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REDUCTION OF TRIMETHYLSILYL-μ_3-*S*,*S*'-ETHYLENEDITHIOLATOHEXACARBONYLDIIRON

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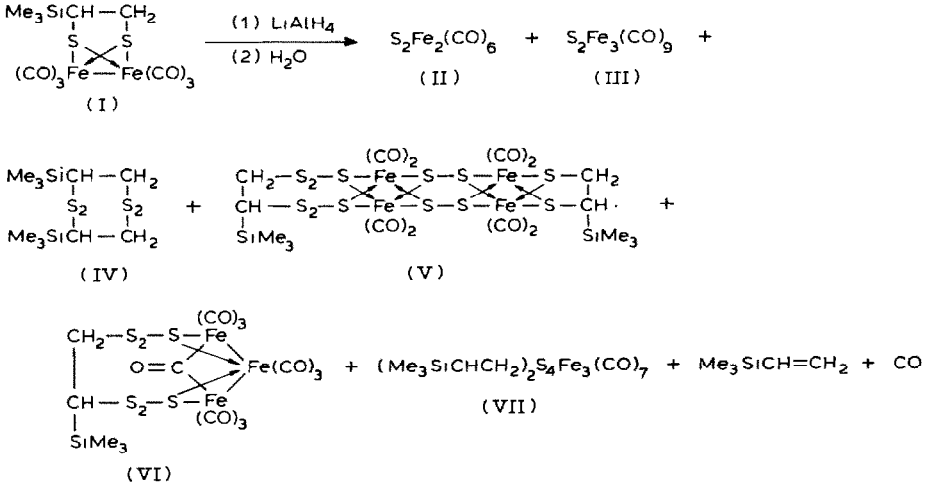
Summary

Reduction of the dithiolatodiiron hexacarbonyl complex of trimethylvinylsilane (I) with $LiAlH_4$ 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 $LiAlH_4$ unexpectedly gives complex thioiron carbonyl clusters of trimethylvinylsilane:



* Deceased (June 1983).

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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 °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.

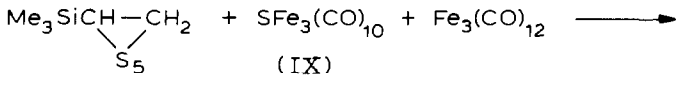
The reaction of compound V with $Fe_3(CO)_{12}$ showed that the clusters II, III and VI are formed under the influence, on V, of $Fe(CO)_3$ or $Fe(CO)_4$ species, which are generated in the decomposition of the reaction mixture with water apparently from the intermediate hydride complexes:

$$V + Fe_3(CO)_{12} \rightarrow I + II + III + VI + CO$$

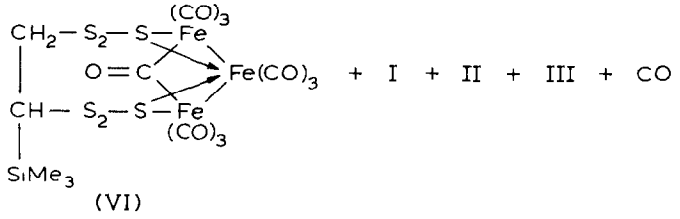
The formation of the tetrasulfide IV possibly follows a similar mechanism.

We have established that the unusual C–S bond reduction in compound I is not accompanied with the formation of a $(HS)_2Fe_2(CO)_6$ cluster, which was isolated in the reduction of $S_2Fe_2(CO)_6$ [3].

The structure of complexes V and VI, obtained for the first time, were established on the basis of mass, IR and ^1H 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 ($M^+ - 7CO$), 296 ($Fe_3S_4^+$). The structure of cluster VI was also confirmed by its synthesis from the cyclic pentasulfide VIII and thiotriiron decacarbonyl (IX) under mild conditions (50 °C, THF):

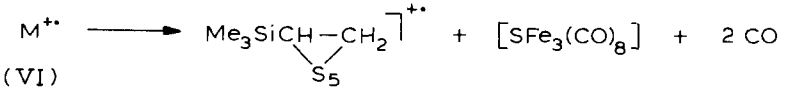


(VIII) (IX)



(VI)

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



(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 °C

and at an ionization energy of 70 eV. ^1H NMR spectra were recorded on a Varian T-60 (60 MHz) spectrometer with C_6H_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 $LiAlH_4$ was carried out under Ar. A suspension of 3 g (0.08 mol) of $LiAlH_4$ 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 $MgSO_4$. 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 °C), III (m.p. 114–115 °C), IV (m.p. 137 °C, cf. [6]), VI and VII. V: Decomp. p. 110 °C. Molecular weight: found, 1020; calcd., 1032.718. IR spectrum (ν, cm^{-1}, KBr): 2960, 2900, 2860 (C-H), 2063, 2042, 2000 (C≡O), 844 (Si–C). ^1H NMR spectrum (δ, ppm): 0.10 s (6 CH_3); 2.3–3.3 m ($2CHCH_2$). 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. $C_{18}H_{24}Si_2S_{12}Fe_4O_8$ calcd.: C, 20.93; H, 2.34; S, 37.25; Fe, 21.62%. VI: Crimson oil. Mass spectrum (m/e): 740 (M^+), 460 ($M^+ - 10$ CO), 360 ($Fe_3S_6^+$), 424 ($[SFe_3(CO)_8]^+$), 200 (SFe_3^+), 260 ($[Me_3SiC_2H_3S_5]^+$), 228 ($[Me_3SiC_2H_3S_4]^+$), 196 ($[Me_3SiC_2H_3S_3]^+$), 164 ($[Me_3SiC_2H_3S_2]^+$), 132 ($[Me_3SiC_2H_3S]^+$), 73 (Me_3Si^+). IR spectrum (ν, cm^{-1}, C_6H_{14}): 2078, 2042, 2023, 1982, 1908 (C≡O), 1763 (C=O), 850 (Si–C). Found: C, 25.00; H, 1.79; Fe, 22.12; S, 26.29. $C_{15}H_{12}SiS_6Fe_3O_{10}$ calcd.: C, 24.34; H, 1.63; Fe, 22.63; S, 25.98%. VII: Crimson oil. IR spectrum (ν, cm^{-1}, C_6H_{14}): 2050, 2012, 2008, 1999, 1946 (C≡O), 1746 (C=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.