Table VIII. Hydrogen Bonds and Short Contacts in $[Ni(ATSC)_2X]^+X^-\cdot H_2O$ Salts, $X^- = NO_3^-$ and Cl^-

Bond D-H···A[a]	Position of A	D-H, Å	H···A, Å	D···A, Å	D-H···A, deg	Bond D-H···A[a]	Position of A	D-H, Å	H···A, Å	D···A, Å	D-H···A, deg
	(a) $NiCl_2(ATSC)_2\cdot H_2O$						(b) $Ni(NO_3)_2(ATSC)_2\cdot H_2O$				
NA2-H1···Cl2	B(00$\bar{1}$)	1.02	2.43	3.298 (5)	143	NA2-H1···OD1	B(00$\bar{1}$)	0.99	2.44	3.194	133
NA3-H2···Cl2	B(00$\bar{1}$)	0.92	2.35	3.230 (6)	162	NA2-H1···OD2	B(00$\bar{1}$)	0.99	2.45	3.190	131
NA3-H3···Ow	D($\bar{1}$00)	0.83	2.17	2.927 (9)	152	NA3-H2···OD1	B(00$\bar{1}$)	1.18	2.21	3.271	147
NB2-H10···Cl2	C(00$\bar{1}$)	0.99	2.27	3.223 (6)	163	NA3-H3···Ow	D(000)	1.07	1.81	2.758	145
NB3-H12···Cl2	C(00$\bar{1}$)	1.13	2.19	3.245 (8)	154	NB2-H10···OD1	C(00$\bar{1}$)	1.01	2.67	3.328	123
Ow-H19···Cl1	C(000)	0.89	2.29	3.166 (6)	168	NB2-H10···OD3	C(00$\bar{1}$)	1.01	2.61	3.287	124
Ow-H20···Cl2	D(010)	0.85	2.42	3.164 (6)	147	NB3-H12···OD1	C(00$\bar{1}$)	1.09	1.96	2.852	137
NB3-H11···Ow	B(10$\bar{1}$)	1.05	2.49	3.072 (8)	114	Ow-H19···OC1	C(000)	1.23	1.94	2.935	134
NB3-H11···SA1	C(00$\bar{1}$)	1.05	2.85	3.380 (7)	111	Ow-H20···OD2	D(010)	1.28	1.41	2.522	140
						NB3-H11···Ow	B(10$\bar{1}$)	0.90	2.93	3.257	105
						NB3-H11···SA1	C(00$\bar{1}$)	0.90	3.17	3.426	99
						NA3-H2···OC3	B(000)	1.18	2.41	3.074	114
						NA3-H3···OC3	B(000)	1.07	2.69	3.074	101

[a] Donor-hydrogen···acceptor. D-H at x, y, z. (A) x, y, z; (B) $\bar{x}, \bar{y}, {}^1/_2 + z$; (C) ${}^1/_2 - x, y, {}^1/_2 + z$; (D) ${}^1/_2 + x, \bar{y}, z$. The numerals after the molecular designation give the unit cell translations in the order a, b, c.

In summary, we see that ATSC is capable of functioning as a bidentate, chelating S,N ligand, with resulting severe steric constraints. The question of whether a more bulky ketone would lead to tetrahedral complexes while aldehydes might give octahedral complexes is being pursued. In addition, the soft-hard combination of donor atoms might be utilized to prepare complexes of heavier transition elements in unusual or distorted geometries.

Registry No. $[Ni(ATSC)_2X]^+X^-\cdot H_2O$ ($X = Cl$), 25087-96-1; $[Ni(ATSC)_2X]^+X^-\cdot H_2O$ ($X = NO_3$), 37523-49-2.

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Chelative Addition of Hydrazines to Coordinated Isocyanides. The Structure of Chugaev's Red Salt

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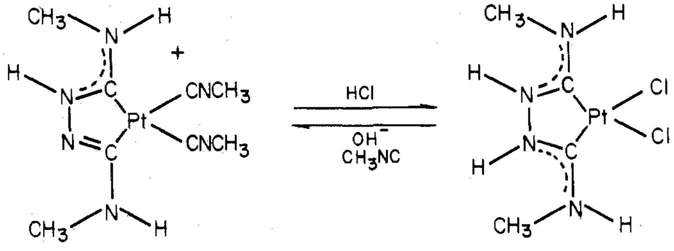
The structures of the monocations produced by the addition of hydrazines to $(CH_3NC)_4M^{2+}$ (M = Pd, Pt) have been elucidated by X-ray diffraction and nuclear magnetic resonance data. The compound $[(C_4H_8N_4CH_3)Pt(CNCH_3)_2][B(C_6H_5)_4]$, which was prepared by adding methylhydrazine to $(CH_3NC)_4Pt^{2+}$, crystallizes in the space group $C2/c$ with eight molecules in a unit cell of $a = 25.64$ (2), $b = 12.23$ (1), $c = 21.34$ (1) Å; $\beta = 105.5$ (2)°. The observed and calculated densities are 1.52 (2) and 1.489 (2) g cm^{-3}, respectively. Full-matrix least-squares refinement of the structure has resulted in $R = 0.053$ for the 1563 data having $F_o^2 > 3\sigma(F_o^2)$. The Pt atom is coordinated by two methyl isocyanide ligands and by two C atoms of the $(CH_3)_3N_4H_2C_2^-$ chelating ligand formed by the addition of methylhydrazine to two methyl isocyanide ligands. The entire cation is nearly planar, but steric interactions result in angular distortions within the plane. The Pt-C(chelate) distances are 1.95 (2) and 2.06 (3) Å; the average Pt-$CNCH_3$ distance is 1.96 (2) Å. The distances in the chelate ring are C-N = 1.24 (3) and 1.32 (2) Å and N-N = 1.45 (2) Å. The H atoms were not located directly, but the C-N distances and the nmr spectra show that a proton has been lost from an N atom of the chelate ring. In acidic media the N atom can be protonated to yield cations of the type $[(C_4H_9N_4R)M(CNCH_3)_2]^{2+}$ which have been isolated and characterized by their nmr spectra.

Introduction

Some years ago Chugaev and coworkers reported that hydrazine reacts with isocyanide complexes of Pt(II) to yield bright red compounds for which binuclear, hydrazine-bridged structures were proposed.[2] These complexes were converted by treatment with hydrochloric acid into yellow compounds which could be transformed back to the red forms by treatment with isocyanide and base.[2] Recent investigations have revealed that these complexes are formed by the chelative addition of hydrazine to coordinated isocyanide and that the red and yellow complexes should be formulated as 1 and 2,



1 2

respectively. The assignment of structure 2 to Chugaev's yellow compound is supported by the X-ray structure deter-

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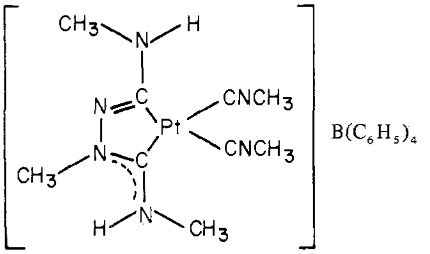
[1] (a) University of Arizona. (b) University of California.

[2] L. Chugaev, M. Skanavy-Grigorieva, and A. Posniak, *Z. Anorg. Allg. Chem.*, **148**, 37 (1925).

mination of the palladium analog.[3] Some further chemistry of **2** has also been described.[4] Chemical and proton magnetic resonance studies have shown that in the transformation of **2** into **1** the chelate ring retains its basic skeleton but that a proton is lost from this portion of the molecule.[5] Preliminary investigations led us originally to propose that a proton had been lost from one of the terminal nitrogens of the chelating ligand in this reaction. Although initially suggesting a rather different proton distribution of the chelate skeleton of **1** and a different structure for **2**,[6a] Rouschias and Shaw have accepted structure **2** for Chugaev's yellow compounds but have inferred that the site of deprotonation in the red compounds was one of the inner, chelate-ring nitrogens.[6b] Here we present X-ray and pmr data which firmly establish that the structure of Chugaev's red cation is **1** and that deprotonation occurs at one of the interior chelate-ring nitrogens, as proposed previously.[6b]

In addition the structure determination of $[(C_4H_8N_4CH_3)Pt(CNCH_3)_2][B(C_6H_5)_4]$ reveals some interesting features about the bonding within the chelating ligand. In the palladium analog of **2** the rigorous planarity of the ligand and the short C-N(CH$_3$)H distance of 1.31 Å indicate appreciable multiple-bond character for the C-N(CH$_3$)H bonds.[3] Molecular models reveal that significant steric interactions would attend the formation of analogs of **1** and **2** from substituted hydrazines. Consequently a determination of the structure of the complex **3** obtained from methylhydrazine has been undertaken to determine the consequences of such steric complications.



3

Experimental Section

Preparation of Compounds. Methyl isocyanide (*toxic*) was prepared *via* the literature method.[7]

$[(C_4H_9N_4)Pt(CNCH_3)_2][B(C_6H_5)_4]$. This salt was prepared by adding aqueous sodium tetraphenylborate to an aqueous solution of Chugaev's red salt[2] $[(C_4H_9N_4)Pt(CNCH_3)_2]Cl$. The yellow precipitate was recrystallized from acetone–methanol to give deep yellow crystals which were dried at 100° for 24 hr; mp 175–177° dec. *Anal.* Calcd: C, 54.17; H, 4.97. Found: C, 54.09; H, 5.30.

$[(C_4H_8N_4CH_3)Pt(CNCH_3)_2][B(C_6H_5)_4]$. Methyl isocyanide (0.5 ml) and methylhydrazine (0.7 ml) were added successively to a cold solution of 0.5 g of potassium tetrachloroplatinate in 20 ml of water. A saturated aqueous solution of sodium iodide was added to precipitate the red cation. The red-brown iodide salt was collected and dried. The iodide salt was dissolved in 60 ml of methanol and an excess of sodium tetraphenylborate in methanol solution was added. On cooling, the product formed orange crystals. These were collected and purified by recrystallization from acetone–methanol and vacuum-dried at 100° for 24 hr; mp 207–210° dec. *Anal.* Calcd: C, 54.78; H, 5.15; N, 11.61; Pt, 26.91. Found: C, 54.91; H, 4.97; N, 11.69; Pt, 27.07.

$[(C_4H_8N_4CH_3)Pd(CNCH_3)_2][BF_4]$. Methyl isocyanide (0.75 ml) and methylhydrazine (1.00 ml) were added successively to a cold solution of 0.60 g of palladium chloride and 0.50 g of sodium chloride in 15 ml of water. A saturated aqueous solution of sodium tetrafluoroborate was added dropwise to precipitate the orange product. After collection by filtration and drying, the product was recrystallized from a small volume of acetone, yield 0.31 g (44%); mp 170–175° dec. *Anal.* Calcd: C, 26.86; H, 4.26; N, 20.89. Found: C, 26.01; H, 4.35; N, 21.31.

$[(C_4H_9N_4)Pd(CNCH_3)_2][BF_4]$. This salt was prepared from hydrazine using the method described above. *Anal.* Calcd: C, 24.73; H, 3.89; Pd, 27.39. Found: C, 24.59; H, 3.81; Pd, 27.38.

$[(C_4H_9N_4CH_3)Pd(CNCH_3)_2][BF_4]_2\cdot H_2O$. Aqueous fluoroboric acid was added dropwise to a solution of 0.14 g of $[(C_4H_8N_4CH_3)Pd(CNCH_3)_2][BF_4]$ in 45 ml of acetonitrile until the orange solution became nearly colorless. Diethyl ether was added to the resulting solution until cloudiness persisted. After cooling this mixture to 0° for 24 hr, the pale yellow crystalline product was collected and dried. Purification was achieved by dissolving the product in a minimum volume of acetonitrile, filtering, and reprecipitating by the addition of ether; yield 0.14 g (84%), mp 122–126°. *Anal.* Calcd: C, 21.27; H, 3.96; N, 16.53. Found: C, 21.28; H, 3.73; N, 16.54.

$[(C_4H_{10}N_4)Pd(CNCH_3)_2][BF_4]_2$. This salt was prepared using the method described above for its methylated derivative. *Anal.* Calcd: C, 19.44; H, 3.67; Pd, 21.52. Found: C, 19.52; H, 3.53; Pd, 22.00.

Pmr Measurements. Acetone-d_6 and acetonitrile-d_3 were obtained from Diaprep, Inc., and were dried by standing for several days over freshly activated Linde 3A molecular sieves. Solvents so prepared showed an HDO resonance corresponding to 1–3 m*M* HDO. Solutions prepared were approximately 10–20 m*M* in complex. Spectra were run on a JEOL JNM-MH-100 spectrometer operating at 100 MHz, which was equipped with a JES-VT-3 temperature controller. Chemical shifts were read from the chart paper; instrument calibration was checked *via* the CHCl$_3$-TMS separation. Temperatures were measured with the methanol sample and calibration chart provided by JEOL.

X-Ray Structure Determination. Crystals of $[(C_4H_8N_4CH_3)Pt(CNCH_3)_2][B(C_6H_5)_4]$ were grown from acetone–methanol solutions by evaporation. Two forms were obtained, neither of which gave large crystals of high quality. Preliminary precession photographs of form 1 indicated that the crystals were monoclinic with cell constants of $a = 12.24$ (3), $b = 17.52$ (5), $c = 14.70$ (3) Å, and $\beta = 93.9$ (1)° with diffraction conditions $0k0$, $k = 2n$, and $h0l$, $l = 2n$, consistent with space group $P2_1/c$. These crystals were of poorer quality than form 2 and no intensity measurements were taken. Preliminary precession photographs (Mo Kα) on form 2 indicated that these crystals were monoclinic with the diffraction conditions hkl, $h + k = 2n$, and $h0l$, $l = 2n$. These conditions are consistent with space groups Cc or $C2/c$. The space group $C2/c$ was assumed and verified by successful solution and refinement of the structure.

A crystal of dimensions 0.10 × 0.10 × 0.07 mm was mounted on a Picker FACS-I four-circle diffractometer. Twelve reflections in diverse regions of reciprocal space with 2θ in the range 10–20° were carefully centered using Mo K$\bar{\alpha}$ radiation (λ 0.71069 Å). An ω scan on each of the reflections gave half-height widths of <0.1° at a takeoff angle of ~0.6°. A least-squares refinement of the setting angles for the 12 reflections gave unit cell parameters at 23 ± 2° of $a = 25.64$ (2), $b = 12.23$ (1), $c = 21.34$ (1) Å; $\beta = 105.5$ (2)°.

The density was measured by the gradient column and flotation techniques. There was interaction between the carbon tetrachloride–bromobenzene mixture and the crystals which led to the eventual decomposition of the crystals. However, the observed density of 1.52 (2) g cm^{-3} is in acceptable agreement with the value of 1.489 (2) g cm^{-3} calculated for eight molecules of $[(C_5H_{11}N_4)Pt(CNCH_3)_2][B(C_6H_5)_4]$ per unit cell. The observed and calculated molecular weights are 737.7 and 723.6, respectively. Although no peaks attributable to solvent molecules could be found in the final difference electron density map (*vide infra*), it is possible that some lattice water is present in the crystal as has been suggested previously.[6b]

An incident beam monochromator equipped with a graphite crystal was used to obtain Mo Kα radiation. The 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 $2\theta_{\mathrm{MoK}\alpha_1} - 0.85°$ to $2\theta_{\mathrm{MoK}\alpha_2} + 0.85°$ at a takeoff angle of 1.7°. The scan rate was 2°/min and stationary-crystal, stationary-counter background counts of 10 sec were taken at both ends of the scan. The pulse height analyzer was set to admit ~90%

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[3] W. M. Butler and J. H. Enemark, *Inorg. Chem.*, 10, 2416 (1971).

[4] A. L. Balch, *J. Organometal. Chem.*, 37, C19 (1972).

[5] A. Burke, A. L. Balch, and J. H. Enemark, *J. Amer. Chem. Soc.*, 92, 2555 (1970).

[6] (a) G. Rouschias and B. L. Shaw, *Chem. Commun.*, 183 (1970); (b) G. Rouschias and B. L. Shaw, *J. Chem. Soc. A*, 2097 (1971).

[7] R. E. Schuster, J. E. Scott, and J. Casanova, Jr., *Org. Syn.*, 46, 75 (1966).

of the Mo Kα peak and the scintillation counter was 24 cm from the crystal. During data collection the intensities of three reflections in diverse regions of reciprocal space were monitored every 50 reflections. None of the standards showed any systematic changes of intensities during data collection. The relative standard deviation of the mean intensity of each standard reflection was less than 2%. A total of 2905 reflections having $2\theta \leqslant 40°$ was obtained. The final structural parameters derived from this data set (*vide infra*) gave errors of ~0.03 Å on a C–C bond. This was larger than had been hoped. However, additional attempts to grow larger crystals of high quality were not successful. Therefore, a second data set was gathered on the same crystal using different experimental conditions in an attempt to improve the signal to noise ratio on weak reflections. For the second data set the scan rate was 0.5°/min and the background count time was 20 sec. The detection aperture was 16 mm^2. Other experimental parameters were the same as for the first data set. The relative standard deviation of the mean intensity of each standard reflection was about 4%. An equipment failure during the data collection required two separate scale factors to be assigned for this data set.

The data were reduced to F^2 and $\sigma(F^2)$ by procedures similar to those previously described.[8-10] 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 corrected intensities by the formula $\sigma(F^2) = [CT + 0.25(t_c/t_b)^2(B_1 + B_2) + (pF^2)^2]^{1/2}$ where CT is the total integrated peak count obtained in time t_c, B_1 and B_2 are the background counts obtained in time t_b, F^2 is the corrected intensity, and p was taken as 0.04. Set 1 had 1458 data and set 2 had 1622 data with $F^2 \geqslant 3\sigma(F^2)$.

The absorption coefficient for the compound for Mo Kα radiation is 47.0 cm^{-1}. The faces of the crystal were identified as $[1\bar{1}\bar{1}]$, $[11\bar{1}]$, $(00\bar{1})$, (102), and $(\bar{1}00)$, and the crystal was carefully measured. Both data sets were corrected for absorption;[10] the correction factor ranged from 1.32 to 1.55. No correction for extinction was necessary.

Solution and Refinement of Structure

The structure was first solved and refined using data set 1. The positions of the Pt atoms were readily determined from a three-dimensional Patterson function. Refinement was based upon F_o, with $\Sigma w(|F_o| - |F_c|)^2$ being minimized. The weights were taken as $4F_o{}^2/\sigma^2(F_o{}^2)$. The atomic scattering factors for Pt were from Cromer and Waber;[11] the factors for C, N, and B were from the usual tabulation.[12] The effects of anomalous dispersion for Pt were included in F_c[13] using the values of $\Delta f'$ and $\Delta f''$ calculated by Cromer.[14] Phenyl rings of the tetraphenylborate anion were treated as rigid groups[15] (C–C = 1.392 Å, D_{6h}/mmm symmetry) with a single isotropic thermal parameter assigned to each ring. Anisotropic thermal parameters were assigned to Pt and individual isotropic thermal parameters were assumed for the remaining nongroup atoms. Refinement of the scale factor and Pt atom coordinates gave $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.265$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2} = 0.321$. Three successive cycles of least-squares refinement and difference electron density maps revealed all of the remaining nonhydrogen atoms. After the data were corrected for absorption, four additional cycles of refinement resulted in convergence of the model (102 variable parameters) to $R_1 = 0.057$ and $R_2 = 0.060$ for the 1458 data having $F_o{}^2 \geqslant 3\sigma(F_o{}^2)$. The hydrogens of the tetraphenylborate anion were then included in their idealized positions (C–H = 1.084 Å) as fixed contributions to F_c assuming isotropic thermal parameters (B = 7.4 Å^2). A final difference electron density map contained no peaks greater than 0.6 e Å^{-3}. On the same scale a C atom had a height of 2.9 e Å^{-3}. Positions for the remaining protons in the molecule could not be deduced from the final difference map. Attempts to refine all nongroup atoms anisotropically resulted in the thermal ellipsoids for several light atoms becoming nonpositive definite. The same model was then refined using the second data set. The final results were $R_1 = 0.068$ and $R_2 = 0.079$ for the 1622 data with $F_o{}^2 \geqslant 3\sigma(F_o{}^2)$ and all parameters were within three estimated standard deviations of those from set 1. The estimated standard deviations of the parameters from the refinement of data set 2 were about 8% larger than those from set 1. The two data sets were then merged.[10] Refinement of the same model converged to $R_1 = 0.053$ and $R_2 = 0.060$ for the 1563 averaged data with $F_o{}^2 \geqslant 3\sigma(F_o{}^2)$.

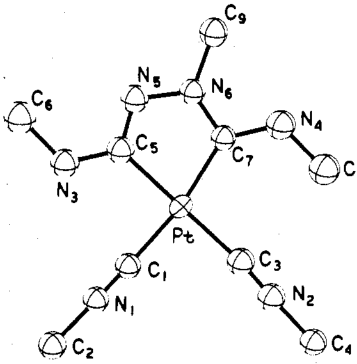

Figure 1. Numbering scheme and view of the $[(C_5H_{11}N_4)Pt(CNCH_3)_2]^+$ anion.

An analysis of the weighting scheme showed that $w(\Delta F)^2$ was not a function of the indices, $|F_o|$, or $(\sin\theta)/\lambda$. Thus, the relative weights are reasonable. The standard deviation of an observation of unit weight was 1.28 electrons.

Final structure parameters appear in Table I, and Table II shows the derived fractional coordinates of the group carbon atoms. A list of $10|F_o|$ and $10|F_c|$ is available.[16]

Description of the Structure

Figure 1 is a perspective view of the $[(C_4H_8N_4CH_3)Pt(CNCH_3)_2]^+$ cation showing the numbering scheme and the relative thermal motion of the atoms. A perspective view of the tetraphenylborate ion is shown in Figure 2. Interatomic distances and angles are given in Table III and Figure 3. The estimated standard deviations of the distances and angles were derived from the variance–covariance matrix from the final cycle of least-squares refinement.

For compound **2** the space group imposed C_{2v}-mm symmetry on the molecule.[3] In the present determination no symmetry need be imposed by the space group, but the cation is nearly planar with effective coordination symmetry m. The equation of the weighted least-squares plane is $12.99x + 5.80y - 17.70z - 3.04 = 0$ (monoclinic coordinates). Distances from this plane are shown in Table IV. The cations are packed in pairs around the inversion centers as shown by the stereoview of the cell in Figure 4. Each pair of least-squares planes is 3.30 Å apart; the Pt · · · Pt distance is 3.55 Å. The intermolecular methyl–methyl contacts are $C_4 \cdots C_4 = 3.23$, $C_2 \cdots C_9 = 3.90$, $C_4 \cdots C_9 = 4.21$, and $C_6 \cdots C_8 = 4.55$ Å. These methyl interactions may be responsible for the cation's slight deviation from planarity (Table IV). Inspection of Figure 3 shows that the

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(8) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

(9) J. H. Enemark, M. S. Quinby, L. L. Reed, M. J. Steuck, and K. K. Walthers, *Inorg. Chem.*, 9, 2397 (1970).

(10) The program used for data reduction was Raymond's UCFACS, itself a modification of Doedens and Ibers' PIKOUT. Other computer programs used included Zalkin's FORDAP Fourier summation program, Hamilton's GONO general absorption program, Iber's NUCLS group least-squares refinement program based upon Busing and Levy's ORFLS, Busing and Levy's ORFFE, Johnson's ORTEP plotting program, Corfield's RANGER weighting analysis program, Hamilton's INSCALA data-averaging program, and the general absorption program AGNOST. All computations were performed on a CDC 6400 computer.

(11) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18, 104 (1965).

(12) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

(13) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 17, 781 (1964).

(14) D. T. Cromer, *Acta Crystallogr.*, 18, 17 (1965).

(15) S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, 18, 511 (1965); R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965).

(16) 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-73-451.

Table I. Final Atomic Parameters

Atoms[a]	x	y	z	B, Å^2
Pt	0.20678 (4)	0.20858 (9)	0.04813 (5)	b
N_1	0.2555 (7)	0.388 (2)	0.1480 (9)	6.9 (5)
N_2	0.0997 (8)	0.344 (2)	0.0167 (9)	8.0 (5)
N_3	0.3215 (8)	0.157 (2)	0.1188 (10)	8.3 (5)
N_4	0.1371 (8)	0.036 (2)	−0.0474 (10)	8.6 (5)
N_5	0.2774 (8)	0.031 (2)	0.0422 (10)	8.2 (5)
N_6	0.2261 (7)	0.003 (2)	−0.0034 (9)	7.0 (5)
C_1	0.2385 (9)	0.326 (2)	0.1074 (12)	7.3 (6)
C_2	0.2793 (10)	0.466 (2)	0.2046 (12)	8.7 (7)
C_3	0.1390 (10)	0.293 (2)	0.0251 (10)	8.0 (6)
C_4	0.0486 (10)	0.414 (2)	0.0056 (11)	7.5 (6)
C_5	0.2767 (10)	0.117 (2)	0.0725 (11)	7.2 (6)
C_6	0.3704 (11)	0.078 (2)	0.1417 (13)	10.9 (8)
C_7	0.1862 (10)	0.078 (2)	−0.0048 (11)	6.7 (6)
C_8	0.0859 (10)	0.102 (2)	−0.0592 (12)	9.5 (7)
C_9	0.2249 (10)	−0.102 (2)	−0.0380 (12)	8.8 (7)
B_1	0.1146 (10)	0.758 (2)	0.1377 (12)	6.0 (7)

Group[c]	x_c	y_c	z_c	δ	ϵ	η	B, Å^2
R_1	0.0698 (4)	0.5351 (10)	0.1668 (4)	1.09 (1)	−2.84 (1)	−0.32 (1)	8.0 (3)
R_2	0.2417 (4)	0.7668 (7)	0.1858 (5)	−3.23 (2)	−2.13 (1)	−0.17 (2)	8.1 (3)
R_3	0.0750 (4)	0.7674 (8)	−0.0148 (5)	0.82 (1)	−2.88 (1)	1.37 (1)	8.6 (3)
R_4	0.0883 (3)	0.9674 (11)	0.2021 (5)	−0.47 (2)	2.24 (1)	−1.00 (2)	9.2 (3)

[a] x, y, and z are in fractional monoclinic coordinates. B is the isotropic thermal parameter. Anisotropic thermal parameters for Pt are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The standard deviation of the least significant figure is given in parentheses. [b] $10^5\beta_{11} = 217$ (2), $10^5\beta_{22} = 1070$ (10), $10^5\beta_{33} = 434$ (3), $10^5\beta_{12} = 105$ (6), $10^5\beta_{13} = 36$ (2), and $10^5\beta_{23} = 1$ (8). [c] x_c, y_c, and z_c are the fractional coordinates of the center of the ring. The angles δ, ϵ, and η (in radians) are the orientation angles which bring about alignment of the internal-coordinate system of the ring with a fixed external-coordinate system and have been described previously.[15] The rings are numbered so that C_1 is attached to boron and C_4 is para to C_1.

Table II. Derived Parameters for Group Carbon Atoms[a]

	x	y	z
		R_1	
C_1	0.0899 (8)	0.636 (1)	0.1539 (7)
C_2	0.1212 (5)	0.542 (2)	0.1568 (8)
C_3	0.1011 (7)	0.441 (1)	0.1695 (8)
C_4	0.0497 (8)	0.434 (1)	0.1796 (8)
C_5	0.0185 (5)	0.528 (2)	0.1767 (8)
C_6	0.0386 (7)	0.629 (1)	0.1640 (8)
		R_2	
C_1	0.1857 (4)	0.760 (1)	0.1621 (8)
C_2	0.2160 (7)	0.815 (1)	0.1267 (6)
C_3	0.2720 (7)	0.822 (1)	0.1504 (8)
C_4	0.2978 (4)	0.773 (1)	0.2096 (8)
C_5	0.2675 (7)	0.718 (1)	0.2449 (6)
C_6	0.2115 (7)	0.712 (1)	0.2212 (8)
		R_3	
C_1	0.0934 (7)	0.764 (1)	0.0528 (5)
C_2	0.1186 (5)	0.701 (1)	0.0152 (9)
C_3	0.1002 (6)	0.704 (1)	−0.0523 (9)
C_4	0.0566 (7)	0.770 (1)	−0.0823 (6)
C_5	0.0314 (5)	0.834 (1)	−0.0448 (9)
C_6	0.0498 (7)	0.831 (1)	0.0228 (9)
		R_4	
C_1	0.0987 (7)	0.873 (1)	0.1715 (10)
C_2	0.0799 (7)	0.866 (1)	0.2269 (10)
C_3	0.0695 (7)	0.960 (2)	0.2575 (7)
C_4	0.0779 (7)	1.062 (1)	0.2328 (10)
C_5	0.0967 (7)	1.069 (1)	0.1774 (10)
C_6	0.1070 (6)	0.974 (2)	0.1468 (7)

[a] The estimated standard deviations are derived from those of the group parameters and are meant to be used in error analysis on inter-ring distances. The intra-ring C–C distance is 1.392 Å.

Table III. Selected Interatomic Distances and Angles[a]

Atoms	Distance, Å	Atoms	Angle, deg
B_1-R_1C_1	1.70 (3)	Pt-C_1-N_1	172 (2)
B_1-R_2C_1	1.76 (3)	Pt-C_3-N_2	175 (2)
B_1-R_3C_1	1.75 (3)	C_1-N_1-C_2	177 (2)
B_1-R_4C_1	1.68 (3)	C_3-N_2-C_4	179 (2)
C_8-C_3	3.04 (3)	R_1C_1-B_1-R_2C_1	113 (2)
N_4-C_9	2.78 (3)	R_1C_1-B_1-R_3C_1	102 (2)
N_5-C_6	2.80 (3)	R_1C_1-B_1-R_4C_1	119 (2)
		R_2C_1-B_1-R_3C_1	109 (2)
		R_2C_1-B_1-R_4C_1	102 (2)
		R_3C_1-B_1-R_4C_1	111 (2)

[a] Only those distances and angles not shown in Figure 3 appear in this table.

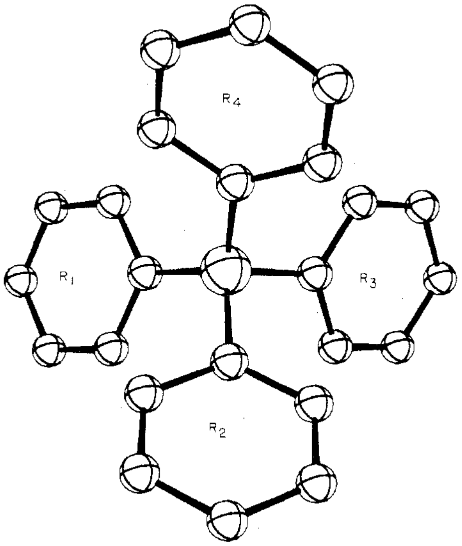

Figure 2. Numbering scheme and view of the $[B(C_6H_5)_4]^-$ cation.

cation achieves planarity at the expense of distortion. The most obvious and significant distortion involves the angles C_1-Pt-C_5 and C_3-Pt-C_7. These two angles differ by 9° (9σ). This difference arises from interaction between the C_8 methyl group and the isocyanide ligand cis to it. The $C_3 \cdots C_8$ contact is only 2.8 Å, and this interaction is probably also responsible for the Pt-C_7-N_4 angle being 135°, 8σ greater than the Pt-C_5-N_3 angle of 119°. Although the bond angles in the cation show that steric interactions of the

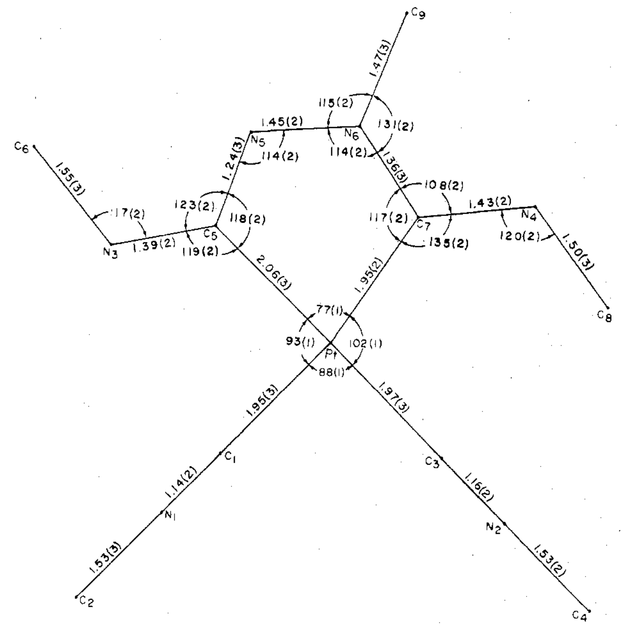

Figure 3. Distances and angles in the $[(C_5H_{11}N_4)Pt(CNCH_3)_2]^+$ anion.

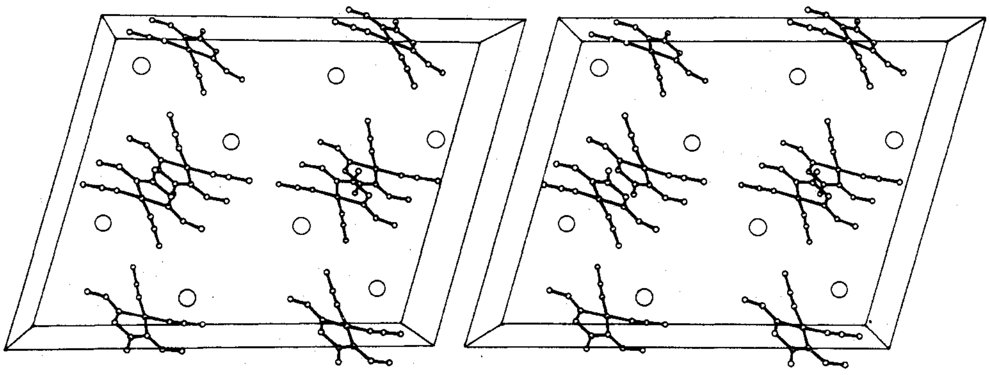

Figure 4. Stereopair showing the crystal structure of $[(C_5H_{11}N_4)Pt(CNCH_3)_2][B(C_6H_5)_4]$ viewed along *b*. The contents of one unit cell are shown. For clarity, the $B(C_6H_5)_4^-$ ions are represented by large open circles. The origin of the cell is in the upper left-hand corner; *a* is horizontal, *c* is nearly vertical, and *b* comes out of the page to complete the right-hand system.

C_8 methyl group result in some distortion, the interactions would be much worse if the orientation of the C_8 methyl group relative to the ring were the same as the orientation of the C_6 methyl group. Such a structure would have a $C_8 \cdots C_9$ distance of 2.8 Å, about 1.2 Å less than the estimated van der Waals contact[17] for two methyl groups.

It is apparent that the steric strain discussed above could be alleviated if the C_8 methyl group were rotated out of the plane of the cation or if the bonding about N_4 were pyramidal rather than trigonal. The near planarity of the complex in spite of steric strain suggests that π-electron delocalization is important in stabilizing the C_2N_4 skeleton of the ligand.

The Pt-C(chelate) distances of 1.95 (2) and 2.06 (3) Å are similar to the 1.98 (2),[18] 2.00 (3),[19] and 2.06 (1) Å[20] observed for Pt-C(sp^2) bonds in other complexes. The average $Pt-CNCH_3$ distance of 1.96 (2) Å does not differ significantly from the Pt-C(chelate) distances. In *trans*-$(CH_3NC)_2Pt[C(NHCH_3)(SC_2H_5)]_2^{2+}$ the $Pt-CNCH_3$ distance is 1.96 (1) Å.[20]

Table IV. Distances of Atoms from the Least-Squares Plane $12.99x + 5.80y - 17.70z - 3.04 = 0$ (Monoclinic Coordinates)

Atom	Distance, Å	Atom	Distance, Å
Pt	0.005 (1)	C_2	−0.33 (2)
N_1	−0.09 (2)	C_3	0.02 (2)
N_2	−0.04 (2)	C_4	−0.11 (2)
N_3	−0.06 (2)	C_5	−0.05 (2)
N_4	−0.21 (2)	C_6	−0.28 (3)
N_5	−0.01 (2)	C_7	−0.08 (2)
N_6	−0.02 (2)	C_8	−0.29 (2)
C_1	0.05 (2)	C_9	−0.04 (2)

The coordination of the methyl isocyanide ligands to the metal is essentially linear. The average C-N distance of 1.15 (2) Å is similar to values observed for coordinated methyl isocyanide in other metal complexes.[20-22] The distance in gaseous CH_3NC is 1.166 Å.[23]

The tetraphenylborate anion has the expected tetrahedral geometry. Group refinement of the anion has led to an average B-C distance of 1.72 (2) Å. This is longer than the 1.640 (9) Å recently observed[24] for a structure in which all the B and C atoms of the anion were refined independently.

One of the primary objectives of this study was to determine the position of deprotonation in **3**. Unfortunately hydrogen atoms could not be located directly in the final difference electron density map. However, comparison of the C-N distances in the cation shows that the two distances external to the ring (C_5-N_3 and C_7-N_4) differ by only 0.04 Å (2σ). On the other hand, the two C-N distances within the chelate ring (C_5-N_5 and C_7-N_6) differ by 0.12 Å (4σ) with C_5-N_5 being 1.24 (3) Å. The shortening of this bond is consistent with deprotonation of the ring N atom (N_5). This has been verified by pmr spectroscopy.

Pmr Results

In carefully dried acetonitrile-d_3 at 30° the pmr spectrum of the tetraphenylborate salt of **1** consists of a doublet at τ 7.17 (6)[25] ($J_{H-N-C-H} = 4.4$ Hz) with further splitting due

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[17] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

[18] E. M. Badley, J. Chatt, R. L. Richards, and G. A. Sim, *Chem. Commun.*, 1322 (1969).

[19] D. J. Cardin, B. Cetinkaya, M. F. Lappert, Lj. Manojlovic-Muir, and K. W. Muir, *Chem. Commun.*, 400 (1971).

[20] W. M. Butler and J. H. Enemark, *Proc. Int. Conf. Coord. Chem.*, 14, 268 (1972).

[21] J. Miller, A. L. Balch, and J. H. Enemark, *J. Amer. Chem. Soc.*, 93, 4613 (1971).

[22] F. A. Cotton, T. G. Dunn, and J. S. Wood, *Inorg. Chem.*, 4, 318 (1965).

[23] C. C. Costain, *J. Chem. Phys.*, 29, 864 (1958); T. S. Jaseja, *Proc. Indian Acad. Sci., Sect. A*, 50, 108 (1959).

[24] R. J. Sime, R. P. Dodge, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, 10, 537 (1971).

[25] In this discussion of the pmr spectra the number in parentheses denotes the relative intensity of the resonance.

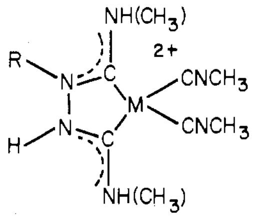
to ^{195}Pt ($J_{\text{Pt-H}} = 4.4$ Hz), a singlet at 6.58 (6) ($J_{\text{Pt-H}} = 12.2$ Hz), a broad resonance at 4.34 (2), and a set of multiplets at 2.86 and 2.58 (20).[26] Similar spectra have been obtained in acetone-d_6[26] and nitrobenzene. The multiplets at τ 2.86 and 2.56 are assigned to the protons of the tetraphenylborate anion. Decoupling experiments have demonstrated that the resonance at τ 7.17 is coupled to the broad resonance at τ 4.34; these resonances are assigned to the methyl groups and the terminal N-H groups of the chelate ring, respectively. The singlet at τ 6.58 is assigned to the methyl group of the unreacted isocyanide ligands. These assignments are consistent with those made for the related complexes of iron of the type $(CH_3NC)_4Fe(C_4H_9N_4R)^{2+}$.[27] No signal ascribable to the internal chelate N-H was observed at room temperature.

The equivalence of the two methyl groups of the chelate ring, of the two terminal N-H groups, and of the two isocyanide ligands can be explained by postulating rapid proton exchange between the two interior chelate nitrogens. Support for this hypothesis comes from temperature-dependent studies. Upon lowering the temperature, the signal at τ 4.34 was observed to broaden and disappear; at −48° two broad resonances appeared at τ 3.6 (1) and 5.1 (1). At the same time a new broad resonance appeared at τ 0.9 (1) and the doublet structure of the signal at τ 7.19 was almost obscured by line broadening. The isocyanide signal at τ 6.58 remained a sharp singlet. Coupling between the methyl signal at τ 7.19 and *both* N-H resonances at τ 3.6 and 5.1 was demonstrated by decoupling experiments. The solution froze at lower temperatures. These observations indicate that the rate of proton migration is slowing down so that the spectra reveal the intrinsic asymmetry of the molecule. Further experiments at lower temperatures in acetone-d_6 support this conclusion. At −80 to −90° both the terminal chelate methyl resonance and the isocyanide signal split, giving separations of 20 and 4 Hz, respectively.[28] Further experiments aimed at delineating the mechanism of proton transfer on this and related systems are in progress.

Because **3** cannot undergo the proton exchange exhibited by **1**, the pmr spectrum of **3** at room temperature resembles that of **1** at low temperatures. Resonances at τ 8.79 (3) ($J_{\text{H-N-C-H}} = 4.9$ Hz, $J_{\text{Pt-H}} = 4.2$ Hz) and 6.82 (3) ($J_{\text{H-N-C-H}} = 4.6$ Hz, $J_{\text{Pt-H}} = 3.4$ Hz) in the spectrum of **3** as the tetraphenylborate salt in acetone-d_6 are assigned to the terminal methyl groups of the chelate ring. The methyl group on the interior of the chelate ring produces a resonance at τ 6.78 (3) ($J_{\text{Pt-H}} = 5.8$ Hz). The isocyanide ligands produce resonances at τ 6.52 (3) ($J_{\text{Pt-H}} = 5.4$ Hz) and 6.48 (3) ($J_{\text{Pt-H}} = 6.4$ Hz). The terminal N-H groups give rise to broad resonances at τ 4.75 (1) (coupled to the doublet at τ 8.79) and at τ 3.46 (1) (coupled to the doublet at τ 6.82). A similar spectrum has been observed for the palladium analog of **3** in acetonitrile-d_3. In this case the spectrum consists of resonances at τ 7.18 (3) ($J_{\text{H-N-C-H}} = 5.0$ Hz) and 6.87 (3) ($J_{\text{H-N-C-H}} = 5.0$ Hz) due to the two inequivalent terminal methyl groups of the chelate ring, at τ 6.84 (3) due to the methyl group on the chelate ring, at τ 6.50 (6) due to the two inequivalent isocyanide ligands, and at τ 5.12 (1) (coupled to the doublet at τ 7.18) and 4.04 (1) (coupled to the doublet at τ 6.78) due to the terminal N-H groups.

Synthetic studies also produce evidence which indicates that **1** and its analogs lack a proton on one of the chelate-ring nitrogen atoms. Monosubstituted hydrazines and hydroxylamine will react to produce analogs of **1**. However reagents, such as 1,2-dimethylhydrazine, pyrazolidine, and methoxyamine, which could undergo chelative addition to adjacent isocyanides but which could not undergo subsequent proton loss from a ring nitrogen atom, do not, upon addition to tetrakis(methyl isocyanide)platinum(II), produce the red color which is specifically characteristic of the formation of monodeprotonated complexes such as **1**.

Treatment of **1** or **3** or their palladium analogs with acid under mild conditions yields pale yellow complexes 4 in



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which protonation of the chelating ligand has occurred without loss of the isocyanide ligands. Procedures for the isolation of the palladium complexes **4** (R = H or CH_3) as the tetrafluoroborate salts are given in the Experimental Section. The preparation of the platinum complex **4** (R = H) as the chloride salt has been reported.[6b] The pmr spectrum of **4** (M = Pd, R = CH_3) is entirely consistent with this structure. The inequivalent terminal methyl groups produce a pair of doublets at τ 7.12 (3) ($J = 5.0$ Hz) and 6.87 (3) ($J = 5.0$ Hz); the methyl group on the chelate ring gives a singlet at τ 6.72 (3); the inequivalent isocyanide ligands produce a single resonance at τ 6.48 (6); the terminal N-H groups give two broad resonances at τ 3.05 (1) and 2.45 (1); and the N-H group of the chelate ring produces a broad resonance at τ 0.8 (1). The N-H resonance at τ 3.05 is coupled to the methyl resonance at τ 6.87 while the N-H resonance at τ 2.45 is coupled to the methyl doublet at τ 7.12

Discussion

The addition of protic nucleophiles to coordinated isocyanides is now well known.[29] Several investigators have designated the resulting complexes as "carbene" complexes, because of their obvious relationship to the complexes first

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(26) Rouschias and Shaw have reported that in acetone-d_6 the terminal chelate methyl resonance appears as a singlet at τ 7.25.[6b] We previously reported that two resonances (a doublet at τ 7.25 and a superimposed singlet at τ 7.26) occurred in this region and proposed that the singlet was due to deprotonation of one terminal nitrogen of the chelate ring. The observation of a singlet at τ 7.26 could be due to the presence of basic or acid impurities in the solvent. These impurities could cause rapid proton exchange at the terminal nitrogens and consequently collapse the doublet structure. We have observed that addition of pyridine or trifluoroacetic acid to acetone solutions of 1 results in the collapse of this doublet into a singlet. Related observations have been made for the iron complexes, $(C_4H_9N_4R)Fe(CNCH_3)_4{}^{2+}$.[27] A second complication arises because of hydrogen-deuterium exchange. Deuteration of an appreciable fraction of the N-H sites in 1 occurs upon dissolution in commercial acetone-d_6, presumably because the solvent contains a significant quantity of D_2O. This deuteration has been verified by adding microliter amounts of D_2O to samples of 1 in very dry acetone and observing the growth of the resonance at τ 7.26. Upon addition of H_2O to this sample, this resonance is caused to decrease in intensity. These studies also demonstrate that the signal at τ 7.26 is not due to water itself (as has been suggested)[6b] since a separate water resonance, which is concentration and temperature dependent, is also observed when water has been added.

(27) A. L. Balch and J. Miller, *J. Amer. Chem. Soc.*, 94, 417 (1972).

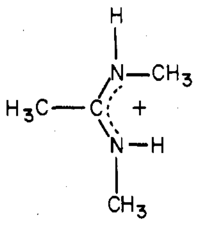
(28) At this temperature these resonances were still too broad to allow resolution of the N-H and ^{195}Pt-H coupling.

(29) E. M. Badley, J. Chatt, and R. L. Richards, *J. Chem. Soc. A*, 21 (1971); B. Crociani, T. Boschi, and U. Belluco, *Inorg. Chem.*, 9, 2021 (1970); R. J. Angelici and L. M. Charley, *J. Organometal. Chem.*, 24, 205 (1970); H. C. Clark and L. E. Manzer, *Inorg. Chem.*, 11, 503 (1972); P. M. Treichel and W. J. Knebel, *ibid.*, 11, 1285 (1972).

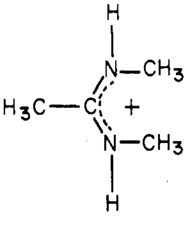
prepared by Fischer and his coworkers[30] by the addition of strong nucleophiles to metal hexacarbonyls. Following this nomenclature, Chugaev's red and yellow compounds contain chelating dicarbene ligands. However, as discussed above, the planarity of the chelate ligands and the multiple-bond character of the C-N and N-N bonds indicate that there is considerable electron delocalization in these ligand systems. These then are not simple carbenes but fall into the category of "resonance-stabilized carbenes."[31]

While carbene nomenclature has become generally used in describing the complexes derived from the addition of nucleophiles to coordinated isocyanide ligands, the stereochemistry of the resulting complexes can also easily be interpreted by comparison to the stereochemistry of amidinium ions.

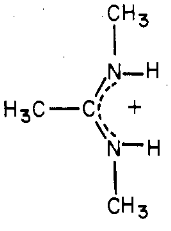
In 1963 nmr studies by Hammond and Neuman[32] showed that rotation about the C-N bond of amidinium ions, **5**, is restricted, and that the ions exist in the amphi configuration, **5a**, in solution. (Models show that the symmetric structures **5b** and **5c** are sterically more crowded than **5a**.)



5a

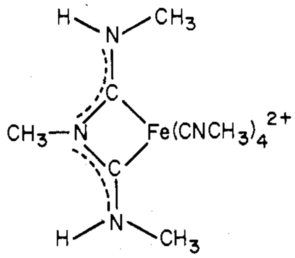


5b



5c

If the methyl group attached to the central carbon atom is conceptually replaced by a metal atom, then a relationship between amidinium ions and a whole series of metal complexes is apparent. Each metal-bound carbon of the chelating ligands in **2** and **3** has adopted this configuration. X-Ray studies have shown that the carbon donors in the chelate skeleton of **6** have also taken on this rearrangement.[33]



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Persuasive evidence exists to support an amphi configuration in other complexes of carbenoid ligands including $M[C(NHCH_3)_2]_4^{2+}$ (M = Pd, Pt),[34] $Au[C(NHCH_3)_2]_2^{2+}$,[35] *trans*-$PtX[C(NHR)_2](PEt_3)_2^{+}$,[36] *trans*-$Pt[C(NHR\text{-}NHR')_2(CNC_2H_5)(PR_3)_2]^{2+}$,[37] and ($t$-BuNC)$PdX_2[C[NH\text{-}t\text{-}Bu][N(CH_3)_2]]$.[38]

Registry No. $[(C_4H_9N_4)Pt(CNCH_3)_2][B(C_6H_5)_4]$, 33308-32-6; $[(C_4H_8N_4CH_3)Pt(CNCH_3)_2][B(C_6H_5)_4]$, 37035-84-0; $[(C_4H_8N_4CH_3)Pd(CNCH_3)_2][BF_4]$, 37035-85-1; $[(C_4H_9N_4)Pd(CNCH_3)_2][BF_4]$, 37035-86-2; $[(C_4H_9N_4CH_3)Pd(CNCH_3)_2][BF_4]_2$, 38194-29-5; $[(C_4H_{10}N_4)Pd(CNCH_3)_2][BF_4]_2$, 37035-87-3.

Acknowledgments. This research was sponsored by grants GP-12299 and GP-28564 from the National Science Foundation and by grants GM 18357 and AM 12182 from the National Institutes of Health. We thank Drs. A. Burke and J. Miller for some experimental assistance.

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(30) See, for example, E. O. Fischer and A. Maasbol, *Angew. Chem.*, 76, 645 (1964).

(31) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 204.

(32) G. S. Hammond and R. C. Neuman, Jr., *J. Phys. Chem.*, 67, 1655 (1963).

(33) J. Miller, A. L. Balch, and J. H. Enemark, *J. Amer. Chem. Soc.*, 93, 4613 (1971).

(34) J. S. Miller and A. L. Balch, *Inorg. Chem.*, 11, 2069 (1972).

(35) J. H. Parks and A. L. Balch, unpublished results.

(36) E. M. Badley, B. J. L. Kilby, and R. L. Richards, *J. Organometal. Chem.*, 27, C37 (1971).

(37) H. C. Clark and L. E. Manzer, *Inorg. Chem.*, 11, 503 (1972).

(38) G. A. Larkin, R. P. Scott, and M. G. H. Wallbridge, *J. Organometal. Chem.*, 37, C21 (1972).