Compounds containing Platinum–Carbon Bonds. Part VI.[1] Crystal and Molecular Structure of *cis*-Carbonyldichlorotriphenylphosphineplatinum(II)†

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The X-ray analysis of the title compound was based on 4 198 diffractometric intensity data, corrected for absorption. Crystals are triclinic, space group $P\bar{1}$, a = 10.4822(9), b = 9.5929(7), c = 11.0065(8) Å, α = 97.57(1), β = 117.96(1), γ = 93.80(1)°, Z = 2. The structure was solved by the heavy-atom method and refined by full-matrix least-squares to R 0.037.

The crystals are built of discrete monomeric molecules with *cis*-square-planar geometry. The Pt–C [1.858(7) Å] and Pt–Cl(*trans* to C) [2.276(1) Å] distances indicate that the carbonyl ligand possesses π-acceptor properties and exerts an extremely small *trans*-influence on the Pt–Cl bond. The Pt–P [2.282(2) Å] and Pt–Cl(*trans* to P) [2.343(2) Å] bond lengths may reflect a weak *cis*-influence of the carbonyl group.

THE chemistry and the spectroscopic properties of carbonyl complexes of platinum(II) have been extensively investigated [2] and the crystal structures of a few complexes [3-6] have been determined. However, the bond lengths obtained are of low or unstated accuracy and consequently of limited use in the discussions of the nature of platinum(II)–carbonyl bonding. To extend our study of the *trans*-influence and the σ-donor–π-acceptor properties of carbon-donor ligands in platinum(II) complexes,[7-9] we have carried out an accurate X-ray crystal structure analysis of *cis*-[$PtCl_2(CO)(PPh_3)$]. A preliminary account of this work has appeared.[10]

EXPERIMENTAL

Crystal Data.—$C_{19}H_{15}Cl_2OPPt$, $M = 556.3$, Triclinic $a = 10.4822(9)$, $b = 9.5929(7)$, $c = 11.0065(8)$ Å, $\alpha = 97.57(1)$, $\beta = 117.96(1)$, $\gamma = 93.80(1)°$, $U = 958.6$ Å^3, $Z = 2$, $D_c = 1.927$ gm cm^{-3}, $F(000) = 528$. Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 80.6 cm^{-1}. Space group $P\bar{1}$.

The crystals are air-stable transparent plates. The specimen chosen for the analysis displayed all members of the {100}, {010}, and {001} forms, and the perpendicular distances between parallel faces were 0.40, 0.24, and 0.09 mm.

The crystal system and the preliminary dimensions of a Delaunay unit cell were obtained from rotation and Weissenberg photographs. Unit-cell dimensions were later adjusted by a least-squares treatment of the setting angles of 12 reflections centred on a Hilger and Watts' Y 290 four-circle diffractometer, controlled by a PDP 8 computer. The space group $P\bar{1}$ led to a satisfactory structural model.

Intensity Measurements.—The intensities of all independent reflections with θ(Mo-K_α) $\leqslant 30°$ were measured on the Y 290 diffractometer, by use of zirconium-filtered molybdenum radiation and a pulse-height analyser. The θ—2θ scan technique was applied, with a scan step in 2θ of 0.04° and a counting time for each step of 2.5 s. Each reflexion was scanned through a 2θ range of 1.2° and the local background counted for 10 s at each end of the scan range. The intensities of three strong low-angle reflexions measured periodically throughout the experiment, showed only random fluctuations of up to $\pm 5\%$ of their mean values.

The integrated intensities, I, and their standard deviations, $\sigma(I)$, were derived using relationships described previously and assigning a value of 0.04 to the empirical factor q.[11] They were corrected for Lorentz, polarisation, and counting-loss effects. An absorption correction was also applied, using a Gaussian integration grid of 12 × 12 × 14 points. The transmission factors on $|F_o|$ ranged from 0.41 to 0.72.

Of 5 618 reflections measured, only 4 198, for which $I \geqslant 3\sigma(I)$, were used in the subsequent calculations.

Structure Analysis.—The position of the platinum atom was derived from a Patterson synthesis, and those of the other non-hydrogen atoms from subsequent difference syntheses. The structure was refined by the method of full-matrix least-squares. The function minimised was $\Sigma w \Delta^2$, where $w = 1/\sigma^2(F_o)$, $\Delta = |F_o| - |F_c|$. Atomic scattering factors were taken from ref. 12, except those of platinum [13] and hydrogen.[14] Anomalous scattering of platinum, chlorine, and phosphorus was accounted for, using $\Delta f'$ and $\Delta f''$ values taken from ref. 15.

The refinement of the scale factor and of the positional and isotropic thermal parameters of the platinum atom led to R 0.28. After the other non-hydrogen atoms were included, oxygen and carbon atoms with isotropic temperature factors and all the remaining atoms with anisotropic temperature factors, R decreased to 0.09. The oxygen and carbon atoms of the carbonyl group were then also assigned anisotropic thermal parameters. The positions of the hydrogen atoms were determined from those of the phenyl-group carbon atoms, assuming C–H 1.0 Å; the scattering of

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† No reprints available.

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these atoms was allowed for in the subsequent structure-factor calculations, but their positional parameters were not varied. The refinement converged at R 0.037 and R' 0.041 $[R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}]$. In the last cycle of refinement all parameters shifted by $<0.1\ \sigma$. The standard deviation of an observation of unit weight was 1.3. The mean values of $w\Delta^2$ showed no systematic trends when analysed as a function of $|F_o|$ or sin θ. The extreme function values in the final difference synthesis (1.7 and -1.1 eÅ^{-3}) were associated with the positions of the Pt and C(24) atoms, respectively. Extinction corrections did not appear necessary.

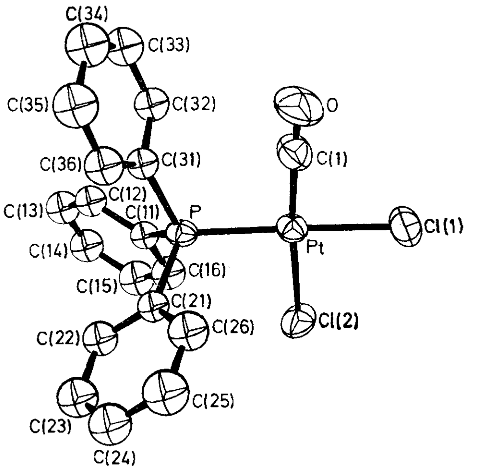
The observed structure amplitudes and the calculated structure factors are listed in Supplementary Publication SUP 21708 (19 pp., 1 microfiche).* Final atomic parameters are presented in Table 1 and a view of the molecular structure is shown in the Figure.

The computer programs used were the Hilger and Watts' software package for the Y290 diffractometer, K. W. Muir's cell reduction program, J. G. Sime's data processing program, J. M. Stewart's '*X*-ray '70 System', W. R. Busing, K. O. Martin, and H. Levy's ORFEE, and C. K. Johnson's ORTEP.

RESULTS AND DISCUSSION

The crystals are built of discrete monomeric molecules. A calculation of all intermolecular distances $\leqslant 3.8$ Å indicated that the interactions between the molecules are of the van der Waals type.

The molecules adopt a *cis*-square-planar configuration. The orientation of the phosphine ligand (Figure) is such as to bring an α-carbon atom, C(31), close to the carbonyl group and to the co-ordination plane of platinum, the C(31)–P–Pt–C(1) torsion angle being only 2.7(3)°. There is also a rather short contact between a β-carbon and a chlorine atom [C(16) $\cdots$ Cl(2) 3.34 Å]. The resulting H $\cdots$ Cl(2) distance of *ca.* 2.55 Å, shorter by 0.45 Å than the sum of van der Waals radii of hydrogen (1.2 Å) and chlorine (1.8 Å),[16] and the C(16)–H $\cdots$ Cl(2) angle of 147° may indicate a weak hydrogen-bonding interaction.



A view of the molecular structure; thermal vibration ellipsoids enclose 50% of probability

TABLE 1

Fractional co-ordinates (× 10^4) and vibrational parameters of atoms

Atom	x	y	z	B × 10 Å^2
Pt	2 422.6(3)	2 223.8(2)	832.6(3)	*
P	1 393(2)	1 363(1)	−1 510(2)	*
Cl(1)	3 496(2)	3 174(2)	3 227(2)	*
Cl(2)	1 798(2)	4 399(2)	382(2)	*
C(1)	3 136(8)	556(7)	1 359(7)	*
O	3 648(8)	−395(6)	1 723(7)	*
C(11)	−549(6)	1 389(5)	−2 598(6)	31(1)
C(12)	−1 416(7)	236(6)	−3 643(7)	39(1)
C(13)	−2 857(8)	300(7)	−4 570(8)	47(1)
C(14)	−3 434(8)	1 512(7)	−4 459(8)	49(1)
C(15)	−2 611(9)	2 664(8)	−3 441(9)	54(2)
C(16)	−1 157(8)	2 606(7)	−2 470(8)	47(1)
C(21)	2 285(6)	2 341(6)	−2 275(6)	32(1)
C(22)	1 524(7)	2 602(6)	−3 597(7)	40(1)
C(23)	2 258(9)	3 349(8)	−4 161(8)	52(1)
C(24)	3 697(9)	3 813(8)	−3 379(9)	54(2)
C(25)	4 467(10)	3 567(9)	−2 068(10)	62(2)
C(26)	3 764(8)	2 825(7)	−1 482(8)	49(1)
C(31)	1 629(6)	−483(6)	−1 811(6)	33(1)
C(32)	909(7)	−1 476(6)	−1 444(7)	40(1)
C(33)	1 066(8)	−2 899(7)	−1 625(8)	50(1)
C(34)	1 985(10)	−3 314(9)	−2 113(10)	61(2)
C(35)	2 705(10)	−2 344(9)	−2 502(9)	61(2)
C(36)	2 513(8)	−929(7)	−2 358(8)	46(1)

* These atoms were assigned anisotropic temperature factors of the form $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$. The final values of the B_{ij} parameters (× 10^4) are:

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	95.0(3)	84.7(2)	88.9(3)	23.7(2)	46.1(2)	23.9(2)
P	93(2)	70(1)	95(2)	20(1)	49(1)	22(1)
Cl(1)	197(3)	154(2)	91(2)	36(2)	52(2)	22(2)
Cl(2)	154(2)	83(1)	128(2)	33(2)	31(2)	14(1)
C(1)	164(11)	134(9)	106(9)	40(8)	59(8)	33(7)
O	281(12)	162(8)	188(10)	108(8)	103(9)	91(7)

The non-bonding intramolecular contacts C(1) $\cdots$ C(31) and C(1) $\cdots$ C(32) (3.06 and 3.14 Å respectively) suggest that the molecule is subject to some steric strain. Some of the ligand–ligand repulsions, especially those between the bulky phosphine and the carbonyl group, appear to be relieved by distortions of the co-ordination plane of platinum from ideal square-planar geometry. Thus the P–Pt–C(1) and C(1)–Pt–Cl(1) angles deviate from 90° by 4.6° and −3.2°, respectively, and the C(1)–Pt–Cl(2) angle is only 173.5(2)°. In addition, the C(1) and O atoms of the carbonyl group are displaced by −0.12 and −0.27 Å, respectively, from the plane through the Pt, P, Cl(1), and Cl(2) atoms. The individual displacements of the last four atoms from their least-squares plane do not exceed 0.02 Å.

The Pt–C(1)–O fragment is slightly bent, by 4.4°, but this may be due to steric rather than electronic effects. The Pt–C(1) bond length [1.858(7) Å] is in the range of those found in other platinum(II) carbonyls [1.74(4) to 1.97(5) Å].[3-6] It is considerably shorter than the Pt–C (*sp*) distance [1.98(2) Å] in *trans*-[PtCl(C:CPh)(PPhEt$_2$)$_2$],[17] and the Pt–C (*sp*^{2}) distances in *cis*-[PtPh(GePh$_2$-

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

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OH)(PEt$_3$)$_2$][18] [2.04(1) Å] and *cis*-[PtPh$_2$(Ph$_2$PCH$_2$PPh$_2$)][19] [2.05(1) Å]. Allowing for the effect of hybridisation on the covalent radius of carbon (0.69 and 0.74 Å for *sp*- and *sp*^{2}-carbon atoms), these distances indicate that in *cis*-[PtCl$_2$(CO)(PPh$_3$)] the co-ordinated carbonyl possesses appreciable π-acceptor properties.

The carbonyl group exerts a weak *trans*-influence on the Pt–Cl(2) bond. The Pt–Cl(2) distance is 2.276(1) Å, and the mean length of Pt–Cl (*trans* to Cl) bonds in five platinum(II) complexes is 2.303(5) Å.[9] However, the *trans*-influence of the σ-bonded carbon-donor ligand in *cis*-[PtCl(C⋮CPh)(PPhEt$_2$)$_2$] is high, the Pt–Cl (*trans* to C) distance being 2.407(6) Å.[17] The bond-length data therefore support our view[9] that the π-acidity of ligands reduces their *trans*-influence on Pt–Cl bonds, by depleting the metal atom of its electrons through d_{π}–d_{π} back-donation and thus enhancing the electrostatic attraction between the metal and chlorine atoms.

The other interesting features of the molecular geometry are the Pt–P [2.282(2) Å] and Pt–Cl(1) [2.343(2) Å] bond lengths. They are, respectively, 0.045(3) longer and 0.036(4) Å shorter than the mean Pt–P [2.237(2) Å] and Pt–Cl (*trans* to P) [2.379(3) Å] distances in other complexes of the type *cis*-[PtCl$_2$LA] [L = PMe$_3$, C(OEt)NHPh, C(NPhCH$_2$)$_2$, CNPh, or CNEt; A = PMe$_3$, PEt$_3$, or PPhEt$_2$].[10] These differences are highly significant. Moreover, they are consistent with the trends in *J*(Pt–P) coupling constants[20–21] and ν(Pt–Cl) stretching frequencies[20,22] of the complexes *cis*-[PtCl$_2$L(PEt$_3$)], where L = PEt$_3$, CNPh, or CO; these trends also indicate that the Pt–P bond is weakest and the Pt–Cl (*trans* to P) bond strongest when L = CO. Accordingly, while accepting that the bond lengths in *cis*-[PtCl$_2$LA] complexes may depend to some extent on the nature of the phosphine substituents and on the steric requirements of the ligands, we consider it likely that the long Pt–P and the short Pt–Cl (*trans* to P) bond in *cis*-[PtCl$_2$(CO)(PPh$_3$)] reflect predominantly an electronic *cis*-influence of the carbonyl ligand.

The geometry of the phosphine ligand is normal, the Pt–P–C and C–P–C angles showing the expected deviations[23] from the ideal tetrahedral value. The mean P–C and C–C bond lengths are 1.815(3) and 1.380(4) Å, respectively, and the phenyl rings are planar within ±0.02 Å.

TABLE 2

Interatomic distances and angles

(*a*) Bond lengths (Å)

Pt–Cl(1)	2.343(2)	C(16)–C(11)	1.389(8)
Pt–Cl(2)	2.276(1)	C(21)–C(22)	1.360(8)
Pt–P	2.282(2)	C(22)–C(23)	1.408(10)
Pt–C(1)	1.858(7)	C(23)–C(24)	1.344(11)
C(1)–O	1.114(8)	C(24)–C(25)	1.346(11)
P–C(11)	1.819(6)	C(25)–C(26)	1.402(11)
P–C(21)	1.815(6)	C(26)–C(21)	1.382(9)
P–C(31)	1.813(5)	C(31)–C(32)	1.390(8)
C(11)–C(12)	1.387(8)	C(32)–C(33)	1.385(9)
C(12)–C(13)	1.382(10)	C(33)–C(34)	1.362(11)
C(13)–C(14)	1.363(9)	C(34)–C(35)	1.390(12)
C(14)–C(15)	1.365(11)	C(35)–C(36)	1.386(10)
C(15)–C(16)	1.403(11)	C(36)–C(31)	1.384(9)

(*b*) Bond angles (°)

Cl(1)–Pt–Cl(2)	88.4(1)	C(21)–C(22)–C(23)	119.6(6)
Cl(1)–Pt–C(1)	86.8(2)	C(22)–C(23)–C(24)	119.6(7)
Cl(2)–Pt–P	90.1(1)	C(23)–C(24)–C(25)	121.7(8)
P–Pt–C(1)	94.6(2)	C(24)–C(25)–C(26)	119.9(8)
Cl(1)–Pt–P	178.3(2)	C(25)–C(26)–C(21)	119.0(7)
Cl(2)–Pt–C(1)	173.5(2)	C(26)–C(21)–C(22)	120.3(6)
Pt–C(1)–O	175.6(7)	C(31)–C(32)–C(33)	120.8(6)
Pt–P–C(11)	118.3(2)	C(32)–C(33)–C(34)	119.3(7)
Pt–P–C(21)	110.3(2)	C(33)–C(34)–C(35)	121.0(8)
Pt–P–C(31)	110.2(2)	C(34)–C(35)–C(36)	119.5(8)
C(11)–P–C(21)	105.4(3)	C(35)–C(36)–C(31)	120.1(7)
C(11)–P–C(31)	104.9(3)	C(36)–C(31)–C(32)	119.3(5)
C(21)–P–C(31)	107.2(3)	P–C(11)–C(12)	120.3(4)
C(11)–C(12)–C(13)	120.8(6)	P–C(11)–C(16)	120.3(5)
C(12)–C(13)–C(14)	119.7(7)	P–C(21)–C(22)	121.2(5)
C(13)–C(14)–C(15)	121.0(7)	P–C(21)–C(26)	118.6(5)
C(14)–C(15)–C(16)	120.1(7)	P–C(31)–C(32)	118.0(4)
C(15)–C(16)–C(11)	119.2(7)	P–C(31)–C(36)	122.7(5)
C(16)–C(11)–C(12)	119.1(6)		

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