

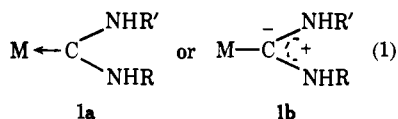
Characterization of the Complexes Obtained from the Addition of Hydrazine to Hexakis(methyl isocyanide)iron(II)

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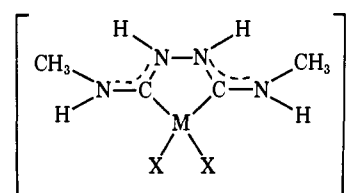
Abstract: The reaction between hydrazine, methylhydrazine, or phenylhydrazine and hexakis(methyl isocyanide)iron(II) yields complexes, $(\text{CH}_3\text{NC})_6\text{Fe}(\text{C}_4\text{H}_9\text{RN})_2^{2+}$ ($\text{R} = \text{H}, \text{CH}_3, \text{C}_6\text{H}_5$), in which the hydrazine has attacked two isocyanide ligands to yield a chelating ligand which is bonded to iron through two, planar, tricoordinate carbon atoms. The structures of the new complexes, which have been isolated as their hexafluorophosphate salts, have been determined from conductivity, infrared, and pmr data and comparison with other related complexes. The pK_a values for the complexes, which are weak acids, have been determined and the site of deprotonation is discussed.

Reactions of the isocyanide function of isocyanide ligands in transition metal complexes have recently attracted widespread interest. Zero-valent isocyanide complexes of palladium and nickel have been shown to act as homogeneous catalysts for the oxidation of isocyanides to isocyanates.¹ The N-protonation of bridging, but not terminal, isocyanides has been reported.² A number of reagents including amines,³ alcohols,^{3a,c,e} pentafluorophenyllithium,⁴ and tetrahydroborate⁵ have been found to add to coordinated isocyanides. In the case of amine addition, the resulting ligand may be formulated as a coordinated carbene ligand **1a** or alternately as a C-metal substituted amidinium ion **1b**.



Isocyanides have also been found to insert into metal-carbon σ bonds.^{2,6} Similar addition and insertion reactions are known to occur with carbon monoxide which is isoelectronic with an isocyanide. These addition and insertion reactions may also be involved in the metal ion catalyzed formation of derivatives of formimidic acid by insertion of an isocyanide into N-H, P-H, O-H, S-H, or Si-H bonds.⁷

Although hydrazine has frequently been used as a reducing agent for the preparation of low-valent metal isocyanide complexes,⁸ the reaction of hydrazine with $(\text{CH}_3\text{NC})_6\text{Pt}^{2+9}$ or $(\text{CH}_3\text{NC})_6\text{Pd}^{2+}$ does not produce a reduced species but rather involves attack of hydrazine on the coordinated isocyanide ligands to yield **2**.¹⁰



- 2**, X = CNCH₃; z = +2
3, X = Cl; z = 0

This reaction represents one of the few cases in which more than one isocyanide ligand in a particular complex has undergone nucleophilic attack. Complex **2** may be readily deprotonated to yield a monocationic species and it may also undergo ligand exchange with chloride ion to give **3**.¹¹ In order to determine if this type of reaction may be extended to complexes of other metal ions with different coordination geometries, the reactions of hydrazines with the extremely stable, octahedral, hexakis(methyl isocyanide)iron(II) cation have been examined.

Experimental Section

Preparation of Compounds. Methylation of potassium ferrocyanide was accomplished using dimethyl sulfate according to the procedure of Hartley.¹² The bisulfate salt which crystallized from the reaction mixture was utilized without further purification.

$[(\text{CH}_3\text{NC})_6\text{Fe}][\text{PF}_6]_2$. A solution containing 1.0 g (6.2 mmol) of ammonium hexafluorophosphate dissolved in a minimum volume of methanol was added to a solution of 1.0 g of $[(\text{CH}_3\text{NC})_6\text{Fe}][\text{HSO}_4]_2$ dissolved in a minimum of methanol. The white pre-

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(11) The X-ray structure of **3** ($\text{M} = \text{Pd}$)¹⁰ has been redetermined and the location of the nitrogen bound hydrogen atoms has been verified: W. M. Butler and J. H. Enemark, *Inorg. Chem.*, **10**, 2416 (1971).

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cipitate, which formed immediately, was collected by filtration and washed with methanol. Purification was achieved by recrystallization from acetonitrile: conductivity, $\Lambda = 167 \text{ cm}^2 \text{ mol}^{-1} \text{ ohm}^{-1}$ (nitromethane); ir 3029 w, 2965 w ($\nu_{\text{C-H}}$), 2238 s ($\nu_{\text{C=N}}$), 1449 m, 1418 cm^{-1} m ($\delta_{\text{C-H}}$).

Anal. Calcd: C, 24.34; H, 3.06; N, 14.20. Found: C, 24.53; H, 2.90; N, 14.24.

$[(\text{CH}_3\text{NC})_6\text{Fe}][\text{B}(\text{C}_6\text{H}_5)_4]_2$. A methanolic solution of sodium tetraphenylborate was added to a methanolic solution of $[(\text{CH}_3\text{NC})_6\text{Fe}][\text{HSO}_4]_2$ and the white precipitate was collected. A pure product was obtained by recrystallization from acetone: conductivity, $\Lambda = 130 \text{ cm}^2 \text{ mol}^{-1} \text{ ohm}^{-1}$ (nitromethane).

Anal. Calcd: C, 76.61; H, 6.21; N, 8.93. Found: C, 76.72; H, 6.28; N, 9.24.

$[(\text{CH}_3\text{NC})_4\text{Fe}(\text{C}_4\text{H}_{10}\text{N}_4)][\text{PF}_6]_2$. Hydrazine (1 ml) was added to a filtered solution of 0.75 g of $[(\text{CH}_3\text{NC})_6\text{Fe}][\text{HSO}_4]_2$ in 50 ml of methanol. The solution was filtered to remove a small quantity of white precipitate and then heated under reflux for 12 hr. The solution was cooled and a filtered methanol solution containing 1.00 g of ammonium hexafluorophosphate was added to it. The white precipitate which formed immediately was removed by filtration and 20 ml of 2-butanol was added to the filtrate. Solvent was distilled from the filtrate until its volume was reduced to 20 ml. The solution was cooled to 0° and allowed to remain at that temperature for several hours during which time the product precipitated as pale yellow crystals. The product and mother liquor were decanted from a small quantity of viscous oil which had formed, and the crystalline product was collected by filtration. Purification was effected by two recrystallizations from methanol-2-butanol. The yield is 0.20 g (25%). The product was dried at 80° *in vacuo*: conductivity, $\Lambda = 172 \text{ cm}^2 \text{ mol}^{-1} \text{ ohm}^{-1}$ (nitromethane); ir 3450 m, 3375 m ($\nu_{\text{N-H}}$); 2958 ($\nu_{\text{C-H}}$); 2236 m, 2192 s ($\nu_{\text{C=N}}$), 1570 m, 1524 m, 1486 m ($\nu_{\text{C=N}}$, $\delta_{\text{N-H}}$), 1443 m, 1416 m, 1356 cm^{-1} ($\delta_{\text{C-H}}$).

Anal. Calcd: C, 23.13; H, 3.56; N, 17.98; F, 36.57. Found: C, 23.46; H, 3.52; N, 18.01; F, 34.96.

$[(\text{CH}_3\text{NC})_4\text{Fe}(\text{C}_6\text{H}_{12}\text{N}_4)][\text{PF}_6]_2$. This complex was prepared from methylhydrazine using the procedure described for the hydrazine adduct: conductivity, $\Lambda = 175 \text{ cm}^2 \text{ mol}^{-1} \text{ ohm}^{-1}$ (nitromethane); ir 3459 m, 3382 m, 3333 m ($\nu_{\text{N-H}}$); 2960 w ($\nu_{\text{C-H}}$); 2237 m, 2197 s ($\nu_{\text{C=N}}$), 1588 m, 1559 m, 1526 w ($\nu_{\text{C=N}}$, $\delta_{\text{N-H}}$), 1454 w, 1428 w, 1401 w, 1378 cm^{-1} m ($\delta_{\text{C-H}}$).

Anal. Calcd: C, 30.87; H, 3.79; N, 17.56. Found: C, 24.61; H, 3.89; N, 17.33.

$[(\text{CH}_3\text{NC})_4\text{Fe}(\text{C}_{10}\text{H}_{14}\text{N}_4)][\text{PF}_6]_2$. This complex was prepared from phenylhydrazine using the procedure described for the hydrazine adduct: conductivity, $\Lambda = 174 \text{ cm}^2 \text{ mol}^{-1} \text{ ohm}^{-1}$ (nitromethane); ir 3446 m, 3333 m ($\nu_{\text{N-H}}$), 2953 w ($\nu_{\text{C-H}}$), 2237 m, 2192 s ($\nu_{\text{C=N}}$), 1594 w, 1569 m, 1549 s, 1495 vw ($\nu_{\text{C=N}}$, $\delta_{\text{N-H}}$), 1456 w, 1446 w, 1430 w, 1418 w, 1410 w, 1374 cm^{-1} m ($\delta_{\text{C-H}}$, $\nu_{\text{C=C}}$).

Anal. Calcd: C, 30.87; H, 3.74; N, 16.00. Found: C, 30.56; H, 3.64; N, 16.77.

$[(\text{CH}_3\text{NC})_4\text{Fe}(\text{C}_8\text{H}_{10}\text{N}_4)][\text{B}(\text{C}_6\text{H}_5)_4]_2$. The salt was prepared in the same way as the hexafluorophosphate analog except that sodium tetraphenylborate replaced the ammonium hexafluorophosphate: conductivity, $\Lambda = 119 \text{ cm}^2 \text{ mol}^{-1} \text{ ohm}^{-1}$ (nitromethane).

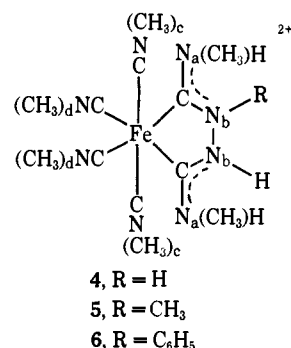
Anal. Calcd: C, 74.09; H, 6.42; N, 11.52. Found: C, 74.22; H, 6.51; N, 11.68.

Physical Measurements. Conductivities were determined by use of a Serfass conductivity bridge with $\sim 10^{-3} M$ nitromethane solutions. Infrared spectra were obtained from fluorocarbon and Nujol mulls and recorded on a Beckman IR-12 spectrometer. Varian A-60 and HA-100 spectrometers were utilized for pmr measurements. A Beckman Expandomatic pH meter with a calomel reference electrode and silver-silver chloride working electrode was utilized for pH titrations of the complexes against standard aqueous sodium hydroxide.

Results

The salt $[(\text{CH}_3\text{NC})_6\text{Fe}][\text{HSO}_4]_2$ has been prepared by the methylation of potassium ferrocyanide with dimethyl sulfate according to the method of Hartley.¹² This salt has been converted into a variety of other salts by metathesis. All of these are 1:2 electrolytes. The salts are air stable and, unlike some isocyanide complexes,^{3a,c,e} unaffected by neutral alcoholic solvents. In basic alcoholic media they undergo extensive decom-

position accompanied by the precipitation of iron metal and the liberation of free methyl isocyanide. Refluxing $[(\text{CH}_3\text{NC})_6\text{Fe}][\text{HSO}_4]_2$ with hydrazines in methanol followed by precipitation as the hexafluorophosphate or tetraphenylborate salts yields the new complexes 4-6 in which hydrazine attack on two isocyanide



functions has occurred.¹³ Attempts to induce further attack of hydrazine on 4 have been unsuccessful. The pale yellow, crystalline complexes are air stable and as solids the hexafluorophosphate salts are stable to 180° (at higher temperature decomposition occurs). The compositions of these salts are confirmed by the analytical data. The conductivity data are consistent with their formulation as 1:2 electrolytes.

Infrared spectra of $[(\text{CH}_3\text{NC})_6\text{Fe}][\text{PF}_6]_2$, 4, 5, and 6 in the region $4000\text{--}1300 \text{ cm}^{-1}$ are presented in the Experimental Section. In addition very strong P-F stretching vibrations are found in the region $840\text{--}860 \text{ cm}^{-1}$ for all of these salts. The $[(\text{CH}_3\text{NC})_6\text{Fe}]^{2+}$ salts all exhibit, as expected for an octahedral complex, a single CN stretching frequency in the region $2230\text{--}2250 \text{ cm}^{-1}$. Although four infrared-active $\text{C}\equiv\text{N}$ stretching modes should be observed for the $(\text{RNC})_6\text{Fe}$ group with local C_{2v} symmetry, only two distinct absorptions are observed for 4 and its substituted derivatives 5 and 6 in the solid state. The inability to observe all the predicted absorptions is undoubtedly due to the poor resolution obtainable from the solid state, and consistent with this the low energy $\nu(\text{C}\equiv\text{N})$ band is quite broad. In addition to C-H stretching modes found for both the $[(\text{CH}_3\text{NC})_6\text{Fe}]^{2+}$ salts and for 4, 5, and 6, the latter three compounds exhibit infrared absorbances which are assigned to the N-H stretches in the region $3460\text{--}3330 \text{ cm}^{-1}$ and absorbances which are probably due to $\delta(\text{N-H})$ and $\nu(\text{C}=\text{N})$ in the $1600\text{--}1450\text{ cm}^{-1}$ region.

The nmr spectra of the new complexes 4-6 support and confirm the structural assignments. The nmr spectrum of 4 in deuterioacetone consists of a doublet ($J = 4.5 \text{ Hz}$) at $\tau 7.00$ (6) which is assigned to the terminal methyl groups on nitrogen a of the chelating ligand, a pair of singlets at 6.56 (6) and 6.43 (6) which are assigned to the two nonequivalent pairs of unreacted isocyanide ligands c and d, a very broad quartet ($J = 4.5 \text{ Hz}$) at 2.50 (2) which is assigned to the terminal $\text{N}_a\text{-H}$ protons of the chelating ligand, and a broad resonance at $-\text{0.23}$ (2) which is assigned to the interior

(13) Amines also react with the isocyanide functions of these complexes. The nature of the products obtained from amine attack has been described separately: J. Miller, A. L. Balch, and J. H. Enemark, *J. Amer. Chem. Soc.*, **93**, 4613 (1971).

N_b -H protons of the chelating ligand. The coupling between the terminal methyl groups and the N_a -H proton has been verified by double resonance experiments. In addition the H_3C-N-H coupling constant is consistent with the values found for *N*-methylacetamide¹⁴ and *N,N'*-dimethylacetamidium ion.¹⁵ The chemical shifts for the various protons in **4** are all in regions similar to those found for the related palladium complex **2**.¹⁰

The pmr spectrum of **5** is similar to that of **4** except that the lower symmetry caused by the introduction of an additional methyl group creates a more complex spectrum. The resonances of the nonequivalent, terminal, methyl groups of the chelating ligand occur as two doublets at 7.04 ($J = 5$ Hz, 3) and 6.74 ($J = 4.7$ Hz, 3). A resonance at 6.58 (6) is assigned to the two equivalent, out-of-plane methyl isocyanide ligands (c). Three singlets at 6.55' (3), 6.47 (3), and 6.46 (3) are assigned to the two, nonequivalent, in-plane methyl isocyanide ligands and the methyl group bound to the inner nitrogen of the chelating ligand.¹⁶ The two, nonequivalent protons on the terminal nitrogens of the chelating ligand give rise to broad absorptions at 2.76 (1) and 2.52 (1). Double resonance experiments indicate that the nitrogen bound proton at 2.76 is coupled to the methyl resonance at 6.74 and the nitrogen bound proton at 2.52 is coupled to the methyl resonance at 7.04. The remaining resonance at -0.48 is assigned to the proton which is bound to one of the inner nitrogens of the chelating ligand.

In the phenyl-substituted complex **6** the nonequivalent, terminal methyl groups of the chelating ligand appear to be accidentally degenerate. They are assigned to a pmr doublet at τ 7.06 ($J = 5.0$ Hz, 6). The resonance at 6.49 (6) is assigned to the two, equivalent, out-of-plane, methyl isocyanide ligands, while the resonances at 6.47 (3) and 6.44 (3) are assigned to the two, nonequivalent, in-plane methyl isocyanide ligands. The phenyl group gives rise to a broad absorption pattern centered at 7.5; the protons bound to the terminal nitrogens of the chelating ligand may be under this pattern. A broad absorption at -0.27 (1) is assigned to the proton bound to the inner nitrogen of the chelating ligand.

Each of the complexes **4**, **5**, and **6** behaves as a weak acid in aqueous solution. Values of pK_a obtained for each are: **4**, $pK_a = 8.4$; **5**, $pK_a = 8.1$; **6**, $pK_a = 7.9$. Similar proton-transfer reactions have been observed for the related platinum and palladium compounds **2**¹⁰ and for other complexes obtained from the addition of alcohols¹⁷ or the pentafluorophenyl anion to isocyanide ligands.² Attempts to isolate the deprotonated forms of the iron complexes **4-6** have not been successful; only mixtures of the di- and monocations were obtained.

However, it has been possible to obtain some interesting information about the sites of proton exchange in these complexes by observing their nmr spectra in

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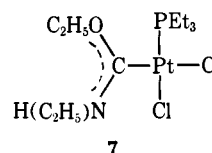
(16) Comparison of the spectra of **4** and **5** leads to the following detailed assignment: the resonances at 6.56 in **4** and 6.58 in **5** assigned to the two, equivalent out-of-plane isocyanide ligands, the resonances at 6.43 in **4** and 6.47 and 6.43 in **5** to the in-plane isocyanide ligands, and the resonance at 6.55 in **5** to the methyl group attached to the inner nitrogen of the chelating ligand.

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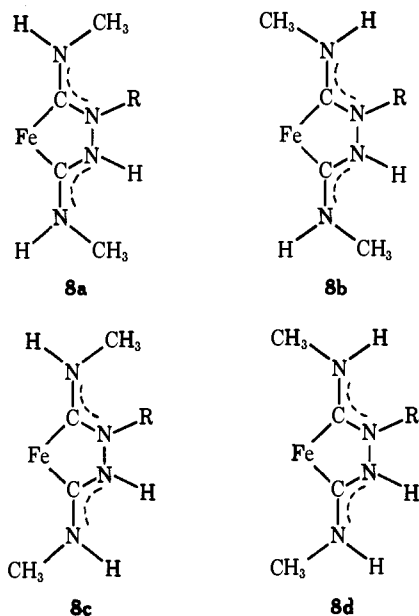
acetone- d_6 -pyridine (20:1 v/v) mixtures. Under these conditions the pmr methyl doublet of **4** at τ 7.00 collapses into a singlet of the same relative intensity and the resonance (originally at -0.23) due to the protons bound to the inner nitrogens of the chelating ligand disappears. The other methyl resonances are unaffected except for slight changes in their chemical shifts. It is not possible to observe effects in the region in which the protons on the terminal nitrogens of the chelate originally resonated because of the presence of resonances due to pyridine. These results are consistent with rapid exchange of all the nitrogen bound protons of the chelating ligand in **4**. Similarly, in **6** all three of the nitrogen bound protons undergo rapid exchange in the presence of pyridine. The terminal methyl doublet of **6** collapses into an equally intense singlet and the resonance due to the internal nitrogen bound proton of the chelate ring disappears in the presence of pyridine. However, in **5** only two of the three available protons undergo rapid exchange. In the presence of pyridine the resonance of the proton bound to the inner nitrogen of the chelate cannot be detected and the methyl resonance at τ 7.04, which in the absence of base appears as a doublet, occurs as a singlet. The other methyl resonances, including the doublet assigned to one of the terminal methyl groups on the chelating ligand, undergo only slight changes in their chemical shifts. Consequently the proton bound to that terminal nitrogen is not undergoing rapid exchange.

Discussion

It is anticipated that the chelating ligands in the complexes **4-6** will be constrained to a planar configuration with restricted rotation of the carbon-nitrogen bonds due to their partial double bond character. In amidinium ions, which contain a similar bonding situation, restricted rotation about the carbon-nitrogen bond has been established.¹⁵ Moreover, a planar arrangement of this ligand has been established by X-ray crystallography for **3** ($M = Pd$).^{10,11} Similarly a planar PtCON unit has been found in the related complex **7**.^{3a} Although three



or four different ligand configurations **8a-d** are possible for each of the complexes **4-6**, there is no evidence, such as doubling of pmr signals or temperature dependence of the spectrum over the range -50 to $+60^\circ$, to suggest the presence of more than a single isomer in our samples. Inspection of space-filling models indicates that these molecules are quite crowded. In **8b**, **8c**, and **8d** the terminal methyl groups which are oriented toward the in-plane, cis ligands are in sterically unfavorable positions. Consequently in **4** the preferred configuration would be **8a**; this is exactly the configuration found in the palladium complex **3**.^{10,11} In the methyl- and phenyl-substituted complexes **5** and **6**, the most probable configurations are **8a** or **8b**; however the experimental evidence does not allow an unambiguous determination of configuration. It is



especially difficult to speculate on **6** because of the accidental degeneracy of the resonances of the two non-equivalent, terminal methyl groups. However some suggestions on the configuration and proton-exchange characteristics of **5** are possible.

The pmr resonance of one of the terminal methyl groups of the chelating ligand in **5** is shifted to lower

field relative to the other terminal methyl of that ligand and relative to the terminal methyl groups of the chelate in **4**. The methyl group which experiences this low field shift is probably the one which is adjacent to the methyl substituent on one of the inner nitrogen atoms of the chelating ligand. Models indicate that in either of the two most probable configurations for this ligand, **8a** or **8b** ($R = CH_3$), the terminal methyl group is in close proximity to either the inner methyl substituent or the methyl isocyanide ligand cis to this terminal methyl group, respectively. Consequently it is likely that the pmr shift to low field of this terminal methyl group is due to steric compression.¹⁸ The absence of rapid, pyridine-induced, proton exchange of the nitrogen bound proton which is coupled to the low-field methyl group may also be understood in terms of the crowded environment in this portion of the molecule. Deprotonation at this terminus of the chelate would necessarily result in increased C-N double bond character and a shorter terminal C-N bond. Since this bond shortening would serve only to increase unfavorable steric interactions, the acidity of the effected N-H proton is decreased to the point that, in pyridine containing solution, rapid proton exchange is not observed at this end of the chelating ligand.

Acknowledgment. This research was supported by Grant GM 18357 from the National Institutes of Health.

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