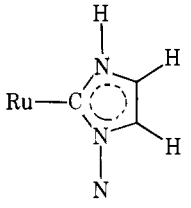
A Comparison of Isomeric Carbene (Ylide) and Amidine Complexes of Cobalt(III). An Approach to the Study of Carbon-Coordinated Imidazole

Daniel J. Doonan, John E. Parks, and Alan L. Balch*

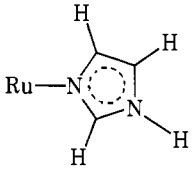
Contribution from the Department of Chemistry, University of California, Davis, California 95616. *Received April 18, 1975*

Abstract: The Co(III) carbene complexes $[Co(DMGH)_2(L)_2][PF_6]$ and $[Co(CH_3)(DMGH)_2(L)]$ (DMGH = dimethylglyoximato, L = $:C(NHCH_3)_2$) and the isomeric formamidine complexes (L = $:N(CH_3)CH(NHCH_3)$) have been prepared and characterized. These systems are viewed as acyclic analogues of C- and N-coordinated imidazole complexes. Proton magnetic resonance (^1H NMR) spectra indicate that the carbene and amidine ligands both contain planar, conjugated N-C-N units similar to those observed in amidinium ions. Specific assignments of the ligand conformations have been made on the basis of ^1H NMR parameters. The effects of internal steric interactions and solvents on the observed conformer distributions are discussed. $[Co(CH_3)(DMGH)_2(C(NHCH_3)_2)]$ undergoes irreversible themal isomerization in solution to form the isomeric formamidine complex. Possible mechanisms for this novel linkage isomerization are considered. Protic acids induce rapid solvolysis of the formamidine ligands in both types of complexes. Under similar conditions the carbene complexes remain intact but undergo rapid proton exchange at the carbene nitrogens.

Recent studies of ruthenium complexes of imidazole have revealed the existence of complexes containing imidazole coordinated through a ruthenium carbon bond, **1**, as well as the more common coordination through nitrogen, **2**.[1,2]



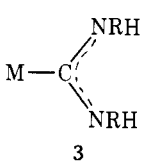
1



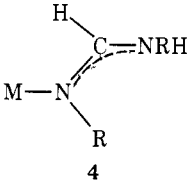
2

Under acidic conditions it has been shown that some complexes of type **2** undergo isomerization to species of type **1**. At present this novel type of linkage isomerism appears to be limited to a few complexes of ruthenium. However, the C-bound linkage isomer is related to a number of other ylide or carbene complexes which have been prepared by other routes.[3,4] Other complexes containing bonds from a metal to C-2 of various imidazole derivatives have been prepared, but in these cases the positioning of substituents on both of the imidazole nitrogen atoms has effectively blocked these atoms as potential coordination sites.[3,4]

Because of the frequent occurrence of imidazole units at the metal binding sites of naturally occurring macromolecules, it has been suggested[1] that this form of linkage isomerism may have considerable biological significance. An important question which arises in this context concerns the ability of more common metal ions to engage in binding imidazole through C-2. Since the stability of such species with biologically important metals like iron, cobalt, and copper is not established, it is not certain whether failure to observe C-bound imidazole complexes of these metals is due to their instability or to the lack of a facile synthetic route to the C-bound linkage isomer. In order to explore these questions a rational route to the preparation of similar linkage isomers has been devised. Acyclic carbene complexes **3** are readily available through the reaction of amines with coordinated isocyanides. Complexes containing this unit offer a convenient analogue to the C-bound imidazole **1**. Amidine complexes **4**, which are acyclic analogues of **2**, may be prepared by either the reaction of an amine with a coordinated nitrile[5,6] or, as reported here, by the direct reaction of an amidine with a metal ion.



3



4

Herein, the synthesis of low spin cobalt(III) complexes of types **3** and **4** are reported. Such complexes are of potential relevance to the chemistry of coenzyme B_{12} which contains a benzimidazole function that acts as one of the axial ligands of the central cobalt.[7] This work, along with previous preparations of low spin iron(II) carbene complexes,[8-10] indicates that at least two common metals have the potential for forming complexes with imidazole through C-2. Although the structural similarities between carbene complexes and free amidinium ions have been emphasized in previous studies,[8,11] few comparisons between amidine ligands and carbene ligands have been made. In addition to the structural relationships between coordinated carbenes and amidines, these moieties are related in another way. When carbene ligands are separated from a metal, they isomerize into the corresponding formamidine. Consequently, it appears that carbene complexes are intermediates in the metal catalyzed synthesis of formamidines via the α-addition of amines to isocyanides.[12] In addition to the syntheses of these carbene and amidine complexes, an investigation of the conformation of both types of ligands, the behavior of both types of ligands upon protonation, and an example of the isomerization **3** → **4** is reported.

Experimental Section

Preparation of Compounds. Methyl isocyanide[13] (caution, *toxic*), *N,N'*-dimethylformamidine,[14] methylatobis(dimethylglyoximato)cobalt(III) dimer,[15] and bis{di(methylamino)carbene}-gold(I) hexafluorophosphate (**14**)[12] were prepared by the reported procedures.

$[(CH_3NC)_2Co(DMGH)_2][PF_6]$. A solution containing 928 mg (8.00 mmol) of dimethylglyoxime in 50 ml of ethanol was added to a solution of 952 mg (4.00 mmol) of cobalt chloride hexahydrate in 5 ml of water. Methyl isocyanide (0.6 ml, 10 mmol) was added to the blue-green solution. An air stream was bubbled through the solution for 20 min. After filtration, 648 mg (4.00 mmol) of ammonium hexafluorophosphate dissolved in 10 ml of water was added to the filtrate. The brown crystalline product was collected by filtration. Purification was achieved by recrystallization from nitro-

methane–acetone (yield 750 mg, 41%): conductivity, Λ = 96 cm^2 mol^{-1} ohm^{-1}; ir 2270 cm^{-1} ($\nu_{C\equiv N}$); ^{1}H NMR in dimethyl-d_6 sulfoxide, τ 7.76 (methyl groups of DMGH), 6.62 (CH_3NC), −6.95 (O-*H*···O). Anal. Calcd for $C_{12}H_{20}CoF_6N_6O_4P$: C, 27.92; H, 3.91; N, 16.28. Found: C, 28.15; H, 3.74; N, 16.40.

[{(CH$_3$NH)$_2$C}$_2$Co(DMGH)$_2$][PF$_6$]. An ethanol-water solution containing $[(CH_3NC)_2Co(DMGH)_2]^+$ was prepared via the above procedure. Methylamine (1.0 ml of a 40% aqueous solution) was added to the mixture and aeration was continued for an additional 20 min. The mixture was filtered and a solution of 1.0 g (6.1 mmol) of ammonium hexafluorophosphate in 10 ml of water was added to the red-orange filtrate. The crude solid product was collected and recrystallized from nitromethane to give 1.0 g (49%) of light yellow crystals: conductivity, Λ = 95 cm^2 mol^{-1} ohm^{-1}; ir 3365 (ν_{N-H}), 1575 (ν_{N-O}, $\nu_{N\cdots C\cdots N}$). Anal. Calcd for $C_{14}H_{30}CoF_6N_8O_4P$: C, 29.08; H, 5.23; N, 19.38. Found: C, 28.77; H, 4.76; N, 19.37.

[(CH$_3$NH$_2$)$_2$Co(DMGH)$_2$][PF$_6$]. Methylamine (2 ml of 40% aqueous) was added to a solution prepared by adding 928 mg of dimethylglyoxime dissolved in 50 ml of ethanol to a solution of 952 mg of cobalt chloride hexahydrate in 5 ml of water. The solution was aerated for 30 min and filtered. Addition of 648 mg of ammonium hexafluorophosphate to the filtrate produced orange crystals. Purification was achieved by recrystallization from nitromethane (yield 1.9 g, 96%): conductivity, Λ = 92 cm^2 mol^{-1} ohm^{-1}; ir 3300, 3220, 3140 (ν_{N-H}), 1595, 1570, 1560 sh (ν_{N-O}, δ_{N-H}); ^{1}H NMR in acetone-d_6, τ 8.40 (CH_3N, triplet, $^3J_{H-H}$ = 6.5 Hz), 7.86 (methyl groups of DMGH), 7.28 (H_2–N, broad, $^3J_{H-H}$ not resolved). Anal. Calcd for $C_{10}H_{24}CoF_6N_6O_4P$: C, 27.92; H, 3.91; N, 16.28. Found: C, 28.15; H, 3.74; N, 16.40.

[{(CH$_3$NH)$_2$C}$_2$Co(DMGBF$_2$)$_2$][BF$_4$]. Boron trifluoride etherate (2.0 ml) was added to a suspension of 200 mg (0.346 mmol) of $[\{(CH_3NH)_2C\}_2Co(DMGH)_2][PF_6]$ in 20 ml of ether. The mixture was stirred at room temperature for 72 h. The solid was then collected, washed with ether, and recrystallized from acetonitrile–1-propanol to give 210 mg (96%) of product: ir 3415 (ν_{N-H}), 1615, 1585, 1569, 1550 (ν_{N-O}, $\nu_{N\cdots C\cdots N}$, δ_{N-H}), 1065, 1012 (ν_{B-F}). Anal. Calcd for $C_{14}H_{28}B_3CoF_8N_8O_4$: C, 27.31; H, 4.58; N, 18.20. Found: C, 27.53; H, 4.81; N, 18.02.

[{(CH$_3$NH)CHN(CH$_3$)}$_2$Co(DMGH)$_2$][PF$_6$]. *N,N'*-Dimethylformamidine (2.0 ml, 20 mmol) was added to a solution prepared by mixing a solution of 952 mg of cobalt chloride hexahydrate in 5 ml of water with a solution of 928 mg of dimethylglyoxime in 50 ml of ethanol. Air was bubbled through the solution for 45 min. After filtration 3 ml of 65% aqueous hexafluorophosphoric acid was added to the filtrate. The mixture was stored at −10 °C for 1 h and then filtered to collect the yellow-brown crystalline product. Recrystallization from nitromethane–ether gave 350 mg (19%) of pure material: conductivity, Λ = 100 cm^2 mol^{-1} ohm^{-1}; ir 3650 sh, 3570, 3350 (ν_{N-H}), 1670, 1560 ($\nu_{N\cdots C\cdots N}$, ν_{N-O}, δ_{N-H}). Anal. Calcd for $C_{14}H_{30}CoF_6N_8O_4P$: C, 29.08; H, 5.23; N, 19.38. Found: C, 28.64; H, 5.38; N. 19.27.

(CH$_3$NC)(CH$_3$)Co(DMGH)$_2$. This compound was prepared from $[CH_3Co(DMGH)_2]_2$ and methyl isocyanide as described previously:[16] ir 2202 ($\nu_{C\equiv N}$), 1535 (ν_{N-O}); ^{1}H NMR in dimethyl-d_6 sulfoxide τ 9.27 (CH_3-Co), 7.92 (methyl groups of DMGH), 6.61 ($CNCH_3$, triplet, $^2J_{N-H}$ = 2.5 Hz), −8.40(O-*H*···O).

(CH$_3$NH$_2$)Co(CH$_3$)(DMGH)$_2$. Anhydrous methylamine was bubbled through a suspension of 0.3 g (0.5 mmol) of $[CH_3Co(DMGH)_2]_2$ in 10 ml of dichloromethane. The solids dissolved within 1 min to give a clear yellow solution. The product was precipitated by addition of ether (15 ml). Following recrystallization from dichloromethane–ether 310 mg (92%) of dark yellow crystals was obtained: ir 3280 sh, 3240, 3160 (ν_{N-H}), 1560 (ν_{N-O}, δ_{N-H}); ^{1}H NMR in dimethyl-d_6 sulfoxide τ 9.76 (CH_3-Co), 8.24 (CH_3N, triplet, $^3J_{H-H}$ = 6.5 Hz), 7.91 (methyl groups of DMGH), 7.20 (H_2N, broad quartet, $^3J_{H-H}$ = 6.5 Hz), −8.45 (O-*H*···O). Anal. Calcd for $C_{10}H_{22}CoN_5O_4$: C, 35.83; H, 6.61; N, 20.89. Found: C, 36.31; H, 6.50; N, 21.12.

{(CH$_3$NH)$_2$C}Co(CH$_3$)(DMGH)$_2$. Anhydrous methylamine was passed through a solution of 345 mg of $[(CH_3NC)(CH_3)Co(DMGH)_2]$ in 10 ml of CH_2Cl_2. The solution color changed from light yellow to orange after 1 min. Addition of methylamine was discontinued and three drops of methyl isocyanide were added. The solution was allowed to stand, protected from light, for 48 h. The light yellow solution was evaporated to dryness under vacuum. The residue was recrystallized from chloroform–hexane to give 330 mg (90%) of yellow crystals: ir 3390, 3290, 3170 (ν_{N-H}), 1565 (ν_{N-O}, $\nu_{N\cdots C\cdots N}$, δ_{N-H}). Anal. Calcd for $C_{12}H_{25}CoN_6O_4$: C, 38.30; H, 6.70; N, 22.33. Found: C, 38.36; H, 6.81; N, 22.44.

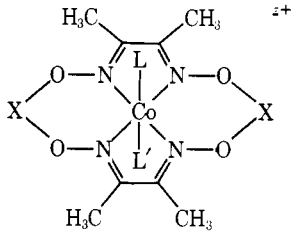
{(CH$_3$NH)CHN(CH$_3$)}Co(CH$_3$)(DMGH)$_2$. *N,N'*-Dimethylformamidine (0.10 ml, 1.4 mmol) was added dropwise to a stirred suspension of 0.4 g (0.66 mmol) of $[CH_3Co(DMGH)_2]_2$ in 15 ml of dichloromethane. Hexane (25 ml) was added to the resulting yellow solution to precipitate the product. Recrystallization from dichloromethane–hexane yielded 0.42 g (77%) of yellow crystals: ir 3330 sh, 3280 (ν_{N-H}), 1665, 1560 (ν_{N-O}, $\nu_{N\cdots C\cdots N}$, δ_{N-H}). Anal. Calcd for $C_{12}H_{25}CoN_6O_4$: C, 38.30; H, 6.70; N, 22.33. Found: C, 38.52; H, 6.78; N, 22.15.

Physical Measurements. These were performed as outlined previously.[10] Infrared spectra were recorded for powdered solids in fluorocarbon (4000–1300 cm^{-1}) or mineral oil (1300–600 cm^{-1}) mulls.

Thermal Isomerization Reactions. Solutions of the complexes in NMR tubes were degassed on a vacuum line and the tubes were then sealed under vacuum. A Kontes NMR tube heater served as a constant (±0.5°) temperature bath. ^{1}H NMR spectra were recorded periodically at ambient temperatures (ca. 30°). The samples underwent no perceptible change in compostion during the times required to obtain the spectra.

Results and Discussion

Preparation and Characterization of Complexes. Two pairs of linkage isomers have been prepared. Both involve Co(III) and utilize two dimethylglyoxime monoanions (DMGH) as in-plane donors. The first pair of isomers are cations **5** and **6**. The two axial sites, L and L', are occupied



5, X = H; L = L' = C(NHCH$_3$)$_2$; z = 1
6, X = H; L = L' = N(CH$_3$)CH(NHCH$_3$); z = 1
7, X = BF$_2$; L = L' = C(NHCH$_3$)$_2$; z = 1
8, X = H; L = CH$_3$; L' = C(NHCH$_3$)$_2$; z = 0
9, X = H; L = CH$_3$; L' = N(CH$_3$)CH(NHCH$_3$); z = 0

by di(methylamino)carbene ligands in **5** and isomeric *N,N'*-dimethylformamidine ligands in **6.** The carbene complex **5** was prepared in a one-step synthesis which involved the aerial oxidation of Co(II) in the presence of dimethylglyoxime, methyl isocyanide, and methylamine. In the absence of methylamine this procedure gives the bisisocyanide complex $[(CH_3NC)_2Co(DMGH)_2]^+$. In the preparation of **5** the intermediate bisisocyanide complex has undergone nucleophilic addition of methylamine to each isocyanide donor carbon. Complex **6** was also prepared by oxidation of Co(II) in the presence of dimethylglyoxime and, in this case, *N,N'*-dimethylformamidine. This procedure yielded only ca. 20% of the desired product. Since a sufficient quantity of **6** was available for characterization, no effort was made to improve the yield. The complexes **5, 6,** $[(CH_3NC)_2Co(DMGH)_2]^+$, and $[(CH_3NH_2)_2Co(DMGH)_2]^+$ were isolated as crystalline, analytically pure, hexafluorophosphate salts. Conductivity data from nitromethane solutions indicate that each salt is a 1:1 electrolyte. The infrared spectra of these cations are consistent with their formulations and clearly indicate that the isomers **5** and **6** are distinguishable. Both isomers show strong N–H stretching vibrations in the 3500–3100 cm^{-1} region and absorbtions due to δ_{N-H} and $\nu_{N\cdots C\cdots N}$ in the 1600–1500 cm^{-1} region. The ^{1}H NMR spectra of the complexes are also in

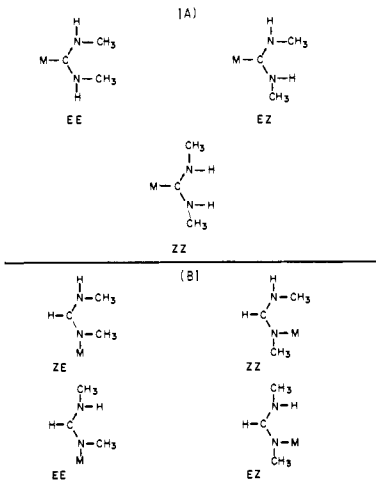


Figure 1. Possible conformations of (A) di(methylamino)carbene and (B) *N,N'*-dimethylformamidine ligands.

accord with their formulation and allow the conformation of the axial ligand to be ascertained (vide infra).

The reaction of **5** with boron trifluoride etherate results in the introduction of BF_2 bridges between the glyoxime ligands to give **7.** The carbene ligands remain intact during this procedure although their conformations are altered.[17] Attempts to introduce BF_2 bridges into **6** have been unsuccessful; **6** is decomposed by boron trifluoride etherate.

The second pair of linkage isomers are the neutral complexes, **8** and **9,** with L = methyl. The amidine complex **9** was prepared by addition of *N,N'*-dimethylformamidine to $[CH_3Co(DMGH)_2]_2$. The carbene complex **8** was prepared by the addition of methylamine to $(CH_3NC)CH_3Co(DMGH)_2$. Since methylamine also caused ligand substitution of methyl isocyanide, this reaction was performed with excess methyl isocyanide present. The carbene ligand of **8** was resistant to replacement by methylamine or methyl isocyanide. Analytical and infrared data for **8** and **9** are given in the experimental section. These complexes are nonelectrolytes with appreciable solubility in chloroform and dichloromethane.

Conformation of Carbene and Amidine Ligands. A number of x-ray structures have established that the donor carbon and the two nitrogen atoms of diaminocarbene ligands are trigonal planar. The length of the C–N bonds and the observations of restricted rotation about these bonds indicate that there is appreciable double bond character in these bonds as would be anticipated for a three-center, four π electron system.[3,4,11] Extensive structural data for amidine complexes are not available. It is to be expected that coordinated amidines will adopt a planar geometry with partial double bond character in both C–N bonds. Proton magnetic resonance studies of amidinium ions have been interpreted in terms of a planar, conjugated N–C–N unit with restricted rotation about the C–N bonds.[18] Similar structural features should occur when a metal ion, rather than a proton, coordinates an amidine.

As a result of these considerations, several conformations are possible for amidine and carbene ligands. These are shown in Figure 1. For the carbene ligands under consideration three configurations are possible while for the isomeric amidine ligand four configurations must be considered. A number of carbene ligands and the *N,N'*-dimethylacetamidinium ion adopt the *EZ* or amphi configuration.[8,11,18]

The ^1H NMR spectra of the complexes **5** through **9** allow the ligand conformations to be identified. The relevant ^1H NMR data are presented in Figure 2 where the resonance positions and coupling constants are assigned to particular

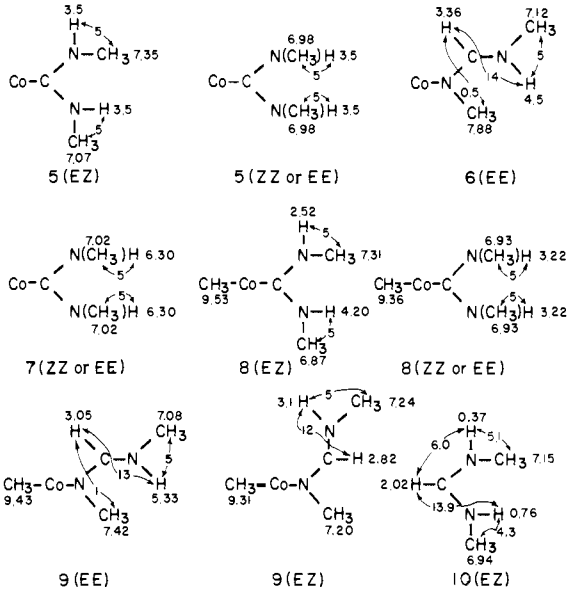


Figure 2. ^1H NMR parameters for di(methylamino)carbene complexes (**5, 7,** and **8**), *N,N'*-dimethylformamidine complexes (**6** and **9**), and the *N,N'*-dimethylformamidinium ion (**10**). Data are obtained for solutions of **5, 6,** and **7** in acetonitrile-d_3, **8** and **9** in chloroform-*d*, and **10** in dimethyl-d_6 sulfoxide. In these solvents the conformer distributions of **5, 8,** and **9** are as follows: **5**(*EZ*):**5**(*ZZ* or *EE*) $\simeq$ 1:2.3; **8**(*EZ*):**8**(*ZZ* or *EE*) = 1:1; **9**(*EZ*):**9**(*EE*) = 1:2. Chemical shifts are in τ units. Coupling constants are in hertz and are represented here between arrows which connect the coupled protons. The dimethylglyoximato (DMGH) ligands of the cobalt complexes have been omitted for clarity. The DMGH methyl resonances are conformation independent and occur at 7.84 (**5**), 7.65 (**6**), 7.56 (**7**), 7.86 (**8**), and 7.83 (**9**).

conformers. All coupling assignments have been verified by double resonance techniques. ^1H NMR data are included for the *N,N'*-dimethylformamidinium ion, **10.** This ion adopts the *EZ* conformation and its ^1H NMR spectrum forms part of the basis for the following conformational analysis. The two $^3J_{HCNH}$ of 6.3 and 13.9 Hz in **10** are assigned as cis and trans coupling constants, respectively. This assignment results in associating the inner methyl group with the high field doublet centered at τ 7.15. Others have assigned the higher field methyl resonances of N-methylated amidines and amides to interior, rather than exterior, resonances on the basis of a variety of arguments.[18,19]

The spectra of the isomeric complexes **8** and **9** in chloroform-*d* solution indicate that two conformers of each complex are present. Here, as is generally the case in this series of compounds, the resonances of the axial ligands, including the cobalt bound methyl groups, are sensitive to conformation, but the resonances of the dimethylglyoxime ligands do not reveal the presence of different conformers. Only one resonance due to all the dimethylglyoxime methyl groups is seen. The O–H protons of the dimethylglyoxime ligands have, in general, not been examined since they occur at inconveniently low fields and are not expected to produce any additional information. Of the two isomers of **8** that are detected, one possesses two different carbene methyl groups and must be the *EZ* isomer. Assignment of the second conformer is more difficult. Since the methyl group of this conformer appears at a resonance position closer to the position of the exterior methyl group of **8EZ** than that of the interior methyl group, this isomer may have the *ZZ* conformation. In chloroform solution the abundances of the two conformers of **8** are 50% *EZ*, 50% *ZZ*. This distribution is, however, solvent dependent. In acetonitrile solution, the same two conformers are present but the ratio is 85% *EZ*, 15% *ZZ*, while in dimethyl sulfoxide the distribution is ca. 95% *EZ*,

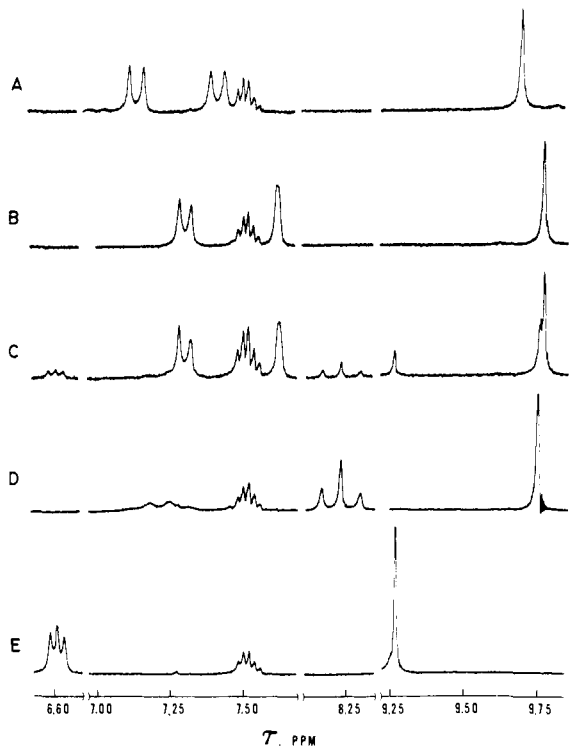


Figure 3. ^{1}H NMR spectra of methylcobaloxime complexes $Co(CH_3)(DMGH)_2(L)$ in dimethyl-d_6 sulfoxide solution: (A) L = $:C(NHCH_3)_2$, ~95% *EZ*; (B) L = $:N(CH_3)CH(NHCH_3)$, *EE*; (C) mixture obtained by heating sample (A) for 21 h at 70°; (D) L = $:NH_2CH_3$; (E) L = $:CNCH_3$. The recurring multiplet at τ 7.52 is due to residual undeuterated solvent. Resonances occurring at τ >9.25 are due to the cobalt bound methyl group while the other resonances shown belong to methyl groups on the other axial ligands and to the NH protons of the methylamine ligand.

5% *ZZ*. For **9** two of the four possible conformers are detectable. Both exhibit $^2J_{HNCH}$ of about 14 Hz so the N-H and C-H protons of the amidine ligand are trans. Consequently the two conformers present are *EE* and *EZ*. The specific assignments shown in the figure were based on the observation of $^4J_{HH}$ of 1.5 Hz in one conformer (assigned as *EE*) but no detectable, analogous coupling in the other conformer (assigned as *EZ*). This assignment again rests on the assumption that trans coupling will be greater than cis coupling. This is in part verified: the trans coupling constant in *N,N*-dimethylformamide is 1.12 Hz, while the cis coupling constant is 0.56 Hz.[19] In chloroform the distribution of conformations of **9** is 67% *EE* and 33% *EZ*. As is the case with the carbene complex, the conformer population of the amidine complex is solvent dependent. In acetonitrile the *EE* conformer is the most prominent (>90%) although a second isomer is detectable in the ^{1}H NMR spectrum. It has not been possible to obtain sufficient data to identify this conformer. In dimethyl sulfoxide solutions of **9** the *EE* conformer is observed exclusively.

With the complexes **5, 6,** and **7,** the presence of two axial ligands, which may independently assume the conformations shown in Figure 1, increases the complexity of the conformational analysis. If each axial ligand can independently assume the conformations shown in Figure 1, then there are six conformers possible for the carbene complexes **5** and **7** and ten conformers possible for the amidine complex **6.** The ^{1}H NMR spectrum of **5** reveals the presence of several conformers. The carbene ligands are present in at least two conformations: one, with two types of methyl groups, must be the *EZ* conformer; the second is assigned as the *ZZ* conformer on the basis of the low field methyl group resonance position. All of the carbene methyl resonances of **5** are unusually broad. It appears that not only are the carbene ligands present in two conformations but that the ligand trans to a particular conformation of the carbene ligand may be either the *EZ* or *ZZ* conformer. Thus it appears that at least three—(*EZ,EZ*), (*EZ,ZZ*), and (*ZZ,ZZ*)—of the possible six conformers of **5** are present. In distinct contrast in **7** only one conformer is present, one with identical methyl groups on the carbene ligands. This is probably the *EE* conformer. The conformational change induced by the transformation of **5** into **7** may result from an increase in the bulk of the in-plane ligand. Examination of space filling models (Corey, Pauling, Koltum) indicates that **7** is appreciably more crowded than **5** and that some of this crowding may be alleviated by folding the carbene ligands into the *EE* conformation.

Complex **6** also appears to exist as only a single conformer in acetonitrile-d_3 solution. The conformational assignment is based on the observation of a 13 Hz coupling between the C-H and N-H protons and on the observation of only a 0.5 Hz coupling along the CH_3-N-CH unit.

These data clearly demonstrate that both carbene and amidine ligands possess a planar 4π electron system extending over a CN_2 unit. Previous discussions of carbene conformations have stressed the importance of steric interactions within the carbene ligand itself. The data for these cobalt complexes indicates that internal steric effects, solvent effects and interactions with other ligands are all important in determining the conformational preferences of carbene and amidine ligands. Similar effects of solvent on carbene ligand conformation have been reported once previously.[20]

Interconversion of Isomers. A number of comparative studies of the chemical stability of the carbene and amidine ligands have been made. Upon heating in dimethyl sulfoxide solution, **8** undergoes both isomerization to the N-bound form **9** (eq 1) and separate decomposition (eq 2) to produce amidine and isocyanide complexes.

$$CH_3Co(DMGH)_2\{C(NHCH_3)_2\} \rightarrow CH_3Co(DMGH)_2\{N(CH_3)CH(NHCH_3)\} \quad (1)$$

$$CH_3Co(DMGH)_2\{C(NHCH_3)_2\} \rightarrow CH_3Co(DMGH)_2CNCH_3 + NH_2CH_3 \quad (2)$$

$$\downarrow\uparrow$$

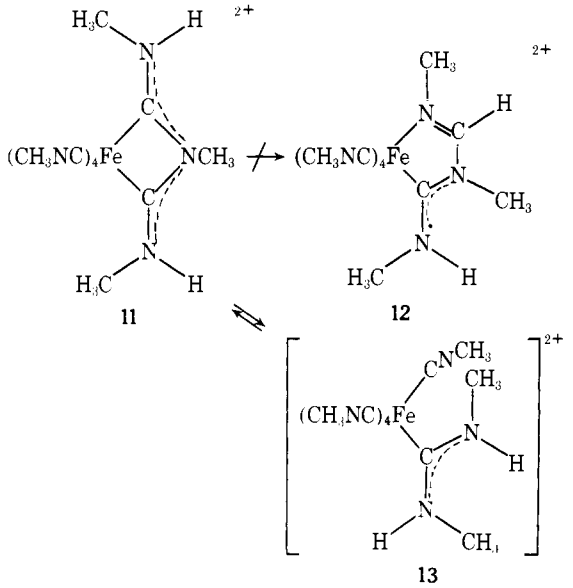
$$CH_3Co(DMGH)_2NH_2CH_3 + CH_3NC$$

This thermal reaction has been monitored by ^{1}H NMR spectroscopy. Representative data are shown in Figure 3. Traces A and C of the figure show the same solution of **8** before and after heating. The components giving rise to spectrum C may be readily identified by comparison with traces B, D, and E which are respectively the spectra of the complexes with *N,N'*-dimethylformamidine, methylamine, and methyl isocyanide as one axial ligand.[21] Disappearance of the carbene complex was complete when a 0.15 M solution of **8** was heated for 21 h at 70°. Under these conditions the formamidine complex is formed in 80% yield, the balance of the cobaloxime material being converted to roughly equal amounts of $Co(CH_3)(DMGH)_2(CNCH_3)$ and $Co(CH_3)(DMGH)_2(NH_2CH_3)$. No other products were detected and no further reaction occurred during an additional 24-h heating period. When the same reaction was carried out at 130° the carbene complex was consumed within 1 h, but the yield of formamidine complex was reduced to 64% while production of the methylamine and methyl isocyanide complexes increased proportionately. Under identical heating conditions solutions of complex **9** remained unchanged. In contrast, it was not possible to effect thermal interconversion between **5** and **6.** These cation-

ic complexes gradually decomposed to yield unidentified products when dimethyl sulfoxide solutions were heated at 70° for several hours.

The conversion of **8** to **9** is the first example of this type of isomerization. A reasonable mechanism for this reaction would involve dissociation of the carbene ligand followed by isomerization to the free amidine and recapture by the ligand-deficient cobalt center. Such a dissociative process would be consistent with the established mode of axial ligand exchange in a number of methyl cobaloxime complexes.[22,23] It is also known that when diaminocarbene ligands are liberated from metal complexes, either by heating or by ligand displacement, they are converted to the isomeric amidine.[12] However, preliminary kinetic investigations of the isomerization indicate that the reaction is more complex than outlined above. The isomerization **8** → **9** is autocatalytic; the rate of disappearance of **8** increases during the course of the reaction. Additionally it has been possible to detect, in the reaction mixture after isomerization, small amounts of paramagnetic Co(II) species by electron spin resonance measurements. It is not known whether the Co(II) species influences the kinetics of isomerization. The second thermal reaction of **8** (eq 2) is just the reverse of the reaction which was used to form **8.** Such a decomposition of a carbene ligand has been observed previously for iron[24] and gold[12] complexes.

The reactions of the carbene ligand in **8** may be compared to the thermal reaction of the chelated carbene found in **11.**[25] Upon heating **11** does not isomerize to give **12** al-

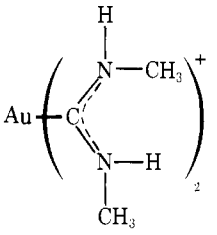


11 ⇌ 12 ⇌ 13

though the five-membered chelate ligand present in **12** has been prepared[26] and this conversion would appear to relieve ring strain present within the four-membered ring of **11.** Rather **11** undergoes reactions which have been ascribed to opening of the C–N bonds of the chelate ring. The nonchelated form **13** has been implicated as an intermediate in these reactions.[27]

Behavior toward Acids. The carbene complexes described here, and other carbene complexes as well, appear to retain their integrity upon treatment with protic acids. In contrast the amidine complexes **6** and **9** are decomposed by treatment with acid. Treatment of **6** in acetonitrile or dimethyl sulfoxide solution and **9** in chloroform solution with trifluoroacetic acid results in rupture of the Co–N (amidine) bonds and the formation of *N,N'*-dimethylformamidinium ion. This reaction is due to protonation of the amidine ligand. Experimental evidence has been presented which demonstrates that analogous amidinium ions may be protonated.[18] Both nitrogen atoms of an amidine ligand would be expected to be subject to protonation. Protonation of the cobalt-bound nitrogen would be expected to weaken that Co–N bond and facilitate the departure of the completely formed amidinium ion.

The nitrogen atoms of carbene ligands are also subject to protonation. In this case, however, the cobalt–carbon bond is not appreciably weakened since protonation does not occur at the cobalt bound carbon. Consequently the greater stability of carbene complexes over amidine complexes may be explained. However, protic acids do facilitate proton exchange at the carbene nitrogen atoms. The ^{1}H NMR spectra of **5** and **7** show a loss of the coupling between the N–H and the methyl protons when trifluoroacetic acid is added. A more extensive examination of this protonation has been made with the less complicated carbene compound **14.** The



14

hexafluorophosphate salt of this cation in acetonitrile-d_3 solution shows two methyl doublets at τ 7.36 ($^3J_{H-H}$ = 4 Hz) and 6.85 ($^3J_{H-H}$ = 4 Hz). Upon addition of trifluoroacetic acid to an acetonitrile solution of **14,** the ^{1}H NMR spectrum undergoes a series of changes. These changes are reversible upon dilution. Initial acid addition causes the methyl doublets to broaden slightly. The upfield methyl doublet collapses into a single line when the mole fraction of trifluoroacetic acid is in the range 0.29–0.36. The downfield doublet undergoes similar collapse with the mole fraction of trifluoroacetic acid in the range 0.36–0.48. With further increases in the trifluoroacetic acid concentration the two methyl resonances broaden and when the mole fraction of trifluoroacetic acid reaches the range 0.63–0.66, these resonances merge into a single broad resonance. Further increases in the mole fraction of trifluoroacetic acid cause only a narrowing of this resonance. Two separate processes are responsible for these changes. The initial collapse of the methyl doublets and loss of $^3J_{HH}$ is due to rapid exchange of the N–H protons. This occurs via protonation of the carbene nitrogens. Since the two nitrogen atoms are nonequivalent, different rates of proton exchange at each nitrogen are expected. The coalescence of the two methyl resonances into a single resonance results from rapid rotation about the CN bonds at increasing acid concentrations. Protonation of the carbene nitrogens localizes the π electrons into a nitrogen–hydrogen bond and destroys the multiple bond character of the C–N bond. Consequently rotation about the C–N bonds is facilitated by high acid concentrations. Completely analogous observations have been made for amidinium ions.[18] For the *N,N'*-dimethylacetamidinium ion the collapse of the high field, interior methyl doublet was found to occur at lower acid concentrations than necessary for the collapse of the low field, external methyl doublet.[28] For this ion higher acid concentrations caused the coalescence of both methyl singlets.

The ability of boron trifluoride etherate to convert **5** into **7,** while **6** undergoes decomposition under identical conditions, may be understood in the context of the protonation studies. Boron trifluoride may be expected to act as an acid toward the nitrogens of either the carbene or amidine ligand. With the amidine ligand of **6,** attack of the Lewis

acid at the cobalt-bound nitrogen would result in weakening of that cobalt-nitrogen bond and would facilitate loss of amidine. Under similar reactions, however, the cobalt-carbon bond of **5** would remain largely unaffected.

Conclusions

This work demonstrates that carbene or ylide complexes of Co(III) are stable, isolable species even in the presence of a trans methyl group. However, a route for the conversion of the amidine ligands into the isomeric carbene ligands has not been found with these cobalt complexes. The transformation of N bound to C bound imidazole or formamidine probably depends strongly on the activation of the C–H bond involved. In the known cases in which this isomerism occurs, it may be that a key isomerization step involves transfer of a proton from the imidazole carbon to the filled d orbitals of ruthenium. Evidence for electrophilic attack on the filled d orbitals of ruthenium has been presented;[29] similar attack is expected to be much less significant for cobalt(III) which would have a much reduced radial extention for its filled d orbitals.

Acknowledgments. This work was supported by Grant GM 18357 from the National Institutes of Health.

References and Notes

(1) R. J. Sundberg, R. F. Bryan, I. F. Taylor, Jr., and H. Taube, *J. Am. Chem. Soc.*, **96**, 381 (1974).
(2) R. J. Sundberg and G. Gupta, *Bioinorg. Chem.*, **3**, 39 (1973).
(3) D. J. Cardin, B. Cetinkaya, and M. F. Lappert, *Chem. Rev.*, **72**, 545 (1972).
(4) F. A. Cotton and C. M. Lukehart, *Prog. Inorg. Chem.*, **16**, 487 (1972).
(5) G. Rouschias and G. Wilkinson, *J. Chem. Soc. A*, 489 (1968).
(6) N. C. Stephenson, *J. Inorg. Nucl. Chem.*, **24**, 801 (1962).
(7) J. M. Pratt, "Inorganic Chemistry of Vitamin B_{12}", Academic Press, New York, N.Y., 1972.
(8) R. J. Angelici and L. M. Charley, *J. Organomet. Chem.*, **24**, 205 (1970).
(9) A. L. Balch and J. Miller, *J. Am. Chem. Soc.*, **94**, 417 (1972).
(10) D. J. Doonan and A. L. Balch, *Inorg. Chem.*, **13**, 921 (1974).
(11) W. M. Butler, J. H. Enemark, J. Parks, and A. L. Balch, *Inorg. Chem.*, **12**, 451 (1973).
(12) J. E. Parks and A. L. Balch, *J. Organomet. Chem.*, **71**, 453 (1974).
(13) R. E. Schuster, J. E. Scott, and J. Casanova, Jr., *Org. Synth.*, **46**, 75 (1966).
(14) E. C. Taylor and W. E. Erhart, *J. Org. Chem.*, **28**, 1103 (1963).
(15) G. N. Schrauzer, *Inorg. Synth.*, **11**, 61 (1968).
(16) A. W. Herlinger and T. L. Brown, *J. Am. Chem. Soc.*, **93**, 1790 (1971).
(17) When this treatment was applied to the hexafluorophosphate salt of $\mathbf{8}^+$ the tetrafluoroborate salt of $[\{(CH_3NH)_2C\}_2Co(DMGBF_2)_2]^+$ was obtained. The chemical analysis and the absence in the infrared spectrum of ν_{P-F} in the 800–900-cm^{-1} region are in accord with the formulation. An independent synthesis from the tetrafluoroborate salt of **8** further substantiates the formulation. The conversion of hexafluorophosphate salts into tetrafluoroborate salts upon treatment with boron trifluoride etherate appears to be a general reaction (J. J. Watkins, unpublished results).
(18) G. S. Hammond and R. C. Neuman Jr., *J. Phys. Chem.*, **67**, 1655 (1963).
(19) M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).
(20) B. Crociani and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 693 (1974).
(21) The observed ^1H NMR spectra (Figure 3) do not show the presence of the free methyl isocyanide and methylamine which are required to be present by eq 2. We suspect that these two volatile species are vaporized into the evacuated headspace of the sealed NMR tube. It has been possible, however, to verify the reversible equilibrium portion of eq 2 in a separate experiment. Methylamine and methyl isocyanide will replace one another as the ligand trans to the methyl group in the $CH_3Co(DMGH)_2$ ligand complexes.
(22) R. J. Guschl and T. L. Brown, *Inorg. Chem.*, **12**, 2815 (1973), and references therein.
(23) D. Dodd and M. D. Johnson, *J. Organomet. Chem.*, **52**, 1 (1973).
(24) K. Öfele and C. G. Kreiter, *Chem. Ber.*, **105**, 529 (1972).
(25) J. Miller, A. L. Balch, and J. H. Enemark, *J. Am. Chem. Soc.*, **93**, 4613 (1971).
(26) A. L. Balch and J. E. Parks, *J. Am. Chem. Soc.*, **96**, 4114 (1974).
(27) D. J. Doonan and A. L. Balch, *J. Am. Chem. Soc.*, **95**, 4769 (1973).
(28) Although the rates of proton exchange at the two nitrogens of the *N,N'*-dimethylacetamidinium ion and of **14** are expected to differ, the magnitude of this difference in the *N,N'*-dimethylacetamidinium ion has been interpreted as resulting from slow rotation (in comparison to the exchange rate) about the $C-{}^+NH_2CH_3$ bond. C. L. Perrin, *J. Am. Chem. Soc.*, **96**, 5631 (1974).
(29) H. Taube, *Surv. Prog. Chem.*, **6**, 1 (1973).

Catalytic Hydrogenation Using Cationic Rhodium Complexes. I. Evolution of the Catalytic System and the Hydrogenation of Olefins

Richard R. Schrock[1a] and John A. Osborn*[1b]

Contribution from The Mallinckrodt Laboratory, Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. *Received August 22, 1975*

Abstract: Homogeneous hydrogenation catalysts are prepared in situ by reductive elimination of a diene from a class of precursors of the type $[Rh(diene)L_n]^+A^-$ (L = tertiary phosphine or arsine, or phosphite, n = 2 or 3; L_2 = chelating phosphine or arsine; A^- = ClO_4^-, BF_4^-, or PF_6^-), on reaction with molecular hydrogen in polar solvents (S = acetone, tetrahydrofuran, or 2-methoxyethanol). We present evidence for two metal–hydride complexes, $[RhH_2L_nS_x]^+$ and $RhHL_nS_y$, in solution. The equilibrium between the two is sensitive to the nature of L and S and can be shifted by addition of acid or base. They are active catalysts in two of three basic catalytic cycles. The neutral monohydride is a powerful hydrogenation catalyst but also concomitantly isomerizes olefins (path A). Path B involves the cationic dihydride, which is a moderately active hydrogenation catalyst but a poor isomerization catalyst. Path C involves the cationic complex $[Rh(olefin)L_n]^+$ and probably occupies a minor catalytic role for weakly coordinating olefins. This system may serve as a model for homogeneous hydrogenation with cationic catalysts in general. Elucidation of its essential features led to its use to selectively reduce alkynes to cis olefins and chelating dienes to monoenes to be described in Parts II and III, respectively.

Interest in catalytic hydrogenation using soluble transition metal complexes continues to be intense.[2a] Unfortunately, relatively few homogeneous hydrogenation catalysts[2b] are commonly used by the practicing organic chemist since most, if not all, suffer, to varying degrees, from one or more of the following disadvantages: (i) they function satisfactorily only under conditions too vigorous or inconvenient for practical, routine applications; (ii) they cannot be greatly modified by altering the ligands to give, for example, regio- or stereoselectivity; and (iii) they usually reduce