

Preliminary communication

THE REACTIONS OF CYCLOPENTADIENYL CARBONYLALKYNYLIRON COMPOUNDS WITH ELECTROPHILES

II. CYCLOADDITION REACTIONS WITH TETRACYANOETHYLENE AND HEXAFLUOROACETONE

ALAN DAVISON and JEFFREY P. SOLAR

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

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Summary

Cyclopentadienylcarbonylalkynylirons react with the neutral electrophiles tetracyanoethylene and hexafluoroacetone. These reactions lead to a (2 + 2) cycloaddition to the alkynyl ligand and involve a two step mechanism. Initial electrophilic attack forms a dipolar complex which by a cyclization reaction can form a σ -cyclobutenyl complex.

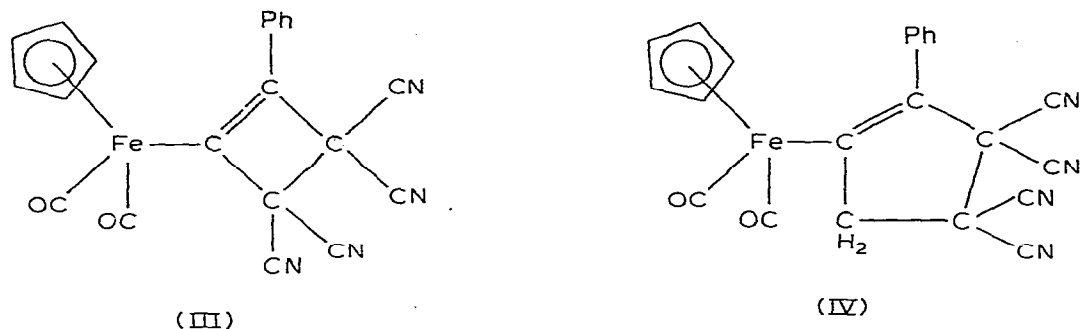
We recently have demonstrated that the reactions of the alkynes $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{C}\equiv\text{CPh}$ (I) and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{PPh}_3)(\text{CO})\text{C}\equiv\text{CPh}$ (II) with protic acids generate cationic vinylidene-metal complexes [1]. It was expected that alkyne complexes such as I and II would react similarly with other electrophiles. The neutral electrophiles tetracyanoethylene (TCNE) and hexafluoroacetone were of interest in that these reagents have been found to undergo (3 + 2) cycloaddition reactions with several organometallic complexes [2]. These reactions have been found to proceed via a dipolar intermediate resulting from electrophilic attack on the complexes [2]. The related (2 + 2) cycloaddition reactions of metal alkyne complexes have not been reported previously.

The phenyl complex I reacts rapidly with TCNE. In CH_2Cl_2 an 82% yield of yellow-brown, crystalline III can be isolated. The infrared spectrum of III has two bands assignable to $\nu(\text{CO})$, at 2050 and 2005 cm^{-1} , and no band assignable to $\nu(\text{C}\equiv\text{C})$ could be observed. The mass spectrum (parent ion at m/e 406) and elemental analysis* indicate that III is a 1/1 adduct of I and

*Analysis: Found: C, 62.34; H, 2.61; N, 13.80. $\text{C}_{21}\text{H}_{10}\text{N}_4\text{O}_2\text{Fe}$ (III) calcd.: C, 62.11; H, 2.46; N, 13.80%.

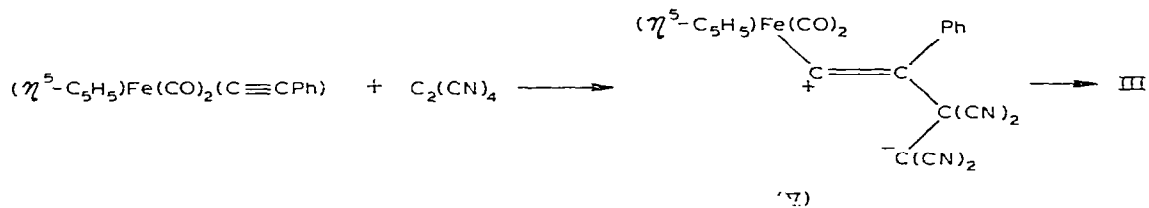
TCNE. The mass spectrum of III also indicates that TCNE has reacted with the alkyne ligand: sequential loss of the carbonyls and loss of the cyclopentadienyl ligand are observed and a fragment is found at m/e 285 from $\text{Fe}(\text{C}\equiv\text{CPh})\text{C}_2(\text{CN})_4$. The NMR spectrum of III contains a singlet at δ 5.13 ppm due to the cyclopentadienyl protons.

Thus III is assigned the structure shown below which results from cycloaddition of the TCNE to the acetylide. The infrared and NMR spectra of III are similar to those of the known cycloadduct IV, which has $\nu(\text{CO})$ at 2040 and 1980 cm^{-1} and a cyclopentadienyl resonance at δ 5.13 ppm [3].



The reaction of I and TCNE in diethyl ether, however, gives a different product. A green solution, assumed to be due to a charge-transfer complex, is formed on addition of ether to a 1/1 mixture of the solids. This color fades and, after a few minutes, a yellow solid (V) precipitates. The infrared spectrum (Nujol mull) of V contains two $\nu(\text{CO})$, at 2040 and 1990 cm^{-1} . A freshly prepared NMR sample of V shows a cyclopentadienyl resonance at δ 5.45 ppm. Over the period of ca. 1 h, however, this signal disappears, and the spectrum for III grows in. Attempted recrystallization or heating in the solid state converts V into III in high yield.

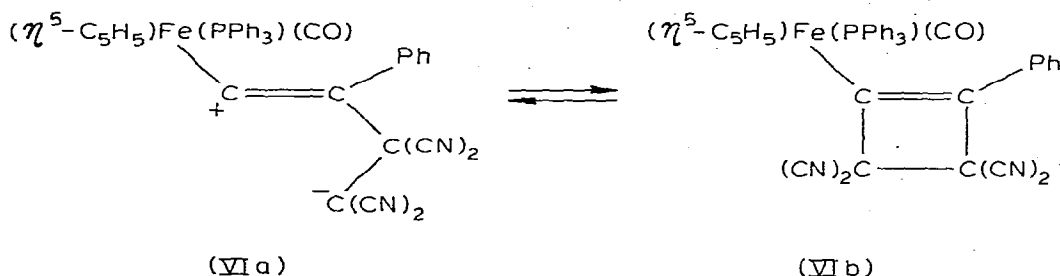
Thus V is suggested to be a dipolar, σ -bonded intermediate formed from electrophilic attack on the alkyne. We have previously demonstrated that electrophilic attack on acetylides I and II occurs in this manner to generate vinylidene-metal complexes [1].



This reaction is analogous to the reactions of vinyl ethers with TCNE which have been reviewed recently by Huisgen [4]. Huisgen has reported that the dipolar intermediates in the reactions of vinyl ethers are in equilibrium with the final products (cyclobutanes) and can be trapped by reaction with dipolarophiles [4]. In contrast, V does not react with the dipolarophiles acetone, acetonitrile, or ethanol. In all cases, only compound III or mixtures

of III and V could be isolated. Furthermore, no evidence for formation of V from an opening of III was observed by NMR spectroscopy.

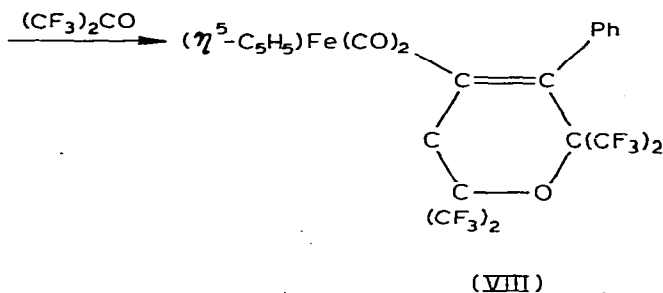
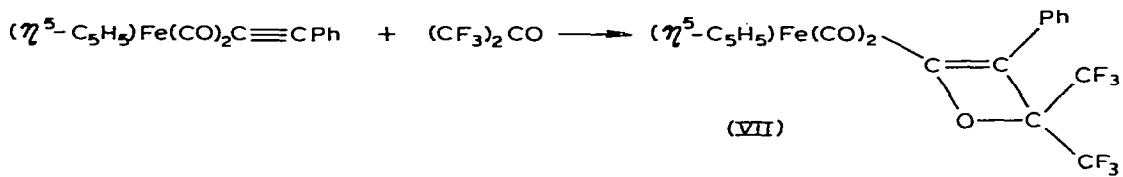
Acetylide II also reacts with TCNE. After chromatography on Florisil (CH_2Cl_2), a 64% yield of a red solid (VI) that analyzed as a 1/1 complex* was isolated. This product, however, was a mixture of two forms, VIa and VIb. Two bands assignable to $\nu(\text{CO})$, at 1950 and 1935 cm^{-1} , are observed in the mull infrared spectrum of VI and the relative intensities of these two bands are dependent on the method of crystallization. However, in solution, both bands are observed and all samples of VI are found to have an NMR spectrum containing two cyclopentadienyl resonances. Furthermore, while these signals vary in intensity initially, the intensities are always in a ca. 7/3 ratio after the system has stood for ca. 2 h. These results suggest that the two forms VIa and VIb are analogous to V and III and are in equilibrium in solution.



Like V, the dipolar complex VIa does not react with dipolarophiles. The NMR spectrum of VI is solvent dependent, indicating an interaction between the solvent and at least one of the two complexes, VIa and VIb. Thus, in CDCl_3 , two ^{31}P coupled doublets are found at δ 4.44 and 4.79 ppm which are due to the cyclopentadienyl protons; in acetone- d_6 , these are found at δ 4.70 and 4.75 ppm. The mull infrared spectrum of the acetone solvate of VI, however, has $\nu(\text{CO})$ identical to those observed for other solvates of VI and a stretch at 1710 cm^{-1} due to the acetone $\text{C}=\text{O}$ frequency. Thus, this interaction does not involve formation of a stable complex in the manner described by Huisgen [4].

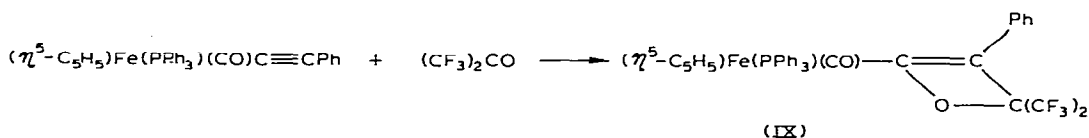
The reaction of alkyne I with hexafluoroacetone also yields a mixture of products. Chromatography on alumina gives a mixture of two compounds, VII and VIII, which cannot be further separated. Two cyclopentadienyl resonances in a ratio of 1.45/1 are found at δ 4.6 and 5.0 ppm in the ^1H NMR spectrum and three signals, at δ 68.3, 72.3, and 75.3 are found in the ^{19}F NMR spectrum of the mixture. Four bands at 2042, 2035, 1995, and 1990 are observed in the $\text{C}\equiv\text{O}$ stretching region of the infrared spectrum of the mixture. Also, the mass spectrum indicates the presence of two compounds, with parent peaks found at m/e 444 and 610, corresponding to the formulas $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{C}\equiv\text{CPh}\cdot(\text{CF}_3)_2\text{CO}$ and $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{C}\equiv\text{CPh}\cdot 2[(\text{CF}_3)_2\text{CO}]$, respectively. Structures for VII and VIII resulting from cycloaddition to the

*Complex VI forms solvates with several solvents including CH_2Cl_2 , CHCl_2 , CHCl_3 , acetone, and toluene. Analysis was as a CH_2Cl_2 solvate. Found: C, 67.07; H, 4.07; N, 8.39. $\text{C}_{38}\text{H}_{25}\text{N}_4\text{OPFe}\cdot 2/3\text{CH}_2\text{Cl}_2$ calcd.: C, 66.66; H, 3.79; N, 8.05; Cl, 6.79%.



acetylide ligand and ring expansion by addition of a second molecule of hexafluoroacetone are consistent with these data. Similar ring expansion reactions are known for Group VII and VIII complexes of hexafluoroacetone [5].

In contrast to these results, a 1/1 complex (IX) can be prepared cleanly by the reaction of alkyne II and one equivalent of hexafluoroacetone. The parent ion at m/e 678 is observed in the mass spectrum of IX and a satisfactory analysis was obtained*. A single $\nu(\text{CO})$ occurs at 1937 cm^{-1} and a phosphorus-split doublet is found at δ 4.63 ppm. The presence of two quartets, at ϕ 72.67 and 73.33 (J 7 Hz), in the ^{19}F NMR spectrum is consistent with the expected structure from cycloaddition to the alkyne. A similar splitting of the trifluoromethyl signals due to an asymmetric center at iron has been noted for $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{PPh}_3)(\text{CO})\text{C}=\text{C}(\text{Ph})\text{C}(\text{CF}_3)_2\text{OCH}_2$ [6].



No reaction was observed on treatment of an NMR sample of IX with an excess of hexafluoroacetone. Similarly, no change was observed in the relative intensities of the C_5H_5 resonances in the mixture of VII and VIII, in the presence of an excess of hexafluoroacetone. Thus it would seem that both of the 1/1 adducts are stable with respect to ring opening reactions once they have been formed.

*Found: C, 62.21; H, 3.71; F, 16.37. $\text{C}_{35}\text{H}_{25}\text{F}_6\text{O}_2\text{PFe}$ calcd.: C, 61.97; H, 3.71; F, 16.80%.

References

- 1 A. Davison and J.P. Solar, *J. Organometal. Chem.*, 155 (1978) C8.
- 2 M. Rosenblum, *Acc. Chem. Res.*, 1 (1974) 122; A. Wojcicki, *Ann. N.Y. Acad. Sci.*, 239 (1974) 100.
- 3 S. Raghu and M. Rosenblum, *J. Amer. Chem. Soc.*, 95 (1973) 3060.
- 4 R. Huisgen, *Acc. Chem. Res.*, 10 (1977) 117; R. Huisgen, *Acc. Chem. Res.*, 10 (1977) 199.
- 5 F.G.A. Stone, *Pure Appl. Chem.*, 30 (1972) 551.
- 6 D.W. Lichtenberg and A. Wojcicki, *Inorg. Chem.*, 14 (1975) 1295.