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Reactions of Dicarbonylthiocarbonylcyclopentadienyliron(II) with Various Nucleophiles

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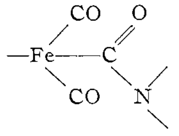
Some reactions of the cation $C_5H_5Fe(CO)_2(CS)^+$ with nucleophilic agents bearing nitrogen or oxygen as donor atoms have been examined. Based on the product obtained, these reactions can be grouped into three sets: (i) reactions with N_3^- and hydrazine with formation of $C_5H_5Fe(CO)_2(NCS)$ through fission of the nitrogen–nitrogen bond of the attacking nucleophile; (ii) reaction with RNH_2 and RO^- leading to thiocarboxamide, $C_5H_5Fe(CO)_2(C(S)NHR)$, and thiocarbalkoxy derivatives, $C_5H_5Fe(CO)_2(C(S)OR)$; (iii) reactions with NCO^- and NCS^- yielding the complex $C_5H_5Fe(CO)_2(CN)$. The varying character of the carbon atom in the CO and CS groups toward nucleophilic agents is discussed.

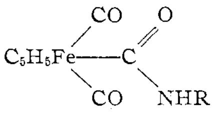
Nucleophilic attacks at the carbonyl carbon in transition metal–carbonyl complexes are rather common.[1] This carbon acquires an electrophilic character upon coordination to transition metals. Thus the reaction of CH_3O^- with the cation $Mn(CO)_4(P(C_6H_5)_3)_2^+$ yielding the ester $Mn(CO)_3(P(C_6H_5)_3)_2(CO_2CH_3)$ has been described.[2] The carbonyl carbon in $Fe(CO)_5$ was also found to be attacked by various amines.[3]

Some reactions of $C_5H_5Fe(CO)_3^+$ with nucleophilic agents have been recently reported.[4,5] These agents were as follows: (i) hydrazine, N_3^-, and NCO^-; (ii) amines and RO^-; (iii) NCS^- and CN^-. The nucleophiles of the first type display attack at the carbonyl carbon through the nitrogen end giving unstable intermediates of the type



These give the stable compound $C_5H_5Fe(CO)_2(NCO)$ *via* intramolecular rearrangement with liberation of NH_3 (from N_2H_4), N_2 (from N_3^-), and CO (from NCO^-). The nucleophiles of the second type also attack the carbonyl ligand giving stable addition products.[5] For instance, with amines, carboxamido derivatives are obtained according to the reaction

$C_5H_5Fe(CO)_3^+ + RNH_2 \longrightarrow$



$$C_5H_5Fe(CO)_2C(O)NHR + H^+ \quad (1)$$

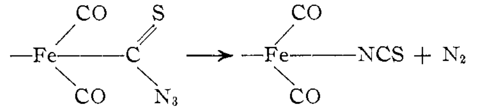
With CN^- and NCS^- (Y^-) one carbonyl group is replaced with formation of $C_5H_5Fe(CO)_2Y$.

We have now examined various reactions of the thiocarbonyl cation $C_5H_5Fe(CO)_2(CS)^+$ [6,7] with these types of reagents with the aim of determining the preferred site of nucleophilic attack on the ligands (CO or CS) coordinated to the central metal. Scheme I reports the reactions investigated.

Based on the products obtained, the nucleophilic agents that have been employed give rise to three different types of reaction.

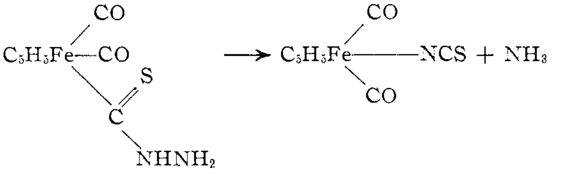
1. Reaction with N_3^- and Hydrazine.—With these, the thiocarbonyl complex undergoes nucleophilic attack at the carbon atom of coordinated CS.

The reaction with N_3^- proceeds *via* a reactive intermediate



$$\text{—Fe(CO)}_2\text{C(S)N}_3 \longrightarrow \text{—Fe(CO)}_2\text{NCS} + N_2 \quad (2)$$

The reaction with hydrazine is likely to involve formation of the thiocarbazoyl intermediate followed by elimination of ammonia and formation of the N-bonded thiocyanate complex



$$C_5H_5Fe(CO)_2C(S)NHNH_2 \longrightarrow C_5H_5Fe(CO)_2NCS + NH_3 \quad (3)$$

In this regard it is worth mentioning that the carbazoyl intermediate could be isolated from the reaction of $C_5H_5Fe(CO)_3^+$ with N_2H_4.[4] In reactions 2 and 3 the driving force probably is the high stability of N_2 and NH_3, respectively, liberated. The common product of these reactions, the N-bonded thiocyanate complex, was identified by its ir spectrum which shows ν(CO) at 2072 (s), 2031 cm^{-1} (s) and ν(CN) at 2133 cm^{-1} (m). The CS absorption was not observed in the solution spectrum but appeared in the Nujol mull at 829 cm^{-1} (m). These spectral features support a structure in which the NCS grouping is bonded to iron through the nitrogen.[8] No N→S linkage isomerization was observed either in solution or on Florisil chromatography. By chromatography on alumina of the N-bonded isomer using CH_2Cl_2 as eluent this isomerization was observed, probably catalyzed by the column's material.

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* To whom correspondence should be addressed.

[1] K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, **7**, 1282 (1968).

[2] T. Kruck and M. Noack, *Chem. Ber.*, **97**, 1693 (1964).

[3] W. F. Edgell and B. J. Bulkin, *J. Amer. Chem. Soc.*, **88**, 4839 (1966).

[4] R. J. Angelici and L. Busetto, *ibid.*, **91**, 3197 (1969).

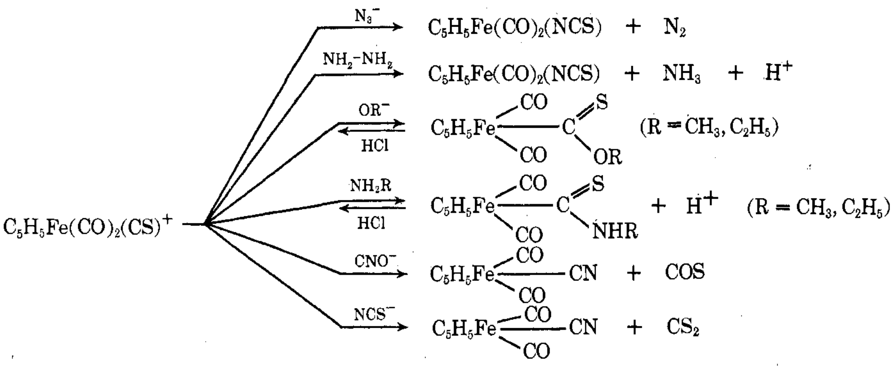
[5] L. Busetto and R. J. Angelici, *Inorg. Chim. Acta*, **2**, 391 (1968).

[6] L. Busetto and R. J. Angelici, *J. Amer. Chem. Soc.*, **90**, 3283 (1968).

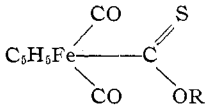
[7] L. Busetto, U. Belluco, and R. J. Angelici, *J. Organometal. Chem.*, **18**, 213 (1969).

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

SCHEME I

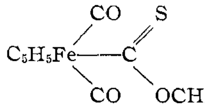


2. **Reactions with RO⁻ and Amines.**—The complex $C_5H_5Fe(CO)_2(CS)^+$ reacts with alkoxides in anhydrous alcohol to give thiocarboxyl derivatives of type

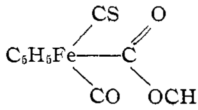

$C_5H_5Fe(CO)_2C(=S)OR$

These react with hydrogen chloride in ether or benzene to give the starting thiocarbonyl complex.

The proton resonance absorption of the thiocarboxyl derivative ($R = CH_3$) occur at τ 5.16 (cyclopentadienyl ring protons) and 5.97 (methyl protons), with relative intensity of 5:3. Its infrared spectrum in cyclohexane shows two CO stretching absorptions at 2031 (s) and 1993 cm^{-1} (s). A strong C=S stretching absorption occurs at 1193 cm^{-1}. This spectrum supports the proposed structure. The same product was obtained from the reaction of $CH_3OC(S)Cl$ with $Na[C_5H_5Fe(CO)_2]$.[7] It should be noted that the product of the reaction of $C_5H_5Fe(CO)_2(CS)^+$ with CH_3O^- in nondried methanol is a mixture of the thiocarboxylate and carboxylate isomers


$C_5H_5Fe(CO)_2C(=S)OCH_3$

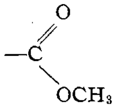
thiocarboxylate complex (A)


$C_5H_5Fe(CS)(CO)C(=O)OCH_3$

carboxylate complex (B)

The presence of these two isomers was confirmed by ir and ^1H nmr spectra. The ir spectrum of the mixture, in fact, shows three bands in the carbonyl stretching region (2031 (s), 1990 (s), and 2020 cm^{-1} (s)), of which the first two can be assigned to the dicarbonyl derivative (A) and the third to the monocarbonyl derivative (B). Further, a medium band at 1658 cm^{-1} is assigned to the carboxyl C=O stretching[9] and a strong band at 1316 cm^{-1} is attributed to $\nu(C\equiv S)$;[5] finally, a strong band at 1196 cm^{-1} is due to $\nu(C=S)$. Ir spectra were recorded in cyclohexane or carbon disulfide, depending on the spectral region examined.

The nmr spectrum of the mixture of the thiocarboxylate and carboxylate complexes shows four signals. Those at τ 5.12 and 6.50 are assigned to the cyclopentadienyl ring protons and to the methyl protons of the


$-C(=O)OCH_3$

grouping. The remaining two signals correspond to those of the above-described thiocarboxyl derivative (see Figure 1).

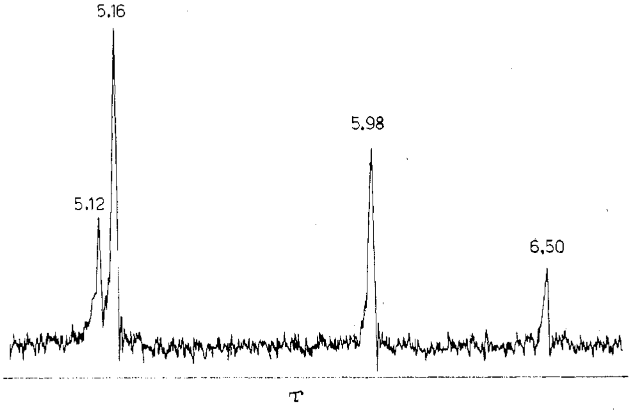
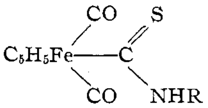


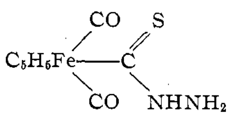
Figure 1.—Nmr spectrum in CS_2 solvent of the thiocarboxylate and carboxylate mixture.

The reactions of $C_5H_5Fe(CO)_2CS^+$ with amines (CH_3NH_2 and $C_2H_5NH_2$) in anhydrous ether yield the thiocarboxamide derivative ($-C(=S)NHR$) which undergoes fast reaction with hydrogen chloride. The rather unstable

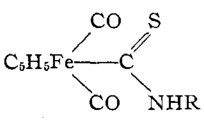

$C_5H_5Fe(CO)_2C(=S)NHR$

complexes were characterized by their infrared spectra in hexane which show two strong terminal carbonyl stretching absorptions at 2007 (s) and 1965 cm^{-1} (s) and one C=S stretching absorption at 1158 cm^{-1}.

The similarity of the reaction with RNH_2 to that with hydrazine rests on the attack of the unshared electron pair of nitrogen at the carbon atom of coordinated thiocarbonyl with formation of the two derivatives


$C_5H_5Fe(CO)_2C(=S)NHNH_2$

thiocarbazoyl derivative (labile)


$C_5H_5Fe(CO)_2C(=S)NHR$

thiocarboxamido derivative (stable)

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[9] R. B. King, M. B. Bisnette, and A. Fronzaglia, *J. Organometal. Chem.*, **5**, 341 (1966).

3. Reactions with NCS⁻ and NCO⁻.—The reactions of $C_5H_5Fe(CO)_2(CS)^+$ with these anions both lead to formation of the complex $C_5H_5Fe(CO)_2(CN)$, CS_2 (detected by gas chromatography) and probably COS being liberated, respectively. The cyano complex was identified by its elemental analysis and ir spectrum.[10] These reactions were carried out with the expectation that nucleophilic attack by the nitrogen of cyanate group at the thiocarbonyl carbon would yield the thiocyanate derivative $C_5H_5Fe(CO)_2(NCS)$ in analogy to the course of the similar reaction with the isoelectronic N_3^-.

Although for the corresponding reactions of $C_5H_5Fe(CO)_3^+$ with N_3^- and NCO^- the derivative $C_5H_5Fe(CO)_2(NCO)$ is the product in both cases,[4] the reaction products for the thiocarbonyl products are different. Thus, the reaction with N_3^- involves breaking of the N–N bond with liberation of molecular nitrogen, whereas the reaction with cyanate or thiocyanate involves a more complex rearrangement of the reaction intermediate.

Conclusion.—The results described above suggest the following remarks.

(i) The electrophilic character of the carbon of the CS group linked to the moiety $C_5H_5Fe(CO)_2$ is markedly greater than that of the carbonyl carbon. This explains the fact that in the reactions with nucleophiles examined the reaction site is the CS group instead of the CO group.

(ii) The thiocarbonyl complex reacts with each nucleophile much faster than its tricarbonyl analog $C_5H_5Fe(CO)_3^+$, under comparable experimental conditions.

(iii) Reaction rates of either tricarbonyl or thiocarbonyl complexes with nucleophiles are generally enhanced by increasing solvent polarity, suggesting a considerable charge separation in the activation process that leads to the rearrangement of the intermediate and liberation of a small molecule.

(iv) Thiocarboxyl intermediates are generally more reactive than the corresponding carbonyls (*cf.* the reactions with hydrazine).

Experimental Section

A. Preparation of $C_5H_5Fe(CO)_2(NCS)$ from $[C_5H_5Fe(CO)_2CS)]^+PF_6^-$. (i) **$N_3^-$.**—A solution of 0.0325 g (0.5 mmol) of NaN_3 dissolved in 3 ml of water was added with stirring to a solution of 0.183 g (0.5 mmol) of $[C_5H_5Fe(CO)_2(CS)]PF_6$ in 30 ml of acetone.

Nitrogen was rapidly evolved, and the solution turned from yellow to deep red. After stirring for 15 min at room temperature, the acetone was removed in a rotary evaporator and 15 ml of water was added to the residue. The $C_5H_5Fe(CO)_2(NCS)$ was extracted from the mixture with 20 ml of $CHCl_3$ and the solution was dried over $CaCl_2$. Evaporation of the chloroform solution to 5 ml followed by addition of 50 ml of hexane gave the red $C_5H_5Fe(CO)_2(NCS)$; yield 55%; mp 118–119°. *Anal.* Calcd for $C_8H_5NO_2SFe$: C, 40.9; H, 2.1; N, 6.0; S, 13.6. Found: C, 40.5; H, 2.3; N, 5.9; S, 13.9.

The nature of the solvent exerted a striking effect upon the rate of reaction. In tetrahydrofuran and ethyl ether the reaction was very slow (31–24 hr); it was faster (0.5 hr) in acetone whereas in water and methanol it was virtually complete within a few minutes.

(ii) **H_2N-NH_2.**—A solution of 0.183 g (0.5 mmol) of $[C_5H_5Fe(CO)_2(CS)]PF_6$ and 0.05 ml (1 mmol) of H_2N-NH_2 in CH_2Cl_2 was allowed to react at room temperature under nitrogen with stirring.

The reaction mixture turned red immediately. After 30 min the solvent was evaporated off under vacuum, and the residue was dissolved in 20 ml of $CHCl_3$ and filtered. Concentration of this solution followed by addition of pentane gave $C_5H_5Fe(CO)_2(NCS)$ in 35% yield.

B. Preparation of $C_5H_5Fe(CO)_2C(S)OCH_3$.—A mixture of 1 g of $[C_5H_5Fe(CO)_2(CS)]PF_6$ in 50 ml of anhydrous methanol was stirred for 20 min at room temperature under nitrogen in the presence of an excess of Na_2CO_3. The solution was then filtered and the solvent was removed under reduced pressure leaving an orange-brown material which was dissolved in 20 ml of ether and filtered. Elimination of the solvent followed by vacuum sublimation at 40° gave the orange-red $C_5H_5Fe(CO)_2C(S)OCH_3$ in a 70% yield; mp 75–76°. *Anal.* Calcd for $C_9H_8O_3SFe$: C, 42.9; H, 3.2; S, 12.7. Found: C, 43.1; H, 3.0; S, 12.6.

On bubbling HCl into an ether solution of the thioalkoxycarbonyl derivative and on precipitating the cation with NH_4PF_6, the starting $[C_5H_5Fe(CO)_2(CS)]PF_6$ was recovered.

C. Preparation of $C_5H_5Fe(CO)_2C(S)OCH_2CH_3$.—This compound was prepared from $C_5H_5Fe(CO)_2(CS)^+$ and $C_2H_5O^-$ in ethanol solution following the same procedure described for the methyl derivative.

The ir spectrum in CS_2 solution shows ν(CO) at 2031 and 1980 cm^{-1} and ν(CS) at 1172 cm^{-1}.

D. Preparation of $C_5H_5Fe(CO)_2C(S)NHCH_3$.—Methylamine was slowly bubbled into a stirred suspension of 0.5 g of $[C_5H_5Fe(CO)_2(CS)]^+PF_6^-$ in 50 ml of nitrogen-saturated ethyl ether. After 20 min the reaction was stopped and the solution was filtered. The filtrate was evaporated under reduced pressure leaving a brown oil. The spectrum of this oil in hexane shows two strong terminal CO stretching absorptions (2007 and 1965 cm^{-1}) and one C=S absorption at 1158 cm^{-1}. Attempts to isolate the thiocarboxamide complex $C_5H_5Fe(CO)_2CSNHCH_3$ were unsuccessful, but on treatment with hydrogen chloride the starting thiocarbonyl complex was obtained.

E. Reactions of $C_5H_5Fe(CO)_2(CS)^+$ with NCO^- and NCS^-.—A dry acetone solution (20 ml) containing 0.5 mmol of $[C_5H_5Fe(CO)_2(CS)]^+PF_6^-$ and 1 mmol of KNCO was stirred at room temperature for 1 hr. After evaporating the solvent under vacuum, the red residue was dissolved in $CHCl_3$ and filtered, and the volume was reduced to 10 ml. Addition of pentane gave in low yield (20%) the red compound $C_5H_5Fe(CO)_2CN$. The ir spectrum is identical with that of an independently prepared sample.

The same product was obtained from $C_5H_5Fe(CO)_2(CS)^+$ and KCNS using the procedure described above.

F. Materials and Instrumentation.—The $[C_5H_5Fe(CO)_2(CS)]PF_6$ was synthetized as described previously,[7] commercial $H_2N_2-NH_2$ (Baker) was used as purchased, and other chemicals were reagent grade materials.

Infrared spectra were recorded on a Beckman IR-5 A spectrophotometer using a polystyrene standard; nmr spectra were recorded on a Varian DP 60 spectrometer, using TMS as internal standard.

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