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Carbene Complexes Resulting from the Addition of Various Amines to Isocyanide Complexes of Iron(II) and Ruthenium(II)

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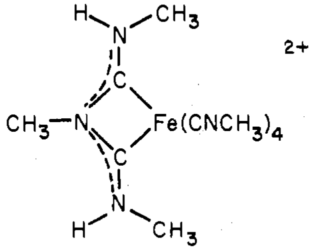
Treatment of $Ru(CN)_6^{4-}$ and $Fe(o\text{-phen})_2(CN)_2$ with dimethyl sulfate produces $Ru(CNCH_3)_6^{2+}$ and $Fe(o\text{-phen})_2(CNCH_3)_2^{2+}$. Electrochemical studies of these and related isocyanide complexes indicate that Fe(III) and Ru(III) isocyanide complexes can only exist under strongly oxidizing conditions. The addition of simple amines to $Fe(CNCH_3)_6^{2+}$ and $Ru(CNCH_3)_6^{2+}$ may produce either monodentate carbene ligands or chelating ligands with two carbene donor centers. Steric effects appear to determine which mode of addition occurs. The chelative addition of hydrazine to $Ru(CNCH_3)_6^{2+}$ produces $Ru(C_4H_{10}N_4)(CNCH_3)_4^{2+}$ and $Ru(C_4H_{10}N_4)_2(CNCH_3)_2^{2+}$. Hydrazine adds to *cis*-$Fe(o\text{-phen})_2(CNCH_3)_2^{2+}$ to give *cis*-$Fe(o\text{-phen})_2(C_4H_{10}N_4)^{2+}$. Acetamidine adds to two isocyanide ligands of both $Fe(CNCH_3)_6^{2+}$ and $Ru(CNCH_3)_6^{2+}$ to give chelated complexes, the possible structures of which are discussed. All new complexes have been characterized by elemental analysis, conductivity, infrared spectra, and pmr spectra. The electronic spectrum of $Fe(o\text{-phen})_2(C_4H_{10}N_4)^{2+}$ is discussed, and it is concluded that the chelating carbene ligand in this complex strongly resembles cyanide ion in its bonding to iron.

Introduction

Although the addition of protic nucleophiles to isocyanide ligands to produce carbene ligands has been extensively investigated for planar complexes of platinum and palladium, relatively little effort has been made to investigate the effects of other metal ions on this reaction.[1,2] This paper presents results relating to the addition of simple amines and polyfunctional amine derivatives to six-coordinate isocyanide complexes of iron(II) and ruthenium(II). These complexes differ in two significant aspects from the well-studied platinum(II) and palladium(II) species. The octahedral geometry of the d^6 complexes makes them sterically more crowded than the d^8 complexes and the d^6 complexes also show diminished substitutional lability in comparison to the d^8 complexes.

The planarity of carbene ligands leads to steric effects which impose limitations on their formation. With sterically unencumbered isocyanide complexes such as $Pt(CNCH_3)_4^{2+}$, $Pd(CNCH_3)_4^{2+}$, and $Au(CNCH_3)_2^{+}$, it is possible to convert all of the isocyanide ligands into carbene ligands. The reactions of these complexes with methylamine produce $M\{C(NHCH_3)_2\}_4^{2+}$ (M = Pt and Pd)[3] and $Au\{C(NHCH_3)_2\}_2^{+}$.[4] However, as we have briefly reported the reaction of methylamine with $Fe(CNCH_3)_6^{2+}$ results in the addition of only a single amine and formation of the chelated complex **1** rather than the anticipated, isomeric complex **2** (M = Fe; R = CH_3).[5]



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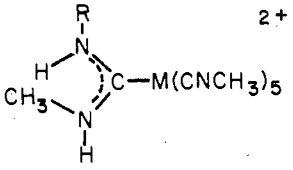

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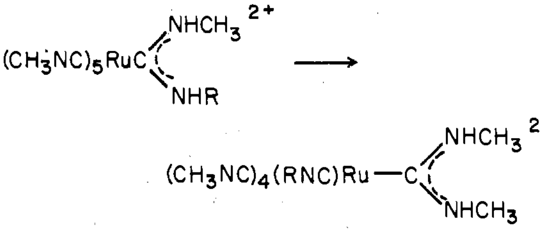
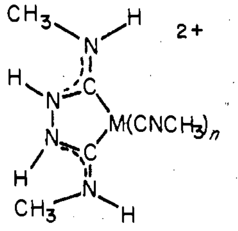
Further studies have shown that complexes of the type **2** are obtained when methylamine is added to $Ru(CNCH_3)_6^{2+}$ and when ammonia is added to $Fe(CNMe)_6^{2+}$.[6] The synthesis and characterization of complexes of the type **1** and **2** will be described within; however, the novel isomerization reactions of these complexes (*e.g.*, eq 1), which result in the transfer of NR groups between isocyanide and carbene ligands,[6] will be described in detail separately.

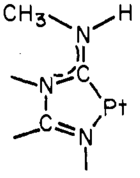


(1)

With polyfunctional amine derivatives it has been possible to construct chelating carbene ligands. Hydrazines have already been shown to react as bidentate nucleophiles toward cis isocyanide ligands in both four-coordinate platinum and palladium complexes[7] and six-coordinate iron complexes.[8] The complexes **3a**, **3b**, and **3c** have been obtained in this way. Acetamidine and 2-aminopyridine have been shown to add to $Pt(CNCH_3)_4^{2+}$ to give bidentate ligands containing the basic unit **4**.[9] In this case an amine center has been



3a, M = Pt; *n* = 2
b, M = Pd; *n* = 2
c, M = Fe; *n* = 4
d, M = Ru; *n* = 4



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[7] W. M. Butler, J. H. Enemark, J. Parks, and A. L. Balch, *Inorg. Chem.*, 12, 451 (1973), and references therein.

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

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added to one isocyanide while an imino center has displaced a second isocyanide. We shall show that this last reaction is strongly altered by the steric effects and lack of lability exhibited by the six-coordinate isocyanide complexes.

Experimental Section

Preparation of Compounds. Dicyanobis(1,10-phenanthroline)-iron(II), Fe(*o*-phen)$_2$(CN)$_2$, was prepared according to the procedure of Schilt.[10]

[Ru(CNCH$_3$)$_6$][PF$_6$]$_2$. Anhydrous $K_4Ru(CN)_6$ (5 g) was stirred with 65 ml of dimethyl sulfate at 95° for 6 hr. The mixture was filtered hot and the filtrate allowed to stand, loosely covered at room temperature. The first crop of white crystalline salt was collected after 48 hr. During the following 10 days several milliliters of viscous oil separated from the reaction mixture. This oil was collected and added dropwise with stirring to 30 ml of 1-propanol. The crude product precipitated immediately as fine white crystals. The combined crops of crude material were recrystallized once from methanol. This material, which is presumed to be the bisulfate salt $Ru(CNCH_3)_6(HSO_4)_2$, was sufficiently pure to use in subsequent reactions. Yields of the salt ranged from 3.5 to 4.0 g. Conversion of this salt into the hexafluorophosphate salt was achieved by dissolving 0.54 g of $Ru(CNCH_3)_6(HSO_4)_2$ in 20 ml of methanol and adding 0.33 g of ammonium hexafluorophosphate dissolved in 20 ml of methanol. The white precipitate which formed immediately was collected and purified by recrystallization from acetonitrile: conductivity, Λ = 206 cm^2 mol^{-1} ohm^{-1}.

Anal. Calcd for $[Ru(CNCH_3)_6][PF_6]_2$: C, 22.61; H, 2.85; N, 13.19. Found: C, 22.73; H, 2.85; N, 13.20.

[Ru(CNCH$_3$)$_6$][BF$_4$]$_2$. A saturated aqueous solution (5 ml) of sodium tetrafluoroborate was added to a solution containing 0.5 g of $[Ru(CNCH_3)_6][HSO_4]_2$ in 5 ml of water. The white precipitate which formed was collected and washed with methanol. Purification was achieved by recrystallization from methanol: conductivity, Λ = 204 cm^2 mol^{-1} ohm^{-1}.

Anal. Calcd for $[Ru(CNCH_3)_6][BF_4]_2$: C, 27.67; H, 3.48; N, 16.13. Found: C, 28.00; H, 3.47; N, 15.99.

[Fe(*o*-phen)$_2$(CNCH$_3$)$_2$][PF$_6$]$_2$. Dicyanobis(1,10-phenanthroline)-iron(II), 936 mg (2 mmol), was stirred in 8 ml of dimethyl sulfate for 1 hr at 75°. The dark red solution was extracted with two 15-ml portions of water. The product was precipitated from the combined aqueous extracts by the addition of an aqueous solution of ammonium hexafluorophosphate. After recrystallization from acetonitrile-1-propanol, 1.4 g (89%) of the yellow, crystalline product was obtained: conductivity, Λ = 187 cm^2 mol^{-1} ohm^{-1}.

Anal. Calcd for [Fe(*o*-phen)$_2$(CNCH$_3$)$_2$][PF$_6$]$_2$: C, 42.02; H, 2.77; N, 10.50. Found: C, 42.79; H, 3.02; N, 10.53.

[Fe(*o*-phen)$_2$(CNCH$_3$)$_2$][BF$_4$]$_2$. The preparation of this salt followed that outlined for the analogous hexafluorophosphate salt except that sodium tetrafluoroborate was used as the precipitating agent: conductivity, Λ = 204 cm^2 mol^{-1} ohm^{-1}.

Anal. Calcd for [Fe(*o*-phen)$_2$(CNCH$_3$)$_2$][BF$_4$]$_2$: C, 50.05; H, 3.30; N, 12.50. Found: C, 49.82; H, 3.29; N, 12.25.

[Ru(CNCH$_3$)$_5${C(NHCH$_3$)$_2$}][PF$_6$]$_2$. Aqueous 40% methylamine (1.0 ml) was added to a solution containing 540 mg (1 mmol) of $[Ru(CNCH_3)_6][HSO_4]_2$ in 40 ml of methanol. The solution was heated under reflux for 15 min, cooled, and added to a filtered solution containing 500 mg of ammonium hexafluorophosphate in 20 ml of methanol. The volume of the solution was reduced to 5 ml under aspirator vacuum, and 20 ml of water was added. The white precipitate which formed was collected and washed with water. After recrystallization from methanol-2-propanol, 405 mg (61%) of colorless crystalline product was obtained: conductivity, Λ = 197 cm^2 mol^{-1} ohm^{-1}.

Anal. Calcd for $[Ru(CNCH_3)_5\{C(NHCH_3)_2\}][PF_6]_2$: C, 23.36; H, 3.46; N, 14.67. Found: C, 23.62; H, 3.46; N, 14.80.

[Ru(CNCH$_3$)$_4${C(NHCH$_2$)$_2$}$_2$][PF$_6$]$_2$. This complex was prepared in the same manner as $Ru(CNCH_3)_5\{C(NHCH_3)_2\}[PF_6]_2$ except that the reflux period was extended to 12 hr: conductivity Λ = 193 cm^2 mol^{-1} ohm^{-1}.

Anal. Calcd for $[Ru(CNCH_3)_4\{C(NHCH_2)_2\}_2][PF_6]_2$: C, 24.04; H, 4.04; N, 16.04. Found: C, 23.84; H, 4.06; N, 15.87.

[Fe(CNCH$_3$)$_5${C(NHCH$_3$)NH$_2$}][PF$_6$]. Concentrated aqueous ammonia (1 ml) was added to a solution of 0.5 g (1 mmol) of $[Fe(CNCH_3)_6][HSO_4]_2$ in 25 ml of methanol. The precipitate of $(NH_4)_2SO_4$ which formed was filtered off and the filtrate heated under reflux for 1 hr. The crude product precipitated as a pale yellow solid upon addition of 0.5 g of NH_4PF_6 in 5 ml of methanol. Recrystallization from acetone-ether gave 0.4 g (66%) of pure material: conductivity, Λ = 181 cm^2 mol^{-1} ohm^{-1}.

Anal. Calcd for $[Fe(CNCH_3)_5\{C(NHCH_3)NH_2\}][PF_6]$: C, 23.66; H, 3.48; N, 16.10. Found: C, 23.79; H, 3.37; N, 15.93.

[Ru(CNCH$_3$)$_4${C$_4$H$_{10}$N$_4$}][PF$_6$]$_2$. Hydrazine hydrate (0.5 ml) was added to a solution of 540 mg (1 mmol) of $[Ru(CN\text{-}CH_3)_6][HSO_4]_2$ in 25 ml of methanol. The precipitate of hydrazine sulfate which formed was filtered off, and the filtrate was heated under reflux for 1 hr. The colorless solution was cooled to room temperature and excess hydrazine precipitated by dropwise addition of 4 ml of 2 *M* H_2SO_4 in methanol. The mixture was filtered and the filtrate volume was reduced to 5 ml under aspirator vacuum. The crude product was precipitated by the addition of 1 g of ammonium hexafluorophosphate in 5 ml of water. Recrystallization from acetone-ether gave 400 mg (57%) of pure material: conductivity, Λ = 193 cm^2 mol^{-1} ohm^{-1}.

Anal. Calcd for $[Ru(CNCH_3)_4\{C_4H_{10}N_4\}][PF_6]_2$: C, 21.53; H, 3.31; N, 16.74. Found: C, 21.50; H, 3.42; N, 16.68.

[Ru(CNCH$_3$)$_2${C$_4$H$_{10}$N$_4$}$_2$][PF$_6$]$_2$. This complex was prepared by the procedure described for the monohydrazine adduct with the following modifications. The initial reflux period was extended to 4 hr after which a second 0.5-ml portion of hydrazine hydrate was added and the reflux continued for 3 hr. The crude product was isolated from the pale yellow solution in the same fashion as described for the monohydrazine adduct. Recrystallization from acetone-2-propanol gave 350 mg (50%) of shiny white crystals: conductivity, Λ = 184 cm^2 mol^{-1} ohm^{-1}.

Anal. Calcd for $[Ru(CNCH_3)_2\{C_4H_{10}N_4\}_2][PF_6]_2$: C, 20.55; H, 3.74; N, 19.96. Found: C, 20.65; H, 3.72; N, 19.89.

[Fe(*o*-phen)$_2${C$_4$H$_{10}$N$_4$}][BF$_4$]$_2$. Anhydrous hydrazine (0.5 ml) was added to a solution containing 672 mg of [Fe(*o*-phen)$_2$(CNCH$_3$)$_2$][BF$_4$]$_2$ dissolved in 20 ml of acetonitrile. The yellow solution became deep purple during a 1-hr reflux period. The cooled solution was then acidified with 3 ml of 48% aqueous fluoroboric acid. Upon addition of dry ether (40 ml) the crude product precipitated as a dark red powder mixed with colorless crystals of hydrazine salts. Following extraction with two 15-ml portions of 5% aqueous HBF_4, the dark red solid was dissolved in 5 ml of acetonitrile containing 5 drops of 48% aqueous HBF_4. The pure product was precipitated as dark, shiny crystals by slow addition of 15 ml of water. The net yield is 400 mg (57%): conductivity, Λ = 186 cm^2 mol^{-1} ohm^{-1}.

Anal. Calcd for [Fe(*o*-phen)$_2${C$_4$H$_{10}$N$_4$}][BF$_4$]$_2$: C, 47.77; H, 3.72; N, 15.92. Found: C, 47.59; H, 3.76; N, 15.65.

[Fe(CNCH$_3$)$_4$(C$_6$H$_{12}$N$_4$)][PF$_6$]$_2$. A methanolic solution of acetamidine was prepared by adding 945 mg (10 mmol) of acetamidine hydrochloride to a solution containing 540 mg (10 mmol) of $NaOCH_3$ in 20 ml of methanol. The precipitate of NaCl was removed by filtration, and 0.50 g (1 mmol) of $[Fe(CNCH_3)_6][HSO_4]_2$ was added to the filtrate. The resulting mixture was heated under reflux for 1 hr and filtered, and the bright yellow filtrate acidified with 1 ml of HPF_6 (65% aqueous). The clear yellow solution was evaporated to 5 ml under aspirator vacuum and 20 ml of water added slowly with stirring. The pure product precipitated as bright yellow crystals (550 mg, 82% yield): conductivity, Λ = 194 cm^2 mol^{-1} ohm^{-1}.

Anal. Calcd for $[Fe(CNCH_3)_4(C_6H_{12}N_4)][PF_6]_2$: C, 25.86; H, 3.72; N, 17.23. Found: C, 25.59; H, 3.86; N, 17.02.

[Ru(CNCH$_3$)$_4$(C$_6$H$_{12}$N$_4$)][PF$_6$]$_2$. This complex was prepared from $[Ru(CNCH_3)_6][HSO_4]_2$ using the procedure described for the corresponding iron complex: conductivity, Λ = 182 cm^2 mol^{-1} ohm^{-1}.

Anal. Calcd for $[Ru(CHCH_3)_4(C_6H_{12}N_4)][PF_6]_2$: C, 24.18; H, 3.48; N, 16.11. Found: C, 23.78; H, 3.25; N, 16.06.

Physical Measurements. Conductivities were determined for ~10^{-3} *M* nitromethane solutions of the complexes through the use of an Industrial Instruments conductivity bridge. Infrared spectra were recorded on a Beckman IR-12 spectrophotometer. Proton magnetic resonance spectra were recorded by a JEOL-MH-100 spectrometer operating at 100 MHz or a Varian A-60 spectrometer at 60 MHz. Electronic spectra were recorded on a Cary 14 spectrometer. A Beckman Expandomatic pH meter was utilized for pH titrations of the complexes in aqueous solution with standard sodium hydroxide titrant.

Electrochemical measurements were made on a Chemtrix Model SSP-2 polarograph in acetonitrile solutions with sample concentrations of ~1 m*M*. The supporting electrolyte was 0.05 *M* tetrapropylammonium perchlorate; a saturated aqueous calomel electrode was utilized as the reference electrode, and a platinum electrode served as the working electrode.

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Results and Discussion

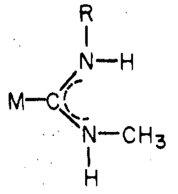
Preparation and Properties of Isocyanide Complexes. The conversion of $Ru(CN)_6^{4-}$ and $Fe(o\text{-phen})_2(CN)_2$ into $Ru(CNCH_3)_6^{2+}$ and $Fe(o\text{-phen})_2(CNCH_3)_2^{2+}$, respectively, was achieved through methylation with dimethyl sulfate. The methylation of $Fe(o\text{-phen})_2(CN)_2$ in this fashion has been reported previously without experimental details.[11] These cations, which are stable to air and moisture, have been isolated as the hexafluorophosphate and tetrafluoroborate salts. In accord with its formulation, colorless $Ru(CNCH_3)_6(PF_6)_2$ exhibits a single isocyanide stretching frequency at 2241 cm^{-1} and a single resonance in the pmr spectrum at τ 6.43 (acetonitrile-d_3). The observation of two isocyanide stretching frequencies (2210 and 2197 cm^{-1}), the pmr spectrum, and the reaction with hydrazine (*vida infra*) establish that $Fe(o\text{-phen})_2(CNCH_3)_2^{2+}$ exists as the cis isomer as is generally the case for bis-*o*-phenanthroline complexes.[12] The pmr spectral parameters obtained for $Fe(o\text{-phen})_2(CNCH_3)_2^{2+}$ are set out in Table I. The appearance of this spectrum in the region of the *o*-phenanthroline protons is very similar to that reproduced[13] for the related complex $Fe(o\text{-phen})_2(CNH)_2^{2+}$ dissolved in liquid hydrogen fluoride, and our results substantiate the contention that no *o*-phenanthroline resonance of $Fe(o\text{-phen})_2(CNH)_2^{2+}$ is obscured by the hydrogen fluoride resonance. As expected for a complex ion with C_2 symmetry, the two *o*-phenanthroline ligands of $Fe(o\text{-phen})_2(CNCH_3)_2^{2+}$ are equivalent but within each ligand all of the protons have been rendered inequivalent. The analysis of the spectrum and the *o*-phenanthroline numbering system for $Fe(o\text{-phen})_2(CNCH_3)_2^{2+}$ correspond to that given in ref 13 for $Fe(o\text{-phen})_2(CNH)_2^{2+}$. Protons 9 and 8 are assigned to the end of the ligand which overlies the other *o*-phenanthroline ring. As a result of the *o*-phenanthroline ring current the positions of the resonance of protons 9 and 8 are shifted upfield from their positions in the free ligand. From this information and the coupling scheme, the assignment of resonances to the 2, 3, 4, and 7 protons follows unambiguously. In assigning chemical shifts to the 5 and 6 protons, the more upfield chemical shift is arbitrarily assigned to the 6 proton. With the exception of $J_{5,6}$, which cannot be measured for free *o*-phenanthroline, the coupling constants in the coordinated heterocyclic ligands correspond rather closely to those found for the free ligand and related pairs of coupling constants (*e.g.*, $J_{2,3}$ and $J_{8,9}$, $J_{2,4}$ and $J_{7,9}$) in the coordinated *o*-phenanthroline are quite similar.

Table I. Pmr Data for Phenanthroline Protons

	Chemical shifts in acetonitrile-d_3 (τ, ppm)		
Proton	$[Fe(o\text{-phen})_2(CNCH_3)_2][BF_4]_2$	$[Fe(o\text{-phen})_2(C_4H_{10}N_4)][BF_4]_2$	*o*-Phenanthroline
H_2	0.31	1.29	0.78
H_3	1.70	2.18	2.27
H_4	0.95	1.40	1.60
H_5	1.56	1.85	2.10
H_6	1.65	1.89	2.10
H_7	1.23	1.59	1.60
H_8	2.30	2.60	2.27
H_9	2.45	2.79	0.78
	Coupling constants, Hz		
$J_{2,3}$	5.3	5.3	4.3
$J_{2,4}$	1.4	1.2	1.8
$J_{3,4}$	8.2	8.2	8.2
$J_{5,6}$	9.0	9.0	
$J_{7,8}$	8.6	8.3	8.2
$J_{7,9}$	1.1	1.3	1.8
$J_{8,9}$	5.4	5.2	4.3

Electrochemical studies of these and other related isocyanide complexes have been performed in order to determine if other oxidation states of these complexes might play a significant role in their chemistry. Over the potential range −2 to +3 V (in acetonitrile solution *vs.* an aqueous saturated calomel electrode), $Ru(CNCH_3)_6^{2+}$ is electrochemically inactive while $Fe(CNCH_3)_6^{2+}$ exhibits a quasireversible, one-electron oxidation with $E_p^a = +2.4$ V. For this process the ratio of the anodic to cathodic peak current ($i_{p,a}/i_{p,c}$) was 1.0, the peak current divided by the square root of the scan rate was a constant, and the separation (ΔE_p) between the anodic and cathodic peaks was 0.08 V. Oxidation of $Fe(o\text{-phen})_2(CNCH_3)_2^{2+}$ is accomplished more easily. This species undergoes a reversible, one-electron oxidation at $E_p = +1.55$ V with $i_{p,a}/i_{p,c} = 1.0$ and $\Delta E_p = 0.06$ V. In comparison, $Fe(o\text{-phen})_3^{2+}$ is even more easily oxidized; a reversible, one-electron oxidation occurs at $E_p^a = +1.17$ V with $i_{p,a}/i_{p,c} = 1.0$ and $\Delta E_p = 0.06$ V. Consequently, it may be concluded that the presence of isocyanide ligands stabilizes iron(II) and ruthenium(II) against oxidation to the trivalent ions, and in general the trivalent state will be relatively unimportant in regard to the chemistry of these particular complexes.

Reactions with Amines. In refluxing methanol solution, methylamine adds to $Ru(CNCH_3)_6^{2+}$ to give $(CH_3NC)_5Ru\{C(NHCH_3)_2\}^{2+}$ (structure **2**) within 15 min. Upon extending the reflux period to 12 hr, addition of a second amine is effected to yield $(CH_3NC)_4Ru\{C(NHCH_3)_2\}_2^{2+}$. These colorless cations have been isolated as hexafluorophosphate salts which exhibit conductivities consistent with their formulation. Infrared and pmr spectral data relating to the characterization of these and other new adducts are set out in Tables II and III. The planar carbene ligands in these complexes exist in the amphi configuration **5** (R = CH_3). This



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arrangement minimizes steric interactions within the carbene ligand and has been found for numerous diaminocarbene complexes.[2-8] Because of this configuration, each of the methyl groups of a carbene ligand produces a separate pmr signal and in the infrared spectrum two N-H stretching frequencies are observed for the carbene ligand. However, the pmr resonances of the two N-H groups are degenerate; this has also been observed for some related palladium and platinum carbene complexes.[3] As is generally the case for diaminocarbene ligands, coupling between the *N*-methyl group and the N-H gives rise to splitting of their resonances with $J = 5$ Hz. In the case of $(CH_3NC)_5Ru\{C(NHCH_3)_2\}^{2+}$, the pmr spectrum does not distinguish between cis and trans isocyanide ligands over a temperature range of −63 to 35°. This is probably due to an accidental degeneracy of the chemical shifts, although a rapid exchange process cannot be eliminated as a possibility. The splitting of the methyl isocyanide

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(11) N. K. Hamer and L. E. Orgel, *Nature (London)*, **190**, 439 (1961).

(12) E. D. McKenzie, *Coord. Chem. Rev.*, **6**, 187 (1971).

(13) M. F. A. Dove and J. G. Hallet, *J. Chem. Soc. A*, 1204 (1969).

Table II. Infrared Data for Iron and Ruthenium Complexes[a]

Compd	ν(NH)	ν(C–H)	ν(C≡N–)	$\nu(\mathrm{N}\overset{\cdots}{-}\mathrm{C}\overset{\cdots}{-}\mathrm{N})$, δ(C–H)
$[(CH_3NC)_5Ru\{C(NHCH_3)_2\}][PF_6]_2$	3460 m, 3395 m	2962 m, 2930 m, 2865 w	2268 m, 2217 s	1568 m, 1516 m, 1454 m, 1413 m
$[(CH_3NC)_4Ru\{C(NHCH_3)_2\}_2][PF_6]_2$	3476 m, 3391 m	2954 m, 2923 m, 2859 w	2267 m, 2212 s	1577 m, 1516 m, 1454 m, 1413 m
$[(CH_3NC)_5Fe\{C(NHCH_3)NH_2\}][PF_6]_2$	3538 m, 3451 m, 3414 m	2943 m, 2889 w	2239 m, 2198 s	1638 s, 1534 s, 1464 m, 1456 m, 1423 m, 1407 m
$[(CH_3NC)_4Fe\{C_5H_{11}N_3\}][PF_6]_2$, **1**	3330 m	2963 w, 2888 w	2244 m, 2205 s	1614 w, 1590 m, 14227 m, 14145 m, 1401 w
$[(CH_3NC)_4Ru\{C_4H_{10}N_4\}][PF_6]_2$, **3d**	3453 m, 3381 m	2956 w	2248 m, 2217 s	1576 m, 1524 m, 1489 m, 1453 m, 1415 m
$[(CH_3NC)_2Ru\{C_4H_{10}N_4\}_2][PF_6]_2$, **6**	3453 m, 3384 m	2962 w	2194 s, 2166 s	1564 m, 1512 m, 1484 w, 1444 w, 1416 m
$[(o\text{-phen})_2Fe\{C_4H_{10}N_4\}][BF_4]_2$, 7	3627 w, 3562 w, 3417 m, 3297 m	3100 w, 2950 w		1425 m, 1474 w, 1453 w, 1412 w
$[(CH_3NC)_4Fe\{C_6H_{12}N_4\}][PF_6]_2$	3402 m	2959 w, 2888 w	2237 m, 2196 s	1660 m, 1555 s, 1498 m, 1459 m, 1420 m, 1412 m
$[(CH_3NC)_4Ru\{C_6H_{12}N_4\}][PF_6]_2$	3398 m	2961 w	2241 m, 2001 s	1661 m, 1554 m, 1496 w, 1460 m, 1419 w, 1412 m

[a] Solids in fluorocarbon mull.

Table III. Pmr Spectral Data for Iron and Ruthenium Complexes

	τ (intensity) in acetonitrile-d_3				
Complex	*CH*$_3$-N-H	*CH*$_3$NC	*H*-N	*H*-N chelate	Other
$[(CH_3NC)_5Ru\{C(NHCH_3)_2\}][PF_6]_2$	7.20 (3) 6.90 (3)	6.52 (15)	3.45 (2)		
$[(CH_3NC)_4Ru\{C(NHCH_3)_2\}_2][PF_6]_2$	7.25 (6) 7.03 (6)	6.57 (6) 6.55 (6)	3.45 (4)		
$[(CH_3NC)_5Fe\{C(NHCH_3)NH_2\}][PF_6]_2$	7.21 (3)	6.53 (15)	3.43 3.20		
$[(CH_3NC)_4Fe\{C_5H_{10}N_3\}][PF_6]_2$, **1**	6.75 (6)	6.62 (6) 6.59 (6)	1.73 (2)		7.13 (3)[a]
$[(CH_3NC)_4Ru\{C_4H_{10}N_4\}][PF_6]_2$, **3d**	7.06 (6)	6.66 (6) 6.46 (6)	3.11 (2)	0.93 (2)	
$[(CH_3NC)_2Ru\{C_4H_{10}N_4\}_2][PF_6]_2$, **6**	7.24 (6) 7.03 (6)	6.46 (6)	3.89 (2) 3.11 (2)	0.93 (4)	
$[(o\text{-phen})_2Fe\{C_4H_{10}N_4\}][BF_4]_2$, 7	7.18 (6)		4.12 (2)	0.17 (2)	*b*
$[(CH_3NC)_4Fe\{C_6H_{12}N_4\}][PF_6]_2$, **8** or **9**	6.92 (6)	6.63 (6) 6.52 (6)	1.84 (2) 1.40 (1)		7.62 (3)[c]
$[(CH_3NC)_4Ru\{C_6H_{12}N_4\}][PF_6]_2$, **8** or **9**	6.97 (6)	6.65 (6) 6.54 (6)	1.82 (2) 1.49 (1)		7.65 (3)[c]

[a] Interior methyl of chelate ring. [b] Resonances of 1,10-phenanthroline reported in Table I. [c] Dangling methyl group from the chelate ring.

resonance in the pmr spectrum of $(CH_3NC)_4Ru\{C(NHCH_3)_2\}_2^{2+}$ into a symmetrical doublet is consistent with cis geometry; however, this splitting could also occur in a trans isomer if the carbene ligands were locked into a particular geometric orientation relative to the four isocyanide ligands by steric constraints. A trans structure appears unlikely in view of the infrared band shapes and intensities in the –C≡N– region which are virtually identical for $(CH_3NC)_4Ru\{C(NHCH_3)_2\}_2^{2+}$ and the hydrazine adduct $(CH_3NC)_4Ru(C_4H_{10}N_4)^{2+}$. A cis geometry is imposed on the latter complex by the chelating dicarbene ligand.

Similarly, reaction of ammonia with $Fe(CNCH_3)_6^{2+}$ results in the formation of the complex $(CH_3NC)_5Fe\{C(NH_2)NHCH_3\}^{2+}$ (structure **2**, R = H) with a single, monodentate carbene ligand. Work on other carbene complexes indicates that methyl substituents on the "inside" of the ligand give rise to pmr resonances at higher fields than do methyl groups on the "outside" positions.[14] Since the methyl group of the carbene ligand in $(CH_3NC)_5Fe\{C(NH_2)NHCH_3\}^{2+}$ resonates at about the same position as the upfield methyl group of the carbene ligands in the ruthenium complexes, the iron complex probably exists in the carbene configuration **5** (R = H) with the single methyl group in an inside position. This arrangement also minimizes steric interaction between the carbene and isocyanide ligands.

The reaction of methylamine with $Fe(CNCH_3)_6^{2+}$ produces the complex **1** in which a chelating dicarbene ligand has been formed. The structure of this unusual complex has been firmly established by an X-ray crystal structure determination.[5] In addition, the pmr and infrared spectra contain features which are diagnostic for the formation of the chelated structure. Invariably, it has been found that the methyl substituents of monodentate diaminocarbene ligands occur at positions upfield from unreacted methyl isocyanide ligands. In addition to features of this type, the pmr spectrum of **1** exhibits a unique methyl resonance at higher fields; this signal is assigned to the interior methyl group of the chelate ring. Further, the cis and trans isocyanide ligands in this and other chelated complexes[8] give rise to two different resonances. Due to the weakness of long-range vibrational coupling, only a single N-H stretching vibration is observed in the chelated complex **1**, and this vibration occurs at a significantly lower energy than the N-H stretching vibrations of monodentate carbene ligands.

We ascribe the formation of the chelate in **1** to a suitable combination of steric effects. Undoubtedly, the initial attack of an amine on $M(CNCH_3)_6^{2+}$ results in formation of a monodentate carbene ligand as in **2**. In the cases described above, this complex is the stable product, but in the case of the $Fe(CNCH_3)_6^{2+}$-methylamine reaction, the carbene ligand

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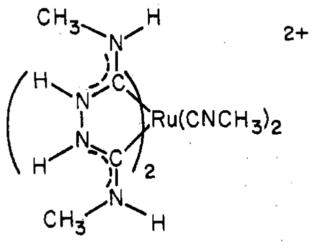
(14) C. G. Kreiter and E. O. Fischer, "XXIIIrd International Congress of Pure and Applied Chemistry," Vol. 6, Butterworths, London, p 151.

acts as a nucleophile toward a second isocyanide ligand to effect chelate ring closure. In this context we note that amidines, which these carbene ligands strongly resemble in structure and chemical behavior, undergo nucleophilic addition to coordinated isocyanides[9] (*vida infra*). The comparison between the ruthenium(II) and iron(II) complexes suggests that the slightly larger radius of ruthenium alleviates some of the interligand interactions so that the monodentate carbene ligand is stable. Similarly, the monodentate carbene ligand generated by the addition of ammonia to $Fe(CNCH_3)_6^{2+}$ is apparently sufficiently smaller than the analogous dimethyl carbene ligand so that the monodentate form does not react further to form a chelate. Significantly, in $(CH_3NC)_5Fe\{C(NH_2)NHCH_3\}^{2+}$ the methyl group of the carbene ligand is located at an interior position (structure **5**, R = H) where interligand interactions are minimized. Unsuccessful attempts to prepare chelating dicarbene ligands from four-coordinate planar isocyanide complexes have been reported.[15] Owing to the ability of a carbene ligand to be positioned in a plane perpendicular to the coordination plane in square planar complexes, it is unlikely that the coordination sphere will force the ligands into the orientation and proximity that is requisite for chelate formation.

Despite the presence of the undoubtedly strained, four-membered chelate ring in **1**, this complex is remarkably stable. Both in the solid state and in solution, the complex is unaffected by oxygen, moisture, or dilute acid. The pmr spectrum of **1** dissolved in trifluoroacetic acid[5] is virtually identical with the pmr spectrum obtained from acetonitrile solution. However, the complex does undergo degenerate, reversible, chelate ring opening upon heating[6] which will be described in greater detail elsewhere.

Attempts to prepare an amine adduct of methylamine with $Fe(o\text{-phen})_2(CNCH_3)_2^{2+}$ have been unsuccessful. Although a reaction clearly occurs, the only product which we have been able to isolate is $Fe(o\text{-phen})_3^{2+}$.

Reactions with Hydrazines. The reaction of hydrazine with $Ru(CNCH_3)_6^{2+}$ yields the chelated complex **3d**. Under more extensive treatment with hydrazine, the bis-chelate complex **6** may be obtained. The physical, chemical, and spectroscopic properties of the ruthenium complex **3d** are analogous to those of the iron complex **3c**, which has been described previously.[8] The bis-chelate complex **6** clearly has cis geometry. The infrared spectrum of this cation exhibits two isocyanide stretching vibrations as required for the cis isomer. The pmr spectrum of **6** presents complementary data which indicates that the ends of the chelate ligands are rendered inequivalent by the overall symmetry of the cation. Thus in **6** the pmr absorptions due to the terminal methyl groups of the chelates appear as two doublets of equal intensity while only one such doublet appears in the spectrum of **3c** and **3d**. Similarily, there are two resonances in the spectrum of **6** due to terminal N-H groups of the chelate ligand. These observations are exactly what is required of a cis cation with C_2 symmetry. Although the chelate N-H groups produce only a single resonance, whereas an AB doublet is anticipated, this degeneracy is not unexpected. As one moves from the ends toward the middle of an otherwise symmetrical bidentate ligand in a complex of C_2 geometry, the overall symmetry-induced differences become smaller. This effect has been noted elsewhere. In $Fe(o\text{-phen})_2(CNH)_2^{2+}$ [13] and $Fe(o\text{-phen})_2(CNCH_3)_2^{2+}$, the resonance due to the 5 and 6 protons shows a much smaller separation than do any other analogous pair of protons.[13] Similarily, in $Ir(bipy)_2Cl_2^+$ the chemical shift difference for the 3 and 3′ protons of the chelate is again the least of any pair of this type.[16]



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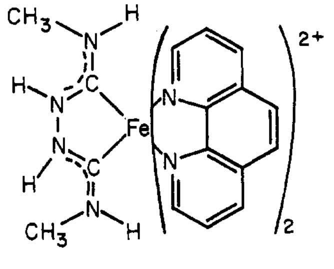
The observation that **6** exists exclusively as the cis isomer is related to the observation[11] that almost all bis(*o*-phenanthroline) and bis(α,α-bipyridyl) complexes also exist as the cis isomer. In all these cases the geometry is governed by the steric influence of the protons which are located α to the metal coordination sites. This steric interaction may be, in part, responsible for the failure of attempts to add a second hydrazine to the planar complexes **3a** and **3b**. We have observed (by pmr spectroscopy) the formation of the iron analog of **6** when $Fe(CNCH_3)_6^{2+}$ is treated with hydrazine over prolonged periods, but we have not attempted to isolate the pure bis-chelate complex.

Hydrazine also adds to the two isocyanide ligands of $Fe(o\text{-phen})_2(CNCH_3)_2^{2+}$ to produce the violet cation **7** which has been isolated as the tetrafluoroborate salt. The infrared spectrum of **7** reveals the absence of any isocyanide stretching frequency but features which are indicative of the formation of the chelating dicarbene ligand and the presence of *o*-phenanthroline ligands. The pmr spectrum of **7** exhibits resonances characteristic of a chelating dicarbene ligand and of *cis-o*-phenanthroline ligands. Since the pmr spectra of relatively few examples of complexes containing *cis*-diimine chelates have been reported and analyzed, the spectrum obtained from **7** is reproduced in Figure 1. The assignment of the pmr spectrum of **7** parallels that of $Fe(o\text{-phen})_2(CNCH_3)_2^{2+}$; however, changes in the various chemical shifts alter the appearance of the spectrum. The data and assignments for the *o*-phenanthroline portion are tabulated in Table I where they may be compared with the data for free *o*-phenanthroline and for $Fe(o\text{-phen})_2(CNCH_3)_2^{2+}$.



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The electronic spectra of low-spin complexes of the type $Fe(o\text{-phen})_2X_2$ (Figure 2) are dominated by intense, low-energy transitions which have been ascribed to inverted metal d to phenanthroline π* charge transfer.[10,17] In considering spectra of such complexes it has been assumed that the energies of the π* *o*-phenanthroline orbitals will be unaffect-

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(15) P. R. Branson and M. Green, *J. Chem. Soc. A*, 1303 (1972).

(16) R. E. DeSimone and R. S. Drago, *Inorg. Chem.*, 8, 2517 (1969).

(17) D. F. Shriver and J. Posner, *J. Amer. Chem. Soc.*, 88, 1672 (1966), and references therein.

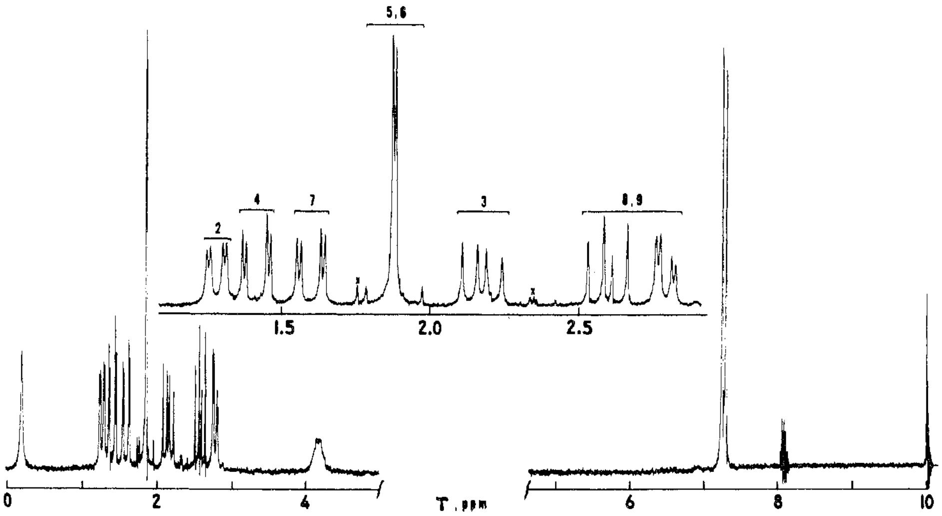

Figure 1. The pmr spectrum of $[Fe(o\text{-phen})_2(C_4H_{10}N_4)][BF_4]_2$ in acetonitrile-d_3 solution. The complete spectrum at the bottom is interrupted to allow the expanded portion of the spectrum due to the *o*-phenanthroline ligands to be inserted above.

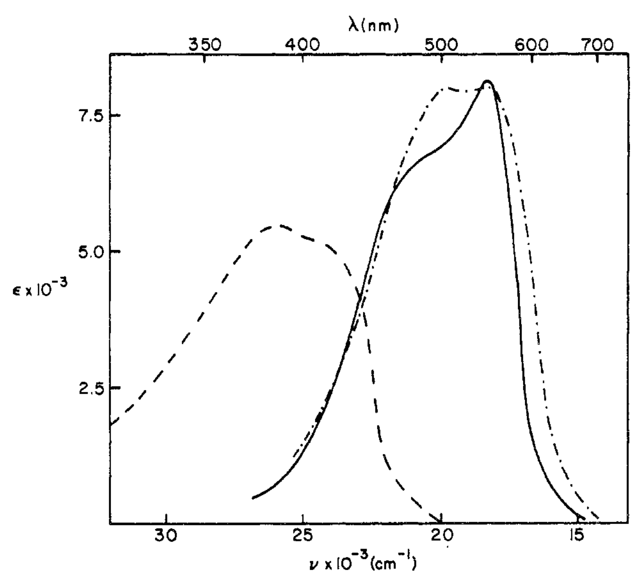

Figure 2. The electronic spectrum of (—) $Fe(o\text{-phen})_2(CN)_2$, (- - - -) $Fe(o\text{-phen})_2(CNCH_3)_2{}^{2+}$, and (- · · ·) $Fe(o\text{-phen})_2(C_4H_{10}N_4)^{2+}$ in methanol solution.

ed by changes in the other ligands X. However, alterations in X which make these ligands better π acceptors and poorer σ donors will lower the energies of the filled iron d orbitals. Consequently, protonation, methylation, or addition of Lewis acids to the cyanide ligands of $Fe(o\text{-phen})_2(CN)_2$ causes the metal → ligand charge-transfer absorbtions to occur at higher energies in these adducts than in unperturbed $Fe(o\text{-phen})_2(CN)_2$ itself. However, in complex 7 with carbene centers as donors the charge-transfer absorptions occur at low energies, energies which are quite similar to those found for $Fe(o\text{-phen})_2(CN)_2$.[18] Thus, the chelating carbene ligand in this complex is a poorer π acceptor than are two isocyanide ligands, and the carbene ligand acts as a strong field donor similar to cyanide ion. Consequently, with metals in high-oxidation states where they are poor π donors, the extent of double bond character in the metal-C-(diaminocarbene) bond may be expected to be small. However, with metals in lower oxidation states, it may still be possible for the diaminocarbene ligands to act as π acceptors.

Previous studies have shown that both chelating[3,7,8] and monodentate[19] ligands containing diaminocarbene centers may be deprotonated. In the case of the chelates **3a** and **3b** it has been demonstrated that deprotonation of an interior, chelate N-H group occurs in preference to loss of a proton from a terminal N-H group.[7] Of the complexes, **1**, $(CH_3NC)_5Ru\{C(NHCH_3)_2\}^{2+}$, $(CH_3NC)_4Ru\{C(NHCH_3)_2\}^{2+}$, $(CH_3NC)_4Ru\{C_4H_{10}N_4\}^{2+}$, and $(CH_3NC)_2Ru\{C_4H_{10}N_4\}_2{}^{2+}$, only $(CH_3NC)_4Ru\{C_4H_{10}N_4\}^{2+}$ is sufficiently acidic to allow measurement of its pK_a in aqueous solution. The pK_a of 8.3 for this complex (**3d**) is similar to the value of 8.4 reported[8] for the analogous iron complex **3c**. Clearly, the chelating carbene ligands contain N-bound protons which are more acidic than are the N-bound protons of the nonchelating carbene ligands. By analogy with the platinum and palladium complexes **3a** and **3b**, we assume that the protons of the chelate ring nitrogens are more acidic than the protons of the terminal N-H groups. Charge dispersion is also important in determining the acidity of various sites in these complexes since the bis-chelate complex **6** is less acidic than the monochelate complexes **3c** and **3d**.

Amidine Additions. The reaction of acetamidine with $Fe(CNCH_3)_6{}^{2+}$ or $Ru(CNCH_3)_6{}^{2+}$ yields similar complexes which have been isolated as the hexafluorophosphate salts. Elemental analysis and conductivity data indicate that a single acetamidine molecule has been added to these complexes and that no loss of isocyanide has occurred. The pmr spectra indicate that in addition to the presence of a unique methyl group and a unique nitrogen-bound proton, these complexes contain two pairs of equivalent, unreacted isocyanide ligands and two equivalent $NH(CH_3)$ groups. From these data it is possible that the amidine added to form the four-membered chelate ring in **8** or that a six-membered chelating ring, **9**, is formed. An unambiguous distinction between these two possibilities cannot be made; however, the data available favor structure **8**. The infrared spectrum shows, in addition to features indicative of the presence of N–H, C–H, C≡N–, and $N\overset{...}{=}C\overset{...}{=}N$ units, an absorption at 1660 cm^{-1} which is

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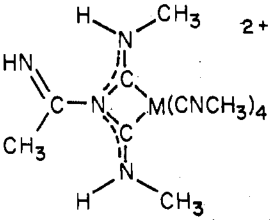
[18] The visible absorption of 7 cannot be attributed to charge transfer involving the chelating dicarbene ligand since 3c is completely transparent throughout the visible and near-infrared regions.

[19] L. Busetto, A. Palazzi, B. Crociani, U. Belluco, E. M. Badley, B. J. L. Kilby, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1800 (1972).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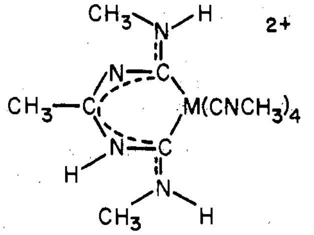
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readily accounted for as ν(C=N) in structure 8 but is of an energy somewhat higher than expected for the six-membered chelate ring in 9. Furthermore, the chemical shifts for the various pmr resonances are very similar to those of the complex 1 which also contains a four-membered chelate ring. The pmr data can only be rationalized in terms of structure 9 if rapid proton exchange is occurring between the two nitrogens in the chelate ring. This proton exchange would serve to make the two terminal NH(CH_3) groups and the two in-plane isocyanide ligands equivalent. A similar phenomenon has been observed for the deprotonated form of **3a** and **3b**[7] except that in these platinum and palladium complexes the proton moves between immediately adjacent nitrogen atoms. At lower temperatures the pmr spectrum of the ruthenium acetamidine adduct undergoes only one change. The terminal N-H resonance at τ 1.82 broadens and splits into two resonances. In acetone-d_6 at −80° these resonances occur at τ 0.64 and 0.12. This indicates that at low temperatures the terminal NH(CH_3) groups become nonequivalent. Presumably, the effect on the chemical shift of the associated methyl resonance is too small to detect. This nonequivalence can be explained in terms of structure **8** if rotation of the $CH_3C(NH)$ group about the C-N (chelate) bond is restricted at low temperatures. However, the low-temperature spectrum is also consistent with structure **9** if the proton exchange described above is slowed sufficiently at low temperatures to reflect the intrinsic asymmetry of the six-membered chelate ring.

Attempted Reactions with 2-Aminopyridine. Refluxing methanolic solutions of 2-aminopyridine with $Fe(CNCH_3)_6^{2+}$ or $Ru(CNCH_3)_6^{2+}$ under conditions more than adequate to effect the additions described above, leads to no reaction. The failure of 2-aminopyridine to add to these complexes although it does add to $Pt(CNCH_3)_4^{2+}$ may be ascribed to a combination of the following effects: the weaker basicity of 2-aminopyridine compared to the other amines, the greater bulk of this amine, and the inability of the pyridine nitrogen to replace an isocyanide ligand in the more substitutionally inert iron and ruthenium complexes.

Acknowledgment. This research was sponsored by grant GM 18357 from the National Institutes of Health.

Registry No. $[Ru(CNCH_3)_6][PF_6]_2$, 49631-67-6; $[Ru(CNCH_3)_6][BF_4]_2$, 49631-68-7; $[Fe(o\text{-phen})_2(CNCH_3)_2][PF_6]_2$, 49664-77-9; $[Fe(o\text{-phen})_2(CNCH_3)_2][BF_4]_2$, 49627-00-1; $[Ru(CNCH_3)_5\{C(NHCH_3)_2\}][PF_6]_2$, 49631-69-8; $[Ru(CNCH_3)_4\{C(NHCH_3)_2\}_2][PF_6]_2$, 49631-70-1; $[Fe(CNCH_3)_5\{C(NHCH_3)NH_2\}][PF_6]_2$, 49716-69-0; $[Ru(CNCH_3)_4\{C_4H_{10}N_4\}][PF_6]_2$, 49849-46-9; $[Ru(CNCH_3)_2\{C_4H_{10}N_4\}_2][PF_6]_2$, 49631-71-2; $[Fe(o\text{-phen})_2\{C_4H_{10}N_4\}][BF_4]_2$, 49631-72-3; $[Fe(CNCH_3)_4(C_6H_{12}N_4)][PF_6]_2$, 49631-73-4; $[Ru(CNCH_3)_4(C_6H_{12}N_4)][PF_6]_2$, 49631-74-5; $[Fe(CNCH_3)_4\{C_5H_{11}N_3\}][PF_6]_2$, 41654-40-4; $[Ru(CNCH_3)_6][HSO_4]_2$, 49627-01-2; $[Fe(CNCH_3)_6][HSO_4]_2$, 15334-25-5; $K_4Ru(CN)_6$, 15002-31-0; $Fe(o\text{-phen})_2(CN)_2$, 15362-08-0; methylamine, 74-89-5; ammonia, 7664-41-7; hydrazine, 302-01-2; acetamidine, 143-37-3.

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Spectral and Structural Studies of Iron(III) Salicylaldimine Complexes. A Six-Coordinate Dinuclear Complex

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The dimeric, five-coordinate complex $[Fe(SALPA)Cl]_2$ (SALPA = the dianion of the potentially tridentate Schiff-base ligand formed from salicylaldehyde and 3-aminopropanol) reacts readily with sodium peroxide to give a red crystalline product, $[Fe_2(SALPA)_2(SALPAH)_2]$, which exhibits antiferromagnetic behavior (μ_{eff}/g-atom of iron = 4.45 and 2.34 BM at 298 and 77°K, respectively). The three-dimensional X-ray crystal structure analysis of the toluene solvate of the complex revealed the presence of six-coordinate iron atoms linked closely by bridging propoxide groups into dinuclear units having a planar, four-membered Fe–O–Fe–O ring (Fe–O = 1.93 (2), 2.00 (2) Å; O–Fe–O = 70.9 (8), 70.2 (8)°; Fe–O–Fe = 108.2 (9), 110.6 (9)°). Hydrogen bonding between the uncoordinated alcohol groups and the phenolic oxygens connects the dimeric units into infinite, doubly linked chains. The iron atoms have virtually identical geometries (distorted octahedron with trans nitrogens, two bridging cis μ_2 oxygens, two terminal oxygens); the iron atoms are nevertheless nonequivalent since the two bridging propoxide groups are chelated to the same iron atom. The preparation of $Fe_2(SALPA)_2(SALPAH)_2$ is discussed and the structure is correlated with the magnetic and spectral properties of several mononuclear and dinuclear iron(III) complexes. Crystal data for $[Fe_2(SALPA)_2(SALPAH)_2]\cdot$toluene: *Pcab*, $a = 20.050$ (3) Å, $b = 24.269$ (4) Å, $c = 18.608$ (3) Å, $Z = 8$, $\rho_{calcd} = 1.34$ g cm^{-3}, $\rho_{obsd} = 1.35$ g cm^{-3}. Final agreement factors are $R = 0.098$ and $R_w = 0.071$ for 1160 reflections above background.

Introduction

Schiff base complexes of iron(III) are of considerable interest because of the diversity of coordination geometries and the unusual magnetic properties which have been observed.[1-7] Thus, mononuclear and polynuclear complexes have been found to have distorted trigonal-bipyramidal,[1,2] square-pyra-

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