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STRUCTURE OF A CHELATE YLIDE COMPLEX : DICHLORO(BENZOYLMETHYLENE-DIPHENYL-2-DIPHENYLPHOSPHINOETHYLPHOSPHORANE)PALLADIUM

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X-ray structure analysis of dichloro(benzoylmethylenediphenyl-2-diphenylphosphinoethylphosphorane)palladium indicates that the ylide carbon, the phosphine phosphorus and two chlorine atoms coordinate to palladium forming a square planar configuration.

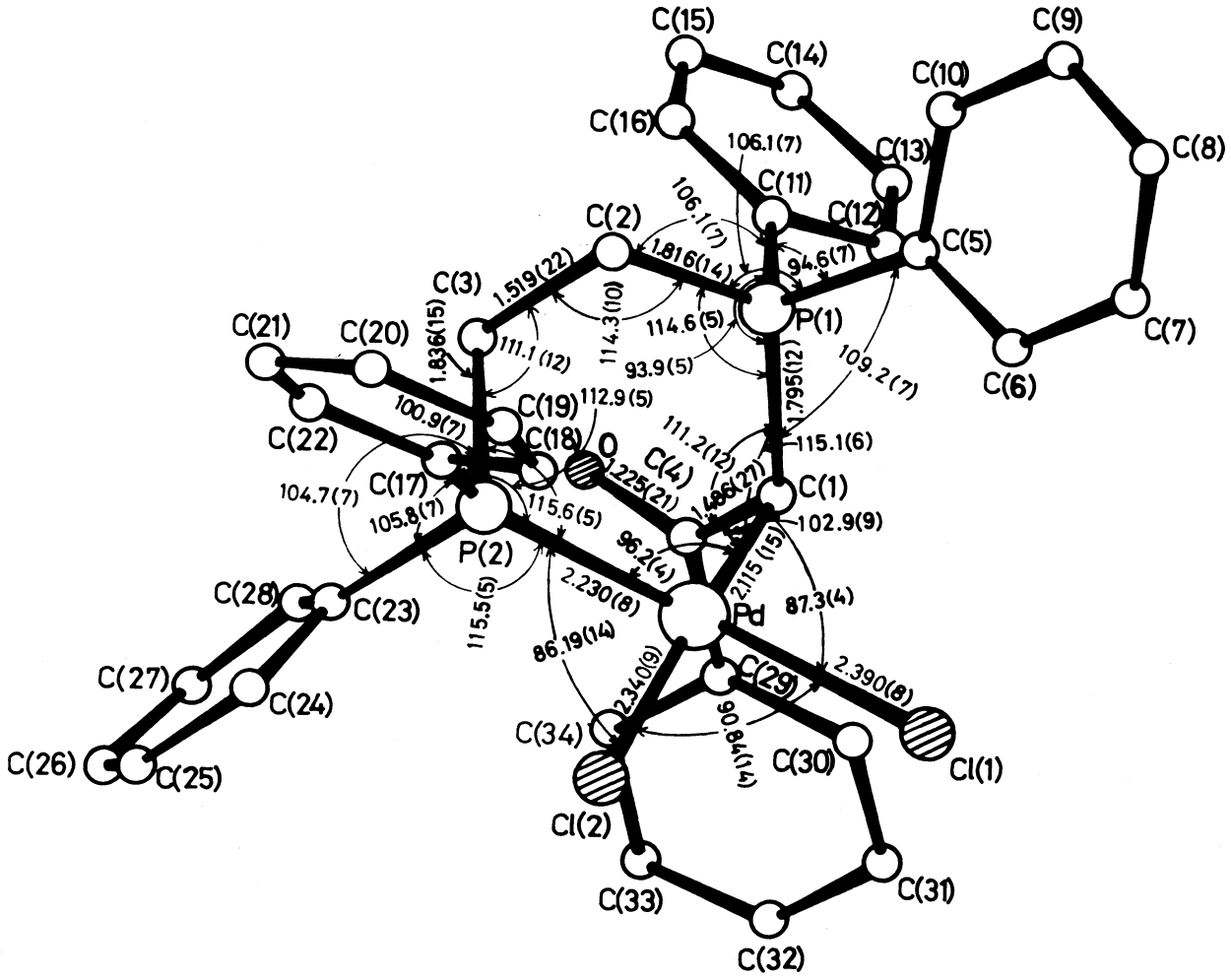
In a previous letter,[1] we reported the synthesis of palladium and platinum chloride complexes of benzoylmethylenediphenyl-2-diphenylphosphinoethylphosphorane (BDEP*) which is a new type mono ylide of 1,2-bisdiphenylphosphinoethane coordinating to the metals as a chelate ligand. We concluded from the shift in the ir spectra of stretching frequencies of the carbonyl group of benzoyl group that the ylide carbon of the ligand coordinates to palladium or platinum. The present study has been carried out to confirm the above conclusion using X-ray crystal structure analysis of one of the complexes, $PdCl_2(BDEP)$.

The compound was synthesized according to the previous method,[1] and recrystallized from a nitromethane solution diluted with toluene. ^1H nmr spectra indicated that the crystals contained one mole toluene per mole of the compound. A single crystal of approximate dimensions of $0.25 \times 0.25 \times 0.10$ mm was used for the structure determination.

The crystal data : $PdCl_2C_{34}H_{30}OP_2 \cdot C_7H_8$, M.W. 786.0, monoclinic, space group $P2_1/c$, $a = 13.39(5)$, $b = 16.88(1)$, $c = 19.85(6)$ Å, $\beta = 123.54(1)°$, $V = 3740$ Å^3, $Z = 4$, $D_o = 1.42$, $D_x = 1.40$ g/cm^3, $\mu = 7.47$ cm^{-1} for Mo-Kα.

The intensity data were collected on a Rigaku four-circle automated diffractometer using Mo-Kα radiation monochromatized with graphite. The independent reflections up to $2\theta = 55°$ were measured by the ω-2θ scan technique and significant counts were recorded for 2652 reflections ($|F_o| > 3\sigma$) which were used for the structure analysis. The structure was solved by the standard heavy-atom method. All the atoms except fifteen hydrogens were located and refined to a final R value of 0.065. The molecular structure of the complex is illustrated in the Figure.

* BDEP = $Ph_2P\text{-}(CH_2)_2\text{-}P^+(Ph_2)\text{-}C^-H\text{-}\underset{\underset{O}{\|}}{C}\text{-}Ph$, Ph = C_6H_5



It is evident that BDEP coordinates to palladium through P(2) and the ylide carbon C(1). The distance between the ylide carbon and palladium is 2.115(15) Å. The remaining two coordination sites are occupied by two chlorine atoms in cis positions. The five atoms [P(2), C(1), Cl(1), Cl(2), and Pd] are nearly coplanar thus forming a square-planar coordination around palladium. Although the hydrogen atom bonded to the ylide carbon could not be located, the bond angles around the ylide carbon suggest that the carbon orbital is probably sp^3 hybrid. The geometrical configuration around the phosphorus atom of the phosphonium ylide is almost tetrahedral. The Pd-Cl(2) distance 2.340(9) Å is shorter than Pd-Cl(1) distance 2.390(8) Å.

Reference

1) Y. Oosawa, T. Miyamoto, T. Saito, and Y. Sasaki, Chem. Lett., 33 (1975).

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