Compounds containing Platinum–Carbon Bonds. Part V.[1] Crystal and Molecular Structure of a Carbenoid Complex of Platinum(IV), $[PtCl_2\{C(Cl{\cdot}C_6H_3NH)(NHMe)\}(PEt_3)_2]ClO_4$ †

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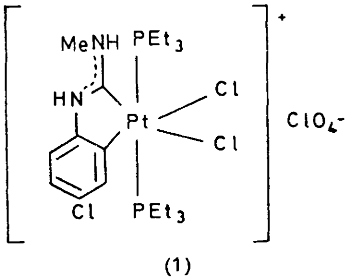
The molecular structure of the title complex has been determined by single-crystal *X*-ray analysis. Crystals are monoclinic, space group $P2_1/a$, a = 13·451(2), b = 21·381(5), c = 13·368(2) Å, β = 130·73(1)°, Z = 4. The structure was solved by the heavy-atom method and refined by full-matrix least-squares to R 0·048 for 3811 diffractometric intensity data corrected for absorption.

In each complex cation mutually *cis* chlorine atoms, *trans*-phosphorus atoms, and *cis*-carbenoid and -phenyl carbon atoms define an octahedron about the platinum atom. The metal–ligand distances are: Pt–P 2·388(4), Pt–C(Ph) 2·034(11), Pt–C(carbenoid) 1·973(11), Pt–Cl 2·415(4) *trans* to phenyl, and 2·372(3) Å *trans* to carbenoid.

RECENTLY Chatt *et al.* have shown that the platinum(II) carbenoid complexes *cis*-$[PtCl_2\{C(NHR^1)(NHR^2)\}(PEt_3)]$ and *trans*-$[PtCl\{C(NHR^1)(NHR^2)\}(PEt_3)_2]ClO_4$, where $R^1 = R^2 =$ Me, undergo oxidative addition with chlorine to give the expected platinum(IV) carbenoid compounds. However, when $R^1 =$ Me or Et and $R^2 =$ Ph the reaction appears to follow a different course, involving 2-metallation and 4-chlorination of the phenyl ring; thus the product from *trans*-$[PtCl\{C(NHMe)(NHPh)\}(PEt_3)_2]ClO_4$ was formulated as the platinum(IV) species (1).[2] Verification of this structure by *X*-ray analysis seemed desirable, since reactions involving co-ordinated carbenoid ligands are relatively unusual.[3] Moreover, metallation occurs more commonly under reducing conditions.[4]



(1)

We also expected that a determination of the bond lengths in (1) would allow us to compare the relative

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† No reprints available.

[1] Part IV, Lj. Manojlović-Muir and K. W. Muir, *J.C.S. Dalton*, 1974, 2427.

[2] J. Chatt, R. L. Richards, and G. H. D. Royston, personal communication; see also ref. 9.

[3] F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 1973, **16**, 487; D. J. Cardin, B. Çetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, 1973, **2**, 99.

[4] A. J. Cheney, W. S. McDonald, K. O'Flynn, B. L. Shaw, and B. L. Turtle, *J.C.S. Chem. Comm.*, 1973, 128, and refs. therein.

trans-influences of σ-phenyl and carbenoid ligands in platinum(IV) complexes. This work thus forms part of our continuing investigation of the *trans*-influence and bonding of carbon donor ligands in platinum complexes.[1,5-8]

A preliminary account of this work has already been published.[9] Prior to that, structural data were available only for carbenoid complexes of metals in oxidation states 0 to II.[3] However, the molecular structure of a carbenoid complex of rhodium(III) has been described recently.[10]

EXPERIMENTAL

Crystal Data.—$C_{20}H_{38}Cl_4N_2O_4P_2Pt$, M = 769·4, Monoclinic, a = 13·451(2), b = 21·381(5), c = 13·368(2) Å, β = 130·73(1)°, U = 2913 Å^3, Z = 4, D_c = 1·754 g cm^{-3}, F(000) = 1520. Mo-K_α radiation, λ = 0·71069 Å; μ(Mo-K_α) = 55·7 cm^{-1}. Space group $P2_1/a$ from systematic absences ($h0l$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$) and subsequent successful refinement.

Measurements.—The crystals are white air-stable prisms. The monoclinic Laue symmetry $2/m$, systematic absences, and approximate unit-cell dimensions were obtained from a preliminary photographic study. Final values of the cell parameters and the intensities of all independent reflections with θ(Mo-K_α) $\leqslant$ 25° were measured on a Hilger and Watts Y 290 four-circle diffractometer by standard methods previously described in detail.[11] The crystal employed was of equant habit and it was set with its c axis approximately coincident with the diffractometer ϕ axis. To check crystal and electronic stability the intensities of three strong reflections were periodically remeasured during the experiment. Apparently random fluctuations of up to ±7% of the mean values were observed.

The integrated intensities were derived in the way described previously;[11] the factor q was assigned a value of 0·05. They were scaled according to the variation of the intensities of the standard reflections. For 45 reflections the maximum counting rate exceeded 8 × 10^3 counts s^{-1}. In order to correct for the resulting counting losses the intensities of all independent reflections with θ(Mo-K_α) $\leqslant$ 8° were remeasured at reduced X-ray generator settings. The coefficients of the equation $J = rI + sI^2$, where J and I are respectively the integrated intensities at reduced and normal generator settings, were obtained by the method of least squares. The corrected intensity was taken as J/r. The maximum counting loss correction was 30% of the final integrated intensity. Lorentz and polarisation factors were applied. A correction for absorption was made, using a Gaussian integration grid of 8 × 8 × 10 points for the crystal, the dimensions of which were 0·3 × 0·3 × 0·3 mm. The transmission factors on $|F_o|$ ranged from 0·50 to 0·57.

A total of 3811 independent reflections with $I \geqslant 3\sigma(I)$ were used in the analysis.

Structure Analysis.—The position of the platinum atom was derived from a Patterson synthesis, and the remaining non-hydrogen atoms were located in subsequent electron-density syntheses.

TABLE 1

Fractional atomic co-ordinates and vibrational parameters

	x	y	z	$10^3 \times U$/Å^2
Pt	0·06375(3)	0·15076(2)	0·90764(4)	*
P(1)	−0·0711(3)	0·0743(1)	0·7399(3)	*
P(2)	0·1967(3)	0·2254(1)	1·0816(3)	*
Cl(1)	0·1733(4)	0·1546(2)	0·5076(3)	*
Cl(2)	0·0503(3)	0·0907(1)	1·0477(3)	*
Cl(3)	−0·1275(3)	0·2105(1)	0·8293(3)	*
Cl(4)	0·5046(4)	−0·0175(2)	1·2034(3)	*
O(1)	0·2278(24)	0·1157(12)	0·4765(23)	269(10)
O(2)	0·2647(20)	0·1749(9)	0·6261(20)	212(7)
O(3) †	0·1159(41)	0·1106(19)	0·5370(38)	210(14)
O(4) †	0·0469(31)	0·1569(12)	0·4669(30)	155(10)
O(5) †	0·1208(40)	0·1671(17)	0·3861(41)	206(14)
O(6) †	0·1703(31)	0·2211(16)	0·4773(32)	189(12)
C(1)	0·3617(17)	0·2043(8)	1·2087(17)	124(5)
C(2)	0·3816(20)	0·1579(9)	1·3040(20)	139(7)
C(3)	0·2038(29)	0·3018(15)	1·0045(28)	199(11)
C(4)	0·2668(47)	0·3397(19)	1·0497(46)	284(21)
C(5)	0·1236(15)	0·2458(7)	1·1499(15)	102(4)
C(6)	0·2006(17)	0·2937(8)	1·2691(17)	121(5)
C(7)	−0·1340(16)	0·1013(7)	0·5789(16)	112(5)
C(8)	−0·2192(20)	0·0619(10)	0·4574(19)	144(6)
C(9)	−0·2104(16)	0·0552(8)	0·7307(15)	109(5)
C(10)	−0·3066(19)	0·0098(9)	0·6365(18)	134(6)
C(11)	0·0078(12)	−0·0003(6)	0·7693(12)	83(3)
C(12)	0·0962(15)	−0·0071(7)	0·7345(15)	107(4)
C(13)	0·2283(9)	0·1085(4)	0·9625(9)	54(2)
C(14)	0·2996(10)	0·0617(5)	1·0553(10)	62(2)
C(15)	0·4138(11)	0·0428(5)	1·0869(11)	72(3)
C(16)	0·4587(12)	0·0687(5)	1·0297(12)	77(3)
C(17)	0·3850(11)	0·1143(5)	0·9327(11)	72(3)
C(18)	0·2712(10)	0·1339(4)	0·9026(9)	56(2)
C(19)	0·0846(10)	0·1967(4)	0·7943(10)	60(2)
C(20)	0·0168(13)	0·2760(6)	0·6214(13)	90(4)
N(1)	0·0040(9)	0·2411(4)	0·7095(9)	71(2)
N(2)	0·1887(8)	0·1792(4)	0·8073(8)	64(2)

* These atoms were assigned anisotropic temperature factors of the form $\exp\left[-2\pi^2 10^{-4} \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} a_i^* a_j^* h_i h_j\right]$.

The final values of the U_{ij} parameters are:

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	459(2)	535(2)	519(2)	24(2)	279(2)	42(2)
P(1)	565(16)	787(18)	577(16)	−114(14)	317(14)	−64(14)
P(2)	640(17)	694(18)	802(20)	−76(14)	396(16)	−179(15)
Cl(1)	894(23)	1068(26)	715(19)	−122(19)	483(18)	−231(18)
Cl(2)	791(18)	733(17)	684(17)	12(14)	509(15)	92(13)
Cl(3)	574(15)	792(18)	936(20)	186(14)	424(15)	110(16)
Cl(4)	951(24)	996(23)	833(21)	475(20)	459(19)	249(18)

† Occupancies of 0·5 were assigned to these atoms.

The structure was refined by the method of full-matrix least-squares. The function minimised was $\Sigma w\Delta^2$, where $\Delta = ||F_o| - |F_c||$ and $w = 4F_o^2/\sigma(F_o^2)$. Atomic scattering factors were taken from ref. 12, except for those of platinum[13] and hydrogen.[14] Allowance was made for the anomalous scattering of the platinum, chlorine, and phosphorus atoms, by use of values for $\Delta f'$ and $\Delta f''$ from ref. 15.

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[11] K. W. Muir, *J. Chem. Soc.* (*A*), 1971, 2663.

[12] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[13] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[14] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[15] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

Refinement of the positional and isotropic vibrational parameters for all non-hydrogen atoms except platinum, which was assigned an anisotropic temperature factor, led to *R* 0·078. When allowance was made for the anisotropic thermal motion of the phosphorus and chlorine atoms *R* fell to 0·058. It then became apparent from a difference synthesis that both the perchlorate anion and the ethyl group containing C(3) and C(4) were disordered. Several disordered structural models were considered but none proved entirely satisfactory. In the model finally adopted no attempt was made to describe the disorder of the ethyl group. However six sites were assigned to perchlorate oxygen atoms. Two of these [O(1) and O(2)] were given population parameters of unity and the remaining four population parameters of 0·5. The population parameters were not refined. Refinement of this model terminated at *R* 0·048 and *R'* 0·066. In the final calculations fixed contributions for the scattering of the hydrogen atoms bonded to the nitrogen atoms, and to the phenyl and methylene carbon atoms [apart from those bonded to C(3)], were added to the structure factors; the positions of the hydrogen atoms were deduced from those of the heavier atoms, assuming normal bond lengths and valency angles. In the final cycle of refinement no parameter shifted by >0.8 of its standard deviation (σ), except *z* of O(5) which shifted by 1·1σ. Mean values of $w\Delta^2$ showed no consistent trend when analysed as a function either of $|F_o|$ or of sin θ, suggesting that the weighting scheme employed was satisfactory. In the final difference synthesis the extreme function values of 1·1 and −1·5 eÅ^{-3} occurred in regions close to the platinum atom.

TABLE 2

Selected interatomic distances (Å) and angles (°)

(*a*) Bond lengths

Pt–P(1)	2·384(3)	Pt–P(2)	2·392(3)
Pt–Cl(2)	2·372(3)	Pt–Cl(3)	2·415(4)
Pt–C(19)	1·973(11)	Pt–C(13)	2·034(11)
N(1)–C(19)	1·327(13)	N(2)–C(19)	1·347(17)
N(1)–C(20)	1·496(18)	N(2)–C(18)	1·394(13)
C(13)–C(14)	1·38(1)	Cl(1)–O(1)	1·34(3)
C(14)–C(15)	1·36(2)	Cl(1)–O(2)	1·29(2)
C(15)–C(16)	1·36(2)	Cl(1)–O(3)	1·43(5)
C(16)–C(17)	1·39(2)	Cl(1)–O(4)	1·41(4)
C(17)–C(18)	1·37(2)	Cl(1)–O(5)	1·31(4)
C(18)–C(13)	1·37(2)	Cl(1)–O(6)	1·47(4)
Mean	1·373(7)	Mean	1·38(3)
P(1)–C(7)	1·82(2)	C(7)–C(8)	1·49(3)
P(1)–C(9)	1·84(2)	C(9)–C(10)	1·44(3)
P(1)–C(11)	1·81(1)	C(11)–C(12)	1·54(3)
P(2)–C(1)	1·76(2)	C(1)–C(2)	1·50(3)
P(2)–C(3)	1·97(3)	C(3)–C(4)	1·04(5) *
P(2)–C(5)	1·78(2)	C(5)–C(6)	1·58(2)
Mean	1·83(3)	Mean	1·51(2)
C(15)–Cl(4)	1·760(12)		

(*b*) Interbond angles

P(1)–Pt–Cl(2)	88·2(1)	Pt–C(19)–N(2)	114·8(4)
P(1)–Pt–Cl(3)	90·8(1)	N(1)–C(19)–N(2)	121(1)
P(2)–Pt–Cl(2)	89·2(1)	C(19)–N(1)–C(20)	126(1)
P(2)–Pt–Cl(3)	88·7(1)	C(18)–N(2)–C(19)	117(1)
P(1)–Pt–C(13)	90·9(3)		
P(1)–Pt–C(19)	91·2(3)	Pt–P(1)–C(7)	112·1(4)
P(2)–Pt–C(13)	89·9(3)	Pt–P(1)–C(9)	109·4(5)
P(2)–Pt–C(19)	91·4(3)	Pt–P(1)–C(11)	114·9(4)
Cl(2)–Pt–C(13)	95·8(3)	Pt–P(2)–C(1)	116·1(5)
Cl(3)–Pt–C(19)	92·8(3)	Pt–P(2)–C(3)	107·8(7)
Cl(2)–Pt–Cl(3)	91·2(1)	Pt–P(2)–C(5)	110·5(5)
C(13)–Pt–C(19)	80·3(4)	Mean	111·8(13)
P(1)–Pt–P(2)	177·4(1)		
Cl(2)–Pt–C(19)	176·0(3)	C(7)–P(1)–C(9)	109(1)
Cl(3)–Pt–C(13)	172·9(8)	C(7)–P(1)–C(11)	107(1)
Pt–C(13)–C(14)	126·9(6)	C(9)–P(1)–C(11)	104(1)
Pt–C(13)–C(18)	112·8(4)	C(1)–P(2)–C(3)	105(1)
C(14)–C(13)–C(18)	120(1)	C(1)–P(2)–C(5)	110(1)
C(13)–C(14)–C(15)	118(1)	C(3)–P(2)–C(5)	107(1)
C(14)–C(15)–C(16)	122(1)	Mean	107·0(9)
C(14)–C(15)–Cl(4)	119(1)		
C(16)–C(15)–Cl(4)	119(1)	P(1)–C(7)–C(8)	123(1)
C(15)–C(16)–C(17)	120(1)	P(1)–C(9)–C(10)	120(1)
C(16)–C(17)–C(18)	118(1)	P(1)–C(11)–C(12)	118(1)
C(17)–C(18)–C(13)	122(1)	P(2)–C(1)–C(2)	114(1)
C(17)–C(18)–N(2)	123(1)	P(2)–C(3)–C(4)	130(2)
C(13)–C(18)–N(2)	115(1)	P(2)–C(5)–C(6)	117(1)
Pt–C(19)–N(1)	124·5(6)	Mean	120·5(23)

(*c*) Interionic non-bonded distances less than the sum of the appropriate van der Waals radii

N(2) · · · Cl(3$^{\mathrm{I}}$)	3·29	C(6) · · · C(7$^{\mathrm{IV}}$)	3·89
Cl(4) · · · C(8$^{\mathrm{II}}$)	3·43	C(2) · · · C(10$^{\mathrm{III}}$)	3·94
C(11) · · · Cl(2$^{\mathrm{III}}$)	3·58	C(4) · · · C(12$^{\mathrm{V}}$)	3·94
C(2) · · · C(20$^{\mathrm{IV}}$)	3·64	C(10) · · · C(10$^{\mathrm{VI}}$)	3·97
C(6) · · · C(8$^{\mathrm{IV}}$)	3·67		

Roman numerals refer to the following transformations of the co-ordinates in Table 1:

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

* Not used in calculation of the mean.

TABLE 3

Mean planes

(*a*) Deviations (Å) of atoms from least-squares planes. Atoms not used to define the plane are italicised.

Plane (*A*): C(19) 0·005, N(1) −0·002, N(2) −0·002, Pt −0·001, *C(18)* 0·060, *C(20)* −0·015

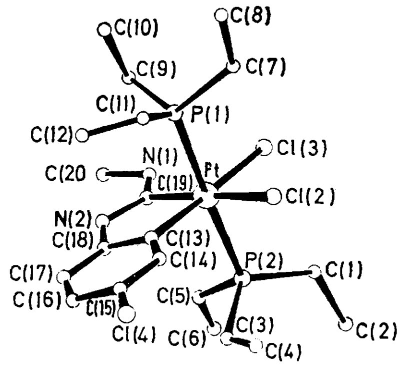
Plane (*B*): Pt −0·007, C(13) 0·023, C(19) −0·020, Cl(2) −0·015, Cl(3) 0·018, *P(1)* −2·390, *P(2)* 2·385

Plane (*C*): Pt 0·011, C(13) −0·026, C(18) 0·034, C(19) 0·003, N(2) −0·021, *N(1)* 0·004, *C(20)* −0·020

Plane (*D*): C(13) 0·009, C(14) −0·009, C(15) −0·004, C(16) 0·016, C(17) −0·015, C(18) 0·003, *Pt* 0·165, *N(2)* −0·027, *Cl(4)* −0·048

(*b*) Equations of planes

(*A*) $1.636x + 14.679y + 6.201z = 7.947$
(*B*) $1.781x + 14.313y + 6.250z = 7.951$
(*C*) $1.460x + 14.736y + 6.310z = 8.031$
(*D*) $0.594x + 14.896y + 6.868z = 8.353$



A view of the cation of (1) showing the atomic numbering scheme

Final atomic parameters and a selection of functions derived from them are presented in Tables 1—3. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21152 (23 pp., 1 microfiche).* A

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1973, Index issue.

view of the structure of the complex cation is shown in the Figure.

Computer programs used include the Hilger and Watts software package for the Y 290 diffractometer and the Edinburgh Regional Computer Centre version of J. M. Stewart's '*X*-Ray '70' system.

DISCUSSION

The crystal structure is built of discrete $[PtCl_2\{C(Cl{\cdot}C_6H_3NH)(NHMe)\}(PEt_3)_2]^+$ cations and perchlorate anions. Adjacent cations and anions appear to be well separated, but there are several contacts between different cations which are shorter than the sum of the van der Waals radii of the participating atoms (Table 2). The $N(2) \cdots Cl(3^I)$ contact of 3·29 Å is short enough to represent the donor–acceptor distance in a weak $N-H \cdots Cl$ hydrogen bond.[16] Assuming that N(2) is in a state of sp^2 hybridisation (*vide infra*), and that the N–H bond length is 1·0 Å, the $H \cdots Cl(3^I)$ distance can be estimated to be *ca.* 2·6 Å, which is appreciably shorter than 3·0 Å, the sum of the van der Waals radii of chlorine and hydrogen. However, the average $H \cdots Cl$ distance in $N-H \cdots Cl$ hydrogen bonds is *ca.* 2·40 Å,[16] and in the neutron diffraction study of methylglyoxal bisguanylhydrazone dihydrochloride monohydrate values between 2·17 and 2·82 Å were observed.[17] The $N(2)-H \cdots Cl(3^I)$ angle is estimated to be 122° which is a value acceptable for hydrogen bonds of this type.[16,17] The other non-bonded contacts in Table 2 all involve carbon atoms of the phosphine ethyl groups.

The perchlorate oxygen atoms are disordered. Two sites, O(1) and O(2), appear to have an occupancy of unity, and they subtend an angle of 108(1)° at Cl(1). The O–Cl–O angles involving partially occupied oxygen sites range between 73(2) and 142(2)°. The mean Cl–O distance [1·38(3) Å] can be compared with the value (1·46 Å) typical of ordered perchlorate groups.[18]

Disorder also affects two of the phosphine carbon atoms, C(3) and C(4), giving rise to an unreasonable C(3)–C(4) bond length of 1·04(5) Å. It is therefore clear that, for the atoms which it involves, the disorder has led not only to systematic errors in the positional (and thermal) parameters, but also to underestimates of the standard deviations of these parameters. Hence, no weight should be attached to the formally significant differences which exist, *inter alia*, between the P–C bond lengths involving P(2), or between the O–Cl–O angles within the perchlorate group.

Despite the disorder, and the rather large vibrational amplitudes of all the phosphine carbon atoms, the mean values of the P–C and CH_2-CH_3 bond lengths and of the Pt–P–C, C–P–C, and P–C–C angles are in fair agreement with those we have observed in platinum(II) carbenoid complexes containing triethylphosphine ligands.[1]

There is no evidence that disorder has affected the platinum, chlorine, and phosphorus atoms, or any of the atoms of the chelate ligand. Therefore, we consider it unlikely that the parameters of these atoms are subject to systematic errors. Furthermore, there are no significant correlations between the parameters of these atoms and those of the disordered atoms. We therefore conclude that the standard deviations of the ordered atoms are realistic estimates of the experimental errors.

The structure of the complex cation agrees with that predicted by Chatt *et al.*[2] Mutually *cis* phenyl and carbenoid carbon atoms, *trans*-phosphorus atoms, and *cis*-chlorine atoms define a slightly distorted octahedron about the platinum atom. The constraint imposed by the chelate ring leads to a C(13)–Pt–C(19) angle of 80·3(4)°, and also to a slight opening of the C(13)–Pt–Cl(2) and C(19)–Pt–Cl(3) angles to 95·8(3) and 92·8(3)° respectively. Other angles subtended at the platinum atom by mutually *cis* ligand donor atoms are close to 90°.

The carbenoid carbon atom, C(19), is coplanar with the atoms N(1), N(2), and Pt, to which it is directly bonded. The methyl carbon atom, C(20), attached to N(1), also lies in this plane. The mean N–C(carbenoid) bond distance [1·337(10) Å] is much shorter than the other N–C bonds in the cation and is consistent with a bond order of *ca.* 1·7.[3]

The Pt–C(carbenoid) bond distance [1·973(11) Å] is 0·061(16) Å shorter than Pt–C(Ph) [2·034(11) Å]. The latter distance is in turn 0·02 Å shorter than the mean Pt^{IV}–C(Me) distance (2·054 Å) in several trimethylplatinum(IV) complexes,[19] and this difference can be almost entirely accounted for by the difference in covalent radii of sp^2 and sp^3 hybridised carbon atoms. The Pt–C(Ph) bond thus appears to be single in character. It has been suggested that the order of a metal–carbon bond which is 0·1 Å shorter than the corresponding single bond will be *ca.* 1·2.[19] On this basis it may be argued that the shortening of the Pt–C(carbenoid) bond is consistent with a bond order of *ca.* 1·1; such multiple character could arise from a small amount of Pt–C(carbenoid) back donation.

From the lengths and coplanarity of the bonds involving the carbenoid carbon atom it may be concluded that the platinum–carbenoid bonding is predominantly that indicated by the canonical structure (1), in which the main interaction of the vacant *p* orbital of the sp^2 hybridised carbenoid carbon atom is with the filled *p* orbitals of the adjacent nitrogen atoms, which are also sp^2 hybridised. [The C–N–C angles at atoms N(1) 125·5(11), and N(2) 116·8(9)°, appear consistent with this view.] There also appears to be a minor contribution from a second canonical structure, in which platinum *d* electrons are donated to the vacant *p* orbital of the carbenoid carbon atom. The platinum(IV)–carbenoid bonding found here is thus very similar to that observed in *cis*- and *trans*-$[Pt^{II}Cl_2\{C(PhNCH_2)_2\}PEt_3]$.[1,8]

The C–C bond lengths in the phenyl ring bonded to

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platinum do not differ significantly from their mean value of 1·373(7) Å ($\chi^2 = 2·7$ on 5 degrees of freedom). The average internal C–C–C angle within the ring is 120·0(7)°, and the ring is planar. The platinum and Cl(4) atoms are displaced respectively by 0·17 and −0·05 Å from the plane of the ring. The dihedral angle of 4·5° between the phenyl ring plane and the co-ordination plane of the carbenoid carbon atom results in a slight puckering of the five-membered chelate ring (see Table 3). The C–Cl bond length [1·760(12) Å] is slightly longer than the corresponding value (1·745 Å) in chlorobenzene.[20]

The Pt–Cl(2) bond length [2·372(3) Å] is 0·043(5) Å shorter than Pt–Cl(3) [2·415(4) Å], but 0·040(6) Å longer than the mean Pt–Cl distance [2·332(5) Å] in *trans*-[$PtCl_4(PEt_3)_2$].[21] These differences suggest that in platinum(IV) complexes the *trans*-influence of the carbenoid ligand is less than that of σ-phenyl but greater than that of chloride. The same *trans*-influence series has been established for platinum(II) complexes. Thus Pt^{II}–Cl bond lengths *trans* to Cl^- and $C(PhNCH_2)_2$ are found to be 2·303(5) and 2·362(3) Å respectively; the length of a Pt^{II}–Cl bond *trans* to σ-phenyl has not yet been reported, but a value of 2·398(4) Å *trans* to σ-vinyl has been observed.[8]

As noted earlier, the atom Cl(3) may be involved in an interionic hydrogen bond. This atom may also participate in an intramolecular N–H ··· Cl hydrogen bond with N(1), since Cl(3) ··· N(1) is 3·13 Å. If it is assumed that N(1) is sp^2 hybridised and that N–H is 1·0 Å, then estimates of 2·4 Å for the H ··· Cl(3) distance and of 130° for the N–H ··· Cl angle are obtained. The difference in the lengths of the Pt–Cl(2) and Pt–Cl(3) bonds could thus be ascribed to the involvement of Cl(3) in hydrogen bonding. However, N–H ··· Cl hydrogen bonds are believed to be rather weak,[16] and we therefore consider this factor less important than the difference in the nature of the ligands *trans* to the bonds involved.

The mean Pt–P bond length [2·388(4) Å] is in good agreement with the corresponding value [2·393(5) Å] for *trans*-[$PtCl_4(PEt_3)_2$].[21] In square-planar complexes of platinum(II), however, mutually *trans* Pt–P bond lengths lie in the range 2·27—2·32 Å.[5] The greater length of Pt–P bonds in octahedral platinum(IV) complexes is probably related to the presence of six, rather than eight, *d* electrons at the metal atom. In octahedral *trans*-[$M^{IV}Cl_4(PR_3)_2$] complexes, where M is a third-row transition metal, addition of one *d* electron to M leads to a contraction of 0·05 Å in the M–P bond length.[21] It is, however, remarkable that the lengths of the Pt–C and Pt–Cl bonds in the cation of (1) are nearly the same as those of comparable bonds in square-planar platinum(II) complexes.

We thank Dr. R. L. Richards for a gift of crystals and for bringing this problem to our attention, and the S.R.C. for a grant (to R. W.).

[4/1296 *Received*, 28*th June*, 1974]

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