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Preliminary communication

THE MOLECULAR STRUCTURE OF *cis*-DICHLOROCARBONYL(TRIPHENYLPHOSPHINE)PLATINUM(II)

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Our interest in the *trans* influence of carbon-donor ligands in platinum(II) complexes has led us to determine the structure of the title compound by X-ray analysis.

Structural data for mononuclear platinum(II) carbonyl complexes are scarce and of low or unstated accuracy [1-3]. Furthermore, in *trans*-$[PtCl(CO)(PEt_3)_2]^+$ the Pt—P distances (2.34 and 2.35 Å) are slightly longer than the values (2.27 - 2.32 Å) usually found [4] for Pt^{II}—P(*trans* to P) bonds; Pt^{II}—Cl (*trans* to Cl) distances are normally close to 2.31 Å [4] whereas in *trans*-$PtCl_2(CO)(ONC_6H_4OMe)$ the Pt—Cl bond lengths are 2.25(3) and 2.26(3) Å [2].

Spectroscopic data for *cis*-$PtCl_2L(PEt_3)$ complexes, where L is a neutral ligand, also suggest that the Pt—Cl bonds are strongest and the Pt—P bond weakest when L = CO. The *J*(Pt—P) coupling constants (Hz) are: 2754, L = CO; 3049, L = CNPh; and 3520, L = PEt_3 [5, 6]. The mean ν(Pt—Cl) stretching frequencies (cm^{-1}) are: 330, L = CO; 307, L = CNPh; and 294, L = PEt_3 [5, 7].

The crystals of *cis*-$PtCl_2(CO)(PPh_3)$ are triclinic, space group $P\bar{1}$. The unit cell of dimensions *a* 10.482(1), *b* 9.593(1), *c* 11.007(1) Å, α 97.57(1), β 117.96(1), γ 93.80(1)° contains two molecules. The intensities of 4150 independent reflexions ($I \geqslant 3\sigma(I)$) were measured on a four circle diffractometer and corrected for absorption. The structure has been refined by least-squares methods to *R* 0.067 and *R* ′ 0.075 (128 parameters, fixed hydrogen contributions). The molecules have the expected *cis*-square planar configuration. The geometry around the platinum atom is slightly distorted, with C—Pt—P and Cl—Pt—C angles of 95.2(4) and 172.4(3)°. Similar distortions are found in *cis*-$PtCl_2(CNEt)(PEt_2Ph)$ [8]. The Pt—C—O angle is 180(3)°. The Pt—C distance of 1.849(14) Å is somewhat shorter than the mean value of 1.896(16) Å in *cis*-$PtCl_2(CNPh)_2$ [9], suggesting increased Pt—C back donation in the carbonyl complex.

The Pt—Cl and Pt—P distances are compared with those in related complexes [3, 5, 8, 10, 11], in Table 1. The extremely short Pt—Cl (*trans* to C) distance indicates that the *trans* influence of CO is significantly less than that of CNEt. The Pt—Cl (*trans* to P) and Pt—P distances are respectively 0.037(4)

TABLE 1

BOND LENGTHS (Å) IN *cis*-$PtCl_2L(R_3P)$ COMPLEXES

L	R_3P	Pt—Cl (*trans* L)	Pt—Cl (*trans* P)	Pt—P	Ref.
PMe_3	PMe_3	2.376(12)[a]	2.376(12)[a]	2.248(9)[a]	11
C(OEt)NHPh	PEt_3	2.365(5)	2.368(7)	2.240(8)	3
$C(NPhCH_2)_2$	PEt_3	2.362(3)	2.381(3)	2.234(3)	10
CNPh	PEt_3	2.333(12)	2.365(11)	2.238(8)	3,5
CNEt	$PPhEt_2$	2.314(10)	2.390(8)	2.244(8)	8
Weighted means		—	2.379(3)	2.237(2)	
CO	PPh_3	2.277(3)	2.342(3)	2.279(3)	Present work

[a] Mean values

shorter, and 0.042(4) Å longer, than the weighted mean values of corresponding distances in five other *cis*-$PtCl_2L(PR_3)$ complexes. These differences, though small, are statistically highly significant and are compatible with the spectroscopic and structural evidence discussed above. They imply either that CO exerts a *cis* effect which strengthens the Pt—Cl bond and weakens the Pt—P bond, or that PPh_3 forms a weaker bond to platinum and has a lower *trans* influence than PEt_3, PMe_3, or $PPhEt_2$. To establish which of these effects is of prevailing importance we plan further structural studies.

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