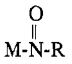
angles are found, for example, in the coordinated phenyldiazonium cation of $HB(C_3N_2H_3)_3Mo(CO)_2N_2C_6H_5$ (~20°)[37] and *trans*-azobenzene (~17°).[38] The nonbonded contact between the hydrogen atom bound to carbon atom 5 and the nitrosyl oxygen atom is 2.75 Å in length. Examination of molecular models shows that approach of additional ligands perpendicular to the coordination plane is effectively blocked by the phenyl ring, in particular by the hydrogen atom bound to C(6). This hydrogen atom makes an estimated 2.69-Å nonbonded contact with the Pd atom.

The monodentate coordination of the nitrosobenzene contrasts with the involvement of both N and O atoms in metal coordination in bis[tricarbonyl(3-chloro-2-methylnitrosobenzene)iron].[5] The configuration of the bonded RNO group in the iron dimer differs substantially from that which we observe. The principal variations are a longer N-O distance of 1.40 (1) Å, a smaller C-N-O angle of 112.2 (7)°, and a greater torsional angle (20.2°) about the N-C bond. The distinction between N and O bonding in metal-RNO complexes has in general been difficult to draw. This difficulty stems in part from uncertainty as to the assignment of vibrational spectra of the aromatic nitroso compounds themselves.[39,40] O bonding has been favored in some instances[9,10] and could well prevail in complexes of "hard" metal ions. Authentic examples of O-bonded arylnitroso ligands would be useful in formulating spectroscopic criteria for distinguishing between the various bonding possibilities.

Demonstration of this mode of metal coordination for nitrosobenzene gives rise to the interesting question of whether this type of



$$\overset{O}{\overset{\|}{M\text{-}N\text{-}R}}$$

linkage could be obtained by nucleophilic attack on a coordinated nitrosyl group or by a nitrosyl insertion reaction, analogous to the well-known reactions of metal-coordinated carbonyl groups. Nucleophilic attack of hydroxide[15b] or methoxide[16] ion on coordinated NO is known, as are a few reactions in which NO is inserted into a metal-carbon bond.[41,42] However, to date these reactions have not been shown to yield simple metal-arylnitroso complexes of the sort found here.

Registry No. *trans*-$(C_6H_5NO)_2PdCl_2$, 37680-12-9.

Acknowledgment. Support of this work by the National Science Foundation (Grant GP-20603) is gratefully acknowledged.

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Addition of Ethanethiol to Coordinated Isocyanides. Structure of *trans*-Bis(methyl isocyanide)bis(methylamino(thioethoxy)carbene)platinum(II) Hexafluorophosphate, $[Pt(CH_3NC)_2\{C(NHCH_3)(SCH_2CH_3)\}_2][PF_6]_2$

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Received August 23, 1972

The structure of *trans*-bis(methyl isocyanide)bis(methylamino(thioethoxy)carbene)platinum(II) hexafluorophosphate, $[Pt(CH_3NC)_2\{C(NHCH_3)(SCH_2CH_3)\}_2][PF_6]_2$, has been determined from three-dimensional X-ray diffraction data collected by counter methods. The compound crystallizes in the triclinic space group $P\bar{1}$ with one molecule in a cell of dimensions $a = 8.913$ (6), $b = 10.526$ (6), and $c = 7.750$ (5) Å with $\alpha = 94.77$ (3), $\beta = 88.30$ (3), and $\gamma = 117.20$ (3)°. The observed and calculated densities are 1.98 (2) and 1.980 (1) g/cm³, respectively. Full-matrix least-squares refinement has resulted in $R = 0.039$ for the 2198 data with $F_o^2 \geqslant 3\sigma(F_o^2)$. The coordination about the Pt atom is square planar and the cation is required to have $\bar{1}$-C_i symmetry. The Pt-C(carbene) distance is 2.058 (7) Å and the Pt-$CNCH_3$ distance is 1.968 (9) Å. The C-N and C-S distances of the carbene ligand are 1.30 (1) and 1.681 (8) Å, respectively. The structural trans influence of carbene ligands is shown to be similar to that of phosphine ligands.

Introduction

A number of metal "carbene"[1,2] complexes resulting from addition reactions of coordinated isocyanide ligands have been structurally characterized by single-crystal X-ray diffraction.[3-8] Several of these complexes[4-8] involve chelative addition to two cis isocyanide ligands to give "dicarbene" com-

(1) "Carbene" nomenclature has become generally used for C(R)R′ ligands derived from reactions of coordinated carbonyls and isocyanides. Since extensive electron delocalization is possible in these ligands, they are not simple carbenes but fall into the category of resonance-stabilized carbenes.[2]

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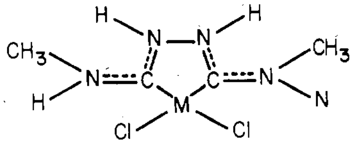

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plexes such as **1**.[4] There is evidence[3,4,9-11] that carbene ligands exhibit a trans influence similar to phosphines in four-coordinate complexes of Pt(II). To our knowledge, however, the structure of a trans dicarbene complex has not been reported. In order to better assess the trans influence of carbene ligands and to compare cis and trans dicarbene complexes, we have determined the structure of the trans complex resulting from the addition of 2 mol of ethanethiol to tetrakis(methyl isocyanide)platinum(II).[12] This complex was of further interest because at the time that this work was begun no structural results were available for thiocarbenes. Subsequently the structure of the methyl(phenylthio)carbene complex, $Cr(CO)_5\{C(CH_3)(SC_6H_5)\}$, has been reported.[13]

Experimental Section

A sample of $[Pt(CH_3NC)_2\{C(NHCH_3)(SCH_2CH_3)\}_2][PF_6]_2$ was kindly supplied by Drs. A. L. Balch and J. S. Miller. Crystals suitable for X-ray analysis were obtained from the sample as received and recrystallization was not necessary. Preliminary precession photographs (Mo Kα) suggested that the crystals were triclinic. Neither a Delaunay reduction nor a systematic search of reciprocal space by precession photography revealed any additional symmetry elements. Successful solution and refinement of the structure confirmed the choice of space group as $P\bar{1}$.

A crystal was chosen which had ω scan widths of <0.10° (peak widths at half-heights at a takeoff angle of 0.7°). The crystal had dimensions 0.42 × 0.16 × 0.15 mm. Eleven reflections with 2θ in the range 15–27° were manually centered on the Mo $K\bar{\alpha}$ peak (λ 0.71069 Å). A least-squares refinement of the setting angles for the eleven reflections gave unit cell parameters at 23 ± 2° of $a = 8.913$ (6), $b = 10.526$ (6), and $c = 7.750$ (5) Å with $\alpha = 94.77$ (3), $\beta = 88.30$ (3), and $\gamma = 117.20$ (3)°. All results and discussion are based on this triclinic cell. The reduced right-handed triclinic cell has parameters $a = 8.91$, $b = 7.75$, and $c = 12.54$ Å; $\alpha = 123.2$, $\beta = 111.5$, and $\gamma = 91.7°$. The reduced cell is related to the working cell by $a_r = a$, $b_r = -c$, $c_r = b + c$. The density of the compound was measured by the gradient column technique using CH_3I and CCl_4 solutions and found to be 1.98 (2) g/cm³. The calculated density assuming one molecule per cell is 1.980 (1) g/cm³.

An incident beam monochromator equipped with a graphite crystal was used to obtain Mo Kα radiation. The θ–2θ axis of the monochromator was perpendicular to the θ–2θ axis of the diffractometer. Data were collected using the θ–2θ scan technique and a scan range from $2\theta_{\text{MoK}\alpha_1} - 0.7°$ to $2\theta_{\text{MoK}\alpha_2} + 0.7°$ at a takeoff angle of 1.7°. The scan rate was 2°/min and background measurements of 10 sec were taken at each end of the scan. The pulse height analyzer was set to admit ~90% of the Mo Kα peak and the scintillation counter was 24 cm from the crystal. During data collection the intensities of three reflections were monitored every 100 reflections. There was no systematic change in the intensity of the three standards. A total of 2413 reflections were collected with $2\theta \leqslant 50°$. The data were reduced to F^2 and $\sigma(F^2)$ by procedures similar to those previously described.[14-16,17] The polarization correction used was $P = 0.5(\cos^2 2\theta_m + \cos^2 2\theta)$ where θ_m is the Bragg angle of the monochromator crystal and θ is the Bragg angle of the observed reflection. Standard deviations were assigned to the intensities by the formula

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

where CT is the total integrated peak count obtained in time t_c and B_1 and B_2 are the background counts each obtained in time t_b; I is the intensity and p was taken as 0.04.

The absorption coefficient for the compound for Mo Kα radiation is 60.49 cm⁻¹. The faces of the crystal were identified as $\{001\}$, $\{010\}$, $\{4\bar{3}0\}$, and $(01\bar{2})$ and the crystal was carefully measured. Sample calculations showed that the absorption correction ranged from 2.15 to 2.61 and the data were corrected for absorption.[16,17]

Solution and Refinement

With one molecule in the cell, space group $P\bar{1}$ requires that the Pt atom be located on an inversion center. An electron density map phased by the structure factors calculated for Pt at the origin revealed all of the structure except the ethyl group. One cycle of least-squares refinement assuming isotropic thermal parameters resulted in $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.187$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2} = 0.230$. A difference electron density map located the C atoms of the ethyl group.

Refinement of the structure was based upon F_o, with $\Sigma w(|F_o| - |F_c|)^2$ being minimized. Weights were evaluated by $w = 4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for Pt were from Cromer and Waber;[18] the factors for S, P, C, N, and F were from the usual tabulation.[19] The effects of anomalous dispersion for Pt, P, and S were included in F_c[20] using Cromer's[21] values for $\Delta f'$ and $\Delta f''$. Four cycles of least-squares refinement assigning the ethyl group isotropic thermal parameters and the other atoms anisotropic thermal parameters and treating the hexafluorophosphate anion as a rigid group gave $R_1 = 0.063$ and $R_2 = 0.087$. A difference map revealed large residual electron density in the hexafluorophosphate anion and the ethyl group. Attempts to fit the density near the PF_6^- group to a twofold disorder were not successful. A difference electron density map based upon a structure factor calculation from which the ethyl group had been omitted revealed a region of high electron density ~1 Å from C_5, the methylene C atom of the ethyl group. A disordered C_5 atom was assumed, and an occupancy factor was included as one of the least-squares variables. Five additional cycles of refinement in space group $P\bar{1}$ with all atoms assigned individual positional parameters and anisotropic thermal parameters resulted in convergence with $R_1 = 0.039$ and $R_2 = 0.048$ for the 2198 data with $F_o^2 \geqslant 3\sigma(F_o^2)$. The occupancy factor for C_{5a} was 0.33 (3). The standard deviation of an observation of unit weight was 1.81.

The implied disorder of the methylene group over two conformations raised the possibility that the true space group was $P1$ rather than $P\bar{1}$. Structure factor calculations in space group $P1$ suggested several reflections for which intensity differences between Friedel pairs could be as large as 10%. The intensities of these Friedel pairs were measured but no significant differences could be observed. It was concluded that $P\bar{1}$ is the preferred space group.

A final difference density map had a maximum residual density of 1.0 e/Å³ near the disordered ethyl group. All other peaks were less than 0.75 e/Å³. Hydrogen atoms could not be located in this map. An analysis of the weighting scheme as a function of $|F_o|$, $(\sin\theta)/\lambda$, and the indices showed that $w(\Delta F)^2$ decreased with increasing $(\sin\theta)/\lambda$. This is not surprising considering the disorder of the ethyl group and the inadequacy of individual anisotropic thermal parameters for describing the motion of the PF_6^- ion. All correlation coefficients between parameters of the ethyl group or the PF_6^- ion and other variables in the least-squares refinement had absolute values

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Table I. Final Atomic Parameters for *trans*-$[Pt(CNCH_3)_2\{C(CHNH_3)(SC_2H_5)\}_2][PF_6]_2$

Atom	x^a	y	z	$10^4\beta_{11}{}^b$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Pt	0	0	0	190 (1)	143 (1)	201 (1)	85 (1)	79 (1)	45 (1)
S	0.1500 (5)	0.1880 (5)	−0.3418 (6)	455 (8)	549 (10)	626 (11)	378 (8)	353 (9)	457 (10)
P	0.3595 (4)	−0.2804 (3)	−0.1781 (3)	316 (5)	201 (4)	273 (5)	107 (4)	19 (4)	1 (3)
N_1	0.1774 (10)	0.2973 (9)	0.2007 (10)	322 (16)	165 (11)	254 (14)	115 (11)	77 (12)	39 (10)
N_2	0.3010 (8)	0.0650 (8)	−0.2087 (8)	195 (11)	208 (10)	221 (12)	103 (9)	76 (9)	36 (9)
C_1	0.1105 (10)	0.1870 (9)	0.1340 (10)	253 (15)	154 (11)	208 (14)	104 (11)	85 (12)	33 (10)
C_2	0.2697 (20)	0.4425 (11)	0.2777 (17)	542 (38)	153 (13)	368 (28)	90 (18)	66 (26)	−15 (15)
C_3	0.1680 (9)	0.0857 (8)	−0.1965 (10)	211 (13)	162 (10)	217 (14)	92 (10)	66 (11)	46 (9)
C_4	0.4372 (11)	0.1261 (12)	−0.3355 (13)	221 (15)	267 (17)	310 (20)	107 (13)	138 (14)	57 (14)
$C_{5a}{}^c$	−0.0842 (32)	0.1507 (37)	−0.3465 (72)	131 (43)	174 (49)	189 (89)	46 (35)	−23 (38)	73 (42)
$C_{5b}{}^c$	−0.0307 (44)	0.2186 (51)	−0.2513 (47)	355 (53)	482 (69)	277 (59)	282 (57)	62 (52)	133 (62)
C_6	−0.0742 (19)	0.2906 (19)	−0.3420 (33)	303 (28)	300 (28)	1051 (90)	142 (24)	38 (41)	110 (40)
F_1	0.1860 (15)	−0.3877 (15)	−0.1365 (23)	465 (27)	477 (26)	1157 (67)	−111 (21)	297 (34)	−211 (34)
F_2	0.4435 (17)	−0.3310 (11)	−0.0450 (12)	917 (42)	401 (19)	426 (21)	391 (25)	−7 (23)	94 (16)
F_3	0.5467 (12)	−0.1627 (11)	−0.2173 (14)	434 (21)	386 (18)	605 (28)	104 (16)	127 (19)	129 (18)
F_4	0.3054 (19)	−0.2112 (14)	−0.3180 (13)	998 (49)	571 (29)	468 (24)	533 (34)	−218 (29)	−62 (21)
F_5	0.3510 (12)	−0.1645 (9)	−0.0371 (10)	599 (24)	318 (13)	368 (16)	250 (15)	53 (16)	−20 (12)
F_6	0.3694 (16)	−0.3855 (11)	−0.3243 (12)	898 (42)	420 (20)	453 (23)	374 (25)	−54 (25)	−177 (18)

[a] x, y, and z are fractional triclinic coordinates. The standard deviation of the least significant figure is given in parentheses. [b] Anisotropic thermal parameters are in the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [c] C_{5a} and C_{5b} are the two crystallographically independent positions for the disordered methylene carbon atom. The occupancy factor of the C_{5a} position is 0.33 (3).

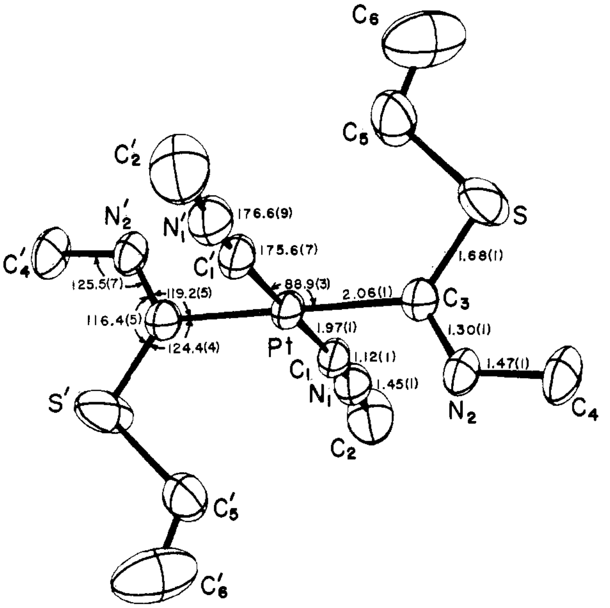

Figure 1. Perspective view of the $[Pt(CNCH_3)_2\{C(NHCH_3)(SC_2H_5)\}_2]^{2+}$ cation. For clarity, only C_{5b} has been shown in position C_5. Primed atoms are related to unprimed atoms by a center of inversion at the Pt atom. Atoms are drawn to enclose 30% of the probability distribution.

Table II. Interatomic Distances (Å) and Angles (deg)

Atoms	Distance		Atoms	Angle	
$Pt-C_1$	1.968 (9)		C_3-Pt-C_1'	88.8 (3)	
$Pt-C_3$	2.058 (7)		$Pt-C_1-N_1$	175.6 (7)	
C_1-N_1	1.120 (10)		$C_1-N_1-C_2$	176.6 (9)	
N_1-C_2	1.448 (14)		$Pt-C_3-N_2$	119.2 (5)	
C_3-N_2	1.300 (10)		$Pt-C_3-S$	124.4 (4)	
C_3-S	1.681 (8)		N_2-C_3-S	116.4 (5)	
N_2-C_4	1.474 (10)		$C_3-N_2-C_4$	125.5 (7)	
$S-C_{5a}{}^a$	1.94 (2)	1.92 (2)[b]	C_3-S-C_{5a}	107.6 (10)	105 (2)[b]
$S-C_{5b}$	1.89 (2)		C_3-S-C_{5b}	102.1 (10)	
$C_{5a}-C_6$	1.43 (4)	1.34 (8)[b]	$S-C_{5a}-C_6$	104 (2)	109 (5)[b]
$C_{5b}-C_6$	1.26 (2)		$S-C_{5b}-C_6$	114 (2)	
$P-F_1$	1.48 (1)	1.56 (4)[b]			
$P-F_2$	1.55 (1)				
$P-F_3$	1.60 (1)				
$P-F_4$	1.56 (1)				
$P-F_5$	1.60 (1)				
$P-F_6$	1.55 (1)				

[a] C_{5a} and C_{5b} are the two crystallographically independent positions of the disordered methylene carbon atom. [b] For the averages of chemically equivalent distances and angles $\hat{\sigma}(\bar{x}) = (\Sigma_i(x_i - \bar{x})^2/n)^{1/2}$, where x_i is the value of an individual determination, $\bar{x}$ is the arithmetic mean, and n is the number of observations. See W. C. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., 1964, p 43.

less than 0.5. Since neither the PF_6^- ion nor the ethyl group were the principal points of interest, the refinement was terminated at this point. A final structure factor calculation on all 2271 unique data gave $R_1 = 0.041$ and $R_2 = 0.050$.

Final atomic parameters appear in Table I. A list of $10|F_o|$ and $10|F_c|$ is available.[22]

Description and Discussion

The numbering scheme and a perspective view of the cation are shown in Figure 1, and a stereoview of the unit cell is shown in Figure 2. The sizes and shapes of the atoms are determined by the vibrational ellipsoids associated with the final anisotropic thermal parameters and by the perspective view. Interatomic distances and angles computed from the final atomic parameters of Table I appear in Figure 1 and Table II. The estimated standard deviations for the distances and angles were derived from the inverse least-squares matrix for the final refinement.

From Figure 1 it is apparent that the cation results from the addition of two molecules of ethanethiol to two trans isocyanide ligands of a $Pt(CNCH_3)_4{}^{2+}$ ion to produce a trans dicarbene complex. The space group imposes $\bar{1}$ symmetry on the cation and the coordination about the Pt atom is nearly square planar. The $Pt-C_1$ distance of 1.968 (9) Å is similar to the average $Pt-CNCH_3$ distance of 1.96 (2) Å found in $(C_5H_{11}N_4)Pt(CNCH_3)_2{}^+$ [8] but longer than the distances of 1.83 (4) and 1.90 (2) Å found in *cis*-$PtCl_2(CNC_2H_5)[P(C_2H_5)_2(C_6H_5)]$ and *cis*-$PtCl_2(CNC_6H_5)_2$, respectively.[23] The $Pt-C_3$ distance of 2.058 (7) Å compares with values of 1.95 to 2.06 Å found for other $Pt-C(sp^2)$ distances.[3,8,10]

The geometry about atom C_3 is essentially planar, as has been found in other metal-carbene complexes.[3-8,10,13,24] Atoms C_3, C_4, N_2, and S describe the weighted least-squares

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(22) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth 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-73-540.

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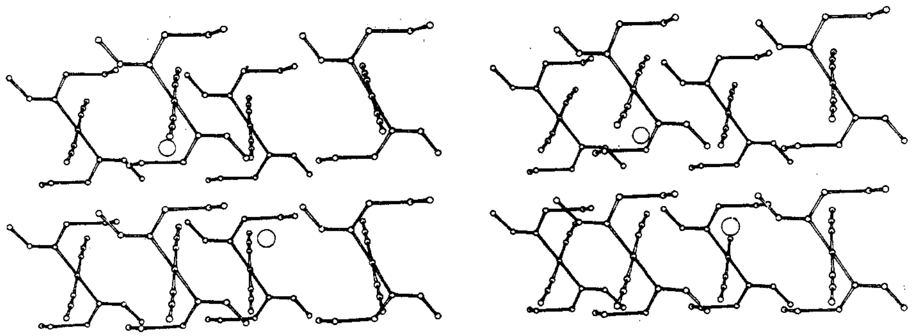
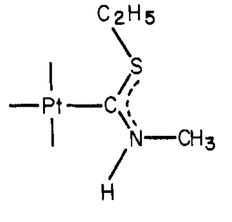


Figure 2. Stereopair showing the crystal structure of $[Pt(CNCH_3)_2\{C(NHCH_3)(SC_2H_5)\}_2][PF_6]_2$. The PF_6^- ions are represented by large spheres and the Pt atoms occur at the corners of the cell. The view is normal to the *ac* plane with the origin in the lower left corner; *a* is horizontal, *b* goes obliquely into the page, and *c* is nearly vertical.

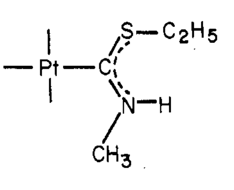
plane $1.32x + 6.44y + 4.43z - 0.10 = 0$ (triclinic coordinates), and all four atoms are within 0.01 Å of this plane. Atoms Pt, C_{5a}, C_{5b}, and C_6 are, respectively, 0.10, −0.78, 0.15, and 0.16 Å from this plane.

Figures 1 and 2 show that the plane of the carbene ligand is nearly perpendicular to the coordination plane of the platinum defined by C_1, Pt, and C_3. The dihedral angle between these planes is 81.5°. The C_3-S distance of 1.681 (8) Å agrees with the C-S distance of 1.690 (3) Å found in coordinated methyl(phenylthio)carbene.[13] Both of these distances are considerably shorter than the single-bond value of 1.801 Å found in dimethyl sulfide[25] but agree well with the C-S double-bond distances observed in 1-thiocarbamoylimidazolidine-2-thione[26] and tetraethylthiuram.[27] The C_3-N_2 distance of 1.30 (1) Å is indicative of multiple-bond character and is similar to the C-N distances found in a variety of aminocarbene complexes.[3-8,10,24a,c]

It has been pointed out previously[8,12] that diaminocarbene complexes can also be viewed as metalated amidinium ions. This interpretation is particularly useful for understanding the conformations of the ligands because the complexes exhibit the amphi configuration characteristic of amidinium ions.[28] If this analogy is applied to complexes of methylamino(thioethoxy)carbene, then two structures (**2**) are possible. Figure 1 shows that **2a** is the correct structure in the solid state. This conformation has also been observed in a phenylamino(ethoxy)carbene complex.[3]

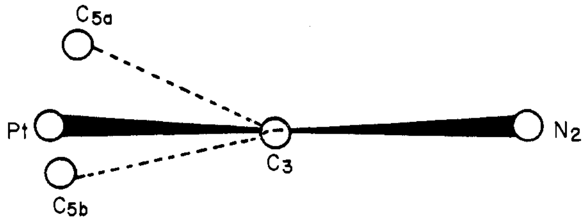


2a



2b

The finer details of the thioethoxy group are obscured by the torsional disorder of the methylene group about the C_3-S bond as shown schematically in **3**, a projection along the C_3-S bond. The torsional angle between C_{5a} and C_{5b} is 29°; the torsional angles between the Pt-C_3 bond and the C_{5a}-S and C_{5b}-S bonds are 19 and 10°, respectively. In the final refined model C_{5a} and C_{5b} are separated by 0.95 (3) Å with occupancies of 0.33 and 0.67, respectively. The shapes of the thermal ellipsoids for S, C_5, and C_6 are not unusual (Figure 1), but the principal root-mean-square amplitudes of vibration for S and C_6 are as large as 0.6 Å. In addition the average C_5-C_6 single bond distance of 1.34 (8) Å is abnormally short and poorly defined, suggesting that the description of the thioethoxy group is overly simple.



3

The PF_6^- ion has the expected octahedral geometry. The average P-F distance of 1.56 (4) Å agrees with values observed previously.[29]

One of the objectives of our structural investigations of carbene complexes of Pt(II) and Pd(II) has been to assess the structural trans influence of the -C(sp^2) group. Recent proton magnetic resonance (pmr) studies[11] of a series of *trans*-$[PtCH_3(L)\{P(CH_3)_2(C_6H_5)\}]^+$ complexes have shown that the coupling constants *J*(Pt-C-H) and *J*(Pt-P-C-H) are rather similar when L is a tertiary phosphine and when L is the carbene ligand $\overline{CH_2CH_2OC}CH_2$. These results have been interpreted as indicating that phosphines and carbenes have a similar trans influence in complexes of Pt(II).

Table III summarizes the structural data for several square-planar complexes of Pt(II) and Pd(II). In this table the structural trans influence of Cl is arbitrarily defined as zero. Thus, Δ(M-L) is the difference between an M-L distance with L′ trans to L and the distance with Cl trans to L. The upper section of the table examines the structural trans influence of various ligands upon M-Cl distances. It can be seen that both phosphines and carbenes lead to Δ(M-L) ≈ 0.06 Å, *i.e.*, M-Cl distances ~10σ longer than observed in *trans*-ML_2Cl_2 compounds. In marked contrast isocyanide ligands have no influence on the trans M-Cl distance. The middle section of the table presents similar results for M-P distances. Thus, the trans influence of -C(sp^2) on M-Cl and M-P distances support the hypothesis that carbenes are strongly σ-bonding ligands

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Table III. Structural Trans Influence in Pt(II) and Pd(II) Complexes

L′-M-L

Compound	L′	L	M-L, Å	Δ(M-L),[a] Å	Ref
$PtCl_4^{2-}$	Cl	Cl	2.308 (2)		*b*
$PdCl_4^{2-}$	Cl	Cl	2.313 (2)		*b*
trans-$Pt(P(C_2H_5)_3)\{C(NC_6H_5CH_2)_2\}Cl_2$	Cl	Cl	2.31 (1)		*c*
trans-$Pt(P(C_6H_5)_2(C_2H_5))_2HCl$	H	Cl	2.422 (9)	0.11	*d*
cis-$Pt(P(CH_3)_3)_2Cl_2$	P	Cl	2.376 (8)	0.07	*e*
cis-$Pt(P(C_2H_5)_3)\{C(NHC_6H_5)(OC_2H_5)\}Cl_2$	P	Cl	2.368 (7)	0.06	*f*
cis-$Pt(CNC_2H_5)[P(C_2H_5)_2(C_6H_5)]Cl_2$	P	Cl	2.390 (8)	0.08	*g*
	CNR	Cl	2.314 (10)	0.00	*g*
cis-$Pt(CNC_6H_5)_2Cl_2$	CNR	Cl	2.309 (5)	0.00	*g*
cis-$Pt(P(C_2H_5)_3)\{C(NHC_6H_5)(OC_2H_5)\}Cl_2$	$C(sp^2)$	Cl	2.365 (5)	0.06	*f*
$Pd(C_2N_4H_4(CH_3)_2)Cl_2$	$C(sp^2)$	Cl	2.387 (1)	0.08	*h*
cis-$Pt(P(CH_3)_3)_2Cl_2$	Cl	P	2.247 (7)		*e*
cis-$Pt(CNC_2H_5)[P(C_2H_5)_2(C_6H_5)]Cl_2$	Cl	P	2.244 (8)		*g*
trans-$Pt(P(C_2H_5)_3)_2Br_2$	P	P	2.315 (4)	0.07	*i*
$Pd(C_2N_4H_4(CH_3)_2)Cl_2$	Cl	$C(sp^2)$	1.948 (5)		*h*
cis-$Pt(P(C_2H_5)_3)\{C(NHC_6H_5)(OC_2H_5)\}Cl_2$	Cl	$C(sp^2)$	1.98 (2)		*f*
$Pt(CNCH_3)_2(C_5H_{11}N_4)^+$	$CNCH_3$	$C(sp^2)$	1.95 (2), 2.06 (3)	?	*j*
trans-$Pt(CNCH_3)_2\{C(NHCH_3)(SC_2H_5)\}_2^{2+}$	$C(sp^2)$	$C(sp^2)$	2.058 (7)	~0.10	*k*
trans-$Pt(P(C_2H_5)_3)\{C(NC_6H_5CH_2)_2\}Cl_2$	P	$C(sp^2)$	2.00 (3)	?	*c*

[a] The structural trans effect of Cl is arbitrarily defined as zero; Δ(M-L) is the difference between the M-L distance with L′ trans to L and the distance with Cl trans to L. [b] R. H. B. Mais, P. G. Owston, and A. M. Wood, *Acta Crystallogr., Sect. B*, 28, 393 (1972). [c] See ref 10. [d] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965). [e] G. G. Messmer, E. L. Amma, and J. A. Ibers, *ibid.*, 6, 725 (1967). [f] See ref 3. [g] See ref 23. [h] See ref 4. [i] G. G. Messmer and E. L. Amma, *Inorg. Chem.*, 5, 1775 (1966). [j] See ref 8. [k] This work.

with a trans influence similar to phosphines. The bottom section of Table III considers the susceptibility of M-C(sp^2) distances to the trans influence of other ligands. Here the results are less definitive because the errors on the Pt-C distances are rather large for three of the examples, but the two compounds whose M-C distances are well defined, $Pd(C_2N_4H_4(CH_3)_2)Cl_2$ (1) and *trans*-$[Pt(CNCH_3)_2\{C(NHCH_3)(SC_2H_5)_2\}_2]^{2+}$, do give Δ(M-L) ≈ 0.10 Å (14σ). Some caution is required in ascribing this difference solely to the susceptibility of M-C(sp^2) distances to trans influence because the carbene ligands in these two complexes are not identical. It has been shown that in the series of compounds $(CO)_5Cr\{CR(R')\}$ (where R = OMe, R′ = Ph; R = NHMe, R′ = Me; R = NEt_2, R′ = Me)[24] the metal-carbene bond length ranges from 2.04 to 2.16 Å.

Registry No. $[Pt(CH_3NC)_2\{C(NHCH_3)(SCH_2\text{-}CH_3)\}_2]\cdot(PF_6)_2$, 37668-70-5.

Acknowledgments. We thank Professor A. L. Balch for the sample and for several helpful discussions. We are grateful to the National Science Foundation for financial support and to the University of Arizona Computing Center for an allocation of computer time.

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Crystal Structure of Mercury(II) Hydroxide Fluoride

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Received April 13, 1972

Mercury(II) hydroxide fluoride, Hg(OH)F, crystallizes in the orthorhombic system, space group $P2_12_12_1$, with four formula units per unit cell. The unit cell dimensions are $a = 4.963 \pm 0.005$ Å, $b = 5.920 \pm 0.005$ Å, and $c = 6.857 \pm 0.005$ Å; the measured and calculated densities are 7.77 and 7.80 g/cm^3, respectively. The structure was solved from Patterson and electron density maps and refined by least-squares methods to a conventional R index of 0.091 for 222 independent, nonzero reflections collected by the use of equiinclination Weissenberg photographs. The mercury atom is surrounded by three fluorine and three oxygen atoms in an irregular octahedral coordination. By sharing two opposite edges the octahedra form infinite columns along the c axis. These columns are linked by shared corners and by O-H· · ·F hydrogen bonds of length 2.76 ± 0.10 Å. The closest Hg-O distances of 2.06 ± 0.06 and 2.11 ± 0.06 Å occur within a column in the planar zigzag -O-Hg-O-Hg- chain. The compound may be conveniently described as polymeric mercurioxonium fluoride, $[Hg(OH)]_n^{n+},nF^-$.

Introduction

Mercury(II) hydroxide fluoride, Hg(OH)F, described for the first time by Djordjevic,[1] is the only known basic fluoride of this metal. At the same time all other basic mercury(II) halides are oxide halides defined by the general formula $Hg_nX_2O_{n-1}$, with n = 1.5, 3, 4, and 5, but with oxygen functioning differently in the various structures.[2,3] In

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