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Reactions of Cyclopentadienyliron Carbonyl Cations with Amines

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$[C_5H_5Fe(CO)_2L]^+$ ($L{=}CO$, $P(C_6H_5)_3$) reacts with primary and secondary amines to form carboxamido complexes, $C_5H_5Fe(CO)(L)(CONHR)$:

$$[C_5H_5Fe(CO)_2L]^+ + 2RNH_2 \longrightarrow C_5H_5Fe(CO)(L)(CONHR) + RNH_3^+$$

Their reaction with HCl removes the –NHR group from the carboxamido group:

$$C_5H_5Fe(CO)(L)(CONHR) + HCl \longrightarrow [C_5H_5Fe(CO)_2L]^+Cl^- + RNH_2$$

The $[C_5H_5Fe(CO)_3]^+$ cation reacts with $NaOCH_3$ to form the alkoxycarbonyl derivative, $C_5H_5Fe(CO)_2C(O)OCH_3$, according to the equation:

$$[C_5H_5Fe(CO)_3]^+ + OCH_3^- \longrightarrow C_5H_5Fe(CO)_2C(O)OCH_3$$

A mechanism of nucleophilic attack at the carbonyl carbon is proposed for the formation of the carboxamido and alkoxycarbonyl derivatives. The properties of the new compounds are listed, and the carbonyl stretching frequencies are discussed.

Introduction

Although carboxamido complexes of manganese(I), $Mn(CO)_4(NH_2R)(CONHR)$, have recently been prepared[2] by reaction of $Mn(CO)_5Br$ with primary aliphatic amines, relatively little work has been done on complexes containing the –CONHR group. The first compound of this type, $C_5H_5Fe(CO)_2C(O)N(CH_3)_2$,[3] was prepared by reacting $Na[C_5H_5Fe(CO)_2]$ and dimethylcarbamoylchloride. $R_2NCOCo(CO)_4$ [4,5] has been proposed as an intermediate in the cobalt catalyzed carbonylation of primary and secondary amines to form formamide derivatives. Carboxamido complexes of iron pentacarbonyl have been also proposed to be formed in the first steps of the reaction between $Fe(CO)_5$ and pyrrolidine, piperidine, and *n*-butylamine.[6,7]

Reported in this paper are the reactions between $[C_5H_5Fe(CO)_2L]^+$ ($L{=}CO$ or $P(C_6H_5)_3$) and nucleophiles such as primary and secondary amines and OR^- to produce carboxamido and alkoxycarbonyl derivatives. The reverse reactions will also be discussed.

Experimental Section

Materials. The compounds $[C_5H_5Fe(CO)_2]_2$,[8] $C_5H_5Fe(CO)_2Cl$ [9] and $[C_5H_5Fe(CO)_2P(C_6H_5)_3]Cl$ [10,11] were synthesized as described in the literature.

All solvents were reagent grade. Infrared spectra were measured on a Beckman IR-8 spectrophotometer using a polystyrene standard.

Preparation of $[C_5H_5Fe(CO)_3]^+PF_6^-$. This compound was prepared following the same method used for the preparation of $[C_5H_5Fe(CO)_2(CS)]^+$.[12] Thus a mixture of $Na[C_5H_5Fe(CO)_2]$ (from 7.08 g., 0.02 mole, of cyclopentadienyl iron dicarbonyl dimer and excess 1% sodium amalgam) and ethyl chloroformate (4.34 g., 0.04 mole) in 80 ml. of freshly distilled tetrahydrofuran was stirred under nitrogen for 10 hrs. Removal of the solvent at room temperature (~20 mm), extraction of the residue with 100 ml. of benzene in 5-20 ml. portions, and filtration through celite filter aid were followed by treatment with gaseous HCl for 20 minutes. The resulting pale yellow precipitate was washed with ether and pentane, dissolved in water and the $[C_5H_5Fe(CO)_3]^+$ precipitated by adding a solution of excess NH_4PF_6. The pale yellow $[C_5H_5Fe(CO)_3]PF_6$ was dried under vacuum and recrystallized from acetone-ether. Yield 5.80 g. (41%). The IR spectrum in nujol mull of the compound shows two CO stretching absorptions at 2120 and 2068 cm^{-1}, in good agreement with those reported in the literature.[10,13,14]

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(1) On leave from the University of Padua, Padua, Italy.
(2) R. J. Angelici and D. L. Denton, *Inorg. Chim. Acta*, *2*, 3 (1968).
(3) R. B. King, *J. Am. Chem. Soc.*, *85*, 1918 (1963).
(4) H. W. Sternberg and I. Wender, *Chem. Soc.* (London), *Spec. Publ.* No. *13*, 35 (1959).
(5) H. W. Sternberg, I. Wender, R. A. Friedel, and M. Orchin, *J. Am. Chem. Soc.*, *75*, 3148 (1953).
(6) W. F. Edgell, M. T. Yang, B. J. Bulkin, R. Bayer, and N. Koizumi, *J. Am. Chem. Soc.*, *87*, 3080 (1965).
(7) W. F. Edgell and B. J. Bulkin, *J. Am. Chem. Soc.*, *88*, 4839 (1966).
(8) See procedures described in R. B. King, «Organometallic Syntheses», Vol. 1, Academic Press Inc., New York, N. Y. (1965).
(9) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, *1*, 165 (1955).
(10) A. Davison, M. L. H. Green, and G. Wilkinson, *J. Chem. Soc.*, 3172 (1961).
(11) P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, *5*, 1177 (1966).
(12) L. Busetto and R. J. Angelici, *J. Am. Chem. Soc.*, *90*, 3283 (1968) and ref. therein.
(13) E. O. Fisher and K. Fichtel, *Chem. Ber.*, *94*, 1200 (1961).
(14) R. B. King, *Inorg. Chem.*, *1*, 964 (1962).

Preparation of $C_5H_5Fe(CO)_2(CONHR)$. The gaseous amine was slowly bubbled into a mixture of 0.5 g. of $[C_5H_5Fe(CO)_3]PF_6$ stirred in 50 ml. of nitrogen-saturated ethyl ether. After 30 min. the reaction was stopped and the solution filtered, leaving on the filtration frit a white precipitate ($RNH_3^+PF_6^-$). The filtrate was evaporated using a water-aspirator vacuum until pale yellow crystals began to separate from the solution. Addition of 30 ml. of pentane, cooling in a dry ice-acetone bath and filtration gave $C_5H_5Fe(CO)_2(CONHR)$.

In the case of liquid amines a slight variation was required. A ten-fold excess of the amine was added to the ether solution, and after filtration the solvent was evaporated to dryness under a water-aspirator vacuum and the solid dissolved in 10 ml. of ether. After filtration, the product was precipitated by adding 20 ml. of pentane.

Preparation of $C_5H_5Fe(CO)[P(C_6H_5)_3](CONHCH_3)$. It was prepared following the method used above and purified by recrystallization from ether-hexane. Other primary aliphatic amines such as ethyl amine and isopropylamine also react to give analogous $C_5H_5Fe(CO)[P(C_6H_5)_3](CONHR)$ complexes which were identified only from their infrared spectra in solution (Table II).

Preparation of $C_5H_5Fe(CO)_2(CONC_5H_{10})$ and $C_5H_5Fe(CO)_2(CONC_4H_8)$. These compounds were prepared from piperidine and pyrrolidine following the method used for the liquid primary amines. Both of these carboxamido complexes were purified by recrystallization from benzene-heptane.

Properties of the Carboxamido Complexes. All of the derivatives are yellow solids, their stability in solution decreases as the size of the R group increases. In the solid state they slowly decompose in air but can be stored for several weeks in the dark under vacuum. Upon melting, considerable decomposition to $[C_5H_5Fe(CO)_2]_2$ occurs as identified by its infrared spectrum. $[C_5H_5Fe(CO)_3]^+PF_6^-$ also reacts with ammonia to give a pale yellow, extremely unstable solid having an infrared spectrum identical to the $C_5H_5Fe(CO)_2(CONHR)$ derivatives (Table II).

All the carboxamido complexes studied react with water to give yellow basic (pH ~ 9-10) solutions that in a few minutes turn dark producing a brown precipitate.

Reaction of $C_5H_5Fe(CO)_2(CONHR)$ with HCl. Gaseous HCl was bubbled into a solution of 0.1 g. of $C_5H_5Fe(CO)_2(CONHR)$ dissolved in 30 ml. of ether, and after a few minutes a pale yellow precipitate appeared. After 10 min. the reaction was stopped. The solid was filtered under nitrogen and dissolved in water. The product $[C_5H_5Fe(CO)_3]PF_6$ precipitated upon addition of an aqueous solution of NH_4PF_6.

Reaction of $C_5H_5Fe(CO)[P(C_6H_5)_3](CONHCH_3)$ with HCl. When the reaction was carried out as noted above for $C_5H_5Fe(CO)_2(CONHR)$, $C_5H_5Fe(CO)_2[P(C_6H_5)_3]Cl$ was obtained as determined from its C-O stretching absorptions at 2060 and 2018 cm^{-1}.[10]

Preparation of $C_5H_5Fe(CO)_2C(O)OCH_3$. A mixture of 0.5 g. of $[C_5H_5Fe(CO)_3]PF_6$ in 50 ml. of absolute methanol was stirred for 4 hrs. at room temperature in the presence of a ten-fold excess of $NaOCH_3$. Then the methanol was eliminated under a water aspirator vacuum leaving an orange-brown material that was dissolved in 20 ml. of pentane and filtered. Cooling overnight at −78° gave $C_5H_5Fe(CO)_2C(O)OCH_3$ which was identified by its infrared spectrum.[15] By bubbling HCl into an ether solution of the alkoxy-carbonyl derivative and precipitating the cation with NH_4PF_6, 0.32 g. of the starting $[C_5H_5Fe(CO)_3]PF_6$ were recovered.

Attempted decarbonylation of $C_5H_5Fe(CO)_2(CONHCH_3)$. In an attempt to decarbonylate $C_5H_5Fe(CO)_2(CONHCH_3)$ to the unknown $C_5H_5Fe(CO)_2(NHCH_3)$, a solution of $C_5H_5Fe(CO)_2(CONHCH_3)$ in tetrahydrofuran was irradiated with ultraviolet light for 15 hrs. After filtration the solution was evaporated to give a brown material. Its infrared spectrum showed the presence of only $[C_5H_5Fe(CO)_2]_2$. Other unidentified materials which were not soluble in organic solvents were also formed .

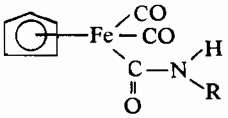
Results and Discussion

The reaction of $[C_5H_5Fe(CO)_2L]^+$ (L=CO or $P(C_6H_5)_3$) with primary aliphatic amines, RNH_2, yields $C_5H_5Fe(CO)(L)(CONHR)$ according to equation (1).

$$[C_5H_5Fe(CO)_2L]^+ + 2RNH_2 \longrightarrow C_5H_5Fe(CO)(L)(CONHR) + RNH_3^+ \qquad (1)$$

The nature of the carboxamido complexes was established from elemental analyses and their IR spectra (Table II). The mass spectra of $C_5H_5Fe(CO)_2(CONHCH_3)$ and $C_5H_5Fe(CO)[P(C_6H_5)_3](CONHCH_3)$ show the parent ions along with fragments corresponding to the loss of CO and $NHCH_3$. The proton NMR spectrum of $C_5H_5Fe(CO)_2(CONHCH_3)$ in $CDCl_3$ shows a doublet at 2.88 p.p.m. downfield from tetramethylsilane due to the methyl protons, a singlet due to the five ring protons at 4.94 p.p.m., and a broad peak at 6.80 p.p.m. in deuterated dimethylsulfoxide solvent due to the nitrogen proton. Secondary amines such as piperidine, pyrrolidine or dimethylamine and ammonia also react with $C_5H_5Fe(CO)_3^+$ according to equation (1) giving carboxamido derivatives. With aniline no product could be isolated. Under conditions where $[C_5H_5Fe(CO)_3]^+$ reacted readily with amines, the isoelectronic and isostructural $C_5H_5Mn(CO)_3$ gave no reaction. It appears that the carbonyl complex must be cationic in order to react with amines to produce carboxamido complexes.

The IR spectra of these compounds are completely in accord with structure I.



(I)

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

Table I. Analytical Data for the Carboxamido Complexes

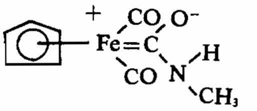
Complex	M.P. °C	Crystallization method	Yield %	Analyses Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
$C_5H_5Fe(CO)_2(CONHCH_3)$	118 dec	ether-pentane	60	46.0	3.9	6.0	45.7	3.7	6.1
$C_5H_5Fe(CO)_2(CONHC_2H_5)$	97 dec	»	62	48.2	4.5	5.6	47.6	4.4	5.9
$C_5H_5Fe(CO)_2[CONHCH(CH_3)_2]$	78-80 dec	»	70	50.2	5.0	5.3	50.2	4.8	5.5
$C_5H_5Fe(CO)_2(CONC_5H_{10})$	70 dec	benzene-heptane	45	54.0	5.2	4.9	54.3	5.6	5.0
$C_5H_5Fe(CO)_2(CONC_4H_8)$	68 dec	»	40	52.4	4.8	5.1	53.2	5.1	5.2
$C_5H_5Fe(CO)[P(C_6H_5)_3](CONHCH_3)$	114 dec	ether-hexane	50	66.5	5.2	3.0	64.5	4.9	2.8

Table II. Infrared Stretching Frequencies (cm^{-1}) of the Carboxamido Complexes

Compound	Solvent	$-C{\equiv}O$	$C{=}O$
$C_5H_5Fe(CO)_2(CONH_2)$	CH_2Cl_2	2015 (s), 1963 (s)	1593 (m)
$C_5H_5Fe(CO)_2(CONHCH_3)$	methylcyclohexane	2015 (s), 1972 (s)	1625 (m)
$C_5H_5Fe(CO)_2(CONHCH_2CH_3)$	»	2015 (s), 1968 (s)	1622 (m)
$C_5H_5Fe(CO)_2[CONHCH(CH_3)_2]$	»	2015 (s), 1965 (s)	1620 (m)
$C_5H_5Fe(CO)_2[CONH(CH_2)_3CH_3]$	»	2019 (s), 1968 (s)	1622 (m)
$C_5H_5Fe(CO)_2[CON(CH_3)_2]$	CH_2Cl_2	2015 (s), 1960 (s)	1612 (m)
$C_5H_5Fe(CO)_2(CONC_4H_8)$	heptane	2023 (s), 1967 (s)	1566 (m)
$C_5H_5Fe(CO)_2(CONC_5H_{10})$	cyclohexane	2020 (s), 1968 (s)	1560 (m)
$C_5H_5Fe(CO)[P(C_6H_5)_3](CONHCH_3)$	CH_2Cl_2	1915 (s)	1558 (m)
$C_5H_5Fe(CO)[P(C_6H_5)_3](CONHCH_2CH_3)$	»	1911 (s)	1560 (m)
$C_5H_5Fe(CO)[P(C_6H_5)_3][CONHCH(CH_3)_2]$	cyclohexane	1924 (s)	1585 (m)

The $C_5H_5Fe(CO)_2(CONHCH_3)$ complex shows two strong bands at 1972 and 2015 cm^{-1} in methylcyclohexane solvent which are assigned to the $-C{\equiv}O$ stretching frequencies of the terminal carbonyl groups and a medium intensity band at 1625 cm^{-1} due to the $>C{=}O$ stretching frequency of the carboxamido group. The intensity and position of the $>C{=}O$ stretching frequencies are consistent with previous observations on systems of this kind.[3,6,7,16,17]

It is interesting to note that the $>C{=}O$ stretching frequency in the $-CONHR$ group is shifted 80-100 wave numbers toward lower frequencies with respect to HCONHR ($\sim$1700 cm^{-1}) and that these stretching frequencies in the compounds $C_5H_5Fe(CO)[P(C_6H_5)_3](CONHR)$ are lower than those in the parent dicarbonyl compounds $C_5H_5Fe(CO)_2(CONHR)$. The same trend has been observed in the compound $C_5H_5Fe(CO)(L)(COCH_3)$, ($L{=}CO$, $P(C_6H_5)_3$).[18,19] It has been suggested that this lowering may arise from π-electron donation from the metal to the $-CONHR$ group causing a reduction in the $>C{=}O$ bond order. Additional evidence that the resonance structure,



is of importance in this system comes from the fact that the $>C{=}O$ stretching frequency is lower in $C_5H_5Fe(CO)[P(C_6H_5)_3](CONHCH_3)$ than in $C_5H_5Fe(CO)_2(CONHCH_3)$.

The carboxamido complexes $C_5H_5Fe(CO)(L)(CONHR)$ react with HCl in non-polar solvents to yield the cationic $[C_5H_5Fe(CO)_2L]^+$ according to equation (2).

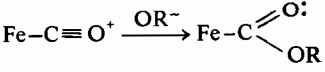
$$C_5H_5Fe(CO)(L)(CONHR)+2HCl \longrightarrow [C_5H_5Fe(CO)_2L]^+Cl^- + RNH_3^+Cl^- \qquad (2)$$

The cation has been isolated as the hexafluorophosphate salt and was identified by its IR spectrum. An attempted reaction of $C_5H_5Fe(CO)_2COCH_3$ with HCl did not give $[C_5H_5Fe(CO)_3]^+$ and CH_4.[20]

The cation $[C_5H_5Fe(CO)_3]^+$ reacts with sodium methoxide in methanol giving the methoxycarbonyl $C_5H_5Fe(CO)_2C(O)OCH_3$ compound that may be converted into the cation by adding HCl to its benzene solution. The forward and reverse reaction can be represented by the equilibrium (3).

$$C_5H_5Fe(CO)_3^+ + OCH_3^- \underset{HCl}{\overset{NaOCH_3}{\rightleftharpoons}} C_5H_5Fe(CO)_2C(O)OCH_3 \qquad (3)$$

It has been shown[21,22] that nucleophilic agents react with cationic carbonyl compounds, and it has been proposed that these reactions take place by attack at the carbonyl carbon. Although a mechanistic investigation of reaction (3) was not conducted, it appears that the forward reaction proceeds by such a mechanism.



$$Fe{-}C{\equiv}O^+ \xrightarrow{OR^-} Fe{-}C\begin{matrix}{\nearrow}\ddot{O}: \\ {\searrow}OR\end{matrix}$$

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[16] D. M. Adams and G. Booth, *J. Chem. Soc.*, 1112 (1962).

[17] W. Beck, W. Hieber, and H. Tengler, *Chem. Ber.*, *94*, 862 (1961).

[18] M. L. H. Green and C. R. Hurley, *J. Organometall. Chem.*, *10*, 188 (1967).

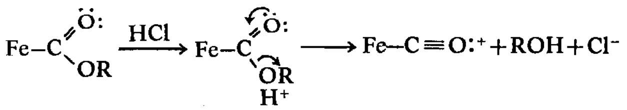
[19] J. P. Bibler and A. Wojcicki, *Inorg. Chem.*, *5*, 883 (1966).

[20] C. Green, unpublished observation. See reference 18.

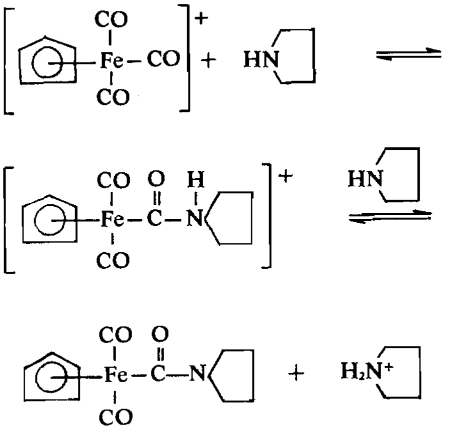
[21] T. Kruck and M. Noack, *Chem. Ber.*, *97*, 1693 (1964).

[22] E. L. Muetterties, *Inorg. Chem.*, *4*, 1841 (1965).

The reverse of this reaction may be similar to the acid catalyzed hydrolysis of organic esters:

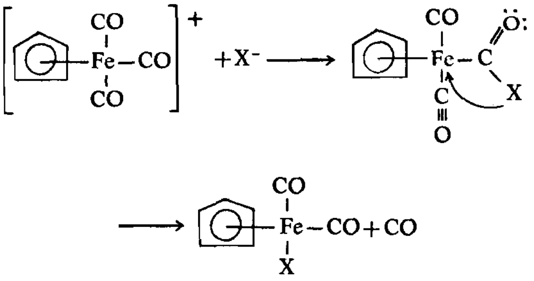


Likewise a similar mechanism is postulated for the formation of $C_5H_5Fe(CO)_2(CONHR)$: the amine first attacks the carbonyl carbon forming an intermediate which loses a proton giving the carboxamido derivative as summarized in the following scheme:



A mechanism in which the amine first attacks the iron atom then undergoes a rearrangement in which the amine migrates to a carbon site to yield the carboxamido complex can also be postulated but seems less reasonable. Nucleophilic attack on the iron atom has been proposed in the reaction of $[C_5H_5Fe(CO)_3]^+$ with halide ions to form $C_5H_5Fe(CO)_2X$.[23]

Since it has been inferred from recent calculations that the carbonyl carbon is the most electron-deficient site in the molecules in the isoelectronic series $V(CO)_6^-$, $Cr(CO)_6$, $Mn(CO)_6^+$,[24] a mechanism of direct attack on the carbonyl carbon could also explain the reaction of $[C_5H_5Fe(CO)_3]^+$ and X^- *via* the formation of an acyl halide intermediate that rearranges by an internal displacement mechanism analogous to that suggested for the decarbonylation of $RCOMn(CO)_5$.[25]



In the reaction with amines the reaction stops at the carboxamido intermediate, $C_5H_5Fe(CO)_2(CONHR)$, without subsequent rearrangement to $C_5H_5Fe(CO)_2(NHR)$. There is no evidence of such rearrangement even under ultraviolet irradiation.

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(23) R. K. Kochhar and R. Pettit, *J. Organom. Chem.*, *6*, 272 (1966).
(24) K. G. Caulton and R. Fenske, *Inorg. Chem.*, *7*, 1273 (1968).
(25) K. Noack and F. Calderazzo, *J. Organometall. Chem.*, *10*, 101 (1967).