bicyclobutanes into **13** and **14** appears not to require any further elaboration.

This and the preceding communication have demonstrated that there are not sufficient data that compel one to invoke the intermediacy of carbenoid–Ag(I) or argentocarbonium ions[2a] in nearly all the Ag(I)-catalyzed reactions. All the experimental evidence presently available to us tends to suggest that the initial one-bond cleavage intermediate I is *the dividing point leading to various types of products for the bicyclobutanes examined thus far.*[9] Evidence is (i) trapping of I, (ii) the stereoselectivity observed in the reactions of **10a**, **10b**, and the corresponding dimethylbicyclobutanes, (iii) formation of **5** from **1** and **9**, and (iv) reasonable explanation for the formation of uncommon products, **13** and **14**. However, several assumptions have been made and, in the absence of detailed knowledge of C–Ag and C:–Ag(I), additional work is demanded before one can define the precise mechanism of the Ag(I)-catalyzed reaction. An issue central to the whole subject is concerned with the origin of different behavior exhibited by Ag(I) and Pd(II) and certainly it remains to be answered.

Acknowledgment. We are grateful to the National Research Council for financial support.

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[9] Since we have not studied extensively the trapping experiment, we are at present unable to state that the C-1,2 bond is *invariably* the one initially cleaved by Ag(I). Therefore, the possibility exists that the C-1,3 bond may be in some cases attacked to provide cyclobutyl cations which collapse into products, following pathways reasonably expected for this type of species.

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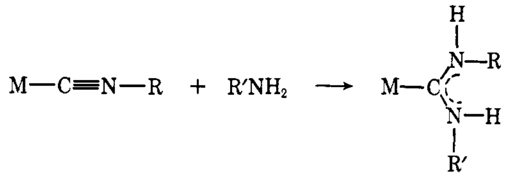
Addition of Methylamine to Hexakis(methyl isocyanide)iron (II). The Formation of an Unusual Chelating Ligand

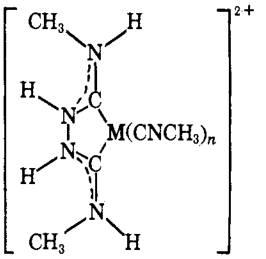
Sir:

Several cases of addition of amines to coordinated isocyanides (eq 1) have been described.[1–6] In all of



$$\text{M—C}\equiv\text{N—R} + \text{R}'\text{NH}_2 \longrightarrow \text{M—C}\begin{cases}\text{N(H)—R}\\ \text{N(H)—R}'\end{cases} \quad (1)$$

these cases, the addition has been limited to a single isocyanide. However, hydrazine has been shown to react with the complexes $Pd(CNCH_3)_4^{2+}$,[7,8] $Pt(CNCH_3)_4^{2+}$,[7,8] and $Fe(CNCH_3)_6^{2+}$ [9] to yield products **1**, **2**, and **3**, respectively, in which addition to two adjacent isocyanide ligands has occurred to form a chelate ring. We now report the first example of addition of a monofunctional amine to two isocyanide ligands.



1, M = Pd; $n = 2$
2, M = Pt; $n = 2$
3, M = Fe; $n = 4$

Refluxing a methanolic solution of $Fe(CNCH_3)_6(HSO_4)_2$ with an excess of methylamine for 12 hr yields, after precipitation with ammonium hexafluorophosphate and recrystallization from methanol–2-butanol, the very pale yellow complex **4** having the empirical formula $[Fe(CNCH_3)_6 \cdot CH_3NH_2][PF_6]_2$. In nitromethane, **4** is a 2:1 electrolyte (Λ = 182 ohms^{-1} cm^2 M^{-1} at 10^{-3} M). The infrared spectrum (fluorocarbon mull, 4000–1500 cm^{-1}) exhibits absorptions at 3330, ν(N—H); 2960, ν(C—H); 2244, 2205, ν(C$\equiv$N); 1613, 1589, ν(N$\underline{\cdots}$C$\underline{\cdots}$N) and δ(N—H).

Crystals of **4** belong to the monoclinic space group $P2_1/c$. Unit cell data are: a = 8.17 (1), b = 20.08 (2), c = 16.32 (2) Å, cos β = −0.0997 (14); Z = 4; d_{calcd} = 1.526, d_{obsd} = 1.53 (1) g cm^{-3}. A crystal of dimensions 0.06 × 0.05 × 0.36 mm was mounted about a, the needle axis, and 797 data having $F_o{}^2 > \sigma(F_o{}^2)$ and $2\theta \leqslant 30°$ were collected using Mo Kα radiation and a four-circle diffractometer. The positions of the Fe and P atoms were located from a Patterson function, and the C, N, and F atoms appeared in successive electron-density maps. These maps also revealed a twofold disorder of one of the PF_6^- ions. An occupancy factor was included as a variable in the least-squares refinement, and the PF_6^- ions were treated as rigid groups.[10] Isotropic refinement converged to a conventional R factor of 0.147. A difference electron-density map shows that there is still complex thermal motion and/or disorder of the PF_6^- ions which is not adequately described by the present isotropic model. The geometry of the cation is that shown for **4**; distances and angles in the novel chelate system appear in Figure 1. The limited number of nonzero data obtained from the small crystal and the overly simple model for the PF_6^- ions have resulted in rather large uncertainties for interatomic distances and angles. These large errors preclude any detailed comparisons of the distances found here to those observed in other related complexes. However, the average Fe–C(chelate) distance of 2.02 (4) Å is similar to the Fe–C(sp^2) distance of 1.987 (5) Å reported[11] for $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2C_2H_4$.

The pmr spectrum of **4** in trifluoroacetic acid is consistent with the X-ray structure and provides unambiguous evidence for the locations of the protons.

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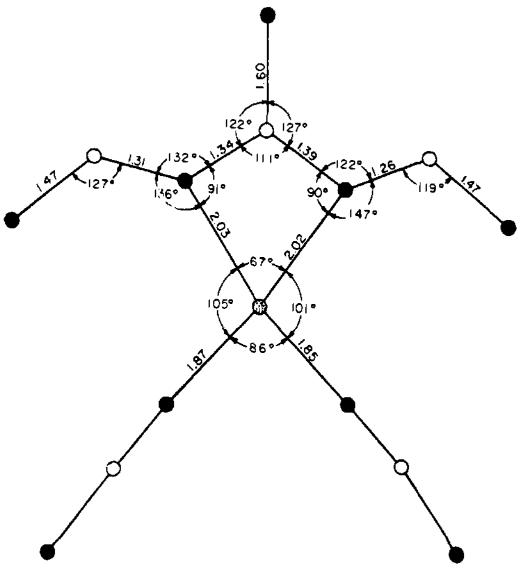
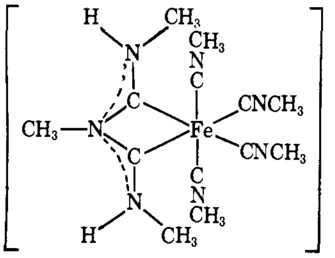


Figure 1. Distances and angles within the chelate ring of the $(CH_3NC)_4Fe(C_2N_3(CH_3)_3H_2)^{2+}$ ion: ○, N; ●, C; ◉, Fe. H atoms are not shown, and the two out-of-plane CH_3NC ligands have been omitted for clarity. Estimated standard deviations are 0.04 Å for Fe–C(chelate) and 0.05 Å for C–N. The average distances for the four isocyanide ligands are Fe–C, 1.86 (2), C–N, 1.15 (2), and N–CH_3, 1.48 (4) Å.

The spectrum consists of resonances at τ 6.92 (singlet (s), relative intensity 3), which is assigned to the internal methyl group of the chelate; 6.50 (s, 6), which is assigned to one of the pairs of equivalent unreacted isocyanide ligands; 6.50 (doublet, J_{H-N-CH_3} = 5.0 Hz, 6), which is assigned to the terminal methyl groups of the chelate; 6.45 (s, 6), which is assigned to the second pair of equivalent unreacted isocyanide ligands; and a broad resonance at 1.62 (s, 2), which is assigned to the two nitrogen-bound protons. The coupling between the doublet at τ 6.50 and the broad resonance at τ 1.62 has been confirmed by double-resonance experiments.



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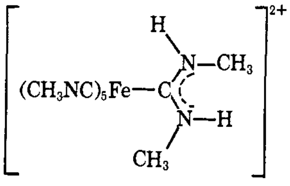
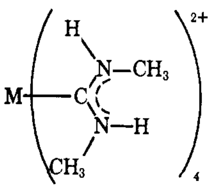
Presumably, the addition of methylamine to Fe-$(CNCH_3)_6{}^{2+}$ to give **4** occurs stepwise *via* reaction **1**, with **5** formed as an intermediate. In **5**, a relatively



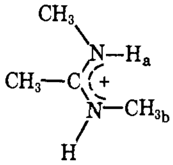
5

small isocyanide ligand has been converted into a bulky new ligand. In a six-coordinate complex, this ligand is forced close enough to the adjacent isocyanide groups so that a second addition reaction takes place to form **4**. The square-planar isocyanide complexes $M(CNCH_3)_4{}^{2+}$ (M = Pd, Pt) do not undergo chelative addition with methylamine, but instead add 4 mol of methylamine to yield **6**.[9] Molecular models show that **6** is sterically crowded and that the ligands must be oriented so that the remaining coordination sites of the metal are effectively blocked. Therefore, multiple additions of this type are not likely for six-coordinate complexes.



6, M = Pd, Pt

The configurations adopted by the planar ligands in complexes such as **1**–**4** and **6** follow a common pattern which is related to the configuration of the *N,N′*-dimethylacetamidinium ion **7**. This ion adopts the amphi configuration with one proton (a) and one methyl group (b) in the "inside" positions.[12] The configuration about each metal-bound carbon of the chelating ligand in **4** similarly has one proton and one methyl group in the inside positions. An X-ray study[7,8] of a derivative of **1** shows that the configuration about each metal-bound carbon of the chelate is such that one proton and one methyl group occupy inside positions. The ligands in **6**[9] and in some related complexes[6] also adopt amphi configurations.



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Effect of Ion-Pair Structure on Electron-Transfer and Proton-Transfer Equilibria

Sir:

The difference in electron affinities of acceptors[1,2] is the dominant factor determining the position of

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