Preparation and the Properties of π-Allylic Palladium(II) Complexes of Amino Acid

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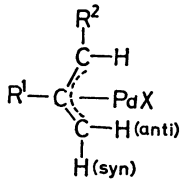
The preparation of π-allylic and related organopalladium(II) complexes with amino acid anions as bidentate ligands is described. The complexes were characterized by means of ^{1}H NMR.

In a previous communication[1] we reported a variable-temperature ^{1}H NMR spectral survey of π-allylic palladium complexes of α-amino acid without giving details of the preparation of the complexes. Some complexes were later found to show an interesting catalytic activity in oligomerizing butadiene preferentially to tetramers.[2] We report herewith on the preparation and characterization of the metal complexes concerned.

Results and Discussion

The principle in preparing the complexes was to displace the di-μ-chloro bridge of dimeric organopalladium complexes by bidentate and chelating amino acid anions. The latter was used as silver salts. After publication of our communication, Benedetti *et al.*[3] reported the preparation of similar amino acid complexes, in which potassium salts of amino acids were utilized. The alkali metal salts can not always be prepared. However, the corresponding silver salts are readily available. Thus the use of the latter salts is preferable for the present study. The π-allylic palladium complexes prepared are given in Table 1 along with the ^{1}H NMR chemical shifts of allylic protons. The aryl- or alkylpalladium(II) amino acid complexes of similar type could also be

TABLE 1. π-ALLYLIC PROTON CHEMICAL SHIFTS OF PALLADIUM COMPLEXES
(δ, ppm from TMS, 60 MHz, 35 °C)[a]



Complex	R^1	R^2	X[b]	Solvent[c]	*syn*-H	*anti*-H	R^1(H,CH$_3$)
1	H	H	Gly	D_2O	4.10	3.02	5.43
2	H	H	Ala	M	3.93	2.86	5.46
				D_2O	3.70	2.99	5.41
3	H	H	Val	M	3.93	2.84	5.44
4	H	H	Phe	D_2O	3.95	2.73	5.48
5	H	H	Pro	M	3.92	2.96, 2.82	5.52
				C	3.91	2.89, 2.67	5.40
				D_2O	4.05	3.05, 2.95	5.61
6	H	H	Bz-Ala	C	3.90	2.86	5.30
7	H	H	Cbz-Gly	C	3.8—4.0	2.85	5.40
8	CH_3	H	Gly	M	3.70	2.71	2.10
9	CH_3	H	Ala	M	3.70	2.70	2.10
10	CH_3	H	Phe	M	3.56	2.41	1.99
11	CH_3	H	Pro	M	3.65	2.77, 2.63	2.12
12	CH_3	H	His	M	3.6—3.9	2.7—3.1	2.12
13	CH_3	H	Bzl-Ala	M	3.95, 3.82	2.56, 2.1—2.3	1.85
14	CH_3	H	6-MP	M	4.15	3.17	2.20
15	CH_3	H	BTA	M	3.90	2.95	2.04
16	H	CH_3[d]	Ala	M	3.5—4.1	2.62	5.31
17	H	C_6H_5	Ala	M	3.92	4.56, 2.97	5.94
18	H	$CO_2C_2H_5$	Ala	C	4.0—4.3	3.21, 3.53	6.05

a) When signals were broad or no definite assignment could be made, the region where the signals appeared is indicated. Coupling constants between the central and terminal protons were 6.5—7.5 Hz and 11—12.5 Hz for *syn* and *anti* positions, respectively. Geminal couplings of the terminal protons were $\lesssim$1 Hz. b) Amino acids are of natural (L-) configuration. Bz-Ala, *N*-benzoylalaninate; Cbz-Gly, *N*-benzyloxycarbonylglycinate; Bzl-Ala, *N*-benzylalaninate; 6-MP, 6-methylpicolinate; BTA, (benzylthio)acetate. c) M, CD_3OD; C, $CDCl_3$. d) The methyl group is in *anti* position.

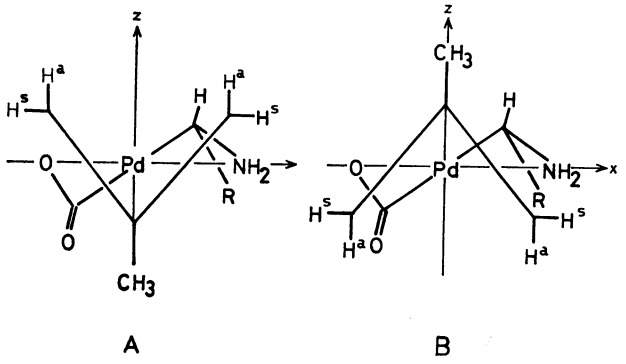


Fig. 1. Schematic view of [π-(2-methylallyl)]Pd(II) complex of α-amino acid.

prepared, including those derived from *N,N*-dimethylbenzylamine-,[4] *N*-benzylideneaniline-[5] or methoxydicyclopentadiene[6]-palladium(II) chloride (see Experimental).

Figure 1 shows a schematic picture of π-(2-methylallyl)palladium complex of amino acid as viewed down Cartesian y axis. Because of the "ligand atom effect" and "chirality effect,"[1] the four front octants in which allylic protons H^s and H^a are placed should differ from each other in their magnetic environment. If the relative configuration of the allylic ligand and the amino acid ligand is fixed as in pictures A and B, then four *anti* proton signals as well as the same number of *syn* proton signals should be observed. The low temperature ^1H NMR at 90 MHz was studied for π-(2-methylallyl)-palladium glycinate (**8**), alaninate (**9**) and prolinate (**11**) complexes at temperatures between 0 and −90 °C. No further change in spectral pattern was observed by lowering the temperature below −40 °C in line with the previous study at 60 MHz. However, the signals were sharpened, and additional small splittings (1—3 Hz) were disclosed. A schematic representation of the experimentally observed spectra is given in Fig. 2 for selected signals. Splittings of *syn* or *anti* proton signal(s) into four signals or less for **9** and **11** are in line with the expectation that the relative configuration of the two ligands on the metal is fixed at low temperature, and all or at least three out of the four front octants differ from each other in their magnetic environment. Examination of intensities of the signals reveals that the relative population of configuration A and B are equal. This is reasonable since no direct steric or dipolar interaction can be expected between the coordinated allylic ligand and the amino acid ligand. Glycinate complex **8** gave the splitting of *syn* and *anti* proton signals (which are singlets at room temperature) into doublets, but the absence of chirality in the glycine molecule allowed no further splitting. The freezing of the chelate ring conformation of the glycine ligand might have occurred at low temperature (−90 °C), but the effect was not sufficient to bring about measurable splittings of the signals.

The dynamic process as revealed by the temperature-dependent ^1H NMR signals was most satisfactorily rationalized either by π-allyl rotation[1] or base assisted N,O-ligand atom exchange of amino acid ligand.[1,7] No

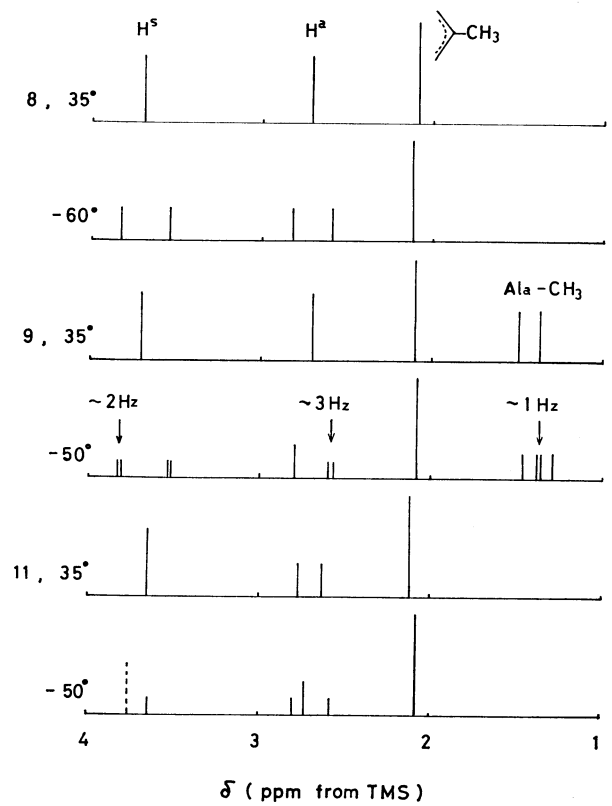


Fig. 2. A schematic representation of selected proton signals observed for π-allylic complexes. Low temperature spectra (−50, −60 °C) were obtained at 90 MHz, and those at 35 °C were at 60 MHz.

effect of the complex concentration[7] on the spectral shape was observed, indicating that the process is unimolecular with respect to the complex. Preference of the π-allyl rotation as a plausible mechanism is suggested. However, the possibility that the solvent molecule (methanol-d_4) acts effectively as base and that the process is the N,O-ligand atom exchange can not be excluded. As to the ^1H NMR behavior of other π-allyl- or π-(2-methylallyl)palladium complexes (Table 1), most of them seem to be grouped into one of the three typical types (Fig. 2). Complex **13** shows a complicated temperature-dependent behavior, rejecting simplified spectral interpretation.

Experimental

General. The ^1H NMR spectra were obtained with a Varian A-60 spectrometer at 60 MHz and a Hitachi R-22 spectrometer at 90 MHz. Natural (L-) amino acids and their derivatives were used. π-Allylic palladium(II) chloride complexes were prepared according to the reported procedures[8] and used as obtained or after purification by column chromatography.

Silver Salts of Amino Acid. The general procedure for the preparation of the salts is as follows. Silver nitrate (1 mmol) dissolved in water or aqueous methanol was added under stirring to an equimolar mixture (1 mmol each) of lithium hydroxide monohydrate and an amino acid in a similar solvent. Silver salt precipitated as withe powder. The solvent was chosen considering the solubility of the starting material and the product. For silver salt easily

hydrolyzable in water (typically, those of proline, *N*-phenylglycine and tryptophan), 80—90% methanol was used. For the stable salts (*e.g.*, those of glycine and β-phenylalanine), water was used. In each case the use of minimum amount of the solvent was preferred. Yields were 60% to quantitative.

π-Allylic Palladium(II) Complexes of Amino Acid. The complexes were prepared according to the following general procedure. π-Allylic palladium(II) chloride (1 mmol) was stirred with the suspension of excess silver salt of amino acid (3 mmol) in methanol or chloroform (20—40 ml) in the dark until the yellow coloration due to the starting complex disappeared (5—20 min). Filtration and concentration of the reaction mixture followed by gradual addition of ether produced the amino acid complex as pale yellowish crystalline powder. Yields were 60% to quantitative. The product was in most cases analytically pure, but in some cases reprecipitation was needed for further purification after treatment with decolorizing charcoal. The stable complexes could be purified by recrystallization. Numerous complexes other than those given in Table 1 were also prepared according to the procedure outlined above. The complexes of Phe were the most stable, while those containing Pro were air-sensitive, the manipulation of the solution being preferably carried out under dry nitrogen. The proline complexes could not be stored more than a week. The elemental analyses of the complexes were statisfactory except for a few cases. No analyses were made for **12** and **17**. The IR and NMR spectra are in line with the composition and structure of the complexes. Details for the selected complexes are given in the following. **4.** π-Allylpalladium(II) chloride[8] was reacted with silver salt of Phe in methanol. The complex was recrystallized from water or water containing a small amount of ethanol, yield 73—95%, dec 160—175 °C, $\nu_{C=O}$ 1600 cm^{-1}. NMR for Phe (δ, ppm from TMS; D_2O): 2.2—2.6 (t, J=5.0 Hz, >CH–), 3.31 (d, J=5.0 Hz, –CH_2–), 7.75 (s, –C_6H_5). Found: C, 46.24; H, 4.76; N, 4.52%. Calcd for $C_{12}H_{15}NO_2Pd$: C, 46.25; H, 4.85; N, 4.49%. **9.** π-(2-Methylallyl)palladium(II chloride[8] was reacted with silver alaninate in chloroform, yield 80—87%, dec 138—150 °C, MW (vapour pressure osmometer) 236 (Calcd: 249.6), $\nu_{C=O}$ 1603 cm^{-1}. NMR for Ala (CD_3OD): 3.54 (q, J=7.0 Hz, >CH–), 1.41 (d, J=7.0 Hz, –CH_3). Found: C, 33.04; H, 5.21; N, 5.54%. Calcd for $C_7H_{13}NO_2Pd$: C, 33.69; H, 5.25; N, 5.61%. **11.** π-(2-Methylallyl)palladium(II) chloride[8] was reacted with silver prolinate in chloroform, yield 60—90%, dec 110—138 °C, MW 294 (Calcd: 275.6), $\nu_{C=O}$ 1608 cm^{-1}. NMR for Pro (CD_3OD): 1.7—2.2(m, C–CH_2CH_2–C), 3.1—3.4 (m, N–CH_2–C), 3.7—3.9 (m, >CH–). Found: C, 39.00; H, 5.41; N, 5.01%. Calcd for $C_9H_{15}NO_2$-Pd: C, 39.22; H, 5.49; N, 5.08%. **15.** The silver salt of BTA was obtained as white precipitate from aqueous reaction mixture. The reaction with π-(2-methylallyl)palladium(II) chloride[8] was carried out in chloroform, yield 76%, dec 110—125 °C, $\nu_{C=O}$ 1634 cm^{-1}. NMR for BTA ($CDCl_3$): 3.47 (s, benzyl-CH_2–), 4.08 (s, –$COCH_2S$–), 7.38 (s, –C_6H_5). Found: C, 45.69; H, 4.70%. Calcd for $C_{13}H_{16}O_2PdS$: C, 45.56; H, 4.71%. π-(1-Ethoxycarbonylallyl)palladium(II) glycinate. π-(1-Ethoxycarbonylallyl)palladium(II) chloride[8] was reacted with silver glycinate in methanol, yield 80—97%, dec 150—160 °C, $\nu_{C=O}$ 1600, 1620 cm^{-1}. Found: C, 32.73; H, 4.33; N, 4.95%. Calcd for $C_8H_{13}NO_2Pd$: C, 32.73; H, 4.33; N, 4.77%. The complex is stable at room temperature. Other complexes. *o*-(Dimethylaminomethyl)-phenylpalladium(II) alaninate. The organopalladium chloride[4] was reacted with silver alaninate in chloroform in the usual way, white crystalline powder, yield 97%, $\nu_{C=O}$ 1625 cm^{-1}. NMR (CD_3OD): 6.8—7.0 (m, Ar–H), 3.88 (s, benzyl CH_2), 3.57 (q, J=7.0 Hz, –CH–), 2.79 (s, N–CH_3), 1.49 (d, J=7.0 Hz, C–CH_3). Found: C, 42.82; H, 5.58; N, 8.47%. Calcd for $C_{12}H_{18}N_2O_2Pd$: C, 42.85; H, 5.52; N, 8.52%. 3a,4,7,7a-Tetrahydro-*exo*-6-methoxy-*endo*-4,7-methanoindene-*endo*-5σ,2π-palladium(II) alaninate. The organopalladium(II) chloride[6] was reacted with silver alaninate in methanol. Manipulation under nitrogen produced white powder, yield 88%, $\nu_{C=O}$ 1632, ν_{C-O} 1090 cm^{-1}. NMR for Ala (CD_3OD): 3.3—3.6 (q, >CH–), 1.58 (d, J=7.5 Hz, –CH_3). The signals for the π-enyl moiety were similar to those of the chloride complex.[6]

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