Journal of Organometallic Chemistry, 253 (1983) C55—C58
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

SYNTHESIS OF A CHIRAL ANIONIC COMPLEX OF HEXACOORDINATED PALLADIUM(II) HAVING A PALLADIUM—CARBON σ-BOND STARTING FROM OPTICALLY ACTIVE DI-μ-CHLOROBIS(DIMETHYLAMINOMETHYLFERROCENYL-*C,N*)DIPALLADIUM

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(Received June 1st, 1983)

Summary

Starting from the enantiomeric title compound I, several complexes with amino acids, such as glycine (II), L-lysine (IV), L-aspartic acid (V), L-cysteine (VI), were prepared. Complex II, when treated with excess sodium glycinate, gave a new ionic complex $(Fc_R PdGly_2)^- Na^+$, III, which was isolated column-chromatographically. CD spectra suggest that III is a unique example of a hexacoordinated palladium(II) complex. Additional coordination in the cysteine complex VI is another possibility.

Our recent work on asymmetric cyclopalladation has afforded a facile route to an optically active ferrocene series via the title compound (I) of high enantiomeric purity [1]. Starting from I, we prepared several square planar palladium(II) complexes with chelated amino acid and dipeptide ligands [2]. The diastereomeric complex with L-proline has been used for the resolution of I by other workers [3].

Now we report that the monoglycinate complex II [2] is capable to react with another equivalent of sodium glycinate in alkaline solution to give the ionic diglycinate complex III. This can be obtained directly without isolation of II when I is allowed to react with a large excess of GlyNa.

We believe that III is an octahedral complex since its CD spectrum remarkably disagrees with the CD spectra of II and of similar complexes with one amino acid ligand as shown in Fig. 1. The preparation of a hexacoordinated octahedral anionic complex from a tetracoordinated complex by addition of a second amino acid ligand has been previously reported for nickel(II) glycinates, one of the isomers being studied by X-ray method [4]. Perhaps in our case the reaction is

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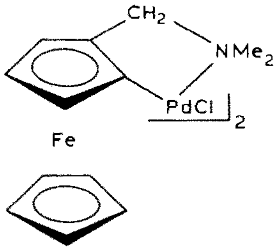

(I)

$$\equiv \; \mathrm{Fc_RPdCl} + \mathrm{GlyNa} \longrightarrow \underset{(\mathrm{II})}{\mathrm{Fc_RPdGly}}$$

$$\underset{(\mathrm{II})}{\mathrm{Fc_RPdGly}} + \mathrm{GlyNa} \rightleftharpoons \underset{(\mathrm{III})}{[\mathrm{Fc_RPdGly_2}]^- \; \mathrm{Na^+}}$$

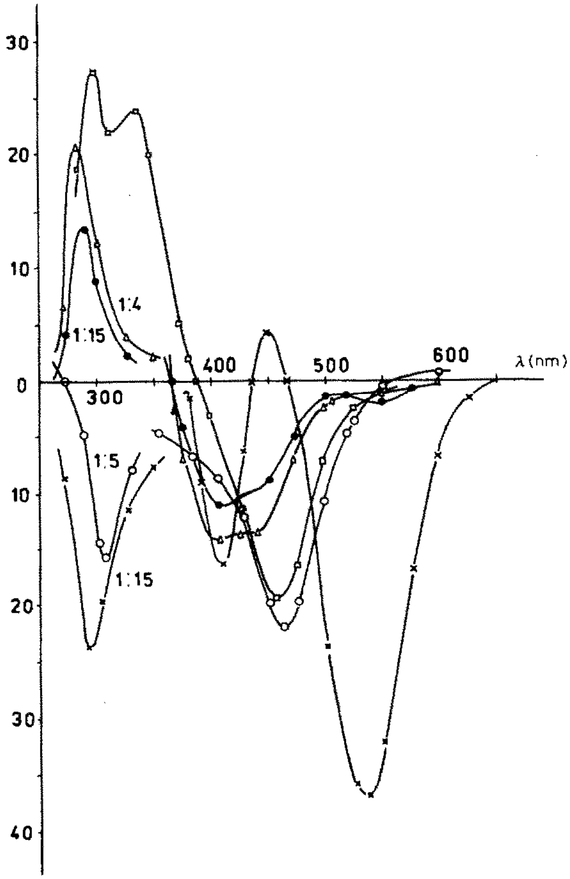

Fig. 1. CD spectra in methanol of complexes II—VI.
II ●—● $\mathrm{Fc_RPdGly}$, III X—X $\mathrm{Fc_RPdGly_2Na}$, IV △—△ $\mathrm{Fc_RPdLys}$, V □—□ $\mathrm{Fc_RPdAsp}$, VI ○—○ $\mathrm{Fc_RPdCys}$.

reversible due to lesser stability of the hexacoordinated complex which has the following features: (i) it is a very rare example, if any known, of a palladium(II) complex which has coordination number 6 with an amino acid ligand; (ii) to the best of our knowledge, the formation of the octahedral complex with a palladium—carbon σ-bond is unprecedented.

The capacity of palladium in complexes like II to expand its coordination sphere prompted us to investigate complexes of amino acids which have additional functional groups, such as L-lysine (IV), L-aspartic acid (V) and L-cysteine (VI). The fifth coordination site at the palladium atom could be occupied in these complexes by NH_2, COO^- or S^- ligands, respectively. However, the CD study revealed that the curves of II, IV (both in neutral and acidic solution) and V (both in neutral and alkaline solution) are very similar and they differ sharply from that of III (Fig. 1). Evidently, the metal atom in IV and V avoids additional coordination. The situation is different with the cysteine complex VI, in this case the CD curve tends to approach that of III which is likely to reflect the occurrence of pentacoordination.

A sulfur atom in cysteine is known to act as a very good ligand for palladium, see, for example ref. 5. However, substitution of S for O while the square planar arrangement is preserved is hardly able to influence the CD spectrum significantly. The most remarkable feature in the CD spectra of III and VI is the same negative sign of a strong Cotton effect near 300 nm while other complexes show positive signs (Fig. 1). UV-visible spectra of II and III have no clear differences except a broad band near 520 nm in III which is optically active and determines a rather strong Cotton effect. There are two Cotton effects in the ferrocene region which are present for all complexes: near 450 and 405 nm but only in III the former is positive. The other complexes exhibit two badly resolved negative maxima. Besides, there is evidence for a positive Cotton effect near 360 nm in III.

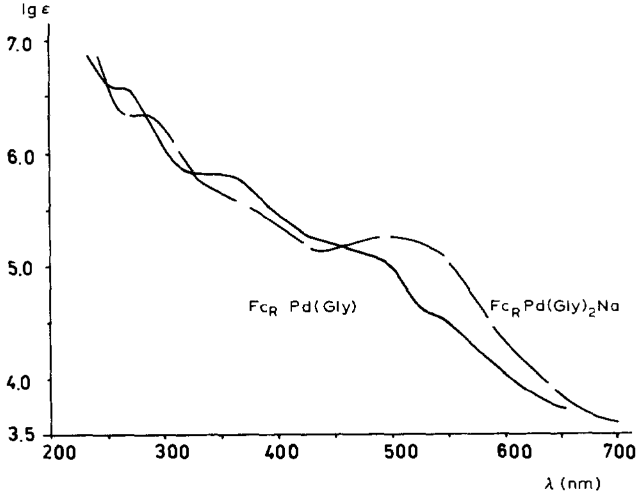

Fig. 2. Absorption spectra in methanol of complexes II and III.

The starting compound I was about 68% enantiomerically pure, the spectra were re-calculated to 100%. It should be emphasized that upon formation of an octahedral complex the metal atom becomes the centre of chirality and hence a number of diastereomers are possible of the same absolute configuration of a chiral plane which are shown in Fig. 3. Therefore further interpretation of the CD spectrum seems to be premature until the X-ray investigation of diastereomeric III is made.

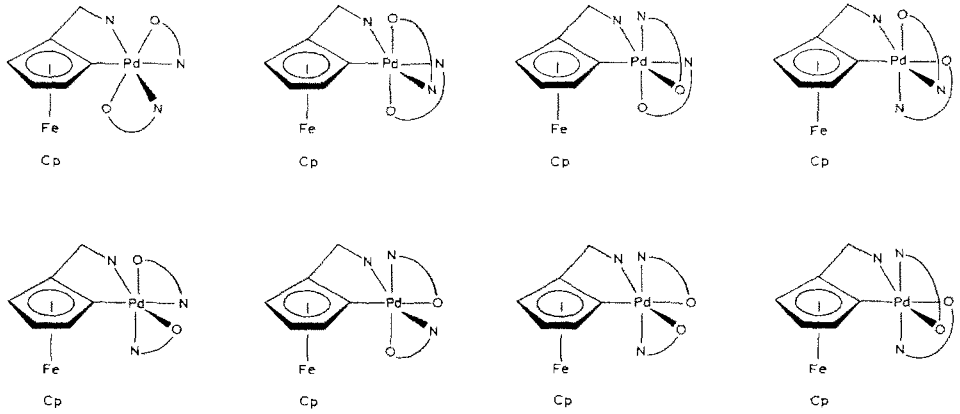

Fig. 3. Possible diastereomers.

Experimental

UV-visible absorption spectra and CD spectra were obtained in methanol at concentrations ca. 10^{-5} mol l^{-1}, with CARY and JASCO J-20 instruments.

To sodium glycinate in 10 ml of methanol (prepared from 0.06 g of sodium metal and 0.2 g of glycine) was added with stirring 1.0 g of (–)I, $[\alpha]^{20}_{578}$ –508° (CH_2Cl_2) in 10 ml of benzene. After 3 h at room temperature the reaction mixture was chromatographed on SiO_2 and 1.1 g of yellow II (98%) was eluted with methanol. Found: C, 42.40; H, 4.68; N, 6.84. $C_{15}H_{20}FeN_2O_2Pd$ calcd.: C, 42.65; H, 4.76; N, 6.63%.

0.8 g of II in methanol was treated with an equimolar quantity of GlyNa and the mixture was stirred and heated for two days. Chromatography on an SiO_2 column with water as eluent afforded 0.22 g (22.4%) of pink-red III. Found: C, 39.73; H, 5.12; N, 8.49. $C_{17}H_{24}FeN_3NaO_4Pd$ calcd.: C, 39.31; H, 4.62; N, 8.09%.

References

1 V.I. Sokolov, L.L. Troitskaya and O.A. Reutov, J. Organomet. Chem., 182 (1979) 537.
2 V.I. Sokolov, K.S. Nechaeva and O.A. Reutov, Russ. J. Org. Chem., 19 (1983) 1003.
3 T. Komatsu, M. Nonoyama and J. Fujita, Bull. Chem. Soc. Japan, 54 (1981) 186.
4 C.F. Campana, D.F. Shepard and W.M. Litchman, Inorg. Chem., 20 (1981) 4039.
5 A. Nakamura et al., Bull. Chem. Soc. Japan, 55 (1982) 2364.