

CHEMISTRY OF μ -DITHIOBIS(TRICARBONYLIRON), AN INORGANIC MIMIC OF ORGANIC DISULFIDES

II *. NUCLEOPHILIC S–S BOND CLEAVAGE BY ORGANOLITHIUM AND ORGANOMAGNESIUM REAGENTS **

DIETMAR SEYFERTH*, RICHARD S. HENDERSON, LI-CHENG SONG,
 and GARY B. WOMACK

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

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Summary

Organolithium and Grignard reagents cleave the S–S bond of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ at -78°C to give intermediates of type $(\mu\text{-RS})(\mu\text{-MS})\text{Fe}_2(\text{CO})_6$ ($\text{M} = \text{Li}$ or MgX). These may be alkylated with organic halides to produce complexes of type $(\mu\text{-RS})(\mu\text{-R}'\text{S})\text{Fe}_2(\text{CO})_6$ and protonated to yield $(\mu\text{-RS})(\mu\text{-HS})\text{Fe}_2(\text{CO})_6$.

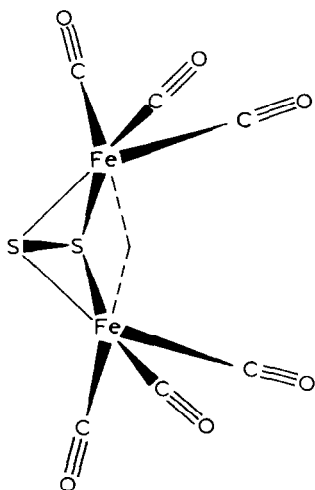
Introduction

μ -Dithiobis(tricarbonyliron) (**1**) [2] contains an S_2 ligand which has a S–S σ bond and which bridges two $\text{Fe}(\text{CO})_3$ units which are bonded by a “bent” Fe–Fe bond [3]. In Part I of this series we showed that the S–S bond of **1** could be reduced to the sulfur-centered dianion, **2**, by the action of LiBEt_3H and other complex metal hydrides [1]. This reaction most likely proceeds in two steps: (1) nucleophilic cleavage of the S–S bond (eq.1) and (2) deprotonation of the SH function generated in the first step (eq.2). Such reactions are characteristic of the S–S bond in organic disulfides [4]. Furthermore, **1** could be reduced to dianion **2** by elemental sodium; such reduction of the S–S bond is also readily effected with organic disulfides [5].

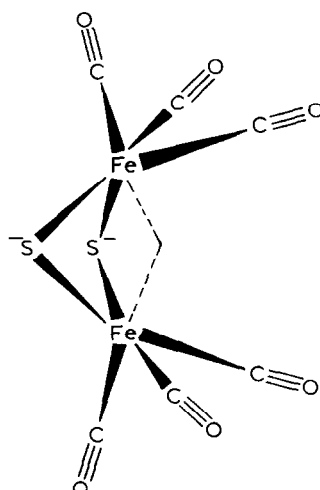
These similarities of **1** with organic disulfides led us to search for other reactions of **1** for which there are known precedents in organic disulfide reactivity. Nucleophilic cleavage of the S–S bond of organic disulfides is a very general and important process [6] and it was of interest to us that such cleavage could be readily effected

* For part I see ref. 1.

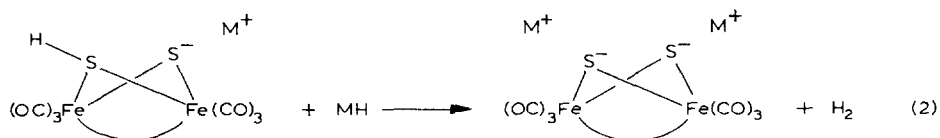
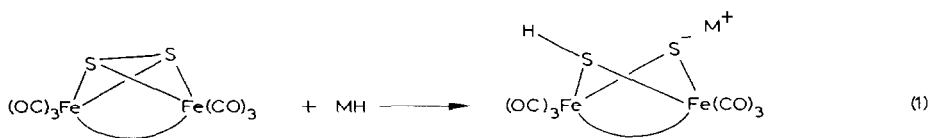
** Dedicated to my friend, Professor Oleg A. Reutov, on the occasion of his 65th birthday on September 5, 1985 and in recognition of his outstanding contributions to organometallic chemistry.



(1)



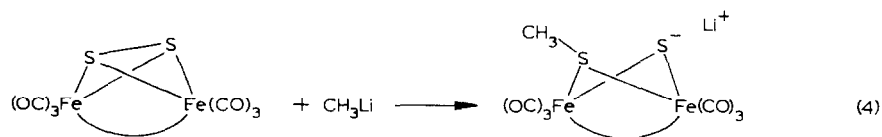
(2)

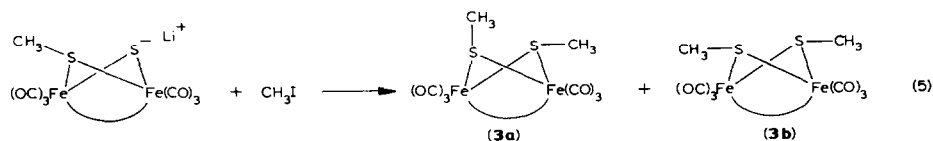


with organolithium compounds [7] and with Grignard reagents [8] (eq.3). We report $RSSR + R'M \rightarrow RSR' + RS^-M^+$ (3) here the results of our studies of the reaction of **1** with such organometallic reagents.

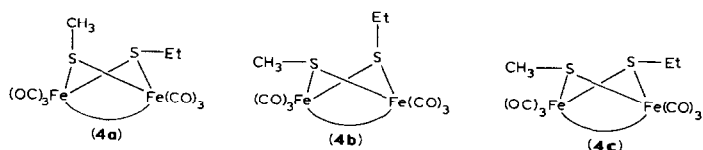
Results and discussion

When a red tetrahydrofuran (THF) solution to μ -dithiobis(tricarbonyliron) at $-78^\circ C$ was treated (under nitrogen) with a solution of $CH_3Li/LiBr$ in diethyl ether, an abrupt color change to green occurred when exactly one molar equivalent of the lithium reagent had been added. Addition of iodomethane to this mixture caused a green-to-red color change. Subsequent workup, gave the two isomers of $(\mu-CH_3S)_2Fe_2(CO)_6$ (**3a** and **3b**) [9] in 82% yield. These conversions are summarized in eq. 4 and 5. The **3a/3b** ratio was 3.2.



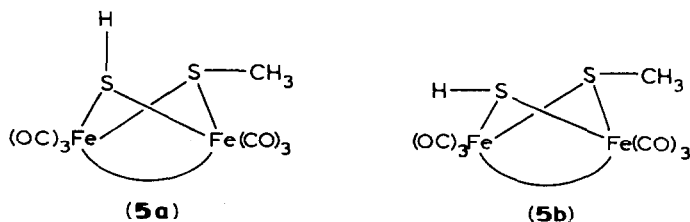


Symmetrically substituted $(\mu\text{-RS})_2\text{Fe}_2(\text{CO})_6$ complexes are more readily prepared by other means (including the alkylation of dianion **2** [1]) and the RLi cleavage of **1** is of unique utility in its application to the preparation of unsymmetrically substituted complexes, $(\mu\text{-RS})(\mu\text{-R}'\text{S})\text{Fe}_2(\text{CO})_6$. For instance, cleavage of **1** with $\text{CH}_3\text{Li}/\text{LiBr}$ at -78°C , followed by addition of iodoethane, gave $(\mu\text{-CH}_3\text{S})(\mu\text{-C}_2\text{H}_5\text{S})\text{Fe}_2(\text{CO})_6$ as an air-sensitive red oil in 77% yield. Three isomers were present, with **4a** and **4b** predominating. A number of such $(\mu\text{-RS})(\mu\text{-R}'\text{S})\text{Fe}_2(\text{CO})_6$ complexes



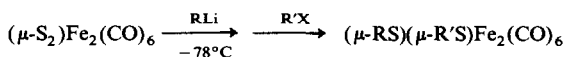
were prepared in this manner. The reactions employed are given in Table 1. The unsymmetrical products were *a,e/e,e* isomer mixtures and were isolated as air-sensitive red oils.

In one $\text{CH}_3\text{Li}/(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ reaction the intermediate bridging thiolate complex was protonated (with $\text{CF}_3\text{CO}_2\text{H}$ at -78°C) rather than alkylated. The product obtained in 94% yield was an air-sensitive red solid whose NMR spectrum showed it to be a 7.9/1 mixture of **5a** and **5b**.



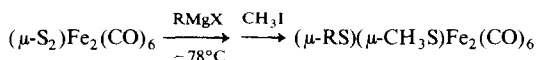
As expected, Grignard reagents reacted equally well with $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ under the same conditions (in THF at -78°C). The intermediate in this case, **6**, also is

TABLE 1



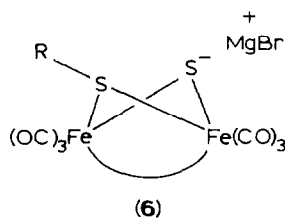
RLi	R'X	Product yield (%)
CH_3Li	CH_3I	82
CH_3Li	$\text{C}_2\text{H}_5\text{I}$	77
CH_3Li	PhCH_2Cl	85
CH_3Li	$\text{CH}_2=\text{CHCH}_2\text{Cl}$	82
<i>n</i> -BuLi	CH_3I	87
PhLi	CH_3I	70
PhLi	$\text{CH}_2=\text{CHCH}_2\text{Cl}$	75

TABLE 2



RMgX	Product yield (%)
CH ₃ MgI	81
CH ₂ =CHMgBr	89
PhMgBr	83
CH ₂ =CHCH ₂ MgBr	99
(CH ₃) ₂ CHMgBr	90
n-C ₃ H ₇ MgBr	96
(CH ₃) ₂ CHCH ₂ MgBr	99
(CH ₃) ₃ CCH ₂ MgCl	43
cyclo-C ₃ H ₅ MgBr	92
cyclo-C ₅ H ₉ MgBr	91
(CH ₃) ₂ C=CHMgBr	94
p-CH ₃ C ₆ H ₄ MgBr	89

green in THF solution. Examples of $(\mu\text{-RS})(\mu\text{-R}'\text{S})\text{Fe}_2(\text{CO})_6$ preparation by the Grignard route are given in Table 2.



This nucleophilic cleavage/alkylation sequence using either an organolithium or a Grignard reagent thus is an excellent route for the preparation of $(\mu\text{-RS})_2\text{Fe}_2(\text{CO})_6$, $(\mu\text{-RS})(\mu\text{-R}'\text{S})\text{Fe}_2(\text{CO})_6$ and $(\mu\text{-RS})(\mu\text{-HS})\text{Fe}_2(\text{CO})_6$ complexes in high yield. It would seem that diverse organic substituents may be introduced via the organometallic reagents (alkyl, vinyl, allyl, aryl groups in the present examples). The introduction of the second substituent, in view of the broad reactivity of the mercaptide function [10], should be equally versatile in its diversity.

Experimental

General comments. The general comments in Part 1 [4] are applicable. μ -Dithio-bis(tricarbonyliron) was prepared as described in detail in Part 1 [1].

Product characterization. In general, the 70 eV electron impact mass spectra of the $(\mu\text{-RS})(\mu\text{-R}'\text{S})\text{Fe}_2(\text{CO})_6$ complexes showed the molecular ion and fragment ions resulting from the successive loss of the six CO ligands, as well as other fragment ions such as RFe_2S_2^+ and/or $\text{R}'\text{Fe}_2\text{S}_2^+$, Fe_2S_2^+ , Fe_2S^+ , FeS^+ , Fe_2^+ and Fe^+ . Typically, their IR spectra showed four terminal carbonyl bands, e.g., for $\text{R} = \text{CH}_3$, $\text{R}' = \text{C}_2\text{H}_5$, 2080(m), 2048(s), 2005(vs), 1995(vs) cm^{-1} ; for $\text{R} = \text{CH}_3$, $\text{R}' = n\text{-C}_4\text{H}_9$, 2077(s), 2040(vs), 1997(vs), 1986(vs) cm^{-1} .

Since the organic substituents which were introduced were all quite simple ones, the spectral data will not be given except in those cases where clear 250 MHz NMR

spectra were available. In many cases the chemical shift of the protons of the methyl group introduced via the CH_3I reactant served to indicate the isomer ratio. For the $(\mu\text{-CH}_3\text{S})_2\text{Fe}_2(\text{CO})_6$ isomers (which are separable by column chromatography), the NMR spectrum of the *e,e* isomer shows the CH_3 resonance at δ 2.07 ppm; the spectrum of the *a,e* isomer shows the axial CH_3 resonance at δ 1.62 ppm and the equatorial CH_3 resonance at δ 2.13 ppm. However, in some other cases the isomer ratio could not be determined. All NMR spectra showed the expected signals in the correct integrated area ratio. The NMR spectra were recorded for samples in CDCl_3 solution.

Organolithium cleavage of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$. The reactions of *n*-BuLi with $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$, followed by CH_3I quench (which gives a liquid product), and of phenyllithium with $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$, followed by CH_3I quench (which gives a solid product), are described in order to illustrate the procedures used.

A 200 ml Schlenk flask equipped with a serum cap and a magnetic stir-bar was charged with 1.00 g (2.91 mmol) of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ and was flushed with nitrogen. THF (75 ml) was added and the red solution was cooled to -78°C . Subsequently, 1.3 ml (3.0 mmol) of 2.4 *M* *n*-butyllithium in hexane was added, with stirring, by syringe in three portions over 15 min to the solution, causing a color change to dark green. The mixture was stirred for 20 min and then 0.9 ml (14.4 mmol) of iodomethane was added. Following this, the reaction mixture was allowed to warm slowly to room temperature. After 1 h, the solvent was removed from the red solution on a rotary evaporator, leaving a red-brown oil which was chromatographed (silicic acid/pentane) to give 0.853 g (2.05 mmol, 70% yield) of $(\mu\text{-CH}_3\text{S})(\mu\text{-n-BuS})\text{Fe}_2(\text{CO})_6$ as an air-sensitive red oil. The product was purified further by short-path distillation at 50°C and 0.2 mmHg. The exact isomer ratio could not be determined by NMR, but it was estimated that equal amounts of the *e,e* and the two *a,e* isomers were present ($\mu(\text{CH}_3)$, 1.67, 2.12, 2.17).

A similar reaction of 3.0 ml (2.91 mmol) of 0.98 *M* phenyllithium in cyclohexane/diethyl ether with 2.91 mmol of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ in 75 ml of THF at -78°C , followed by addition of 0.9 ml of CH_3I , gave a brown-red, oily solid. Chromatography (silicic acid/20% CH_2Cl_2 /pentane) resulted in isolation of 1.102 g (2.53 mmol, 87% yield) of $(\mu\text{-CH}_3\text{S})(\mu\text{-C}_6\text{H}_5\text{S})\text{Fe}_2(\text{CO})_6$, a red solid, m.p. $83\text{--}85^\circ\text{C}$ after recrystallization from pentane. According to the NMR spectrum (CH_3 resonances at δ 1.77, 2.10 and 2.20 ppm), the CH_3 *a/Ph e*, CH_3 *e/Ph e* and CH_3 *e/Ph a* isomers were present in 3/2.1/1 ratio.

The following compounds were prepared by this procedure (cf. Table 1):

- $(\mu\text{-CH}_3\text{S})_2\text{Fe}_2(\text{CO})_6$ [1], red solid, *a,e* to *e,e* isomer ratio of 3.2.
 $(\mu\text{-CH}_3\text{S})(\mu\text{-C}_2\text{H}_5\text{S})\text{Fe}_2(\text{CO})_6$, red oil, three isomers by NMR, $4\mathbf{a} \cong 4\mathbf{b} > 4\mathbf{c}$; $\delta(\text{CH}_3)$ 1.57 ($4\mathbf{a}$), 2.03 ($4\mathbf{c}$), 2.06 ($4\mathbf{b}$). Anal. Found: C, 27.82; H, 2.15. $\text{C}_9\text{H}_8\text{O}_6\text{S}_2\text{Fe}_2$ calcd.: C, 27.86; H, 2.08%.
 $(\mu\text{-CH}_3\text{S})(\mu\text{-C}_6\text{H}_5\text{CH}_2\text{S})\text{Fe}_2(\text{CO})_6$, dark red solid, m.p. $85\text{--}87^\circ\text{C}$, (CH_3 *e*, PhCH_2 *a*): (CH_3 *e*, PhCH_2 *e*) isomer ratio 5.5 by NMR (δ 2.02 (*e,a*), 2.12 (*e,e*) (s, SCH_3), 2.21 (*e,a*), 3.53 (*e,e*) (s, CH_2Ph), 6.97–7.33 (Ph) ppm) Anal. Found: C, 37.46; H, 2.23. $\text{C}_{14}\text{H}_{10}\text{O}_6\text{S}_2\text{Fe}_2$ calcd.: C, 37.36; H, 2.24%.
 $(\mu\text{-CH}_3\text{S})(\mu\text{-CH}_2=\text{CHCH}_2\text{S})\text{Fe}_2(\text{CO})_6$, red oil, b.p. 80°C at 0.4 mmHg; by NMR (CH_3 *e*, allyl *a*) > (CH_3 *e*, allyl *e*) > (CH_3 *a*, allyl *e*) (δ 1.77 (*a,e*), 2.21 (*e,e*), 2.25 (*e,a*) (s, SCH_3), 2.85, 3.17 (d, *J* 6 Hz, S- CH_2), 4.95–6.10 (m, $\text{CH}=\text{CH}_2$) ppm). Anal. Found: C, 30.06; H, 2.05. $\text{C}_{10}\text{H}_8\text{O}_6\text{S}_2\text{Fe}_2$ calcd.: C, 30.03; H, 2.02%.

$(\mu\text{-CH}_3\text{S})(\mu\text{-n-C}_4\text{H}_9\text{S})\text{Fe}_2(\text{CO})_6$, red oil, b.p. $50^\circ\text{C}/0.2$ mmHg; by NMR (CH_3 *a*, Bu *e*) \cong (CH_3 *e*, Bu *e*) \cong (CH_3 *e*, Bu *a*); δ (CH_3) 1.67, 2.12, 2.17 ppm. Anal. Found: C, 31.96; H, 2.74. $\text{C}_{11}\text{H}_{12}\text{O}_6\text{S}_2\text{Fe}_2$ calcd.: C, 31.76; H, 2.91%.

$(\mu\text{-CH}_3\text{S})(\mu\text{-C}_6\text{H}_5\text{S})\text{Fe}_2(\text{CO})_6$, red solid, m.p. $83\text{--}85^\circ\text{C}$ (from pentane), isomer ratio given above. Anal. Found: C, 36.05; H, 1.91. $\text{C}_{13}\text{H}_8\text{O}_6\text{S}_2\text{Fe}_2$ calcd.: C, 35.81; H, 1.85%.

$(\mu\text{-C}_6\text{H}_5\text{S})(\mu\text{-CH}_2=\text{CHCH}_2\text{S})\text{Fe}_2(\text{CO})_6$, red oil, by NMR (CH_2 doublets at δ 2.84, 3.01, 3.12 ppm) 2/9/5 *e,e,a* allyl group orientations, but specific assignments not possible. Anal. Found: C, 38.99; H, 2.30. $\text{C}_{15}\text{H}_{10}\text{O}_6\text{S}_2\text{Fe}_2$ calcd.: C, 39.03; H, 2.18%.

Grignard cleavage of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$. A 300 ml. three-necked flask equipped with a serum cap and a magnetic stir-bar was charged with $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ (2–3 mmol) and flushed with nitrogen. THF (75 ml) was added; the red solution was cooled to -78°C and then the appropriate Grignard reagent solution was added dropwise with stirring, resulting in a color change to green. The mixture was stirred at -78°C for 15–30 min and then 1.0 ml (16.1 mmol) of iodomethane was added. The reaction mixture was stirred for 30 min at -78°C and 2–3 h at room temperature. The solvent was removed at reduced pressure, leaving a red oil, which was purified by filtration chromatography (silicic acid) and short path distillation, or a red solid which was chromatographed and recrystallized from pentane.

The following compounds were prepared by this procedure (cf. Table 2):

$(\mu\text{-CH}_3\text{S})_2\text{Fe}_2(\text{CO})_6$, red solid, *a,e* to *e,e* isomer ratio of 3.8.

$(\mu\text{-CH}_3\text{S})(\mu\text{-CH}_2=\text{CHS})\text{Fe}_2(\text{CO})_6$, CH_3 *a*, $\text{CH}_2=\text{CH}$ *e* isomer, red solid, m.p. $77\text{--}78^\circ\text{C}$, separated by column chromatography, recrystallized from pentane; 61% yield; $\delta(\text{CH}_3)$ 1.66 ppm. Anal. Found: C, 27.99; H, 1.59. $\text{C}_9\text{H}_6\text{O}_6\text{S}_2\text{Fe}_2$ calcd.: C, 28.01; H, 1.57%. CH_3 *e*, $\text{CH}_2=\text{CH}$ *a* or *e* isomer, orange powder, m.p. $84\text{--}85^\circ\text{C}$ (from pentane), 28% yield; $\delta(\text{CH}_3)$ 2.16 ppm. Anal. Found: C, 28.01; H, 1.65%.

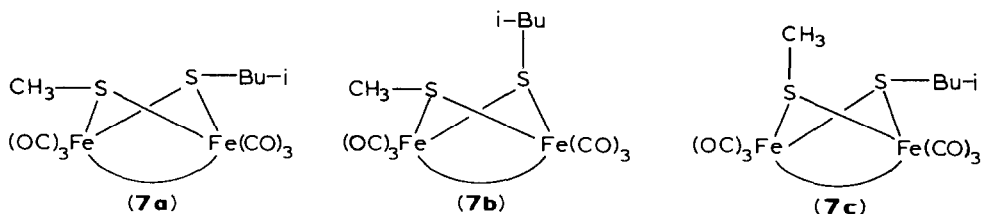
$(\mu\text{-CH}_3\text{S})(\mu\text{-C}_6\text{H}_5\text{S})\text{Fe}_2(\text{CO})_6$, red oil. Recrystallization from pentane after short-path distillation (b.p. $142.5^\circ\text{C}/0.3$ mmHg) gave a red powder, m.p. $71\text{--}73^\circ\text{C}$, which was more soluble in pentane and a deep red powder, m.p. $84\text{--}85^\circ\text{C}$, less soluble in pentane. Both products had identical mass spectra, in agreement with the formula given. Thus some fractionation of isomers occurred.

$(\mu\text{-CH}_3\text{S})(\mu\text{-CH}_2=\text{CHCH}_2\text{S})\text{Fe}_2(\text{CO})_6$, red oil, b.p. $108\text{--}110^\circ\text{C}/0.4$ mmHg; by NMR (CH_3 *e*, allyl *a*) $>$ (CH_3 *e*, allyl *e*) $>$ (CH_3 *a*, allyl *e*). δ (CH_3) at 2.07, 2.12, and 1.62 ppm, respectively.

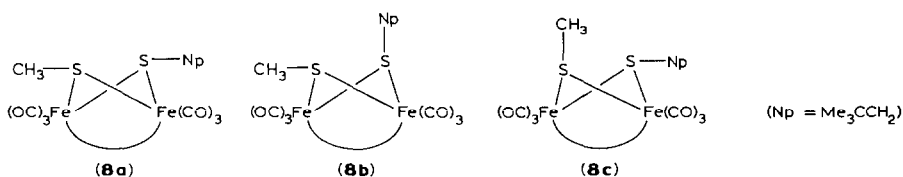
$(\mu\text{-CH}_3\text{S})(\mu\text{-Me}_2\text{CHS})\text{Fe}_2(\text{CO})_6$, red oil, b.p. $100\text{--}103^\circ\text{C}/0.4$ mmHg; by NMR (CH_3 *a*, *i*-Pr *e*) $>$ (CH_3 *e*; *i*-Pr *e*) $>$ (CH_3 *e*; *i*-Pr *a*) δ 1.6 (*a,e*), 2.03 (*e,e* and *e,a*) (s, SCH_3), 1.10 (*e,a*), 1.26 (*e,e*), 1.33 (*e,a*) (d, *J* 6 Hz, CH_3), 2.24–2.92 (m, SCH) ppm. Anal. Found: C, 29.99; H, 2.59. $\text{C}_{10}\text{H}_{10}\text{O}_6\text{S}_2\text{Fe}_2$ calcd.: C, 29.88; H, 2.51%.

$(\mu\text{-CH}_3\text{S})(\mu\text{-n-C}_3\text{H}_7\text{S})\text{Fe}_2(\text{CO})_6$, red oil, b.p. $114\text{--}116^\circ\text{C}/2.0$ mmHg, a mixture of three isomers whose ratio could not be determined because of overlapping CH_3 and propyl proton signals; $\delta(\text{CH}_3)$ 1.65, 2.06, 2.14 ppm. Anal. Found: C, 29.99; H, 2.52. $\text{C}_{10}\text{H}_{10}\text{O}_6\text{S}_2\text{Fe}_2$ calcd.: C, 29.88; H, 2.51%.

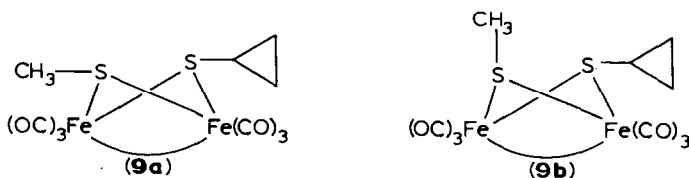
$(\mu\text{-CH}_3\text{S})(\mu\text{-(CH}_3)_2\text{CHCH}_2\text{S})\text{Fe}_2(\text{CO})_6$, red oil, b.p. $130^\circ\text{C}/0.5$ mmHg. A 250 MHz NMR spectrum allowed determination of the isomer ratio of $7\mathbf{a}/7\mathbf{b}/7\mathbf{c} = 2.5/1/3.3$: δ 1.64 (**7c**), 2.10 (**7a**), 2.11 (**7b**) (s, SCH_3); 1.95 (**7b**) (d, *J* 7.0 Hz, SCH_2), 2.32 (**7a**) and 2.33 (**7c**) (d, *J* 6.6 Hz, SCH_2), 0.93 (**7b**), 1.03 (**7a**), 1.08 (**7c**) (d, *J* 6.6 Hz, $\text{CH}(\text{CH}_3)_2$), 1.77–1.91 and 1.52–1.58 (m, CHMe_2) ppm.



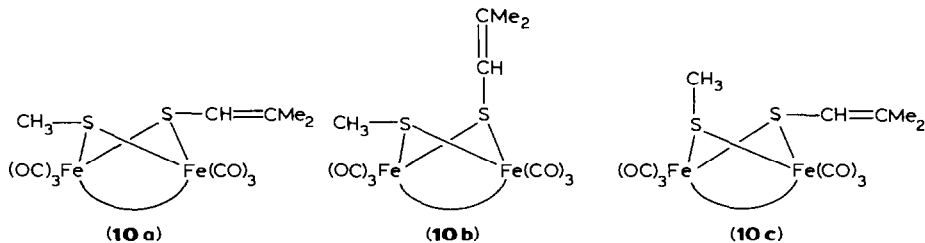
Anal. Found: C, 31.81; H, 2.94. $C_{11}H_{12}O_6S_2Fe_2$ calcd.: C, 31.76; H, 2.91%.
 $(\mu-CH_3S)(\mu-Me_3CCH_2S)Fe_2(CO)_6$, red oil, b.p. $112^\circ C/0.24$ mmHg. Isomer ratio **8a/8b/8c** = 1.3/1/1.3. 250 MHz NMR: δ 0.93 (**8b**), 1.03, 1.09 (**8a, 8c**) (s, $C(CH_3)_3$), 2.10 (**8a, 8b**), 1.66 (**8c**) (s, SCH_3), 1.99 (**8b**), 2.35 and 2.36 (**8a, 8c**) (s, CH_2) ppm.



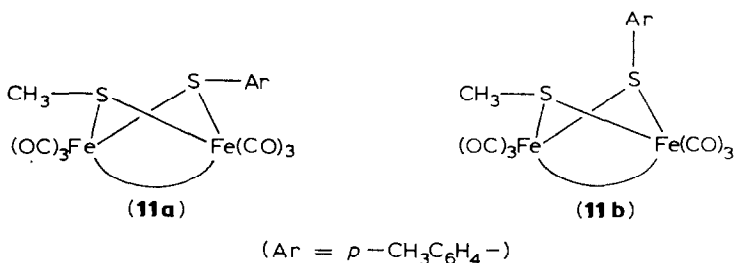
Anal. Found: C, 33.81; H, 3.41. $C_{12}H_{14}O_6S_2Fe_2$ calcd.: C, 33.52; H, 3.28%.
 $(\mu-CH_3S)(\mu-cyclo-C_3H_7S)Fe_2(CO)_6$, a red solid, m.p. $63-68^\circ C$ (from pentane), a 1/1 mixture of **9a** and **9b**. 250 MHz NMR: δ 1.54 (**9b**),



2.07 (**9a**) (s, SCH_3), 1.62 to 1.74 (m, SCH), 0.70–0.86 and 1.0–1.14 (m, ring CH_2) ppm. Anal. Found: C, 30.25; H, 2.10. $C_{10}H_8O_6S_2Fe_2$ calcd.: C, 30.03; H, 2.02%.
 $(\mu-CH_3S)(\mu-cyclo-C_3H_9S)Fe_2(CO)_6$, red oil, b.p. $120^\circ C/0.2$ mmHg, a mixture of three isomers whose ratio could not be determined because of overlapping CH_3 and cyclopentyl proton signals; $\delta(CH_3)$ 1.62, 2.08, 2.12 ppm. Anal. Found: C, 33.82; H, 2.91. $C_{12}H_{12}O_6S_2Fe_2$ calcd.: C, 33.67; H, 2.83%.
 $(\mu-CH_3S)(\mu-Me_2C=CHS)Fe_2(CO)_6$, a red oil, b.p. $85^\circ C/0.06$ mmHg, a 1.6/1/1.9 mixture of **10a**, **10b** and **10c** by NMR. 250 MHz NMR: δ 1.66 (**10c**), 2.09 (**10a**), 2.12 (**10b**) (s, SCH_3), 1.79, 1.98 (**10c**); 1.76, 1.89 (**10a**); 1.70, 1.83 (**10b**) (all s, $=CMe_2$), 5.40 (**10b**), 5.54 (**10a**), 5.62 (**10c**) (s, $=CH$) ppm. Anal. Found: C, 31.90; H, 2.45. $C_{11}H_{10}O_6S_2Fe_2$ calcd.: C, 31.91; H, 2.43%.



$(\mu\text{-CH}_3\text{S})(\mu\text{-}p\text{-CH}_3\text{C}_6\text{H}_4\text{S})\text{Fe}_2(\text{CO})_6$, red solid, m.p. 106–108°C (from pentane). Two isomers, **11a** and **11b**, were present in 4/1 ratio (by NMR), but assignments could not be made. 250 MHz NMR: δ 2.05, 2.15, 2.27 (s, SCH_3 and $\text{C}_6\text{H}_4\text{CH}_3$), 6.9–7.1 (m, C_6H_4) ppm. Anal. Found: C, 37.39; H, 2.33. $\text{C}_{14}\text{H}_{10}\text{O}_6\text{S}_2\text{Fe}_2$ calcd.: C, 37.37; H, 2.24%.



Preparation of $(\mu\text{-CH}_3\text{S})(\mu\text{-HS})\text{Fe}_2(\text{CO})_6$. The monoanion was prepared by the usual method by reaction of 1.82 ml of 1.6 M $\text{CH}_3\text{Li}/\text{LiBr}$ in diethyl ether with 2.91 mmol of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ in 75 ml of THF at -78°C . To this solution was added, with stirring at -78°C , 0.50 ml (5.70 mmol) of $\text{CF}_3\text{CO}_2\text{H}$. An immediate color change from green to red occurred. The reaction mixture was allowed to warm to room temperature and the volatiles were removed in vacuo. The red-brown solid which remained was extracted with three 25 ml portions of pentane. The extracts were filtered and evaporated in vacuo to leave 0.98 g (2.72 mmol, 94% yield) of $(\mu\text{-CH}_3\text{S})(\mu\text{-HS})\text{Fe}_2(\text{CO})_6$, an air-sensitive red solid, m.p. 82–84°C after recrystallization from hexane. NMR: δ -2.47 (*a* SH), -0.52 (*e* SH), 2.18 (*e* SCH_3) ppm. Isomer ratio (*a* SH/*e* SH) 7.9. The mass spectrum (70 eV) showed the molecular ion and, inter alia, fragment ions corresponding to $[\text{M}^+ - n\text{CO}]$ ($n = 1\text{--}6$). Anal. Found: C, 23.36; H, 1.21. $\text{C}_7\text{H}_4\text{O}_6\text{S}_2\text{Fe}_2$ calcd.: C, 23.36; H, 1.12%.

References and notes

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