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

ADDITIONS TO THE COORDINATED ETHYLENE LIGAND IN THE $[C_5H_5Fe(CO)_2(C_2H_4)]^+$ COMPLEX

L. BUSETTO, A. PALAZZI, R. ROS AND U. BELLUCO
Faculty of Industrial Chemistry, The University, Viale Risorgimento 4, 40136 Bologna (Italy)

(Received June 25th, 1970)

SUMMARY

Reaction of $[C_5H_5Fe(CO)_2C_2H_4]^+$ with methylamine or methoxide ion (L) yields the stable σ-bonded carbon–iron complexes $[C_5H_5Fe(CO)_2(C_2H_4L)]$, which regenerate the original iron cationic complex when treated with hydrogen chloride. Reactions with other nucleophiles, such as N_3^-, NCO^-, CN^- have also been examined. With N_3^- the nucleophilic attack occurs at the CO group to give the cyanato complex $[C_5H_5Fe(CO)(C_2H_4)(NCO)]$, while with NCO^- and CN^- (X) ethylene is replaced to give $[C_5H_5Fe(CO)_2X]$ complexes.

INTRODUCTION

We recently described the reactions of cationic iron carbonyl derivatives of the type $[C_5H_5Fe(CO)_3]^+$ and $[C_5H_5Fe(CO)_2(CS)]^+$ with various nucleophiles, such as primary and secondary amines, hydrazines, methoxide, N_3^-, NCO^- and CN^-[1,2], and showed that with the $[C_5H_5Fe(CO)_2(CS)]^+$ complex reaction occurs at the carbon of the thiocarbonyl group rather than at the carbonyl group. We now describe the reactions of $[C_5H_5Fe(CO)_2(C_2H_4)]^+BF_4^-$ with nucleophilic agents with nitrogen or oxygen donor atoms.

EXPERIMENTAL

Materials

The complex $[C_5H_5Fe(CO)_2(C_2H_4)]BF_4$[3,4] was made as described previously. $(C_6H_5)_3CBF_4$ was prepared from $(C_6H_5)_3COH$ and fluoroboric acid[5]. Absolute methanol was refluxed with $Mg(OCH_3)_2$ and distilled from it. Dichloromethane was dried over molecular sieves. All the other chemicals used were Reagent Grade.

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, with TMS as internal standard.

1. *Reactions of* $[C_5H_5Fe(CO)_2(C_2H_4)]^+$ *with* CH_3O^-

A mixture of 1 g (3.4 mmoles) of $[C_5H_5Fe(CO)_2(C_2H_4)]BF_4$ in 50 ml of anhydrous methanol was stirred for 7 h at room temperature under nitrogen in the presence of an excess of Na_2CO_3. The solution was then filtered and the solvent removed under reduced pressure to leave a red-orange material which was dissolved in 20 ml of CH_2Cl_2 and filtered. Elimination of the solvent followed by vacuum sublimation at 40° of the resulting red oil gave the orange-red $C_5H_5Fe(CO)_2(CH_2CH_2OCH_3)$ in 36% yield. (Found: C, 51.8; H, 5.04. $C_{10}H_{12}FeO_3$ calcd.: C, 50.9; H, 5.09%.)

The complex is air sensitive, and rapidly decomposes in solution to form $[C_5H_5Fe(CO)_2]_2$. When HCl is bubbled into ether solution of $[C_5H_5Fe(CO)_2(CH_2CH_2OCH_3)]$ and NH_4PF_6 is added, the starting cation $[C_5H_5Fe(CO)_2(C_2H_4)]^+$ is recovered as the hexafluorophosphate salt.

2. *Reactions of* $[C_5H_5Fe(CO)_2(C_2H_4)]^+$ *with* CH_3NH_2

Methylamine was slowly bubbled into a stirred suspension of 0.5 g of $[C_5H_5Fe(CO)_2(C_2H_4)]BF_4$ in 50 ml of ethyl ether saturated with nitrogen. After 20 min the reaction was stopped and the solution filtered under nitrogen. The filtrate was evaporated under reduced pressure leaving a brown oil. Vacuum sublimation of the oily compound gave an unstable solid which showed two strong terminal CO stretching absorptions, at 2004 and 1950 cm^{-1}. Because of the low stability of this compound satisfactory analyses were not obtained, but on treatment with hydrogen chloride the starting $[C_5H_5Fe(CO)_2(C_2H_4)]^+$ complex was obtained.

3. *Reaction of* $[C_5H_5Fe(CO)_2(C_2H_4)]^+$ *with* N_3^-

When a solution of 0.13 g (2 mmoles) of NaN_3, dissolved in 5 ml of water, was added with stirring to a solution of 0.584 g (2 mmoles) of $[C_5H_5Fe(CO)_2(C_2H_4)]BF_4$ in 50 ml of acetone the mixture immediately turned from yellow to red. After 1 h of stirring at room temperature, the acetone was removed under water-pump vacuum, and 20 ml of water was added to the residue. The $C_5H_5Fe(CO)(C_2H_4)(NCO)$ was extracted from the mixture with 20 ml of $CHCl_3$. The solution was dried over calcium chloride and the solvent was removed under reduced pressure. The red-orange residue was dissolved in CH_2Cl_2 and filtered. Chromatography of this solution on an alumina column, with CH_2Cl_2 as eluent, gave a red band and a green band. The red band was eluted off, the volume of the solution was reduced to ca. 5 ml, and 50 ml of hexane was added. Red-brown crystals were filtered off; yield 65%; m.p. 123–124°. (Found: C, 48.9; H, 4.21; N, 6.25. $C_9H_9FeNO_2$ calcd.: C, 49.7; H, 4.11; N, 6.39%.)

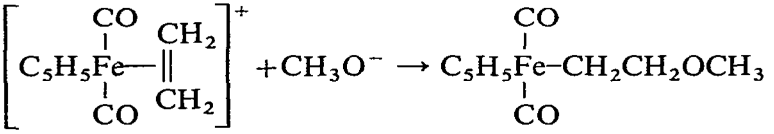
4. *Reactions of* $[C_5H_5Fe(CO)_2(C_2H_4)]^+$ *with* CN^- *and* NCO^-

These compounds were prepared by general procedures as previously described [6,7]. Thus an acetone solution (50 ml) containing 1 g (3.4 mmoles) of $[C_5H_5Fe(CO)_2(C_2H_4)]BF_4$ and a ten-fold excess of KCN or KNCO was stirred at room temperature for 10 h. The solvent was evaporated off under vacuum and the red residue was dissolved in 10 ml of CH_2Cl_2. In both cases ($X = CN^-, NCO^-$) the solution was chromatographed on alumina and the red band was eluted off with CH_2Cl_2 and the solution concentrated to small volume. The complexes precipitated by adding pentane. The yield was 65% for $C_5H_5Fe(CO)_2(CN)$ and 72% for $C_5H_5Fe(CO)_2(NCO)$, and the products were characterized by their infrared spectra which were identical with those of samples made by other methods[6,8].

RESULTS

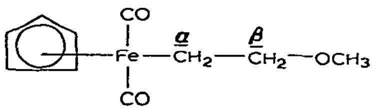
It was shown recently that nucleophilic agents such as amines or methoxide react with $[C_5H_5Fe(CO)_3]^+$ to give aminocarbonyl or alkoxycarbonyl derivatives[1,6]. With the thiocarbonyl complex $[C_5H_5Fe(CO)_2(CS)]^+$ the corresponding thioderivatives are formed[2]. It has been suggested that the electrophilic character of the carbon of the carbonyl or thiocarbonyl groups is the driving force for these reactions.

The complex $[C_5H_5Fe(CO)_2(C_2H_4)]^+$ reacts with methoxide in anhydrous methanol to give the σ-methoxyethyl derivative $[C_5H_5Fe(CO)_2(CH_2CH_2OCH_3)]$, according to eqn. (1).



$$\left[\underset{CO}{\overset{CO}{C_5H_5Fe}}\!-\!\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}\right]^{+} + CH_3O^- \rightarrow C_5H_5\underset{CO}{\overset{CO}{Fe}}\text{-}CH_2CH_2OCH_3 \qquad (1)$$

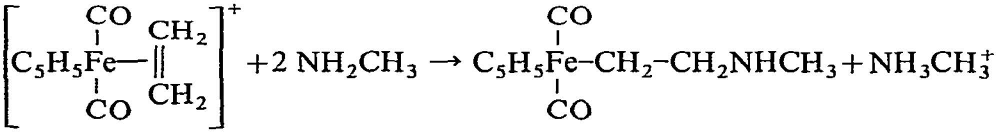
The product was identified by elemental analysis and spectroscopy. Its IR spectrum in CH_2Cl_2 shows two strong terminal $\nu(CO)$ absorptions at 2006 and 1954 cm^{-1} and the proton NMR spectrum in CS_2 shows a singlet due to the five ring protons at 5.24 downfield from TMS, a triplet at 6.49 partially superimposed on a sharp singlet at 6.60 due to the methyl protons of the methoxy group and a triplet at 8.31. This spectrum is consistent with the following formulation:



where the two triplets at 8.31 and 6.49 are assigned to the α and β methylene protons respectively. The σ-methoxyethyl derivative can be converted into the starting $[C_5H_5Fe(CO)_2C_2H_4]^+$ complex by treating its ether solution with hydrogen chloride. No evidence for the formation of a chloro derivative of the type $[C_5H_5Fe(CO)_2CH_2CH_2Cl]$ was obtained. Such a product is formed in the reaction of $(C_5H_5Fe(CO)_2(CH_2OCH_3)]$ with HCl[9,10]:

$$[C_5H_5Fe(CO)_2(CH_2OCH_3)] + HCl \rightarrow [C_5H_5Fe(CO)_2CH_2Cl] + CH_3OH$$

Methylamine reacts with $[C_5H_5Fe(CO)_2(C_2H_4)]^+$ according to the equation:



$$\left[\underset{CO}{\overset{CO}{C_5H_5Fe}}\!-\!\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}\right]^{+} + 2\,NH_2CH_3 \rightarrow C_5H_5\underset{CO}{\overset{CO}{Fe}}\text{-}CH_2\text{-}CH_2NHCH_3 + NH_3CH_3^+$$

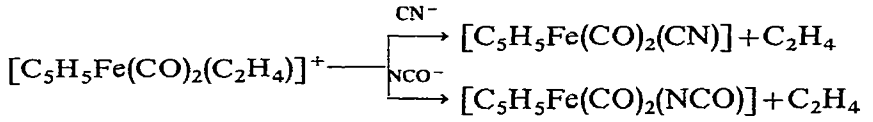
The IR spectrum of the product showed two strong terminal carbonyl stretching frequencies at 2004 and 1950 cm^{-1}. Because of the instability of the complex a satisfactory elemental analysis was not obtained. Treatment with hydrogen chloride in ether regenerated the original $[C_5H_5Fe(CO)_2(C_2H_4)]^+$ complex in almost quantitative yield.

The reaction between $[C_5H_5Fe(CO)_2(C_2H_4)]^+$ and NaN_3 leads to the formation of the cyanato derivative, $[C_5H_5Fe(CO)(C_2H_4)(NCO)]$.

$$[C_5H_5Fe(CO)_2(C_2H_4)]^+ + N_3^- \rightarrow C_5H_5Fe(CO)(C_2H_4)(NCO) + N_2$$

The IR spectrum of the cyanato complex in $CHCl_3$ shows a carbonyl stretching absorption at 1943(s), and two bands due to the asymmetric and symmetric NCO stretching modes at 2225 (s) and 1320 (w) cm^{-1}, respectively. This reaction presumably proceeds by a mechanism similar to that for the interaction of $C_5H_5Fe(CO)_3^+$ and N_3^- [6].

Nucleophilic agents such as CN^- and NCO^- displace ethylene from the $[C_5H_5Fe(CO)_2(C_2H_4)]^+$ cation to form the known cyano, $[C_5H_5Fe(CO)_2(CN)]$, and cyanato, $[C_5H_5Fe(CO)_2(NCO)]$, complexes.



$$[C_5H_5Fe(CO)_2(C_2H_4)]^+ \xrightarrow{CN^-} [C_5H_5Fe(CO)_2(CN)] + C_2H_4$$
$$[C_5H_5Fe(CO)_2(C_2H_4)]^+ \xrightarrow{NCO^-} [C_5H_5Fe(CO)_2(NCO)] + C_2H_4$$

Although the complex $[C_5H_5Fe(CO)_2(CH_2CH_2CN)]$ has been prepared by treating hydrido(dicarbonyl)cyclopentadienyliron $[C_5H_5Fe(CO)_2H]$ with acrylonitrile[11], under the conditions we used there was no evidence of nucleophilic attack at the coordinated olefin.

DISCUSSION

Studies of the reactions of nucleophiles with diene complexes of Pt^{II} and Pd^{II} have shown that aliphatic amines or methoxide are very effective in attacking a coordinated diene[12]. With π-olefinic complexes of transition metals only a few examples are known of nucleophilic attack on the carbon of coordinated olefins in which the alkyl product is sufficiently stable to be isolable[13,14]. For example, Paiaro *et al.*[14], have described the preparation of stable, σ-bonded carbon–platinum derivatives by treating complexes of the type *cis*-$[PtCl_2(Ol)(PR_3)]$ with amines. The stability of these alkyl derivatives is related to the presence of π-bonding ligands coordinated to the central metal[15]. In the complexes we studied the π-ligands such as cyclopentadienyl and carbon monoxide play the same role and favour the formation of the stable alkyl derivative, $[C_5H_5Fe(CO)_2(C_2H_4OCH_3)]$. This complex does not decompose to give the vinyl ether $CH_2{=}CHOCH_3$, whereas in the case of the reaction of $[Pd(C_2H_4)Cl_3]^-$ with acetic acid vinyl acetate $CH_3COOCH{=}CH_2$ is formed[16] *via* the unstable σ-alkyl derivative $[Cl_3Pd(CH_2CH_2OCOCH_3)]^{2-}$.

The cationic complex $[C_5H_5Fe(CO)_2(C_2H_4)]^+$ has carbon atoms prone to nucleophilic attack, that of the carbonyl group and that of the π-coordinated olefin, and we think that the electrophilic character of the carbon of the olefin is greater than that of the carbonyl carbon. However $[C_5H_5Fe(CO)_2(C_2H_4)]^+$ reacts with azide ion to form the cyanato derivative $C_5H_5Fe(CO)(C_2H_4)(NCO)$, the formation of which is presumably favoured by the loss of N_2 and by its greater stability relative to the azido adduct $C_5H_5Fe(CO)_2(C_2H_4N_3)$.

ACKNOWLEDGEMENTS

Financial support of this work by the SNAM–Progetti (S. Donato Milanese, Milan) is gratefully acknowledged.

REFERENCES

1 L. Busetto and R. J. Angelici, *Inorg. Chim. Acta*, 2 (1968) 391.
2 L. Busetto, M. Graziani and U. Belluco, *Inorg. Chem.*, 9 (1970) in press.
3 M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, 1 (1963) 58.
4 E. O. Fisher and K. Fichtel, *Chem. Ber.*, 94 (1961) 1200.
5 H. J. Dauben Jr., L. R. Honner and K. M. Harmon, *J. Org. Chem.*, 25 (1960) 1442.
6 R. J. Angelici and L. Busetto, *J. Amer. Chem. Soc.*, 91 (1969) 3197.
7 R. K. Kochhar and R. Pettit, *J. Organometal. Chem.*, 6 (1966) 272.
8 T. S. Piper, F. A. Cotton and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1 (1955) 165.
9 P. W. Jolly and R. Pettit, *J. Amer. Chem. Soc.*, 88 (1966) 5044.
10 M. L. H. Green, M. Ishaq and R. N. Whiteley, *J. Chem. Soc. A*, (1967) 1508.
11 J. K. P. Ariyaratne and M. L. H. Green, *J. Chem. Soc.*, (1963) 2976.
12 J. Chatt, L. M. Vallarino and L. M. Venanzi, *J. Chem. Soc.*, (1957) 2496.
13 M. L. H. Green, A. G. Massey, J. T. Moelwyn-Hughes and P. L. I. Nagy, *J. Organometal. Chem.*, 8 (1967) 511, and references cited therein.
14 A. Panunzi, A. De Renzi, R. Palumbo and G. Paiaro, *J. Amer. Chem. Soc.*, 91 (1969) 3879.
15 J. Chatt and B. L. Shaw, *J. Chem. Soc.*, (1959) 705 and 4020.
16 I. I. Moissev, M. N. Vargeftik and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, 133 (1960) 377.