is also supported by the extreme high-field shift of the $^{31}P$ resonance of 3 ($\delta$ −188.7 vs external 85% $H_3PO_4$) and by the low-field shift of the carbenic carbon ($\delta(^{13}C)$ + 266.3).

**Registry No.** 1, 83603-06-9; 2, 60635-78-1; 3, 111495-74-0.

**Supplementary Material Available:** Anisotropic thermal parameters (Table S1), hydrogen atom parameters (Table S2), complete set of bond lengths (Table S3), and complete set of bond angles (Table S4) (8 pages); observed and calculated structure factor amplitudes for all observed reflections (×10) (Table S5) (11 pages). Ordering information is given on any current masthead page.

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# Unexpected Formation of $[\mu\text{-}\eta^2\text{-(S)(S)}\underline{\mathrm{CSC_2H_4S}}][\eta^1\text{-}\underline{\mathrm{CSC_2H_4S}}]\mathrm{Fe_2(CO)_5}$: Structure and Dynamic Behavior

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*Summary:* Ethylene trithiocarbonate reacts with diiron nonacarbonyl to afford the coordination compound $[\mu\text{-}\eta^3\text{-S}\underline{\mathrm{CSC_2H_4S}}]\mathrm{Fe_2(CO)_6}$ in which the carbon of the thione is $\sigma$-bonded to one iron atom; upon warming, this complex is transformed into $[\mu\text{-}\eta^2\text{-(S)(S)}\underline{\mathrm{CSC_2H_4S}}][\eta^1\text{-}\underline{\mathrm{CSC_2H_4S}}]\mathrm{Fe_2(CO)_5}$. The formation of this new coordination compound implies that the association of two fragments containing the heterocyclic moieties is followed by a redistribution of the sulfur atoms affording the planar carbenic ligand ($=\underline{\mathrm{CSC_2H_4S}}$) and the original bridging system $[\mathrm{(S)(S)}\underline{\mathrm{CSC_2H_4S}}]$ in which a carbon atom is linked to four sulfur atoms.

Organic molecules containing the thiocarbonyl group are good ligands for zerovalent metal carbonyls and lead to families of mono- and polynuclear coordination compounds.[1] In this field we have shown that the behavior of the >C=S group toward diiron nonacarbonyl depends considerably on the nature of neighboring atoms. For instance, complexation of *O*-alkyl *S*-alkyl dithiocarbonate 1 affords compounds 3 in which the carbon atom of the thione is $\sigma$-bonded to one iron atom.[2] Upon warming or on electron-transfer catalysis, compound 3 rearranges to the carbenic binuclear complex 5.[2,3] With trithiocarbonates 2 the fragmentation is not regiospecific and the two isomers 6 and 7 are obtained.[4] Finally, dithioesters 8 afford compounds 4 possessing a stable carbon–iron $\sigma$-bond.[5] All these coordination compounds are good models for study of the stereochemical aspects of ligand exchange under thermal activation or by electron-transfer catalysis.[6,7] Up to now, we have studied conformationally mobile sulfur ligands, but in this paper we describe the reactivity of the cyclic trithiocarbonate 9 which initially behaves like a dithioester ligand, affording 10. Then 10, under thermal activation, leads to the new compound 11.

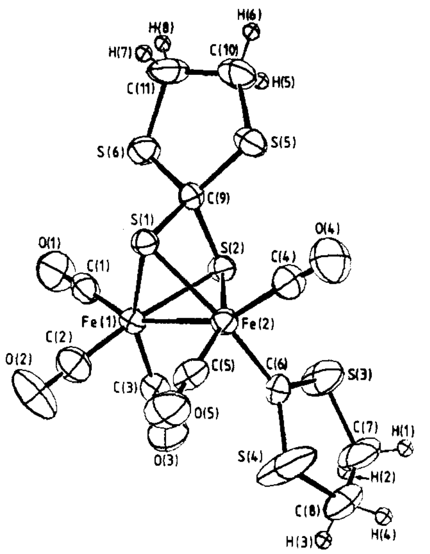

**Figure 1.** Molecular structure and labeling scheme for compound 11. Relevant bond distances (Å) and angles (deg): Fe(1)–Fe(2), 2.489 (1); Fe(1)–S(1), 2.273 (2); Fe(1)–S(2), 2.275 (2); Fe(2)–S(1), 2.281 (2); Fe(2)–S(2), 2.282 (2); Fe(2)–C(6), 1.900 (6); S(1)–C(9), 1.850 (6); S(2)–C(9), 1.829 (6); S(3)–C(6), 1.680 (7); S(4)–C(6), 1.668 (7); S(5)–C(9), 1.803 (6); S(6)–C(9), 1.811 (6); Fe(1)–S(1)–Fe(2), 66.25 (5); Fe(1)–S(2)–Fe(2), 66.21 (5); Fe(2)–C(6)–S(3) 123.5 (4); Fe(2)–C(6)–S(4), 124.5 (4); S(3)–C(6)–S(4), 112.0 (4); S(1)–C(9)–S(2), 93.6 (3); S(1)–C(9)–S(5), 111.4 (3); S(1)–C(9)–S(6), 113.5 (3); S(2)–C(9)–S(5), 114.9 (3); S(2)–C(9)–S(6), 113.2 (3); S(5)–C(9)–S(6), 109.5 (3).

In contrast to the behavior of ligands of type 2, the reaction of 9 with $Fe_2(CO)_9$ does not lead to the insertion of iron into a carbon–sulfur bond. Complex 10 was rapidly formed,[8] but the production of the more polar product 11

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[1] For a leading reference see: Seyferth, D.; Womack, G. B.; Cowie, M.; Hames, B. W. *Organometallics* **1984**, *3*, 1891.

[2] Lhadi, E. K.; Patin, H.; Darchen, A. *Organometallics* **1984**, *3*, 1128.

[3] Patin, H.; Mignani, G.; Benoit, A.; Le Marouille, J. Y.; Grandjean, D. *Inorg. Chem.* **1981**, *20*, 4351.

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[6] Darchen, A.; Lhadi, E. K.; Patin, H. *J. Organomet. Chem.* **1983**, *259*, 196.

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[8] To a solution of 9 (1.64 g, 12 mmol) in toluene (20 mL) was added 6 g of $Fe_2(CO)_9$ (16 mmol), and the mixture was allowed to react for 45 min at 55 °C under $N_2$ with stirring. The solvent was removed under vacuum and the residue chromatographed on silica plates (petroleum ether–diethyl ether (1/1)). The strips of $R_f$ 0.6 and 0.3 were extracted and afforded, after crystallization, respectively 2.66 g of 10 (53%) and 1.05 g of 11 (19%). Compound 10 also is one of the components of the mixture obtained by irradiation[9] of $[\mathrm{Cr(CO)_5\{S}\underline{\mathrm{CSC_2H_4S}}\}]$ in the presence of $Fe(CO)_5$. 10: mp 100–102 °C (pentane–ether) (lit.[9] mp 101–102 °C); mass spectrum, $m/z$ calcd 415.786, found 415.786 ($M^{\cdot+}$), successive loss of six CO's, 248 ($C_3H_4S_3Fe_2$), 220 ($CS_3Fe_2$), 176 ($Fe_2S_2$), 144 (FeS), 136 ($C_3H_4S_3$); IR (Nujol) terminal carbonyl region 1950–2085 cm$^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 2.5 (m, 1 H), 3.45 (m, 3 H); $^{13}C$ NMR ($CDCl_3$ at 36 °C) $\delta$ 38.2 ($CH_2$), 49.5 ($CH_2$), 74.9 (CS), 208.7 (3 CO), 210.5 (3 CO). Anal. Calcd for $C_9H_4Fe_2O_6S_3$: C, 25.96; H, 0.96; S, 23.07. Found: C, 25.90; H, 0.89; S, 23.44.

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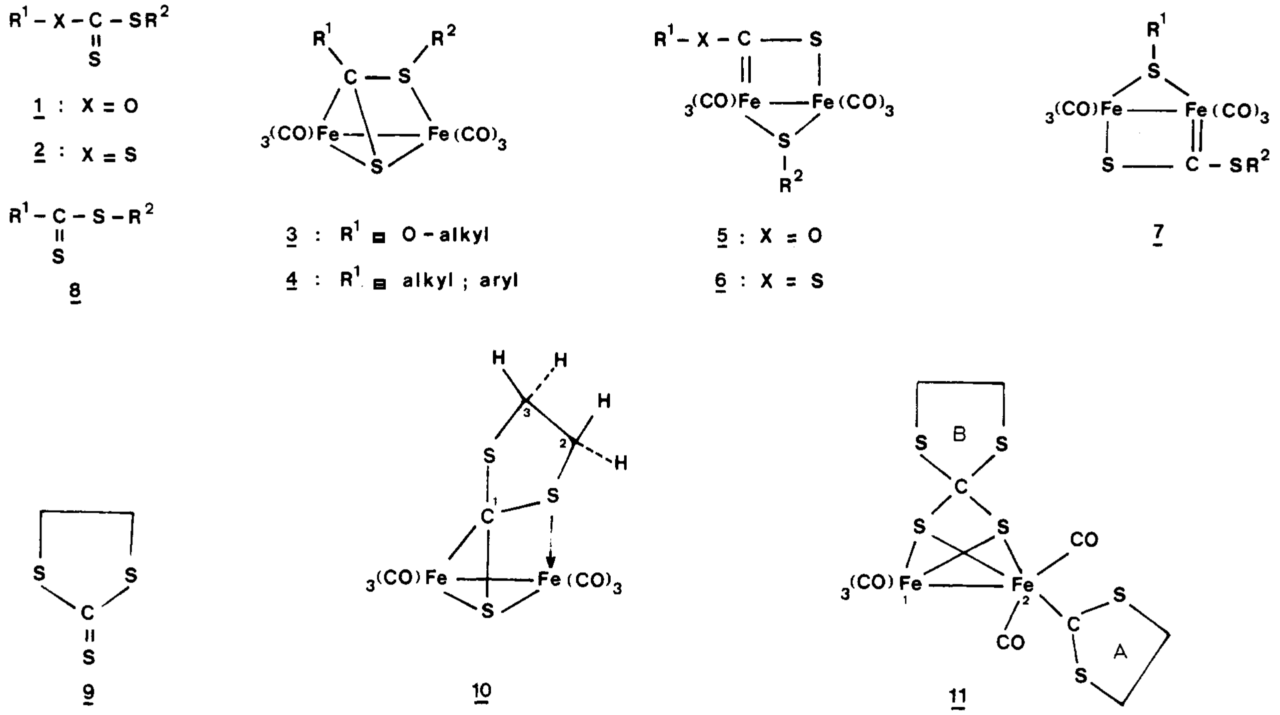
**Chart I**



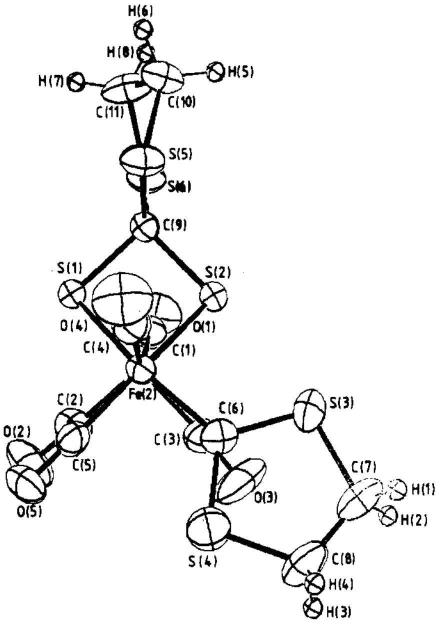


**Figure 2.** A projection view of compound 11 on the metal–metal axis.

could not be avoided even by using lower temperatures or shorter reaction times. Pure compound **10** obtained after chromatography is easily transformed[10] (in hot toluene) into **11**. The structure of **10** was readily established, but the spectroscopic data obtained for **11** were not sufficient to propose a formula, and an X-ray diffraction study was undertaken[11] (Figures 1 and 2). The structure determination of **11** reveals the unusual nature of this molecule which basically is made of the $Fe_2(CO)_6S_2$ framework in which one of the terminal CO ligands is replaced by one molecule of partially desulfurized ligand **9** (heterocycle A). Moreover, the two bridging sulfur atoms are linked to another desulfurized molecule of **9** (heterocycle B). However, the heterocycle B is not planar by comparison to heterocycle A because in the first one the carbon atom C(9) is tetrahedral while in the second one the carbon atom C(6), directly bonded to Fe(2), is sp$^2$ hybrided. The bond length Fe(2)–C(6) (1.90 Å) and the chemical shift of C(6) (303 ppm) are in agreement with classical values for iron–carbene bonds,[3] and the shortening of the C(6)–S(3) and C(6)–S(4) bond lengths (1.68 Å) by comparison to S(4)–C(8) and S(3)–C(7) (1.78 Å) show a significant participation of the sulfur orbitals in carbene stabilization. In contrast, the resonance of C(9) occurs at 100,5 ppm and the bond angles are close to the theoretical value for an sp$^3$ carbon atom except for S(1)–C(9)–S(2) because of the

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[9] Kruger, G. J.; Linford, L.; Raubenheimer, H. G.; Chalmers, A. A. *J. Organomet. Chem.* **1984**, *262*, 69.

[10] A solution of 1.1 g (2.6 mmol) of 10 in toluene (15 mL) was stirred at 80 ° C under $N_2$ for 30 h (TLC control showed complete disappearance of 10). The solvent was removed under vacuum and the crude mixture purified on silica plates, eluting with petroleum ether–diethyl ether (1/1). The orange strip was recovered, and 0.280 g (43%) of pure compound 11 was obtained after crystallization from hexane, mp 145–146 °C. Complex 11 was identical with the compound previously obtained:[8] mass spectrum, $m/z$ calcd for $C_3H_4S_4Fe_2$ 279.789, found 279.780 ($M^+$ - 5 CO - $C_3H_4S_2$), 420 ($M^+$ - $C_3H_4S_2$), then successive loss of five CO's; $^1H$ NMR ($CDCl_3$) $\delta$ 3.3 (s, 4 H), 3.5 (s, 4 H) at 36 °C; at -90 °C ($CD_3COCD_3$), the low field signal is splitted into peaks at $\delta$ 4.15, 4.05, 3.92, 3.87, 3.77, 3.65; $^{13}C$ NMR ($CDCl_3$ at 36 °C) $\delta$ 41.8 ($CH_2$), 42.3 ($CH_2$), 46.5 (two equivalent $CH_2$), 101.2 ($CS_4$), 210.6 (3 CO), 213.1 (2 CO), 303.8 (carbene); at -90 °C, the carbonyl region shows five peaks at $\delta$ 215.2, 212.6, 211.9, 211.4, 207.5 ($CD_2Cl_2$) (Figure 3); IR (Nujol) $\nu_{CO}$ 2070–1940 cm$^{-1}$. Anal. Calcd for $C_{11}H_8O_5S_6Fe_2$: C, 25.19; H, 1.52; S, 36.64; Fe, 21.37. Found: C, 25.50; H, 1.59; S, 36.31; Fe, 21.29.

[11] Crystal data for $C_{11}H_8O_5S_6Fe_2$: space group $P2_1/n$, $a$ = 10.136 (4) Å, $b$ = 18.397 (8) Å, $c$ = 10.728 (8) Å, $\beta$ = 110.94 (2)°, $V$ = 1868.4 Å$^3$, $\rho$(calcd) = 1.864 g cm$^{-3}$ for $M_r$ 524.3, $Z$ = 4, $\mu$ = 22.16 cm$^{-1}$ for Mo K$\alpha$. Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer at room temperature. All data were corrected for Lorentz and polarization effects. An empirical absorption correction was made. Crystallographic computations were carried out on a PDP 11/60 computer using the SDP (Structure Determination Package). The structure was solved by the direct method using the MULTAN program and difference Fourier syntheses. $R_F$ = 0.0323 and $R_{wF}$ = 0.0356 (218 parameters refined, including the extinction coefficient) for 1486 reflections [$I \geq 3\ \sigma(I)$] of 2886 unique reflections collected in the range of 1° $\leq \theta \leq$ 25°.

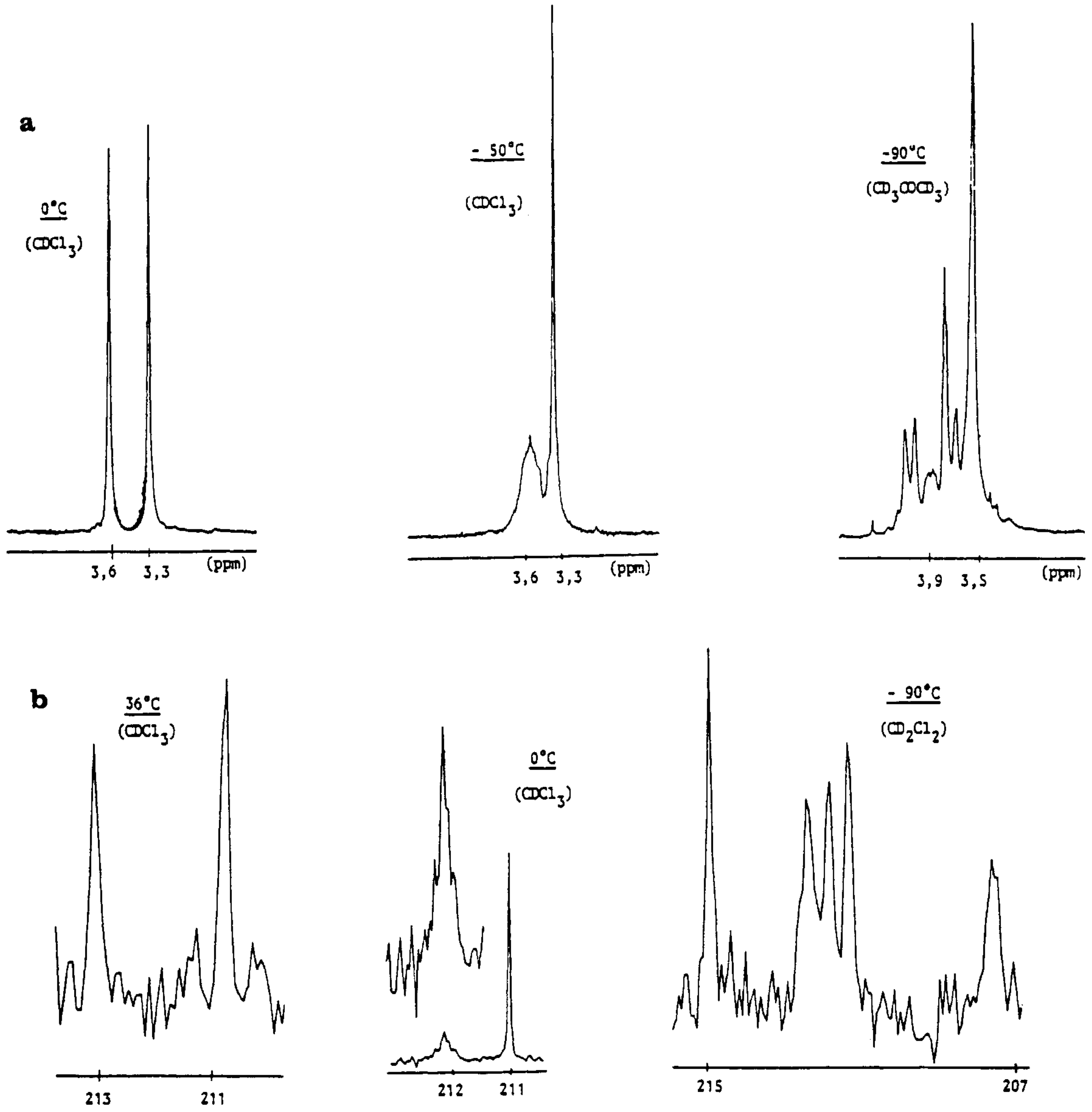

**Figure 3.** (a) Temperature-dependent $^1$H NMR spectra of 11 (δ 3.3, 4 H of ring A; δ 3.6, 4 H of ring B). (b) Temperature-dependent $^{13}$C NMR spectra of 11 in the carbonyl region.

demands of the $Fe_2S_2$ skeleton. Similar angle values are reported for analogous structures, but the carbon resonance of C(9) is by far at the lowest field among the published data.[12,13] All the carbon–sulfur bonds around C(9), in the range 1.82 Å, are longer than intracyclic C–S bonds [1.79 Å for S(5)–C(10) and S(6)–C(11)]. The X-ray structure reveals also that in the crystal the five carbonyl ligands are nonequivalent and that in heterocycle B the atoms C(11) and C(10) and the four hydrogens linked to them are also nonequivalent (Figure 2). These observations are in agreement with the $^1$H and $^{13}$C NMR temperature-dependent spectra showing the fluxionality in compound 11 (Figure 3).

The formation of **11** on heating of **10** implies a dimerization. We proposed that the loss of $Fe(CO)_3$ from **10** is favored because it releases the torsional strain. Then by coupling of two electron-deficient intermediates a binuclear compound such as **12** with no metal–metal bond can be formed and subsequently rearranged to give **11**. The reaction of HC(S)OEt with $Fe_2(CO)_9$ gives such a dimer[1] (with no metal–metal interaction), the stability of which can be attributed to the presence of the ethoxy substituents.

**Registry No.** **9**, 822-38-8; **10**, 90697-86-2; **11**, 111559-59-2; Fe, 7439-89-6.

**Supplementary Material Available:** Tables of selected interatomic distances, selected bond angles, positional parameters, anisotropic thermal parameters, and hydrogen parameters (4 pages); a listing of observed and calculated structure amplitudes (8 pages). Ordering information is given on any current masthead page.

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(13) Seyferth, D.; Womack, G. B.; Henderson, R. S.; Cowie, M.; Hames, B. W. *Organometallics* **1986**, *5*, 1568.