Compounds containing Platinum–Carbon Bonds. Part IV.[1] Crystal and Molecular Structures of *trans*- and *cis*-Dichloro(1,3-diphenylimidazolidin-2-ylidene)(triethylphosphine)platinum(II) †

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The crystal structures of the *trans* (I) and *cis* (II) isomers of $[PtCl_2\{C(PhNCH_2)_2\}(PEt_3)]$ have been determined by *X*-ray diffraction methods. The structural models were refined by full-matrix least-squares, both to *R* 0·048 [(I), 2356 and (II), 1822 independent reflections measured on a diffractometer]. Crystal data are: (I), triclinic, space group $P\bar{1}$, $a = 13·961(6)$, $b = 11·782(4)$, $c = 10·659(5)$ Å, $\alpha = 92·98(3)$, $\beta = 125·29(3)$, $\gamma = 114·54(3)°$, $Z = 2$; (II), orthorhombic, space group *Pnam*, $a = 15·991(2)$, $b = 8·601(2)$, $c = 16·703(2)$ Å, $Z = 4$.

Crystals of both compounds are built of discrete monomeric molecules, in which the co-ordination around the platinum atom is square planar. In (I) selected bond lengths are: Pt–Cl 2·302(10), Pt–P 2·291(4), and Pt–C 2·020(16) Å; in (II) they are Pt–Cl (*trans* to C) 2·362(3), Pt–Cl (*trans* to P) 2·381(3), Pt–P 2·234(3), and Pt–C 2·009(13) Å. These results indicate that the order of the Pt–C bonds is little greater than unity, and that the *trans*-influence of the carbene ligand is similar to that of phosphine and appreciably greater than that of chlorine.

STRUCTURAL investigations described in this paper represent part of our continuing study of the relative *trans*-influence of various carbon-donor ligands in square-planar platinum(II) complexes.[1-3] In this context, determination of the molecular structures of isomeric compounds, such as the *trans* (I) and *cis* (II) isomers of $[PtCl_2\{C(PhNCH_2)_2\}(PEt_3)]$, is of particular importance, since it permits comparison between corresponding bond lengths in different molecules containing the same metal atom bonded to the same set of ligands. Prior to this work *cis*- and *trans*-$[PtCl_2(NH_3)_2]$ were the only pair of isomeric platinum(II) complexes for which accurate structural results were available.[4] A preliminary report on the molecular structures of isomeric bis(phosphine) complexes of platinum(II) has recently appeared.[5]

The first general synthesis of carbenoid complexes of platinum(II) involved 1,2-addition of alcohols or amines to the C–N bond of an isocyanide complex.[6] It has been found more recently that bridged binuclear complexes, such as $[\{PtCl_2(PEt_3)\}_2]$, react with a variety of electron-rich olefins to give carbenoid complexes.[7,8] In view of

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† No reprints available.

[1] Part III, B. Jovanović, Lj. Manojlović-Muir, and K. W. Muir, *J.C.S. Dalton*, 1974, 195.

[2] B. Jovanović, Lj. Manojlović-Muir, and K. W. Muir, *J.C.S. Dalton*, 1972, 1178.

[3] B. Jovanović and Lj. Manojlović-Muir, *J.C.S. Dalton*, 1972, 1176.

[4] G. H. W. Milburn and M. R. Truter, *J. Chem. Soc.* (*A*), 1966, 1609.

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

[6] E. M. Badley, J. Chatt, R. L. Richards, and G. A. Sim, *Chem. Comm.*, 1969, 1322.

[7] D. J. Cardin, B. Cetinkaya, M. F. Lappert, Lj. Manojlović-Muir, and K. W. Muir, *Chem. Comm.*, 1971, 400.

[8] B. Cetinkaya, E. Cetinkaya, and M. F. Lappert, *J.C.S. Dalton*, 1973, 514.

the apparent generality of this reaction it seemed desirable to examine the molecular structure of a typical product, such as (I), by *X*-ray analysis.

The lemon-yellow crystals of (I) are converted by heating into a white solid (II). The extreme insolubility of (II) in organic solvents made its spectroscopic characterisation difficult. On the basis of chemical analysis and mass spectroscopic data, (II) was formulated as the *cis*-isomer of (I).[7] The *X*-ray diffraction study of (II) has confirmed this formulation.

Preliminary accounts of this work have been published.[7,9]

EXPERIMENTAL

Crystal Data.—(i) *trans*-$[PtCl_2\{C(PhNCH_2)_2\}(PEt_3)]$, (I). $C_{21}H_{29}Cl_2N_2PPt$, $M = 606{\cdot}4$, Triclinic, $a = 13{\cdot}961(6)$, $b = 11{\cdot}782(4)$, $c = 10{\cdot}659(5)$ Å, $\alpha = 92{\cdot}98(3)$, $\beta = 125{\cdot}29(3)$, $\gamma = 114{\cdot}54(3)^\circ$, $U = 1196{\cdot}9$ Å^3, $D_c = 1{\cdot}682$, $Z = 2$, $F(000) = 592$. Space group $P\bar{1}$. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; $\mu(\text{Mo-}K_\alpha) = 64{\cdot}6$ cm^{-1}.

(ii) *cis*-$[PtCl_2\{C(PhNCH_2)_2\}(PEt_3)]$, (II). Orthorhombic, $a = 15{\cdot}991(2)$, $b = 8{\cdot}601(2)$, $c = 16{\cdot}703(2)$ Å, $U = 2297{\cdot}3$ Å^3, $D_c = 1{\cdot}753$, $Z = 4$, $F(000) = 1184$. Space group *Pnam* (No. 62, D_{2h}^{16}), equivalent positions: $\pm(x, y, z)$, $\pm(x, y, \tfrac{1}{2} - z)$, $\pm(\tfrac{1}{2} + x, \tfrac{1}{2} - y, z)$, $\pm(\tfrac{1}{2} - x, \tfrac{1}{2} + y, \tfrac{1}{2} + z)$. Mo-$K_\alpha$ radiation; $\mu(\text{Mo-}K_\alpha) = 67{\cdot}3$ cm^{-1}.

Crystallographic Measurements.—(i) *Isomer* (I). Weissenberg and precession photographs revealed that the crystals belong to the triclinic system. A satisfactory structural model was derived in the space group $P\bar{1}$. The unit cell chosen is a Delaunay cell.

Final values of the cell parameters and the intensities of 3011 independent reflections, with $\theta(\text{Mo-}K_\alpha) \geqslant 22^\circ$, were measured on a Hilger and Watts Y290 four-circle diffractometer, by use of techniques described previously.[10] Integrated intensities, I, and their standard deviations, $\sigma(I)$, were derived from the relationships $I = C - (t_p/t_b)(B_1 + B_2)$ and $\sigma^2(I) = C + (t_p/t_b)^2(B_1 + B_2) + (qI)^2$, where C is the peak count, B_1 and B_2 the background counts, t_p the time taken to measure the peak, t_b the total time taken to measure the backgrounds, and $q = 0{\cdot}04$. Intensities of 2382 independent reflections, having $I/\sigma(I) \geqslant 3$, were used in the subsequent analysis. Corrections were applied for Lorentz, polarisation, and absorption effects. Transmission factors on $F_0{}^2$, calculated by an analytical method,[11] ranged from 0·30 to 0·64.

(ii) *Isomer* (II). Weissenberg and precession photographs indicated orthorhombic *mmm* Laue symmetry. Systematically absent reflections ($0kl$ when $k + l$ odd, and $h0l$ when h odd) were consistent with the space groups $Pna2_1$ (No. 33) and *Pnam*, the latter being a non-conventional setting of *Pnma* (No. 62). With $Z = 4$, each molecule would be required to have *m* symmetry if the space group is *Pnam*.

The intensities of *ca.* 3300 independent reflections with $\theta(\text{Mo-}K_\alpha) \geqslant 28^\circ$ were measured on a Y290 diffractometer. Values of I and $\sigma(I)$ were obtained as before ($q = 0{\cdot}05$), and 1822 reflections, having $I/\sigma(I) \geqslant 3$, were used in the subsequent calculations. Lorentz, polarisation, and absorption corrections were applied. Transmission factors[11] on $F_0{}^2$ varied between 0·36 and 0·60.

Structure Analyses.—For both complexes the positions of the non-hydrogen atoms were initially determined by Patterson and Fourier methods. The refinement of the structural models was by the method of full-matrix least-squares. The function minimised was $\Sigma w\Delta^2$, where $\Delta = ||F_0| - |F_c||$ and $w = 4F_0{}^2/\sigma^2(F_0{}^2)$. 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 platinum, chlorine, and phosphorus atoms, using values of $\Delta f'$ and $\Delta f''$ from ref. 15.

(i) *Isomer* (I). With allowance for the scattering of the platinum atom only R was 0·27. Subsequent refinement of the positional and isotropic thermal parameters of all the non-hydrogen atoms led to R 0·13. Refinement of anisotropic temperature factors for the platinum, chlorine, and phosphorus atoms and also for the atoms of the imidazolidine ring brought R to 0·051 and R' to 0·067. Positions of the non-methyl hydrogen atoms were then derived from those of the heavier atoms, assuming normal bond lengths and valency angles; the scattering of these hydrogen atoms was allowed for in the subsequent calculations, but their positions were not refined. The refinement of 153 atomic parameters and of a scale factor converged at R 0·048 and R' 0·065. The standard deviation of an observation of unit weight was 1·6. Analysis of the variation of mean $w\Delta^2$ with sin θ, and with $|F_0|$, revealed no systematic trends. In a final-difference synthesis, function values ranged between $\pm 1{\cdot}7$ eÅ^{-3}, the extreme values being associated with the position of the heavy atom; in the final electron-density synthesis the mean and minimum peak heights for carbon atoms were 5·3 and 3·1 eÅ^{-3}.

Final atomic parameters, and a selection of functions derived from them are presented in Tables 1—3. A view of the molecule is shown in Figure 1.

(ii) *Isomer* (II). When the platinum scattering only was considered, R was 0·29. Refinement of the coordinates and isotropic temperature factors of the non-hydrogen atoms gave R 0·17. Allowance for anisotropic vibrations of the platinum, chlorine, and phosphorus atoms reduced R to 0·059 and R' to 0·083. The positions of all hydrogen atoms were then determined from a low-angle difference synthesis, and these atoms were accordingly included in the structure-factor calculations and their positional and isotropic thermal parameters were refined. The refinement finally converged at R 0·048 and R' 0·060; the standard deviation of an observation of unit weight was 1·4. Hence, agreement between observed and calculated structure factors was substantially improved by allowing for the scattering of the hydrogen atoms. Final values of their temperature factors (Table 4), and also the bond lengths and valency angles in which they are involved (Tables 5 and 7), appear physically reasonable if not particularly accurate.

The choice of the centrosymmetric space group *Pnam* thus led to a satisfactory refinement of a structural model which included the hydrogen atoms. We could find no evidence for any deviation of the molecules from the exact mirror symmetry required of them by the space group

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[9] D. J. Cardin, B. Cetinkaya, E. Cetinkaya, M. F. Lappert, Lj. Manojlović-Muir, and K. W. Muir, *J. Organometallic Chem.*, 1972, **44**, C59.

[10] Lj. Manojlović-Muir, *J. Chem. Soc.* (*A*), 1971, 2796; K. W. Muir, *ibid.*, p. 2663.

[11] J. de Meulenaar and H. Tompa, *Acta Cryst.*, 1965, **19**, 1014.

[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.

Pnam and we conclude that such deviations, if they exist, are so slight as to be undetectable given the accuracy of our data. Accordingly, no effort has been made to refine the structure in the alternative space group $Pna2_1$ which imposes no symmetry requirement on the molecules.

Function values in the final difference synthesis vary from 1·6 to −2·2 e$Å^{-3}$. The weighting scheme employed appeared adequate in view of the lack of systematic variation of mean $w\Delta^2$ with $\sin\theta$ or $|F_o|$. A view of the molecule is given in Figure 2; least-squares planes are listed in Table 6.

TABLE 1

Fractional atomic co-ordinates and vibrational parameters in (I)

Atom	*x*	*y*	*z*	*B*/Å^2
Pt	0·37275(7)	0·16943(6)	0·13509(9)	*
Cl(1)	0·3231(6)	0·1608(5)	0·3084(7)	*
Cl(2)	0·4273(7)	0·1858(5)	−0·0317(8)	*
P	0·2869(5)	−0·0577(4)	0·0651(6)	*
N(1)	0·5634(14)	0·4703(12)	0·3486(18)	*
N(2)	0·3824(15)	0·4254(14)	0·0996(19)	*
C(1)	0·4423(17)	0·3684(16)	0·1973(22)	*
C(2)	0·5819(21)	0·6050(16)	0·3538(28)	*
C(3)	0·4662(22)	0·5769(16)	0·1776(28)	*
C(4)	0·6597(17)	0·4554(16)	0·4810(22)	4·5(4)
C(5)	0·7081(20)	0·3799(18)	0·4598(25)	5·6(4)
C(6)	0·8032(24)	0·3609(23)	0·6083(31)	7·6(6)
C(7)	0·8503(21)	0·4233(21)	0·7601(28)	6·4(5)
C(8)	0·8043(21)	0·4990(20)	0·7758(27)	6·4(5)
C(9)	0·7093(20)	0·5157(19)	0·6439(26)	5·8(4)
C(10)	0·2513(19)	0·3548(18)	−0·0707(24)	5·3(4)
C(11)	0·1355(20)	0·2362(19)	−0·1102(25)	5·7(4)
C(12)	0·0049(23)	0·1628(22)	−0·2803(30)	7·2(5)
C(13)	0·0036(27)	0·2171(26)	−0·3952(34)	8·4(6)
C(14)	0·1073(27)	0·3300(26)	−0·3546(34)	9·0(7)
C(15)	0·2386(23)	0·4060(21)	−0·1887(29)	7·0(5)
C(16)	0·1106(21)	−0·1548(20)	−0·0074(27)	6·4(5)
C(17)	0·0087(27)	−0·1420(26)	−0·1697(35)	9·2(7)
C(18)	0·3909(19)	−0·0967(18)	0·2451(24)	5·4(4)
C(19)	0·5439(23)	−0·0290(22)	0·3252(30)	7·5(6)
C(20)	0·2748(19)	−0·1377(17)	−0·0978(23)	5·2(4)
C(21)	0·1985(21)	−0·2950(20)	−0·1649(27)	6·6(5)

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

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	107(1)	78(1)	156(1)	56(1)	84(1)	44(1)
Cl(1)	232(9)	128(6)	234(11)	101(6)	183(9)	74(6
Cl(2)	300(11)	140(6)	387(15)	138(7)	291(12)	131(8)
P	128(6)	78(5)	193(10)	54(5)	102(7)	40(6)
N(1)	126(20)	91(16)	184(31)	47(16)	99(23)	60(19)
N(2)	156(21)	115(18)	187(31)	85(17)	83(23)	61(20)
C(1)	136(23)	107(21)	159(34)	64(20)	113(26)	78(24)
C(2)	191(31)	71(19)	287(50)	72(21)	147(36)	46(25)
C(3)	203(32)	76(19)	286(50)	76(21)	144(36)	90(25)

TABLE 2

Selected interatomic distances (Å) and angles (°) in (I)

(*a*) Bond lengths

Pt–Cl(1)	2·311(6)	Pt–Cl(2)	2·292(6)
Pt–P	2·291(4)	Pt–C(1)	2·020(16)
C(1)–N(1)	1·37(2)	C(1)–N(2)	1·33(2)
N(1)–C(2)	1·49(2)	N(2)–C(3)	1·49(2)
N(1)–C(4)	1·36(2)	N(2)–C(10)	1·44(2)
C(4)–C(5)	1·40(3)	C(10)–C(11)	1·42(3)
C(5)–C(6)	1·47(3)	C(11)–C(12)	1·44(3)
C(6)–C(7)	1·36(3)	C(12)–C(13)	1·41(4)
C(7)–C(8)	1·35(3)	C(13)–C(14)	1·29(4)
C(8)–C(9)	1·37(3)	C(14)–C(15)	1·42(3)
C(9)–C(4)	1·44(3)	C(15)–C(10)	1·37(3)
P–C(16)	1·83(2)	C(16)–C(17)	1·55(4)
P–C(18)	1·85(2)	C(18)–C(19)	1·53(3)
P–C(20)	1·81(2)	C(20)–C(21)	1·56(3)
C(2)–C(3)	1·49(3)		

TABLE 2 (*Continued*)

(*b*) Bond angles

Cl(1)–Pt–Cl(2)	178·1(2)	C(1)–N(2)–C(3)	114·4(14)
Cl(1)–Pt–P	88·5(2)	C(1)–N(2)–C(10)	125·9(14)
Cl(1)–Pt–C(1)	89·6(6)	C(3)–N(2)–C(10)	119·6(14)
Cl(2)–Pt–P	93·3(2)	N(1)–C(2)–C(3)	104·1(13)
Cl(2)–Pt–C(1)	88·7(6)	N(2)–C(3)–C(2)	101·6(13)
P–Pt–C(1)	177·6(5)	N(1)–C(4)–C(5)	120·9(17)
Pt–P–C(16)	111·5(7)	N(1)–C(4)–C(9)	119·2(16)
Pt–P–C(18)	112·8(6)	C(5)–C(4)–C(9)	119·8(17)
Pt–P–C(20)	115·8(6)	C(4)–C(5)–C(6)	116·4(19)
C(16)–P–C(18)	104·4(9)	C(5)–C(6)–C(7)	121·4(21)
C(16)–P–C(20)	105·7(9)	C(6)–C(7)–C(8)	119·9(21)
C(18)–P–C(20)	105·8(9)	C(7)–C(8)–C(9)	123·1(21)
P–C(16)–C(17)	109·6(16)	C(8)–C(9)–C(4)	119·1(19)
P–C(18)–C(19)	114·2(15)	N(2)–C(10)–C(11)	118·4(18)
P–C(20)–C(21)	117·0(14)	N(2)–C(10)–C(15)	120·0(17)
Pt–C(1)–N(1)	125·6(13)	C(11)–C(10)–C(15)	121·5(18)
Pt–C(1)–N(2)	127·2(12)	C(10)–C(11)–C(12)	119·1(20)
N(1)–C(1)–N(2)	107·2(14)	C(11)–C(12)–C(13)	115·6(20)
C(1)–N(1)–C(2)	111·9(15)	C(12)–C(13)–C(14)	124·1(25)
C(1)–N(1)–C(4)	125·7(14)	C(13)–C(14)–C(15)	122·3(26)
C(2)–N(1)–C(4)	122·4(14)	C(14)–C(15)–C(10)	117·0(20)

(*c*) Intermolecular distances

C(3) · · · Cl(2^{I})	3·48	C(9) · · · C(17^{III})	3·64
C(2) · · · Cl(1^{II})	3·57	C(8) · · · C(16^{III})	3·66

Superscripts refer to the following transformations of the fractional co-ordinates:

I $1 - x, 1 - y, -z$
II $1 - x, 1 - y, 1 - z$
III $1 + x, 1 + y, 1 + z$

TABLE 3

Equations of least-squares planes in (I), and, in square brackets, deviations (Å) of atoms from these planes

Plane (*A*): Pt, Cl(1), Cl(2), P, C(1)

$$8·980x - 4·133y + 2·434z = 2·976$$

[Pt −0·001, Cl(1) 0·012, Cl(2) 0·016, P −0·003, C(1) −0·047, N(1) 0·988, N(2) −1·058]

Plane (*B*): Pt, C(1), N(1), N(2)

$$12·783x - 1·714y - 8·986z = 3·261$$

[Pt 0, C(1) −0·011, N(1) 0·002, N(2) 0·003, C(2) −0·039, C(3) 0·114, C(4) 0·069, C(10) −0·022]

Plane (*C*): C(1)—(3), N(1), N(2)

$$12·916x - 1·994y - 8·881z = 3·227$$

[C(1) −0·001, N(1) 0·016, C(2) −0·059, C(3) 0·068, N(2) −0·021, Pt 0·050, C(4) 0·114, C(10) −0·061]

Plane (*D*): C(4)—(9)

$$7·788x + 5·909y - 4·611z = 5·616$$

[C(4) −0·005, C(5) 0·023, C(6) −0·033, C(7) 0·002, C(8) 0·019, C(9) −0·014, N(1) −0·0057]

Plane (*E*): C(10)—(15)

$$11·796x - 9·494y - 5·011z = -0·075$$

[C(10) 0·025, C(11) −0·017, C(12) −0·009, C(13) 0·036, C(14) −0·016, C(15) −0·020, N(2) 0·0048]

Plane (*F*): C(1), N(1), C(2), C(4)

$$12·520x - 1·300y - 9·194z = 3·242$$

[C(1) 0·003, N(1) −0·005, C(2) 0·004, C(4) 0·003]

Plane (*G*): C(1), N(2), C(3), C(10)

$$12·843x - 2·315y - 9·041z = 3·039$$

[C(1) 0·006, N(2) −0·013, C(3) 0·008, C(10) 0·006]

Observed and calculated structure factors for both compounds are listed in Supplementary Publication No. SUP 21122 (27 pp., 1 microfiche).* The computer pro-

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

TABLE 4

Fractional atomic co-ordinates and vibrational parameters in (II)

Atom	x	y	z	B/Å^2
Pt	0·05158(3)	0·08785(5)	1/4	*
Cl(1)	−0·0886(2)	0·1742(4)	1/4	*
Cl(2)	0·0006(2)	−0·1722(4)	1/4	*
P	0·0875(2)	0·3388(4)	1/4	*
N	0·2158(5)	−0·0084(9)	0·1843(5)	3·6(2)
C(1)	0·1707(8)	0·0134(17)	1/4	3·8(2)
C(2)	0·3028(7)	−0·0504(14)	0·2060(7)	4·7(2)
C(3)	0·1919(6)	0·0048(12)	0·1043(6)	4·3(2)
C(4)	0·2382(8)	0·0990(15)	0·0536(8)	5·4(2)
C(5)	0·2164(10)	0·1121(18)	−0·0260(10)	7·3(3)
C(6)	0·1475(11)	0·0332(19)	−0·0557(11)	7·1(3)
C(7)	0·1024(9)	−0·0610(16)	−0·0072(8)	6·2(3)
C(8)	0·1231(7)	−0·0755(14)	−0·0726(7)	5·0(2)
C(9)	0·0452(8)	0·4419(15)	0·1637(7)	5·1(2)
C(10)	0·0786(10)	0·3862(19)	0·0842(10)	6·9(3)
C(11)	0·1976(10)	0·3799(17)	1/4	3·9(2)
C(12)	0·2208(11)	0·5573(20)	1/4	4·7(3)
H(2A) †	0·335(6)	0·037(11)	0·178(6)	5(2)
H(2B)	0·319(6)	−0·163(14)	0·180(6)	6(2)
H(4)	0·284(7)	0·148(13)	0·078(6)	6(2)
H(5)	0·250(11)	0·145(20)	−0·075(10)	11(5)
H(6)	0·151(10)	0·042(17)	−0·116(11)	13(5)
H(7)	0·046(8)	−0·145(16)	−0·030(8)	7(3)
H(8)	0·094(6)	−0·140(11)	0·120(5)	3(2)
H(9A)	0·048(7)	0·571(16)	0·179(8)	8(3)
H(9B)	0·004(13)	0·431(19)	0·175(10)	13(5)
H(10A)	0·058(9)	0·427(17)	0·032(10)	11(4)
H(10B)	0·142(7)	0·415(12)	0·080(6)	6(2)
H(10C)	0·061(8)	0·243(19)	0·080(8)	7(4)
H(11)	0·216(6)	0·346(12)	0·200(6)	3(2)
H(12A)	0·283(12)	0·569(19)	1/4	7(4)
H(12B)	0·205(4)	0·589(8)	0·205(4)	2(2)

* These atoms were assigned anisotropic temperature factors as defined in Table 1, with $\beta_{13} = \beta_{23} = 0$ by symmetry. Final β_{ij} values are:

Atom	β_{11}	β_{22}	β_{33}	β_{12}
Pt	22(1)	68(1)	52(1)	1(1)
Cl(1)	21(1)	108(5)	85(3)	6(2)
Cl(2)	37(2)	61(4)	72(2)	−10(2)
P	26(1)	61(4)	59(2)	2(2)

† Each hydrogen atom is numbered according to the carbon atom to which it is attached.

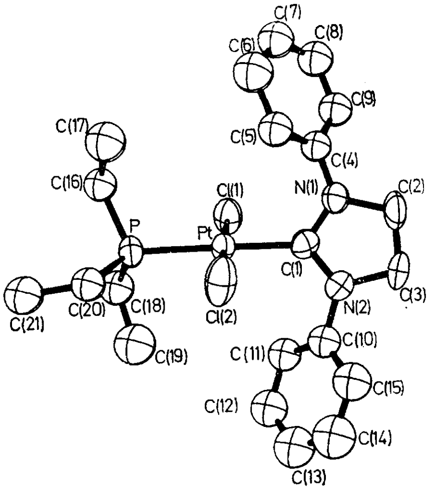


FIGURE 1 Perspective view of the structure of the *trans*-complex (I), showing the atomic numbering scheme. Thermal ellipsoids enclose 50% of probability. Hydrogen atoms are omitted for clarity

TABLE 5

Selected interatomic distances (Å) and angles (°) in (II)

(*a*) Bond lengths

Pt–Cl(1)	2·362(3)	C(11)–C(12)	1·570(23)
Pt–Cl(2)	2·381(3)	C(2)–H(2A)	1·02(10)
Pt–P	2·234(3)	C(2)–H(2B)	1·10(12)
Pt–C(1)	2·009(13)	C(4)–H(4)	0·94(12)
C(1)–N	1·327(11)	C(5)–H(5)	1·02(18)
C(2)–N	1·482(14)	C(6)–H(6)	1·01(18)
C(3)–N	1·395(13)	C(7)–H(7)	1·22(13)
C(2)–C(2′)	1·471(23)	C(8)–H(8)	1·08(9)
C(3)–C(4)	1·387(16)	C(9)–H(9A)	0·70(20)
C(4)–C(5)	1·379(21)	C(9)–H(9B)	1·14(14)
C(5)–C(6)	1·386(23)	C(10)–H(10A)	0·99(16)
C(6)–C(7)	1·353(22)	C(10)–H(10B)	1·05(12)
C(7)–C(8)	1·379(18)	C(10)–H(10C)	1·26(16)
C(8)–C(3)	1·402(15)	C(11)–H(11)	0·94(10)
P–C(9)	1·823(13)	C(12)–H(12A)	1·00(19)
P–C(11)	1·796(16)	C(12)–H(12B)	0·84(7)
C(9)–C(10)	1·510(20)		

(*b*) Bond angles

Cl(1)–Pt–Cl(2)	88·3(1)	N–C(3)–C(8)	122·5(9)
Cl(1)–Pt–P	86·6(1)	C(3)–C(4)–C(5)	120·1(12)
Cl(1)–Pt–C(1)	179·8(4)	C(4)–C(5)–C(6)	120·4(15)
Cl(2)–Pt–P	174·9(1)	C(5)–C(6)–C(7)	120·1(16)
Cl(2)–Pt–C(1)	91·5(4)	C(6)–C(7)–C(8)	120·4(13)
P–Pt–C(1)	93·7(4)	C(7)–C(8)–C(3)	120·6(11)
Pt–C(1)–N	124·1(6)	C(8)–C(3)–C(4)	118·4(10)
N–C(1)–N′	111·6(16)	Pt–P–C(9)	112·0(4)
C(1)–N–C(2)	110·1(8)	Pt–P–C(11)	116·3(5)
C(1)–N–C(3)	129·1(9)	C(9)–P–C(9′)	104·6(8)
C(2)–N–C(3)	120·8(8)	C(9)–P–C(11)	105·5(5)
N–C(2)–C(2′)	104·1(13)	P–C(9)–C(10)	114·2(10)
N–C(3)–C(4)	119·1(10)	P–C(11)–C(12)	115·0(11)

(*c*) Intermolecular distances

H(10C) ··· H(7^{I})	2·07	H(12A) ··· Cl(1^{IV})	2·93
H(5) ··· H($12B^{II}$)	2·33	C(11) ··· Cl(1^{IV})	3·45
H(9A) ··· Cl(2^{III})	2·62		

Co-ordinates of primed atoms are derived from those of the corresponding unprimed atom in Table 4 by the transformation $x, y, \frac{1}{2} - z$.

Superscripts refer to the following transformations of fractional co-ordinates

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

TABLE 6

Equations of least-squares planes in (II), with, in square brackets, deviations (Å) of atoms from planes

Plane (*A*): Pt, C(1), N, N′

$$-4·824x - 8·200y + 0·114z = -0·941$$

[Pt −0·001, C(1) 0·036, N −0·011, N′ 0·005, C(2) −0·083, C(3) −0·013]

Plane (*B*): C(3)—(8)

$$9·470x - 6·654y - 3·765z = 1·396$$

[C(3) −0·003, C(4) 0·001, C(5) 0·007, C(6) −0·010, C(7) 0·007, C(8) −0·001, N 0·010]

Plane (*C*): C(1)—(3), N

$$-4·038x - 8·322y - 0·114z = -0·825$$

[C(1) −0·004, N 0·003, C(2) −0·002, C(3) −0·002]

grams used were C. K. Johnson's ORTEP, the ATLAS versions of J. M. Stewart's '*X*-ray '63' and '*X*-ray '70' systems including N. W. Alcock's ABSCOR absorption correction program, the Hilger and Watts software package for the Y 290 diffractometer, the HILGA data processing program of M. A. Bush, K. W. Muir, and D. White, and the REDUX cell reduction program of K. W. Muir.

DISCUSSION

Crystals of (I) and (II) contain discrete monomeric molecules which are separated by normal van der Waals contacts. A somewhat greater efficiency in packing appears to be achieved in crystals of (II), where each molecule occupies a volume of 574 Å^3, as compared with (I), where the corresponding value is 598 Å^3. However, this difference may merely indicate that within individual molecules of (II) the atoms are more compactly arranged. Intermolecular contacts do not appear to be on average shorter in (II) than they are in (I) (Tables 2 and 5).

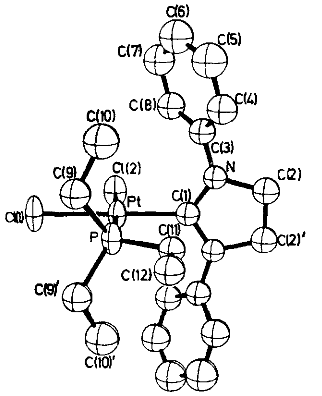


FIGURE 2 Perspective view of the structure of the *cis*-complex (II), showing the atomic numbering scheme. Thermal ellipsoids enclose 50% of probability. Hydrogen atoms are omitted for clarity

In each structure there is excellent agreement between chemically equivalent bond lengths and valency angles. Indeed, only in the case of the P–C–C angles in (II) does a χ^2 test indicate that the deviations of individual values from the mean are significant at a probability level of <0·1%. Accordingly, we consider the mean bond lengths and valency angles in Table 7 and Figure 3 as the best values obtainable from each analysis, and these are used in the subsequent discussion.

Co-ordination of the Metal Atoms.—In both molecules a square plane about the platinum atom is defined by two chlorine atoms, the phosphorus atom of the triethylphosphine ligand, and the donor carbon atom of the carbenoid ligand. Deviations from ideal square planar co-ordination of the metal atoms are small. In (I) individual atoms are displaced by <0·05 Å from the co-ordination plane of the platinum atom. The corresponding plane in (II) coincides with a crystallographic mirror plane. In both molecules the triethylphosphine ligands adopt a conformation in which one ethyl group lies in the co-ordination plane of the metal atom. [In (I) the Pt–P–C(20)–C(21) torsion angle is 172°; in (II) the Pt–P–C(11)–C(12) torsion angle is exactly 180° since all the atoms involved lie on the mirror plane at $z = 1/4$.] Steric repulsion between the ethyl group so situated and the appropriate *cis*-ligand leads to the opening of the P–Pt–Cl(2) angle in (I) to 93·3(2)°, and of the P–Pt–C(1) angle in (II) to 93·7(4)°.

TABLE 7

Mean bond lengths (Å) and angles (°) in (I) and (II)

(*a*) Bonds

	(I)	(II)
CH_2–CH_3	1·545(17) [a]	1·540(30)
C(sp^2)–C(sp^2)	1·399(13)	1·381(8)
P–C	1·830(12)	1·810(14)
C–H		1·02(4)

(*b*) Angles

	(I)	(II)
C(sp^2)–C(sp^2)–C(sp^2)	119·9(8)	120·0(5)
N–C(sp^2)–C(sp^2)	119·6(9)	120·8(17)
Pt–P–C	113·4(13) [b]	114·2(22)
C–P–C	105·3(5)	105·1(5)
P–C–C	113·6(22) [b]	114·6(7) [c]
X–C(sp^3)–H [d]		109·7(21)
C(sp^2)–C(sp^2)–H		119·3(35)
H–C(sp^3)–H		110·9(43)

[a] The standard deviation of each mean is the larger of σ_A and σ_B. σ_A is calculated from the individual standard deviations, σ_j, by the relation $\sigma_A = (\sum_j 1/\sigma_j^2)^{-\frac{1}{2}}$. σ_B is calculated from the deviations of individual values x_j from their mean, $\bar{x}$, by $\sigma_B = [\sum_j (x_j - \bar{x})^2/n(n-1)]^{\frac{1}{2}}$. [b] Differences between individual values significant at 1% but not at 0·1% level. [c] Difference between individual values significant at <0·1%. [d] X = N or C.

Triethylphosphine Ligands.—Corresponding bond lengths and valency angles in the phosphine ligands of (I) and (II) agree well. The interbond angles at the phosphorus atoms show the usual departures from the ideal tetrahedral value of 109° 28′. The P–C–C angles are greater than this value, presumably because of intramolecular overcrowding. In each molecule the substituents adopt approximately staggered conformation relative to the P–CH_2 bonds. Thus in (I) the C(18)–P–C(16)–C(17) and C(16)–P–C(18)–C(19) torsion angles are 175(2) and 178(2)°, while the comparable C(9′)–P–C(9)–C(10) angle in (II) is 174(1)°.

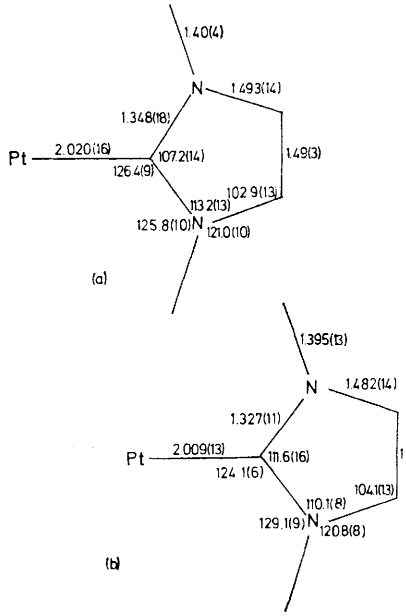


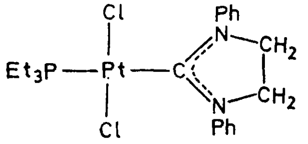
FIGURE 3 Mean bond lengths and valency angles in the imidazolidine rings of (a) complex (I) and (b) complex (II)

Geometry of the Carbenoid Ligands.—The different environments of the carbenoid ligands in (I) and (II) are reflected in small, but significant, conformational differences. In each compound the carbenoid carbon atom and the three atoms directly bonded to it are coplanar. Furthermore, each nitrogen atom is coplanar with the three carbon atoms to which it is bonded. However, in (I) the imidazolidine ring is slightly puckered, and the displacements of the Pt and C(4) atoms from the mean plane through the ring are 0·050 and 0·114 Å. In (II) the atoms of the imidazolidine ring deviate by <0·001 Å from the plane $4{\cdot}020x + 8{\cdot}325y = 0{\cdot}798$, and the displacements of the Pt and C(3) atoms are respectively 0·141 and 0·014 Å. Despite these conformational differences corresponding valency angles at the ring atoms in (I) and (II) agree well (Figure 3), as do chemically equivalent bond lengths. The N–C(carbenoid) distances (1·35 and 1·33 Å) are much shorter than the formally single N–C(Ph) bonds (1·40 Å), which suggests that they possess appreciable multiple character. It has been pointed out recently that such bond lengths in complexes of several metals vary only slightly, and that the mean of 1·31(1) Å is consistent with an N–C bond order of 1·7.[16]

The C–C distances [1·49(3) and 1·471(16) Å] in the imidazolidine rings appear rather short, possibly because of the effects of librational shrinkage.

The co-ordination plane of the carbenoid carbon atom makes a dihedral angle with that of the platinum atom of 71° in (I) and 90° in (II).

Platinum–Carbenoid Bonding.—The Pt–C bond lengths in (I) and (II) are slightly but not significantly shorter than the Pt–C(*trans* to Cl) distance [2·03(2) Å] in *trans*-$[PtCl(CH{:}CH_2)(PPhEt_2)_2]$[17] and the Pt–C(*trans* to I) bond length [2·029(11) Å in *trans*-$[PtI\{C(NC_6H_4Cl)Me\}(PEt_3)_2]$.[18] It therefore appears that there is little Pt–C multiple bonding in (I) and (II), and that the vacant *p* orbital of the carbenoid carbon atom accepts *p* electrons from nitrogen in preference to *d* electrons from platinum, as indicated by the Lewis structure (1).



(1)

However, the *trans*-influence of $C(PhNCH_2)_2$ on Pt–Cl bonds is less than that of σ-vinyl, as may be seen by comparison of the Pt–Cl(*trans* to C) bond length in (II) with the corresponding value [2·398(4) Å] in *trans*-$[PtCl(CH{:}CH_2)(PPhEt_2)_2]$. A small degree of $Pt \rightarrow C$ back-donation in the carbenoid complex, but not in the vinyl complex, would explain this difference. Such back-donation would reduce the electron population in the metal *d* orbital and, consequently, the electrostatic repulsion experienced by the *trans*-chlorine atom. Some confirmation of this view is obtained from the high correlation[19] between the π-acidity of a carbon donor ligand and its ability to shorten the *trans*-Pt–Cl bond in a platinum(II) complex.

In Table 8 Pt–C bond lengths in (I) and (II) are compared with similar ones in other carbenoid complexes of platinum(II).[6,20–22] Although the variations in these bond lengths are difficult to explain in detail, they appear to involve at least three separate electronic effects. (i) It is now well established[16] that multiple M–C bonding in an M–CXY carbenoid complex decreases as the ability of X and Y to donate electrons into the vacant *p* orbital of the carbenoid carbon atom becomes greater. The order[16,23] of increasing donor ability of X and Y is Me < OR ∼ SR < NR_2. For the ligands listed in Table 8 this leads to the following π-acidity series: $C(OMe)Me > C(OEt)NHPh \sim C(SEt)NHMe > C(PhNCH_2)_2 \sim C_4H_8N_4CH_3$. The correlation between this series and the Pt–C bond lengths is poor. (ii) The data in Table 8 suggest that the *trans*-influence of the various ligands on Pt–C(carbenoid) bonds decreases in the order: Me > C(SEt)NHMe > PEt_3 ∼ Cl ⩾ CNMe. This series is similar to those derived from Pt–Cl bond lengths[19] and from spectroscopic data.[24] However, it should be considered tentative, in view of the limited accuracy of the Pt–C bond lengths quoted in Table 8. It is, perhaps, surprising that the Pt–C bond lengths in (I) and (II) differ by only 0·011(21) Å since PEt_3 has a substantially greater *trans*-influence than Cl on both Pt–Cl and Pt–P bonds (see later). (iii) The tendency of dipositive platinum to donate electrons to a carbenoid ligand may be smaller in cationic than in electroneutral complexes.

TABLE 8

Selected Pt–C bond lengths (Å) in platinum(II) carbenoid complexes

Complex	Pt–C	*trans*-Ligand
trans-$[PtMe\{C(OMe)Me\}(PMe_2Ph)_2]^+$	2·13(2) [a]	Me
trans-$[Pt(CNMe)_2\{C(SEt)NHMe\}_2]^{2+}$	2·058(7) [b]	C(SEt)NHMe
trans-$[PtCl_2\{C(PhNCH_2)_2\}(PEt_3)]$	2·020(16) [c]	PEt_3
cis-$[PtCl_2\{C(PhNCH_2)_2\}(PEt_3)]$	2·009(13)	Cl
cis-$[PtCl_2\{C(OEt)NHPh\}(PEt_3)]$	1·98(2) [d]	Cl
cis-$[Pt(C_4H_8N_4CH_3)(CNMe)_2]^+$	1·95(2) [e]	CNMe

[a] Ref. 20. [b] Ref. 21. [c] This work. [d] Ref. 6. [e] Ref. 22.

trans-*Influence of the Ligands*.—It may be argued, from the trends in both the Pt–P and the Pt–Cl bond

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[16] F. A. Cotton and C. M. Lukehart, *Progr. Inorg. Chem.*, 1973, **16**, 487.

[17] C. J. Cardin, D. J. Cardin, M. F. Lappert, and K. W. Muir, *J. Organometallic Chem.*, 1973, **60**, C70.

[18] K. P. Wagner, P. M. Treichel, and J. C. Calabresse, *J. Organometallic Chem.*, 1973, **56**, C33.

[19] Lj. Manojlović-Muir and K. W. Muir, *Inorg. Chim. Acta*, 1974, **10**, 47.

[20] R. F. Stepaniak and N. C. Payne, *J. Organometallic Chem.*, 1973, **57**, 213.

[21] W. M. Butler and J. H. Enemark, *Inorg. Chem.*, 1973, **12**, 540.

[22] W. M. Butler, J. H. Enemark, J. Parks, and A. L. Balch, *Inorg. Chem.*, 1973, **12**, 451.

[23] R. J. Hoare and O. S. Mills, *J.C.S. Dalton*, 1972, 653.

[24] T. G. Appleton, H. C. Clark, and L. E. Manzer, *Co-ordination Chem. Rev.*, 1973, **10**, 335.

lengths in (I) and (II), that the *trans*-influence of the carbenoid ligand is comparable with that of tertiary phosphine and significantly greater than that of chloride. Similar conclusions have been made from far-i.r. and from n.m.r. spectroscopic results.[9]

Thus the Pt–P(*trans* to C) distance [2·291(4) Å] in (I) is comparable with Pt–P(*trans* to P) distances in *trans*-[$PtCl(Me_3SiCH_2)(PMe_2Ph)_2$] [1] [2·293(3) Å] and in *trans*-[$PtBr_2(PEt_3)_2$] [2·315(4) Å].[25] The Pt–P(*trans* to Cl) distances are much shorter, the mean for five such bonds being 2·237(2) Å,[26] close to that of 2·234(3) Å in (II).

Furthermore, the Pt–Cl(*trans* to C) distance [2·362(3) Å] in (II) is the same as the corresponding distance [2·365(5) Å] in *cis*-[$PtCl_2\{C(OEt)NHPh\}(PEt_3)$].[6] These distances are only slightly shorter than Pt–Cl(*trans* to P) [2·381(3) Å] in (II) but are significantly longer than the mean Pt–Cl(*trans* to Cl) bond length [2·302(10) Å] in (I). Mean Pt–Cl(*trans* to P) and Pt–Cl(*trans* to Cl) distances in several platinum(II) compounds are respectively 2·376(5) and 2·303(5) Å.[19]

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[25] G. G. Messmer and E. L. Amma, *Inorg. Chem.*, 1966, **5**, 1775.

[26] Lj. Manojlović-Muir, K. W. Muir, and R. Walker, *J. Organometallic Chem.*, 1974, **66**, C21.