Asymmetrical Dimer - allyl-palladiu Complexes
II. Data from Infrared Spectra and Chemical Behaviour

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The previous data obtained by 1H-NMR spectroscopy established the existence of an asymmetry of the bond between Pd and \( \pi \)-allylic groups, even in the \( \pi \)-allyl-Pd complexes dimers which are considered usually symmetric dimers. The asymmetry of the bond depends by the substitutes of the allylic group. Other analytical methods were investigated for additional proof of the obtained results. Thus, this paper discusses how this asymmetry would be reflected in the infrared spectra and in the reaction of the complexes with carbon monoxide.

Keywords: \( \pi \)-allyl paladium complexes, infrared spectra, asymetrical dimer

The amount of infrared spectroscopic data about \( \pi \)-alilic complexes present in literature is scarce. The bond between the metallic atom and the halogen bridge (Cl, Br) or that between the metallic atom and the carbonylic group from \( \pi \)-allylic substituent gives absorptions in the field of 200-500 cm\(^{-1}\). A literature search yielded some studies about the infrared spectra of the simplest complexes such as: \( \pi \)-allylic-Pd [C\(_3\)H\(_5\)PdCl] , \( \pi \)-metalyl Pd [C\(_4\)H\(_7\)PdCl] , and \( \pi \)-crotyl Pd[C\(_4\)H\(_7\)PdCl] [2, 3]. On the basis of the previously deduced asymmetry [1] we have tried to bring additional proof for this using IR spectroscopy for the complexes 1-6.

Complex 7b:
IR (CCl\(_4\), cm\(^{-1}\)): \( \nu \)(C=O) 1740. RMN (CDCl\(_3\), \( \delta \), ppm): 1.28 (d, 3H, CH\(_3\), J 6 Hz), 3.49 and 3.79 (2s, 6H, OCH\(_3\) and COOCH\(_3\)), 4.33 (q, 1allylic H, J 6 Hz), 6.90 - 7.20 (m, 10 aromatic H).

Lactone 8:
m. p. 136 : IR (CCl\(_4\), cm\(^{-1}\)): \( \nu \)(C=O) 1770. RMN (CDCl\(_3\), \( \delta \), ppm): 1.43 (d, 3H, CH\(_3\), J 6.5Hz), 5.46 (q, 1allylic H), 7.31 (broad s, 10 aromatic H). UV (EtOH) : \( \lambda \)\(_{max}\) 286.1 nm (log\( \epsilon \) 4.062).

Complex 9:
IR (KBr, cm\(^{-1}\)): \( \nu \)(C=O) 1725. RMN (CDCl\(_3\), \( \delta \), ppm), 1.16 (d, 3H, CH\(_3\)-3, J 6.5Hz), 3.29 (s, 3H, COOCH\(_3\)), 4.46 (q, 1allylic H, J 6.5 Hz), 6.80 - 7.80 (m, 10 aromatic H).

Results and discussions
The unsubstituted \( \pi \)-allylic group presents in IR suitable bands of asymmetric stretching vibration in the field of 1450-1500 cm\(^{-1}\), of the symmetric stretching vibration in the field of 1015-1045 cm\(^{-1}\) and of the deformations vibration in the field of 510-567 cm\(^{-1}\).

The IR spectra of the six complexes show two closed absorption bands \( \nu \)\(_{asim}\) in the field of 1450-1500 cm\(^{-1}\) having comparable intensities.

The analysis of the 1H-NMR spectra of complexes 1-6 shows that the two double bonds between the carbon atoms of the allylic groups could have a weaker or a stronger \( \pi \) bond character. This means that the bonds between C2 and C3 have a stronger sp\(_2\) character than the bonds between Cl and C2. Consequently, the two double bonds appear in infrared spectrum as two distinct vibrations with a small difference in frequencies as can be observed in the table 1.

This explains the appearance of two absorption bands in the field of the stretching vibrations of the skeleton of the \( \pi \)-allylic group (figs. 1, 2). The splitting of the absorption band corresponding to the stretching vibration \( \nu \)\(_{asim}\) of the \( \pi \)-allylic skeleton is not surprising. The same effect in the appearance of the two absorption bands of in the field of frequency of the stretching vibration, \( \nu \)\(_{asim}\) was also observed in the case of substituted alenes [4].

It was noticed for the complexes 1, 3 and 5, with substituents at carbon C-2, that the values of the chemical shifts \( \delta \) for H-3 were bigger than the chemical shifts of the

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Experimental part
The \( ^1\)H-NMR spectra were carried out with a Varian Gemini 300 MHz spectrometer in CDCl\(_3\) and the IR spectra with a Bruker instrument, Vertex 70 with Fourier transformation (FTIR), equipped with diamond crystal, solid in ATR.

Complex 7a:
IR (CCl\(_4\), cm\(^{-1}\)): \( \nu \)(C=O) 1740. RMN (CDCl\(_3\), \( \delta \), ppm): 1.10 (d, 3H, CH\(_3\), J 6 Hz), 3.25 and 3.30 (2s, 6H, OCH\(_3\) and COOCH\(_3\)), 4.11 (q, 1allylic H, J 6 Hz), 7.20 - 7.45 (m, 10 aromatic H).
same proton in the series of the complexes without substituent at C-2, respectively of the complexes 2, 4 and 6. On the other hand, the difference in the frequencies of vibration of the two bands of absorption for the stretching vibrations $\nu_{\text{asim}}$ is bigger in the case of the complexes having substituent at C-2 than that observed for the series without substituent at C-2. The analysis of the NMR and IR spectra strengthens the hypothesis of the existence of the same

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\nu_{\text{asim}}$ (cm$^{-1}$)</th>
<th>$\Delta \nu_{\text{asim}}$ (cm$^{-1}$)</th>
<th>$\delta_{\text{H-3}}$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1491 1442</td>
<td>49</td>
<td>4.38</td>
</tr>
<tr>
<td>3</td>
<td>1495 1474</td>
<td>21</td>
<td>3.55</td>
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<tr>
<td>5</td>
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<td>37</td>
<td>5.38</td>
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<tr>
<td>2</td>
<td>1475 1450</td>
<td>25</td>
<td>3.98</td>
</tr>
<tr>
<td>4</td>
<td>1475 1460</td>
<td>15</td>
<td>3.28</td>
</tr>
<tr>
<td>6</td>
<td>1476 1459</td>
<td>17</td>
<td>4.84</td>
</tr>
</tbody>
</table>

**Table 1**

THE IR $\nu_{\text{asim}}$ ABSORPTION BANDS AND THE $^1$H-NMR DATA FOR THE ALLYLIC PROTON H3 OF THE COMPLEXES 1-6

**Fig. 1.**
IR spectrum of the complex 1

**Fig. 2.**
IR spectrum of the complex
kind of asymmetry in the \( \pi \)-allylic dimers complexes [5, 6]. The degree of asymmetry varies in relation with the presence or the absence of a substituent at C-2.

Chemical arguments about the asymmetry of the bond Pd-allylic complex

The reaction of the \( \pi \)-allyl Pd with carbon monoxide may bring additional proof for the asymmetry of the bond \( \pi \)-allyl Pd. It was considered that the carbon monoxide inserts at the \( \sigma \) bond, between palladium and allylic carbon [7].

The reaction between the complexe 1 with carbon monoxide was carried out by barbotation of the carbon monoxide in a solution of the complex in a mixture of methanol and methylene dichloride. From complex 1, a mixture of two isomeric methoxyesters (7a and 7b), a lactone (8) and a carbomethoxy complex (9) was obtained [8, 12].

The analysis of the NMR and IR spectra of the products 7a,b showed that the carbon monoxide inserts at carbon C-1 of the allylic group while the methoxy group inserts at C-3. The principal argument consists in the chemical shift of the signal given by the allylic proton H-3, in NMR spectra. This appears at \( \delta = 4.05-4.33 \) ppm, for the two methoxy esters 7a,b. A reverse position of these functional groups would have induced a chemical shift for the H-3 proton, of about 3.00 ppm [13], suitable for a proton binded to a carbon placed between a double bond and a carbonyl group.

For the lactones it was considered two possible structures: conjugated structure 8a and the unconjugated structure 8b. The choice between these formulas was made on the basis of NMR and IR spectra.

Analysis of the IR, UV, NMR spectra has confirmed the structure 8a for the lactones. All these reaction products between the complex 1 and the carbon monoxide show that the reagent enters at carbon C-1 of the allylic system. So, it results also from the reaction products that the carbon atom C-1 is most likely capable to form an \( \sigma \) bond with palladium atom.

Conclusions

The structure of the products 7-9 of the reaction is an argument for the presence of an asymmetry in the bond between Pd and allyl group and for the fact that short life reaction intermediate contains a C-1-Pd bond possessing a strong \( \sigma \) character.

On the other hand, the appearance of the two methoxy ester isomers is an additional argument for the asymmetry of the bond allylic-Pd. Only by a \( \sigma \) binding of palladium at C-1 may be obtained the turning of the substitutes. This turning explains the formation of the two methoxy esters isomers.

Bibliography

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Manuscript received: 9.07.2007