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# CARBONIUM ION DERIVED FROM SUBSTITUTED π-ALLYLPALLADIUM CHLORIDE COMPLEXES

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## SUMMARY

Cationic butadienylpalladium chloride complexes, assumed to be intermediates in the nucleophilic substitutions at [1-(1-chloroalkyl)-π-allyl]palladium chlorides, can be prepared by abstraction of chloride from [1-(1-chloroalkyl)-π-allyl]- or hydride from (1-alkyl-π-allyl)palladium chlorides by strong acids or $SbF_5$. NMR data indicate that the butadienyl group is bonded as a cisoid, *tetrahapto* ligand.

Solutions of a cationic (trimethylenemethane palladium complex can be obtained analogously by chloride abstraction from [2-(dichloromethyl)-π-allyl]-palladium chloride.

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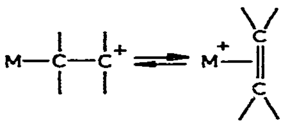
## INTRODUCTION

Two extreme cases of stabilization of a carbonium ion by a transition metal may be visualized[1,2]:

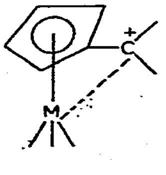
(*a*). Stabilization of a β-carbonium ion by direct transfer of electron density from the metal to the cationic centre, which may result in the formation of an olefin complexed with a metal cation (I).

(*b*). When the cationic centre overlaps a π system of the ligand, the electron density can be transferred via this system.

Formula (II) represents a combination of these two principles.

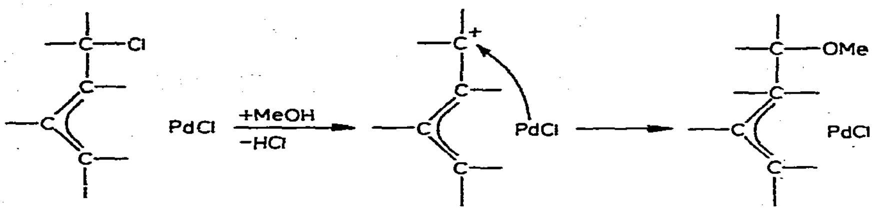


(I)



(II)

To explain the ready solvolysis of [1-(1-chloroalkyl)-π-allyl]palladium chlorides[3] a (1-π-allylpalladium chloride)carbonium ion has been postulated:



In view of the configurations of reactant and product the reaction intermediate was considered to have the $C^+$ in the *syn* position. Stabilization was assumed to proceed according to (*a*).

It occurred to us that this cationic intermediate species might be sufficiently stable to permit its preparation, so that we would be able to investigate its structure and chemical behaviour.

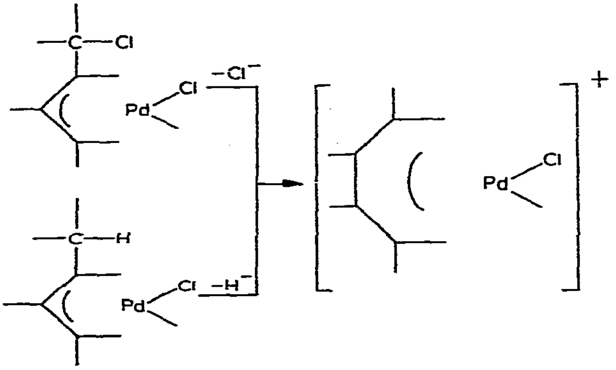
## RESULTS

Formation of the complexed cations was achieved by two different methods:

(*a*). Abstraction of chloride from [1-(1-chloroalkyl)-π-allyl]palladium chlorides by strong acids [*e.g.* $H_2SO_4$, $HSO_3F$, $HSO_3F/SbF_5$ (1/1 *m*/*m*) and $SbF_5$].

(*b*). Abstraction of hydride from (1-alkyl-π-allyl)palladium chlorides by $SbF_5$[4].

All reactions were performed without solvent except for those with $SbF_5$, which were carried out in a solution of $SO_2ClF$. Depending on the degree of methyl substitution of the substrate the reaction temperatures ranged from −80° to 0°. Substitution at carbon atom 4 facilitates the abstraction considerably, which is in accordance with the fact that secondary and tertiary carbonium ions are more stable than primary ones.



The NMR spectra of these carbonium ions (Table 1, Fig. 1) unequivocally demonstrate the similarity in the chemical shifts of the protons at carbon atoms 1 and 4. This led us to assign to these ions a general cisoid, *tetrahapto* structure rather than the reported π-allylcarbonium ion structure.

By following the formation of the cationic complexes by NMR we discovered that the complexes containing a secondary or tertiary cationic centre [(III)–(VI)] were

TABLE 1

NMR SPECTRA OF CATIONIC DIENYLPALLADIUM CHLORIDE COMPLEXES

The spectra were recorded in solutions of $SbF_5/SO_2ClF$ mixtures, unless otherwise indicated. See Fig. 1 for structural assignments.

| Diene | No. | Chemical shifts (ppm)[a] of H at | | | | | | Coupling constant J(Hz) |
|---|---|---|---|---|---|---|---|---|
| | | $C_1$ | | $C_4$ | | $C_2$ | $C_3$ | |
| | | *anti* | *syn* | *anti* | *syn* | | | |
| Butadiene | (I) | 5.65 | 6.90 | 5.65 | 6.90 | 8.40 | | $H_{anti}$–$H_{syn}=3$<br>$H_2$–$H_{anti}=10$<br>$H_2$–$H_{syn}=5$ |
| 2-Methylbutadiene | (II) | 5.20 | 6.40 | 5.42 | 6.60 | 3.35[b] | 8.05 | $H_{1anti}$–$H_{1syn}=4$<br>$H_{4anti}$–$H_{4syn}=3.5$<br>$H_3$–$H_{4anti}=12$<br>$H_3$–$H_{4syn}=7$ |
| 1,3-Pentadiene | (III)[c] | 4.90 | 5.90 | 6.40 | 2.10[b] | 7.3 | | $H_{1anti}$–$H_{1syn}=3$<br>$H_{1anti}$–$H_2=14$<br>$H_{1syn}$–$H_2=10$ |
| 2-Methyl-1,3-pentadiene | (IV) | 5.84 | 5.86 | 8.92 | 1.94[b] | 2.18[b] | 5.51 | $H_{1anti}$–$H_{1syn}=3$<br>$H_3$–$H_4=13$ |
| | (IV)[c] | 4.05 | 5.07 | 5.68 | 1.55[b] | 2.39[b] | 6.49 | $H_4$–$H_{CH_3}=6$ |
| 2,4-Hexadiene | (V) | 8.90 | 2.20[b] | 8.90 | 2.20[b] | 6.10 | | $H_{anti}$–$H_{CH_3}=7$ |
| | (V)[c] | 6.15 | 2.00[b] | 6.15 | 2.00[b] | 7.05 | | $H_{anti}$–$H_2=11$ |
| 2,5-Dimethyl-2,4-hexadiene | (VI)[d] | 2.20[b] | 2.58[b] | 2.20[b] | 2.58[b] | 5.90 | | |
| | (VI)[e] | 2.38 | | | | 5.90 | | |

[a] Downfield from TMS (external). [b] $CH_3$ group. [c] In $FSO_3H$. [d] At −60°. [e] At −20°.

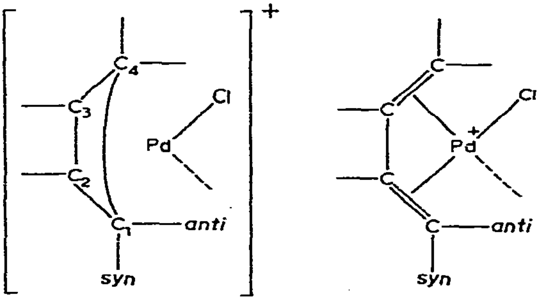


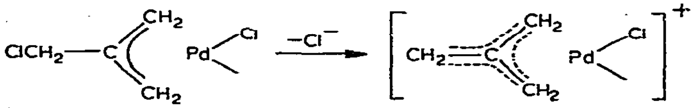
Fig. 1. The cisoid, *tetrahapto* structure of the ligand in cationic butadienylpalladium chloride complexes (see also Table 1); (I): 1–4=H; (II): 1,3,4=H; 2=$CH_3$; (III): 1,2,3,4*anti*=H; 4*syn*=$CH_3$; (IV): 1,3,4*anti*=H; 2,4*syn*=$CH_3$; (V): 1*anti*,2,3,4*anti*=H; 1*syn*,4*syn*=$CH_3$; (VI): 2,3=H; 1,4=$CH_3$.

formed immediately upon mixing; on the other hand, the final spectra of complexes with a primary cationic centre [(I) and (II)] were preceded by spectra showing rather broad absorption bands. In the case of complex (I) two broad signals appeared at 6.12 and 6.05 ppm in a ratio of 2/1. This phenomenon may be interpreted as an exchange of chloride between the starting material and the corresponding cationic species.

Complex (VI) was the only one with an NMR spectrum that was temperature-dependent: two methyl singlets at 2.20 and 2.58 ppm coalesced into one signal at 2.38 ppm at −25°. [$k_1(-25°)=2.5\times10\ s^{-1}$; $E_A=13$ kcal/mole$^{-1}$, $SO_2ClF$ as solvent].

The NMR spectra of complexes (IV) and (V) were found to be greatly dependent on the reagent ($FSO_3H$ or $SbF_5$; see Fig. 3). We succeeded in obtaining two of the complexes [(I), (VI)] in the crystallized form. But analysis revealed that the orange red crystals contained five antimony atoms per palladium atom, and thus we had to assume that a cluster of, on an average, four $SbF_5$ molecules crystallizes with the salt. (Such cluster gegenions are a known phenomenon for $SbF_6^-/SbF_5$ mixtures[5]).

Naturally, this finding destroyed our hopes of being able to elucidate the structure by means of X-ray analysis. Abstraction of chloride from [2-(chloromethyl)-π-allyl]palladium chloride at −20° by $SbF_5$ yielded a (trimethylenemethane)-palladium complex:



The NMR spectrum showed a singlet at 5.70 ppm, which broadened below −20°. A lower limiting spectrum could not be obtained since the complex crystallized at −80°.

Quenching of the carbonium ion complexes derived from [1-(chloroalkyl)-π-allyl]- and [2-(chloroalkyl)-π-allyl]palladium chlorides in $CH_3OH/K_2CO_3$ or $H_2O/NaOH$ yielded the corresponding 1- and 2-methoxy or [(hydroxyalkyl)-π-allyl]palladium chloride complexes.

Treatment of the methoxy and hydroxy compounds with $FSO_3H$ regenerated the original cationic species.

## DISCUSSION

The symmetrical structure of a cisoid, *tetrahapto* ligand is clearly demonstrated by the NMR spectra of the complexes. For the six hydrogen atoms in complex (I) only three absorptions can be observed (see Table 1).

The doublet of doublets at low field (8.40 ppm) is due to the hydrogens on $C_2/C_3$ since they will couple with *anti* and *syn* hydrogens on $C_1/C_4$. The assignment of the signal at the highest field (5.65 ppm) to the *anti* hydrogens is based on the close proximity of these protons to the metal atom and the shielding effect of the latter; it is supported by the value of the coupling constant ($J$ 10 Hz), which is indicative of *trans* coupling (to H on $C_2/C_3$). The remaining signal with the intermediate chemical shift (6.90 ppm) must then be due to the *syn* hydrogens, which is confirmed by the correspondingly smaller coupling constant ($J$ 5 Hz, *cis* coupling). As contrasted with π-allyl complexes, this complex exhibits geminal coupling $H_{anti}/H_{syn}$ ($J$ 3 Hz).

The other ions of the homologous series have analogous features; as an example the NMR spectrum of complex (II) is given in Fig. 2. The NMR spectra are all strikingly similar to those of π-pentadienyltricarbonyliron cations[6].

Two features deserve special notice:

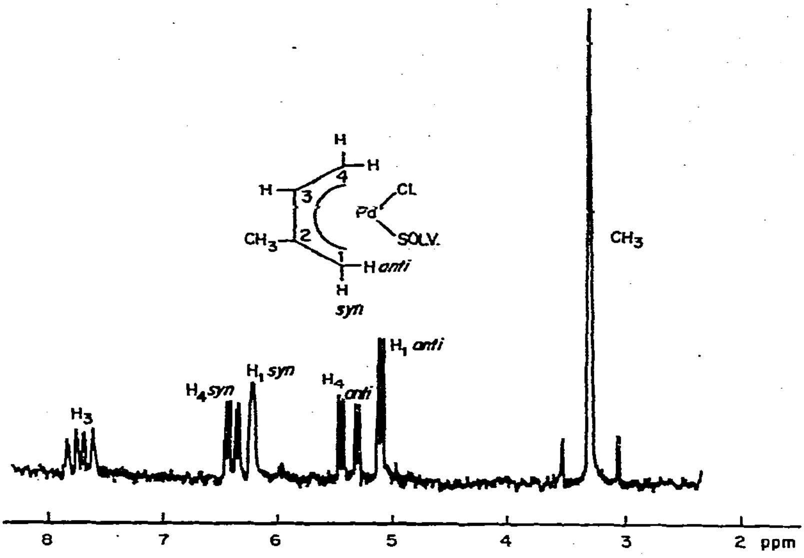


Fig. 2. NMR spectrum of complex (II) (external TMS).

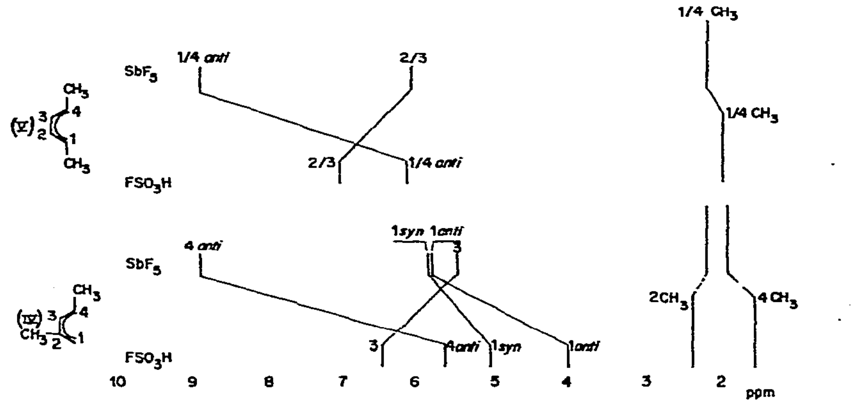


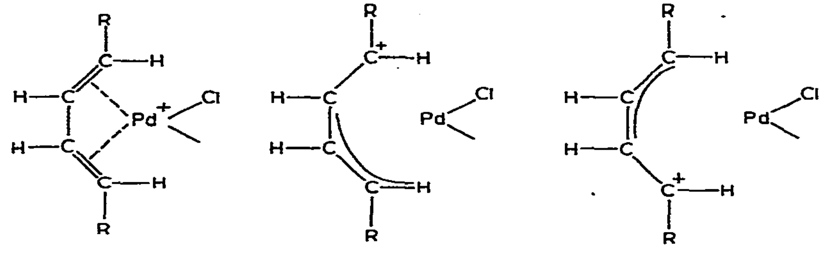
Fig. 3. Effect of solvent on the NMR spectra of complexes (IV) and (V).

(*a*). The dependence of the spectra of complexes (IV) and (V) on the nature of the gegenion (or the solvent).

(*b*). The coalescence of the methyl signals in complex (VI).

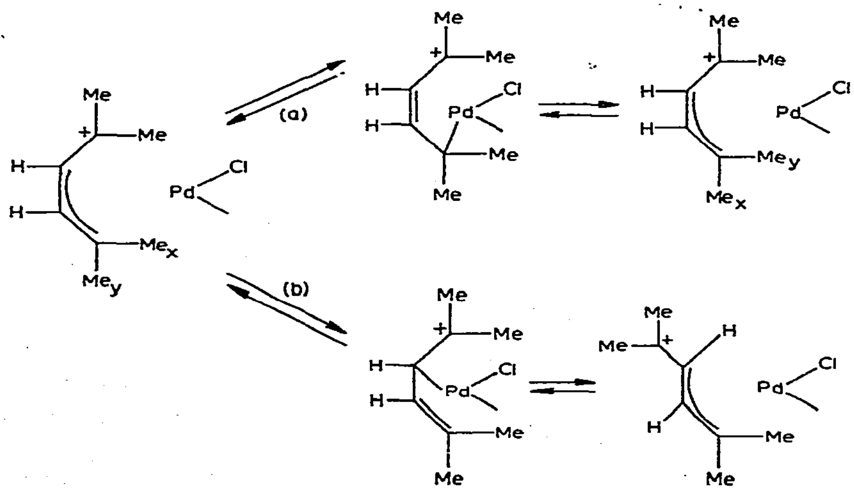
The first point is illustrated in Fig. 3, which is a schematic representation of the spectra of complexes (IV) and (V) (without indication of coupling).

When going from $SbF_6^-$ ($SbF_5$) to $FSO_3^-$ ($FSO_3H$) it is seen that the resonances for the hydrogens on $C_2/C_3$ shift to lower and those for the hydrogens on the terminal carbons $C_1/C_4$ to higher field. The methyl groups behave in the same way. The upfield shift of the hydrogens on $C_1/C_4$, which are geminal to a methyl group, is particularly pronounced [see complex (IV)]. It may be tried to interpret these observations by assuming that the bond between the gegenion (or a solvent molecule) and the cation has partially homeopolar character (for example via bridging fluorine). With the more nucleophilic species $SO_3F^-$ ($FSO_3H$) the degree of homopolarity in this bond will be higher than with $SbF_6^-$ ($SbF_5$). Electron density donated in this way to the metal atom will be relayed to the terminal carbon atoms (1/4) opposite to the coordinated gegenion (*trans* effect). This explains why the protons and methyl groups on these carbon atoms shift to higher field. However, these changes in overall electron density in the complex cation as a whole, do not explain why the chemical shifts of hydrogens on $C_2/C_3$ move downfield and why the upfield shifts of the hydrogen on $C_1/C_4$ when geminal to a methyl group become more pronounced. The spectra in $FSO_3H$ resemble the general pattern of uncoordinated dienes, in which the hydrogens on $C_2/C_3$ appear at lower field than those on $C_1/C_4$. We therefore assume that canonical form A makes a greater contribution than B′ and B″ in $FSO_3H$ and that the reverse applies in $SbF_5$, where moreover for $R = CH_3$ B′ will be the larger contributor thus accounting for the influence of a *geminal* methyl group on the shift of terminal hydrogens.

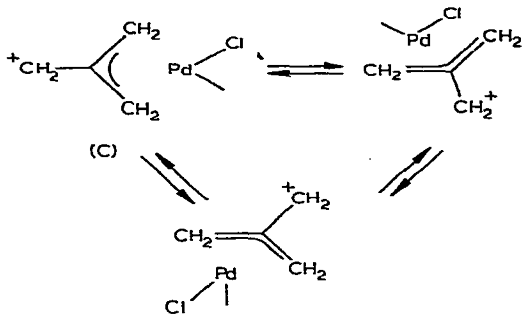


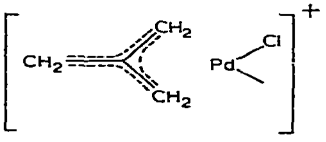
A B′ B″ R = H or $CH_3$

The second feature which attracted our attention was the coalescence of the methyl signals of complex (VI). The four methyl substituents at $C_1/C_4$ stabilize the cationic centre and favour a π-allyl structure similar to that in B′ and B″. A π→σ→π rearrangement can then lead to equilibration of *anti* and *syn* methyl groups (a).



A similar rearrangement (b) gives rise to an equilibration of π-allylic complexes with the cationic centre in the *anti* and *syn* positions. The cationic character of the "*syn*" complex will be more pronounced than that of the "*anti*" complex owing to lack of direct stabilization via the metal. This might well explain why quenching leads exclusively to reaction at the more reactive (cationic) centre, yielding *syn*-substituted π-allylic complexes, just as observed in solvolysis. The alternative explanation, *viz.* reaction at the cationic centre in the *anti* position, followed by *anti–syn* equilibration of the neutral π-allylic complexes via π→σ→π rearrangement, seems less plausible. This is concluded from earlier experiments with tert-butyl-substituted π-allylic complexes in which, for steric reasons, the necessary rearrangement only occurred at elevated temperatures[7] and from the consideration that the steric requirements of a tert-butyl and a $C(CH_3)_2(OCH_3)$ group are about the same. The cation derived from [2-(chloromethyl)-π-allyl]palladium chloride could be either a static (2-carbinyl-π-allyl)palladium chloride cation (C), a degenerate equilibrium of three cations of type C or a static (trimethylenemethane)palladium chloride cation (D) in which all four *p* orbitals of the ligand are simultaneously coordinated to the metal. The singlet at 5.70 ppm in the NMR spectrum and its collapse upon cooling can only be accounted for by the equilibrium situation.


(C)


(D)

EXPERIMENTAL

*Starting materials*

All [1-(1-chloroalkyl)-π-allyl]palladium chlorides were prepared according to the method suggested by Slade and Jonassen[8], in which the diene in question is added to dibenzonitriledichloropalladium.

The 1-(1-methoxyalkyl) complexes were prepared with the aid of palladium chloride (which is soluble in methanol), rather than with the previously used sodiumchloropalladate tetrahydrate. The [2-(chloromethyl)-π-allyl]palladium chloride complex was prepared from 2-(chloromethyl)allyl chloride with $PdCl_2$ and CO in $CH_3OH$ according to the method of Dent *et al.*[9]. Commercially available $FSO_3H$ and $SbF_5$ were distilled before use.

### *Ionization reactions*

The abstractions of chloride and hydride were effected by adding, at −80°, a slurry of the π-allyl complex in $SO_2ClF$ to a solution of the acid ($SbF_5$, $FSO_3H$, $H_2SO_4$) in the same solvent. The solutions were then warmed until no further changes in the NMR spectra occurred. The salts were isolated by evaporating the solvent and washing the residue with $SO_2$ to remove excess $SbF_5$.

### *Quenching reactions*

The solutions of the cationic complexes in $SO_2ClF$ were poured slowly into a stirred slurry of a large excess of $K_2CO_3$ in methanol at −80°. The reaction mixture was then allowed to warm up to room temperature. Water was added and the products were extracted with methylene chloride.

The antimony contents of the salts isolated were determined as follows: the salt was added to dilute $H_2SO_4$, and the mixture heated to destroy the organic material and to drive off the water. Zinc dust was added to reduce the antimony to oxidation state (III), which was subsequently titrated with sodium bromate.

### *NMR spectra*

The spectra were recorded on a Varian HA-100 instrument with variable temperature probe. Kinetic parameters were determined by known methods[10].

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