Journal of Organometallic Chemistry, 182 (1979) C39—C42

Preliminary communication

PHOTOCHEMICALLY INDUCED INSERTION OF ACETYLENES INTO μ-DITHIOBIS(TRICARBONYLIRON)

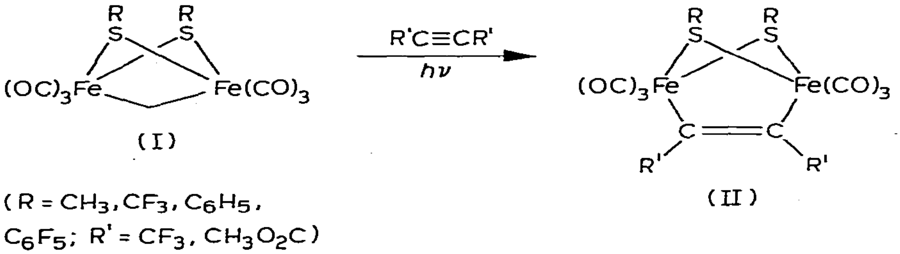
DIETMAR SEYFERTH and RICHARD S. HENDERSON
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (U.S.A.)

(Received October 4th, 1979)

Summary

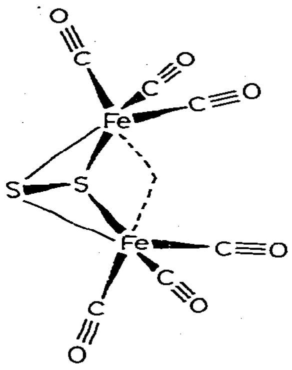
Hexafluoro-2-butyne and the dimethyl and diethyl esters of acetylenedicarboxylic acid insert into the sulfur—sulfur bond of μ-dithiobis(tricarbonyliron) upon UV irradiation to give dithiolene complexes of type IV.

The photochemically induced reactions of activated acetylenes such as hexafluoro-2-butyne and esters of acetylenedicarboxylic acid with di-μ-alkylthiobis-(tricarbonyliron) complexes (I) result in insertion of the acetylene into the Fe—Fe bond (eq. 1) [1—3]. The σ-bonded structure II was confirmed in the case of the complex where R = CF_3 and R′ = CF_3 by an X-ray diffraction study [1]. μ-Dithiobis(tricarbonyliron) (III) contains both an iron—iron bond of the type found in I and a sulfur—sulfur bond. Since the photochemically-induced insertion of acetylenes into the S—S bond of organic disulfides also is a known reaction [4], it was by no means clear how III would react with acetylenes.



(1)

We have found that μ-dithiobis(tricarbonyliron) also reacts with hexafluoro-2-butyne and with acetylenedicarboxylic acid esters upon irradiation with ul-

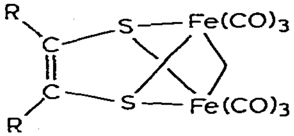


(III)

traviolet light to give 1/1 insertion products. Thus a solution of 2.91 mmol of $S_2Fe_2(CO)_6$ (III) and 12.2 mmol of $CH_3O_2CC{\equiv}CCO_2CH_3$ in 30 ml of dry THF in a quartz flask was stirred and irradiated at room temperature for 8 h under nitrogen in a Rayonet photoreactor (350 nm). After removal of solvent at reduced pressure the residue was passed through a silicic acid column (elution with dichloromethane). The resulting 1.082 g of dark red liquid was maintained under a dynamic high vacuum overnight, leaving 0.46 g (33%) of dark red solid which was recrystallized from pentane to give a ruby-red, air-stable solid, m.p. 81—83°C. Its infrared spectrum in pentane solution showed bands at 2087s, 2053vs, 2015vs, 1965w and 1979w cm^{-1} in the terminal CO region and ester carbonyl bands at 1740(sh) and 1730s cm^{-1}. Its combustion analysis (as well as those of all new compounds reported here) was satisfactory. In the 70 eV mass spectrum no parent ion was observed, but the consecutive loss of six CO ligands was seen. A similar reaction of $S_2Fe_2(CO)_6$ with $EtO_2CC{\equiv}CCO_2Et$ also gave a dark red insertion product, m.p. 73—75°C (from pentane) whose mass spectrum showed successive loss of six CO ligands, then of the two CO_2Et groups. The proton-decoupled ^{13}C FT NMR spectrum (in $DCCl_3$) showed singlets at $\delta(C)$ 206.39 ($C{\equiv}O$), 161.59 (C(O)O), 154.85 (C=C), 62.39 (CH_2) and 13.68 ppm (CH_3).

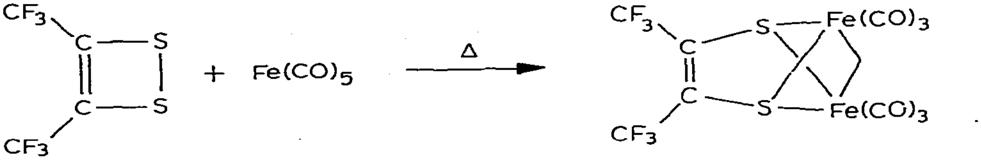
Hexafluoro-2-butyne reacted with $S_2Fe_2(CO)_6$ in a quartz pressure reactor (Rayonet photoreactor, 350 nm) to give a purple-black product, m.p. 79—81°C (from pentane) in 47% yield. Analysis showed it to be the 1/1 insertion product. Its proton-decoupled ^{13}C FT NMR spectrum (in $DCCl_3$) showed resonances at $\delta(C)$ 205.83 ($C{\equiv}O$), 125.97 (C=C) and 113.68 ppm (CF_3). Other acetylenes such as $PhC{\equiv}CPh$, $PhC{\equiv}CCO_2Me$, and $HC{\equiv}CC(O)CH_3$ did not react with $S_2Fe_2(CO)_6$ under these conditions.

The presently available evidence indicates that these 1/1 acetylene/S_2Fe_2-$(CO)_6$ products are formed by insertion of the acetylene into the sulfur—sulfur, not the iron—iron, bond, i.e., that they are dithiolene complexes, IV. Com-



(IV)

plexes of type IV have been prepared previously by other methods [5]. In particular, the complex with R = CF_3 had been prepared by King using the reaction shown in eq. 2 [6]. The product from the $CF_3C{\equiv}CCF_3/S_2Fe_2(CO)_6$ reaction and King's compound (an authentic sample of which was prepared) were found to be identical in all respects: melting point and mixture melting point, behavior on thin layer chromatography, infrared, ^{13}C and mass spectra.



(2)

The ^{13}C NMR spectra of the acetylene/$S_2Fe_2(CO)_6$ insertion products also provided useful structural evidence. At room temperature all showed a single C≡O carbon atom signal, indicating a fluxional system. μ-Dithiobis(tricarbonyliron), which has a bent iron—iron bond [7], also has only a single C≡O carbon atom signal in its ^{13}C NMR spectrum (δ(C) 208.3 ppm in $DCCl_3$) at room temperature. The structurally similar [8] (μ-EtS)$_2$$Fe_2(CO)_6$ has been reported* to show a single C≡O carbon atom signal at room temperature at 209.2 ppm (in 2-methyltetrahydrofuran); as the solution was cooled, the signal broadened and at −90°C three signals of equal intensity were observed at δ(C) 208.0. 209.1 and 210.8 ppm. On the other hand, insertion of an acetylene into the Fe—Fe bond of (μ-RS)$_2$$Fe_2(CO)_6$ complexes gives products whose ^{13}C NMR spectra show more than one C≡O carbon atom signal at room temperature; $(\mu\text{-}CH_3S)_2Fe_2(CO)_6/EtO_2CC{\equiv}CCO_2Et$ product: 200.7, 204.4 and 209.9 ppm; $(\mu\text{-}CH_3S)_2Fe_2(CO)_6/CF_3C{\equiv}CCF_3$ product: 202.85, 204.15, 205.25 ppm. On the basis of these admittedly limited results it would seem that CO scrambling is a facile process at room temperature in bridged systems in which the $Fe_2(CO)_6$ unit with a bent iron—iron bond is present, but not in a complex in which a σ-bonded connecting group, e.g., the vinylene unit, links the iron atoms, i.e., when there is no Fe—Fe bond. Further studies hopefully will provide more evidence for or against this tentative generalization.

We had found in earlier work that it is the sulfur—sulfur bond of μ-dithiobis(tricarbonyliron), not the iron—iron bond, which is reduced by metallic sodium and by potassium hydride and which is cleaved by organolithium reagents [10]. The present study has shown that the sulfur—sulfur bond also is the site of reactivity in reactions with electrophilic acetylenes. We are continuing our investigations of the chemistry of $S_2Fe_2(CO)_6$ with the aim of determining S—S vs. Fe—Fe reactivity with respect to other types of reagents.

Acknowledgment

The authors are grateful to the National Science Foundation for support of this work.

---

*Similar observations, i.e., facile CO scrambling at room temperature, also were made in the case of $(\mu\text{-}Me_2P)_2Fe_2(CO)_6$ and $(\mu\text{-}Me_2As)_2Fe_2(CO)_6$ [9].

References

1 J.L. Davidson, W. Harrison, D.W.A. Sharp and G.A. Sim, J. Organometal. Chem., 46 (1972) C47.
2 J.L. Davidson and D.W.A. Sharp, J. Chem. Soc., Dalton Trans., (1975) 2283.
3 R. Mathieu and R. Poilblanc, J. Organometal. Chem., 142 (1977) 351.
4 E.I. Heiba and R.M. Dessau, J. Org. Chem., 32 (1967) 3837.
5 Gmelin Handbook of Inorganic Chemistry, 8th Edition, Iron—Organoiron Compounds, Part C1, Springer-Verlag, Berlin, 1979, pp. 120—122.
6 R.B. King, J. Amer. Chem. Soc., 85 (1963) 1584.
7 C.H. Wei and L.F. Dahl, Inorg. Chem., 4 (1965) 1.
8 L.F. Dahl and C.H. Wei, Inorg. Chem., 2 (1963) 328.
9 R.D. Adams, F.A. Cotton, W.R. Cullen, D.L. Hunter and L. Mihichuk, Inorg. Chem., 14 (1975) 1395.
10 D. Seyferth and R.S. Henderson, J. Amer. Chem. Soc., 101 (1979) 508.