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DYNAMIC STEREOCHEMISTRY OF π-ALLYLIC Pd(II) α-AMINOACETATE COMPLEXES

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A variety of π-allylic Pd(II) aminoacetate complexes were synthesized, and their temperature dependent NMR study revealed the presence of diastereoisomers which are in dynamic equilibrium by π-allyl rotation mechanism.

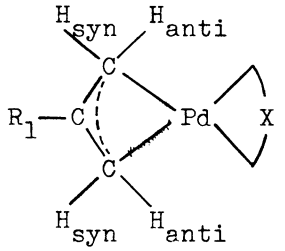
In accordance with the increasing attention in the literature[1~4] to the pseudo-chirality of π-allylic lignad on coordination, we herein wish to report the synthesis of π-allylic Pd(II) α-aminoacetate complexes and discuss their structure as relates to NMR behaviour. The aminoacetate includes those of glycine, (S)-alanine, N-benzyl-(S)-alanine, (S)-phenylalanine, (S)-valine, and (S)-proline, while the π-allylic ligand comprises π-allyl, and π-2-methylallyl, as well as some of the other substituted π-allyl group. The synthetic procedure is also applicable to other complexes of similar type, such as π-allylic Pd(II) β-alaninate, 6-methyl-picolinate, or S-benzylthioglycolate.

The synthesis consists in the reaction of chloro(π-alkenyl)Pd(II) with silver aminoacetate in solvent such as methanol or chloroform. The identification of the complexes resides on IR, NMR, EA, and molecular weight measurement (monomeric in methanol). The isolated complexes (usually in yields 50~80%) are generally not very stable in the air and gradually decompose on storage, making it necessary to carry out any physico-chemical measurement on freshly prepared sample.

All of the NMR spectra of coordinated π-allylic group in π-2-methylallyl (or π-allyl) complexes are of typical AA'BB' (or AA'BB'X) pattern at and above room remperature except for proline and N-benzylalanine complexes. The latter two are different from the rest in that A and A'(anti-protons, those trans to central

substituent) are no more indistinguishable but are clearly differentiated from each other. Some of the typical room temperature NMR spectra are summarized in Table I.

Table I NMR Spectra(60MHz) of π-allylic Pd(II) Complexes at Room Temperature (TMS standard)



No	R_1	X	solvent[a)]	δ_{syn}	δ_{anti}	δ_{H_1}	$J_{H_1-H_{syn}}$,	$J_{H_1-H_{anti}}$
1	CH_3	Gly	M	3.70	2.71 (ppm)			
2	CH_3	Ala	M	3.70	2.70			
3	CH_3	Pha	M	3.56	2.41			
4	CH_3	Pro	M	3.65	2.63, 2.77			
5	H	Gly	W	4.10	3.02	5.43	6.5	12.0 (Hz)
6	H	Ala	M	3.93	2.86	5.46	7.1	12.5
7	H	Pha	W	3.95	2.73	5.48	7.5	11.5
8	H	Pro	M	3.92	2.96, 2.82	5.52	6.9	12.1

a) M: d_4-Methanol, W: d_2-Water

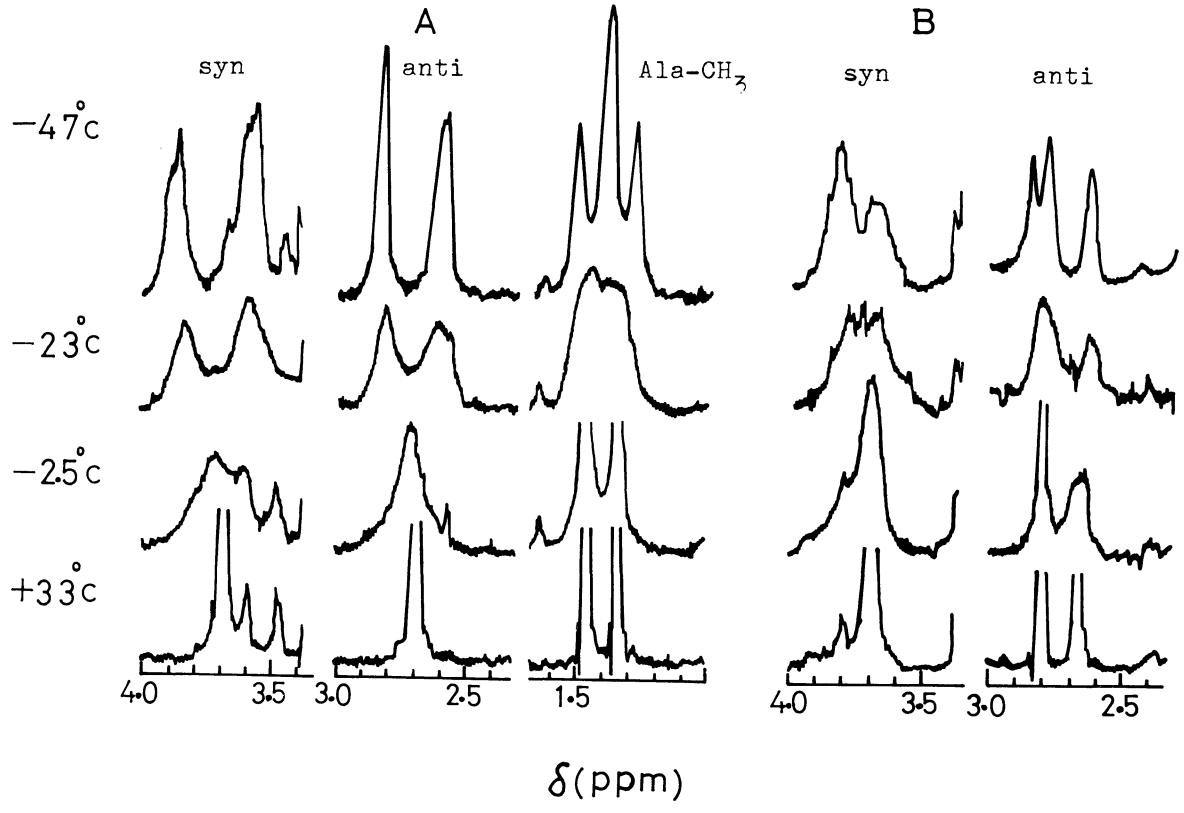


Figure 1. Variable Temperature NMR Spectra(60MHz) of Alaninato(π-2-methylallyl) Pd(II) (A) and Prolinato(π-2-methylallyl) Pd(II) (B) in d_4-Methanol

The typical temperature dependence is illustrated in Figure 1 for alanine and proline complexes of π-2-methylallyl Pd(II). Other complexes in Table I show the similar behaviour, and obviously there is some dynamic process operating in these complexes which becomes frozen below room temperature. Above room temperature, on the other hand, the spectra remain essentially unchanged upto 58°C(in methanol) or even upto 90°C(in nitrobenzene) for some of the stable complexes. This means that in the present experimental conditions there is no syn-anti proton exchange in NMR time scale, the view which is further supported by the fact that the coupling constants of syn- and anti-protons to central proton in π-allyl group remain unchanged. Therefore, any mechanism which involves the exchange of syn- and anti-protons[2,3] is unsatisfactory to interpret the dynamic process observed in the present complexes. There remain two mechanisms to be inspected, i.e., "π-allyl flip" and "π-allyl rotation".

The prominent feature of these complexes lies in the fact that the coordinated α-aminoacetate is, in addition to its chiral nature, much less labile[5] than ordinary monodentate ligand such as chloride or amine, and provides a peculiar material for the detailed study of dynamic stereochemistry of coordinated allylic group which has not yet been covered by the ordinary π-allylic complexes appeared in the literatures[2,4]. Figure 2 is a schematic picture of α-aminoacetato(π-2-methylallyl) Pd(II) as viewed down Cartesian y axis with palladium atom placed at the center of the coordinates. The space around palladium is devided into octants, 1, 1B, 2, 2B, 3, 3B, 4, and 4B(B: backside). If xz-plane is coplanar with the page, then π-2-methylallyl group is above the page in front octants, and aminoacetate, below the page in backside octants. With these in mind, "π-allyl flip", and "π-allyl rotation" mechanism are illustrated in scheme 1, where symbols N, O, and R represent (S)-aminoacetate, and the other simplifications are made. Four possible cases are considered below as to the mechanism of epimerization and the anti-proton resonance pattern to be expected. The similar argument holds to syn-protons.

no flip, no rotation: Four resonances (two pairs of resonances, equal intensities within a pair) should result due to non-equivalent fields in octants, 1, 2, 3, and 4. flip only: Fields of octant 1 and 4, as well as those of octant 2 and 3, are averaged. This leads to two resonances of equal intensity, which is described as due to "ligand atom effect"[7] of aminoacetate. rotation only: Fields of octant 1 and 3, as well as those of 2 and 4, become averaged. There should appear two resonances of equal intensity, which substantiate the "chirality effect"[7] due

to asymmetric disposition of R in aminoacetate moiety. flip and rotation: Single resonance signal represents the averaged field of all the four octants. In summation the effect of optically active α-aminoacetate ligand on the proton resonances of π-allylic group is in double ways, "ligand atom effect", and "chirality effect". The former is nullified by "π-allyl rotation" but not by "π-allyl flip". The latter remains unrevealed under the flip motion but becomes manifested under rotational process.

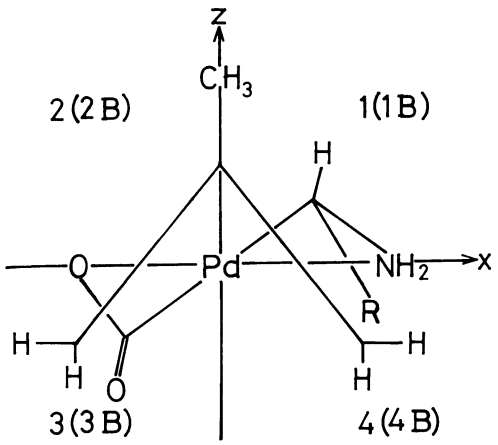
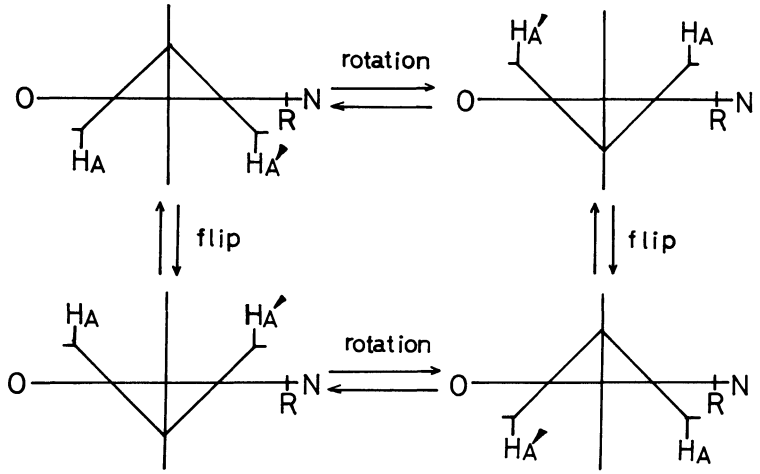


Figure 2



Scheme 1

In Figure 1 the alanine complex shows the splitting of syn- and anti-proton resonances into doublets at low temperature[8]. That this splitting is not the manifestation of chirality effect but that of ligand atom effect is evidenced by the fact that glycine complex which lacks an asymmetric α-carbon gives the almost identical temperature dependent NMR spectra[9]. This verifies the rotational process operating in both complexes at and above room temperature which, however, becomes frozen at low temperature. This view is also consistent with the spectra of 6-methylpicolinate and S-benzylthioglycolate complexes of (π-2-methylallyl)Pd(II) which again lack chiral element on the carboxylate side. Both syn- and anti-protons show sharp singlets at room temperature, and no splitting due to ligand atom effect was observed. Powell reported that π-2-methylallyl Pd(II) picolinate in chloroform at -20°C gave single anti-proton resonance (τ,6.92) and two syn-proton resonances (τ,6.23, 5.92)[11]. This observation provides some measure of ligand atom effect to be expected in the complex of 6-methylpicolinato(π-2-methylallyl) Pd(II). These evidences strongly support the idea that in the present complexes π-allyl rotation process is opperative, essentially freely, at and above room temperature[12]. However, the above argument does not exclude concurrent π-allyl flip

process occurring along with π-allyl rotation, since the alternative explanations for the failure of appearence of chirality effect in alanine complex are (i) negligible chirality effect associated with methyl substitution on α-carbon, and (ii) nullification of chirality effect by means of flip motion. The settlement to this problem is provided by proline complex below, which denies the latter possibility.

It would be reasonable to assume that the π-allyl rotation process is equally well operative in proline complex at and above room temperature as in other complexes. Then, it follows that the invariance of two anti-proton signals observed between 30°C and 90°C must be a manifestation of chirality effect from prolinato ligand. On the other hand, resonance signals start to broaden below room temperature and are finally converted into new multiplets[13]. It seems that for anti-protons two of the formally four resonances happened to occur at the same frequency at -47°C. The behaviour of N-benzylalanine complex is similar to that of proline, although the broadening of resonance signals starts at considerably higher temperature (~90°C in nitrobenzene)[14] rather than at ~10°C for proline complex. All of these observations and other related evidences lead to the conclusion that π-allyl rotation is opperative in (π-2-methylallyl)- or (π-allyl)Pd(II)aminoacetate complexes at and above room temperature, and that the freezing of this process gives rise to the temperature dependent NMR spectrum. While the present system is the first among four coordinated π-allyl metal complexes in which the presence of π-allyl rotation was demonstrated, it has been reported that in the cationic complex 1,2-bis(diphenylphosphino)ethane(2-methylallyl)Pd(II) such process was not detected[3]. The apparent contradiction would be ascribed to the difference in structure, the allyl-Pd bond being presumably much tight in the cationic complex as compared to that in the neutral complex. More study is needed in this context.

References

1) J.Powell, and A.W.L.Chan, J.Organometal.Chem.,35, 203(1972).
2) J.W.Faller, M.E.Thomsen, and M.J.Mattina, J.Am.Chem.Soc.,93, 2642(1971).
3) D.L.Tibbetts, and T.L.Brown, J.Am.Chem.Soc.,92, 3031(1970).
4) P.Ganis, G.Maglio, A.Musco, and A.L.Segre, Inorg.Chim.Acta,3, 266(1969).
5) The absence of intermolecular aminoacetate ligand exchange in NMR time scale was verified by the fact that a equimolar mixture of phenylalaninato(π-2-methylallyl)Pd(II) and glycinato(π-2-methylallyl)Pd(II) in d_4-methanol gave proton resonance spectrum which is just a superposition of those recorded seperately for each component. The similar observation was confirmed with other complexes. A rapid intramolecular nitrogen-oxygen positional exchange

("rotation" of aminoacetate ligand) was arbitrarily excluded in view of the successful isolation of cis-, and trans- isomer of bis(glycinato)Pd(II)[6]. However, the presence of π-allylic group could somewhat labilize aminoacetate for such a process, and in that case there is no basis at present to distinguish between "π-allyl rotation" and "aminoacetate rotation".

6) K.Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", John Wiley and Sons, Inc., New York, N.Y. (1970), p.232.

7) The terms "trans effect" and "chirality effect" were adopted in a review. S.Otsuka, "The Synthesis of Metal Complexes and the Ligand Reactivity", (in Japanese, edited by A.Nakahara, and M.Shibata) Nankodo, Tokyo(1970), p.255.

8) For syn-protons, the free energy of activation as evaluated by the usual coalescence method, $\Delta G^{\ddagger}_{-2.5°C}$=14kcal/mol. For methyl protons of alanine, $\Delta G^{\ddagger}_{-23°C}$=13kcal/mol. Generally, temperature dependence was not limited to syn- and anti-protons, but other protons also reflected the formation of diastereo-isomer.

9) In fact there is another possibility to be considered that this splitting arose from the chirality of aminoacetate chelate ring whose conformation could become frozen at low temperature. However, this possibility is excluded from the energetic consideration upon such a conformational transforamation. A recent calculation[10] indicated that the activation free energy of conformational inversion for an isolated ethylenediamine transition metal chelate ring is less than 6kcal/mol. The energy associated with the glycine chelate ring presumably does not exceed this value, since the chelate ring is less puckered and a number of non-bonded interactions involved is smaller. The observed energy of trans-formation($\Delta G^{\ddagger}$) in the present aminoacetate complexes including glycine complex is invariably around 13～14kcal/mol at the coalescence which is too large to be accepted as associated with such a conformational inversion.

10) J.R.Gollogly, C.J.Hawkins, and J.K.Beattie, Inorg.Chem.,10, 317(1971).

11) E.Ban, A.Chan, and J.Powell, J.Organometal.Chem.,34, 405(1972).

12) Ambiguity remains with the picolinate complexes. Powell briefly described the rapid syn-syn, and anti-anti proton exchanges at room temperature for π-allylic picolinate complexes, and, on the basis of "a marked concentration dependence" of the phenomenon, suggested a bimolecular (nitrogen-oxygen positional) exchange process in which another molecule of complex acts as a base and promotes exchange in a similar manner to the added pyridine[11]. On the other hand in the presnet study, sixfold change in concentration of prolinato(π-2-methylallyl) Pd(II) produced the identical temperature dependent NMR spectra. Thus, for aminoacetate complexes such a process does not seem to be important.

13) For syn-protons, $\Delta G^{\ddagger}_{-23°C}$=13kcal/mol.

14) The situation is much complexed in this compound since the stereochemistry of benzyl group disposition becomes a added factor. It is to be noted here that an appreciable chirality effect was verified only with N-alkylated amino-acetates. It is probably related to the asymmetric nitrogen introduced on coordination to palladium.

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