

## Stereochemistry at Co-ordinated Nitrogen in Chiral Platinum(II) Complexes

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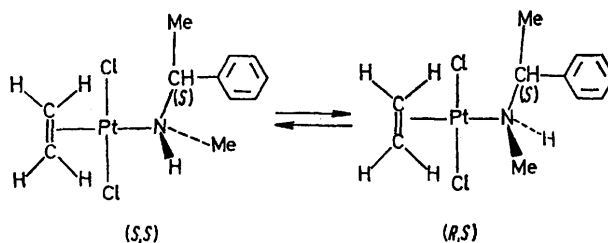
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**Summary** Evidence is reported that the co-ordination of the amine ligand in the complex *trans*-dichloro-[(*S*)-*N*-methyl- $\alpha$ -methylbenzylamine](ethylene)platinum(II) occurs in a highly stereoselective manner.

As model compounds in the study of the stereochemistry of such important catalytic reactions as hydroformylation<sup>1</sup> and the stereospecific polymerization of  $\alpha$ -olefins<sup>2</sup> chiral amine-olefin Pt<sup>II</sup>-complexes have been receiving increasing attention. In complexes involving either a chiral olefin and an achiral amine<sup>3</sup> or a prochiral olefin and a chiral amine<sup>4</sup> stereoselective co-ordination of the olefinic double bond has been reported.

In complexes containing a secondary unidentate amine ligand a dominant chirality could be also induced on the



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asymmetric nitrogen atom<sup>5,6</sup> if at least one other chiral centre is present in the complex. Accordingly, we have investigated *trans*-dichloro-[(*S*)-*N*-methyl- $\alpha$ -methylbenzylamine](ethylene)platinum(II) (I), which has an asymmetric carbon atom  $\alpha$  to the tetravalent nitrogen atom, in order to discover if the co-ordination of the amine occurs in highly stereoselective manner.

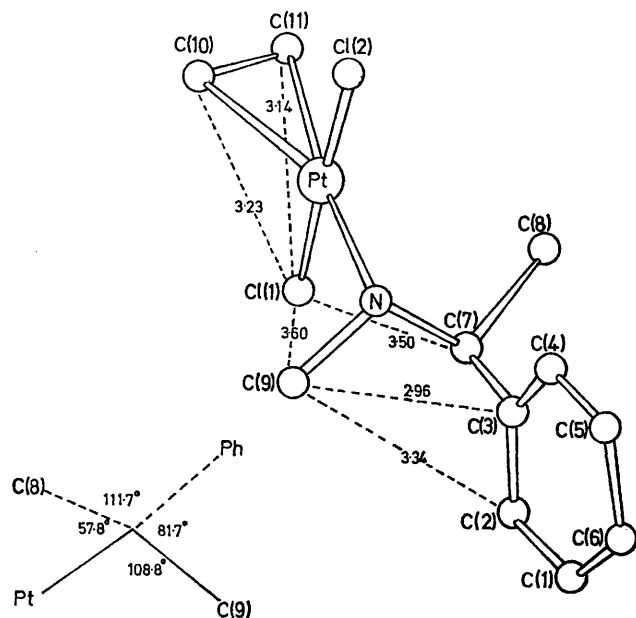


FIGURE 1. Model of the *SS* diastereoisomer of (I) showing some non-bonding distances (Å) and dihedral angles (Newman type projection along  $N \rightarrow C(7)$  bond) taken from X-ray structure analyses at present level of refinement. The e.s.d.s. are 0.05, 0.06 and 0.08 Å for Pt-C, Cl-C, and C-C respectively.

Since (I) was prepared<sup>7†</sup> from a sample of (*S*)-*N*-methyl- $\alpha$ -methylbenzylamine (*ca.* 99% optical purity<sup>8</sup>), a diastereoisomeric mixture of complexes having *SS* and *SR* configurations were formed (Scheme) and these are clearly discernible in the room temperature n.m.r. spectrum of (I) in  $CDCl_3$ . Two unequal doublets centred at 1.62 and 1.95 p.p.m. have been assigned to the  $C-CH_3$  resonances. The low-field signal shows further evidence of coupling to <sup>195</sup>Pt ( $J_{Pt-H}$  7 Hz), which is absent in the high-field  $C-CH_3$  resonance. In addition, the spectrum exhibits two unequal  $N-CH_3$  doublets centred at 2.41 and 2.76 p.p.m. which are flanked by <sup>195</sup>Pt satellites ( $J_{Pt-H}$  29 and 32 Hz respectively<sup>9</sup>).  $D_2O$  exchange eliminates the proton coupling and the  $N-CH_3$  resonances appear as singlets.

The <sup>13</sup>C n.m.r. spectrum is also consistent with a mixture of epimers whose percentage composition (88:12) agrees with the results obtained from the proton spectrum (85:15).

Crystallization of (I) is accompanied by a second-order

asymmetric transformation resulting in the deposition of solid material which is essentially a single diastereoisomer. This has been shown by X-ray analysis to have the absolute *SS* configuration and the conformation, as illustrated in Figure 1, is characterized by having the phenyl group oriented *trans* with respect to the Pt.

Interconversion of the two diastereoisomers in solution is too rapid at room temperature on the n.m.r. time scale to show epimerization. Rapid determination of the n.m.r. spectrum of a diastereoisomerically homogeneous sample of (I) at  $-50^\circ$  provided evidence for the epimerization process (Figure 2). Since the absolute configuration of the single isomer present in the solid has been shown to be *SS*, we can assign the *SS* configuration to the diastereoisomer in

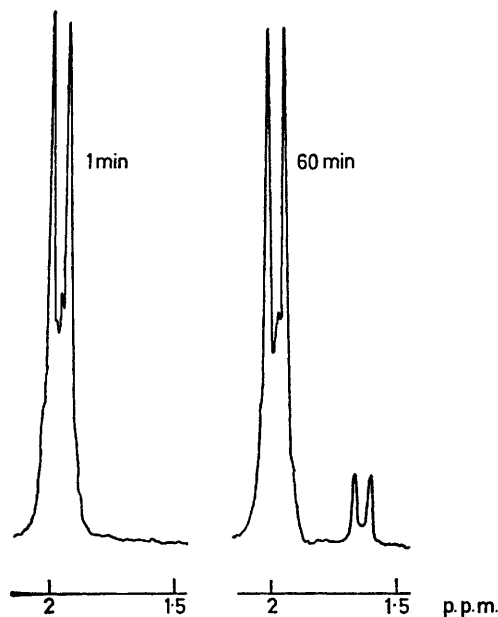


FIGURE 2. Modification of the  $C-Me$  resonance with time in the n.m.r. spectrum of (I) ( $-50^\circ C$ ,  $CDCl_3$ ) owing to configurational inversion at co-ordinated nitrogen.

solution, which gives rise to the downfield  $CH_3-C$  doublet (major) and the *RS* configuration to the diastereoisomer which corresponds to the upfield  $C-CH_3$  doublet (minor).

In conclusion, the co-ordination to  $Pt^{II}$  of a simple secondary amine having an asymmetric carbon atom  $\alpha$  to nitrogen is highly stereoselective, the more stable diastereoisomer in solution being that with the same chirality for the two chiral centres.

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† Complex (I) had satisfactory elemental analyses and spectral properties in accord with the assigned structure.

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