undergo two-electron oxidations, particularly since the HClO oxidation of Fe^{2+} apparently involves formation of an Fe(IV) species,[40] while no evidence was found for Fe(IV) in the oxidation of $Fe(phen)_3{}^{2+}$.[41] At any rate, the present study provides no evidence to distinguish between an initial one-electron or two-electron transfer.

Whatever the underlying reason, it should be emphasized again that there is apparently a correlation between the form of the rate equation and the substitution-inertness of one-equivalent reducing agents. In order to fully understand the mechanism of Cr(VI) oxidations, the above correlation and the formation of Cr(III)–Fe(III) binuclear complexes must be taken into account.

A frequent characteristic of redox reactions between ions of like charge is a catalysis by oppositely charged ions; *e.g.*, the exchange reactions of $Fe(CN)_6{}^{4-}$ with $Fe(CN)_6{}^{3-}$ [42,43] and $MnO_4{}^{2-}$ with $MnO_4{}^{-}$ [44,45] and the reduction of $S_2O_8{}^{2-}$ by $Fe(CN)_6{}^{4-}$ [46] are catalyzed by a number of cations, with various efficiencies. With respect to the present study, it is known that $Fe(CN)_6{}^{4-}$ and $Fe(CN)_6{}^{3-}$ form complexes[47–49] with K^+, so it is somewhat surprising that the reduction of $HCrO_4{}^-$ by $Fe(CN)_6{}^{4-}$ is independent of variations in $[K^+]$ over the range 7×10^{-6} to 9×10^{-2} *M*. Apparently if such catalytic activity is important in this case, K^+, Na^+, and Li^+ are about equally as effective.

The $[H^+]$ dependence of the $HCrO_4{}^-$–Fe(II) reactions can be explained in terms of activated complexes of composition $\{(HCrO_4{}^-)(Fe(II))(H^+)_n\}^{\ddagger}$, where $n = 1$ (or possibly 2, depending on the value of K_4 below) for $Fe(CN)_6{}^{4-}$, $n = 2$ for $Fe(bip)(CN)_4{}^{2-}$, $n = 1$ and 2 for $Fe(bip)_2(CN)_2$, and $n = 0$, 1, and 2 for $Fe(bip)_3{}^{2+}$. The denominator terms in the equations describing the $[H^+]$ dependence of the reactions of the cyanoiron(II) complexes presumably arise from variation in the predominant forms of the reactants with changes in $[H^+]$, and can be accommodated qualitatively by the equilibria

$$H_2CrO_4 \xrightleftharpoons{K_2} H^+ + HCrO_4{}^- \qquad (16)$$

$$H_2Fe^{II} \xrightleftharpoons{K_3} H^+ + HFe^{II} \qquad (17)$$

$$HFe^{II} \xrightleftharpoons{K_4} H^+ + Fe^{II} \qquad (18)$$

Although appropriate values of K_3 and K_4 have not been determined under the same conditions studied here, it is known that protonation of each of the cyanoiron(II) complexes occurs.[7,8,27,50–52] Since the parameters used in the denominators of the various rate equations are composites of these unknown equilibrium constants, it is not possible to make any meaningful statements about the magnitude of these parameters at this time.

Acknowledgment. Partial support of this work by the Advanced Research Projects Agency and by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(40) T. J. Conocchioli, E. J. Hamilton, Jr., and N. Sutin, *J. Am. Chem. Soc.*, **87**, 926 (1965).

(41) B. Z. Shakhashiri and G. Gordon, *Inorg. Chem.*, **7**, 2454 (1968).

(42) M. Shporer, G. Ron, A. Loewenstein, and G. Navon, *ibid.*, **4**, 361 (1965).

(43) R. J. Campion, C. F. Deck, P. King, Jr., and A. C. Wahl, *ibid.*, **6**, 672 (1967).

(44) J. C. Sheppard and A. C. Wahl, *J. Am. Chem. Soc.*, **79**, 1020 (1957).

(45) O. L. Meyers and J. C. Sheppard, *ibid.*, **83**, 4739 (1961).

(46) R. W. Chlebek and M. W. Lister, *Can. J. Chem.*, **44**, 437 (1966).

(47) J. C. James, *Trans. Faraday Soc.*, **45**, 855 (1949).

(48) J. C. James and C. B. Monk, *ibid.*, **46**, 1041 (1950).

(49) W. A. Eaton, P. George, and G. I. H. Hanania, *J. Phys. Chem.*, **71**, 2016 (1967).

(50) A. A. Schilt, *J. Am. Chem. Soc.*, **85**, 904 (1963).

(51) J. Jordan and C. J. Ewing, *Inorg. Chem.*, **1**, 587 (1962).

(52) G. I. H. Hanania, D. H. Irvine, W. A. Eaton, and P. George, *J. Phys. Chem.*, **71**, 2022 (1967).

Reactions of Cyclopentadienyliron Tricarbonyl Cation with Hydrazines and the Azide Ion

Robert J. Angelici and Luigi Busetto

Contribution from the Department of Chemistry, Iowa State University,
Ames, Iowa 50010. Received November 30, 1968

Abstract: Hydrazine reacts with $C_5H_5Fe(CO)_3{}^+$ to form first a carbazoyl intermediate which then loses NH_3 to give an isocyanate complex.

$$C_5H_5Fe(CO)_3{}^+ + 2N_2H_4 \xrightarrow[-N_2H_5{}^+]{} C_5H_5Fe(CO)_2(CONHNH_2) \xrightarrow[-NH_3]{} C_5H_5Fe(CO)_2(NCO)$$

The reaction with some methyl-substituted hydrazines proceeds in the same manner. The isocyanate product may also be prepared by the reaction of $C_5H_5Fe(CO)_3{}^+$ with $N_3{}^-$ or NCO^-. With CN^- and NCS^-, the cationic carbonyl yields $C_5H_5Fe(CO)_2(CN)$ and the N-bonded isomer of $C_5H_5Fe(CO)_2(NCS)$, respectively. Mechanisms of these reactions are discussed.

Recently we have been interested in examining the reactions of cationic metal carbonyls with primary and secondary aliphatic amines. In two such studies,[1,2] it was found that one carbonyl group in the complex reacts with the amine to form a carboxamido group.

---

(1) R. J. Angelici and D. L. Denton, *Inorg. Chim. Acta*, **2**, 3 (1968).

(2) L. Busetto and R. J. Angelici, *ibid.*, **2**, 391 (1968).

$$Mn(CO)_5(NH_2R)^+ + 2NH_2R \longrightarrow cis\text{-}Mn(CO)_4(NH_2R)(CONHR) + RNH_3^+ \quad (1)$$

$$C_5H_5Fe(CO)_3^+ + 2NH_2R \longrightarrow C_5H_5Fe(CO)_2(CONHR) + RNH_3^+ \quad (2)$$

The structure of one of these carboxamido complexes, $Mn(CO)_4(NH_2CH_3)(CONHCH_3)$, has been established by an X-ray structural investigation.[3] In the present paper we wish to report the results of studies of the reactions of $C_5H_5Fe(CO)_3^+$ with hydrazines and the azide ion.

Results and Discussion

Like primary and secondary aliphatic amines, hydrazine first reacts with $[C_5H_5Fe(CO)_3]PF_6$ to form the carbazoyl derivative, $C_5H_5Fe(CO)_2(CONHNH_2)$, as in eq 3. Although it was not possible to purify this

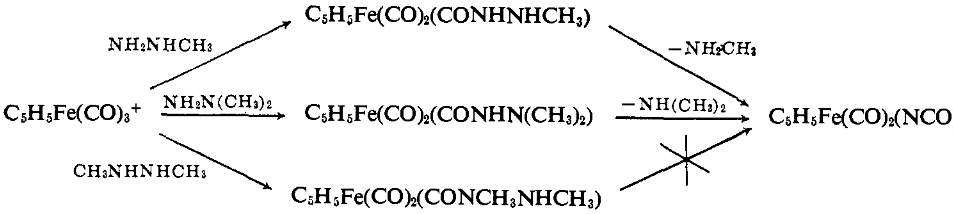
$$C_5H_5Fe(CO)_3^+ + NH_2NH_2 \longrightarrow C_5H_5Fe(CO)_2(CONHNH_2) + NH_2NH_3^+ \quad (3)$$

$$C_5H_5Fe(CO)_2(CONHNH_2) \longrightarrow C_5H_5Fe(CO)_2(NCO) + NH_3 \quad (4)$$

intermediate, the close similarity of its infrared spectrum to that[2] of $C_5H_5Fe(CO)_2(CONH_2)$ strongly suggests that this is indeed the compound which is formed. The other product, $[NH_2NH_3]PF_6$, was not characterized, but its formulation was assumed to be analogous to that of the ammonium product obtained in the reaction with amines[1,2] (eq 1 and 2).

The carbazoyl intermediate, $C_5H_5Fe(CO)_2(CONHNH_2)$, is not stable and loses NH_3 to form the isocyanate complex, $C_5H_5Fe(CO)_2(NCO)$, according to eq 4. This reaction may be followed by infrared spectroscopy; in $CHCl_3$ at room temperature approximately 70% of the carbazoyl compound is converted to the isocyanate in 1 hr. In the solid state, the reaction is much slower with about 10% being converted during the same length of time. The infrared spectrum shows no evidence of other carbonyl-containing products. The NH_3 was identified both mass spectrometrically as well as chemically. Since the $C_5H_5Fe(CO)_2(CONHNH_2)$ was badly contaminated with $[N_2H_5]PF_6$, attempts to quantitatively measure the amount of NH_3 evolved were far short of the theoretical amount calculated on the basis that the $C_5H_5Fe(CO)_2(CONHNH_2)$ was pure. At best only 25% of the theoretical amount was detected by back-titration of an acid solution into which the NH_3 had been discharged.

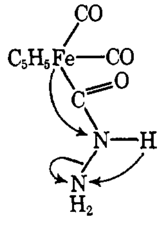
The methyl-substituted hydrazines, NH_2NHCH_3 and $NH_2N(CH_3)_2$, also reacted according to eq 3 and 4 to finally yield $C_5H_5Fe(CO)_2(NCO)$ (eq 5). In the case of NH_2NHCH_3, the carbazoyl intermediate, $C_5H_5Fe(CO)_2(CONHNHCH_3)$, had formed in the CH_2Cl_2 solution 3 min after the reactants had been combined. The infrared absorptions assigned to the terminal C–O stretching modes occurred at 2025 (s) and 1969 (s) cm^{-1}, and that of the carbazoyl carbonyl stretch was observed at 1592 (m) cm^{-1}. These positions are, within experimental error, the same as those of $C_5H_5Fe(CO)_2(CONHNH_2)$ which had analogous absorptions at 2023 (s), 1967 (s), and 1588 (m) cm^{-1}. The reaction of $C_5H_5Fe(CO)_3^+$ with $NH_2N(CH_3)_2$ gave no evidence of the carbazoyl intermediate; it presumably reacted very rapidly to form $C_5H_5Fe(CO)_2(NCO)$. In general, the rates of reaction of the carbazoyl derivatives to form the isocyanate product increased in the order: $NH_2NH_2 < NH_2NHCH_3 < NH_2N(CH_3)_2$. In the reaction of $C_5H_5Fe(CO)_2(CONHNH_2)$, the evolved NH_3 was identified; the NH_2CH_3 and $NH(CH_3)_2$ evolved from the substituted hydrazine derivatives were not specifically identified but assumed by analogy with the unsubstituted hydrazine reaction to be products.



(5)

The symmetrically substituted hydrazine, $CH_3NHNHCH_3$, also reacts to form the carbazoyl compound, $C_5H_5Fe(CO)_2(CONCH_3NHCH_3)$. It was too unstable to isolate, but its spectrum showed the characteristic carbonyl stretching absorptions of the carbazoyl derivatives at 2037 (s), 1957 (s), and 1600 (m) cm^{-1}. Unlike the other carbazoyl complexes, this one does *not* react further to form $C_5H_5Fe(CO)_2(NCO)$.

The over-all mechanism for the reaction of $C_5H_5Fe(CO)_3^+$ with hydrazines to form $C_5H_5Fe(CO)_2(NCO)$ clearly proceeds in the two steps given in eq 3 and 4. Reaction 3 presumably occurs by nucleophilic attack[2] of the hydrazine on a carbonyl carbon atom with loss of a proton, as $NH_2NH_3^+$, to form the carbazoyl derivative. This is the same mechanism[1,2] that was suggested for the reaction of amines with $C_5H_5Fe(CO)_3^+$. The subsequent loss of NH_3 by $C_5H_5Fe(CO)_2(CONHNH_2)$ requires the migration of a proton from the -NH to the NH_2 group and fission of the N–N bond. Migration of the Fe from the carbon to the remaining N must also be involved. The order of these changes is not clear but the migration of the Fe to the nitrogen atom almost certainly assists in the removal of the ammonia. This reaction is similar in many respects to that recently reported by Fischer and Aumann.[4]

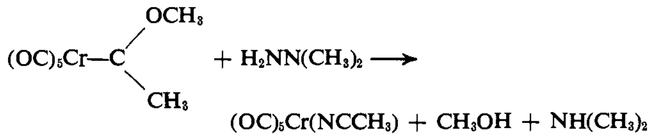


If $C_5H_5Fe(CO)_2(CONCH_3NHCH_3)$ were to react to form $C_5H_5Fe(CO)_2(NCO)$ by the above mechanism, the migration of a $-CH_3$ group rather than H would be required. Such a migration apparently does not occur.

---

(3) D. M. Chipman and R. A. Jacobson, *Inorg. Chim. Acta*, **1**, 393 (1967).

(4) E. O. Fischer and R. Aumann, *Chem. Ber.*, **101**, 963 (1968).



$$(OC)_5Cr{-}C(OCH_3)(CH_3) + H_2NN(CH_3)_2 \longrightarrow (OC)_5Cr(NCCH_3) + CH_3OH + NH(CH_3)_2$$

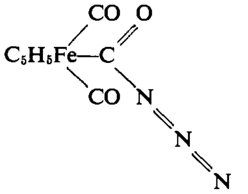
Only in the complexes $C_5H_5Fe(CO)_2(CONHNH_2)$, $C_5H_5Fe(CO)_2(CONHNHCH_3)$, and $C_5H_5Fe(CO)_2(CONHN(CH_3)_2)$, where an H is present on the α nitrogen, is reaction to the isocyanate observed. This observation is a major reason for proposing (eq 5) the carbazoyl structure, *e.g.*, $-CONHNHCH_3$, in which the carbon is bonded to the nonmethylated nitrogen atom. The virtually identical infrared spectra of $C_5H_5Fe(CO)_2(CONHNH_2)$ and $C_5H_5Fe(CO)_2(CONHNHCH_3)$ also support this structure.

From what is currently known,[2] it appears that amines form carboxamido complexes with cationic metal carbonyls more readily than with neutral carbonyl complexes. The reactions of hydrazines with neutral carbonyls were also expected to be less successful. The reaction of $W(CO)_6$ with NH_2NH_2 gave yellow solutions from which low yields of $W(CO)_5(NCO)^-$ could be obtained as the tetraphenylarsonium salts.[5]

The isocyanate complex, $C_5H_5Fe(CO)_2(NCO)$, may also be prepared in good yield from the reaction of the cation with azide ion.

$$C_5H_5Fe(CO)_3^+ + N_3^- \longrightarrow C_5H_5Fe(CO)_2(NCO) + N_2 \qquad (6)$$

This reaction presumably proceeds by a mechanism which is very similar to that[5] involved in the preparation of $W(CO)_5(NCO)^-$ from $W(CO)_6$ and N_3^-. In view of the reactions of $C_5H_5Fe(CO)_3^+$ with hydrazines, it is reasonable to suppose that

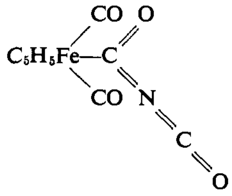


occurs as an intermediate in this reaction and rearranges with loss of N_2 to form the isocyanate product in a manner which is very similar to that involved in the well-known Curtius reaction of organic chemistry. It is of interest to note that the nature of the solvent exerts a tremendous effect upon the rate of reaction 6. In tetrahydrofuran and ethyl ether, the formation of the product is complete in 12–15 hr; in acetone the reaction is faster (7–8 hr), while in water and in methanol the reaction is virtually complete within 10 min. Addition of a few milliliters of water to the acetone solutions decreases the time of reaction to about 10 min. It should be pointed out that both $[C_5H_5Fe(CO)_3]PF_6$ and NaN_3 are insoluble or slightly soluble in tetrahydrofuran, ethyl ether, and methanol, while only $[C_5H_5Fe(CO)_3]PF_6$ is soluble in acetone and only NaN_3 in water.

Finally, the isocyanate complex can be synthesized in good yield using the isocyanate ion.

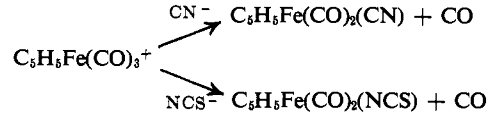
$$C_5H_5Fe(CO)_3^+ + NCO^- \longrightarrow C_5H_5Fe(CO)_2(NCO) + CO \qquad (7)$$

The mechanism of this reaction is uncertain since a CO in the cationic complex may be that which is evolved in the reaction. Or the CO in the NCO^- may be the one which is evolved if the reaction proceeds by attack of NCO^- on a carbonyl carbon atom to give an intermediate



analogous to that involved in the reaction with N_3^-. This may then lose CO from the $-NCO$ group and rearrange to give the isocyanate complex product. Isotopic labeling experiments should distinguish between these two possibilities.

The cation, $C_5H_5Fe(CO)_3^+$, is known[6] to react with halide ions to give $C_5H_5Fe(CO)_2X$, where X = Cl, Br, or I. A similar reaction occurs with the CN^- and NCS^- ions.



(8)

$$C_5H_5Fe(CO)_3^+ \xrightarrow{CN^-} C_5H_5Fe(CO)_2(CN) + CO$$
$$C_5H_5Fe(CO)_3^+ \xrightarrow{NCS^-} C_5H_5Fe(CO)_2(NCS) + CO$$

The $C_5H_5Fe(CO)_2(CN)$ was obtained in good yield and was identified by its infrared spectrum which was very similar to that of the same compound previously prepared[7] from $C_5H_5Fe(CO)_2Cl$ and NaCN. Although $C_5H_5Fe(CO)_2(CNS)$ is known to exist in both the N- and S-bonded isomeric forms[8] and is obtained as a mixture of these isomers from the reaction of $[C_5H_5Fe(CO)_2]_2$ with KNCS and O_2, the reaction according to eq 8 gives only the thermodynamically more stable N-bonded isomer.

Experimental Section

Materials. The $[C_5H_5Fe(CO)_3]PF_6$ was synthesized as described previously.[2] The hydrazines, N_2H_4 (Baker), CH_3NHNH_2, and $(CH_3)_2NNH_2$ (Aldrich), were used as obtained from the commercial sources; $CH_3NHNHCH_3$ was prepared by bubbling CH_3NH_2 into an ether suspension of $CH_3NHNHCH_3 \cdot HCl$ (Aldrich) for 5 or 6 hr at room temperature. The product, $CH_3NHNHCH_3$, was distilled in a nitrogen atmosphere and used soon thereafter. Benzene was dried over sodium and CH_2Cl_2 over molecular sieves. All the other solvents were reagent grade.

Infrared spectra were recorded on a Beckman IR-8 spectrophotometer using a polystyrene standard. Mass spectra were obtained on an Atlas CH-4 mass spectrometer.

Reaction of $[C_5H_5Fe(CO)_3]PF_6$ and NH_2NH_2. Depending upon the reaction conditions, either the carbazoyl compound, $C_5H_5Fe(CO)_2(CONHNH_2)$, or the isocyanate, $C_5H_5Fe(CO)_2(NCO)$, could be obtained.

(a) Identification of $C_5H_5Fe(CO)_2(CONHNH_2)$. To a suspension of 0.5 g (1.43 mmoles) of $[C_5H_5Fe(CO)_3]PF_6$ in 20 ml of benzene at 7° was added 0.1 g (3.03 mmoles) of NH_2NH_2 with stirring. Immediately the $[C_5H_5Fe(CO)_3]PF_6$ disappeared and a voluminous bright-yellow precipitate formed. It was filtered from the solution which was rapidly becoming red in color. The time required to carry out these operations varied from 3 to 5 min. The yellow precipitate consisted of a mixture of $C_5H_5Fe(CO)_2(CONHNH_2)$ and presumably $[NH_2NH_3]PF_6$, although this latter compound was not specifically identified. An infrared spectrum of this mixture taken in CH_2Cl_2 solvent showed two strong terminal C–O stretching absorptions at 2023 and 1967 cm^{-1} and a medium intensity band at

---

(5) W. Beck, H. Werner, H. Engelmann, and H. S. Smedal, *Chem. Ber.*, **101**, 2143 (1968).

(6) R. K. Kochhar and R. Pettit, *J. Organometal. Chem.*, **6**, 272 (1966).

(7) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

(8) T. E. Sloan and A. Wojcicki, *Inorg. Chem.*, **7**, 1268 (1968).

1588 cm^{-1} which may be assigned to the carbazoyl C–O stretching mode. These absorptions were almost identical in position and intensity with those observed[2] in $C_5H_5Fe(CO)_2(CONH_2)$, which occurred at 2015 (s), 1963 (s), and 1593 (m) cm^{-1}.

The yellow precipitate of $C_5H_5Fe(CO)_2(CONHNH_2)$ changed to a red material, $C_5H_5Fe(CO)_2(NCO)$, with the simultaneous evolution of NH_3. The NH_3 was identified by placing the yellow solid in a vacuum distillation apparatus. The receiver vessel was cooled to −196°. The NH_3 collected over a period of 4–5 hr was identified mass spectrometrically and also by adding a solution of Nessler's reagent to give a red-brown color characteristic of a reaction with NH_3.

The carbazoyl compound could also be precipitated in an impure form by carrying out the reaction of $[C_5H_5Fe(CO)_3]PF_6$ with NH_2NH_2 in CH_2Cl_2 instead of in benzene. After allowing the reaction to occur for about 3 min, the solution was filtered. Dropwise addition of pentane to the solution yielded a yellow precipitate which contained $C_5H_5Fe(CO)_2(CONHNH_2)$ as established from its infrared spectrum.

(b) Preparation of $C_5H_5Fe(CO)_2(NCO)$. A solution of 0.5 g of $[C_5H_5Fe(CO)_3]PF_6$ and 0.1 g of NH_2NH_2 in CH_2Cl_2 were allowed to react at room temperature for 1.5 hr. After filtration, the solvent was removed under vacuum leaving a red powder which was dissolved in 20 ml of $CHCl_3$. Concentration of this solution to 5 ml followed by addition of 20 ml of pentane gave red $C_5H_5Fe(CO)_2$-(NCO) in 55% (0.172 g) yield. It was identified by its infrared spectrum (see below).

$C_5H_5Fe(CO)_2(NCO)$ from $[C_5H_5Fe(CO)_3]PF_6$ and NH_2NHCH_3. To a mixture of 0.5 g (1.43 mmoles) of $[C_5H_5Fe(CO)_3]PF_6$ in 25 ml of CH_2Cl_2 at room temperature was added 0.138 g (3.0 mmoles) of NH_2NHCH_3 with stirring. Immediately the reaction mixture turned red. After 30 min, the solvent was evaporated off under vacuum, and the residue was dissolved in 20 ml of $CHCl_3$. After filtration and evaporation of the solvent to 5 ml, the solution yielded a precipitate of $C_5H_5Fe(CO)_2(NCO)$ upon treatment with pentane. The yield was 40% (0.125 g). The product was again identified from its infrared spectrum (see below).

$C_5H_5Fe(CO)_2(NCO)$ from $[C_5H_5Fe(CO)_3]PF_6$ and $NH_2N(CH_3)_2$. The reaction was carried out in the same manner as above. The yield of $C_5H_5Fe(CO)_2(NCO)$ was 35% (0.109 g).

Reaction of $[C_5H_5Fe(CO)_3]PF_6$ and $CH_3NHNHCH_3$. To a suspension of 1.0 g (2.86 mmoles) of $[C_5H_5Fe(CO)_3]PF_6$ in CH_2Cl_2 was added 0.36 g (6.00 mmoles) of $CH_3NHNHCH_3$. The presence of $C_5H_5Fe(CO)_2(CONCH_3NHCH_3)$ in this solution was suggested by the infrared absorptions at 2037 (s), 1957 (s), and 1600 (m) cm^{-1}, which are very similar in position and intensity to those of C_5H_5Fe-$(CO)_2(CONHNH_2)$. This intermediate, however, does not react further to give $C_5H_5Fe(CO)_2(NCO)$ as was observed with the other hydrazines. Even after 3 hr there was no infrared evidence of $C_5H_5Fe(CO)_2(NCO)$ formation. Attempts to isolate $C_5H_5Fe(CO)_2$-$(CONCH_3NHCH_3)$ from solution yielded only the decomposition product $[C_5H_5Fe(CO)_2]_2$, a common decomposition product of the carboxamido-type compounds.[2]

$C_5H_5Fe(CO)_2(NCO)$ from $[C_5H_5Fe(CO)_3]PF_6$ and N_3^-. A solution of 0.30 g (3.1 mmoles) of NaN_3 dissolved in 5 ml of water was added with stirring to a solution of 1.0 g (2.9 mmoles) of $[C_5H_5Fe$-$(CO)_3]PF_6$ in 50 ml of acetone. Nitrogen gas is rapidly evolved, and the solution turns from yellow to deep red. After stirring for 15 min at room temperature, the acetone was removed under a water aspirator vacuum, and 20 ml of water was added to the residue. The $C_5H_5Fe(CO)_2(NCO)$ was extracted from the mixture with 20 ml of $CHCl_3$. Evaporation under vacuum of the chloroform solution to 5 ml followed by addition of 20 ml of pentane gave 0.47 g (75%) of the red precipitate $C_5H_5Fe(CO)_2(NCO)$.

Anal. Calcd for $C_5H_5Fe(CO)_2(NCO)$: C, 43.9; H, 2.3; N, 6.4. Found: C, 43.9; H, 2.4; N, 6.5. In $CHCl_3$ solution, its infrared spectrum exhibits carbonyl stretching absorptions at 2066 (s) and 2020 (s) cm^{-1} and bands due to the assymmetric and symmetric NCO stretching modes at 2252 (m) and 1330 (w) cm^{-1}, respectively.

The mass spectrum of $C_5H_5Fe(CO)_2(NCO)$ was measured using 16-eV electron energies. The major ions and their relative intensities follow: $C_5H_5Fe(CO)_2(NCO)^+$, 59; $C_5H_5Fe(CO)(NCO)^+$, 70; $(C_5H_5)_2Fe^+$, 25; $C_5H_5Fe(NCO)^+$, 100. The lack of ions containing CO groups and no NCO group suggests that the NCO group is more strongly bonded to the Fe than are the CO groups.

$C_5H_5Fe(CO)_2(NCO)$ from $[C_5H_5Fe(CO)_3]PF_6$ and KNCO. To a solution of 1.0 g (2.9 mmoles) of $[C_5H_5Fe(CO)_3]PF_6$ in 50 ml of acetone was added 1.0 g (12.3 mmoles) of KNCO. After stirring for 3 hr at room temperature, the solvent was removed under water aspirator vacuum. The residue was extracted with $CHCl_3$. After filtration and concentration of the solution to 5 ml, the C_5H_5Fe-$(CO)_2(NCO)$ was precipitated by adding 20 ml of pentane. The yield was 80% (0.52 g). Its infrared spectrum was identical with that of the same compound prepared above.

Properties of $C_5H_5Fe(CO)_2(NCO)$. This compound is a red air-stable solid which melts with decomposition at 98–99°. It is soluble in benzene, ethyl ether, CH_2Cl_2, and $CHCl_3$, but only sparingly soluble in pentane and hexane. Its CH_2Cl_2 and $CHCl_3$ solutions decompose very slowly to give a green material.

The chemical reactivity of the –NCO group in $C_5H_5Fe(CO)_2$-(NCO) is greatly different than that of organic isocyanates, RNCO. For example, it does not react with water, alcohols, or amines. In H_2O and CH_3OH, it decomposes slowly but very rapidly in 7 *M* KOH aqueous solutions. In all cases the main product of the decomposition is $[C_5H_5Fe(CO)_2]_2$.

$[(C_6H_5)_4As][W(CO)_5(NCO)]$ from $W(CO)_6$ and NH_2NH_2. To 1.0 g of $W(CO)_6$ in 50 ml of ethanol under a nitrogen atmosphere was added a 10-fold excess of NH_2NH_2. After 24 hr at room temperature, the solution was evaporated under vacuum to 30 ml. After filtration an ethanol solution of excess $[(C_6H_5)_4As]Cl$ was added. Dropwise addition of H_2O with stirring yielded 0.20 g of yellow $[(C_6H_5)_4As][W(CO)_5(NCO)]$ as identified by its infrared spectrum.[5] For no apparent reason, some preparations of $W(CO)_5(NCO)^-$ by this method yielded no product although the characteristic yellow color was produced. With $Mo(CO)_6$ and $Cr(CO)_6$, the solutions turned yellow upon NH_2NH_2 addition, but no isocyanate product could be isolated.

$C_5H_5Fe(CO)_2(CN)$ from $[C_5H_5Fe(CO)_3]PF_6$ and NaCN. A 50-ml acetone solution containing 0.70 g of $[C_5H_5Fe(CO)_3]PF_6$ and 0.9 g of NaCN was stirred at room temperature for 2 hr. After evaporating the solvent under vacuum, the red residue was dissolved in 10 ml of $CHCl_3$. The solution was filtered and again evaporated to dryness. The solid was then dissolved in ethyl ether. After filtering, the $C_5H_5Fe(CO)_2(CN)$ was precipitated by addition of hexane. The yield was 70%, and the product was characterized by its infrared spectrum which was the same as that of the compound prepared by a different method.[7] It contained C–O absorptions at 2068 (s) and 2023 (s) cm^{-1} and the C–N band at 2129 (m) in $CHCl_3$ solution.

$C_5H_5Fe(CO)_2(NCS)$ from $[C_5H_5Fe(CO)_3]PF_6$ and KNCS. A mixture of 0.5 g of $[C_5H_5Fe(CO)_3]PF_6$ and 1.0 g of KNCS in 50 ml of acetone was stirred at room temperature for 2 hr. After evaporating off the solvent under vacuum, the residue was dissolved in $CHCl_3$. This solution was filtered and evaporated to 10 ml. Addition of 50 ml of hexane and cooling to −78° gave a 45% yield of $C_5H_5Fe(CO)_2(NCS)$ which had a melting point of 105–107°.

Anal. Calcd for $C_5H_5Fe(CO)_2(NCS)$: C, 40.9; H, 2.1; N, 6.0. Found: C, 40.4; H, 1.9; N, 6.4. In $CHCl_3$ solution, C–O stretching absorptions occur at 2075 (s) and 2033 (s) cm^{-1}, and that of the C–N stretch is observed at 2123 (m) cm^{-1}. The C–S absorption was not observed in the solution spectrum. In a KBr pellet these absorptions occurred at 2066 (s), 2008 (vs), 2123 (m), and 826 (w) cm^{-1}, respectively. These spectra support a structure[8] in which the NCS group is N-bonded to the Fe.

Acknowledgment. We very much appreciate the support of this research by the National Science Foundation (GP-6034). A departmental grant from the same agency allowed the purchase of the mass spectrometer which was used in this study.