Molecular Structure of *cis*-Dichloro[(*R*)-α-methylbenzylamine][(*S*)-1,2,2-trimethylpropyl (*R*)-vinyl ether]platinum(II)

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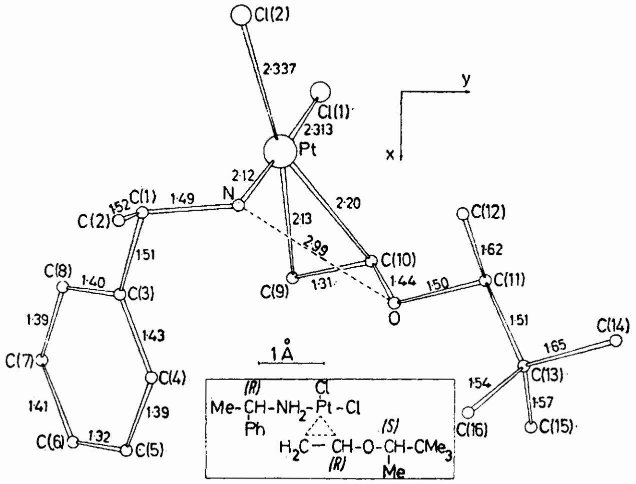
Summary The *X*-ray structural analysis of the title compound showed that the absolute configuration of the chiral centre formed by complexation of the vinyl group to Pt^{II} is *R* and gave indications on the conformation of the amine and olefin ligands.

ALTHOUGH transition metal–olefin complexes have been extensively investigated, complexes of olefinic compounds containing electron releasing substituents have only recently received attention.[1]

As part of our investigation[2] into the stereospecificity of complexation of chiral vinyl derivatives to Pt^{II}, we report here the *X*-ray structure of *cis*-dichloro[(*R*)-α-methylbenzylamine][(*S*)-1,2,2-trimethylpropyl (*R*)-vinyl ether]platinum(II) (I). Complex (I) was prepared by displacement of ethylene with (*S*)-1,2,2-trimethylpropyl vinyl ether† from the corresponding ethylene–Pt^{II} complex.[3] Crystallization from a mixture of acetone, diethyl ether, and pentane (1 : 1 : 2) gave a diastereoisomerically homogeneous sample of (I) (m.p. 134—135°) as supported by an n.m.r. spectrum that showed a single resonance for the t-butyl group of the complexed vinyl ether.

The crystals form plates normal to [100]; $a = 25{\cdot}56 \pm 0{\cdot}03$, $b = 11{\cdot}37 \pm 0{\cdot}01$, $c = 6{\cdot}84 \pm 0{\cdot}01$ Å; $V = 1988$ Å^3; $D_m = 1{\cdot}65$, $D_c = 1{\cdot}67$ g cm^{-3}, $Z = 4$; $F(000) = 968$.



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† The preparation and the optical purity determination will be reported elsewhere.

Space group: $P2_12_12_1$ by systematic absences. Cu-K_α radiation (1·5418 Å), $\mu = 158{\cdot}7\ \mathrm{cm}^{-1}$. The intensities of 1764 symmetrically independent reflections were measured by means of a Nonius microdensitometer on integrated equi-inclination multiple-film Weissenberg photographs taken about *c* axis; the intensities were corrected for Lorentz, polarization, and absorption factors.

The structure was solved by means of the heavy-atom method; the full-matrix least-squares refinement of atomic co-ordinates, platinum and chlorine anisotropic temperature factors, and C, N, and O isotropic temperature factors converged to a final *R* value of 0·071. Further refinement is in progress. Two enantiomorphous solutions of the structure were possible, but knowledge of the absolute configuration of the amine and the vinyl ether used (*R* and *S* respectively) allows us to assign[4] an absolute configuration *R* to the chiral centre of the co-ordinated vinyl group. The shape of the molecule and bond lengths for the examined *SSR* diastereoisomer are shown in the Figure (e.s.d.'s are 0·008 for Pt–Cl, 0·03 for Pt–N and Pt–C, 0·04 for N–C and O–C, and 0·05 Å for C–C bond lengths). The complex shows almost undistorted square-planar arrangement of the ligands around the Pt atom with the two chlorines in a *cis* position. The best plane through Pt, Cl(1), Cl(2), and N does not bisect the co-ordinated double bond, C(9) being 0·32 Å below while C(10) is 0·99 Å above it. Moreover, the double bond is slightly displaced from the perpendicular (5·4°) to the plane, C(9) being closer to Pt. Unlike similar olefin complexes,[5] the plane Pt, C(9), C(10) is perpendicular to the co-ordination plane within the error limits.

The dihedral angles C(9), C(10), O, C(11) and C(10), O, C(11), C(13) are 0° and 42° respectively. The Pt, N, C(1) plane deviates from perpendicularity to the Pt, Cl(1), Cl(2) plane (dihedral angle 77°). Furthermore while C(2) is in a "quasi anti" position with respect to Pt, the benzene ring is bent toward Pt [C(3) · · · Pt distance 3·51 Å] and lies approximately in a plane containing the C(1)–H bond. Finally, the short distance of 2·99 Å between the N and O atoms strongly suggests the presence of an intramolecular hydrogen bond which could play an important role in determining the conformation of co-ordinated vinyl ether.

(*Received*, 10*th December* 1973; *Com.* 1659.)

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