Synthesis and X-Ray Crystal Structure of *cis*-[$PdCl_2\{Ph_2PCH_2CH_2P(CF_3)_2\}$] [*cis*-1-Bistrifluoromethylphosphino-2-(diphenylphosphino)ethane]dichloropalladium(II)

By LJUBICA MANOJLOVIĆ-MUIR,* DOUGLAS MILLINGTON, KENNETH W. MUIR,* and DAVID W. A. SHARP
(*Chemistry Department, University of Glasgow, Glasgow* G12 8QQ, *Scotland*)

W. EUGENE HILL,
(*Chemistry Department, Auburn University, Auburn, Alabama* 36830)

and JAMES V. QUAGLIANO and LIDIA M. VALLARINO
(*Chemistry Department, Florida State University, Tallahassee, Florida* 32306)

Summary A novel unsymmetrical ditertiary phosphine, $Ph_2PCH_2CH_2P(CF_3)_2$, and its chelate complex *cis*-[$PdCl_2\{Ph_2PCH_2CH_2P(CF_3)_2\}$] have been prepared and characterised; the molecular structure of the latter compound shows that the organic substituents on the phosphorus atoms exert a profound effect on the metal–ligand bonding and that the *trans*-influence of the PPh_2 group is considerably greater than that of the $P(CF_3)_2$ group.

IN contrast to the long known symmetrical ditertiary phosphine, $Ph_2PCH_2CH_2PPh_2$, the first unsymmetrical ditertiary phosphines, $Ph_2PCH_2CH_2PPhR$ and $Ph_2PCH_2CH_2PR_2$ (R = alkyl), have been made only recently.[1] Chromium, molybdenum, and tungsten carbonyls of these novel ligands are their only metal complexes described so far.[2] We now report the synthesis of the compounds $Ph_2PCH_2CH_2P(CF_3)_2$ and *cis*-[$PdCl_2\{Ph_2PCH_2CH_2P(CF_3)_2\}$] and the X-ray crystal structure analysis of the palladium complex. This work enables us to examine the effect of organic groups with very different electronic properties (Ph and CF_3) on the metal–ligand bonding.

The diphosphine $Ph_2PCH_2CH_2P(CF_3)_2$ was obtained by addition of $(CF_3)_2PH$ to $Ph_2PCH{:}CH_2$, the reaction being initiated photochemically. The direction of the addition was established by ^1H n.m.r. spectroscopy. The $PdCl_2$ complex was prepared by addition of the diphosphine to $PdCl_2(NCPh)_2$ in refluxing benzene, and was fully characterised by analytical and X-ray crystallographic methods. The i.r. spectrum shows bands at 333 and 295 cm^{-1}, required by the *cis*-$PdCl_2$ fragment.

The crystals of *cis*-$[PdCl_2\{Ph_2PCH_2CH_2P(CF_3)_2\}]$ are monoclinic, space group $P2_1/c$. There are four molecules in a unit-cell of dimensions: a = 10·048, b = 13·700, c = 15·797 Å and β = 108·4°. The intensities, I, of 4882 independent reflexions, for which $\theta(\text{Mo-}K_\alpha) \leqslant 30°$ and $I \geqslant 3\sigma(I)$, were measured on a four-circle diffractometer. The structure was solved by the heavy atom method and has been currently refined to R = 0·050 and R_w = 0·069.

The crystals are built of discrete, square planar molecules of *cis*-$[PdCl_2\{Ph_2PCH_2CH_2P(CF_3)_2\}]$, in which the ditertiary phosphine acts as a chelating bidentate ligand. The Pd, P, and Cl atoms are coplanar to within ±0·03 Å. The methylene carbon atoms are displaced, by 0·25 and 0·38 Å, on opposite sides of the co-ordination plane of the metal atom.

The Pd–P distance involving the phenyl-substituted phosphorus atom [2·253(4) Å] is similar to those observed in arylalkylmonotertiary phosphine complexes *e.g.* *cis*-$[PdCl_2(PMe_2Ph)_2]$.[3] However, the Pd–P distance involving the phosphorus atom bonded to the trifluoromethyl groups is significantly shorter [2·193(4) Å]. This difference in the effects of electron-releasing phenyl groups and electron-withdrawing trifluoromethyl groups on the length of Pd–P bonds is further reflected in the Pd–Cl distances [2·370(4) Å, *trans* to PPh_2 and 2·311(4) Å, *trans* to $P(CF_3)_2$], which indicate that the PPh_2 group exerts considerably greater *trans*-influence on a Pd–Cl bond than the $P(CF_3)_2$ group. This result is in accordance with our qualitative model of *trans*-influence,[4] based on interaction of the metal d_π orbital with two mutually *trans* ligands.

We thank Mr. I. Bryson for technical assistance and N.A.T.O. for a research grant.

(*Received, 7th October* 1974; *Com.* 1253.)

---

[1] S. O. Grim, R. P. Molenda, and R. L. Keiter, *Chem. and Ind.*, 1970, 1378; R. B. King, J. C. Cloyd, Jr., and P. K. Hendrick, *J. Amer. Chem. Soc.*, 1973, **95**, 5083.

[2] S. O. Grim, J. Del Gaudio, C. A. Tolman, and J. P. Jesson, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 1083; S. O. Grim, J. Del Gaudio, R. P. Molenda, C. A. Tolman, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1974, **96**, 3416.

[3] L. L. Martin and R. A. Jacobson, *Inorg. Chem.*, 1971, **10**, 1795.

[4] Lj. Manojlović-Muir and K. W. Muir, *Inorg. Chim. Acta*, 1974, **10**, 47.