

## REDUCTION OF TRIMETHYLSILYL- $\mu_3$ -S,S'-ETHYLENEDITHIOLATOHEXACARBONYLDIIRON

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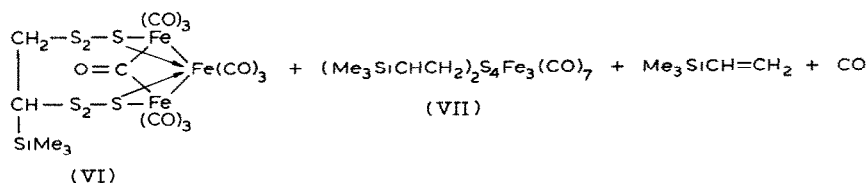
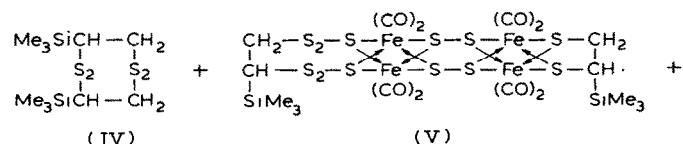
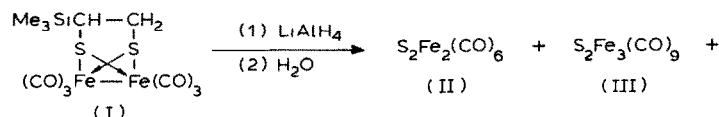
### Summary

Reduction of the dithiolatodiiron hexacarbonyl complex of trimethylvinylsilane (I) with  $\text{LiAlH}_4$  leads to the formation of thioiron carbonyl clusters, and is not accompanied with the generation of the corresponding dithiol.

### Results and discussion

It is known that the reduction of bis(alkylthioiron) tricarbonyls leads to quantitative formation of the corresponding thiols [1].

We found that the interaction of an ether solution of I with  $\text{LiAlH}_4$  unexpectedly gives complex thioiron carbonyl clusters of trimethylvinylsilane:

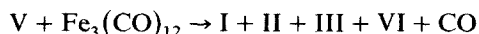


\* Deceased (June 1983).

The yields relative to initial sulfur are: II, 3%; IV, 6%; III, 3%; V, 80%; VI, 3%; and VII, 3%.

The reaction proceeds above  $-40^{\circ}\text{C}$  and does not depend on the order of reagent addition. The main reaction product is the cluster V. We failed to perform an X-ray study of compound V, because of the amorphousness of this complex. Perhaps tetrasulfide IV was discovered in a small amount owing to intermolecular oxidation of dithiol at the time of isolation. The reduction of CO to lower hydrocarbons [2] was not observed.

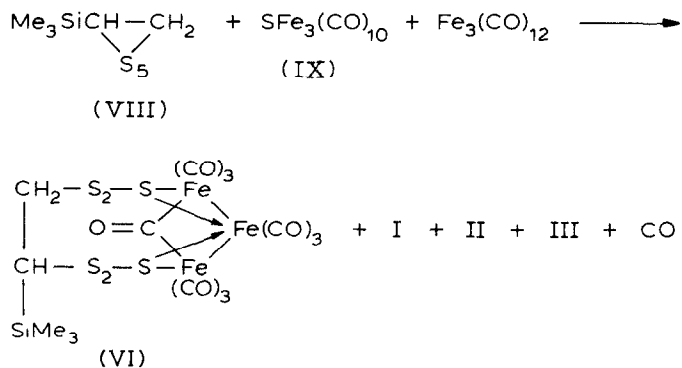
The reaction of compound V with  $\text{Fe}_3(\text{CO})_{12}$  showed that the clusters II, III and VI are formed under the influence, on V, of  $\text{Fe}(\text{CO})_3$  or  $\text{Fe}(\text{CO})_4$  species, which are generated in the decomposition of the reaction mixture with water apparently from the intermediate hydride complexes:



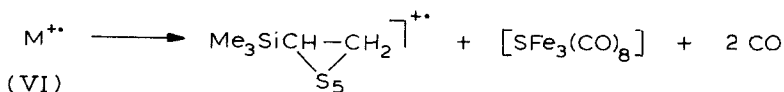
The formation of the tetrasulfide IV possibly follows a similar mechanism.

We have established that the unusual C-S bond reduction in compound I is not accompanied with the formation of a  $(\text{HS})_2\text{Fe}_2(\text{CO})_6$  cluster, which was isolated in the reduction of  $\text{S}_2\text{Fe}_2(\text{CO})_6$  [3].

The structure of complexes V and VI, obtained for the first time, were established on the basis of mass, IR and  $^1\text{H}$  NMR spectra. We failed to identify cluster VII similarly by means of spectra. Its gross formula was determined on the basis of mass spectral data ( $m/e$ ): 692 ( $M^+$ ), 496 ( $M^+ - 7\text{CO}$ ), 296 ( $\text{Fe}_3\text{S}_4^+$ ). The structure of cluster VI was also confirmed by its synthesis from the cyclic pentasulfide VIII and thiotriiron decacarbonyl (IX) under mild conditions ( $50^{\circ}\text{C}$ , THF):



The yield of VI relative to initial sulfur was 5%. This reaction is opposite to the mass spectral dissociation of VI:



## Experimental

IR spectra were measured on a UR-20 spectrophotometer. Mass spectra were taken on an MAT-311A instrument with a direct inlet to the ion source, at  $100^{\circ}\text{C}$

and at an ionization energy of 70 eV.  $^1\text{H}$  NMR spectra were recorded on a Varian T-60 (60 MHz) spectrometer with  $\text{C}_6\text{H}_6$  as the solvent and internal standard. The molecular mass of V was measured by ebullioscopy from THF. The syntheses of compounds I, VIII [4] and IX [5] have been reported previously.

### Reduction of I

The reaction of I with  $\text{LiAlH}_4$  was carried out under Ar. A suspension of 3 g (0.08 mol) of  $\text{LiAlH}_4$  in 75 ml of absolute ether was added dropwise to 4.44 g (0.01 mol) of I in 100 ml of ether under cooling. After 2 h of mixing, the reaction mixture was treated with water. The ether layer was separated and dried over  $\text{MgSO}_4$ . After removal of ether, the residue was washed with absolute pentane, an insoluble (V) being isolated in the hydrocarbon as a dark-brown powder. The extract was concentrated and chromatographed on a silica gel column (eluant pentane), collecting in sequence: II (m.p.  $45^\circ\text{C}$ ), III (m.p.  $114\text{--}115^\circ\text{C}$ ), IV (m.p.  $137^\circ\text{C}$ , cf. [6]), VI and VII. V: Decomp. p.  $110^\circ\text{C}$ . Molecular weight: found, 1020; calcd., 1032.718. IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ , KBr): 2960, 2900, 2860 (C-H), 2063, 2042, 2000 ( $\text{C}\equiv\text{O}$ ), 844 (Si-C).  $^1\text{H}$  NMR spectrum ( $\delta$ , ppm): 0.10 s (6  $\text{CH}_3$ ); 2.3–3.3 m (2CHCH<sub>2</sub>). UV spectrum (THF) has the form of a wing, stretching up to 300 nm. Found: C, 21.17; H, 2.42; S, 36.07; Fe, 21.91.  $\text{C}_{18}\text{H}_{24}\text{Si}_2\text{S}_{12}\text{Fe}_4\text{O}_8$  calcd.: C, 20.93; H, 2.34; S, 37.25; Fe, 21.62%. VI: Crimson oil. Mass spectrum ( $m/e$ ): 740 ( $M^+$ ), 460 ( $M^+ - 10\text{CO}$ ), 360 ( $\text{Fe}_3\text{S}_6^+$ ), 424 ( $[\text{SFe}_3(\text{CO})_8]^+$ ), 200 ( $\text{SFe}_3^+$ ), 260 ( $[\text{Me}_3\text{SiC}_2\text{H}_3\text{S}_5]^+$ ), 228 ( $[\text{Me}_3\text{SiC}_2\text{H}_3\text{S}_4]^+$ ), 196 ( $[\text{Me}_3\text{SiC}_2\text{H}_3\text{S}_3]^+$ ), 164 ( $[\text{Me}_3\text{SiC}_2\text{H}_3\text{S}_2]^+$ ), 132 ( $[\text{Me}_3\text{SiC}_2\text{H}_3\text{S}]^+$ ), 73 ( $\text{Me}_3\text{Si}^+$ ). IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ,  $\text{C}_6\text{H}_{14}$ ): 2078, 2042, 2023, 1982, 1908 ( $\text{C}\equiv\text{O}$ ), 1763 ( $\text{C}=\text{O}$ ), 850 (Si-C). Found: C, 25.00; H, 1.79; Fe, 22.12; S, 26.29.  $\text{C}_{15}\text{H}_{12}\text{Si}_6\text{Fe}_3\text{O}_{10}$  calcd.: C, 24.34; H, 1.63; Fe, 22.63; S, 25.98%. VII: Crimson oil. IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ,  $\text{C}_6\text{H}_{14}$ ): 2050, 2012, 2008, 1999, 1946 ( $\text{C}\equiv\text{O}$ ), 1746 ( $\text{C}=\text{O}$ ), 850 (Si-C).

### References

- 1 N.S. Nametkin, V.D. Tyurin and M.A. Kukina, *J. Organomet. Chem.*, 149(1978) 355.
- 2 M.M. Harris, J.D. Atwood, M.E. Wright and G.O. Nelson, *Inorg. Chem.*, 21 (1982) 2117.
- 3 D. Seyferth and R.S. Henderson, *J. Organomet. Chem.*, 218 (1981) C34.
- 4 E.A. Chernyshev, O.V. Kuz'min, A.V. Lebedev, A.I. Gusev, M.G. Los', N.V. Alekseev, N.S. Nametkin, V.D. Tyurin, A.M. Krapivin, N.A. Kubasova and V.G. Zaikin, *J. Organomet. Chem.*, 252 (1983) 143.
- 5 N.S. Nametkin, V.D. Tyurin, G.G. Aleksandrov, I.V. Petrosyan, B.I. Kolobkov, A.M. Krapivin and Yu.T. Struchkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1981) 2572.
- 6 E.A. Chernyshev, O.V. Kuz'min, A.V. Lebedev, A.I. Gusev, N.I. Kirillova, N.S. Nametkin, V.D. Tyurin, A.M. Krapivin and N.A. Kubasova, *J. Organomet. Chem.*, 252 (1983) 133.