Ligands with Dual Denticity: Crystal and Molecular Structure of Dichloro-bis(*o*-(diphenylphosphino)-benzaldehyde)platinum(II)

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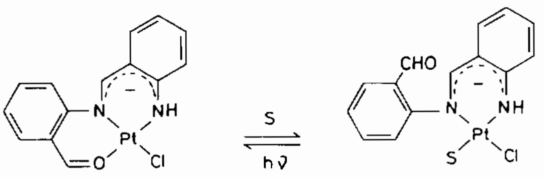
In the investigation of a platinum(II) complex resulting from the Schiff base condensation of *o*-aminobenzaldehyde, a coordinated formyl group was noted to be quite labile in the presence of coordinating solvents. The solvolysis reaction was found to be photoreversible [1]:



1 2

S = CH_3CN, DMSO

A structure determination of an analog of (2), obtained by reacting triphenylphosphine with (1), revealed that while the formyl group was indeed not coordinated, the benzaldehyde was oriented so that the aldehyde was poised above the platinum ion [2]. In order to investigate in greater detail the stereochemical tendencies of potentially coordinating functional groups, a structure analysis of dichloro-bis(*o*-(diphenylphosphino)benzaldehyde)platinum(II), was undertaken. It was anticipated from previously reported physical data that both benzaldehydes would be uncoordinated [3].

Experimental

Synthesis

To 20 ml of a solution of K_2PtCl_4 (0.102 g, 2.46 mmol) in water was added *o*-(diphenylphosphino)-benzaldehyde (0.141 g, 4.86 mmol) as a solid, forming a suspension. Acetonitrile (3 ml) was added to disperse the hydrophobic aldehyde. The bright yellow color of the aldehyde gradually turned pale yellow during stirring for one day at room temperature, at which time the product precipitated. The complex was filtered, washed with ethanol and ether, and dried *in vacuo* at room temperature. Single crystals for X-ray analysis were obtained by slow evaporation of a solution of the complex in a 1:1 chloroform:acetonitrile mixture.

Crystal Data

$C_{38}H_{30}O_2P_2Cl_2Pt$

M = 846.62, monoclinic space group $P2_1/n$, a = 13.63(1), b = 10.17(2), c = 13.07(2) Å, β = 108.4(9)°, D_{calc} = 1.635 g cm^{-3} for Z = 2, D_{meas} = 1.60(1) g cm^{-3}, μ(Mo Kα) = 45.7 cm^{-1}.

A total of 3579 observed reflections were collected with $I > 3\sigma(I)$ on a Syntex $P2_1$ diffractometer as described previously [4] using graphite monochromated Mo Kα radiation (λ = 0.71069 Å). Neither decay nor absorption corrections were applied. The structure was solved by the heavy atom method, and the platinum atom was placed at (½, ½, ½). The positions of all non-hydrogen atoms were determined from subsequent Fourier maps**. Full-matrix least-squares refinement in which hydrogen atoms were included as fixed contributions resulted in final R_1 = 0.053 and R_2 = 0.067. Atom parameters are listed in Table I and bond lengths and angles of interest in Tables II and III, respectively.

Results and Discussion

A perspective view of the complex is shown in Fig. 1 along with that of the aforementioned triphenylphosphine adduct [2]. The immediate coordination sphere of the platinum atom is square planar as required in this case by symmetry. The fist observation of note is the *trans* geometry about the platinum atom. In most bis-phosphine complexes of platinum(II), the *cis*-isomer is the most insoluble in organic solvents and thus crystallizes from solution first [5]. The bright yellow crystals of this complex were the first indication of the *trans* geometry as *cis* isomers are pale yellow to white in general [5].

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TABLE I. Final Positional Parameters.

Atom	*x*	*y*	*z*
Pt	0.5000	0.5000	0.5000
P	0.5368(2)	0.5832(2)	0.3497(2)
Cl	0.5746(2)	0.3047(2)	0.4704(2)
C(1)	0.4660(6)	0.4811(7)	0.2343(6)
C(2)	0.3676(7)	0.4374(10)	0.2301(7)
C(3)	0.3083(7)	0.3637(10)	0.1428(8)
C(4)	0.3462(9)	0.3295(10)	0.0616(8)
C(5)	0.4450(9)	0.3677(11)	0.0659(8)
C(6)	0.5059(8)	0.4450(11)	0.1539(8)
C(7)	0.6684(6)	0.5877(8)	0.3420(6)
C(8)	0.6937(7)	0.6713(11)	0.2713(8)
C(9)	0.7930(9)	0.6774(14)	0.2647(9)
C(10)	0.8698(8)	0.5975(13)	0.3318(10)
C(11)	0.8461(9)	0.5137(11)	0.4043(11)
C(12)	0.7449(7)	0.5074(9)	0.4101(8)
C(13)	0.4885(6)	0.7516(7)	0.3107(6)
C(14)	0.4041(7)	0.7706(9)	0.2190(7)
C(15)	0.3627(8)	0.8963(11)	0.1907(8)
C(16)	0.4046(11)	1.0032(10)	0.2516(12)
C(17)	0.4903(10)	0.9871(8)	0.3423(10)
C(18)	0.5324(7)	0.8628(8)	0.3742(7)
C(19)	0.6210(8)	0.8578(10)	0.4726(8)
O	0.6657(5)	0.7591(8)	0.5147(5)

TABLE II. Interatomic Distances (A).

Pt	2.335(3)
Pt–Cl	2.318(3)
P–C(1)	1.834(8)
P–C(7)	1.828(8)
P–C(13)	1.848(8)
C(1)–C(2)	1.398(11)
C(2)–C(3)	1.391(12)
C(3)–C(4)	1.364(14)
C(4)–C(5)	1.386(14)
C(5)–C(6)	1.424(14)
C(6)–C(1)	1.376(12)
C(7)–C(8)	1.377(12)
C(8)–C(9)	1.385(13)
C(9)–C(10)	1.394(16)
C(10)–C(11)	1.386(17)
C(11)–C(12)	1.408(13)
C(12)–C(7)	1.400(12)
C(13)–C(14)	1.387(10)
C(14)–C(15)	1.399(12)
C(15)–C(16)	1.362(16)
C(16)–C(17)	1.386(19)
C(17)–C(18)	1.396(12)
C(18)–C(19)	1.460(13)
C(18)–C(13)	1.419(11)
C(19)–O	1.213(12)

TABLE III. Bond Angles (deg).

Cl–Pt–P	87.0(1)
Pt–P–C(1)	106.8(3)
Pt–P–C(7)	122.1(3)
Pt–P–C(13)	114.5(2)
C(1)–P–C(7)	103.9(4)
C(1)–P–C(13)	104.4(3)
C(7)–P–C(13)	103.4(4)
P–C(1)–C(2)	117.5(6)
P–C(1)–C(6)	123.1(7)
C(2)–C(1)–C(6)	119.4(8)
C(1)–C(2)–C(3)	120.3(9)
C(2)–C(3)–C(4)	119.9(9)
C(3)–C(4)–C(5)	120.8(9)
C(4)–C(5)–C(6)	119.9(9)
C(5)–C(6)–C(1)	119.6(9)
P–C(7)–C(8)	120.7(7)
P–C(7)–C(12)	119.8(6)
C(8)–C(7)–C(12)	119.5(8)
C(7)–C(8)–C(9)	121.8(10)
C(8)–C(9)–C(10)	119.3(10)
C(9)–C(10)–C(11)	119.8(9)
C(10)–C(11)–C(12)	120.6(10)
C(11)–C(12)–C(7)	119.0(9)
P–C(13)–C(14)	119.6(6)
P–C(13)–C(18)	122.0(6)
C(14)–C(13)–C(18)	118.4(8)
C(13)–C(14)–C(15)	120.7(9)
C(14)–C(15)–C(16)	121.0(10)
C(15)–C(16)–C(17)	119.4(9)
C(16)–C(17)–C(18)	121.2(10)
C(17)–C(18)–C(13)	119.2(9)
C(13)–C(18)–C(19)	124.5(8)
C(17)–C(18)–C(19)	116.2(9)
C(18)–C(19)–O	125.8(8)

As anticipated the Pt–P distance of 2.335(3) Å in the bis-phosphine complex is elongated by 0.06 Å compared to the adduct. This is consistent with the mutual strong *trans* directing effect of the inversion-related phosphorus atoms compared to the weaker *trans*-directing ability of the C=N group *trans* to the Pt–P bond in the adduct. Similar observations are not uncommon and have been noted in other phosphorus ligand complexes containing *trans* imine compared to phosphine ligands [6].

The orientation of the aldehyde is, of course, of major interest. In the perspective view it appears, visually at least, that the aldehyde oxygens are poised at the axial sites of the platinum atom. This is actually not the case, as evidenced by the P–Pt–O angle of 63.1(2)°. Rather, the oxygen is more closely associated with the phosphorus of the same ligand, with a P–O distance of 2.92(8) Å. A similar finding was seen also in the triphenylphosphine analog of

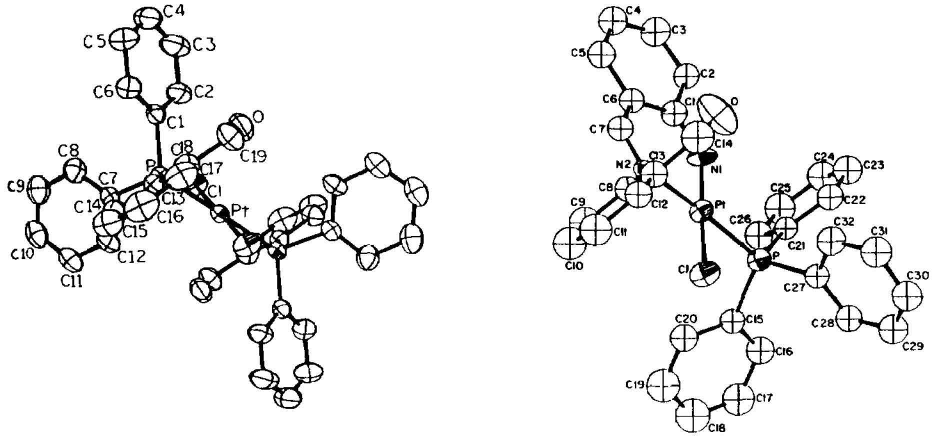

Fig. 1. Perspective views of the bis complex of *o*-(diphenylphosphino)benzaldehyde and the triphenylphosphine adduct analog of (2).

(2), where an N–O distance of 2.87(1) Å was observed. Both distances are less than the sum of the van der Waals radii [7]. On the other hand the rather long Pt–O distances show no real bonding interactions: 3.436(8) Å for the bis-phosphine complex and 3.71(1) Å for the triphenylphosphine adduct [2]. The fact that the aldehyde has not rotated to relieve the close interactions with the phosphorus in one case and the nitrogen in the other, leads to speculation whether there really are weak interactions, or whether the phenomenon is merely a result of packing effects.

Other bond angles and distances are as expected with the exception of a rather large degree of distortion about the phosporus–phenyl bonds. The three Pt–P–C angles are 106.8(2), 122.1(3) and 114.5(2)° for C(1), C(7), and C(13), respectively. This can be compared to a range of 113.4(5) to 113.9(5)° in the triphenylphosphine adduct. No striking cause can be seen for this observation, which merely results in a slight tilting of the phosphorus–phenyl cone from the coordination plane of the platinum.

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