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ISOLATION OF TWO DIASTEREOMERS OF DICHLORO{2-(*S*)-[(*n*-BUTYLPHENYLPHOSPHINO)METHYL]PYRROLIDINE}PALLADIUM(II)

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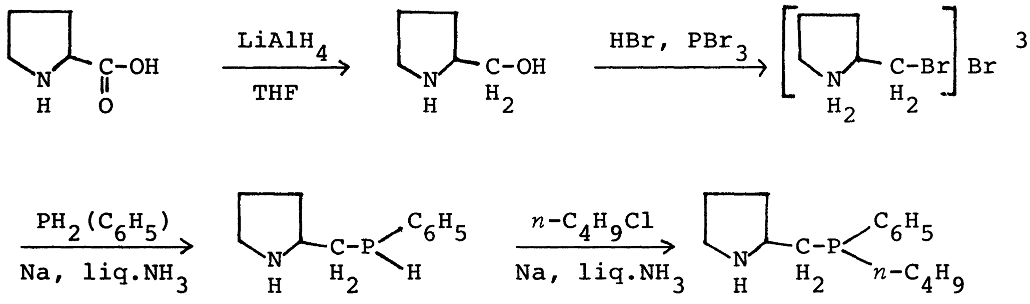
A pair of new diastereomers, the isomerism of which came from a pair of chiral phosphorus atoms were obtained for [PdCl$_2$L], where L denotes 2-(*S*)-[(*n*-butylphenylphosphino)methyl]pyrrolidine prepared from (*S*)-proline. The absolute configurations of these isomers were suggested on the basis of the PMR spectra.

A variety of chiral phosphines have been prepared to investigate asymmetric inductions catalyzed by transition metal complexes.$^{1)}$ Some of optically active natural products are good precursors of such chiral phosphines.$^{2-4)}$

This letter reports the preparation of 2-(*S*)-[(*n*-butylphenylphosphino)methyl]-pyrrolidine (L) which was derived from (*S*)-proline, and the isolation of a pair of diastereomers of the [PdCl$_2$L] complex. The isomers are the first complex of a chiral aminophosphine containing a chiral phosphorus atom.

All the operations for preparing the ligand and the complex were carried out in an atmosphere of nitrogen or *in vacuo*. The ligand was prepared from (*S*)-proline as shown in the following scheme;



b.p. 140-141°C/933 Pa b.p. 135-136°C/13.3 Pa

The [PdCl$_2$L] complex was prepared by the reaction of L with [PdCl$_2$(CH$_3$CN)$_2$] in chloroform at room temperature. Recrystallization of the complex from a mixture of chloroform and ethanol gave two different crystal forms, blocks and needles, which can be separated by hand picking. Both crystals were stable in air and gave the satisfactory results of elemental analysis for [PdCl$_2$L]. The purity of the two isomers may be confirmed by PMR spectra (*vide post*).

The ligand has three chiral centers at the carbon, nitrogen, and phosphorus atoms. Since the chiral carbon atom has the (*S*)-configuration, and the chiral nitrogen one should yield the same (*S*)-configuration stereoselectively upon coordination as seen in bis[(*S*)-prolinato]palladium(II),⁵⁾ the complex is expected to exist in two diastereomers due to the chirality of the phosphorus atom. As stated previously, the complex gives only two isomers, blocks and needles. No indication for the presence of more than two isomers was found. The isomers show nearly the same absorption spectra, but exhibit circular dichroism spectra which are almost mirror images of each other, as shown in Fig. 1. The PMR spectrum of the blocks gives the N-H proton signal at 6.13 ppm and the methyl signal of the *n*-butyl group at 0.97 ppm (in $CDCl_3$, TMS as the internal standard), while that of the needles the corresponding signals at 6.97 and 0.83 ppm, respectively. The complex prepared from the N-deuterated ligand shows no signal at 6.13 and 6.97 ppm. The N-H proton of the needles resonates at a very low magnetic field compared with that of the blocks. When the chiral phosphine has the (*R*)-configuration, the phenyl group on the phosphine is to be located so as to deshield the N-H proton, as seen in Fig. 2. Hence, the needles is suggested to have the (*R*)-configuration. An X-ray analysis on the blocks is under investigation.

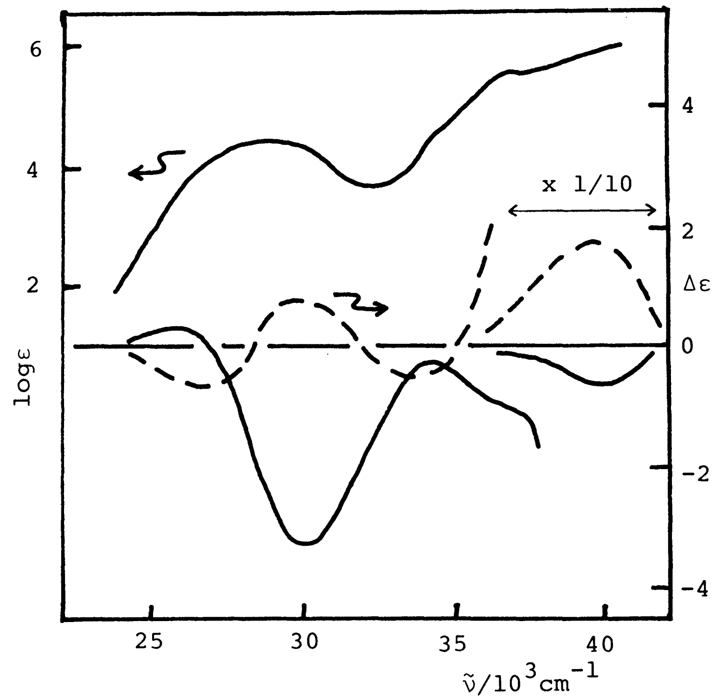


Fig. 1. Absorption and circular dichroism spectra of the blocks (————), and the needles (-----) in $CHCl_3$.

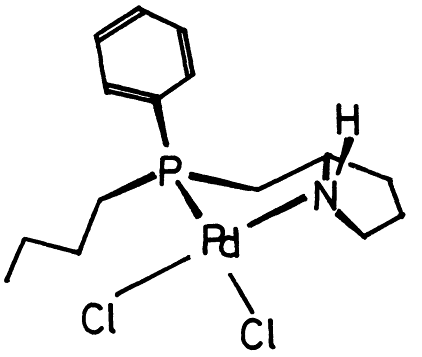


Fig. 2. Schematic structure of the (*R*)-phosphine complex

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