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Maximizing Ligand Intermeshing in Phosphine Complexes: Synthesis and Structural Characterization of *cis*-$Cl_2Pt(PCy_3)_2$

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Considerable information is now accumulating concerning the ways in which bulky ligands intermesh and distort on coordination to a metal centre [1]. Studies of tertiary phosphine complexes of Pt(II) show that with bulky phosphines such as tricyclohexylphosphine (PCy_3), configurations are usually adopted that minimize ligand interactions. Thus, attempts to prepare Pt(II)–bis-phosphine complexes with a *cis* geometry are often unsuccessful either because of the ease of *cis* to *trans* isomerization or because of the lack of steric control which often allows exclusive formation of the *trans* isomer [2]. However, it has been possible to prepare Pt(II) square-planar complexes of bidentate ligands such as dioxygen or carbonate, in which two bulky phosphine ligands are forced into the *cis* configuration [3]. There is no intrinsic reason, therefore, why *cis* complexes of bulky phosphines with monodentate ligands cannot be formed. Careful examination of such complexes could provide useful information on the way in which bulky phosphine ligands intermesh. Moreover, a complex such as *cis*-dichlorobis(tricyclohexylphosphine)platinum(II) would not only possess the *cis*-Cl_2Pt component but would also possess an essentially aliphatic molecular surface, and might thus have interesting solubility behaviour in biological systems. The possible anti-tumour behaviour of such a molecule would then be worth examining [4].

During the course of a study of the reactivity of the complexes $XPt(PR_3)_2$ (where X is a bidentate ligand containing Pt–O bonds and PR_3 is a bulky phosphine) toward chlorosilanes, R_nSiCl_{4-n}, and chlorostannanes, R_nSnCl_{4-n}, we observed the formation of a crystalline product (**1**) in quantitative yield when $O_2Pt(PCy_3)_2$ was allowed to react with $SnCl_4$ in dry methanol. Spectroscopic characterization of **1** by $^{31}P\{^1H\}$ NMR (methanol, $\delta = 16.9$ ppm; $J_{P-Pt} = 3595$ Hz) suggested a Pt(II) complex with a *cis*-phosphine geometry. Single crystals of **1** suitable for X-ray analysis formed overnight when the reaction was performed in a 10-mm NMR tube. The crystallographic analysis showed the crystals to contain a molecule of methanol solvate. Crystal data: $C_{37}H_{70}Cl_2OP_2Pt$; $M = 858.8$, monoclinic, space group $P2_1/n$ (No. 14), $a = 14.706(3)$, $b = 16.212(3)$, $c = 17.215(3)$ Å; $\beta = 91.53(2)°$, $V = 4102.7$ Å^3, $Z = 4$, $D_c = 1.390$ g cm^{-3}. A total of 5697 unique reflections were measured on an Enraf–Nonius CAD-4 diffractometer with Mo Kα radiation. The position of the platinum atom was obtained from the Patterson function and the remaining non-hydrogen atoms were located in

TABLE 1. Bond angles and distances in *cis*-phosphine–platinum complexes

Compound	P–Pt–P (°)	Pt–P–C (°)	Cl–Pt–Cl (°)	Pt–P (Å)	Reference
$(PCy_3)_3Pt$	120			2.303^a	5
$(PCy_3)_2Pt(C_2H_4)$	116.3			2.284(1)	6
$[(PCy_3)_2Pt(Allyl)]^+PF_6^-$	111.2	107.3, 118.0, 115.8 107.2, 118.6, 113.8		2.335(3) 2.327(4)	7
$(PCy_3)_2Pt(C_4F_6)$	110.2	109.5, 120.2, 109.6 105.2, 124.6, 110.5		2.309(2) 2.301(2)	8
$(PCy_3)_2Pt(O_2C_2(CO_2Me))$	109.3	103.8, 121.5, 111.3 105.4, 121.9, 111.5		2.270(4) 2.276(4)	9
$(PCy_3)_2PtCl_2$	107.6	110.1, 105.3, 122.4 107.1, 114.2, 120.5	82.1	2.299(4) 2.289(3)	This work
$(PPh_3)_2PtCl_2$	97.8	110.3, 113.5, 116.5 109.1, 113.5, 122.7	87.1	2.251(2) 2.265(2)	10
$(P(CH_2Ph)_2Ph)_2PtCl_2$	103.0	112.1, 111.1, 120.2	87.9	2.246(4)	11

^{a}Average.

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subsequent difference-Fourier syntheses. Hydrogen atoms were placed by geometric calculation and their positions were not refined. Non-hydrogen atoms were refined anisotropically. The refinement converged at $R = 0.037$, $R_w = 0.041$ for 2956 observed reflections with $I > 2\sigma(I)$. One Cy ring was found to be disordered.

The crystallographic analysis shows **1** to be *cis*-$Cl_2Pt(PCy_3)_2 \cdot MeOH$, the first example of the exclusive formation of the *cis* isomer of such a simple Pt(II) complex containing bulky phosphine ligands.

Table 1 provides comparisons of the principal bond angles and bond distances for a number of *cis*-phosphine–platinum complexes. For less bulky phosphines such as PPh_3 and $P(CH_2Ph)_2Ph$, the P–Pt–P angles are somewhat greater than the expected 90°, as might be expected with the relatively small chloro ligands. In **1**, the P–Pt–P angle is substantially larger but is still the smallest for any *cis*-$(PCy_3)_2$ complex.

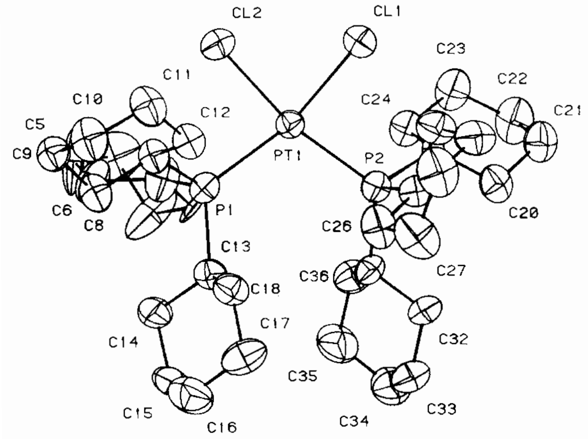

Fig. 1. Molecular structure of *cis*-$Cl_2Pt(PCy_3)_2$ showing thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

The Pt–P distances are not elongated to any significant extent and the degree of distortion in the Pt–P–C angles of **1** is about the same as in other *cis*-$(PCy_3)_2$ species. The large bulk of the PCy_3 ligands in **1** is therefore accommodated entirely by compression of the P–Pt–P angle and by intermeshing of the cyclohexyl rings. As Fig. 1 shows, two cyclohexyl rings, one on each phosphine are bisected by the plane of the complex. The close proximity of these rings to each other opens $Pt–P_1–C_{13}$ to 122.4° and $Pt–P_2–C_{31}$ to 120.5°. On each phosphorus, the remaining two rings are oriented so that the chloro ligand can intermesh between them. It is worth noting that the molecule contains a pseudo two-fold axis running between the two chlorine atoms and C_{13}/C_{31}.

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