

SYNTHESIS, CHARACTERIZATION AND FLUXIONAL BEHAVIOUR OF ALLYLIC PALLADIUM(II) CARBOXYLATE AND *N,N'*-DIARYL-FORMAMIDIDO COMPLEXES

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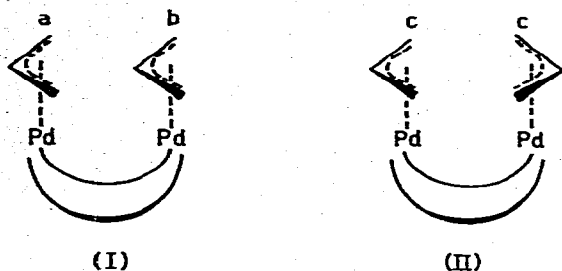
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Summary

$[\text{Pd}(1\text{-}3\text{-}\eta\text{-allyl})\text{Cl}]_2$ reacts with $\text{Li}(\text{N,N}'\text{-diarylformamidido})$ forming dimeric complexes of the type $[\text{Pd}(1\text{-}3\text{-}\eta\text{-allyl})(p\text{-RC}_6\text{H}_4\text{N}\cdots\text{CH}\cdots\text{NC}_6\text{H}_4\text{R}\text{-}p)]_2$ ($\text{R} = \text{CH}_3, \text{H}, \text{Cl}$). ^1H NMR spectra show the presence of two conformers, one of which has two electronically equivalent allyl groups; their concentration ratio is independent of the temperature, suggesting that no intramolecular process takes place. At 80-100 °C the other conformer undergoes an intramolecular process which brings the two allyl groups to equivalence. This together with the mechanism of the process which results in the equivalence of the allyl groups in the closely related dimeric carboxylate systems, is discussed below. The presence of weak bridge-splitting ligands, such as DMSO or the parent *N,N'*-diarylformamidine, does not affect the intramolecular process, which thus occurs without any palladium-formamidido bond breaking, probably through a boat inversion of the $\text{C}_2\text{N}_4\text{Pd}_2$ ring via a chair conformation.

Introduction

Recent studies on dimeric allylpalladium(II) complexes containing bridging acetato [1] or triazenido [2,3] ligands have shown that, although structurally related, they behave differently in solution. Low temperature ^1H NMR spectra suggest the presence of two isomers for both systems, where the line linking the two palladium atoms represents an acetato or a triazenido ligand bridging through the oxygen, or the terminal nitrogen atoms. Structures I and II have been confirmed by X-ray studies for the acetato [4] triazenido [3] systems, respectively.



Variable temperature ^1H NMR studies from -60° up to 100°C established the presence of inter- and intra-molecular processes for the acetato complex [1] which are absent in the other system [2,3]. A possible explanation for their different behaviour is based on (a) a stronger Pd—N bond than a Pd—O one or (b) a less rigid π -conjugation in the acetato ligand than in the 1,3-diaryltriazenido one (in the latter the π -conjugation extends also to the two aryl rings [3]).

With the aim of getting more insight into the situation we have undertaken a study of dimeric allyl(benzoato)palladium(II) and N,N' -diarylformamidido complexes and the results of this study are reported here.

Experimental

Solvents were dried and purged with nitrogen before use. IR and NMR spectra were run on Perkin—Elmer 457 and Jeol C-60HL instruments. Molecular weights were determined on a Mecrolab Osmometer in benzene at 36°C . Melting points were taken in air on a Kofler hot stage.

Allyl(chloro)palladium dimer was synthesized from Na_2PdCl_4 and allyl alcohol by the method of Moiseev et al. [5]; silver benzoate was prepared from AgNO_3 and sodium benzoate; N,N' -diarylformamidine was prepared following the literature method from triethylorthoformate and the appropriate *p*-substituted aniline [6].

Bis(μ - N,N' -di-*p*-tolylformamidido)*bis*(1-3- η -allyl)dipalladium(II)

A solution of *n*-butyllithium in hexane (1.2 ml, ca. 2.5 *M*, 3 mmol) was added to a THF solution of N,N' -di-*p*-tolylformamidine (10 ml, 675 mg, 3 mmol), at room temperature, yielding a pale yellow solution. After 1 min allyl(chloro)palladium dimer (460 mg, 1.25 mmol) was added as a solid. The resulting yellow solution was stirred for 10 min while heating to the b.p. Then the volume was reduced to ca. 2 ml by a vigorous nitrogen flux, cooling the solution to room temperature. Addition of ethanol afforded the complex as pale yellow crystals. Crystallization from benzene/ethanol yielded the analytical sample, m.p. 175 – 176°C (75% yield).

The phenyl and the *p*- ClC_6H_4 derivatives were similarly prepared as pale yellow crystals, m.p. 169 – 170°C (70% yield); m.p. 151 – 152°C (75% yield) respectively.

Di- μ -benzoato-*bis*(1-3- η -allyl)dipalladium(II)

To an acetone solution of allyl(chloro)palladium dimer (365 mg, 1 mmol,

TABLE 1
ANALYTICAL AND IR DATA OF $[(1-3-\eta-C_3H_5)PdX]_2$ ($X = p-RC_6H_4N=CH=NC_6H_4R-p; C_6H_5COO$)

| X,R | M.p. | Analytical found (calcd.) (%) | | | | IR ^a (cm ⁻¹) | |
|-----------------------------------|---------|-------------------------------|----------------|----------------|-----------------|--|-------------------|
| | | C | H | N | Mol. wt. | | |
| C ₆ H ₅ COO | 100 | 44.94 (44.72) | 3.82 (3.75) | | 505 (537.16) | 1593vs, 1388vs | 1553vs, |
| CH ₃ | 175-176 | 58.25 (58.31) | 5.31 (5.44) | 7.76 (7.56) | 736 (741.52) | 1612w, 1354s, | 1573vs, 1228s |
| H | 169-170 | 55.83 (56.07) | 4.96 (4.71) | 8.01 (8.18) | 700 (685.42) | 1608w, 1358s, | 1563vs, 1225s |
| Cl | 151-152 | 46.38 (46.69) | 3.48 (3.43) | 7.29 (7.56) | 842 (823.18) | 1603s, 1363s, | 1554vs, 1228vs |

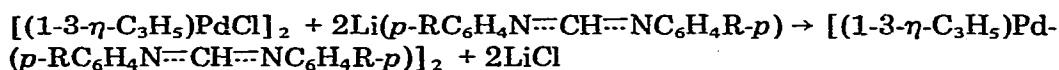
^a Only bands associated with carboxylate and formamidido groups.

10 ml) an equimolar amount of silver benzoate was added as a solid under vigorous stirring. After stirring the suspension for 8 h at room temperature, all the solvent was stripped off. The solid was treated with benzene and centrifugation allowed separation from silver chloride. On adding ethanol to the yellow benzene solution, pale yellow crystals of the pure complex precipitated out, m.p. 100 °C (70% yield).

Analytical and infrared data are listed in Table 1.

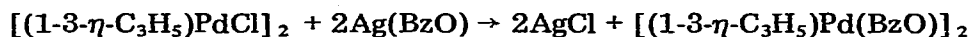
Results and discussion

Similarly to the allyl(triazenido)palladium(II) complexes [3], the *N,N'*-diarylformamidido analogues can be obtained by the following reaction:

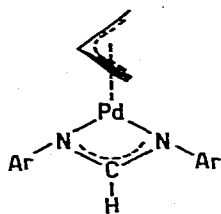


(R = CH₃, H, Cl)

The allyl(benzoato)palladium(II) dimer was prepared from silver benzoate, Ag(BzO), and the chloride dimer by the same procedure used for the acetate analogue [7].



Although in principle the formamidido linkage can act as a bidentate non-bridging ligand to form monomeric complexes of the type:



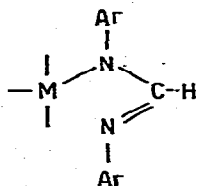
as does the closely related 1,3-diaryltriazenido anion in $Co(\text{triazenido})_3 \cdot \text{tol}$

uene [8] which contains three, strained four-membered rings, a dimeric structure with unstrained formamidido bridging linkages is preferred, as in the isostructural dimer $[(1-3-\eta-C_3H_5)Pd(1,3\text{-diaryltriazenido})]_2$ [3]. The benzoate complex is also dimeric, as is the acetate analogue [4,7] (see below).

In Table 1 are reported the IR absorption bands due to the formamidido and benzoate linkages in the $1600\text{-}1200\text{ cm}^{-1}$ region only, for a mixture of conformers I and II, see below. Because the main difference lies only in the orientation of one allyl group, one predicts a very small difference in the IR frequency. Thus we believe that the IR values reported here should not be different from those of the two conformers taken separately.

The IR spectrum of the benzoate dimer shows the asymmetric $\nu(C=O)$ at a lower value, and the symmetric $\nu(C=O)$ at a higher value than the corresponding $\nu(C=O)$ in complexes where the benzoate anion acts as a monodentate ligand as, for example, in $Pd(PPh_3)_2(BzO)_2$ ($\nu(C=O)$ at 1626 and 1325 cm^{-1} [9]). This agrees with a dimeric structure for $[(1-3-\eta-C_3H_5)Pd(BzO)]_2$ in which the carboxylate anion acts as a bidentate ligand bridging two palladium atoms, as found by a X-ray study for the closely-related acetato analogue [4].

The bridged formamidido gives a band with some shoulders at ca. 1560 cm^{-1} , 100 cm^{-1} higher than $\nu(C=N)$ in the corresponding protonated formamidine. In $M(PPh_3)_2(N,N'\text{-diarylformamidido})Cl$ ($M = Pd, Pt$) such a band occurs at a value 20 cm^{-1} lower [10] than that in the bridged complexes reported* here and the ligand is thought to act as a monodentate:



Thus the trend of the $\nu(C=N)$ frequency contrasts with that of $\nu(C=O)$ for the bridging and monodentate ligands. We cannot suggest a simple rationalization of these facts which are probably complicated by the presence of conjugated aryl rings.

At low temperature the NMR spectrum of the acetate complex shows three different allyl groups, the two non-equivalent for conformer I and the one for the symmetric conformer II [1]. At -32°C the peaks due to the allyl groups of conformer I collapse, and at -20°C equivalence is achieved. At the higher temperature another process occurs resulting in the NMR equivalence of the allyl groups of the two conformers. This has been explained on the basis of a bimolecular exchange [1], which probably also occurs with the benzoate system, since the two complexes behave the same way above -20°C . Below this temperature they behave similarly, the main difference being that the collapse for the peaks of the allyl groups of conformer I for the benzoate occurs at -55°C . On the basis of energetic considerations and chemical shift parameters, Powell [1] proposed as the most likely mechanisms for this process, (a) an inversion of

* Another bridged dimeric complex $[Pd(p\text{-tolyl}N=CH=N\text{tolyl-}p)]_2 \cdot C_6H_6$ presents $\nu(C=N)$ at 1585 cm^{-1} [10].

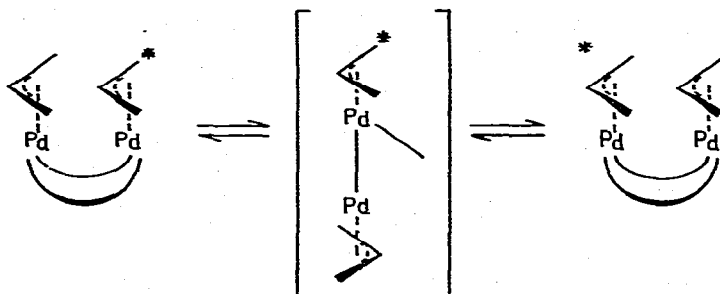
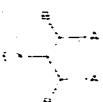


Fig. 1. Proposed mechanism for the NMR equivalence of the allyl groups of the carboxylate conformer I.

the boat conformation through an intermediate chair configuration or (b) a solvolytic cleavage of only one Pd—O bond and rearrangement of the resultant monoacetate bridged intermediate followed by reformation of the Pd—O bond. Below -20°C , if the mechanisms for the acetate and benzoate systems are the same, a solvolytic cleavage is operating; the collapse temperature for a bridge inversion mechanism should be higher than -32°C for the benzoate because of its greater rigidity due to the more extended π -conjugation to the phenyl ring. On the contrary, if the mechanisms are different, it is not possible to discriminate between the two cases; acetate via bridge inversion and benzoate via solvolytic cleavage, or vice versa. However, since the systems are closely related and show the same behaviour above -20°C , it is likely that the same process for both systems is also operative below -20°C , i.e., a solvolytic one as shown in Fig. 1*.

The NMR spectrum of the *N,N'*-diarylformamidido analogue also shows three overlapping AA'BB'X patterns suggesting the presence of two conformers, the major one having electronically equivalent groups, as is shown by the acetate [1] and benzoate systems at low temperature and by the triazenido one from -65° up to 100°C [2,3]. The other conformer presents two non-equivalent allyl groups giving rise to four signals AA'BB' for the *syn*- and *anti*-protons of equal relative intensity; this appears clearer in the region of the *anti* protons,

because here they are spaced farther apart:  $J(\text{AX}) = 12 \text{ Hz}; J(\text{BX}) = 7 \text{ Hz}$,

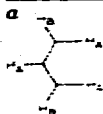
and between 40° and 70°C . Chemical shifts and coupling constants (Table 2) are in agreement with other allylic-palladium(II) complexes. At low temperature, because of a rather sensitive temperature-dependent chemical shift, there is some superposition between the various AA'BB' patterns and the presence of the two

* (1-3- η -Methallyl)palladium(II) dicarboxylates, where a bridge connecting the two carboxylate groups impedes the boat inversion, show the same behaviour as the acetates, except that the process seen there below -20°C does not occur [11]. While this confirms the bimolecular exchange mechanism, it does not establish the boat inversion mode as the one responsible for the NMR equivalence of the allyl groups a and b of the acetate I, because the solvolytic mechanism of Fig. 1 is also no longer possible with these dicarboxylates.

TABLE 2

¹H NMR DATA OF [(1-3- η -C₃H₅)PdX]₂ (X = *p*-RC₆H₄N=CH=NC₆H₄R-*p*; C₆H₅COO) AT ROOM TEMPERATURE.

| X,R | Conformer | Ratio II/I | Allyl ^a | | | Formyl | CH ₃ | Phenyl |
|-----------------------------------|-----------|---------------|--------------------|-------|-------|--------|-----------------|---------------|
| | | | X | B | A | | | |
| C ₆ H ₅ COO | | | 4.40m | 6.00d | 6.97d | | | 2.02m, 2.63 m |
| CH ₃ | I | 2.3 | 5.00m | 6.39d | 7.15d | 2.30s | | |
| | | | | | | 6.57d | 2.34s | |
| | II | | 4.45m | 6.47d | 7.23d | 2.19s | 7.70s | 3.13m |
| | | | | | | 2.25s | | |
| H | I | 2.0 | 4.95m | 6.37d | 7.09d | 2.26s | | |
| | | | | | | 6.50d | 2.30s | |
| | II | | 4.38m | 6.41d | 7.21d | 2.15s | | 2.95m |
| | | | | | | 2.21s | | |
| Cl | I | 2.3 | 4.92m | 6.29d | 7.11d | 2.28s | | |
| | | | | | | 6.46d | 2.33s | |
| | II | | 4.38m | 6.38d | 7.16d | 2.19s | | 2.95m |
| | | | | | | 2.25s | | |



coupling constants (Hz) are the same for all allyls: $J(\text{AX}) = 12$, $J(\text{BX}) = 7$, $J(\text{AB}) < 1$.

conformers becomes harder to detect. Because the systems reported here closely resemble the acetate [1] and the triazenido ones [2,3], which were found by X-ray studies to have structure I and II [3,4], it is likely that conformers of this type are also present with the formamidido ligands. Conformer II presents a plane of symmetry passing through the two palladium atoms and the middle carbon atom of the allyl groups, and a second plane of symmetry perpendicular to the first one and passing between the two metal atoms; this latter plane of symmetry is absent in the second conformer. Thus, for each conformer one should expect only one singlet for the formyl proton. The fact that at least four singlets are detectable, two by two of the same intensity, probably due to the higher asymmetry, since the aryl rings are not co-planar to the same extent as with the N=CH=N linkage. However, the non-equivalence of the formamidido ligands in each conformer does not affect the electronic environment of the allyl groups sufficiently to detect two distinct allyl groups for conformer II and four for I. Thus the formyl protons appear more sensitive than the allyl protons to their electronic environment; the least sensitive are the CH₃ protons of the *N,N'*-di-*p*-tolylformamidido ligand since the different disposition of the allyl and formamidido groups has no effect on the chemical shift of the methyl protons of I and II (Fig. 2).

A closer inspection of the ¹H NMR spectra at low temperature reveals a more sensitive temperature-dependent chemical shift for only one allyl group (probably b) of conformer I (this is the only one differently oriented); on lowering the temperature its AA'BB' pattern reversibly shifts towards lower fields and it appears more separated from the other three AA'BB' patterns. One

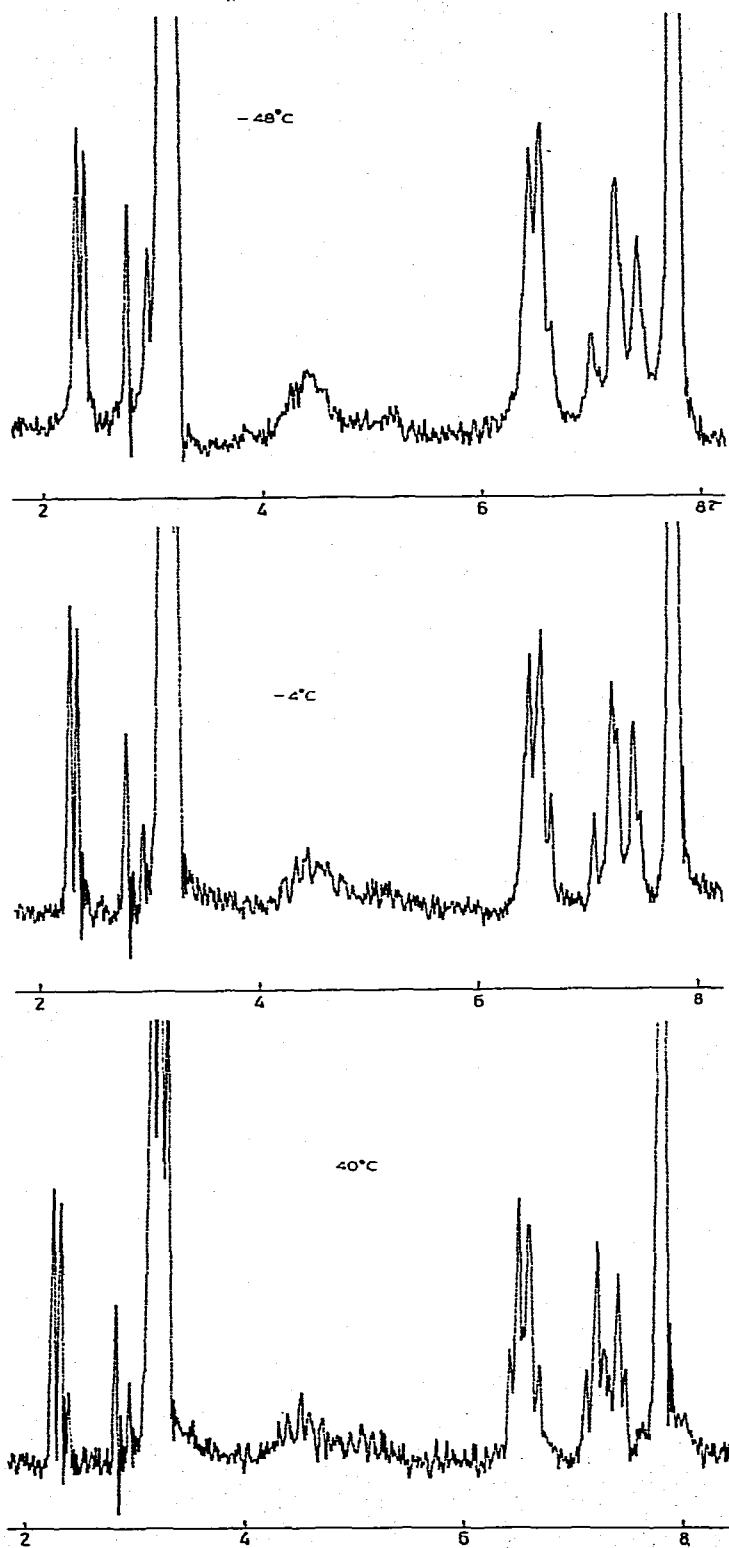


Fig. 2. The variable temperature 60 MHz ^1H NMR spectrum of $[(1-3-\eta\text{-C}_3\text{H}_5)\text{Pd}(p\text{-CH}_3\text{C}_6\text{H}_4\text{=CH=N-C}_6\text{H}_4\text{CH}_3\text{-}p)]_2$.

may speculate that the allyl group b is allowed to rotate to some extent around the Pd—allyl bond, orienting itself to a position closer to a or c at higher temperature, from the chemical shift point of view. Experiments performed up to 110 °C in chlorobenzene show that a reversible dynamic process brings to NMR equivalence the allyl groups of conformer I only and that no interchange be-

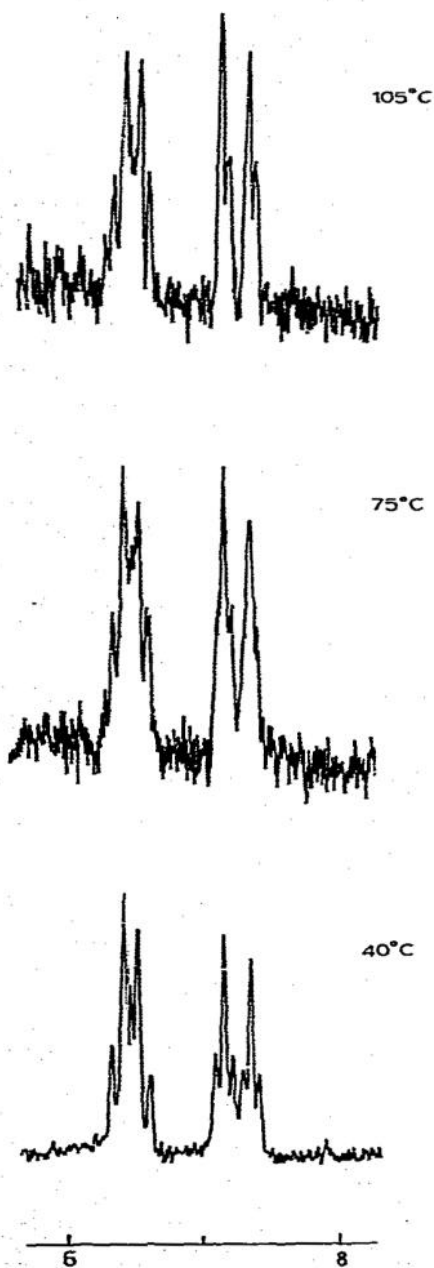


Fig. 3. The variable temperature 60 MHz ^1H NMR spectrum of $[(1\text{-}\eta\text{-C}_3\text{H}_5)\text{Pd}(\text{p-ClC}_6\text{H}_4\text{N}\equiv\text{CH}\equiv\text{N-C}_6\text{H}_4\text{Cl-p})_2]$.

tween conformer I and II occurs (above 110°C extensive decomposition takes place as some metallic palladium forms). This fluxional behaviour cannot be explained by the above rotation (even if complete) and/or allyl flip [13,14], nor by $\pi \rightarrow \sigma \rightarrow \pi$ exchange processes or terminal CH_2 rotations [15]. In fact, the process resulting in the NMR equivalence of the allyl groups of conformer I requires a smaller energy than that of conformer I—conformer II exchange (which does not occur even at 110°C). This exchange would occur at a lower temperature than the fluxional process if rotation (and/or flip) is operating, since it would involve just one allyl group, instead of the synchronized motion of both allyl groups required for the fluxional process of conformer I* (Fig. 3).

No dependence of the temperature of collapse of the signals of the allyl groups of conformer I on the concentration has been observed, so an intermolecular mechanism can be excluded [1] (moreover this would not discriminate between the two conformers and equivalence of the three types of allyl groups would occur simultaneously).

A solvolytic cleavage of only one Pd—N bond, as proposed for the carboxylate systems seen before, or an inversion of the boat conformation through a chair one may be two valid hypotheses to explain the fluxional behaviour of I. In order to discriminate between these two possibilities, we carried out variable temperature NMR experiments in the presence of equivalent amounts of weak bridge-splitting ligands such as DMSO [18] or the protonated parent formamidine. Such agents have no effect on the behaviour of the conformers. Similar experiments carried out on the acetate analogue with DMSO or acetic acid [1] had a marked effect in lowering the temperature of the collapse of the allyl groups of I and in favoring the I—II exchange [1]. Thus the hypothesis that the acetate conformer I is fluxional through a solvolytic cleavage of only one Pd—O bond, confirmed by the NMR variable temperature results on the benzoate analogue, contrasts with the results on the formamidido complexes, for which an inversion mechanism seems more likely. Such a process consists of an inversion of the boat conformation of the $\text{C}_2\text{N}_4\text{Pd}_2$ ring through a chair one, and results in the interchange of the NMR environment of the allyl groups a and b, as shown in Fig. 4.

There is a considerable electronic effect of the *p*-substituent of the aryl ring as the allyl signals of the *p*-Cl derivative collapse at 75°C, while those of the *p*- CH_3 analogue collapse at ca. 100°C**. If the hypothesis of boat inversion holds, this suggests that the *p*-Cl electron-withdrawing character favours the inversion of the $\text{C}_2\text{N}_4\text{Pd}_2$ ring, probably by limiting the extension of the π -conjugation from the aryl ring to the formamidido linkage.

Addition of equimolecular amounts of $[(1-3-\eta\text{-C}_3\text{H}_5)\text{PdCl}]_2$ to the acetate system resulted in a rapid exchange of the electronic environment of all the allyl groups, giving rise to a single AA'BB'X pattern, whose chemical shifts were es-

* The NMR equivalence of the allyl groups of dimeric complexes with bridging nitrogen pyrazolide linkages of type I conformer (the only one present in solution) is achieved at 150-170°C and was ascribed to simple rotation of the allyl groups [16]. In this case boat inversion would involve prohibitive steric strain and be energetically unfavorable, however no experiment was carried out to exclude a solvolytic mechanism which could also explain the equivalence.

** For this last derivative the NMR equivalence is not fully achieved at 110°C, but at higher temperatures extensive decomposition takes place.

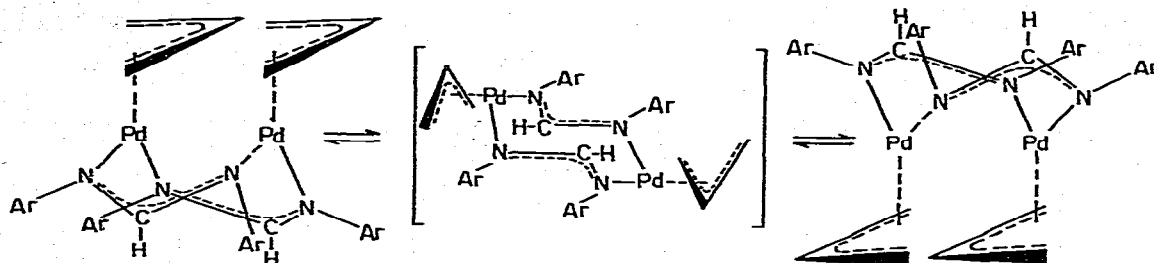


Fig. 4. Proposed mechanism for the NMR equivalence of the allyl groups of the N,N' -diarylformamidido conformer I.

essentially the weighted average of those of the acetate and chloride alone, at the temperature at which exchange occurs between conformers I and II [1]. This process was explained as a bimolecular bridging ligand exchange similar to that observed by Tibbets and Brown in 2-methylallylpalladium halides [17]. The allylpalladium chloride dimer had no effect on the formamidido system indicating that no cleavage of the Pd–N bonds occurs even at 110 °C, thus confirming the intramolecular mechanism for the fluxional behaviour of conformer I.

It is interesting to note that the closely related triazenido system undergoes no dynamic process. Taking into account the hypothesis of the boat inversion mechanism, the rigidity of the analogous triazenido conformer I may be due to stronger π -conjugation of the triazenido linkage compared with formamidido. In fact, while formamidine and the corresponding formamidino complexes are colourless and pale yellow-coloured, respectively, triazene and triazenido complexes are yellow or deeply yellow-orange coloured, suggesting a more extended π -conjugation in the latter case.

Acknowledgements

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