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Crystal and Molecular Structure of Tetrakis(bis(methylamino)carbene)platinum(II) Hexafluorophosphate, $[Pt(C(NHMe)_2)_4](PF_6)_2$

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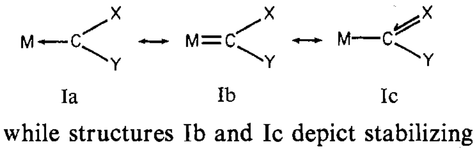
The crystal and molecular structure of tetrakis(bis(methylamino)carbene)platinum(II) hexafluorophosphate, $[Pt(C(NHMe)_2)_4](PF_6)_2$, has been determined from three-dimensional x-ray data collected by counter techniques. The compound crystallizes in the monoclinic space group $P2_1/c$ (C_{2h}^5). There are two formula units within a unit cell of dimensions $a = 8.480$ (4) Å, $b = 9.120$ (4) Å, $c = 17.530$ (9) Å, and $\beta = 96.37$ (1)°. The observed and calculated densities are 1.90 (1) and 1.906 g/cm^3, respectively. The cationic complex has a crystallographically imposed inversion center and nearly ideal square-planar coordination. The average Pt–C bond length is 2.0466 (6) Å, corresponding to a Pt–C(sp^2) single bond. The carbene ligands adopt the amphi configuration in which there exist two stereochemically distinct methyl groups, and the planes of the carbene ligands form angles of 81.8 and 77.1° with the coordination plane of the Pt(II) ion. The orientation of the carbene ligands is such that the complex possesses nearly C_{2h} symmetry. The equivalent C(carbene)–N bonds have an average length of 1.310 (3) Å indicative of significant double-bond character. The structural results thus confirm the importance of $p_\pi \rightarrow p_\pi$ dative bonding in stabilizing amino carbene ligands, and support the notion of hindered rotation about the carbene C–N bond proposed previously based on NMR studies.

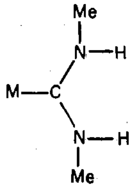
Introduction

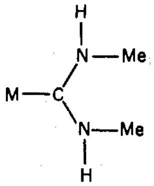
Since the initial report in 1964,[2] the field of transition metal–carbene complexes has become a major area of investigation. Several recent reviews document and summarize the developments in this area.[3-5] The majority of carbene complexes reported to date contain at least one heteroatom (N, O, S) bonded to the carbene carbon which plays an important role in stabilizing the carbene moiety. This can be envisioned in terms of the resonance structures for the metal–carbene unit. Structure Ia corresponds to carbene coordination while structures Ib and Ic depict stabilizing interactions through metal $d_\pi \rightarrow p_\pi$ back-bonding and dative π bonding between the heteroatom and the carbene carbon, respectively. X-ray structural results have shown the importance of the latter interaction, which involves a filled p orbital of the heteroatom and the vacant p orbital of the sp^2-hybridized carbene, through the observation of partial double-bond character in the carbene carbon–heteroatom bond length.[3-5] NMR results have also demonstrated hindered rotation about this bond due to the π interaction.[3-5] The existence of stabilization via structure Ic seriously questions the correctness of viewing these ligands as true carbenes, and alternate suggestions for naming and describing them have been presented by others.[4-7]

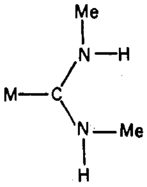


Ia Ib Ic

A principal way in which coordinated carbenes containing a heteroatom have been synthesized involves nucleophilic attack on a coordinated carbonyl or isocyanide, resulting in the formation of alkoxy and amino carbenes, respectively. Usually in reactions of this type, one or at most two coordinated ligands are converted into carbene type ligands. However, in 1972 Miller and Balch reported the addition of methylamine to $M(CNMe)_4^{2+}$ (M = Pt, Pd) to yield the intriguing percarbene complexes of $M(C(NHMe)_2)_4^{2+}$ stoichiometry.[6] Possible conformations for the di(methylamino)carbene ligand in these systems are shown as IIa–c, but


IIa


IIb


IIc

on the basis of the observation of two different methyl resonances over the temperature range −50–90 °C, Miller and Balch assigned the amphi configuration, IIc, to the carbene ligands and viewed the degree of hindered rotation about the C–N bonds as appreciable.[6]

Several questions, however, could not be answered based solely on the NMR results, and they provided the impetus in part for the present study. First, how are the carbene ligands oriented with respect to the coordination plane? Two structures of idealized D_{2d} and C_{2h} symmetry had been proposed,[6] as had a chiral structure in which the planes of the carbene ligands are skewed relative to the coordination plane. Second, is the basis of the hindered rotation primarily electronic or steric, and are the carbene ligands more adequately described as *C*-metal-substituted amidinium ions? The structural parameters could provide insight into this question. Last, what are the metal–carbene bond parameters and are there any unusual interactions to account for these very stable complexes containing only carbene type ligands?

To answer these questions, the structure of $[Pt(C(NHMe)_2)_4](PF_6)_2$ has been determined and the results are presented herein.

Experimental Section

Collection and Reduction of the X-Ray Data. Clear, colorless crystals of $[M(C(NHMe)_2)_4](PF_6)_2$ (M = Pt, Pd) were synthesized by the published procedure[6] and grown from acetonitrile solution. Preliminary investigation by oscillation, Weissenberg, and precession photography of the Pt complex revealed that the crystal had $2/m$ or monoclinic symmetry. Reflections for which $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, were systematically absent, and thus the space group was determined as $P2_1/c$ (C_{2h}^5).[8] Furthermore, reflections for which $k + l = 2n$ were significantly more intense than were those for which $k + l = 2n + 1$. Lattice constants at 24 °C were determined from a least-squares refinement[9] of the setting angles of 12 high-angle reflections ($(\sin\theta)/\lambda \geq 0.430$ Å^{-1}). The reflections were carefully centered, using Mo Kα_1 radiation (λ 0.709261 Å), on a Picker FACS-1 diffractometer equipped with a graphite monochromator. The lattice constants are a = 8.480 (4) Å, b = 9.120 (4) Å, c = 17.530 (9) Å, β = 96.37 (4)°, V = 1347.4 (11) Å^3. The density of 1.90 (1) g/cm^3 as determined by flotation in carbon tetrachloride–bromoform is in excellent agreement with the value 1.906 g/cm^3 calculated for 2 formula units/unit cell. The cationic complex is therefore required to have crystallographically imposed C_i symmetry with the Pt(II) ion located at an inversion center. The greater intensity of the reflections for which $k + l = 2n$ is explained by the fact that Pt, located at $\bar{1}$ special positions, contributes only to those reflections.

The mosaicity of the crystal was examined by means of the narrow-source, open-counter ω-scan technique.[10] The full widths at half-maximum for typical strong reflections were 0.06–0.12°. The crystal, which had a needlelike habit, was mounted such that the a axis (the long axis) was nearly parallel to the ϕ axis of the diffractometer.

Intensities were measured by the θ–2θ scan technique. The takeoff angle for the x-ray tube was 1.5°, a value chosen so that the intensity of the diffracted beam was roughly 80% of its maximum as a function of takeoff angle. Data were collected for $2\theta \leq 45°$ for all reflections in the quadrant with $k \geq 0$, $l \geq 0$. The scan rate was 1°/min. For reflections with $2\theta \leq 35°$ the scan was from 0.65° below the Kα_1 peak to 0.65° above the Kα_2 peak, and backgrounds were counted for 10 s at each end of the scan. For reflections with $2\theta > 35°$ the scan width was from 0.7° below Kα_1 to 0.7° above Kα_2 and backgrounds were counted for 20 s at each end of the scan. Attenuators were automatically inserted when the intensity of the diffracted beam reached roughly 10000 counts/s. The pulse height analyzer was set for a 90% window centered on Mo Kα radiation. During data collection three standard reflections were monitored every 50 observations. The intensities of the standards varied by less than 1% throughout data collection. The intensities of 3405 reflections were collected as data, including 205 reflections which were required to be absent as a result of space group extinctions.

The net intensities and their variances were calculated as described earlier.[11] The ignorance factor, p, was chosen as 0.04. Values of I and $\sigma^2(I)$ were converted to F^2 and $\sigma^2(F^2)$ by application of Lorentz and polarization corrections.[12] Of the 205 reflections systemically absent as a result of the space group extinctions, all had $F^2 < 2.2\sigma(F^2)$. Since the absorption coefficient for Mo Kα radiation was 57.05 cm^{-1}, an absorption correction was carried out. After data collection was complete, the crystal was transferred to an optical goniometer on which the crystal faces were indexed and interplanar distances measured using a Zeiss traveling hairline eyepiece.[13] The analytical method of DeMeulenaer and Tompa[14] was employed for the absorption correction. Transmission coefficients ranged from 0.485 to 0.661 with the average value being 0.582. After application of the absorption correction the 100 reflections with $l = 0$ which had been observed as equivalent forms were averaged. The agreement factor for averaging was 3.3%. The final data set consisted of 3099 independent reflections of which 1899 had $F_o^2 \geq 3\sigma(F_o^2)$.

Solution and Refinement of the Structure. A three-dimensional Patterson map[12] showed no metal–metal vector, thus confirming that the platinum atom was located at a crystallographic inversion center which was chosen as the origin of the unit cell. Further interpretation of the map resulted in the determination of the positions of the carbene carbon atoms and all of the atoms of the hexafluorophosphate anion. Two cycles of refinement of the scale factor, the positional parameters for these nine independent atoms, and isotropic temperature factors for all ten atoms yielded residuals R_1 = 0.16 and R_2 = 0.22.[15] In this and all subsequent refinements the quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where the weights, w, were taken as $4F^2/\sigma^2(F^2)$. Only the 1899 reflections for which $F_o^2 \geq 3\sigma(F_o^2)$ were included in the refinements. Scattering factors for neutral Pt, P, F, N, and C were those of Cromer and Mann.[16] The scattering factors for hydrogen were those of Stewart et al.[17] The effects of anomalous dispersion were included in the calculation of the $|F_c|$; the values for $\Delta f'$ and $\Delta f''$ for Pt and P were those of Cromer and Lieberman.[18]

A difference Fourier phased by the refined model revealed the positions of the eight remaining nonhydrogen atoms. Refinement of a model which included all nonhydrogen atoms treated isotropically yielded R_1 = 0.072 and R_2 = 0.091. When an anisotropic model was used for all 18 nonhydrogen atoms, the refinement converged with R_1 = 0.0298 and R_2 = 0.0365. A difference Fourier at this point showed peaks at the positions expected for the amine protons but did not show strong evidence of the methyl protons. The amine protons were placed at idealized positions (d(N–H) = 0.9 Å, sp^2 hybridization at N) with assigned thermal parameters of 6.0 Å^2; the methyl protons were not included in the refinement. In the final cycles of refinement the amine hydrogen positional and thermal parameters were held constant. Two cycles of refinement converged to R_1 = 0.0288 and R_2 = 0.0355. The final estimated standard deviation for an observation of unit weight was 1.23.[15] This function showed no dependence as a function of either $|F_o|$ or $(\sin\theta)/\lambda$. The two largest peaks in a final difference Fourier were within 1 Å of the metal and had a density of 1.3 e/Å^3, or 25% of the height of a typical carbon peak in this study. All other peaks in the final difference map had densities of less than 0.75 e/Å^3.

The final positional and thermal parameters are given in Table I. A listing of the observed and calculated structure factors for those reflections used in the refinement is available.[19]

Electronic Spectral Measurements. Electronic absorption spectra of $[M(C(NHMe)_2)_4](PF_6)_2$ (M = Pd, Pt) were recorded in ~1 × 10^{-3} M acetonitrile solutions. The spectra were measured on Cary 15 and 118C spectrophotometers purged with dry nitrogen.

Description of the Structure

The crystal structure described by the parameters of Table I, the unit cell dimensions, and the symmetry of the space group consists of the packing of discrete cationic complexes

Table I. Final Positional and Thermal Parameters for $[Pt(C(NHMe)_2)_4](PF_6)_2$

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0	0	0	115.7 (7)[b]	95.5 (6)	24.10 (15)	20.7 (7)	12.29 (14)	0.3 (4)
P	0.310 18 (30)	0.122 90 (29)	0.328 33 (15)	200 (4)	150 (3)	54.7 (10)	−15 (3)	30.9 (16)	−8.7 (16)
F(1)	0.217 6 (10)	−0.024 0 (7)	0.308 3 (5)	504 (20)	180 (12)	93 (4)	−146 (11)	101 (7)	−34 (5)
F(2)	0.170 0 (8)	0.178 3 (7)	0.374 5 (5)	298 (13)	216 (12)	130 (5)	−38 (10)	108 (7)	−55 (6)
F(3)	0.394 1 (6)	0.272 8 (7)	0.349 6 (4)	189 (9)	214 (10)	115 (4)	−50 (8)	10 (5)	−35 (6)
F(4)	0.443 3 (9)	0.076 7 (10)	0.280 3 (5)	340 (16)	345 (16)	127 (5)	−67 (14)	121 (8)	−73 (8)
F(5)	0.218 5 (10)	0.196 6 (9)	0.255 7 (4)	493 (21)	303 (16)	82 (4)	−100 (14)	−44 (7)	40 (6)
F(6)	0.391 5 (14)	0.056 5 (11)	0.401 0 (6)	805 (38)	329 (17)	100 (5)	141 (21)	−108 (11)	37 (8)
N(1)	0.297 8 (8)	−0.055 5 (9)	0.102 0 (4)	148 (10)	212 (12)	41.9 (27)	10 (9)	2 (4)	31 (4)
N(2)	0.311 4 (8)	0.141 9 (8)	0.029 1 (4)	165 (11)	156 (10)	45.4 (28)	−28 (9)	−7 (4)	9 (5)
N(3)	−0.076 1 (9)	0.241 3 (7)	0.105 6 (4)	287 (15)	100 (8)	48.7 (29)	18 (10)	56 (5)	−8 (4)
N(4)	−0.134 6 (7)	0.018 9 (7)	0.146 6 (3)	182 (9)	128 (11)	31.2 (18)	−9 (8)	26 (3)	−9 (4)
C(1)	0.227 8 (8)	0.030 4 (7)	0.049 4 (4)	136 (9)	118 (14)	28.0 (20)	6 (7)	14 (4)	−1 (3)
C(2)	−0.078 8 (8)	0.099 2 (8)	0.093 5 (4)	123 (10)	130 (10)	28.1 (22)	8 (8)	13 (4)	−5 (4)
C(3)	0.223 7 (12)	−0.185 0 (13)	0.131 8 (7)	226 (18)	251 (20)	76 (5)	21 (15)	24 (8)	81 (9)
C(4)	0.473 8 (11)	0.183 4 (13)	0.062 4 (6)	182 (15)	255 (21)	66 (5)	−77 (14)	−23 (7)	−1 (8)
C(5)	−0.016 0 (18)	0.350 7 (11)	0.056 4 (7)	634 (43)	104 (12)	86 (6)	−4 (18)	154 (14)	1 (7)
C(6)	−0.189 7 (10)	0.074 1 (11)	0.218 1 (4)	205 (14)	199 (13)	30.9 (26)	−22 (12)	27 (5)	−21 (5)
H(1)	0.399 8[c]	−0.033 8	0.121 4	6.0[d]					
H(2)	0.265 4	0.200 4	−0.010 0	6.0					
H(3)	−0.118 1	0.274 1	0.149 1	6.0					
H(4)	−0.140 0	−0.082 4	0.138 5	6.0					

[a] Anisotropic thermal parameters have been multiplied by 10^4. The form of the anisotropic thermal ellipsoid is $\exp[-h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] In this and subsequent tables the estimated standard deviations of the least significant figures are given in parentheses. [c] Hydrogen positional and thermal parameters not refined. [d] Isotropic thermal parameter B in the expression $\exp[-(B((\sin \theta)/\lambda)^2)]$.

Table II. Bond Distances (Å) in $[Pt(C(NHMe)_2)_4](PF_6)_2$

Atoms	Dist	Dist cor for riding[a]	Atoms	Dist	Dist cor for riding[a]
Pt-C(1)	2.046 (7)	2.050 (7)	C(1)-N(1)	1.302 (9)	1.329 (10)
Pt-C(2)	2.047 (7)	2.052 (7)	C(1)-N(2)	1.311 (9)	1.331 (9)
Av[b]	2.0466 (6)	2.0508 (7)	C(2)-N(3)	1.313 (9)	1.345 (10)
			C(2)-N(4)	1.314 (9)	1.323 (9)
P-F(1)	1.573 (6)	1.629 (7)	Av	1.310 (3)	1.332 (5)
P-F(2)	1.593 (6)	1.645 (6)			
P-F(3)	1.567 (6)	1.605 (6)	N(1)-C(3)	1.461 (12)	1.494 (12)
P-F(4)	1.540 (7)	1.613 (7)	N(2)-C(4)	1.485 (10)	1.575 (11)
P-F(5)	1.568 (7)	1.639 (8)	N(3)-C(5)	1.448 (11)	1.508 (13)
P-F(6)	1.507 (8)	1.642 (9)	N(4)-C(6)	1.474 (9)	1.487 (9)
Av	1.558 (12)	1.629 (7)	Av	1.467 (8)	1.501 (7)

[a] See ref 20. [b] Average values and their standard deviations are computed from $\bar{x} = \Sigma x_i/n$ and $\sigma(\bar{x}) = [\Sigma(x_i - \bar{x})^2/n(n-1)]^{1/2}$ where n is the number of equivalent values.

Table III. Bond Angles (deg) in $[Pt(C(NHMe)_2)_4](PF_6)_2$

C(1)-Pt-C(2)	88.8 (3)	F(1)-P-F(2)	90.1 (4)
		F(1)-P-F(3)	177.0 (4)
Pt-C(1)-N(1)	123.5 (4)	F(1)-P-F(4)	91.3 (4)
Pt-C(1)-N(2)	120.3 (5)	F(1)-P-F(5)	89.6 (5)
Pt-C(2)-N(3)	124.4 (6)	F(1)-P-F(6)	90.9 (6)
Pt-C(2)-N(4)	119.8 (5)	F(2)-P-F(3)	87.0 (4)
Av[a]	122.0 (12)	F(2)-P-F(4)	176.6 (5)
N(1)-C(1)-N(2)	116.2 (7)	F(2)-P-F(5)	86.9 (5)
N(3)-C(2)-N(4)	115.9 (7)	F(2)-P-F(6)	89.7 (6)
Av	116.0 (2)	F(3)-P-F(4)	91.6 (4)
		F(3)-P-F(5)	89.4 (4)
C(1)-N(1)-C(3)	124.0 (7)	F(3)-P-F(6)	89.8 (5)
C(1)-N(2)-C(4)	126.6 (7)	F(4)-P-F(5)	90.0 (5)
C(2)-N(3)-C(5)	125.8 (7)	F(4)-P-F(6)	93.3 (6)
C(2)-N(4)-C(6)	125.8 (7)	F(5)-P-F(6)	176.6 (6)
Av	125.6 (5)		

[a] See footnote *b* in Table III.

Table IV. Weighted Least-Squares Planes[a] Through the Ligands

Ligand 1		Ligand 2	
Atom	Dev from plane, Å	Atom	Dev from plane, Å
C(1)	−0.008 (6)	C(2)	0.004 (6)
N(1)	0.010 (8)	N(3)	−0.012 (8)
N(2)	0.010 (7)	N(4)	−0.002 (6)
C(3)	−0.005 (13)	C(5)	0.028 (17)
C(4)	−0.016 (12)	C(6)	0.006 (9)

Coefficients of Planes

	Ligand 1	Ligand 2
A	3.820	7.447
B	−5.076	−0.809
C	13.038	6.482
D	0.0801	−0.0656

[a] Planes are of the form $Ax + By + Cz - D = 0$ referred to monoclinic coordinates: see W. C. Hamilton, *Acta Crystallogr.*, 14, 185 (1961).

and octahedral hexafluorophosphate anions. The shortest Pt···Pt separation is 8.480 Å along the *a* axis. A stereoscopic packing diagram is shown in Figure 1. Since the metal atom of the cation is located at a crystallographic inversion center, there are only two crystallographically independent metal–carbon bonds and the inner coordination sphere is rigorously planar. The two metal–carbon bonds are equivalent and their mean value is 2.0466 (6) Å; the angle formed by these two bonds is 88.8 (3)° so the metal coordination deviates only slightly from being perfectly square. Bond distances and angles for the structure are given in Tables II and III. Figure 2 presents a perspective view of the square-planar cation. All intermolecular contacts appear normal and are therefore not tabulated.

The carbene ligands in the structure adopt the amphi configuration, IIc, with two stereochemically different methyl groups. The ligands are planar, and the best least-squares planes for carbene moieties are given in Table IV. The carbene carbon atoms are each bonded to two nitrogens and they exhibit sp^2 hybridization (the sum of the angles about each carbene center averages 360.00 (1)°). The four independent C(carbene)–N bonds are equivalent with an average length of 1.310 (3) Å. The significance of this value in stabilizing the carbene ligands is discussed below.

The Pt–C–N bond angles are significantly larger than the N–C–N angles. In actuality the four Pt–C–N angles comprise two sets, one in which the methyl group bonded to N is in an axial position relative to the coordination plane and one in

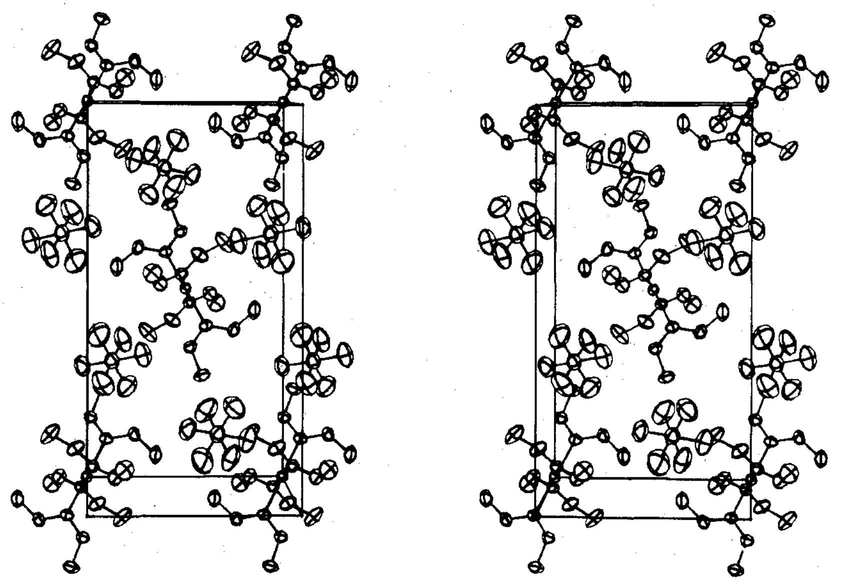


Figure 1. Stereoscopic view of the packing in $[Pt(C(NHMe)_2)_4](PF_6)_2$. The orientation is such that the *b* axis is horizontal and the *c* axis vertical.

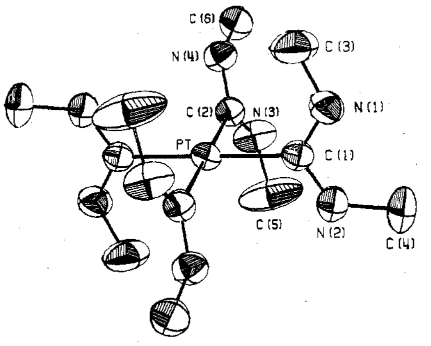


Figure 2. Perspective view of the $Pt(C(NHMe)_2)_4^{2+}$ cation. The thermal ellipsoids enclose 50% probability distributions.

which it is equatorial. The mean value for the former, which involves N(1) and N(3), is 123.9 (4)°, while that for the latter involving N(2) and N(4) is 120.0 (3)°. Figure 2 clearly shows that the axial methyl groups, C(3) and C(5), are directed slightly inward toward the metal. Minimization of nonbonded interactions between the hydrogen atoms of these methyl groups and between them and the Pt(II) ion would be expected to result in enlargement of the Pt–C–N bond angles involving their respective nitrogen atoms, and this is precisely what is observed.

Although the carbene ligands are oriented so that the complex has nearly C_{2h} symmetry, it deviates from this symmetry by torsional movement of the carbene ligands about the metal–carbene bonds. Thus the planes of the ligands are not normal to the metal coordination plane, which is described by the equation $0.661x + 8.100y - 8.040z = 0$ (plane referred to monoclinic coordinates), but form dihedral angles with the coordination plane of 81.8 (4) and 77.1 (3)°, respectively for ligands 1 and 2. The directions of the torsional distortions are such that interactions between the axial methyl protons of C(3) and C(5) are reduced. The symmetry of the cation is thus reduced to C_i which is crystallographically required. To within experimental significance that Pt atom lies in the planes of the carbene ligands, the displacement from the planes being 0.08 (3) Å from the plane of ligand 1 and 0.07 (3) Å from the plane of ligand 2.

The nitrogen to methyl carbon bond lengths have an average value of 1.467 (8) Å. It should be noted, however, that the large anisotropy shown by C(5) (see Table V) leads to a shortening of the N(3)–C(5) bond. The mean value for the other three N–C(methyl) bonds is 1.473 (7) Å. If a riding model[20] is used to correct the bond lengths for thermal motion (Table II) the N(3)–C(5) bond shows the largest correction (0.06 Å compared to 0.01–0.03 Å for the other N–C bonds).

Table V. Root-Mean-Square Amplitudes of Vibration, Å

Atom	Min	Intermed	Max
Pt	0.1743 (9)	0.1944 (9)	0.2229 (9)
P	0.245 (3)	0.248 (3)	0.308 (3)
F(1)	0.226 (8)	0.313 (7)	0.488 (9)
F(2)	0.251 (7)	0.287 (8)	0.489 (9)
F(3)	0.235 (7)	0.309 (7)	0.431 (8)
F(4)	0.258 (7)	0.340 (9)	0.514 (11)
F(5)	0.307 (9)	0.330 (8)	0.489 (10)
F(6)	0.265 (9)	0.413 (10)	0.604 (14)
N(1)	0.214 (9)	0.240 (8)	0.324 (9)
N(2)	0.223 (8)	0.246 (9)	0.295 (9)
N(3)	0.189 (9)	0.237 (8)	0.348 (9)
N(4)	0.195 (7)	0.231 (9)	0.271 (7)
C(1)	0.198 (7)	0.221 (10)	0.230 (9)
C(2)	0.192 (8)	0.220 (8)	0.237 (9)
C(3)	0.215 (12)	0.282 (11)	0.420 (15)
C(4)	0.207 (11)	0.324 (13)	0.364 (13)
C(5)	0.209 (12)	0.249 (11)	0.526 (18)
C(6)	0.191 (10)	0.263 (10)	0.310 (11)

The hexafluorophosphate anion has the expected octahedral geometry. As in other structures containing this anion,[21-25] the fluorine atoms show a large amount of anisotropic thermal motion, but there is no evidence for disorder. The average P–F bond length is 1.558 (12) Å; however, the bond to F(6) shows considerable shortening as a result of the particularly large anisotropic motion of F(6). The average value for the other five P–F bonds is 1.568 (8) Å. Application of a riding correction leads to an elongation of 0.135 Å in the P–F(6) bond as compared with lengthenings of 0.038–0.056 Å for the other P–F bonds.

Electronic Absorption Spectra

The platinum- and palladium-tetrakis(bis(methylamino)carbene) complexes exhibit similar absorption spectra. For $Pt(C(NHMe)_2)_4^{2+}$ the principal features of the spectrum appear at 40 000 cm^{-1} (log ϵ = 3.8), 43 860 (log ϵ = 4.1), and 50 760 cm^{-1} (log ϵ = 4.6), whereas for the Pd analogue these features are found at 39 200 cm^{-1} (sh, log ϵ = 2.7), 48 000 cm^{-1} (sh, log ϵ = 3.9), and >52 000 cm^{-1} (log ϵ = ~4.2). The spectra of these complexes do not exhibit well-resolved bands, as do those of the $M(CNMe)_4^{2+}$ systems,[26] and thus detailed assignments of the observed transitions are precluded, although they probably include d → π^* charge transfers.

Discussion of Results

The structural study shows that the cationic tetracarbene complex $[Pt(C(NHMe)_2)]^{2+}$ possesses a square-planar coordination geometry with the carbene ligands in the amphi configuration. That the carbene ligands must adopt the amphi configuration in the present structure results from an interplay of several factors. First, stabilization of the carbene center by resonance structure Ic leads to a coplanar NCN moiety in which each atom has sp^2 hybridization. Second, minimization of nonbonded repulsions between methyl groups within each carbene ligand eliminates the anti configuration IIb as a preferred arrangement. Last, nonbonded repulsions between methyl groups on different carbene ligands rule out the possibility of more than two methyls occupying axial positions on either side of the coordination plane. Thus, the amphi configuration must be adopted for all of the ligands.

The orientation of the carbene ligands yields a structure of nearly ideal C_{2h} symmetry, which was one of the originally proposed geometries.[6] A closely related structure, which was also proposed, differs from the above arrangement in having two cis carbene ligands rotated by 180°, giving rise to a structure having D_{2d} molecular symmetry. This structure also appears to minimize intra- and intercarbene nonbonded repulsions. The reasons for the complex adopting the observed structure over the arrangement of D_{2d} symmetry are unclear. A recent report of the structure of the related gold(III)–bis(carbene) complex $[AuI_2(C(NH\text{-}p\text{-}C_6H_4Me)_2)_2](ClO_4)$[27] further obscures understanding the nonbonded interactions between carbene ligands in square-planar complexes, since the report is unclear about the configuration of the carbene ligands. A drawing indicates the amphi arrangement for each carbene moiety but with both axial *p*-tolyl groups on the same side of the coordination plane.[27] Significant steric interactions would therefore be anticipated.

The structure reported here represents the first example of a transition metal complex containing only ligands of the resonance-stabilized carbene type. Mercury compounds containing similar ligands have been obtained,[28] and the crystal structure of the gold(III)–tetrazolato complex, $Au(CN_4C_3H_7)_4^-$, has been reported.[29a] The gold complex is somewhat analogous to the system described here. In that structure, the Au–C bonds are single bonds, and the distances within the tetrazole rings are such that the five-membered rings may be considered to be aromatic. Recently, Lappert and coworkers[29b] have reported the structure of a neutral tetrakis(carbene) complex obtained from the reaction of $RuCl_2(PPh_3)_2$ with an electron-rich olefin. The complex $RuCl_2(CN(Et)C_2H_4N(Et))_4$ exhibits a tetragonal structure in which the coordination geometry is octahedral and the carbene ligands adopt a propeller-like arrangement relative to the equatorial plane of the structure.[29b]

The question of the best way to describe the bonding in $Pt(C(NHMe)_2)_4^{2+}$ can be answered in part by a consideration of the Pt–C and C–N distances. To date, there have been a number of structural studies of platinum(II)–carbene complexes reported.[25,30-32] The metal–carbene distance reported in the present structure is in good agreement with the previously reported values of 2.058 (7) Å in *trans*-$Pt(CNMe)_2(C(NHMe)(SEt))_2$,[25] 2.00 (3) Å in *trans*-$PtCl_2(C(NPhCH_2)_2)(PEt_3)$,[32a] 2.079 (13) Å in *trans*-$Pt(Me)(C(Me)(NHMe))(PMe_2Ph)_2$,[32b] and 2.08 (2) Å in $AuI_2(C(NH\text{-}p\text{-}tol)_2)_2^+$;[27] however, it is slightly longer than the value of 1.96 (2) Å in *cis*-$PtCl_2(C(NHPh)(OEt))(PEt_3)$.[30] In the chelating dicarbene complex $Pt(CNMe)_2(C_4H_8N_4Me)^+$,[31] the Pt–C(carbene) distances are 1.95 (2) and 2.06 (3) Å.

In contrast to the above values, the metal–carbon distances in platinum–carbonyl systems are shorter, 1.74 (4) Å being found in *trans*-$PtCl_2(CO)(ONC_6H_4OMe)$[33] and 1.78 Å in *trans*-$[PtCl(CO)(PEt_3)_2](BF_4)$.[34] In platinum isocyanide structures, the Pt–C distances range from values significantly shorter than the platinum–carbene distances to values in near agreement with them. For example in *cis*-$PtCl_2(CNEt)(PEt_2Ph)$,[35] the metal–carbon bond length is 1.83 (4) Å, while in *cis*-$PtCl_2(CNPh)_2$[36] it is 1.896 (16) Å, and in the mixed isocyanide–carbene compounds *trans*-$Pt(CNMe)_2(C(NHMe)(SEt))_2^{2+}$[25] and *cis*-$Pt(CNMe)_2(C_4H_8N_4Me)^+$[31] the distances are 1.968 (9) and 1.96 (2) Å, respectively.

These results are interpreted to mean that whereas metal→ligand π back-bonding is highly significant in platinum carbonyls, it is less important in platinum(II)–isocyanide systems and is virtually inoperative as a means of stabilizing the carbene ligand in platinum–carbene complexes. This view is supported using arguments based on covalent radii. If values of 0.77, 0.73, and 0.71 Å are taken as the single-bond covalent radii for sp^3-, sp^2-, and sp-hybridized carbon atoms, respectively,[37] and if a value of 2.08 Å is assumed for a Pt–C(sp^3) σ bond based on results from known crystal structures,[38-42] then Pt–C bond lengths of 2.04 and 2.02 Å are predicted for Pt–C(sp^2) and Pt–C(sp) bonds, respectively. While the observed platinum–carbonyl and platinum–isocyanide distances are shorter than the predicted 2.02-Å value, the Pt–C distance of 2.0466 (6) Å, which we find in the present structure, agrees with the 2.04-Å predicted value. Hence, the metal–carbene bond in the present structure is a simple σ bond with the carbene ligand acting as a pure σ donor, and resonance structure Ib is deemed unimportant in stabilizing the carbene ligand. This interpretation of the diaminocarbene ligand as a good σ donor (and a weak π acceptor) is in complete accord with recent XPS data on metal–carbene complexes by Brant, Enemark, and Balch.[43]

The principal means of stabilizing the bis(methylamino)carbene ligands in $Pt(C(NHMe)_2)_4^{2+}$ occurs by $p_\pi \rightarrow p_\pi$ dative bonding as shown in resonance structure Ic. This is evidenced by the short C–N distance of 1.310 (3) Å indicative of a high degree of double-bond character. For comparison, the analogous C–N bond length in organic amides is 1.35 Å. The present value of 1.310 (3) Å agrees closely with the corresponding bond length in other aminocarbene complexes,[4,5] although it is slightly longer than the 1.266 (15) Å value found in *trans*-$Pt(Me)(C(Me)(NHMe))(PMe_2Ph)$[32b] which has only one nitrogen serving as the stabilizing heteroatom. The double-bond character in the carbene–heteroatom bond manifests itself in a large barrier to rotation about that bond, thus helping to explain why the axial and equatorial methyl groups maintain their stereochemical integrity in solution at temperatures up to 90 °C.[6]

An unusual aspect of the tetrakis(carbene) complexes $M(C(NHMe)_2)_4^{2+}$ (M = Pt, Pd) is their stability and inertness to reaction relative to that reported for bis(carbene)gold(I) complexes. This is best illustrated by unsuccessful attempts to oxidize the platinum- and palladium–tetrakis(carbene) complexes with halogens,[44] whereas oxidation of the bis(carbene)gold(I) complexes occurs readily.[45-48] The structural results can be used to rationalize the observed chemical inertness. The Pt(II) ion is coordinated by σ-bonding carbene ligands which are resonance stabilized by π donation from the nitrogen heteroatoms. The carbene ligands adopt the amphi configuration, yielding two axial methyl groups above and below the coordination plane. These methyl groups, which Figure 2 reveals to be tilted toward the metal center, then serve to protect the Pt(II) ion from axial attack by various reagents. The Au(I) complexes, possessing only two ligands, do not afford sufficient protection of the metal center by alkyl groups to prevent halogen oxidation.

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Registry No. $[Pt(C(NHMe)_2)_4](PF_6)_2$, 38888-41-4; $[Pd(C(NHMe)_2)_4](PF_6)_2$, 39152-99-3.

Supplementary Material Available: Listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead.

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(13) The crystal was bounded by eight faces, 011, 01$\bar{1}$, 100, 014, and their inverses. For purposes of the absorption correction the crystal origin was chosen as the intersection of the 100, 01$\bar{1}$, and 0$\bar{1}\bar{1}$ faces. The distances to the other faces were $d_{01\bar{1}} = 0.096$, $d_{011} = 0.096$, $d_{0\bar{1}\bar{4}} = 0.057$, $d_{014} = 0.098$, and $d_{\bar{1}00} = 0.394$ mm.
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