Inorganica Chimica Acta, 44 (1980) L245–L246
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Photochemical Preparation, Isolation and Crystal Structure Analysis of Bis(tri-n-propylphosphine)-dichloropalladium(II)

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Received December 12, 1979

Although a number of instances of photoinduced *cis–trans* isomerisation of Pt(II) complexes have been recorded [1], certain isomers having been prepared only by such a route [2], application of photochemical procedures to their Pd(II) analogues is far less developed. While compounds of the type $(R_nPh_{3-n}P)_2PdCl_2$ (R = alkyl, n = 0, 1, 2) exist in both *cis-* and *trans*-forms which maintain a thermal dynamic equilibrium in solution and each of which can be isolated as solid material, when n = 3 only one isomer is found in solution (identified as the *trans* form on the basis of u.v., i.r. and ^{31}P n.m.r. spectroscopy [3]). Recently we have shown, together with Ricevuto and colleagues [4] that photoirradiation of a solution of *trans*-$[(Pr^n_3P)_2PdCl_2]$ yields a steady-state equilibrium mixture of the *cis-* and *trans*-isomers (characterised spectroscopically). Attempts to isolate the labile isomer from the equilibrium mixture in the solvents then utilised produced only the *trans*-isomer.

We have now succeeded in isolating crystalline samples of the *cis*-isomer in two ways. (i) Photolysis (bare Xe arc) of a nitromethane solution (0.08 mol dm^{-3}) at room temperature (or slightly below) yielded a solution containing *ca.* 75% of the *cis*-isomer from ^{1}H n.m.r. (*i.e.* a much higher conversion than in methanol or $CHCl_3$): concentration of the solution with a stream of N_2 to minimal volume followed by addition of diethyl ether yielded a crystalline precipitate of the *cis*-isomer (while the *trans*-form remains in solution). The precipitate was filered, washed with ether and dried. Larger crystals, suitable for an X-ray structure determination, were grown by slow recrystallisation from CH_2Cl_2–ether, using the vapour diffusion procedure. (ii) An alternative route involves photolysis of the *trans*-isomer in hexane at 0 °C when the *cis*-isomer precipitates as the photolysis proceeds. Both of these methods depend on (a) the insolubility of the *cis*-isomer in non-polar solvents and (b) the slowness of the *cis* → *trans* change at temperatures below 25 °C [4]. Method (i) was also applied successfully to the preparations of the *cis*-isomers of $(R_3P)_2PdCl_2$ where R = Et and Bu^n. The structures of the new isomers were verified by spectroscopic measurements, *viz.* (for the n-propyl compound): n.m.r.* (d_4-MeOH) δ 1.11t(CH_3) δ 1.70m($-CH_2$) δ 2.04m($-CH_2$); u.v./vis. ($CHCl_3$) λ_{max} 332 nm (ε = 2.8 × 10^3) λ_{max} 256 (ε = 1.3 × 10^4).

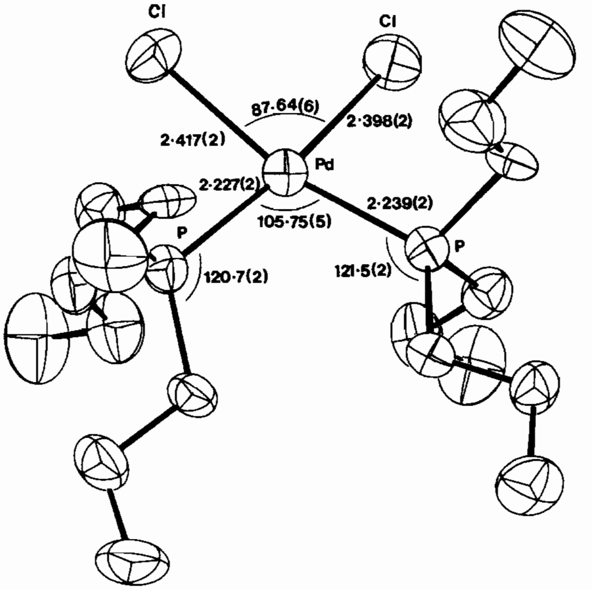

Fig. 1. Unique molecule of *cis*-$[(Pr^n_3P)_2PdCl_2]$. The crystals are monoclinic, *a* = 9.729(2), *b* = 13.816(3), *c* = 9.614(a) A, β = 100.77(1)°, *U* = 1269.4(4) A^3, space group $P2_1/m$, D_m = 1.28 g cm^{-3}, D_x = 1.30 g cm^{-3} for *Z* = 2. Although Pd lies on a mirror plane, the crystal contains two disordered complete molecules without internal symmetry. 1873 observed reflections ($I/\sigma(I) > 3.0$), collected by Syntex P2$_1$ four-circle diffractometer to $2\theta_{max}$ of 50°. *R* = 0.029 for refinement with anisotropic temperature factors for all except hydrogen atoms.

The crystal structure of *cis*-$[(Pr^n_3P)_2PdCl_2]$ was undertaken to give an unequivocal basis for spectroscopic assignments in this series, and to study in detail the overcrowding that is presumed to be the cause of the instability of the *cis*-isomer. The structural results (Fig. 1) confirm the expected geometry and show that the major steric effect is on the P–Pd–P angle, increased to 105.75(6)° from the 90° expected for square planar geometry. There is also a considerable increase in one Pd–P–C angle on each phosphorus to no less than 121°, and the C–P–C

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*t = triplet, m = multiplet.

angles are correspondingly small (avg. 104.5°). All these distortions relate to the conformations around phosphorus. In order to avoid close C–Cl contacts. the PR_3 and Pd–Cl groups are staggered (dihedral angles Cl–Pd–P–C of 55.8(3)°, but this leads to the two PR_3 groups having inward-facing alkyl chains, producing the distortions noted above. It is easy to understand from this why the *cis*-geometry is disfavoured.

Acknowledgements

Mr. P. A. Lampe assisted with the crystal structure analysis. Professor Ricevuto provided useful discussion and the work was funded by the Science Research Council, with the C.N.R. (Italy) and the British Council assisting the Warwick-Ferrara exchange.

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