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Preliminary communication

THE CRYSTAL STRUCTURE OF AN OPTICALLY ACTIVE DIPHOSPHINE—NICKEL COMPLEX

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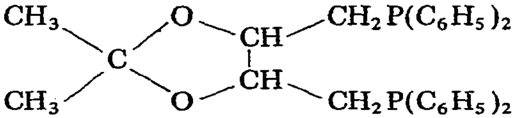
Summary

The molecular structure of dichloro[(—)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane]nickel(II) has been determined by X-ray analysis, and the preliminary isotropic refinement results show the nickel atom to be coordinated by a rather strongly distorted tetrahedron.

Asymmetric homogeneous catalytic reactions such as hydrogenation [1], hydrosilylation [2], hydroformylation [3] and hydrocarboxylation [4] have been successfully carried out using (—)-Diop* (I) in the presence of transition metal complex catalysts. Consiglio and Botteghi [5] and later Kumada and coworkers [6] used $NiCl_2$ [(—)-Diop], the first isolated transition metal complex containing (—)-Diop, for stereospecifically catalysed cross-coupling reaction of secondary racemic Grignard reagents with unsaturated halides. The results obtained in asymmetric catalysis show that at least some of the actual catalytic species contain the asymmetric ligand. However, the structure of the true catalytic species and the mechanism by which the asymmetric induction takes place are not yet understood. Knowledge of the structure of (—)-Diop-containing complexes in the solid state could be of significance in this field, and we give below a preliminary account of the molecular structure of $NiCl_2$ [(—)-Diop].



(I)

Synthesis of the nickel—phosphine complex as described [5] did not yield

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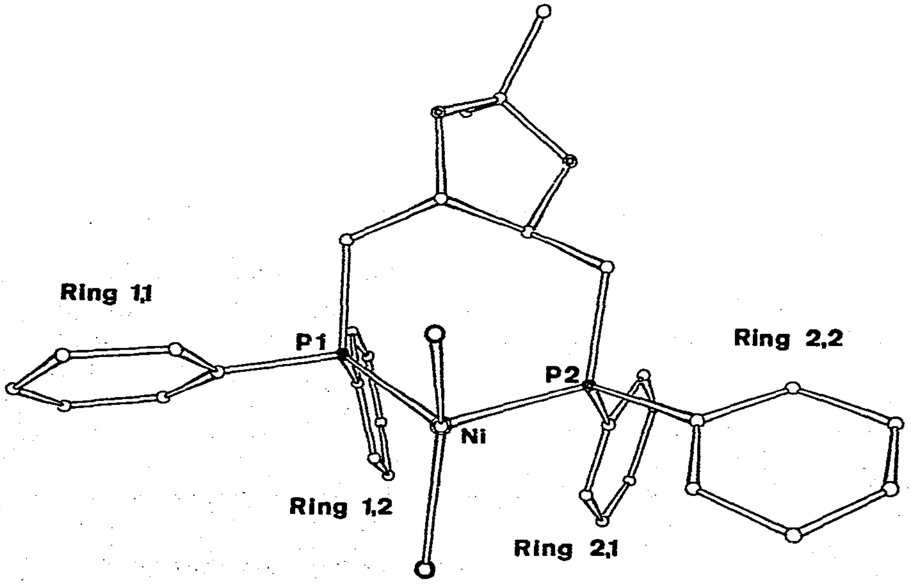
*(—)-Diop= (—)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane.

sufficiently large crystals. Well-shaped crystals up to half a millimeter in all three dimensions were finally obtained as follows: 250 mg (1 mmol) $NiCl_2 \cdot 6H_2O$ dissolved in 5 ml ethanol was slowly added to a solution of 1.0 g (2.1 mmol) (—)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane in 10 ml hot ethanol, a very small quantity of the crystalline powder being introduced with the last drops of the $NiCl_2$ solution. The dark red, transparent crystals grew during very slow cooling of the solution.

A crystal with well developed faces and maximum dimensions of $0.5 \times 0.5 \times 0.35$ mm^3 was selected for the X-ray data collection. 25 reflections with $20° \leqslant 2\theta \leqslant 45°$ were used for the determination of lattice constants by least squares approximation. For the structure determination 1156 ($2\theta \leqslant 35°$) reflections were measured on a Picker four circle automated diffractometer using Mo-K_α radiation (Zr-filtered). No degradation or decomposition could be observed during the measurement. Direct methods (X-ray [7], Multan [8]) were used to find the position of the Ni atom and the phosphorus and chlorine atoms of its first coordination sphere. The remaining C- and O-atoms were found by Fourier methods. No absorption correction nor correction for dispersion was applied.

Space group $P2_1 2_1 2_1$ suggested by systematic absences in the preliminary X-ray photographs was confirmed by the structure analysis. The unit cell with dimensions a 10.785(3), b 14.441(6), c 19.396(4) Å contains 4 molecules of the complex. The isotropic refinement converged to a conventional consistency factor of $R = 0.078$. The "stick-and-ball" model of the molecule drawn with Ortep [9] is given in Fig. 1.

The Ni—Cl distances are both 2.20(1) Å, the Ni—P distances 2.30(1) Å. The bond angles around the nickel atom do not differ by more than ± 10° from the tetrahedral angle (109°28′), except for the Cl—Ni—Cl angle which is 130°. The mean value of the C—P distance is 1.81(3) Å. Kilbourn and Powell have shown that tetrahedral and square planar coordination can coexist in the same unit cell



in two symmetrically independent molecules of dibromobis(benzyldiphenylphosphine)nickel(II) [10]. Furthermore, the planar—tetrahedral interconversion of dihalobis(diarylmethylphosphine)nickel(II) complexes in solution has been observed by Pignolet, Horrocks and Holm [11].

The conformation of the molecule in the crystalline state can be described as follows. The atomic sequence defined by the C(1)-carbon of ring (1,1), P(1), Ni, P(2) and the C(1)-carbon of ring (2,2) is in all-*trans* conformation. The angles between the plane defined by this zig-zag-line and the planes of the two phenyl rings (1,1) and (2,2) are 52 and 11° respectively, whereas the angles between the other two rings (1,2) and (2,1) with the planes defined by the corresponding Ni—P ring bonds are 36 and 41°. The five-membered ring containing the oxygens is planar within the limits of error.

A careful refinement of the structure with an extended data set ($2\theta \leqslant 50°$) is in progress, and details will be published elsewhere.

Acknowledgement

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