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THE CRYSTAL AND MOLECULAR STRUCTURE OF *trans*-[METHYL-(2-OXACYCLOPENTYLIDENE)BIS(DIMETHYLPHENYLPHOSPHINE)-PLATINUM(II)] HEXAFLUOROPHOSPHATE

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Summary

The carbene complex *trans*-$[CH_3(\overline{CH_2COCH_2CH_2})Pt\{P(CH_3)_2C_6H_5\}_2]$-$PF_6$ crystallizes in the centrosymmetric orthorhombic space group *Pcca* (D_{2h}^8) with $a = 15.503(7)$, $b = 18.81(1)$, $c = 17.66(1)$ Å. The measured density of 1.81(1) g cm^{-3} agrees with d(calc) = 1.81 g cm^{-3} for $M = 703.41$ and $Z = 8$. Three dimensional X-ray diffraction data were collected on an automatic four circle diffractometer using Mo radiation. The structure was solved by a combination of Patterson, Fourier and least-squares refinement techniques. The final conventional agreement factor for the converged model is $R_1 = 0.044$, calculated on 1763 observations for which $I > 3\sigma(I)$, with 160 variables. The anion lies on a crystallographic two-fold axis of symmetry, and is disordered. The coordination geometry is essentially square planar about the platinum atom. The cyclic carbene ligand is almost planar and is coordinated approximately perpendicular to the Pt square plane. The mean Pt—P distance is 2.305(5), the Pt—C(sp^3) bond length is 2.080(18) and the C(sp^2) atom lies 2.00(2) Å away from the platinum atom. The stucture is discussed in terms of the *trans*-influences of the ligands, and the character of the Pt—C(sp^2) bond.

Introduction

Carbene has recently become a common word in the study of organometallic compounds. The similarity between the carbene ligands on these metal-stabilized complexes to the generally reactive organic molecules is responsible for this. Two recent reviews [1, 2] exemplify the immense amount of research that has been done in this field.

The carbene ligands are very good σ-donors and are considered to exert a strong *trans*-influence. Thus platinum carbene complexes have attracted special interest, due to the prevalence of the *trans*-influence in platinum chemistry. These ligands are also thought to be π acceptors of varying ability, depending on the electronegativity of the nucleophilic atom stabilizing the $C(sp^2)$ atom. A considerable variety of platinum(II) carbene complexes has been prepared via several routes [1, 3—5].

Crystallographic investigations of several of these compounds have been reported. Badley et al. have examined the structure of *cis*-$[Cl_2(PEt_3)Pt\{CH_3CH_2OCNC_6H_5\}]$ [6]. Butler and Enemark have reported the structural investigations of $[(CH_3N{\equiv}C)_2Pt\{CH_3NHCNN(CH_3)CNHCH_3\}][B(C_6H_5)_4]$ [7] and *trans*-$[(CH_3N{\equiv}C)_2Pt\{C(NHCH_3)SCH_2CH_3\}_2]$ [8]. These complexes are prepared by addition reactions to coordinated isocyanides. Cardin et al. have studied the *cis* and *trans* isomers of the cyclic carbene complex $[Cl_2(PEt_3)Pt\{C(N(C_6H_5)CH_2)_2\}]$ [9] which is prepared by the cleavage of electron rich olefins in the presence of Pt^{II}. We have been investigating complexes with carbene ligands prepared via cationic acetylenic intermediates [5]. These systems provide the possibility of investigating the π character of the $Pt—C(sp^2)$ bond. The electronegative atom stabilizing the $C(sp^2)$ atom is either O or N in these complexes; hence one would expect a difference in the amount of stabilization from the metal atom to the empty p_z orbital of the $C(sp^2)$ atom, if such complexes are indeed metal stabilized carbonium ions as has been predicted [10, 11]. The structural investigations of *trans*-$[CH_3(CH_3COCH_3)Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$ [12] and *trans*-$[CH_3\{CH_3CN(CH_3)_2\}Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$ [13] have been reported so far.

We now present a crystallographic study of the complex *trans*-$[CH_3(\overline{CH_2COCH_2C}H_2)Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$. This single crystal X-ray study was undertaken to examine structural manifestations of the *trans*-influence in this system of compounds and to gain further knowledge of the bonding interactions about the Pt and $C(sp^2)$ atoms. The cyclic nature of the carbene ligand makes this complex particularly interesting.

Experimental section

A sample of *trans*-$[CH_3(\overline{CH_2COCH_2C}H_2)Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$ was prepared by the method of Chisholm and Clark [5] and was kindly supplied by Manzer. Slow evaporation of solvent from a methylene chloride solution produced thick, colourless, tabular crystals of suitable quality for X-ray work.

(Anal. found: C, 35.97; H, 4.31. *trans*-$[CH_3(\overline{CH_2COC}H_2CH_2)Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$ calcd.: C, 35.94; H, 4.41%.)

Weissenberg and precession photographs, taken with Cu-K_α radiation using a large crystal allowed unambiguous assignment of the space group. The crystals were found to be orthorhombic with Laue symmetry *mmm*. The systematic extinctions observed were: $0kl$ for l odd, $h0l$ for l odd, and $hk0$ for h odd. These absences are consistent only with the space group *Pcca*, D_{2h}^8, No. 54 [14].

The density was obtained by the flotation method in a mixture of carbon tetrachloride and 1,2-dibromoethane. The observed density is 1.81(1) g cm^{-3} and the calculated density 1.81 g cm^{-3}. Hence $Z = 8$ and no symmetry constraints need be imposed upon the ions in space group *Pcca*.

The crystal employed for data collection was studied on an optical goniometer. The two largest faces were of the form {001}. Faces of the forms {100}, {010}, and {012} were also present. The crystal dimensions were 0.36 × 0.28 × 0.13 mm as measured with a filar microscope eyepiece. The crystal was mounted in such a way that the long dimension was deliberately offset from coincidence with the diffractometer ϕ axis to minimize the possibility of multiple reflections [15]. Several ω scans of strong reflections were recorded to check the mosaicity of the crystal. The average peak width at half height was 0.06° [16].

16 reflections with 2θ ranging from 15 to 30° were centered manually on a Picker four circle automatic diffractometer at a temperature of 22°. Least-squares refinement of the setting angles of these reflections gave the unit cell parameters and the orientation matrix, using the program PICKTT [17]. The cell constants so obtained are $a = 15.503(7)$, $b = 18.81(1)$ and $c = 17.66(1)$ Å, (Mo-K_α $\lambda = 0.7093$ Å), corresponding to a unit cell volume of 5150 Å^3.

The intensities of 5348 reflections were recorded in the range $2.5° < 2\theta \leqslant 50°$ using Mo-K_α radiation. The incident beam was filtered with 0.07 mm of niobium foil. The take-off angle on the tube was 1.4°. The Bragg intensity of a strong reflection at this angle was about 80% of the maximum attainable as the take-off angle was increased. The counter aperture was positioned 32 cm from the crystal and the aperture dimensions were 0.4 × 0.4 cm. The pulse height analyzer was set to admit only 90% of the Mo-K_α peak. The data were collected by the $\theta - 2\theta$ scan technique, at a scan rate of 1° per minute. A symmetric scan range of 1.4° was used, corrected for dispersion, and stationary background counts of 10 sec were taken at both ends of the scan.

Copper foil attenuators chosen to give attenuator factors of about 2.2 were inserted automatically when the peak intensity exceeded about 7000 counts per sec during the scan. The intensities of six standards were recorded after every 100 reflections collected. This served as a check on the stability of the crystal and of the electronic equipment. The reference reflections were: ($\bar{4}00$), (002), (020), (400), ($0\bar{2}0$) and ($00\bar{2}$).

As we have observed before with crystals of these cationic complexes [12, 13] the most intense reflections seem to be affected by prolonged exposure to the X-ray beam. The intensities of two of the standards ($\bar{4}00$) and (400) increased on average by 10%. The standards (002) and ($00\bar{2}$) showed a 28% decrease. In each case the peak quality was closely examined, and no significant deterioration in the structure of the peaks was observed. No decomposition correction was applied. The two remaining standards showed only random fluctuations. 5348 data were processed [18]. A standard deviation was calculated for each observed intensity from the formula:

$$\sigma(I) = [CT + 0.25\,(t_c/t_b)^2\,(B_1 + B_2) + (pI)^2\,]^{1/2}$$

where CT is the integrated peak count obtained in time t_c, and B_1 and B_2 are the background counts, obtained in time t_b. I is the intensity and the value of p was assigned as 0.03. Corrections for Lorentz and polarization effects were also applied to the observed intensities. All reflections with $I > 2\sigma(I)$ were corrected for absorption [19]. The transmission coefficients ranged from 0.267 to 0.535. Of the 5348 reflections, 1763 had $F^2 > 3\sigma(F^2)$, and only these reflections were used in the solution and refinement of the structure.

TABLE 1

ATOMIC AND GROUP 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	−0.12457(6) [b]	0.25002(6)	0.05895(3)	409(3)	453(3)	368(3)	− 64(5)	− 9(5)	16(11)
P(1)	−0.1838(4)	0.1377(3)	0.0590(4)	715(37)	501(31)	564(35)	−185(28)	− 43(38)	83(34)
P(2)	−0.0670(3)	0.3680(3)	0.0619(3)	467(28)	503(29)	416(29)	− 77(23)	− 35(30)	− 48(30)
P(3)	−¼	½	0.3071(5)	620(19)					
P(4)	0	0.0526(4)	−¼	689(24)					
O	−0.2098(9)	0.2841(7)	−0.0810(8)	719(97)	707(88)	696(108)	159(75)	−175(84)	96(75)
C(1)	−0.1055(16)	0.2402(14)	0.1750(11)	1287(214)	888(181)	433(102)	−527(173)	−180(141)	284(149)
C(2)	−0.1410(13)	0.2606(10)	−0.0529(12)	697(166)	221(132)	568(108)	− 58(95)	196(133)	13(107)
C(3)	−0.0803(14)	0.2302(9)	−0.1128(12)	897(152)	506(154)	620(141)	−108(100)	85(130)	−134(103)
C(4)	−0.1223(26)	0.2521(20)	−0.1904(12)	2273(332)	1412(224)	485(137)	−112(292)	260(236)	−341(270)
C(5)	−0.2123(21)	0.2787(12)	−0.1657(13)	1929(308)	819(167)	380(131)	−235(180)	−391(184)	66(123)
C(11)	−0.1063(14)	0.0664(11)	0.0442(15)	772(166)	543(143)	1411(257)	−242(124)	−805(209)	224(158)
C(12)	−0.2395(17)	0.1076(14)	0.1428(14)	1087(215)	1511(242)	724(173)	−781(190)	−169(163)	99(173)
C(21)	−0.1486(11)	0.4325(11)	0.0452(14)	265(97)	705(157)	1043(205)	144(99)	−378(136)	−104(149)
C(22)	−0.0121(15)	0.3921(11)	0.1464(11)	987(181)	758(145)	415(126)	− 25(134)	−151(128)	−167(113)

GROUP PARAMETERS

Group	x_g [c]	y_g	z_g	δ	ϵ	η	Multiplicity
Ph-1	−0.3256(6)	0.1254(5)	−0.0732(6)	0.862(11)	−2.544(10)	−2.048(11)	
Ph-2	0.0701(5)	0.3740(4)	−0.0732(5)	−2.214(10)	−2.540(8)	−1.990(10)	
1-F_6	−¼	½	0.3075(6)	2.122(10)	3.142	−1.571	0.42(1)
2-F_6	−¼	½	0.2979(26)	2.107(43)	3.142	−1.571	0.08(1)
3-F_6	0	0.0547(8)	−¼	0.000	3.142	−0.991(13)	0.28(1)
4-F_6	0	0.0520(10)	−¼	0.000	3.142	−1.590(18)	0.22(1)

[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 Angstroms. Values are given as U × 10^4. Atoms refined isotropically are given as ($\text{Å}^2 \times 10^4$). [b] Numbers in parentheses given here and in other tables are estimated standard deviations in the least significant digits. [c] x_g, y_g, z_g are the fractional coordinates of the group origin, and δ, ϵ, and η (radians) are the group orientation angles. See ref. 23.

Solution and refinement

The platinum and the two phosphine phosphorus atoms were located from a Patterson synthesis. A series of difference Fourier syntheses, and least-squares calculations yielded positional parameters for the remaining 29 non-hydrogen atoms. Refinement was carried out on F, with $\Sigma w(|F_0|-|F_c|)^2$ being minimized. F_0 and F_c are the observed and calculated structure amplitudes respectively; w is the weight, defined as $4F_0^2/\sigma^2(F_0^2)$. The atomic scattering factors used to obtain F_c for the Pt, P, F, O, and C atoms were those obtained by Cromer and Waber [20]. The H atom scattering factors were from Stewart, Davidson and Simpson [21]. The effects of anomalous dispersion were included in the calculations, and values of $\Delta f'$ and $\Delta f''$ were taken from Cromer and Liberman [22]. Although no symmetry conditions are imposed on the cation in space group $Pccn$, it was found that the phosphorus atoms of the anions lie in two special positions, each with 4 fold multiplicity in the unit cell, such that the anion is constrained to two fold symmetry. Hence two PF_6 anions with multiplicities of 0.5 had to be refined. Furthermore, a close examination of electron density maps in the region of the anions revealed that the F atoms are disordered about the P atoms, though the two-fold symmetry of the sites is maintained. Two disorder models, with the necessary constraints applied to the derivatives were calculated and refined to account for this. The fluorine atoms of the PF_6 anion were constrained as rigid groups, as were the phenyl carbon atoms [23]. A total of 4 F_6 groups was defined, assuming O_h symmetry and a P—F distance of 1.58 Å. The two phenyl rigid groups were assigned D_{6h} symmetry, with a C—C bond length of 1.392 Å. The group parameters refined consisted of a group origin, three orientation angles, and an overall temperature factor. Individual group atom thermal parameters were refined at later stages for the phenyl groups only. An additional occupancy factor had to be refined for each of the disorder models, and suitable constraints were applied to maintain the two fold symmetry about the phosphorus atoms. Two cycles of least-squares refinement with the platinum and two phosphorus atoms vibrating anisotropically and the remaining non-hydrogen atoms undergoing isotropic motion, gave agreement factors:

$$R_1 = \frac{\Sigma(||F_0|-|F_c||)}{\Sigma|F_0|} = 0.079$$

$$R_2 = \left(\frac{\Sigma w(|F_0|-|F_c|)^2}{\Sigma w F_0^2}\right)^{1/2} = 0.095$$

Six subsequent cycles of full matrix least-squares refinement, with all non-hydrogen, non-group atoms vibrating anisotropically, and with the anion disorder calculations included, converged the structure at $R_1 = 0.047$ and $R_2 = 0.054$. The contributions of the 10 phenyl hydrogen atoms were included in F_c, assuming a C—H bond length of 1.0 Å. Similarly, the 6 methylene hydrogen atoms of the carbene ring were accounted for, employing a C—H distance of 1.05 Å and a H—C—H angle of 109.47°. Electron density maps were calculated in the planes where the methyl hydrogen atoms were expected to occur for each of the 5 methyl groups. Three prominent peaks were observed on each Fourier section. Idealized hydrogen positions were calculated to best superimpose

TABLE 2

DERIVED GROUP ATOM PARAMETERS

Atom	x	y	z	B(Å^2)
Ph-1				
1C(1)[a]	−0.2647(9)	0.1271(8)	−0.0153(7)	4.3(5)
1C(2)	−0.3439(11)	0.1608(8)	−0.0058(7)	6.0(8)
1C(3)	−0.4049(7)	0.1591(8)	−0.0637(10)	7.3(6)
1C(4)	−0.3865(9)	0.1237(8)	−0.1310(8)	7.4(6)
1C(5)	−0.3072(11)	0.0900(8)	−0.1405(7)	7.2(6)
1C(6)	−0.2463(7)	0.0917(7)	−0.0826(9)	5.3(5)
Ph-2				
2C(1)	0.0111(8)	0.3729(7)	−0.0138(6)	3.0(4)
2C(2)	0.0919(9)	0.3417(7)	−0.0049(6)	6.0(9)
2C(3)	0.1510(6)	0.3429(7)	−0.0642(8)	5.5(5)
2C(4)	0.1292(7)	0.3752(7)	−0.1325(7)	5.6(5)
2C(5)	0.0484(9)	0.4064(6)	−0.1415(6)	4.7(4)
2C(6)	−0.0107(6)	0.4052(6)	−0.0821(8)	3.9(4)
1-F$_6$				
1F(1)	−0.1632(5)	0.5440(7)	0.3075(6)	*B*(group) = 8.8(4)
1F(2)	−0.3368(5)	0.4560(7)	0.3075(6)	
1F(3)	−0.2123(6)	0.4494(3)	0.2443(6)	
1F(4)	−0.2877(6)	0.5506(3)	0.3707(6)	
1F(5)	−0.2877(6)	0.5506(3)	0.2443(6)	
1F(6)	−0.2123(6)	0.4494(3)	0.3707(6)	
2-F$_6$				
2F(1)	−¼	½	0.2085(26)	*B*(group) = 6.8(21)
2F(2)	−¼	½	0.3873(26)	
2F(3)	−0.1624(22)	0.5430(31)	0.2979(26)	
2F(4)	−0.3376(22)	0.4570(31)	0.2979(26)	
2F(5)	−0.1979(37)	0.4278(18)	0.2979(26)	
2F(6)	−0.3021(37)	0.5722(18)	0.2979(26)	
3-F$_6$				
3F(1)	0.0558(11)	0.0547(8)	−0.3248(7)	*B*(group) = 9.5(7)
3F(2)	−0.0558(11)	0.0547(8)	−0.1752(7)	
3F(3)	−0.0603(5)	−0.0048(8)	−0.2846(7)	
3F(4)	0.0603(5)	−0.0048(8)	−0.2154(7)	
3F(5)	0.0603(5)	0.1141(8)	−0.2154(7)	
3F(6)	−0.0603(5)	0.1141(8)	−0.2846(7)	
4-F$_6$				
4F(1)	−0.0020(19)	0.0520(10)	−0.3394	*B*(group) = 9.1(9)
4F(2)	0.0020(19)	0.0520(10)	−0.1606	
4F(3)	0	−0.0321(10)	−¼	
4F(4)	0	0.1360(10)	−¼	
4F(5)	−0.1019	0.0520(10)	−0.2482(16)	
4F(6)	0.1019	0.0520(10)	−0.2518(16)	

[a] Ring carbon atoms are numbered sequentially. C(1) is bonded to P.

on these peaks, utilizing the known geometry of a methyl group with a C—H distance of 1.05 Å and a H—C—H angle of 109.47°. In the next calculation of structure factors, the contributions for the 31 hydrogen atoms were included. A statistical examination of these structure factors in terms of various combinations of Miller indices, magnitudes of F_0, $\lambda^{-1} \sin\theta$ and diffractometer setting angles, showed F_0 very much greater than F_c for several strong, low-angle reflections.

The background corrections were considered unreliable for the reflections (002), (020), (022) and (122), and these reflections were omitted in the final least-squares calculations. Two final cycles of full matrix refinement with all

TABLE 3

DERIVED HYDROGEN ATOM POSITIONAL PARAMETERS

Atom	x	y	z
C(3)—H(1)	−0.0771	0.1747	−0.1076
C(3)—H(2)	−0.0182	0.2519	−0.1068
C(4)—H(1)	−0.1248	0.2084	−0.2267
C(4)—H(2)	−0.0855	0.2930	−0.2157
C(5)—H(1)	−0.2581	0.2410	−0.1834
C(5)—H(2)	−0.2242	0.3276	−0.1905
C(1)—H(1)	−0.1277	0.1910	0.1932
C(1)—H(2)	−0.0392	0.2453	0.1868
C(1)—H(3)	−0.1390	0.2813	0.2029
C(11)—H(1)	−0.0573	0.0707	0.0847
C(11)—H(2)	−0.1378	0.0175	0.0499
C(11)—H(3)	−0.0802	0.0710	−0.0102
C(12)—H(1)	−0.2765	0.1519	0.1641
C(12)—H(2)	−0.2814	0.0670	0.1288
C(12)—H(3)	−0.1954	0.0926	0.1833
C(21)—H(1)	−0.1870	0.4385	0.0934
C(21)—H(2)	−0.1179	0.4807	0.0323
C(21)—H(3)	−0.1879	0.4173	−0.0010
C(22)—H(1)	0.0335	0.3533	0.1623
C(22)—H(2)	0.0199	0.4402	0.1354
C(22)—H(3)	−0.0568	0.3991	0.1900
Phenyl hydrogen atoms [a]			
1H(2)	−0.3561	0.1870	0.0426
1H(3)	−0.4613	0.1837	−0.0563
1H(4)	−0.4306	0.1224	−0.1718
1H(5)	−0.2946	0.0642	−0.1884
1H(6)	−0.1894	0.0675	−0.0894
2H(2)	0.1080	0.3182	0.0443
2H(3)	0.2093	0.3203	−0.0578
2H(4)	0.1716	0.3758	−0.1751
2H(5)	0.0326	0.4292	−0.1903
2H(6)	−0.0687	0.4270	−0.0882

[a] Ring hydrogen atoms are numbered sequentially 1H(2) is bonded to 1C(2), 1H(3) is bonded to 1C(3), etc. All hydrogen atoms were assigned an isotropic thermal parameter, $B = 4.0$ Å^2.

hydrogen atom contributions included, converged the model at $R_1 = 0.044$ and $R_2 = 0.048$. The standard deviation of an observation of unit weight is 1.71 electrons. The final positional, thermal, and group parameters are presented in Table 1. Refinement of the disorder multiplicity parameters for the PF_6 anions gave values of 0.28(1) and 0.42(1). A final difference Fourier synthesis was calculated. The largest peak had an electron density of 0.73 e Å^{-3} and was situated at (−0.095, 0.075, −0.225). It is therefore associated with a disordered PF_6 anion. The derived positional parameters for the group atoms are given in Table 2. The hydrogen atom positions, which were not refined, are given in Table 3. A list of the observed and calculated structure amplitudes, given as $10|F_0|$ and $10|F_c|$ is available*.

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* The table of structure factors has been deposited as NAPS Document No. 2352, with ASIS/NAPS, c/o Microfiche Publications, 305 E. 46 th Street, New York, New York 10017. A copy may be secured by citing the document and remitting $1.50 for microfiche or $5.00 for photocopies. Advance payment is required. Make checks payable to Microfiche Publications.

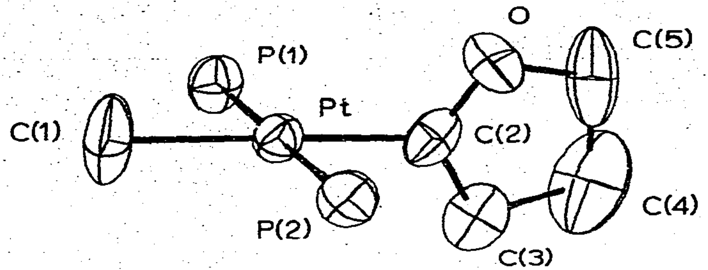

Fig. 1. The inner coordination sphere of the platinum atom, showing the carbene ligand.

Description of the structure

The carbene ligand and the inner coordination sphere of the cation are depicted in Fig. 1. In Fig. 2 is a stereoview of the cation. The shapes and sizes of the atoms in both diagrams are determined by the final isotropic and anisotropic thermal parameters. Table 4 contains a selection of intramolecular bond distances and angles. The nearest approach of the cation to the anion is 3.08 Å between atoms C(4) and 4F(4), and is consistent with that expected for the packing of discrete anionic and cationic components. The PF_6 anion occupies two sets of special positions with 2 symmetry. There are two orientations of the F_6 moiety at each site, due to the disorder of the anion.

The cation has a coordination geometry which is approximately square planar about the platinum atom. The platinum atom, the two phosphorus atoms, the methyl carbon atom, and the carbene $C(sp^2)$ atom all lie in the equatorial plane. In Table 5 is shown the calculation of a weighted least-squares plane through these atoms. P(1) and P(2) deviate from the plane most, being −0.021(6) and −0.015(5) Å below the plane respectively. The P(1)—Pt—P(2) angle is 178.5(2)°, and the C(1)—Pt—C(2) angle is 179.0(8)°.

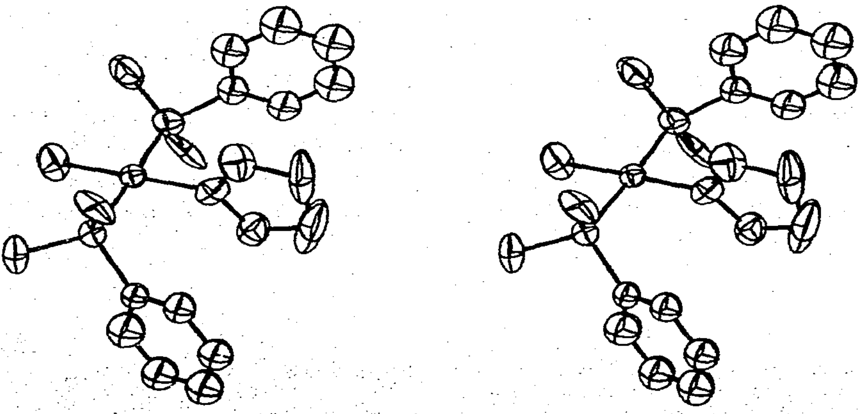

Fig. 2. Stereoview of the cation. Atoms are drawn with 50% probability thermal ellipsoids.

TABLE 4

SELECTED INTRAMOLECULAR BOND DISTANCES AND ANGLES

Atoms	Distance (Å)	Atoms	Angle (°)
Pt—P(1)	2.305(5)	P(1)—Pt—P(2)	178.5(2)
		C(1)—Pt—C(2)	179.0(8)
Pt—P(2)	2.305(5)	C(1)—Pt—P(1)	88.6(7)
		C(1)—Pt—P(2)	90.3(7)
Pt—C(1)	2.080(18)	C(2)—Pt—P(1)	92.3(6)
		C(2)—Pt—P(2)	88.9(6)
Pt—C(2)	2.00(2)	Pt—P(1)—C(11)	114.4(7)
		Pt—P(1)—C(12)	118.6(8)
P(1)—C(11)	1.82(2)	Pt—P(1)—1C(1)	111.9(5)
		Pt—P(2)—C(21)	112.6(6)
P(1)—C(12)	1.81(2)	Pt—P(2)—C(22)	118.8(7)
		Pt—P(2)—2C(1)	109.6(7)
P(1)—1C(1)	1.83(1)	C(11)—P(1)—C(12)	102(1)
		C(11)—P(1)—1C(1)	105.7(9)
P(2)—C(21)	1.84(2)	C(12)—P(1)—1C(1)	103(1)
		C(21)—P(2)—C(22)	104(1)
P(2)—C(22)	1.80(2)	C(21)—P(2)—2C(1)	105.5(8)
		C(22)—P(2)—2C(1)	105(1)
P(2)—2C(1)	1.82(1)	Pt—C(2)—O	122(2)
		Pt—C(2)—C(3)	125(1)
C(2)—O	1.26(2)	C(2)—O—C(5)	113(2)
		C(2)—C(3)—C(4)	105(2)
C(2)—C(3)	1.53(2)	C(3)—C(4)—C(5)	102(2)
		C(4)—C(5)—O	106(2)
C(3)—C(4)	1.57(3)	C(3)—C(2)—O	112(2)
C(4)—C(5)	1.55(4)		
O—C(5)	1.50(2)		

The phosphine ligands have a distorted tetrahedral geometry. The phenyl rings lie on the same side of the platinum atom as does the carbene ligand. This results in a rather lop-sided cation as was observed with the complex *trans*-$[CH_3\{CH_3CN(CH_3)_2\}Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$ [13]. A more balanced configuration has been observed previously for the alkoxycarbene complex *trans*-$[CH_3(CH_3COCH_3)Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$ [12]. The phosphine ligands are

TABLE 5

WEIGHTED LEAST-SQUARES PLANES

Atom	Deviation from Plane (Å)
Atoms included: Pt, P(1), P(2), C(1), and C(2) *Equation of Plane: 14.09x — 7.240y — 2.858z = —3.734*	
Pt	0.001(1)
P(1)	—0.021(6)
P(2)	—0.015(5)
C(1)	0.01(3)
C(2)	0.01(2)
Atoms included: C(2), O, C(3), C(4), and C(5) *Equation of Plane: 6.580x + 17.01y — 9.00z = 3.527*	
C(2)	0.02(2)
O	0.00(1)
C(3)	—0.04(2)
C(4)	0.13(4)
C(5)	—0.03(2)

also twisted relative to each other. The phenyl ring on one phosphine lies well above the platinum equatorial plane, whereas the one on the other phosphine lies well below this plane. This constrains one of the phosphorus—methyl carbon bonds in each phosphine to lie almost parallel to the platinum square plane and the other to lie nearly perpendicular to this plane. The Pt—P distances have identical values of 2.305(5) Å. Comparable values of 2.294(3) and 2.303(3) Å have been obtained for the complexes *trans*-$[CH_3\{CH_3CN(CH_3)_2\}Pt\{P(CH_3)_2 \cdot C_6H_5\}_2]PF_6$ [13] and *trans*-$[CH_3(CH_3C{\equiv}CCH_3)Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$ [24]. All P—C distances are crystallographically equal, the mean being 1.820(6) Å Similar values of 1.796(3) and 1.805(6) Å have been obtained for the complexes *trans*-$[CH_3(CH_3COCH_3)Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$ [12] and *trans*-$[CH_3\{CH_3CN(CH_3)_2\}Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$ [13] respectively. The phosphine tetrahedra are distorted away from the central platinum atom. This has been found in other platinum(II) complexes containing phosphine ligands [12, 13, 24, 25]. The Pt—P—C angles range from 109.6(7) to 118.8(7)°, and the average is 114(2)°. The C—P—C angles vary from 102(1) to 105.7(9)° with a mean value of 104.2(6)°. The corresponding angles in the complex *trans*-$[CH_3\{CH_3CN(CH_3)_2\}Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$ [13] have mean values of 114.4(7) and 103.4(5)°.

The Pt—C(sp^3) distance *trans* to the carbene ligand is 2.080(18) Å. This value differs from that of 2.147(11) Å obtained for the Pt—C(sp^3) bond in the carbene complex *trans*-$[CH_3\{CH_3CN(CH_3)_2\}Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$ [13] by 3.2 σ and by 2.1 σ from the value of 2.130(16) Å in *trans*-$[CH_3(CH_3COCH_3)Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$ [12]. The Pt—C(sp^3) distance is crystallographically equivalent to the value of 2.11(2) Å obtained for the complex *trans*-$[CH_3(CH_3C{\equiv}CCH_3)Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$ [24] where the acetylene ligand is assumed to exert a much weaker *trans*-influence than that expected for carbene ligands [26]. Moreover the Pt—C(sp^3) distance is shorter, although not significantly, than the sum of the covalent radii of the atoms, which is 2.09 Å [27]. In the solid state, for this complex, the *trans*-influence phenomenon is not discernible from the structural parameters, in agreement with the ^1H solution NMR predictions that the carbene ligands CH_3COCH_3, $CH_3CN(CH_3)_2$, and $\overline{CH_2COCH_2CH_2}$ all have similar *trans*-influences [5, 28].

The cyclic carbene ligand approaches planarity. The plane of the carbene ligand intersects the platinum square plane at an angle of 87.3(6)°. Table 5 contains a calculation of a weighted least-squares plane through the five carbene ligand atoms. C(4) is the only atom which deviates significantly from the plane. This atom is 0.13(4) Å above the plane, which may be caused by strain within the ring. The large thermal ellipsoids representing atoms C(4) and C(5) in Fig. 1 give evidence of considerable motion in that region of the carbene ring.

The Pt—C(sp^2) bond length is 2.00(2) Å, which is shorter by 3.3σ than that of 2.079(13) Å observed in *trans*-$[CH_3\{CH_3CN(CH_3)_2\}Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$ [13]. In both cases there is a methyl group *trans* to the carbene. Oxygen is more electronegative than nitrogen and therefore offers much less stabilization to the electron deficient C(sp^2) atom. Indeed, the aminoalkylcarbenes are prepared by direct substitution of the alkoxy group by the aminoalkyl moiety in the noncyclic carbenes [28]. The C(sp^2)—O bond length is 1.26(2) Å, compared to the value of 1.32(3) Å in the complex *cis*-$[\text{Cl}_2\text{PEt}_3\text{Pt}\{\text{C}(\text{NHC}_6\text{H}_5)(\text{OC}_2\text{H}_5)\}]$ [6] which has both an oxygen atom and a nitrogen atom stabilizing the C(sp^2) atom. The O—C(5) bond length is 1.50(2) Å which agrees well with the mean distance of 1.51(4) Å obtained for the cyclic carbene in the complex *cis*-$[\text{MnCl}(\overline{\text{COCH}_2\text{CH}_2\text{O}})(\text{CO})_4]$ [29]. The C(2)—C(3) bond length is 1.53(2) Å and is equivalent to the value of 1.526(18) obtained for *trans*-$[\text{CH}_3\{\text{CH}_3\text{CN}(\text{CH}_3)_2\}\text{-Pt}\{\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5\}_2]\text{PF}_6$ [13]. The mean C(sp^3)—C(sp^3) bond distance in the carbene ring is 1.56(1) Å. The value obtained for *cis*-$[\text{MnCl}(\overline{\text{COCH}_2\text{CH}_2\text{O}})(\text{CO})_4]$ [29] is 1.53(4) Å. Except for the C(sp^2)—O bond length, none of the bond distances around the carbene ring are significantly different.

Of the three angles around C(2), Pt—C(2)—O and Pt—C(2)—C(3) have values of 122(2) and 125(1)° respectively. These approach the expected 120° angle for sp^2 hybridization. The angle within the ring, C(3)—C(2)—O, is only 112(2)°, and the cyclic nature of the ring does impose some strain upon the system. This is further evidenced by the angles about the C(sp^3) atoms which are all less than the ideal value of 109.47°. The mean value of these three angles is 104.3(9)°. The value of the angle C(2)—O—C(5) is 113(2)°, the magnitude expected if the oxygen atom is to contain some sp^2 character. In conclusion, the structural parameters observed in this study are consistent with the view that the carbene ligand is a metal-stabilized carbonium ion.

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