting features in chlorodeuterocarbons at temperatures between −80° and 20°. (Vapour-pressure measurements with a Mechrolab osmometer showed their formulation as dimers to be correct at 33° in dichloroethane.)

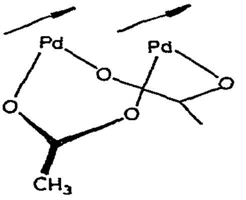
At 20° one methallyl species is present in the spectrum of methallylpalladium acetate. When the temperature is lowered all the signals broaden until at −40° two methallyl groups show up in the ratio of about 5/1. This ratio is solvent-dependent (83/17 in $CDCl_3$, 81/19 in $C_2D_4Cl_2$, 87/13 in $CD_2Cl_2$ at −25°) and evidently a rapid exchange between two different molecules is involved. A further splitting of the smaller absorption lines occurs at still lower temperatures and at −80° we see three sets of lines (with an intensity ratio ≈84/8/8) due to three different methallyl groups. This last splitting cannot be observed in $C_2D_4Cl_2$, because of its high melting point (−35°). The chemical shifts at −80° for the methallyl groups (solvent $CD_2Cl_2$) are: (*a*) 1.98; 2.51; 3.68 ppm downfield from TMS, (*b*) 2.00 and 2.17; 2.72 and 2.97; 3.55 and (not seen) 3.67 ppm downfield from TMS. The latter estimate is based on the fact that the average of the two peaks is seen at 3.61 at higher temperatures (−45° to 55°). The methyl group of the acetate at 2.24 ppm remains unchanged. The splitting of the small lines occurs in a 1/1 ratio, indicating that this must be due to an intramolecular phenomenon.

It was suggested[9,10] that the species with the highest concentration (80–90%) has a symmetric dimeric structure, and the second species an asymmetric dimeric structure. This interpretation is based on the assumption that in solution the ring of the dimer has a conformation like that found[13] in the solid (I):

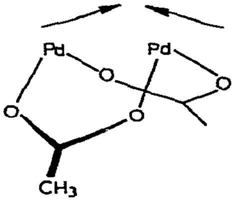


(I)

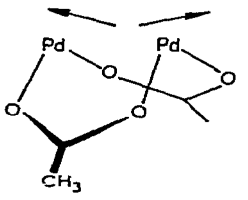
In the crystal structure[13] the two allyl groups are found to point in the same direction (II):



(II)



(IIIa)



(IIIb)

The symmetric conformation indicated by the NMR spectrum is probably structure (IIIb) with the allyl groups pointing in opposite directions and the eight-membered ring again in a boat form*. Scale models show that a crown-like conformation for the eight-membered ring is possible if we neglect the preference of the bidentate acetate to have both metals in the same plane. This requirement is only met in the boat conformation (I), which also brings the palladium atoms into close proximity, although we do not expect a strong metal–metal interaction.

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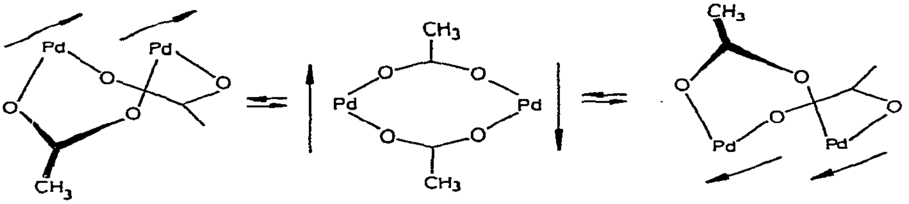
* Structure (IIIa) is unfavourable because of steric factors[9].

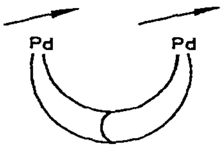
The pair of allyl signals present only to an extent of 10–20% in the methallylpalladium acetates is assigned to the asymmetric species with structure (II). It appears from the spectra that there is a faster exchange between these two small peaks (−80° to 40° in the NMR time scale) than between them and the dominant one (−40 to 0°). A mechanism which may account for the interchange between the allyl arrows in (II) is ring puckering of the type



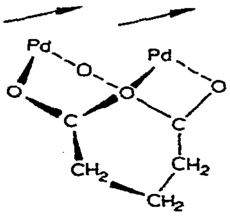
During this rearrangement no $\sigma$-bonds are being broken and only $\pi$-interactions are partially lost.

An interchange between symmetric and asymmetric species requires bond breaking. This may involve palladium acetate oxygen bonds or conversion to $\sigma$-bonding between metal and ligand and a rotation of the allyl group. Experiments with dicarboxylates indicate that we are concerned with palladium–oxygen bond breaking in the symmetric–asymmetric exchange. It is unlikely that the internal rearrangement in the asymmetric compound should occur via $\pi$-rotation (second type of reaction in the Introduction), as this would mean a synchronous rotation of two allyl groups in the asymmetric compound between −80° and −40°. One would anticipate a rotation of one allyl group to be favoured. This would lead to an interchange between symmetric and asymmetric dimers as the first process to occur at low temperatures, which is not the case.

In order to obtain more information about these movements we also studied the dicarboxylates. When the eight-membered ring is supplied with a bridge (connecting the two carboxylate groups) the ring puckering that interconverts the allyl groups of the asymmetric dimer is no longer possible. We synthesized the compounds with the general formula $[(\pi\text{-}C_4H_7)Pd]_2[(CH_2)_n(COO)_2]$ ($n=1$ to 8). The salts of malonic and succinic acid were insoluble in acetone and chloroalkanes. Presumably they are of a condensed nature. The scale models indicate that the number of methylene groups in the bridge should indeed amount to at least three in order to get a bridge structure (IV):

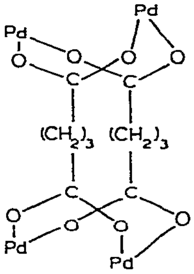


(IV)



The solubilities of the appropriate salts of glutaric acid ($n=3$), adipic acid ($n=4$), octanedioic acid ($n=6$) and nonanedioic acid ($n=7$) were sufficiently high to obtain

NMR spectra. Molecular weight determination in dichloroethane showed the glutaric acid complex to contain exactly four palladium atoms per molecule. The structure is probably (V):


(V)

The aforementioned ring puckering is impossible in structure (V), just as in (IV), although the bridge in (V) is more complicated that expected. The NMR spectra of the bis(methallylpalladium) dicarboxylates exhibited the same behaviour as the acetates except for the fact that the process between −80° and −50° does not occur, although the usual three groups are observed. In the case of adipic acid we prepared the unsubstituted allyl complex and found a symmetric–asymmetric distribution analogous to that found for the acetates by Powell[9]. In the dicarboxylates the exchange between the symmetric and asymmetric forms, and the internal exchange in the asymmetric compound start simultaneously at the same temperature (−20°). Evidently both processes proceed via the same mechanism, *viz.* breaking of palladium oxygen bonds. Besides, this observation proves that the internal movement of the asymmetric compound is not a synchronous $\pi$-rotation, since it is not to be expected that a movement of that type would be effected by bridging the carboxylates.

Within the limits of accuracy the two reactions observed are independent of the concentration in the case of acetates. This requires a simple dissociation mechanism:

$$[(C_4H_7)PdOAc]_2 \rightleftarrows 2\,(C_4H_7)PdOAc$$

In a system with different anions this reaction gives rise to an observable anion exchange. The temperature range (−40 to 0°) found here closely agrees with that found previously[7] for acetate exchange in these compounds. Apparently, the difference in energy between the two conformations is extremely small, as both conformations occur in similar concentrations. The asymmetric conformation is favoured in the solid due to non-bonded interactions in the lattice.

### *Chlorides*

At room temperature the NMR spectrum of methallylpalladium chloride in $CDCl_3$ and benzene indicates, as found for $[(C_3H_5)PdCl]_2$[14], that the allyl groups in solution are equivalent and symmetrically bonded to the palladium atom. At −85° in $CDCl_3$, however, it is seen that the methallyl groups are not equivalent (see Fig. 1). Both the signal of the methyl group and that of the *anti*-protons (2, 3)[6] split into two signals of equal intensity with a splitting of the order of magnitude of 2 Hz. Obviously this splitting is not due to $J$ coupling. (It has been found at higher temperatures, before the $\pi$–$\sigma$ reaction sets in at 90°, that small couplings of 0.4 and 0.2 Hz do exist in

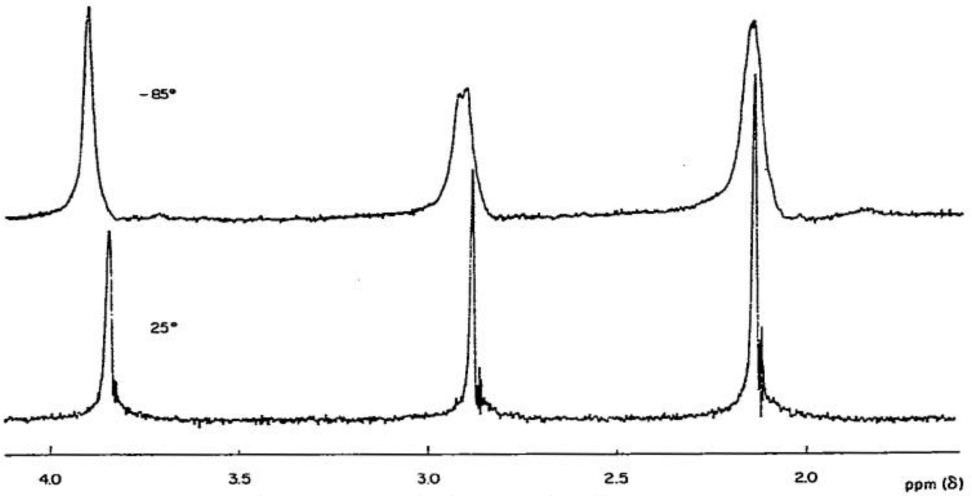


Fig. 1. NMR spectrum of $\pi$-methallylpalladium chloride dimer.

the $\pi$-methallyl group in the dimeric chloride.) No resolved splitting can be observed on the *syn*-protons. Note that in the dimeric acetates the differences found in chemical shifts for the *anti*-protons were also larger than those for the *syn*-protons.

The same splittings have been found in the compound ($\pi$-2-isopentylallyl)-palladium chloride and again the 1,4-protons do not show a resolved splitting at $-80^\circ$.

Another complex studied is (1-tert-butyl-2-methylallyl)palladium chloride[15]. According to NMR[15] and X-ray analysis[16] two isomers exist, *viz.* one with the tert-butyl group in a *syn*-position and the other with the tert-butyl in the *anti*-position. We studied the NMR spectra of these dimers below $-50^\circ$ : both showed a peculiarly similar behaviour. The spectra of the pure *syn*-isomer are reported in detail. At room temperature the spectrum (Fig. 2) consists of absorptions of the tert-butyl group (1.25 ppm downfield from TMS), the methyl group (2.18 ppm), the *anti*-hydrogen geminal to the butyl group (3.48 ppm), the remaining *syn*- (3.62 ppm) and *anti*-proton (2.67 ppm). At $-50^\circ$ large splittings are observed, particularly in the *anti*-protons and the methyl group. The *anti*-proton spectrum indicates that at least three kinds of *anti*-protons can be distinguished.

Spectra of mixtures of dimers showed at $-50^\circ$ to $-80^\circ$ further broadening of the split signals to unresolved overlapping signals.

These results can be interpreted by assuming that the allyl groups in the palladium chloride salts do "see" each other and therefore they are not necessarily equivalent, as was concluded from the room temperature spectrum. In (2-methylallyl)-palladium chloride only two allyls are present, in equal concentrations, and hence it is unlikely that substantial association of the dimers should take place. It is assumed in the following therefore that only dimers need be considered*. From crystal structure determinations it is known that (substituted) allylpalladium chloride occurs in two conformations in the solid, either (VI)[17] $[(\pi\text{-}C_3H_5)PdCl]_2$ or (VII)[18] $\{[1,3\text{-}(CH_3)_2C_3H_3]PdCl\}_2$. The $Pd_2Cl_2$ units may be planar or bent around the Cl–Cl line. The two allyl groups are equivalent in structure (VI), and so are the groups in

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* Monomeric compounds of the type $(C_4H_7)PdClL$ do not show these splittings at $-50^\circ$ to $-80^\circ$.

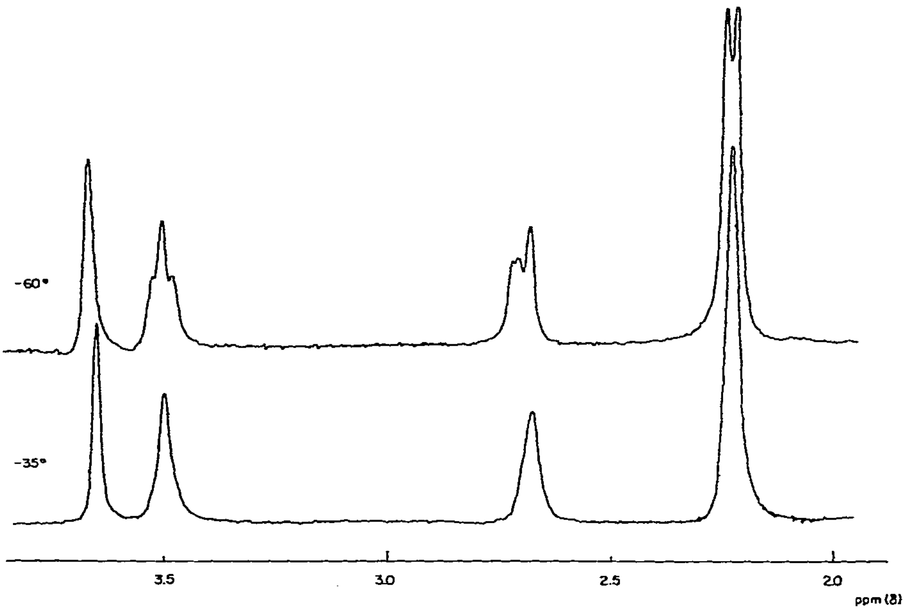
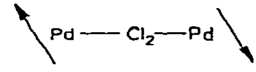
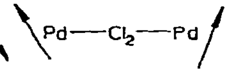


Fig. 2. NMR spectrum of (1-tert-butyl-2-methylallyl)palladium chloride dimer.



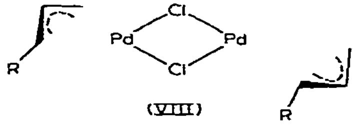
(VI)



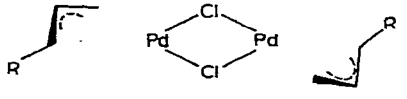
(VII)

(VII), but the allyls in (VI) may differ from those in (VII). This may well be the origin of the appearance of two lines at $-80°$. If so, the concentrations of (VI) and (VII) are equal. The energy difference between (VI) and (VII) is almost zero. Exchange between the isomers takes place via dissociation or association[19] reactions. It is known from systems with mixed anions that these processes occur in this temperature range and can be observed on the NMR time scale[7,19].

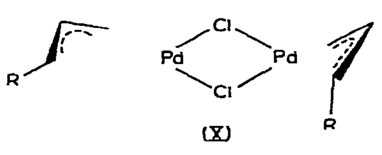
When the allyl group carries a substituent at carbon-1, four isomers [(VIII), (IX), (X) and (XI)] can be distinguished:



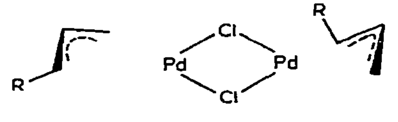
(VIII)



(IX)



(X)



(XI)

All these structures have an axis or plane of symmetry and therefore only four different allyl patterns may be expected in the NMR spectrum. The spectra of the *anti*-protons suggest that there are at least three kinds of groups present. Only two

2-methyl groups are observed, which are assigned to structures (VIII) and (IX) on the one hand and (X) and (XI) on the other, analogous to the compound (2-methylallyl)palladium chloride.

The concentration dependence of the exchange process has been studied using the doublet of the 2-methyl group in the concentration range between 0.053 and 0.212 mole/l at temperatures between −25° and −50°. It was found that the rate of exchange was roughly proportional to the square root of the concentration. This is in accord with a fast reaction of the type:

$$M^* + M_2 \rightleftarrows M^*M + M$$

accompanied by a slow dissociation reaction:

$$M_2 \rightleftarrows 2\,M$$

However, a more complicated system in which besides dissociation also the formation of tetrameric allylpalladium salts is assumed, cannot be rejected. The tetramer formation was observed in $[(C_4H_7)PdSCN]_2$[19], whereas the exchange in the corresponding acetate takes place via dissociation. Hence it is not certain whether the reaction $M_2 +$ M or a mixture of association and dissociation is operative in our system.

## EXPERIMENTAL

The NMR spectra were recorded in $CD_2Cl_2$ and $CDCl_3$ with Varian spectrometer HA 100 and DP, using tetramethylsilane as an internal standard.

Molecular weights of the acetates, glutarate and adipate were determined in dichloroethane with a Mechrolab Osmometer Model 301 A.

The complex $[(\pi\text{-}C_4H_7)Pd(OAc)]_2$ was prepared by the method reported by Robinson and Shaw[11] from the corresponding chloride and silver acetate. The silver dicarboxylates of malonic and adipic acid, octane- and nonanedioic acid, were prepared from the sodium salt and silver nitrate in warm water. The precipitate was filtered, washed with ethanol and acetone and dried at 40°. The silver glutarate was obtained from the corresponding acid (5.3 g) dissolved in 50 ml $H_2O$ and $Ag_2CO_3$ (11.1 g). After refluxing for a few minutes the product was filtered off and dried (13 g) on $P_2O_5$ in a desiccator. The silver carboxylates are much less sensitive to decomposition when exposed to light than silver carbonate and the allylpalladium(II) carboxylates.

Derivatives of π-allylpalladium(II) chloride were prepared from sodium palladium chloride, the appropriate olefin, and sodium acetate according to a method devised by Volger[12].

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