Journal of Organometallic Chemistry, 393 (1990) C49–C52
Elsevier Sequoia S.A., Lausanne
JOM 21188PC

Preliminary communication

Insertion of iron carbonyl into a C–S bond of tetrathiofulvalene

Helgard G. Raubenheimer *, **Lorna Linford**
Department of Chemistry, Rand Afrikaans University, P.O. Box 524, Johannesburg 2000 (Republic of South Africa)

and H. Marita Roos
Department of Chemistry, University of Pretoria, Pretoria (Republic of South Africa)

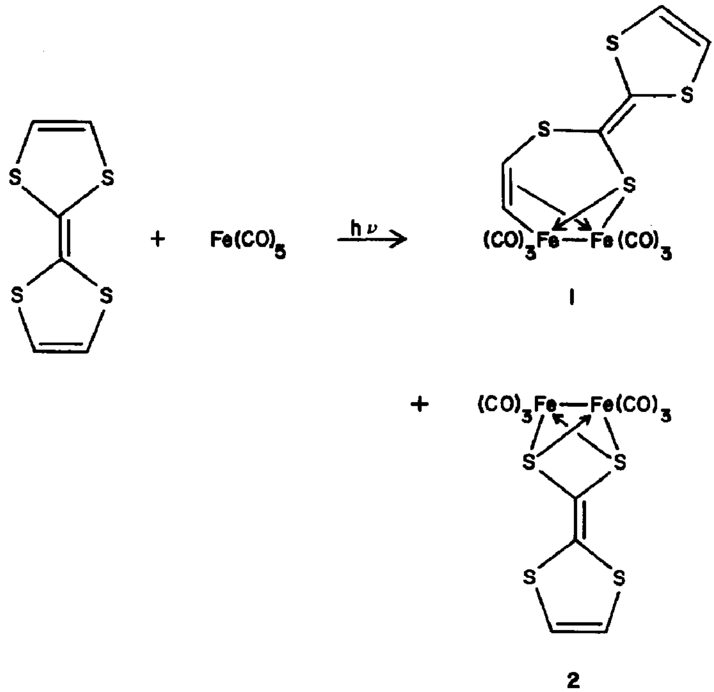
(Received May 29th, 1990)

Abstract

Irradiation of a mixture of tetrathiofulvalene (TTF) and iron pentacarbonyl in THF gives a dinuclear hexacarbonyl iron chelate, $Fe_2(CO)_6[\mu\text{-}SC(=\overline{CSCH{=}CHS})\text{-}SCH{=}CH]$ (**1**), by ring-opening of TTF adjacent to an internal double bond. The donated ligand electrons originate from an sp^2 carbon atom, a sulphur atom, and a carbon–carbon double bond.

An important class of reactions between organosulphur compounds and low oxidation state transition metal complexes involves C–S bond cleavage and formal oxidative addition to the metallic centre(s). Cyclic trithiocarbonates $\overline{(CH_2)_nSC(S)S}$ ($n = 2, 3$) react with $[Pt(PPh_3)_4]$ to give the metallacycle $[\overline{PtSC(S)S(CH_2)_n}]$ [1], and 1,3-dithiane or 1,3,5-trithiane reacts with $[Fe(CO)_5]$ under UV irradiation to form the dinuclear compound $[Fe_2(CO)_6(CH_2R^1)SR^2]$ [$R^1R^2 = S(CH_2)_3$ or SCH_2SCH_2] [2]. Stone and coworkers [3] discovered much earlier that under more drastic conditions the unsaturated heterocyclic compound, thiophene, affords a ferrole complex, as well as a thiaferrole dinuclear complex as a minor product. In the latter compound the ligand donates 6 e^- to the $Fe_2(CO)_6$ unit, of which three were suggested to come from the bonded vinyl group and three from a sulphur atom. This proposal was later substantiated by a crystal structure determination of an analogous compound by Rauchfuss and coworkers [4]. The present study forms part of our continuing interest in the formation and reactions of organosulphur organometallic compounds [5] and was undertaken to establish (i) whether ring-opening would occur during irradiation of $[Fe(CO)_5]$ and heterocyclic sulphur compounds other than those in the cited examples; (ii) the preferred site of such

0022-328X/90/$03.50



C–S bond cleavage in organosulphur ring-systems containing both internal and external double bonds.

Irradiation of TTF with an excess of $[Fe(CO)_5]$ in tetrahydrofuran (THF) afforded, after column chromatography, a green product, **1**, in ca 15% yield [6*]. The compound was fully characterised by all the standard physical measurements [7*] as well as by single crystal X-ray diffraction **. When equimolar amounts of $[Fe(CO)_5]$ and TTF were used a lower yield of **1** was obtained, but another low-yield product (< 0.5%) was formed and gave a pink-purple band ahead of **1** on the silica column [6*]. This product, **2**, belongs to a well-known class of iron

---

* Reference number with asterisk indicates a note in the list of references.

** *Crystal data*: $C_{12}H_4O_6S_4Fe_2$; $M_r = 484.108$. Crystal size 0.15×0.20×0.57 mm, space group *Cc*; monoclinic, *a* 11.866(3), *b* 18.639(4), *c* 7.652(1) Å; β 97.68(1)°, $Z = 4$, *V* 1677.2 Å^3, D_c 1.917 g cm^{-3}.

Data collection, processing and refinement: Enraf-Nonius CAD4 diffractometer, Mo-K_α radiation (μ 21.38 cm^{-1}). Scanning range for $3 \leq \theta \leq 32°$. Number of reflections measured 6199 and 2474 observed [$4\sigma(I)$-criterion]. Data corrected for Lorentz and polarization effects and for absorption. Decay during data collection 2.0% (uncorrected). The structure was solved by Patterson and subsequent Fourier methods and refined anisotropically with a full-matrix method [$1/\sigma^2(F)$-weights] using SHELX 76 [8]. All hydrogen atoms were placed in calculated positions and refined with a common isotropic temperature factor that converged to *U* 0.044(2) Å. The final electron density difference map revealed a few peaks with $\rho > 1$ e$^-$ Å^3. All these peaks were approximately 1 Å from either an iron or a sulphur atom. Final *R* and R_w 11.32, 8.59%. The absolute structure was not determined. A table of atomic coordinates and a full list of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre. Further details of the crystal structure determination as well as lists of thermal factors, fractional coordinates and structure factors are available upon request from the authors (HMR).

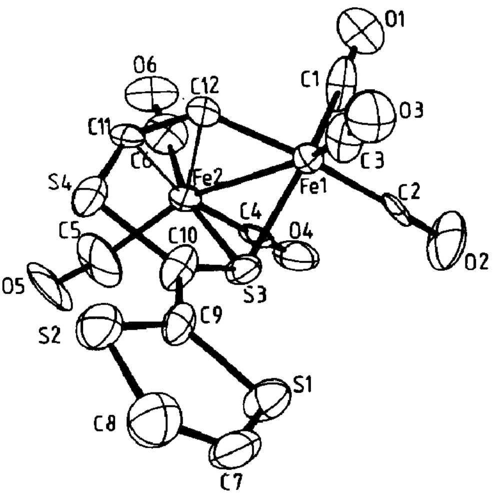
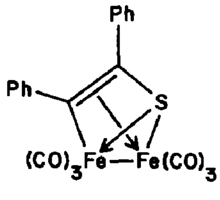


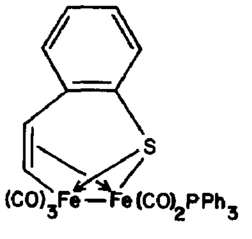
Fig. 1. Perspective drawing of a molecule of compound 1 with atom labels. Selected bond distances (Å): Fe(1)–Fe(2) 2.537(3), Fe(1)–S(3) 2.246(5), Fe(1)–C(12) 1.90(2), Fe(2)–S(3) 2.300(5), Fe(2)–C(11) 2.214(14), Fe(2)–C(12) 2.010(14), S(3)–C(10) 1.68(2), S(4)–C(10) 1.81(2), S(4)–C(11) 1.72(2), C(9)–C(10) 1.37(2), C(11)–C(12) 1.37(2). Selected angles (°): Fe(2)–Fe(1)–S(3) 57.1(1), Fe(1)–Fe(2)–S(3) 55.1(1), Fe(1)–Fe(2)–C(11) 77.3(4), Fe(1)–Fe(2)–C'12) 47.5(4), C(11)–Fe(2)–C(12) 37.3(6), S(1)–C(9)–S(2) 114.3(10), S(3)–C(10)–S(4) 118.4(11).

carbonyls, designated as $[CO)_3Fe(\mu\text{-}S{-}A{-}S)Fe(CO)_3]$ (A = bridging atom or group) in Gmelin's *Handbuch der Anorganischen Chemie* [9]. It is interesting [7*] that all the sp^2 carbons in **2** give rise to only one sharp signal at 118.1 ppm, in the ^{13}C-NMR spectrum. We previously found that 1,3,5-trithiane, but not 1,3-dithiane, also undergoes scission of two CH_2–S bonds, to split out SCH_2S, which then coordinates to the $Fe_2(CO)_6$ unit [2].

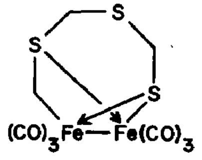
The X-ray structure determination proves that the major neutral, isolable product, **1**, is formed by ring-opening adjacent to the internal double bond in TTF and concomitant oxidative addition to the dinuclear iron system. The $18e^-$ rule is satisfied by additional sulphur and π-bond dative bonding. The structure is shown in Fig. 1, and relevant bond lengths and angles are given in the caption. The various bond distances and bonding patterns in the coordination sphere of the metal atoms of **1** correspond in broad outline with those obtained for compound **3** [10] and essentially agree with those in compound **4**. The latter compound was prepared in the same way as the Stone compound referred to above, and subsequently treated with triphenylphosphine [4]. There is a significant difference in bond lengths in **1** between Fe(2) and C(12) and C(11), respectively [2.010(14) vs. 2.214(14) Å], whereas the corresponding difference in **3** is only 0.072 Å. A feature of compound **1**, containing two sulphurs bonded to an sp^2-hybridized carbon [C(10)] in the chelate ring, is the significantly shorter carbon–sulphur distance between C(10) and the metal-coordinated sulphur atom, S(3) [1.68(2) Å] than between C(10) and S(4) [1.72(2) Å]. The two C(9)–S distances are equal and also identical to the 1.72(2) Å separation between C(11) and S(4). The S(3)–C(10)–S(4) angle in the metallacyclic ring has opened slightly [118.4(11)°] compared to the S(1)–C(9)–S(2) angle in the heterocyclic ring [114.3(10)°].



3



4



5

Apart from the fact that in compound **5** [2] one pair of ligand electrons originates from a sulphur atom α to a CH_2 group rather than from a π-bond next to a carbon donor as in **1**, the coordination geometry of these, respectively, eight- and seven-membered ring chelates is also essentially the same. Significant second-order differences must, however, exist, as indicated by the different number and intensities of CO vibrations exhibited by **5** (2069s, 2026vs, 2002vs, 1981s, 1966w).

References and notes

1 E.D. Dobrzynski and R.J. Angelici, J. Organomet. Chem., 76 (1974) C53.

2 H.G. Raubenheimer, L. Linford and A. van A Lombard, Organometallics, 8 (1989) 2062.

3 H.D. Kaez, R.B. King, T.A. Manuel, R.D. Nichols and F.G.A. Stone, J. Am. Chem. Soc., 81 (1960) 4749.

4 A.E. Ogilvy, M. Draganjac, T.B. Rauchfuss and S.R. Wilson, Organometallics, 7 (1988) 1171.

5 L. Linford and H.G. Raubenheimer, Adv. Organomet. Chem., (accepted; review with 300 references).

6 A solution of TTF (0.20 g, 0.98 mmol) and an excess of $[Fe(CO)_5]$ (1 ml, 8 mmol) in THF was irradiated with UV light in a glass reactor for 7 h. The dark green major product was purified by column chromatography on SiO_2 with CH_2Cl_2/hexane (1:4–1:1) as eluant. The product was dissolved in CH_2Cl_2, the solution filtered through SiO_2, and the solid precipitated as needles by addition of hexane and cooling to −40 °C. Yield 70 mg (14%). M.P. ~167 °C (dec.). Found: C, 29.81; H, 0.91. Mol. mass [M^+] 484. Calcd. for $C_{12}H_4O_6S_4Fe_2$ (484.108): C, 29.77; H, 0,83%.
Purple prisms of compound **2** were isolated (see text). M.p. ~144 °C (dec.). Mol. mass (m/z, 70 eV) 458 and consecutive loss of 6 carbonyl ligands. Calcd. for $C_{10}H_2O_6S_4Fe_2$, 458.070.

7 Characterization data:
1: ^{1}H-NMR ($CDCl_3$): δ 5.78 [d, J 9Hz, C(12)-H], 6.32 and 6.40 [2×d, J_{AB} 6.4 Hz, C(7)-H and C(8)-H], 8.29 [d, J 9 Hz, C(11)-H] ppm. ^{13}C-NMR ($CDCl_3$): δ 93.8 [C(12)], 119.8 and 120.4 [C(7) and C(8)], 151.4 [C(11)], 207.7 (CO) ppm. IR (hexane) ν(CO): 2077m, 2047s, 2013s, 2007s cm^{-1}.
2: ^{1}H-NMR ($CDCl_3$): δ 6.17 (s) ppm. ^{13}C-NMR ($CDCl_3$): δ 118.1 (ligand), 207.4 (CO) ppm. IR (hexane) ν(CO): 2080m, 2046s, 2008s cm^{-1}.
Compounds **1** and **2** both show high intensity mass peaks at m/z 188, 144, 112 and 56 which can be ascribed to the consecutive loss of carbon, sulphur (twice), and iron from the cation, $Fe_2S_2C^+$.

8 G.M. Sheldrick, in: H. Schenk, R. Ollthof-Hazekamp, H. van Koningsveld and G.C. Bassi (Eds.), Computing in Crystallography, Delft University Press, 1978.

9 Gmelin Handbuch der Anorganischen Chemie (U. Krüerke, Ed.) Teil C1, Springer-Verlag, Berlin, 1979, p. 115.

10 G.N. Schrauzer, H.N. Rabinowitz, J.A.K. Frank and I.C. Paul, J. Am. Chem. Soc., 92 (1970) 212.