Compounds containing Platinum–Carbon Bonds. Part I. Crystal and Molecular Structure of *cis*-Dichloro[diethyl(phenyl)phosphine](ethyl isocyanide)platinum(II), *cis*-[$PtCl_2(CNEt)(PEt_2Ph)$]

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The molecular geometry of the title compound has been determined by an *X*-ray analysis based on 1062 photographic data. The crystals are orthorhombic, space-group $P2_12_12_1$, a = 15·16(1), b = 10·72(1), c = 10·48(1) Å, Z = 4. The structure was solved by the heavy-atom method and refined by full-matrix least-squares to R 0·062. The crystals are built of monomeric molecules. Co-ordination around the platinum atom is square planar. The platinum–ligand bond lengths are: Pt–C 1·83(4), Pt–P 2·244(8), Pt–Cl(*trans* to C) 2·314(10), and Pt–Cl (*trans* to P) 2·390(8) Å. The *trans*-influence of isocyanide is thus appreciably smaller than that of tertiary phosphine.

RECENT discussions of the *trans*-influence of ligands (L) in square-planar and octahedral transition-metal complexes emphasise the importance of the σ-donor ability of L.[1,2] Although it has been realised that the *trans*-influence of a ligand also depends on its π-acidity, at least to some extent,[2,3] the importance of this effect has been difficult to assess in the absence of quantitative evidence.

We are therefore carrying out *X*-ray diffraction investigations of a number of platinum(II) complexes, all of which are square planar, uncharged, and contain four unidentate ligands and a platinum–carbon bond. The organic ligands have been chosen so as to display a range of π-acidity. In some cases the complexes have been prepared by novel synthetic routes and *X*-ray analysis has been necessary to establish molecular structure;[4] in others, as in the isocyanide complexes for instance, the geometry of the organic ligand and the mode of platinum–carbon bonding are of interest in the light of recent studies of the reactivity of co-ordinated ligands.[5,6]

We have investigated the structural features of co-ordinated isocyanide in two complexes. The crystal-structure analysis of *cis*-[$PtCl_2(CNEt)(PEt_2Ph)$] will be described here, and that of *cis*-[$PtCl_2(CNPh)_2$] in the following paper.[7] The former compound is one of the series of the type [$PtX_2(CNR^1)(PR^2_3)$] (X = Cl, Br, or I; R^1 = Me, Et, or Ph; PR^2_3 = PMe_2Ph, PEt_2Ph, or PEt_3), prepared and characterised by Badley *et al.*[6b]

EXPERIMENTAL

Crystal Data.—$C_{13}H_{20}Cl_2NPPt$, M = 487·3, Orthorhombic, a = 15·16(1), b = 10·72(1), c = 10·48(1) Å, U = 1703·2 Å^3, D_m (by flotation) = 1·94, Z = 4, D_c = 1·901, F(000) = 928. Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 193·8 cm^{-1}. Space-group $P2_12_12_1$.

The crystals were colourless needles, elongated in the c direction. Their morphology, examined optically, displayed all members of the {110} and {001} forms. For the specimen chosen for the analysis, the distances between parallel faces were 0·019 × 0·019 × 0·060 cm.

The unit-cell dimensions and the space-group were determined from Weissenberg (Cu-K_α radiation) and precession (Mo-K_α radiation, λ = 0·7107 Å) photographs.

For the intensity measurements, the $h0l$ and $hk0$—5 reciprocal-lattice nets were recorded photographically, by use of the multiple-film Weissenberg technique and nickel-filtered copper radiation. Reflexions were indexed in a right-hand co-ordinate system. Unobserved reflexions, and also 12 reflexions which were too intense to be measured reliably, were not included in the subsequent analysis. The intensities of the remaining 1062 independent reflexions were measured on a Joyce–Loebl integrating microdensitometer and corrected for Lorentz, polarisation, and absorp-

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tion effects. The transmission factors on F_o, calculated by Alcock's [8] version of the analytical method of De Meulenaer and Tompa,[9] varied from 0·19 to 0·43. The structure amplitudes of the reflexions from different reciprocal-lattice nets were brought to the same scale by a comparison of common reflexions.

Structure Analysis.—The position of the platinum atom was obtained from a Patterson function, and the positions of the other non-hydrogen atoms from the subsequent difference syntheses.

The structure was refined by full-matrix least-squares. The function minimised and the expressions for conventional and weighted agreement factors, R and R', were as defined previously.[10] The least-squares weights, w, were taken as $\sqrt{w} = 1{\cdot}0$ for $|F_o| \leqslant 60{\cdot}0$ and $\sqrt{w} = 60{\cdot}0/|F_o|$ for $|F_o| > 60{\cdot}0$. The atomic scattering factors were taken from ref. 11 for platinum and from ref. 12 for all other atoms; anomalous scattering was accounted for in the structure-factor calculations, values of $\Delta f'$ and $\Delta f''$ for platinum, chlorine, and phosphorus being taken from ref. 13.

Refinement of the positional and the isotropic thermal parameters of all atoms brought R to 0·092. An allowance was then made for the anisotropic thermal vibrations of platinum, chlorine, phosphorus, and nitrogen atoms, and also for the carbon atom bonded to platinum. The refinement of this model converged at R 0·067 and R' 0·091.

TABLE 1

Final fractional co-ordinates and thermal parameters of atoms

Atom	x	y	z	B/Å^2
Pt	−0·2412(1)	−0·1276(1)	−0·0968(2)	*
Cl(1)	−0·3434(5)	−0·0027(7)	−0·1997(14)	*
Cl(2)	−0·3503(5)	−0·2840(7)	−0·0580(11)	*
P	−0·1397(5)	0·0168(7)	−0·1467(12)	*
N	−0·1127(21)	−0·2878(24)	0·0551(38)	*
C(1)	−0·1646(18)	−0·2289(30)	−0·0098(49)	*
C(2)	−0·0570(25)	−0·3733(38)	0·1256(52)	6·2(9)
C(3)	−0·0536(36)	−0·3052(56)	0·2583(68)	10·5(16)
C(4)	−0·1192(24)	0·0216(34)	−0·3177(54)	5·4(8)
C(5)	−0·0837(27)	−0·1114(41)	−0·3709(52)	6·8(10)
C(6)	−0·1663(17)	0·1751(25)	−0·1096(47)	3·8(5)
C(7)	−0·1797(24)	0·2700(36)	−0·1983(55)	5·7(9)
C(8)	−0·2022(20)	0·3844(30)	−0·1527(44)	4·5(6)
C(9)	−0·2115(19)	0·4163(26)	−0·0309(45)	3·8(6)
C(10)	−0·2056(29)	0·3213(40)	0·0675(54)	6·8(10)
C(11)	−0·1761(23)	0·2002(31)	0·0218(56)	5·4(8)
C(12)	−0·0329(21)	−0·0197(30)	−0·0597(40)	4·9(7)
C(13)	0·0436(24)	0·0719(35)	−0·1206(48)	6·0(8)

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

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	35(1)	63(1)	126(3)	0(1)	−11(1)	2(1)
Cl(1)	42(3)	96(8)	144(19)	11(4)	−27(7)	1(10)
Cl(2)	51(3)	91(7)	128(26)	−16(4)	−20(6)	22(9)
P	42(3)	51(5)	117(30)	0(3)	−4(5)	−1(7)
N	79(18)	72(24)	182(90)	12(16)	4(26)	7(32)
C(1)	31(11)	112(30)	155(78)	19(16)	36(24)	63(42)

To account for the absolute configuration of the structure, the original model was now inverted and refined to convergence, which occurred at R 0·062 and R' 0·087. The absolute configuration of the structure is therefore that enantiomorphic to the one initially chosen.

In the last cycle of refinement all parameters shifted by $< 0{\cdot}95\sigma$. The adequacy of the weighting scheme was confirmed by an analysis of the variation of the mean $w\Delta^2$ with $|F_o|$ and $\sin\theta/\lambda$ (where $\Delta = |F_o| - |F_c|$). The highest peak in the final difference synthesis was 1·5 eÅ^{-3}, and all the peaks $> 0{\cdot}9$ eÅ^{-3} were associated with the position of the platinum atom. The final atomic parameters are shown in Table 1.*

The computer programs used were P. D. Cradwick's Data Processing Program for the ICL 1905 computer, N. W. Alcock's Absorption Correction Program for the Atlas computer, and also those listed previously.[10]

DISCUSSION

The crystal structure consists of monomeric molecular units. All intermolecular interactions are of the van der Waals type (Table 2).

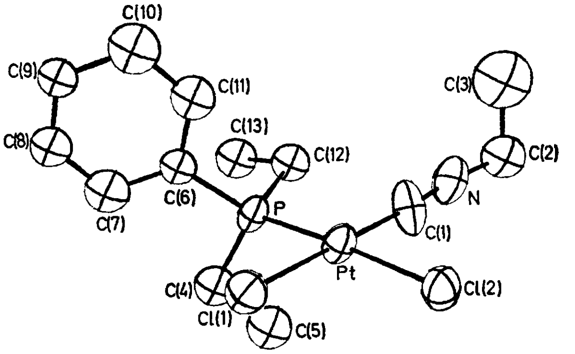
TABLE 2

Intermolecular contacts <3·80 Å

C(13) · · · C(5^{I})	3·45	C(9) · · · C(2^{III})	3·64
C(2) · · · Cl(1^{II})	3·58	C(3) · · · Cl(1^{IV})	3·68
C(2) · · · Cl(2^{II})	3·63	C(11) · · · Cl(1^{IV})	3·62
C(12) · · · Cl(2^{II})	3·69	Pt · · · C(4^{IV})	3·78
C(9) · · · $\mathrm{N}^{\mathrm{III}}$	3·62		

The superscripts refer to the following transformations of the atomic co-ordinates x, y, z:

I $-x, \frac{1}{2} + y, -\frac{1}{2} - z$
II $\frac{1}{2} + x, -\frac{1}{2} - y, -z$
III $x, 1 + y, z$
IV $-\frac{1}{2} - x, -y, \frac{1}{2} + z$



The molecular structure. The thermal-motion ellipsoids enclose 50% of probability

The molecular structure of the complex (Figure) is similar to that of the closely related *cis*-[$\mathrm{PtCl_2(CNPh)(PEt_3)}$].[14] Co-ordination around the platinum atom is square-planar, and the chlorine atoms are mutually *cis*.

The platinum–carbon bonding and the geometry of the isocyanide ligand will be discussed in the following paper.

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* Observed and calculated structure-factors are listed in Supplementary Publication No. SUP 20365 (7 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

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TABLE 3

Molecular geometry

(*a*) Bond lengths (Å)

Pt–Cl(1)	2·314(10)	C(2)–C(3)	1·57(9)
Pt–Cl(2)	2·390(8)	C(4)–C(5)	1·62(6)
Pt–P	2·244(8)	C(12)–C(13)	1·65(5)
Pt–C(1)	1·83(4)	C(6)–C(7)	1·39(6)
P–C(4)	1·82(6)	C(7)–C(8)	1·36(5)
P–C(12)	1·90(4)	C(8)–C(9)	1·33(6)
P–C(6)	1·79(3)	C(9)–C(10)	1·45(6)
C(1)–N	1·22(5)	C(10)–C(11)	1·45(6)
C(2)–N	1·45(5)	C(11)–C(6)	1·41(8)

(*b*) Bond angles (°)

Cl(1)–Pt–Cl(2)	91·2(3)	C(6)–P–C(12)	106(2)
Cl(1)–Pt–P	87·2(3)	C(4)–P–C(12)	109(2)
Cl(2)–Pt–C(1)	86·5(10)	P–C(4)–C(5)	112(3)
P–Pt–C(1)	95·2(10)	P–C(12)–C(13)	107(2)
Cl(1)–Pt–C(1)	177·2(12)	P–C(6)–C(7)	126(4)
Cl(2)–Pt–P	176·3(4)	P–C(6)–C(11)	115(3)
Pt–C(1)–N	174·4(35)	C(11)–C(6)–C(7)	120(3)
C(1)–N–C(2)	172(3)	C(6)–C(7)–C(8)	117(5)
N–C(2)–C(3)	100(4)	C(7)–C(8)–C(9)	127(4)
Pt–P–C(4)	112(1)	C(8)–C(9)–C(10)	120(3)
Pt–P–C(12)	109(1)	C(9)–C(10)–C(11)	114(5)
Pt–P–C(6)	117(1)	C(10)–C(11)–C(6)	122(4)
C(4)–P–C(6)	103(2)		

(*c*) Equations of mean planes and distances (Å) of atoms from the planes

Plane (*A*): $-3{\cdot}275x + 4{\cdot}946y + 9{\cdot}018z = -0{\cdot}730$

[Pt −0·02, Cl(1) −0·04, Cl(2) 0·05, P 0·05, C(1) −0·05]

Plane (*B*): $14{\cdot}649x + 2{\cdot}637y + 0{\cdot}794z = -2{\cdot}063$

[C(6) 0·00, C(7) 0·01, C(8) 0·01, C(9) −0·04, C(10) 0·05, C(11) −0·03]

The Pt–Cl(*trans* to C) bond of 2·314(10) Å is much shorter than Pt–Cl(*trans* to P) bond of 2·390(8) Å. The *trans*-influence of the isocyanide ligand is therefore considerably smaller than that of tertiary phosphine. Judging by the Pt–Cl(*trans* to CO) distance of 2·31(2) Å in *cis*-$[PtCl_2(CO)(PEt_3)]$,[14] and by the Pt–Cl(*trans* to Cl) distances of 2·32(1) and 2·294(9) Å in *trans*-$[PtCl_2(NH_3)_2]$ [15] and *trans*-$[PtCl_2(PEt_3)_2]$,[16] respectively, the *trans*-influence of isocyanide is comparable with those of carbonyl and chlorine.

The Pt–P(*trans* to Cl) bond of 2·244(8) Å is in very good agreement with comparable bonds in other platinum(II) complexes: 2·238(8) in *cis*-$[PtCl_2(CNPh)(PEt_3)]$,[14] 2·240(8) in *cis*-$[PtCl_2\{C(OEt)NHPh\}(PEt_3)]$,[6a] and 2·256(8) and 2·239(6) Å in *cis*-$[PtCl_2(PMe_3)_2]$.[17]

The geometry of the phosphine ligand (Table 3) shows no unusual features.[2b,10,18] Chemically equivalent bond lengths and angles in the phenyl and ethyl groups are equal to each other within the limits of experimental error, and comparable with the expected values. The benzene ring is planar.

We thank Prof. J. Chatt and Drs. E. M. Badley and R. L. Richards for providing the crystals, the Federal Fund for Scientific Research of Yugoslavia for a grant (to B. J.), and the S.R.C. for use of the Chilton Atlas Computer and for financial support.

[1/2482 *Received*, 29*th December*, 1971]

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