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trans-Dichloro(benzylamine)[(2*R*,3*S*)3-methyl-1-pentene] platinum(II) complex. Absolute configuration by X-ray diffraction analysis

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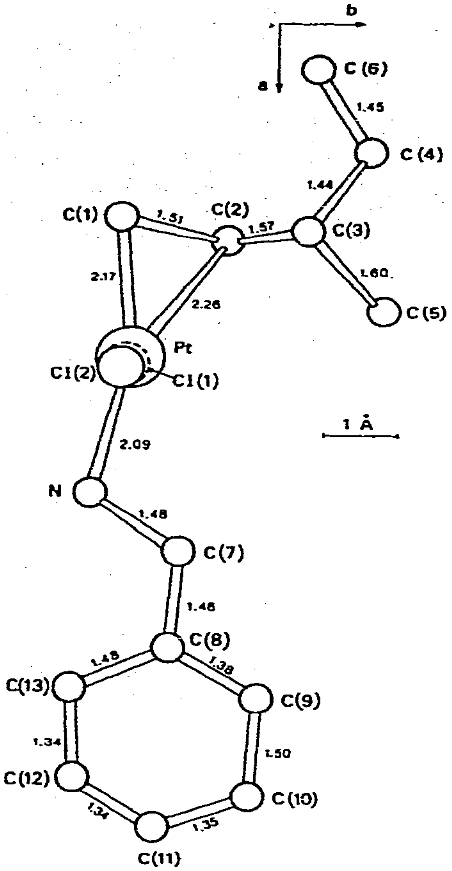
Olefin–platinum complexes with optically active ligands, have received increased attention in the recent years as models for the study of the stereospecific coordination phenomena[1,2]. Recently the synthesis of the *trans*-dichloro(benzylamine)[(*S*)3-methyl-1-pentene] platinum(II) complex was reported[3]. Because of the coordination of the double bond of the olefin to the Pt atom two diastereoisomers should exist, but from the NMR spectrum it was concluded that only one diastereoisomer is obtained in the crystallization[3]. We have investigated the crystal structure of the complex by X-ray diffraction analysis, to establish which diastereoisomer is actually formed in the crystallization and to give some information about the conformation of the molecule in the solid state.

The crystals[3] were acicular [001]; $a = 26.14 \pm 0.03$, $b = 7.16 \pm 0.01$, $c = 8.49 \pm 0.01$ Å; $V = 1589$ Å^3; $D_m = 1.90$ g·cm^{-3} (by a Westphal type balance); $Z = 4$, $D_c = 1.91$ g·cm^{-3}; F(000) = 872. Space group: $P2_12_12_1$ by systematic absences. Cu-K$_\alpha$ radiation (taken as 1.5418 Å), $\mu = 197.8$ cm^{-1}. Cell data are derived from Weissenberg photographs.

A total of 1151 independent non-zero structure amplitudes were obtained from microdensitometer measurements on integrated Weissenberg photographs, collected from a crystal reduced to cilindrical shape ($\mu R = 0.718$): the intensities were corrected for Lorentz, polarization and absorption factors. The structure was solved by means of the heavy atom method and refined by a full-matrix least-squares program, using anisotropic temperature factors for platinum and chlorine atoms, to a R value of 0.077. Further refinement is in progress.

The molecular structure and bond lengths are reported in Fig.1 (ESD's are 0.03 Å for Pt–N, 0.04 Å for Pt–C, 0.05 Å for C–N and 0.06 Å for C–C bond lengths). The platinum–chloride bond lengths are respectively: Pt–Cl(1) 2.32 Å (ESD 0.02 Å) and Pt–Cl(2) 2.46 Å (ESD 0.03 Å). As in similar compounds, the C(1)–C(2) bond is not perpendicular to the coordination plane; the angle between the planes defined respectively by Pt, Cl(1), Cl(2), N and Pt, C(1), C(2) is 73°. The atoms of the benzylamine group lie approximately in a plane, which is also the mean plane for the olefinic group; the methyl groups C(5) and C(6) are in *anti* positions.



The molecules are held together not only by Van der Waals interactions, but in the [001] direction by hydrogen bonds of the type N–H $\cdots$ Cl (with a nitrogen–chlorine distance of 3.31 Å). The presence of association phenomena also in carbon disulfide solution can be inferred from the IR spectra of solutions at different concentrations.

Two enantiomorphous solutions of the structure were possible but the chemical knowledge of the absolute configuration[4] of the α-olefin ligand, which is *S*[5], established with certainty the absolute configuration *R* for the asymmetric center C(2).

As the typical[6] Circular Dichroism band at 400 mμ in CH_2Cl_2 has a negative sign for the (2*R*,3*S*) diastereoisomer[3], these findings confirm the relationship between the absolute configuration of the asymmetric C(2) atom and the sign of the above CD band, as suggested by Scott *et al.*[6], and prove that the Scott's relationship also applies to optically active α-olefins.

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