Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

REACTIONS OF CYCLOPENTADIENYLIRON CARBONYL DERIVATIVES WITH AZIDE ION

M. GRAZIANI, L. BUSETTO AND A. PALAZZI

Facolta' di Chimica Industriale. The University and Centro di Chimica e Tecnologia dei Composti Metallo-Organici degli Elementi di Transizione del C.N.R., Viale Risorgimento, 4-40136 Bologna (Italy)

(Received July 27th, 1970)

SUMMARY

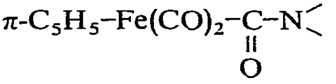
The complex $(\pi\text{-}C_5H_5)Fe(CO)(PPh_3)(NCO)$ has been prepared by treatment of the salt $[(\pi\text{-}C_5H_5)Fe(CO)_2(PPh_3)]PF_6$ with hydrazine or with azide ion. The kinetics of the reaction between azide ion and the salts $[(\pi\text{-}C_5H_5)Fe(CO)_2(L)]PF_6$, where $L = CO$, PPh_3, or C_2H_4 have been studied spectrophotometrically, and in each case the reaction has been shown to be first order with respect to the salt and the azide ion. The rate constants for the sequence $L = CO$, PPh_3, and C_2H_4 are in the ratio 1/67/300. It is suggested that an acyl azide is formed as an intermediate by nucleophilic attack of azide ion on the carbonyl group, and rearranges to the corresponding isocyanate with loss of nitrogen.

Cationic carbonyl complexes such as $[(\pi\text{-}C_5H_5)Fe(CO)_3]^+$ and $[Re(CO)_5(NH_2CH_3)]^+$ have been shown recently to react with hydrazine and azide ion[1,2] to give the corresponding cyanato derivatives, as represented in eqns. (1) and (2).

$$[(\pi\text{-}C_5H_5)Fe(CO)_3]^+ + 2\,NH_2NH_2 \rightarrow (\pi\text{-}C_5H_5)Fe(CO)_2(NCO) + NH_3 + NH_2NH_3^+ \qquad (1)$$

$$(\pi\text{-}C_5H_5)Fe(CO)_3^+ + N_3^- \rightarrow (\pi\text{-}C_5H_5)Fe(CO)_2(NCO) + N_2 \qquad (2)$$

It has been suggested that these reactions proceed via nucleophilic attack on the carbonyl carbon with the formation of the labile intermediate(I)[1,2,3], which rearranges

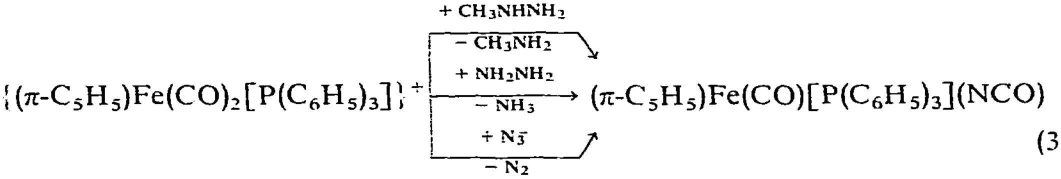


$$\pi\text{-}C_5H_5{-}Fe(CO)_2{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}N\!<$$

(I)

with loss of NH_3 (eqn. 1) or N_2 (eqn. 2) to form the isocyanate.

We have found now that the ion $\{(\pi\text{-}C_5H_5)Fe(CO)_2[P(C_6H_5)_3]\}^+$ reacts analogously with hydrazine and methylhydrazine to give the cyanato derivative, $(\pi\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3](NCO)$. The ethylene derivative, $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_2H_4)]^+$, reacts with hydrazines to give unidentifiable products, whereas with N_3^- only the cyanato derivative, $[(\pi\text{-}C_5H_5)Fe(CO)(C_2H_4)(NCO)]$, is obtained[4].



$$\{(\pi\text{-}C_5H_5)Fe(CO)_2[P(C_6H_5)_3]\}^+ \xrightarrow[\substack{-NH_3\\ +N_3^-\\ -N_2}]{\substack{+CH_3NHNH_2\\ -CH_3NH_2\\ +NH_2NH_2}} (\pi\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3](NCO) \quad (3)$$

In order to clarify the mechanism of the reactions between the $[(\pi\text{-}C_5H_5)Fe(CO)_2L]^+$ $[L=CO, P(C_6H_5)_3, C_2H_4]$ ions and hydrazines and azide ion we planned to examine the kinetics of these reactions. We found that the reactions of the $[(\pi\text{-}C_5H_5)Fe(CO)_2L]^+$ complexes with hydrazines were too fast to be followed by the usual methods and it was possible to study extensively only the reaction (4).

$$[(\pi\text{-}C_5H_5)Fe(CO)_2L]^+ + N_3^- \longrightarrow [(\pi\text{-}C_5H_5)Fe(CO)(L)(NCO)] + N_2 \quad (4)$$

$L=CO, P(C_6H_5)_3, C_2H_4$.

EXPERIMENTAL SECTION

Materials

$[(\pi\text{-}C_5H_5)Fe(CO)_3]BF_4$[5], $\{(\pi\text{-}C_5H_5)Fe(CO)_2[P(C_6H_5)_3]\}Cl$[6,7], $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_2H_4)]BF_4$[8] and $(\pi\text{-}C_5H_5)Fe(CO)(C_2H_4)(NCO)$[4], were synthesized as previously described.

The other chemicals were reagent-grade and were used without further purification. Absolute methanol was dried and purified by distillation after refluxing over $Mg(OCH_3)_2$.

Preparation of $(\pi\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3](NCO)$

(*a*). *From* $\{(\pi\text{-}C_5H_5)Fe(CO)_2[P(C_6H_5)_3]\}PF_6$ *and* N_3^-. A solution of 0.065 g (1 mmole) of NaN_3 dissolved in 5 ml of water was added at room temperature with stirring to a solution of 0.584 g (1 mmole) of $\{(\pi\text{-}C_5H_5)Fe(CO)_2[P(C_6H_5)_3]\}PF_6$ in 50 ml of acetone. After 3 h the solvent was removed under a water aspirator vacuum, the residue dissolved in dichloromethane and the solution filtered. Chromatography of the resulting solution on alumina column, resulted in the appearance of a red band which was eluted from the column with CH_2Cl_2. The continued CH_2Cl_2 fractions were reduced to ca. 5 ml and the red $(\pi\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3](NCO)$ precipitated by adding 50 ml of hexane. Yield 66%. Found: C, 65.50; H, 4.52; N, 3.20. $C_{25}H_{20}FeNO_2$ calcd. C, 66.20; H, 4.43; N, 3.09%.)

(*b*). *From* $\{(\pi\text{-}C_5H_5)Fe(CO)_2[P(C_6H_5)_3]\}PF_6$ *and* NH_2NH_2. A suspension of 0.584 g (1 mmole) of $\{(\pi\text{-}C_5H_5)Fe(CO)_2[P(C_6H_5)_3]\}PF_6$ and 0.10 ml (2 mmole) of NH_2NH_2 in 50 ml of CH_2Cl_2 was allowed to react at room temperature for 1 h. The solvent was removed under vacuum leaving a red powder which was dissolved in 20 ml of CH_2Cl_2. Filtration and concentration of the filtrate to 5 ml followed by addition of 20 ml of pentane gave red $\{(\pi\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3](NCO)\}$ in 56% yield.

(*c*). *From* $\{(\pi\text{-}C_5H_5)Fe(CO)_2[P(C_6H_5)_3]\}PF_6$ *and* NH_2NHCH_3. The reaction was carried out as described above. The yield was 37%.

Properties of $(\pi\text{-}C_5H_5)Fe(CO)[P(C_6H_5)_3](NCO)$

This compound is a red, air-stable solid which melts with decomposition at 131–132°. 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. In $CHCl_3$ solution, its infrared spectrum shows the CO stretching absorption at 1940 (s) cm^{-1} and bands due to the asymmetric and symmetric NCO stretching modes at 2242 (s) and 1325 (w) cm^{-1}, respectively.

Kinetics

The reactions were followed spectrophotometrically using a Beckman DK-2 recording spectrophotometer. The changes of optical density in the ultraviolet region were recorded. All solutions were kept at 22.5° prior to mixing. The reactions were carried out in 1-cm quartz cells in the thermostatically controlled cell compartment of the spectrophotometer. The reference cell contained the reagent blank. The solution of N_3^- was added with a syringe; in the case of fast reactions few seconds elapsed between the mixing and the start of the recording of absorbance. All the kinetic runs were carried out under pseudo-first order conditions using at least a ten-fold ratio of the reagent ligand to the complex.

All the reactions proceed to completion. The pseudo-first-order rate constants k_{obs} were obtained from the slope of the linear plot of log $(A_\infty - A_t)$ against time. A_t and A_∞ are the optical densities of the reaction mixture at the wavelength of maximum change at t seconds and after 7–10 half-lives respectively.

Results and discussion

Recent kinetic studies indicate that in the case of the reactions of the hexacarbonyl complexes of VIA metals with N_3^- the cyanato complex, $[M(CO)_5NCO]^-$,

TABLE 1

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE REACTION:

$$[C_5H_5Fe(CO)_2L]^+ + N_3^- \xrightarrow[\text{MeOH}]{22.5^\circ} C_5H_5Fe(CO)L(NCO)$$

Complex	$[N_3^-] \times 10^3$	$k_{obs} \times 10^2$ (sec^{-1})	k_2 ($M^{-1}\cdot$sec^{-1})
$[C_5H_5Fe(CO)_2(C_2H_4)]^+$	100	5.5	
	80	4.4	
	60	3.4	
	50	2.5	0.55
	35	2.0	
	20	1.0	
	10	0.55	
$\{C_5H_5Fe(CO)_2[P(C_6H_5)_3]\}^+$	10	38.0	
	8	29.3	
	6	22.5	37
	4	13.7	
	2	7.0	
	1	3.8	
$[C_5H_5Fe(CO)_3]^+$	10	Very fast	⩾100

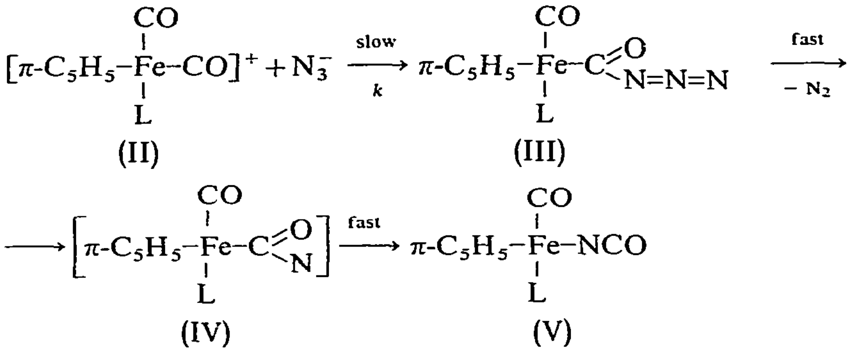
is formed through an S_N2 reaction[9,10].

Attack of a nucleophile on a terminal CO group is well-known[5,11,12], and it seems reasonable to assume that a hard nucleophile attacks the hard carbon atom, as was proposed for the base-catalysed reaction of $Fe(NO)_2(CO)_2$[13] with various nucleophiles. The kinetics of the reaction (4) follow the rate law:

$$\text{Rate} = k \cdot [\text{Complex}] \cdot [N_3^-].$$

The values of k have been obtained from the slope of the linear plots of the pseudo-first order rate constant k_{obs} (sec^{-1}) *vs.* the concentration of azide anion. The rate data for the reaction in methanol at 22.5° are summarized in Table 1.

On this basis, a mechanism involving a direct attack on the carbonyl carbon could explain the reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2L]^+$ with N_3^- an acyl azide being formed as an intermediate. This rearranges with loss of N_2 to form the isocyanate product, as proposed for analogous reactions of the hexacarbonyls of VIB metals[9]. The following scheme shows the proposed mechanism:



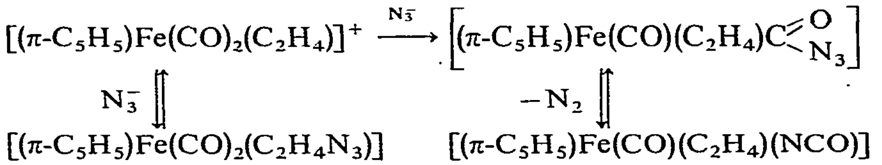
$$[\pi\text{-}C_5H_5\text{-}\overset{CO}{\underset{L}{Fe}}\text{-}CO]^+ + N_3^- \xrightarrow[k]{\text{slow}} \pi\text{-}C_5H_5\text{-}\overset{CO}{\underset{L}{Fe}}\text{-}C{\genfrac{}{}{0pt}{}{\nearrow O}{\searrow N{=}N{=}N}} \xrightarrow[-N_2]{\text{fast}}$$

(II) (III)

$$\longrightarrow \left[\pi\text{-}C_5H_5\text{-}\overset{CO}{\underset{L}{Fe}}\text{-}C{\genfrac{}{}{0pt}{}{\nearrow O}{\searrow N}}\right] \xrightarrow{\text{fast}} \pi\text{-}C_5H_5\text{-}\overset{CO}{\underset{L}{Fe}}\text{-}NCO$$

(IV) (V)

It is worth noting that in the complex $[C_5H_5Fe(CO)_2(C_2H_4)]^+$, there are two possible electrophilic centers, *viz.*, the carbonyl group and the coordinated olefin. With some other nucleophiles such as NH_2CH_3 or OCH_3^- the reaction site is the olefinic carbon and σ-alkyl iron complexes[4] are formed. A possible scheme for the reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_2(C_2H_4)]^+$ with N_3^- is the following:



$$\begin{tikzcd}
{[(\pi\text{-}C_5H_5)Fe(CO)_2(C_2H_4)]^+} \arrow[r, "N_3^-"] \arrow[d, shift left, "N_3^-"'] & \left[(\pi\text{-}C_5H_5)Fe(CO)(C_2H_4)C{\genfrac{}{}{0pt}{}{\nearrow O}{\searrow N_3}}\right] \arrow[d, shift left, "-N_2"'] \\
{[(\pi\text{-}C_5H_5)Fe(CO)_2(C_2H_4N_3)]} \arrow[u, shift left] & {[(\pi\text{-}C_5H_5)Fe(CO)(C_2H_4)(NCO)]} \arrow[u, shift left]
\end{tikzcd}$$

nitrogen being evolved and the nucleophilic attack occurring at the carbonyl carbon.

Data reported in Table 1 show that the reaction is sensitive to the nature of the coordinated ligand L, the sequence being:

$$CO > P(C_6H_5) > C_2H_4$$

The corresponding second-order rate constants, k_2 ($M^{-1} \cdot sec^{-1}$), from Table 1 are in the ratio 1/67/300.

The observed rate law is also consistent with a mechanism involving a rapid pre-equilibrium in the formation of the acyl azide derivative followed by a slow re-arrangement to give the cyanato product. At this point it is worth noting that in the reaction of $[(\pi\text{-}C_5H_5)Fe(CO)_3]^+$ with hydrazine the carbohydrazide intermediate $\{(\pi\text{-}C_5H_5)Fe(CO)_2[C(O)NHNH_2]\}$ is formed. This compound slowly decomposes in $CHCl_3$ to form the $C_5H_5Fe(CO)_2(NCO)$ complex (k at 25° $\simeq 3\times10^{-4}$ sec^{-1})[1], with loss of ammonia. However no such an intermediate has been isolated from the reaction of azide anion with $[(\pi\text{-}C_5H_5)Fe(CO)_2L]^+$.

REFERENCES

1 R. J. Angelici and L. Busetto, *J. Amer. Chem. Soc.*, 91 (1969) 3197.
2 R. J. Angelici and A. E. Kruse, *J. Organometal. Chem.*, 22 (1970) 461.
3 L. Busetto, M. Graziani and U. Belluco, *Inorg. Chem.*, 9 (1970) in press.
4 L. Busetto, A. Palazzi, R. Ros and U. Belluco, *J. Organometal. Chem.*, 25 (1970) 207.
5 L. Busetto and R. J. Angelici, *Inorg. Chim. Acta*, 2 (1969) 391.
6 A. Davidson, M. L. H. Green and G. Wilkinson, *J. Chem. Soc.*, (1961) 3172.
7 P. M. Treichel, R. L. Shubkin, K. W. Barrett and D. Reichard, *Inorg. Chem.*, 5 (1966) 1177.
8 M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, 1 (1963) 58.
9 H. Werner, W. Beck and H. Engelmann, *Inorg. Chim. Acta*, 3 (1969) 331.
10 W. Beck, H. Werner, H. Engelmann and H. S. Smedal, *Chem. Ber.*, 101 (1968) 2143.
11 T. Kruch and M. Noack, *Chem. Ber.*, 97 (1964) 1693.
12 W. F. Edgell, M. T. Yang, B. J. Bulkin, R. Bayer and N. Koizumi, *J. Amer. Chem. Soc.*, 87 (1965) 3080.
13 D. E. Morris and F. Basolo, *J. Amer. Chem. Soc.*, 90 (1968) 2536.