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THE CRYSTAL AND MOLECULAR STRUCTURE OF *trans*-[(METHYL)(METHYLMETHOXYCARBENE)BIS(DIMETHYLPHENYLPHOSPHINE)PLATINUM(II)] HEXAFLUOROPHOSPHATE, $[CH_3\{CH_3C(OCH_3)\}Pt\{P(CH_3)_2(C_6H_5)\}_2]PF_6$.

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SUMMARY

The crystal and molecular structure of *trans*-[(methyl)(methylmethoxycarbene)bis(dimethylphenylphosphine)platinum(II)] hexafluorophosphate has been determined from three dimensional X-ray data collected on an automatic four circle diffractometer using Mo radiation. The complex crystallizes in the orthorhombic system, space group *Pnma*, $Z=4$, and unit cell dimensions $a=15.361(7)$, $b=15.180(7)$ and $c=10.933(6)$ Å. Full-matrix least-squares refinement on F gave a final conventional R factor of 0.047 for 1714 reflections for which the observed intensity $I>3\sigma(I)$. Both ions have crystallographic site symmetry m. The coordination geometry about the platinum atom is approximately square planar. The platinum atom, the methyl-carbon atom, and the carbene ligand all lie on the mirror plane, while the two phosphine ligands are related by reflection in the mirror plane. The methylmethoxycarbene ligand adopts the *trans* configuration, and is disordered in the mirror plane. To account for this disorder, two carbene ligands have been refined as rigid groups, taking multiplicity factors into account. The two ligands are related by a 180° rotation about an axis passing approximately through the methyl-carbon atom and the platinum atom. The Pt–P bond distance is 2.283(3) Å, the $Pt-CH_3$ bond length is 2.13(2) Å, and the $Pt-C(sp^2)$ of the carbene ligand mean bond length is 2.13(2)Å.

INTRODUCTION

The preparation of the first transition metal carbene complexes of tungsten and chromium by Fischer and Maasböl[1] has stimulated research into the coordination of electron-deficient carbon atoms to a transition metal. In such complexes, the electron deficient carbon atom is generally stabilized by an adjacent nucleophilic atom. Both oxygen and nitrogen have been used for this purpose, and crystallographic studies of several alkylamino-[2,3] and alkoxy-carbene[4,5] species have been reported. In the two alkoxy-carbene complexes of chromium examined crystallographically, the carbene ligands are present both in the *cis*[5] and the *trans*[4] configuration.

Several routes for the preparation of carbene complexes of platinum(II) have been described[6,7,8], and crystallographic studies of three such complexes have been completed[7,9]. A recently described route to such complexes is that of Chisholm and Clark[8] via cationic acetylenic platinum(II) intermediates. ^{1}H NMR work[8] on a carbene cation so obtained, *trans*-$[(CH_3)\{CH_3C(OCH_3)\}Pt\{P(CH_3)_2(C_6H_5)\}_2]^+$, was interpreted to show that the methylmethoxy-carbene ligand is present in solution as the *cis* isomer, but previous work[10] has shown that the carbene ligand configurations are often dependent on solvent interactions. Both the carbene ligand and the methyl ligand *trans* to it are found to exhibit strong *trans* influences[8,11] and the alkoxy-carbene ligands are found to be stronger π acceptors than alkylamino-carbene ligands[12,13]. A single crystal X-ray study of *trans*-$[(CH_3)\{CH_3C(OCH_3)\}Pt\{P(CH_3)_2(C_6H_5)\}_2]^+$ was therefore undertaken, to study the geometry of the platinum atom coordination sphere and the configuration of the carbene ligand.

EXPERIMENTAL

Preparation and characterization

trans-$[(CH_3)\{CH_3C(OCH_3)\}Pt\{P(CH_3)_2(C_6H_5)\}_2]PF_6$ was prepared by Chisholm by the method of Chisholm and Clark[8]. The product was recrystallized from a methanol–ether solution over a two week period to produce colourless crystals, which were tabular with rhombohedral cross-section, and of suitable quality for study. Analysis: Found: C, 34.39; H, 4.22. $C_{20}H_{31}F_6OP_3Pt$ calcd.: C, 34.83; H, 4.49%.

Crystal data: $C_{20}H_{31}F_6OP_3Pt$ mol. wt.: 689.45, orthorhombic, $a = 15.361(7)$, $b = 15.180(7)$, $c = 10.933(6)$Å; (20°, $\lambda(\text{Mo-}K_{\alpha_1}) = 0.70926$Å); $V = 2549$Å^3, $d_c = 1.79$ g·cm^{-3} for $Z = 4$, $d_o = 1.76(2)$ g·cm^{-3} (by flotation in $CCl_4/C_2H_4Br_2$); $\mu(\text{Mo-}K_\alpha) = 59.2$ cm^{-1}.

A crystal with well developed faces was selected, and a series of Weissenberg and precession photographs taken with Cu-K_α radiation showed the crystal to be orthorhombic with Laue symmetry *mmm*. The systematic extinctions observed were: $0kl$ for $k+l$ odd, and $hk0$ for h odd. These absences are consistent with the centric space group *Pnma*, D_{2h}^{16}, No. 62, or the acentric space group $Pn2_1a$, alternate setting, C_{2v}^9, No. 33[14].

The density of the compound, determined by flotation in a mixture of carbon tetrachloride and 1,2-dibromoethane, was found to be 1.76(2) g·cm^{-3}. The calculated density is 1.79 g·cm^{-3}, for $Z = 4$. Thus, the molecule is constrained to either have *m* symmetry, or to have a centre of symmetry in space group *Pnma*. No crystallographic symmetry constraints are imposed in $Pn2_1a$. Mo-K_α radiation was chosen for data collection. In an optical goniometric study of the crystal selected for examination, the two largest faces were of the form {100} and the remaining four faces of the form {011}. The crystal was measured with a filar microscope eyepiece and its dimensions were 0.25(5)mm × 0.21(5)mm × 0.21(5)mm. The crystal was mounted on a diffractometer, and the long dimension [100] was deliberately offset 3.5° from coincidence with the spindle axis to minimize the possibility of multiple reflections[15]. Several ω-scans were recorded with a narrow source and wide open counter to check the mosaicity of the crystal. The average width at half height for strong reflections was 0.056 degrees[16].

The cell constants and their standard deviations were determined by a least squares refinement of the setting angles of 16 reflections, that had been centered on a Picker four-circle diffractometer at 20°. A narrow slit width and a take-off angle of 0.5° were used. The refinement of the orientation matrix was carried out using the program PICKTT for the PDP-10 computer*. The cell constants obtained are $a=$ 15.361(7)Å, $b=$15.180(7)Å, and $c=$10.933(6)Å, and the unit cell volume is 2549Å^3. Using Mo-K_α radiation, intensity data were collected from 2471 reflections in the range $2° < 2\theta < 50°$. The diffracted beams were filtered through 3.0 mils of niobium foil. A take-off angle on the tube of 1.8° was used. At this angle, the peak intensity of a strong reflection was about 80% of the maximum value observed as a function of take-off angle. The counter aperture dimensions selected were 0.4 × 0.4 cm positioned 32 cm from the crystal. The pulse height analyzer was set for approximately a 90% window, centered on the Mo-K_α peak.

The data were collected by the θ–2θ scan technique at a scan rate of 1° per minute. A symmetric scan range of 1° was used with corrections applied to account for high angle dispersion. Stationary counter, stationary crystal background counts of 10 seconds were taken at the start and at the end of each scan. Attenuators were inserted automatically when the intensity of the diffracted beam exceeded about 7000 counts per second during the scan. The attenuators were copper foil; their thicknesses chosen to give attenuator factors of approximately 2.2. Throughout the collection of data, the intensities of 3 reference reflections were measured after every 100 reflections as a check on electronic and crystal stability. During the five day period over which data were collected, the intensities of the standards increased on average 12%. However, no significant deterioration in peak quality was observed. No correction was made for this effect.

All data were processed as described previously[17]. The value of p selected was 0.04 in the calculation of $\sigma(I)$. The recorded intensities were corrected for background and for Lorentz and polarization effects. All reflections with $I > 3\sigma(I)$ were corrected for absorption**. The maximum and minimum transmission coefficients were 0.365 and 0.247 respectively. Of the 2471 reflections measured, 1714 had $F^2 > 3\sigma(F^2)$, and only these reflections were used in determining and refining the structure. A sample of the crystals was tested for a piezoelectric effect***. No effect was observed. Values of E, the normalized structure factors, were then calculated, and the calculated distribution of the E values was compared to theoretical calculations for centric and acentric crystals. The results obtained were inconclusive. Since no decision as to space group could be made at this time, the initial solution and refinement of the structure were carried out in space group $Pn2_1a$, equipoints (x,y,z), $(\bar{x},\frac{1}{2}+y,\bar{z})$, $(\frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z)$ and $(\frac{1}{2}+x,y,\frac{1}{2}-z)$.

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* Various local programs were used in the structure determination, but Patterson functions and Fourier syntheses were calculated using a version of Zalkin's FORDAP. Normalized structure factors were calculated using Dewar's FAME. Refinement and structure factor calculations were made with WOCLS, a version of Ibers' NUCLS. Errors in derived quantities were obtained from the Busing–Martin–Levy ORFFE, and drawings were made using Johnson's ORTEP.

** The absorption correction was performed using the analytical method of de Meulenger and Tampa in the program AGNOST as modified by Cahen and Ibers[18].

*** A sample of crystals was sent to Dr. J. A. Ibers, to whom we are grateful for performing the test for piezoelectric effect.

STRUCTURE SOLUTION AND REFINEMENT

Preliminary positional parameters were obtained for the platinum and two phosphorus atoms from a Patterson synthesis. The remaining 28 non-hydrogen atoms were located from a series of difference Fourier syntheses, and least-squares calculations. All refinements were carried out on F; the function minimized being $\Sigma w(|F_o|-|F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes respectively. w is the weight factor, defined by $4F_o^2/\sigma^2(F_o^2)$. In all calculations of F_c, the atomic scattering factors for neutral platinum, phosphorus, fluorine, oxygen and carbon were those obtained by Cromer and Waber[19]. Hydrogen scattering factors were those of Stewart, Davidson and Simpson[20]. The effects of anomalous dispersion were included in the calculations of F. Values of $\Delta f'$ and $\Delta f''$ were those calculated by Cromer and Liberman[21].

One cycle of full-matrix least-squares refinement, with all non-hydrogen atoms assigned isotropic thermal parameters, the platinum and two phosphorus atoms allowed to vibrate anisotropically and the two phenyl rings and the F_6 octahedron refined as rigid groups gave agreement factors

$$R_1 = \frac{\Sigma\big||F_o|-|F_c|\big|}{\Sigma|F_o|} = 0.067 \text{ and } R_2 = \left[\frac{\Sigma w(|F_o|-|F_c|)^2}{\Sigma wF_o^2}\right]^{\frac{1}{2}} = 0.090$$

An examination of the resulting geometry revealed almost perfect m symmetry for the cation. Accordingly, to resolve the question as to the choice of space group, Donohue's criterion[22] was followed, and further refinement cycles were carried out in *Pnma*. One cycle of least-squares refinement showed abnormally large isotropic thermal parameters for the carbon(sp^2) and oxygen atom of the carbene ligand, with a Pt–C(sp^2) bond length of 2.75Å. A set of structure factors was therefore calculated, omitting the carbene atoms, and a difference Fourier synthesis computed. The results are presented in Fig. 1. There are four peaks, with two additional satellite regions, a total of six, to be accounted for by the four carbene ligand atoms. Moreover, the four peaks are not related in any acceptable fashion to the geometries adopted by other carbene ligands in previous structures[4,5]. However, if disorder of a *trans*-carbene ligand is postulated, with a fortuitous superposition of both the methyl groups of the ligand (Fig. 1) then a total of six peaks is expected. This model is supported by the relative peak densities, and the successful refinement of the structure. The model formulated to account for this disorder therefore comprises two carbene ligands, which were refined as rigid groups[23]. The group geometry was taken from an analogous alkoxy-carbene ligand[4,24]. The ligand was constrained to be planar, with interatomic angles of 120°, and bond lengths of C(sp^2)–O, 1.33Å, C(sp^2)–C(sp^3), 1.43Å, and C(sp^3)–O, 1.48Å. The parameters refined for each group were an occupancy factor, the group origin, three orientation angles, and an overall group thermal parameter. During the refinement, the appropriate constraints were applied to the derivatives. In addition to the carbene ligand, the phenyl ring was constrained to a rigid group, with D_{6h} symmetry assumed, and a C–C bond length of 1.392Å. In later stages, individual thermal parameters were refined for the C atoms. Four cycles of refinement, permitting all non-group atoms to vibrate anisotropically, converged the model at $R_1=0.050$ and $R_2=0.059$.

A parallel refinement was carried out on the model in the acentric space group.

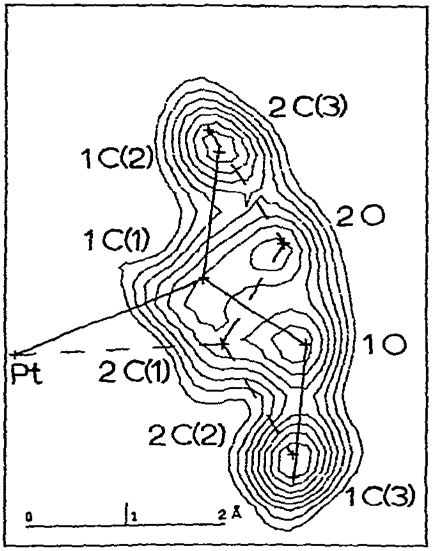


Fig. 1. Difference Fourier synthesis of the plane $y=\frac{1}{4}$ in the region of the disordered carbene ligand. Contours are drawn at intervals of 0.5 e Å^{-3}. The final atomic positions are superimposed.

TABLE 1A. ATOMIC POSITIONAL AND THERMAL PARAMETERS

Atom	*x*	*y*	*z*	*U*(1,1)[a]	*U*(2,2)	*U*(3,3)	*U*(1,2)	*U*(1,3)	*U*(2,3)
Pt	0.22522(4)[b]	$\frac{1}{4}$	0.04290(5)	459(4)	342(3)	430(3)	0	− 3(3)	0
P(1)	0.2184(2)	0.4001(2)	0.0348(2)	531(15)	394(13)	439(13)	− 11(12)	− 2(13)	7(11)
P(2)	0.3077(3)	$-\frac{1}{4}$	0.0640(4)	836(31)	432(21)	602(25)	0	17(22)	0
C(1)	0.0931(10)	$\frac{1}{4}$	−0.0161(15)	611(101)	494(86)	841(108)	0	−208(87)	0
C(2)	0.1989(8)	0.4409(7)	−0.1167(10)	977(92)	588(66)	502(58)	− 19(60)	− 23(58)	127(54)
C(3)	0.3172(7)	0.4577(6)	0.0746(9)	624(64)	377(53)	754(70)	−110(52)	93(59)	−36(47)
F(1)	0.2438(10)	$-\frac{1}{4}$	0.1725(14)	1332(118)	2839(222)	1203(113)	0	700(94)	0
F(2)	0.3736(9)	$-\frac{1}{4}$	−0.0478(9)	1426(110)	1201(93)	856(73)	0	399(70)	0
F(3)	0.3644(6)	−0.3222(4)	0.1281(8)	1550(77)	666(45)	1352(65)	85(47)	−447(62)	274(47)
F(4)	0.2550(7)	−0.1762(5)	−0.0049(11)	1341(71)	777(59)	1553(74)	276(48)	−448(65)	−6(53)

TABLE 1B. GROUP POSITIONAL AND THERMAL PARAMETERS

Group	*xg*[c]	*yg*	*zg*	*δ*	*ε*	*η*	*Multiplicity*
Ph	0.0805(3)	0.4861(3)	0.2174(4)	0.010(5)	2.573(4)	2.264(5)	
CAR[d] 1	0.3512(12)	$\frac{1}{4}$	0.1235(19)	3.142	3.142	2.720(17)	0.46(2)
CAR 2	0.3635(14)	$\frac{1}{4}$	0.0530(17)	0.000	3.142	0.021(16)	0.54(2)

[a] The thermal ellipsoid is given by $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*\cos\gamma^*+2U_{13}hla^*c^*\cos\beta^*+$ $+2U_{23}klb^*c^*\cos\alpha^*)]$ where the U_{ij} are the thermal parameters in terms of mean-square amplitudes of vibration in Ångstroms. Values are given as $U \times 10^4$.

[b] Numbers in parentheses given here and in other tables are estimated standard deviations in the least significant digits. Values without e.s.d.'s were fixed in the refinements.

[c] xg, yg and zg are the fractional coordinates of the group origin, and δ, ε, and η (radians) are the group orientation angles.

[d] CAR = Carbene rigid group, comprising C(1), C(2), C(3) and O.

Attempts to refine non-group carbon atoms anisotropically failed, and after three least-squares cycles with only platinum and phosphorus atoms having anisotropic thermal parameters, the agreement factors were $R_1=0.057$ and $R_2=0.067$. The centric space group *Pnma* is therefore preferred.

The contributions of the five phenyl hydrogen atoms to F_c were calculated utilizing the known geometry of the ring. A C–H distance of 1.049Å and an isotropic thermal parameter of 4.0 Å^2 for each hydrogen atom were assumed. Fourier sections were calculated for each methyl group, for the plane in which the hydrogen atoms are expected to occur. In all cases, even for the disordered carbene methyl groups, rings of positive electron density were observed, though individual peaks were not present. The contributions of the methyl hydrogen atoms to F_c were calculated such that the methyl groups were considered to be undergoing rotation about the three fold axis[25].

A final least-squares cycle, with all hydrogen atom contributions included, generated agreement factors of $R_1=0.047$ and $R_2=0.055$. The final positional, thermal and group parameters are shown in Table 1. Refinement of the disorder multiplicity parameter for the carbene ligand gave a value 0.46(2), so each orientation occurs with approximately equal probability. A statistical examination of the struc-

TABLE 2

DERIVED GROUP ATOM PARAMETERS

Ring C atoms are numbered sequentially. C(1) is bonded to P, H(2) to R-C(2), H(3) to R-C(3), etc.

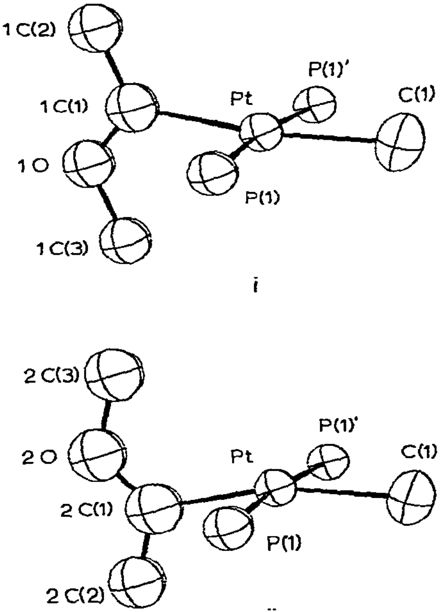
Atom	*x*	*y*	*z*	*B*(Å^2)
Phenyl group				
R-C(1)	0.1388(4)	0.4487(4)	0.1348(5)	3.6(2)
R-C(2)	0.1090(4)	0.5343(4)	0.1167(5)	4.9(2)
R-C(3)	0.0507(4)	0.5717(3)	0.1993(6)	5.4(2)
R-C(4)	0.0222(4)	0.5235(4)	0.3000(5)	5.1(2)
R-C(5)	0.0520(4)	0.4379(4)	0.3181(5)	5.3(2)
R-C(6)	0.1103(4)	0.4005(3)	0.2355(6)	4.6(2)
CAR-1				
1C(1)	0.3512(12)	$\frac{1}{4}$	0.1235(19)	
1C(2)	0.3610(23)	$\frac{1}{4}$	0.2537(18)	*B*(group) = 5.4(6)
1C(3)	0.4116(23)	$\frac{1}{4}$	−0.0825(15)	
1 O	0.4214(11)	$\frac{1}{4}$	0.0522(16)	
CAR-2				
2C(1)	0.3635(14)	$\frac{1}{4}$	0.0530(17)	
2C(2)	0.4121(24)	$\frac{1}{4}$	−0.0587(15)	*B*(group) = 6.9(6)
2C(3)	0.3553(20)	$\frac{1}{4}$	0.2755(17)	
2 O	0.4052(11)	$\frac{1}{4}$	0.1597(15)	
Phenyl hydrogen atoms				
H(2)	0.1304	0.5706	0.0417	4.0
H(3)	0.0283	0.6362	0.1869	4.0
H(4)	−0.0216	0.5516	0.3636	4.0
H(5)	0.0306	0.4014	0.3951	4.0
H(6)	0.1326	0.3358	0.2498	4.0

ture factors in terms of various combinations of Miller indices, magnitudes of F_o, $\sin\theta \cdot \lambda^{-1}$ and diffractometer setting angles indicated no abnormal trends. The error in an observation of unit weight is 1.76 electrons. A final difference Fourier synthesis showed only two peaks with an electron density in excess of 1.0 $e\,Å^{-3}$, one at (0.325, 0.259, 0.100) in the region of the carbene ligand, and a second at (0.225, 0.259, 0.125) which is associated with the platinum atom. The derived positional parameters for the group atoms are shown in Table 2, together with the phenyl hydrogen atom positions. A list of structure amplitudes, observed and calculated, listed as $10|F_o|$ and $10|F_c|$ (electrons) is available*.

DESCRIPTION OF THE STRUCTURE

Figure 2 shows the inner coordination sphere with the two observed carbene ligand orientations, (i) and (ii). Figure 3 gives a stereo-view of the cation with one of the carbene ligands represented. A selection of interatomic bond distances and angles is given in Table 3. The shortest cation–anion distance is 3.14Å, between atoms F(4) and 2 C(3), and is consistent with the packing of discrete anionic and cationic components. The PF_6^- anion is situated on the mirror plane, with a mean P–F distance of 1.57(1)Å. The mean F–P–F angle is 90(1)°.

The coordination geometry about the platinum atom is approximately square planar, with the two phosphorus atoms and the methyl-carbon atom in the equatorial



i

ii

Fig. 2. The inner coordination sphere of the platinum atom, showing the two disordered carbene ligands.

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plane. The C(sp^2) atoms of the two disordered carbene ligands lie slightly above and below the equatorial plane. The two phosphine ligands are related by reflection in the mirror plane, while the methyl ligand and the disordered carbene ligand lie in the mirror plane.

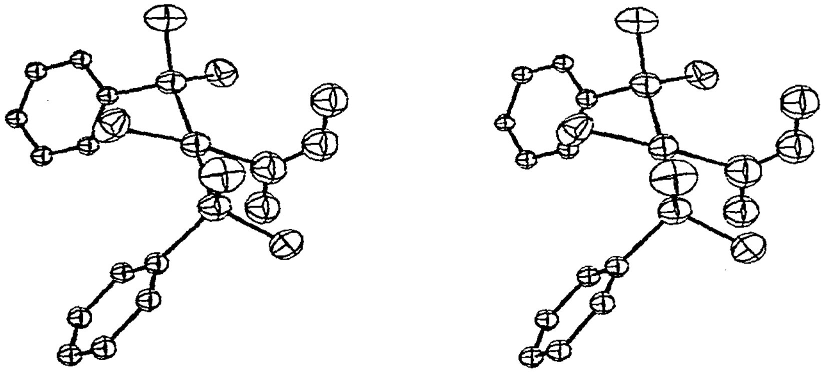

Fig. 3. Stereoview of the cation with only one carbene ligand included for clarity.

TABLE 3

SELECTED INTRAMOLECULAR BOND DISTANCES AND ANGLES

Atoms	*Distance (Å)*	*Atoms*	*Angle (deg.)*
Pt–P(1)	2.283(3)[a]	P(1)–Pt–C(1)	86.83(7)
Pt–C(1)	2.13(2)	P(1)–Pt–P(1)'	173.1(4)
Pt–1C(1)	2.13(1)	P(1)–Pt–1C(1)	93.3(4)
Pt–2C(1)	2.13(1)	P(1)–Pt–2C(1)	92.7(4)
P(1)–C(2)	1.79(1)	C(1)–Pt–1C(1)	173.2(5)
P(1)–C(3)	1.80(1)	C(1)–Pt–2C(1)	165.3(5)
P(1)–R–C(1)	1.799(6)	Pt–P(1)–C(2)	112.8(4)
P(2)–F(1)	1.54(1)	Pt–P(1)–C(3)	115.8(5)
P(2)–F(2)	1.59(1)	Pt–P(1)–R–C(1)	114.7(4)
P(2)–F(3)	1.566(7)	C(2)–P(1)–C(3)	101.3(5)
P(2)–F(4)	1.574(9)	C(2)–P(1)–R–C(1)	107.8(4)
1C(1)–1O	1.33	C(3)–P(1)–R–C(1)	103.1(5)
2C(1)–2O	1.33	F(1)–P(2)–F(2)	180.0(9)
1C(1)–1C(2)	1.43	F(1)–P(2)–F(3)	90.5(6)
2C(1)–2C(2)	1.43	F(1)–P(2)–F(4)	92.3(7)
1O–1C(3)	1.48	F(2)–P(2)–F(3)	89.5(6)
2O–2C(3)	1.48	F(2)–P(2)–F(4)	87.7(6)
		Pt–1C(1)–1O	119.7(9)
		Pt–2C(1)–2O	122(1)
		Pt–1C(1)–1C(2)	120(1)
		Pt–2C(1)–2C(2)	118(1)
		1C(1)–1O–1C(3)	120
		2C(1)–2O–2C(3)	120
		1O–1C(1)–1C(2)	120
		2O–2C(1)–2C(2)	120

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[a] Estimated standard deviations are given in parentheses, with the exception of those values which were constrained as parts of the rigid groups.

The orientation of the dimethylphenylphosphine ligands of the cation is determined mainly by steric factors. The phenyl rings lie to one side of the equatorial plane of the platinum atom, and are directed away from the carbene ligand which is perpendicular to the plane formed by the platinum, methyl-carbon, and the two phosphorus atoms. All P–C distances are equivalent, including that to the phenyl ring, with a mean bond distance of 1.796(3)Å. The bond angles around the phosphorus atom show it to adopt a distorted tetrahedral geometry. The smallest of the C–P–C angles is 101.3(5) degrees between the methyl-carbon atoms. The mean C–P–C angle is 104(2) degrees. Comparative values of 105(1) in *trans*-$[CH_3(CH_3C{\equiv}CCH_3)Pt\{P(CH_3)_2(C_6H_5)\}_2]^+PF_6^-$[26] and 104.3(5) in *trans*-$[CH_3\{CH_3C(N(CH_3)_2)\}Pt\{P(CH_3)_2(C_6H_5)\}_2]^+PF_6^-$[27] have been obtained. Pt^{II}–P distances found in four coordinate complexes are generally much shorter than the sum of the atomic radii 2.42Å[28] and also vary over a relatively large range. In the complex $[Cl_4Pt_2\{P(C_3H_7)_3\}_2]$ the mean Pt–P distance is 2.230(9)Å[29] and in $[CF_3\{(CH_3)_4C_4\}Pt\{P(C_6H_5)(CH_3)_2\}_2]^+SbF_6^-$ the mean Pt–P distance is 2.365(8)Å. The value obtained in this structure, 2.285(3)Å, is midway in this range of distances, and is comparable to Pt–P distances determined in previous Pt^{II} carbene complexes; 2.29(1)Å in *trans*-$[Cl_2\{C|N(C_6H_5)(CH_2)|_2\}PtP(C_2H_5)_3]$[7] and 2.240(8) in *cis*-$[Cl_2\{C(OC_2H_5)(NHC_6H_5)\}PtP(C_2H_5)_3]$[9].

The carbene ligand is present in the *trans* configuration, though the NMR spectrum in solution was interpreted as characteristic of the *cis* isomer[8].

Previous work on the chromium and tungsten complexes of this methyl-methoxy carbene ligand shows that the energy barrier to free rotation about the C–O bond is about 12.4(1) kcal·mole^{-1}, and that in a given solvent one isomer can be more stable than the other[10]. However, the NMR spectra were obtained using a different solvent (deuteroacetone) than that used to grow crystals for this structural examination. A careful examination of the difference Fourier synthesis (Fig. 1) shows no sign of the presence of the *cis* isomer, and it is apparent that under the conditions of crystallization the *trans* isomer is thermodynamically more stable than the *cis*. The mean Pt–C(sp^2) bond length of 2.13(1)Å is significantly longer than that of 1.98(2)Å reported for the complex *cis*-$[Cl_2\{C(OC_2H_5)(NHC_6H_5)\}PtP(C_2H_5)_3]$[9] and also longer than the Pt–C distance of 2.00(3)Å in the amino–carbene complex *trans*-$[Cl_2\{C|N(C_6H_5)(CH_2)|_2\}PtP(C_2H_5)_3]$[7]. However, the Pt–C($sp^2$) bond length is also crystallographically equivalent to the Pt–C(sp^3) methyl distance, 2.130(16)Å, *trans* to it. Whereas the values determined in this analysis are limited by the disorder observed, this suggests very little π interaction between the platinum atom and the sp^2 carbon of the carbene ligand. The methyl and the carbene ligands exert a comparable *trans*-influence, as suggested by the equivalent platinum–methyl-carbon and platinum–carbene-carbon bonds. Such long metal–carbene distances are not usually observed for alkoxy-carbene ligands, since these species tend to be good π acceptors[12,13]. A least-squares plane was calculated through the platinum, methyl-carbon, and two phosphorus atoms. The results are shown in Table 4. The C(sp^2) atoms of the two disordered carbene ligands are above and below the calculated plane. Thus the largest distortion of the square planar complex may be considered as due to the orientation of the carbene ligands. However, this distortion may be a result of a less than ideal representation of the disorder of the carbene ligand, rather than a significant distortion of an ideal square-planar coordination geometry.

TABLE 4

LEAST SQUARES PLANE[a]

Equation of Plane: $-4.423x+10.470z=-0.583$

Atom	*Deviation from plane (Å)*
Pt	0.036
P(1)	−0.019
P(1)′	−0.019
C(1)	0.002
1C(1)	0.322
2C(1)	−0.470

[a] The equation of the least squares plane was calculated using the positions of Pt, P(1), P(1)′, and C(1) only.

The main consequence of the disorder of the carbene ligand is the existence of two isomers of the cation. Thus, for CAR-1, the methoxy substituent on the carbene ligand is on the opposite side of the equatorial plane of the platinum atom to the phenyl ring, while for CAR-2 it lies on the same side. Refinement of the disorder parameter shows that each configuration is equally probable, with multiplicities 0.46(2) and 0.54(2). An explanation of this may be found in an examination of the intramolecular non-bonding interactions with the carbene ligands. Thus, the closest approach of either the carbene methyl-carbon atom, C(2), or the carbene methoxy-carbon atom, C(3), to the phosphine phosphorus atom is 3.88A, and to C(2), the phosphine methyl-carbon atom, is 3.77Å. In the absence of short intermolecular interactions, each configuration is equally favoured energetically. In addition, we may speculate that the disorder arises from attack of the methoxy anion on either of the carbon atoms of the coordinated acetylene ligand in the postulated cationic intermediate[8]. This is further supported by the structural investigation of *trans*-$[CH_3(CH_3C{\equiv}CCH_3)Pt\{P(CH_3)_2(C_6H_5)\}_2]PF_6$, crystals of which are isomorphous with those of the present study, and in which the cations adopt a similar configuration[26].

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