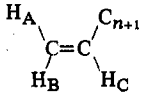
in the monoolefin compound (–)-(fumaric acid)$Fe(CO)_4$ where two of the three crystallographically independent molecules have a carbon–carbon double bond inclined to the equatorial plane at an angle of 17°.[8]

The hydrogen atoms of the double-bond carbon atoms are of considerable interest since they appear to be directed away from the rhodium atom. If the double bond remains olefinic, these hydrogen atoms are expected to be coplanar with the C=C bond. In order to investigate the olefin hydrogens further, the plane C_{n+1}, C_{n+2}, and C_{n+3} (see Figure 5) was calculated and the angles between the respective C-H bonds and the plane were computed. Table X gives the planes, lines, and angles. The angles can be summarized as follows for the structure



H_A-C ranges from 1.2 to 5.8°, H_B-C from 14.2 to 27.2°, and H_C-C from 17.1 to 27.5° out of the plane. Although hydrogen atoms are determined poorly at best in a structure containing heavy atoms, there would seem to be significant nonplanarity of the olefin and this would be consistent with a change from sp^2 toward a more complex hybrid due to metal-carbon bonding.

Selected intermolecular contacts[29] and the appropriate symmetry operations are listed in Table XI.

Table XI. Selected Intermolecular Distances

Carbon ref[a]	Atoms	Distance, Å	Symmetry operation
C(17)	H(29)-Cl(1)	2.75 (9)	$\bar{x}, y - 1/2, 1/2 - z$
C(1)	H(1)-Cl(2)	2.82 (9)	$1 - x, 1/2 + y, 1/2 - z$
C(21)	Cl(1)-H(37)	2.76 (3)	$\bar{x}, 1 - y, \bar{z}$
C(18)	Cl(1)-H(32)	2.95 (9)	$\bar{x}, 1 - y, \bar{z}$
C(10)	Cl(1)-H(18)	3.09 (9)	$\bar{x}, 1/2 + y, 1/2 - z$
C(7)	H(12)-C(12)	2.84 (9)	$\bar{x}, 1/2 + y, 1/2 - z$
C(9)	C(21)-H(16)	2.94 (9)	$x, 1/2 - y, -1/2 + z$
C(14)	H(41)-H(25)	2.53 (9)	$x, 1/2 - y, -1/2 + z$
C(15)	H(42)-H(26)	2.65 (8)	$x, 1/2 - y, -1/2 + z$

[a] Carbon atom to which the hydrogen atom is bonded. Hydrogen atoms are numbered consecutively starting with carbon atom 1; *i.e.*, H(1) and H(2) are attached to C(1), H(3) and H(4) are attached to C(2), etc.

Acknowledgment. The authors wish to thank Dr. L. G. Sneddon for preliminary work on this compound.

Registry No. (+)-$RhClP(CH_2CH_2CH{=}CH_2)_3$, 50276-25-0; (–)-$RhClP(CH_2CH_2CH{=}CH_2)_3$, 50276-26-1.

Supplementary Material Available. Table I, a listing of structure factor amplitudes, will appear following these pages in the microfilm editon of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $7.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-792).

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Crystal and Molecular Structure of *trans*-[(Methyl)(methyl-*N*,*N*-dimethylaminocarbene)bis(dimethylphenylphosphine)platinum(II)] Hexafluorophosphate

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The crystal and molecular structure of *trans*-[(methyl)(methyl-*N*,*N*-dimethylaminocarbene)bis(dimethylphenylphosphine)-platinum(II)] hexafluorophosphate has been determined from three-dimensional X-ray data collected on an automatic four-circle diffractometer using Cu radiation. The compound crystallizes in the monoclinic space group $P2_1/c$, $Z = 4$, with unit cell dimensions $a = 8.515$ (2), $b = 10.934$ (2), and $c = 28.549$ (7) Å with $\beta = 93.93$ (1)°. The observed and calculated densities are 1.77 (1) and 1.76 g cm^{-3}, respectively. Full-matrix least-squares refinement on F gave a final conventional R factor of 0.041 for 1865 reflections with $I > 3\sigma(I)$. The coordination geometry about the Pt atom is square planar, with the carbene ligand lying perpendicular to the plane. The average Pt-P bond distance is 2.294 (3) Å, the Pt-C(methyl) bond length is 2.147 (11) Å, and the Pt-C(sp^2) bond length is 2.079 (13) Å. The C(sp^2)-N bond distance is 1.266 (15) Å. The Pt-C bond lengths are discussed in terms of the trans influences of the methyl and carbene ligands.

Introduction

Square-planar Pt(II) carbene complexes have been prepared in several ways,[1-3] notably by nucleophilic addition to coordinated isocyanides[1,4-7] and by the cleavage of electron-rich olefins in the presence of Pt(II).[2] Both methods yield carbene ligands which contain a C(sp^2) atom stabilized by two adjacent nucleophilic atoms such as O, N, or S. The structures of several of the complexes of this type have been determined by X-ray diffraction methods.[6,8-10]

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A third method has been reported by Chisholm and Clark[3] and involves nucleophilic attack upon a platinum(II)-acetylene complex. This preparation yields square planar, cationic platinum(II)-oxycarbene species. The carbene ligands in these complex cations contain only one nucleophilic atom bonded to and stabilizing the $C(sp^2)$ atom. The ligands are analogous to those in the Cr and W complexes first prepared by Maasbol and Fischer, of which several crystal structures have been reported.[11-15] We have reported the crystallographic investigation of a methylmethoxycarbene compound, *trans*-$[CH_3(CH_3COCH_3)Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$.[16] Treatment of this complex with dimethylamine results in substitution at the $C(sp^2)$ atom and formation of the complex *trans*-$[CH_3\{CH_3CN(CH_3)_2\}Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$.[17]

Carbene complexes of transition metals have been described as metal-stabilized carbonium ions.[18] Hence the mode of attachment of the carbene to the metal atom and the geometry of the ligand are of interest. In addition, nmr studies have suggested that all four ligands coordinated to the Pt atom have comparable trans influences.[19] In particular, both the methyl ligand and the carbene ligand trans to it are believed to have strong trans influences. This single-crystal X-ray diffractometric study was therefore undertaken to study the carbene ligand geometry and the relative trans influences of the ligands present and to compare the structure with that of *trans*-$[CH_3(CH_3COCH_3)Pt\{P(CH_3)_2C_6H_5\}_2]$-$PF_6$.

Experimental Section

A sample of *trans*-$[CH_3\{CH_3CN(CH_3)_2\}Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$ was prepared by Chisholm by the method of Chisholm and Clark.[17] Colorless crystals were obtained by recrystallization from methylene chloride solution. The thick tabular crystals were found to be of suitable quality for X-ray study. *Anal.* Calcd for *trans*-$[CH_3\{CH_3CN(CH_3)_2\}Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$: C, 35.90; H, 4.88; N, 1.99. Found: C, 35.99; H, 5.04; N, 1.88.

A crystal with well-developed faces was chosen for preliminary study and a series of Weissenberg and precession photographs was taken with Cu Kα radiation. The photographs showed the crystal to be monoclinic with Laue symmetry $2/m$. The systematic extinctions observed were $h0l$ for l odd and $0k0$ for k odd. These absences are consistent only with the space group $P2_1/c$, $C_{2h}{}^5$, No. 14.[20]

The density, 1.77 (1) g cm^{-3}, was determined by flotation in carbon tetrachloride and 1,2-dibromoethane. The calculated density is 1.76 g cm^{-3}, for $Z = 4$. No symmetry constraints are imposed on the ions in space group $P2_1/c$.

In an optical goniometric study of the crystal selected for examination, the two largest faces were of the form $\{001\}$. Faces of the forms $\{110\}$, $\{011\}$ and individual faces of indices $(0\bar{1}2)$, $(01\bar{2})$, and (100) were also present. Cu Kα radiation was chosen for data collection. The crystal was measured with a filar microscope eyepiece and had dimensions 0.39 mm × 0.23 mm × 0.17 mm. The crystal was mounted on a diffractometer such that the long dimension [100] was offset slightly from coincidence with the diffractometer ϕ axis to minimize the possibility of multiple reflections.[21] Several ω scans were recorded with a narrow source and a wide open counter to examine the mosaicity of the crystal. The average scan width at half-height for strong reflections was 0.079°.[22]

A least-squares refinement of the setting angles of 14 reflections that had been centered on a Picker four-circle diffractometer gave the unit cell parameters. A narrow slit width and a takeoff angle of 0.5° were used for the centering. Refinement of the orientation matrix was carried out using the program PICKTT.[23] The cell constants obtained at 19° are $a = 8.515$ (2), $b = 10.934$ (2), $c = 28.549$ (7) Å, and $\beta = 93.93$ (1)°. The unit cell volume is 2652 Å^3.

Intensity data were collected in the range $2.5° < 2\theta < 90°$ using Cu Kα radiation. The incident beam was filtered using 0.018 mm of Ni foil. A takeoff angle on the tube of 1.5° was used. At this angle the peak intensity of a strong reflection was about 80% of the maximum value observed as a function of takeoff 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 Cu Kα peak.

The data were collected by the θ-2θ scan technique at a scan rate of 1°/min. A symmetric scan range of 1° was used with a correction applied to account for high-angle dispersion. Stationary-counter, stationary-crystal background counts of 10 sec were taken at the start and at the end of each scan. When the intensity of the diffracted beam exceeded about 7000 counts/sec during the scan, attenuators were inserted automatically. The attenuators were Cu foil; their thicknesses were chosen to give attenuator factors of about 2.2. The intensities of six reference reflections were measured after every 100 reflections recorded. This served as a check on crystal and electronic stability. The six reflections chosen as standards were $\bar{2}00$, 200, 020, 004, 241, and 441. In all, 3064 data were recorded, data collection being terminated when the standard reflections showed a sudden decrease in intensity and a significant deterioration of peak quality. This occurred during the collection of those reflections for which $75 < 2\theta < 90°$. An examination of the standard intensities showed the first 2860 data to be unaffected by decomposition. Over the period these reflections were recorded the intensities of 020 and 004 increased on an average by 8%, and the remaining four standards showed only random fluctuations. No correction for decomposition was applied to the data. All 3064 data were processed.[24] Intensities were assigned standard deviations from the formula

$$\sigma(I) = [\mathrm{CT} + 0.25(t_\mathrm{c}/t_\mathrm{b})^2(B_1 + B_2) + (pI)^2]^{1/2}$$

where CT is the integrated peak count obtained in time t_c, and B_1 and B_2 are the background counts, each obtained in the time t_b. I is the intensity and p was taken as 0.03. The recorded intensities were corrected for background and for Lorentz and polarization effects. All reflections with $I > 3\sigma(I)$ were corrected for absorption.[25] The maximum and minimum transmission coefficients were 0.239 and 0.147, respectively. Of the first 2860 reflections, 1865 had $F^2 > 3\sigma(F^2)$, and only these reflections were employed in the solution and refinement of the structure.

Structure Solution and Refinement

Preliminary positional parameters were obtained for the Pt and the two phosphine P atoms from a Patterson synthesis. The remaining 29 nonhydrogen atoms were located from a series of difference Fourier syntheses and least-squares calculations. The structure was refined on F, minimizing $\Sigma w(|F_\mathrm{o}| - |F_\mathrm{c}|)^2$, where F_o and F_c are the observed and calculated structure amplitudes, respectively. w is the weight and defined as $4F_\mathrm{o}{}^2/\sigma^2(F_\mathrm{o}{}^2)$. In all calculations of F_c, the atomic scattering factors for Pt, P, F, N, and C were those obtained by Cromer and Waber.[26] H atom scattering factors were from Stewart, Davidson, and Simpson.[27] The effects of anomalous dispersion were

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Table I. Atomic and Group Positional and Thermal Parameters

Atom	x	y	z	U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	−0.25377 (6)[b]	0.16554 (4)	0.15203 (2)	459 (7)	367 (5)	385 (5)	−39 (2)	62 (3)	15 (2)
P(1)	−0.1603 (4)	0.0439 (3)	0.0946 (1)	625 (26)	387 (19)	437 (19)	19 (17)	72 (17)	1 (15)
P(2)	−0.3607 (4)	0.2741 (3)	0.2105 (1)	477 (25)	521 (21)	377 (18)	−30 (18)	81 (15)	−8 (16)
P(3)	−0.3485 (4)	0.1853 (3)	0.4178 (1)	597 (11)					
N	−0.1915 (15)	0.3900 (9)	0.0971 (4)	860 (105)	454 (72)	620 (74)	88 (70)	259 (73)	113 (63)
C(1)	−0.3705 (16)	0.0076 (10)	0.1777 (4)	837 (105)	400 (73)	567 (78)	−121 (69)	219 (70)	−42 (63)
C(2)	−0.1359 (18)	0.3182 (10)	0.1290 (5)	796 (128)	316 (80)	600 (89)	41 (72)	122 (83)	−95 (70)
C(3)	0.0287 (16)	0.3458 (10)	0.1510 (5)	484 (105)	524 (86)	722 (92)	−123 (65)	−13 (79)	−41 (63)
C(4)	−0.3492 (17)	0.3707 (12)	0.0732 (4)	580 (111)	737 (92)	560 (84)	145 (80)	44 (79)	235 (72)
C(5)	−0.1093 (19)	0.5007 (12)	0.0804 (5)	1290 (143)	462 (86)	971 (108)	−193 (88)	421 (98)	248 (82)
C(11)	−0.3026 (14)	0.0195 (10)	0.0460 (4)	606 (99)	523 (83)	689 (86)	−153 (68)	−54 (71)	−88 (66)
C(12)	−0.1043 (15)	−0.1109 (11)	0.1104 (4)	695 (104)	493 (81)	797 (94)	161 (75)	160 (76)	37 (73)
C(21)	−0.5680 (16)	0.3030 (12)	0.1991 (5)	486 (107)	779 (96)	971 (109)	−103 (78)	231 (81)	−188 (84)
C(22)	−0.3446 (18)	0.2009 (12)	0.2685 (4)	1145 (132)	644 (89)	483 (81)	−129 (87)	276 (82)	−2 (70)
Group	x_g[c]	y_g	z_g	δ	ϵ	η	Multiplicity		
Ph-1	0.1421 (7)	0.1694 (5)	0.0543 (2)	−2.234 (6)	−2.425 (5)	−2.630 (6)			
Ph-2	−0.2044 (6)	0.5392 (5)	0.2273 (2)	−2.124 (7)	−2.298 (5)	3.006 (7)			
1-F6	−0.3493 (9)	0.1855 (7)	0.4186 (3)	3.363 (10)	2.316 (6)	−3.367 (11)	0.50 (2)		
2-F6	−0.3471 (10)	0.1853 (7)	0.4181 (3)	−1.992 (10)	−2.529 (8)	−2.179 (8)	0.50 (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}'s are the thermal parameters in terms of mean-square amplitudes of vibration in angstroms. Values are given as $U \times 10^4$. 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, and z_g are the fractional coordinates of the group origin, and δ, ϵ, and η (radians) are the group orientation angles.

Table II. Derived Group Atom Parameters

Atom	x	y	z	B, Å^2
		Ph-1		
1C(1)[a]	0.0126 (8)	0.1071 (7)	0.0696 (3)	3.8 (2)
1C(2)	0.1618 (10)	0.0871 (7)	0.0915 (2)	5.0 (3)
1C(3)	0.2913 (8)	0.1494 (8)	0.0762 (3)	6.2 (3)
1C(4)	0.2716 (9)	0.2318 (8)	0.0391 (3)	6.0 (3)
1C(5)	0.1225 (11)	0.2518 (7)	0.0172 (2)	5.8 (3)
1C(6)	−0.0070 (8)	0.1895 (7)	0.0324 (3)	4.4 (3)
		Ph-2		
2C(1)	−0.2757 (9)	0.4252 (5)	0.2214 (3)	3.6 (2)
2C(2)	−0.1597 (9)	0.4436 (6)	0.2576 (2)	5.1 (3)
2C(3)	−0.0885 (8)	0.5577 (8)	0.2635 (3)	5.9 (3)
2C(4)	−0.1332 (10)	0.6533 (6)	0.2332 (3)	6.0 (4)
2C(5)	−0.2491 (10)	0.6348 (6)	0.1970 (3)	5.4 (3)
2C(6)	−0.3204 (8)	0.5208 (7)	0.1911 (2)	3.9 (3)
		1-F6		
1F(1)	−0.1657 (9)	0.1933 (12)	0.4309 (5)	B(group) = 8.8 (4)
1F(2)	−0.3216 (15)	0.0899 (10)	0.3785 (4)	
1F(3)	−0.3606 (18)	0.0774 (9)	0.4549 (4)	
1F(4)	−0.3770 (15)	0.2810 (9)	0.4587 (4)	
1F(5)	−0.3380 (18)	0.2936 (9)	0.3823 (4)	
1F(6)	−0.5329 (9)	0.1777 (12)	0.4063 (5)	
		2-F6		
2F(1)	−0.2235 (15)	0.2327 (14)	0.3836 (4)	B(group) = 9.5 (4)
2F(2)	−0.2082 (15)	0.1369 (13)	0.4529 (4)	
2F(3)	−0.3404 (17)	0.3129 (9)	0.4441 (5)	
2F(4)	−0.4860 (14)	0.2336 (13)	0.3833 (4)	
2F(5)	−0.3537 (16)	0.0576 (9)	0.3921 (4)	
2F(6)	−0.4707 (15)	0.1378 (13)	0.4526 (4)	

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

included in the calculations, and the values of $\Delta f'$ and $\Delta f''$ were those calculated by Cromer and Liberman.[28]

The C atoms of the phenyl rings and the F atoms of the PF_6 anion were constrained as rigid groups.[29] The phenyl rings were assumed to have D_{6h} symmetry, and a C–C bond length of 1.392 Å. The F_6 rigid group was given O_h symmetry and a P–F distance of 1.58 Å. The parameters refined for the rigid groups consisted of a group origin, three orientation angles, and an overall group thermal parameter. Individual group atom thermal parameters were refined at later stages.

Two cycles of full-matrix least-squares refinement with all nonhydrogen atoms assigned isotropic thermal parameters and the Pt and two phosphine P atoms allowed to vibrate anisotropically gave the agreement factors

$$R_1 = \frac{\Sigma(||F_o| - |F_c||)}{\Sigma|F_o|} = 0.083$$

$$R_2 = \left(\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w F_o^2}\right)^{1/2} = 0.141$$

A subsequent difference Fourier synthesis revealed six peaks greater than 2.0 e Å^{-3} in the region of the PF_6 anion. As these peaks form a second octahedron about the P atom, disorder of the anion is apparently present. The model formulated to account for this disorder involved the refinement of a second F_6 octahedron. During the refinement of the two F_6 rigid groups, the appropriate constraints were applied to the derivatives. An occupancy factor was varied for the F_6 groups, in addition to an overall temperature factor, a group origin, and three orientation angles. Five cycles of refinement permitting all nongroup atoms to vibrate anisotropically converged the model at $R_1 = 0.050$ and $R_2 = 0.077$.

The contributions of the ten phenyl H atoms to F_c were calculated utilizing the known geometry of the phenyl rings. A C–H distance of 1.049 Å and an isotropic thermal parameter of 4.0 Å^2 for each H atom were assumed. Fourier sections were calculated for each methyl group, for the plane in which the H atoms are expected to occur. Each Fourier section contained three peaks. Positional parameters were calculated to correspond best to the peak positions utilizing the known geometry of a methyl group with C–H distance of 1.09 Å and H–C–H angle of 109.47°. Contributions to F_c were obtained for all 24 methyl H atoms. The H atoms were assigned isotropic thermal parameters of 4.0 Å^2. Two cycles of full-matrix least squares with all H atom contributions included converged the model at $R_1 = 0.045$ and $R_2 = 0.064$.

For low-angle reflections F_o was observed to be consistently smaller than F_c. This was considered to be a result of secondary extinction. An extinction coefficient was refined in the last cycles of least squares.[30] A final value of 3.8 (4) × 10^{-6} was obtained. Two full-matrix least-squares cycles employing 162 variables and 1865 observations converged to the final model, generating agreement factors $R_1 = 0.041$ and $R_2 = 0.062$. The final positional, thermal, and group parameters are shown in Table I. Refinement of the disorder multiplicity parameter for the PF_6 anion gave a value 0.50 (2), so each orientation occurs with equal probability. A statistical examination of the structure factors in terms of various combinations

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Table III. Derived Hydrogen Atom Positional Parameters

Atom	x	y	z
	Methyl Hydrogen Atoms		
C(1)-H1	−0.3648	−0.0671	0.1526
C(1)-H2	−0.3133	−0.0200	0.2114
C(1)-H3	−0.4937	0.0297	0.1822
C(11)-H1	−0.3432	0.1085	0.0319
C(11)-H2	−0.2489	−0.0312	0.0184
C(11)-H3	−0.4027	−0.0309	0.0575
C(12)-H1	−0.1938	−0.1512	0.1311
C(12)-H2	−0.0924	−0.1644	0.0789
C(12)-H3	0.0083	−0.1092	0.1315
C(21)-H1	−0.6303	0.2160	0.1963
C(21)-H2	−0.6100	0.3546	0.2289
C(21)-H3	−0.5878	0.3552	0.1673
C(22)-H1	−0.2242	0.2084	0.2838
C(22) H2	−0.4243	0.2456	0.2914
C(22)-H3	−0.3765	0.1044	0.2648
C(3)-H1	0.0668	0.2720	0.1748
C(3)-H2	0.1104	0.3538	0.1234
C(3)-H3	0.0273	0.4317	0.1705
C(4)-H1	−0.4144	0.2993	0.0910
C(4)-H2	−0.4208	0.4552	0.0730
C(4)-H3	−0.3423	0.3421	0.0364
C(5)-H1	0.0064	0.5117	0.1015
C(5)-H2	−0.0828	0.4942	0.0436
C(5)-H3	−0.1763	0.5848	0.0853
	Phenyl Hydrogen Atoms[a]		
1-H(2)	0.1765	0.0252	0.1197
1-H(3)	0.4038	0.1337	0.0926
1-H(4)	0.3695	0.2778	0.0273
1-H(5)	0.1077	0.3134	−0.0109
1-H(6)	−0.1196	0.2049	0.0162
2-H(2)	−0.1263	0.3718	0.2805
2-H(3)	−0.0013	0.5720	0.2908
2-H(4)	−0.0794	0.7394	0.2375
2-H(5)	−0.2823	0.7066	0.1739
2-H(6)	−0.4073	0.5064	0.1636

[a] Ring H atoms are numbered sequentially. 1-H(2) is bonded to 1C(2), 1-H(3) is bonded to 1C(3), etc.

Table V. Selected Intramolecular Bond Distances (Å) and Angles (deg)

	Distances		
Pt-P(1)	2.297 (3)	P(2)-C(21)	1.801 (15)
Pt-P(2)	2.290 (3)	P(2)-C(22)	1.834 (13)
Pt-C(1)	2.147 (11)	P(2)-2C(1)	1.821 (8)
Pt-C(2)	2.079 (13)	C(2)-N	1.266 (15)
P(1)-C(11)	1.796 (12)	C(2)-C(3)	1.526 (18)
P(1)-C(12)	1.806 (13)	N-C(4)	1.478 (17)
P(1)-1C(1)	1.819 (8)	N-C(5)	1.495 (15)
	Angles		
P(1)-Pt-P(2)	175.3 (1)	C(11)-P(1)-C(12)	101.9 (6)
C(1)-Pt-C(2)	178.3 (5)	C(11)-P(1)-1C(1)	105.8 (5)
C(1)-Pt-P(1)	88.3 (3)	C(12)-P(1)-1C(1)	104.3 (6)
C(1)-Pt-P(2)	87.2 (3)	C(21)-P(2)-C(22)	104.5 (7)
C(2)-Pt-P(1)	92.3 (3)	C(21)-P(2)-2C(1)	104.1 (6)
C(2)-Pt-P(2)	92.3 (3)	C(22)-P(2)-2C(1)	103.9 (5)
Pt-P(1)-C(11)	112.9 (4)	Pt-C(2)-N	124 (1)
Pt-P(1)-C(12)	117.6 (4)	Pt-C(2)-C(3)	118.6 (9)
Pt-P(1)-1C(1)	113.0 (3)	C(2)-N-C(4)	122 (1)
Pt-P(2)-C(21)	113.2 (5)	C(2)-N-C(5)	125 (1)
Pt-P(2)-C(22)	115.1 (4)	C(4)-N-C(5)	113 (1)
Pt-P(2)-2C(1)	114.8 (3)	N-C(2)-C(3)	117 (1)

of Miller indices, magnitudes of F_o, $(\sin\theta)/\lambda$, and diffractometer setting angles showed no abnormal trends. The largest peak on a final difference Fourier synthesis had an electron density of 0.76 (4) e Å^{-3} at (−0.200, 0.150, 0.380) and is associated with the disordered PF_6 anion.

The derived positional parameters for the group atoms are shown in Table II. The H atom positions were not refined and are presented in Table III. A list of observed and calculated structure amplitudes, given as $10|F_o|$ and $10|F_c|$ (electrons), is presented in Table IV.[31]

Table VI. Weighted Least-Squares Planes

Atom	Dev from plane, Å	Atom	Dev from plane, Å
Atoms Included: Pt, P(1), P(2), C(1), C(2)			
Equation of Plane: $6.441x - 2.436y + 15.98z = 0.391$			
Pt	0.0007 (5)	C(1)	0.043 (13)
P(1)	−0.019 (3)	C(2)	0.019 (16)
P(2)	−0.018 (3)		
Atoms Included: N, C(2), C(3), C(4), C(5)			
Equation of Plane: $3.880x - 6.067y - 20.74z = -5.126$			
N	0.002 (10)	C(4)	0.004 (13)
C(2)	−0.008 (12)	C(5)	−0.004 (14)
C(3)	0.006 (13)		

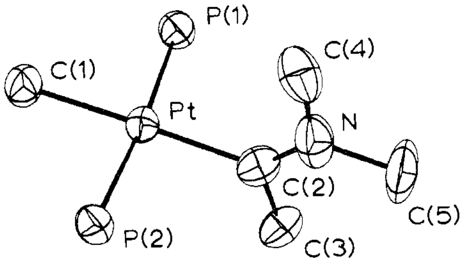

Figure 1. The inner coordination sphere of the platinum atom, showing the carbene ligand.

Description of the Structure

Figure 1 shows the inner coordination sphere of the cation. In Figure 2, a stereoview of the cation is given. Table V contains a selection of interatomic bond distances and angles. The shortest cation–anion distance is 3.18 Å between atoms C(5) and 1-F(1). This distance is of the magnitude expected for the packing of discrete anionic and cationic components. The PF_6 anion occupies one of two equally probable orientations in the lattice.

The coordination geometry about the Pt atom is approximately square planar, with two P atoms, the methyl C atom, and the carbene C(sp^2) atom in the equatorial plane. The angle P(1)-Pt-P(2) is 175.3 (1)°. The phosphine ligands are bent back toward the methyl ligand and the average C(1)-Pt-P angle is 87.8 (5)°. A weighted least-squares plane (Table VI) through the Pt, the two P, the methyl C, and the C(sp^2) atoms shows that the largest deviation from the plane is 0.04 (1) Å. The two phenyl rings of the phosphine ligands lie on the same side of the Pt atom as the carbene ligand. The phosphorus to phenyl ring bonds lie approximately in the Pt equatorial plane. Hence the phosphine methyl groups lie above and below the square plane.

The mean Pt-P distance is 2.294 (3) Å. This is equivalent to the values of 2.283 (3) Å obtained for *trans*-$[CH_3(CH_3COCH_3)Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$[16] and 2.303 (3) Å for *trans*-$[CH_3(CH_3C{\equiv}CCH_3)Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$.[32] The six P-C distances are not significantly different from one another; the mean is 1.812 (6) Å. Comparable means of 1.796 (3) Å in *trans*-$[CH_3(CH_3COCH_3)Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$[16] and 1.804 (7) Å in *trans*-$[CH_3(CH_3C{\equiv}CCH_3)Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$[32] have been obtained. The phosphine ligands have a distorted tetrahedral geometry. The mean Pt-P-C angle is 114.4 (7)°, and the average C-P-C angle is 104.1 (5)°. A similar distortion of the phosphine tetrahedron away from the central metal atom has been observed in several previous structure determinations containing dimethylphenylphosphine ligands.[16,32,33]

The Pt-C(sp^3) distance trans to the carbene is 2.147 (11)

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(31) See paragraph at end of paper regarding supplementary material.

(32) B. W. Davies and N. C. Payne, *Can. J. Chem.*, **51**, 3477 (1973).

(33) D. B. Crump and N. C. Payne, *Inorg. Chem.*, **12**, 1663 (1973).

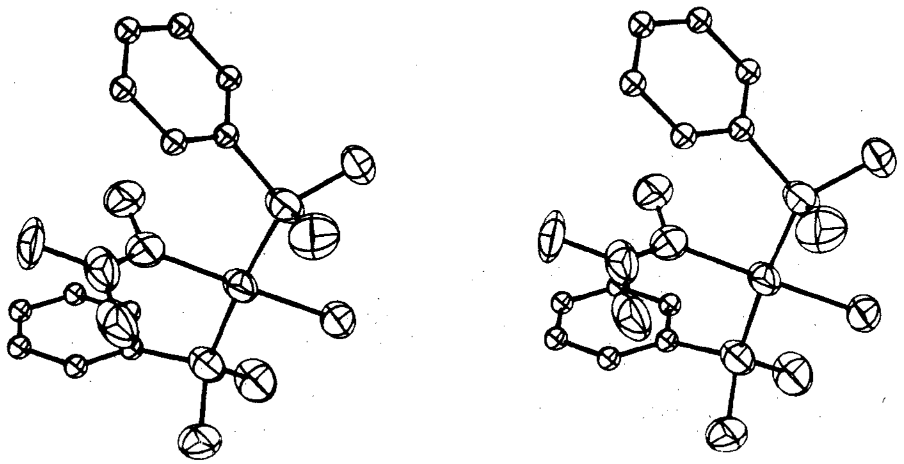

Figure 2. Stereoview of the cation with thermal parameters on carbon atoms of phenyl rings set at 2.0 Å^2 for clarity.

Table VII. Square-Planar Platinum(II)-Carbene Complexes–Structural Data

Complex	N-C(sp^2) (carbene)	Pt-C(sp^2) (carbene)	Ligand trans to carbene	Ref
$[(CH_3N{\equiv}C)_2Pt\{CH_3NHCNN(CH_3)CNHCH_3\}][B(C_6H_5)_4]$	1.36 (3)	1.95 (2)	$CH_3N{\equiv}C$	6
cis-$[Cl_2(P(C_2H_5)_3)Pt\{CH_3CH_2OCNC_6H_5\}]$	1.32 (3)	1.98 (2)	Cl^-	8
trans-$[Cl_2(P(C_2H_5)_3)Pt\{C(NC_6H_5CH_2)_2\}]$	1.348 (18)	2.020 (16)	$P(C_2H_5)_3$	9
cis-$[Cl_2(P(C_2H_5)_3)Pt\{C(NC_6H_5CH_2)_2\}]$	1.327 (11)	2.009 (13)	Cl^-	9
trans-$[(CH_3N{\equiv}C)_2Pt\{C(NHCH_3)SCH_2CH_3\}_2][PF_6]_2$	1.30 (1)	2.06 (1)	$C(NHCH_3)SCH_2CH_3$	10
trans-$[CH_3(CH_3COCH_3)Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$		2.13 (2)	CH_3	16
trans-$[CH_3\{CH_3CN(CH_3)_2\}Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$	1.266 (15)	2.079 (13)	CH_3	This study

Å. This bond length is longer than the sum of the covalent radii, which is 2.09 Å.[34] A slight lengthening of the Pt-C(sp^3) bond could be attributed to a strong trans influence of the carbene ligand. Also, the Pt-C(sp^3) distance in the acetylene complex *trans*-$[CH_3(CH_3C{\equiv}CCH_3)Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$ is 2.10 (2) Å.[32] This distance is shorter than the value found in the present study by 0.05 (3) Å, a result to be expected if, as suggested by nmr studies, the but-2-yne ligand is considered to exert only a weak trans influence. Unfortunately the errors on these bond lengths are too great to permit a detailed comparison of these two ligands in terms of a trans influence using the bond length criterion. A comparable distance of 2.130 (16) Å has been obtained for the carbene complex *trans*-$[CH_3(CH_3COCH_3)Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$.[16] Thus we detect no significant difference in trans influence between the methyl-*N,N*-dimethylamino and the methylmethoxycarbene ligands. Further evidence for this has been postulated from Pt-C-H coupling constants, for the values of *J*(Pt-C-H) differ only slightly for the two complexes.[17]

The carbene ligand is planar within experimental error. The results of a calculation of a least-squares plane through the atoms of the carbene ligand are shown in Table VI. The largest deviation from the plane is 0.008 (12) Å. The angles about the C(sp^2) atom approach 120°, the mean being 120 (2)°. The N atom also displays considerable sp^2 character. The angles about this atom are C(2)-N-C(4) = 122 (1)°, C(2)-N-C(5) = 125 (1)°, and C(4)-N-C(5) = 113 (1)°, corresponding to a mean value of 120 (4)°. The N-C(sp^3) distances are 1.478 (17) and 1.495 (15) Å for N-C(4) and N-C(5), respectively. Values of 1.50 (1) and 1.45 (1) Å in $(CO)_5Cr[CH_3CN(C_2H_5)_2]$[13] and 1.51 (3) Å in $(CO)_5Cr(CH_3CNHCH_3)$[11] have been obtained. The methyl C atom, C(3), is 1.526 (18) Å distant from the C(sp^2) atom. Similar values of 1.50 (1) and 1.51 (3) Å in $(CO)_5Cr[CH_3CN(C_2H_5)_2]$ and $(CO)_5Cr(CH_3CNHCH_3)$, respectively, have been observed. Table VII summarizes some interatomic distances which have been obtained from structural investigations of square-planar platinum(II)-carbene complexes.

The N-C(sp^2) distance of 1.266 (15) Å is significantly shorter than those distances in the compounds $[(CH_3N{\equiv}C)_2Pt(CH_3NHCNN(CH_3)CNHCH_3)][B(C_6H_5)_4]$, *trans*-$[Cl_2(P(C_2H_5)_3)Pt(C(NC_6H_5CH_2)_2)]$, and *cis*-$[Cl_2(P(C_2H_5)_3)Pt(C(NC_6H_5CH_2)_2)]$, all of which contain a C(sp^2) atom stabilized by two nucleophilic N atoms. Only this study of the complexes listed in Table VII has an N-C(sp^2) bond length shorter than 1.30 Å. Values of 1.33 (3) and 1.31 (1) Å were observed in $(CO)_5Cr(CH_3CNHCH_3)$[11] and $(CO)_5Cr(CH_3CN(C_2H_5)_2)$,[13] respectively, in which the C(sp^2) atom is stabilized by only one adjacent nucleophilic atom.

As the carbene ligands in the various complexes of Table VII differ, the Pt-C(sp^2) distances range from 1.95 (2) to 2.13 (2) Å, comparable to the value of 2.079 (13) Å observed in this study. Thus it is not possible to draw conclusions as to the trans influence of the methyl ligand from the Pt-C(sp^2) bond length observed here, since this bond length has been demonstrated to be sensitive to the nature of the substituent groups on the carbene ligand.[10-15]

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Registry No. *trans*-$[CH_3\{CH_3CN(CH_3)_2\}Pt\{P(CH_3)_2C_6H_5\}_2]PF_6$, 49631-76-7.

Supplementary Material Available. Table IV, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-797

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