Chemistry of μ-Dithio-bis(tricarbonyliron), a Mimic of Inorganic Disulfides. 1. Formation of Di-μ-thiolato-bis(tricarbonyliron) Dianion[1]

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Received July 8, 1981

μ-Dithio-bis(tricarbonyliron) is converted to the sulfur-centered dianion, $[(\mu\text{-S})_2Fe_2(CO)_6]^{2-}$, by reduction with sodium in THF or by reaction with 2 molar equiv of potassium hydride or, better, THF-soluble lithium triethylborohydride. The dianion may be alkylated with alkyl halides and forms bridged $-S(CH_2)_nS-$ complexes on reaction with CH_2I_2 and $BrCH_2CH_2Br$. It reacts readily with diverse main group and transition element di- and tetrahalides to give products of type $(\mu\text{-}L_nMS_2)Fe_2(CO)_6$ in which there is a $-SM(L_n)S-$ bridge between the iron atoms.

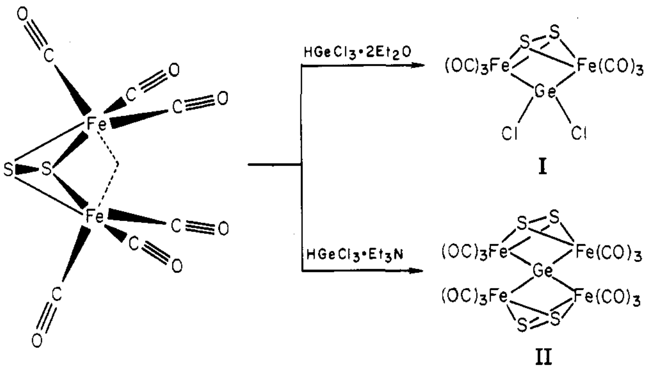
Introduction

The reaction of an aqueous solution of sodium polysulfide of composition Na_2S_5 with a basic aqueous–methanolic solution of iron pentacarbonyl at 0 °C was first carried out by Brendel and described in detail in his Ph.D. thesis in 1956.[3] The products of this reaction were correctly identified by Brendel as $S_2Fe_2(CO)_6$ and $S_2Fe_3(CO)_9$. This work was published in 1958 from the same laboratory by Hieber and Gruber.[4,5]

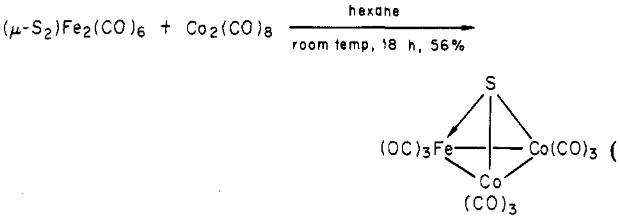
Of these two complexes, $S_2Fe_2(CO)_6$ is particularly interesting. It is isolated in the form of beautiful ruby-red, air-stable crystals. These melt sharply at 46.5 °C, and decompose thermally only above 70 °C. The compound sublimes at 40 °C and is very soluble in nonpolar organic solvents. The structure of $S_2Fe_2(CO)_6$ was determined by Wei and Dahl[6] by X-ray diffraction and is shown in Figure 1. The complex is butterfly shaped (distorted Fe_2S_2 tetrahedron), with an S_2 ligand symmetrically bridging the two $Fe(CO)_3$ units. These are themselves connected by a bent metal–metal bond.[7] The S–S bond distance of 2.01 Å corresponds to the normal S–S single bond distance (2.04 Å, as found in S_2Cl_2 and S_8[8]).

The structure of $S_2Fe_2(CO)_6$ presents interesting opportunities for the study of chemical reactivity. The complex contains potentially reactive S–S and Fe–Fe bonds; the sulfur atoms of the S_2 ligand are potential electron-donor sites, and the CO ligands may be displaced by other Lewis-base ligands. At the time we began our studies in this area, 20 years since μ-dithio-bis(tricarbonyliron) first had been reported, only very few studies of its chemistry had been published. Hieber and Zeidler[9] studied simple CO replacement by triphenylphosphine, a reaction which received more detailed study by later workers.[10]

Scheme I



An interesting fragmentation reaction which proceeded at room temperature (eq 1) was reported by Hungarian workers in 1964.[11] Finally, a Russian group described the reactions of $(\mu\text{-S}_2)Fe_2(CO)_6$ with two $GeCl_2$ precursors (Scheme I).[12] The products, I and II, were identified on the basis of their combustion analysis and IR and mass spectra. The tentative structures shown were postulated solely on the basis of known examples of dihalogermylene insertions into metal–metal bonds of simpler systems.[13,14]



(1)

These were the available reports on the chemistry of $(\mu\text{-S}_2)Fe_2(CO)_6$, and thus, we felt, an exploration of the reactivity of this interesting compound would be fruitful in terms of new chemistry and new iron–sulfur complexes. Focusing on the Fe_2S_2 core, the S–S and the bent Fe–Fe bonds of the molecule, it was not at all clear at which site a given reagent would be expected to attack.

Closely related complexes which have a bent Fe–Fe bond but no S–S bond, $(\mu\text{-RS})_2Fe_2(CO)_6$, have been shown to

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[1] Preliminary communications: (a) Seyferth, D.; Henderson, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 508. (b) Seyferth, D.; Henderson, R. S.; Song, L.-C. *J. Organomet. Chem.* **1980**, *192*, C1.

[2] Visiting Scholar at M.I.T., 1979–1981; on leave from Nankai University, Tian-Jin (P.R.C.).

[3] Brendel, G. Ph.D. Dissertation, Technische Hochschule München, 1956, pp 47–55. We thank Dr. Brendel for calling this work to our attention and for sending us a copy of his thesis.

[4] Hieber, W.; Gruber, J. *Z. Anorg. Allg. Chem.* **1958**, *296*, 91.

[5] Brendel's thesis[3] was mentioned in a footnote.

[6] Wei, C. H.; Dahl, L. F. *Inorg. Chem.* **1965**, *4*, 1.

[7] Dahl, L. F.; Martell, C.; Wampler, D. L. *J. Am. Chem. Soc.* **1961**, *83*, 1761.

[8] (a) Ackermann, P. G.; Mayer, J. E. *J. Chem. Phys.* **1936**, *4*, 377. (b) Abrahams, S. C. *Acta Crystallogr.* **1955**, *8*, 661.

[9] Hieber, W.; Zeidler, A. *Z. Anorg. Allg. Chem.* **1964**, *329*, 92.

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[12] Nametkin, N. S.; Tyurin, V. D.; Kuz'min, O. V.; Nekhaev, A. I.; Mavlonov, M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, 3143.

[13] Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E.; Denisova, Z. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1966**, 2246; **1968**, 142.

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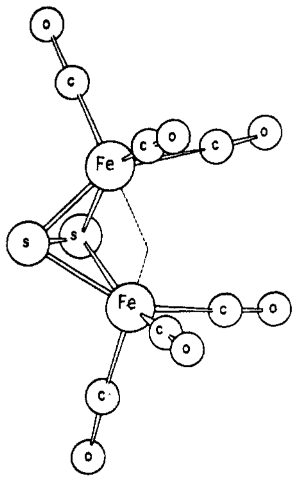
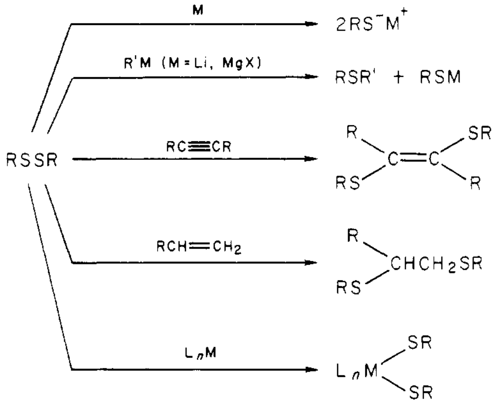
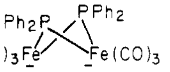


Figure 1. Molecular structure of $(\mu\text{-}S_2)Fe_2(CO)_6$.[6]

Scheme II. Reaction Chemistry of Organic Disulfides



undergo reactions at the metal-metal bond: photoinduced insertion of hexafluoro-2-butyne and esters of acetylenedicarboxylic acid,[15] of tetrafluoroethylene,[16] and, in the case of $(\mu\text{-}RS)_2Fe_2(CO)_4(R_3P)_2$ complexes, of sulfur dioxide.[17] The Fe–Fe bond of the latter type of complex also may be protonated[18] and mercurated.[19] Noteworthy also is the sodium reduction of the diphenylphosphido-bridged complex $(\mu\text{-}Ph_2P)_2Fe_2(CO)_6$, which resulted in formation of the reactive iron-centered dianion, III.[20] Thus there is ample precedent for reactions at a bent Fe–Fe bond of the type found in $(\mu\text{-}S_2)Fe_2(CO)_6$.



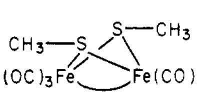
III

On the other hand, the S–S bond of organic disulfides is well-known to be reactive toward diverse nucleophilic, electrophilic, and radical reagents.[21] Some typical reactions which might be of interest in connection with the problem under discussion are shown in Scheme II: reduction to the alkali metal mercaptide with an alkali metal;[22] nucleophilic cleavage by organolithium[23] and Grignard reagents[24] (and by a large number of other nucleophiles[21]); free-radical-induced insertion of acetylenes[25] and olefins;[26] and insertion of low-valent, coordinatively unsaturated transition-metal species.[27]

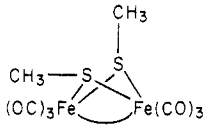
To begin this experimental investigation, we chose one of the reactions common to both the bent Fe–Fe bond of dibridged $Fe_2(CO)_6$ complexes and the S–S bond of organic disulfides, reduction by metallic sodium.

Results and Discussion

In our initial experiment, a red solution of $(\mu\text{-}S_2)Fe_2(CO)_6$ in tetrahydrofuran (THF) (under nitrogen) was treated with an excess of sodium dispersion for 4 h at room temperature. The resulting dark red-brown solution was filtered (under nitrogen), and to the filtrate was added an excess of iodomethane. Evaporation of the reaction mixture and purification of the residue by column chromatography gave $(\mu\text{-}CH_3S)_2Fe_2(CO)_6$ in 31% yield. Use of a longer column separated this product into two geometrical isomers, IVa and IVb (present in 1:2.7 ratio, by NMR).[28]



IVa, e,e



IVb, a,e

A 3:1 mixture of these isomers was obtained in 34% yield when sodium sand was used to reduce $(\mu\text{-}S_2)Fe_2(CO)_6$. A mixture of these isomers had been isolated by King in 1962 from the reaction of CH_3SSCH_3 with $Fe_3(CO)_{12}$,[30,31] and their structures had been inferred to those shown by Dahl and Wei[32] on the basis of their structure determination of $(\mu\text{-}C_2H_5S)_2Fe_2(CO)_6$ and King's ^1H NMR data. The Fe_2S_2 core geometries in $(\mu\text{-}S_2)Fe_2(CO)_6$ and $(\mu\text{-}CH_3S)_2Fe_2(CO)_6$ can be seen to be very similar (for a figure showing a comparison of $(\mu\text{-}S_2)Fe_2(CO)_6$ and $(\mu\text{-}C_2H_5S)_2Fe_2(CO)_6$, see ref 6). This close structural relationship between our

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(15) (a) Davidson, J. L.; Harrison, W.; Sharp, D. W. A.; Sim, G. A. *J. Organomet. Chem.* **1972**, *46*, C47. (b) Davidson, J. L.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* **1975**, 2283. (c) Mathieu, R.; Poilblanc, R. *J. Organomet. Chem.* **1977**, *142*, 351.

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(21) (a) Parker, A. J.; Kharasch, N. *Chem. Rev.* **1959**, *59*, 583. (b) Kharasch, N.; Parker, A. J. *Q. Rep. Sulfur Chem.* **1966**, *1*, 285. (c) Reid, E. E., "Organic Chemistry of Bivalent Sulfur"; Chemical Publishing Co.: New York, 1960; Vol. 1, pp 126–127. (d) Field, L. In "Organic Chemistr of Sulfur"; Oae, S., Ed.; Plenum Press: New York, 1977; Chapter 7.

(22) Moses, C. G.; Reid, E. E. *J. Am. Chem. Soc.* **1926**, *48*, 776.

(23) Schönberg, A.; Stephenson, A.; Kaltschmitt, H.; Petersen, E.; Schulten, H. *Ber.* **1933**, *66*, 237.

(24) (a) de Lattre, J. *Bull. Soc. Chi. Belg.* **1912**, *26*, 323. (b) Wuyts, H., *Bull. Soc. Chim. Fr.* [3] **1906**, *35*, 166.

(25) Heiba, E. I.; Dessau, R. M. *J. Org. Chem.* **1967**, *32*, 3837.

(26) See ref 21c, p 377, and references cited therein.

(27) (a) King, R. B. *Inorg. Chem.* **1963**, *2*, 641. (b) Hayter, R. G.; Humiec, F. S. *J. Inorg. Nucl. Chem.* **1964**, *26*, 807. (c) Davison, A.; Edelstein, N.; Holm, R. H.; Maki, A. H. *Inorg. Chem.* **1964**, *3*, 817. (d) Lam, C. T.; Senoff, C. V. *Can. J. Chem.* **1972**, *50*, 1868. (e) Zanella, R.; Ros, R.; Graziani, M. *Inorg. Chem.* **1973**, *12*, 2737. (f) de Croon, M. H. J. M.; van Gaal, H. L. M.; van der Ent, A. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 1081. (g) Markham, S. J.; Chung, Y. L.; Branum, G. D.; Blake, D. M. *J. Organomet. Chem.* **1976**, *107*, 121. (h) Teo, B. K.; Wudl, F.; Marshall, J. H.; Kruger, A. *J. Am. Chem. Soc.* **1977**, *99*, 2349. (i) Teo, B. K.; Snyder-Robinson, P. A. *Inorg. Chem.* **1978**, *17*, 3489. (j) Teo, B. K.; Snyder-Robinson, P. A. *J. Chem. Soc., Chem. Commun.* **1979**, 255. (k) Gal, A. W.; Gosselink, J. W.; Vollenbroek, F. A. *Inorg. Chim. Acta* **1979**, *32*, 235.

(28) IVa has both CH_3 substituents in equatorial position, and IVb has one equatorial CH_3 and one axial CH_3. Following Shaver et al.,[29] we shall designate isomers of type IVa "e,e" and those of type IVb "a,e". Because of nonbonded repulsions, the third, type of isomer, the one with both alkyl groups in axial positions, a,a, has not been encountered.

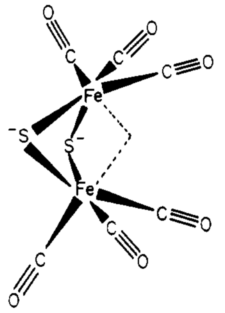
(29) Shaver, A.; Fitzpatrick, P. J.; Steliou, K.; Butler, I. S. *J. Am. Chem. Soc.* **1979**, *101*, 1313.

(30) King, R. B. *J. Am. Chem. Soc.* **1962**, *84*, 2460.

(31) A number of routes, all involving reactions of iron carbonyls with organosulfur compounds (RSH, RSR, RSSR, and others) have served in the preparation of diverse $(\mu\text{-}RS)_2Fe_2(CO)_6$ complexes; cf. "Gmelin Handbuch der Anorganischen Chemie", 8th ed., Fe; Organoiron Compounds, Part C1 (Binuclear Compounds 1); Springer-Verlag: Berlin, 1979; pp 74–122.

(32) Dahl, L. F.; Wei, C.-H. *Inorg. Chem.* **1963**, *2*, 328.

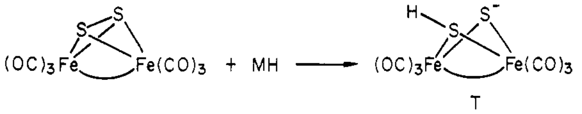
starting material and the isolated product suggested that the intermediate which was formed in the reduction and reacted with iodomethane to give the final product was the novel sulfur-centered dianion V, in which the two $Fe(CO)_3$


V

units are connected by two bridging sulfide anions and a bent Fe–Fe bond.[33] The formation of V can be viewed as involving transfer of two electrons from sodium to $(\mu\text{-}S_2)Fe_2(CO)_6$, the first electron-transfer step giving the radical anion, the second the dianion.

When the solution of dianion V prepared by sodium reduction of $(\mu\text{-}S_2)Fe_2(CO)_6$ was treated with iodoethane, a 2:1 mixture of the a,e and e,e isomers of the known $(\mu\text{-}C_2H_5S)_2Fe_2(CO)_6$ was obtained in 29% yield. Such rather low product yields were not satisfactory for the purposes of the further development of the chemistry of dianion V, and, for this reason, a better route to V was sought.

Metal hydrides, e.g., lithium aluminum hydride,[35] cleave the S–S bond of organic disulfides, so there was a good possibility that the S–S bond of $(\mu\text{-}S_2)Fe_2(CO)_6$ might undergo nucleophilic cleavage, as shown in eq 2, on treatment with a suitable metal hydride. In a subsequent step (eq 3), deprotonation of the monoanionic intermediate VI by a second equivalent of metal hydride would then give the dianion, V. An initial experiment in which potassium hydride in THF[36] was used at room temperature was successful, giving the dianion V whose subsequent reaction with iodomethane produced $(\mu\text{-}CH_3S)_2Fe_2(CO)_6$ (a,e/e,e = 1.4) in 53% yield. (No reaction occurred between KH and $(\mu\text{-}S_2)Fe_2(CO)_6$ at −78 °C.) A similar reaction in which iodoethane was the electrophile used resulted in formation of $(\mu\text{-}C_2H_5S)_2Fe_2(CO)_6$ in 46% yield.



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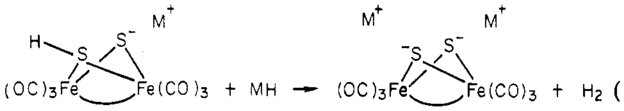
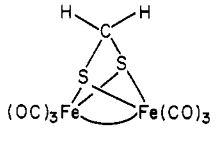


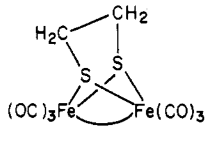
(3)

Still better results were obtained when lithium triethylborohydride ("Super-Hydride"; Aldrich Chemical Co.), which is soluble in THF, was used. This reagent also was known, through the work of Gladysz and his coworkers, to cleave organic disulfides to form lithium thiolates,[38] as well as dinuclear metal carbonyls to give metal-centered anions.[39] The addition of 2 molar equiv of $LiBEt_3H$ to a THF solution of $(\mu\text{-}S_2)Fe_2(CO)_6$ at −78 °C produced dianion V in essentially quantitative yield. Addition of iodomethane to a dianion solution prepared in this manner gave $(\mu\text{-}CH_3S)_2Fe_2(CO)_6$ in 92% isolated yield. The color changes which occur when $LiBEt_3H$ is used are much more pronounced: the red $(\mu\text{-}S_2)Fe_2(CO)_6$ solution first becomes a deeper red as the hydride is added and then dark emerald green when exactly 1 molar equiv of $LiBEt_3H$ has been added (corresponding to eq 2). Addition of the second equivalent of the hydride produces no further color change. Reaction of the green solution with an electrophile usually causes a final color change to red. Dianion V derived product yields were lower (e.g., 63% when CH_3I was the electrophile used) when the formation and reactions of the dianion were carried out at room temperature. This observation, as well as the low yields obtained in the room temperature generation of the dianion using KH, suggests that dianion V is of limited stability in solution at room temperature.

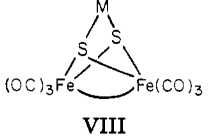
In the generation of $[(\mu\text{-}S)_2Fe_2(CO)_6]^{2-}$ by the reaction of $(\mu\text{-}S_2)Fe_2(CO)_6$ with 2 molar equiv of $LiBEt_3H$, 2 mol of triethylborane are released. In most cases, triethylborane does not interfere in the subsequent reactions of dianion V. However, in reactions in which mercuric chloride or alkylmercuric chlorides were the electrophiles used, ethyl group transfer from boron to sulfur was a complicating process.[40] In dealing with this problem, we found that $LiAl(OBu\text{-}t)_3H$ and $KB(sec\text{-}Bu)_3H$ served equally well as hydride sources for the preparation of dianion V.[40]

The availability of this high yield, complex hydride based route for the preparation of $[(\mu\text{-}S)_2Fe_2(CO)_6]^{2-}$ allowed fuller development of its chemistry. Reactions with simple organic halides occur readily; e.g., $(\mu\text{-}PhCH_2S)_2Fe_2(CO)_6$ was prepared in 83% yield, $(\mu\text{-}CH_2{=}CHCH_2)_2Fe_2(CO)_6$ in 86% yield. Reactions of dianion V with diiodomethane and 1,2-dibromoethane gave cyclic products, VIIa and VIIb, in yields of 25% and 47%, respectively.


VIIa


VIIb

The $[(\mu\text{-}S)_2Fe_2(CO)_6]^{2-}$ anion also is a useful reagent for the synthesis of multinuclear metal (metalloid)–sulfur complexes of type VIII by reaction with main group and


VIII

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[33] The possibility of such a reduction product of $(\mu\text{-}S_2)Fe_2(CO)_6$ and its formal similarity to the dianion of Roussin's red salt, $[(\mu\text{-}S)_2Fe_2(NO)_4]^{2-}$, was pointed out by Brendel in his dissertation.[3] For our initial results of a comparative study of the reactions of $[(\mu\text{-}S)_2Fe_2(CO)_6]^{2-}$ and $[(\mu\text{-}S)_2Fe_2(NO)_4]^{2-}$, see ref 34.

[34] Seyferth, D.; Gallagher, M. K. *J. Organomet. Chem.* **1981**, *218*, C5.

[35] (a) Arnold, R. C.; Lien, A. P.; Alm, R. M. *J. Am. Chem. Soc.* **1950**, *72*, 731. (b) Strating, J.; Backer, H. J. *Rec. Trav. Chim. Pays-Bas* **1950**, *69*, 909.

[36] Potassium hydride also cleaves transition metal–metal bonds,[37] so, in principle, we were dealing here also with a competitive situation, possible nucleophilic attack at the S–S or the Fe–Fe bond.

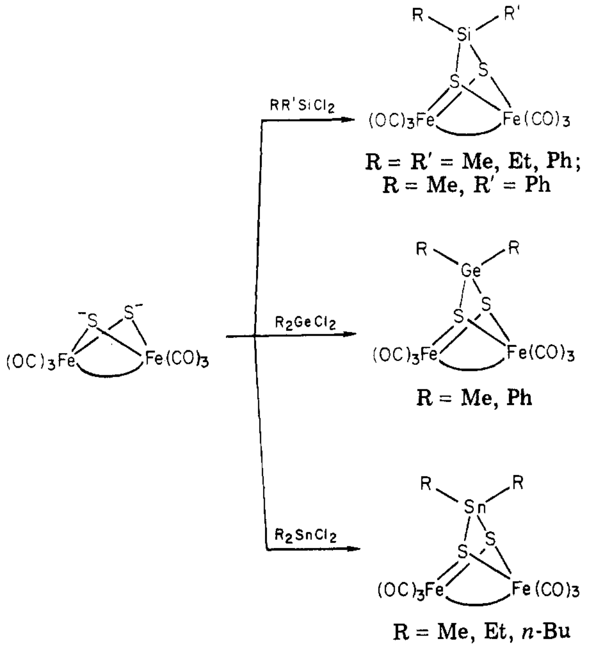
[37] Inkrott, K.; Goetze, R.; Shore, S. G. *J. Organomet. Chem.* **1978**, *154*, 337.

[38] Gladysz, J. A.; Wong, V. K.; Jick, B. S. *Tetrahedron* **1979**, *35*, 2329.

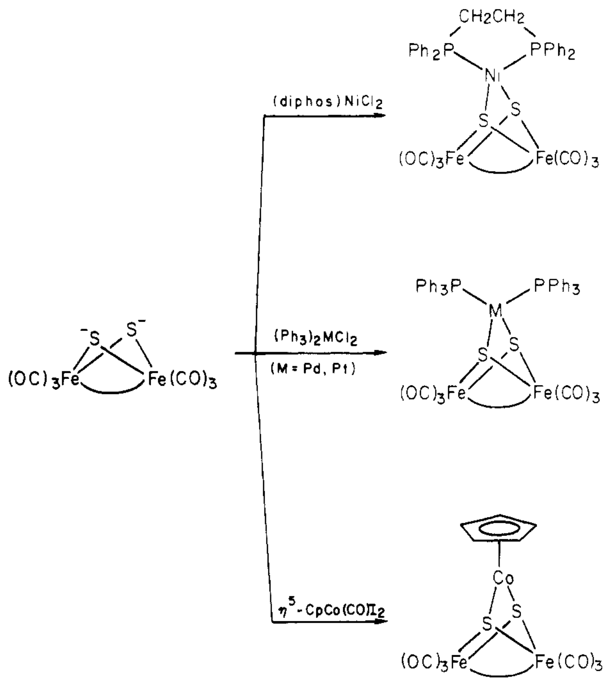
[39] Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553.

[40] Seyferth, D.; Song, L.-C.; Henderson, R. S. *J. Am. Chem. Soc.* **1981**, *103*, 5103.

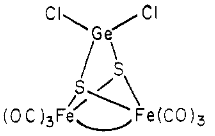
Scheme III



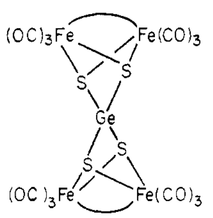
Scheme IV



transition-element dihalides. In the main group series, we have prepared such $S_2Fe_2(CO)_6$ derivatives of silicon, germanium, and tin as shown in Scheme III. Good yields were obtained in all cases. As expected,[41] the complexes containing Si–S bonds were extremely sensitive to hydrolysis by atmospheric moisture. In contrast, those complexes containing Sn–S bonds were very stable and resistant to atmostpheric-moisture hydrolysis, an observation in line with the known hydrolytic and thermodynamic stability of the Sn–S bond.[42] Of particular interest were the reactions of dianion V with $GeCl_4$ in view of the prior Russian work on the reactions of $HGeCl_3$–Lewis base adducts with $(\mu\text{-}S_2)Fe_2(CO)_6$.[12] The reaction of dianion V with an excess of germanium tetrachloride gave $(\mu\text{-}Cl_2GeS_2)Fe_2(CO)_6$, IX, in 78% yield. The slow addition of 0.5 molar equiv of $GeCl_4$ to a solution of dianion V resulted in formation of $GeS_4Fe_4(CO)_{12}$, whose structure we assumed to be one with four Ge–S bonds, X. These



IX



X

products, IX and X, had the same stoichiometry as those obtained in the $HGeCl_3$–Lewis base adduct/$(\mu\text{-}S_2)Fe_2(CO)_6$ reactions. In order to make a detailed comparison, we prepared samples of the latter using the reported procedure;[12] these were found to be identical in all respects with the products obtained in the $(\mu\text{-}S)_2Fe_2(CO)_6{}^{2-}/GeCl_4$ reactions. Thus the "insertion" of $GeCl_2$ occurred into the S–S bond, not the Fe–Fe bond, of $(\mu\text{-}S_2)Fe_2(CO)_6$.[43] This conclusion was reached independently on the basis of an X-ray diffraction study by Struchkov and his co-workers,[44] who showed the $GeS_4Fe_4(CO)_{12}$ obtained in the insertion reaction to have the structure indicated in X.

The silicon-spiro complex analogous to X was prepared by reaction of 0.5 molar equiv of silicon tetrachloride with dianion V in 99% yield. This compound was prepared independently by the Russian group by the action of $HSiCl_3$ and Et_3N on $(\mu\text{-}S_2)Fe_2(CO)_6$,[44] a reaction very likely involving initial nucleophilic cleavage of the S–S bond by the trichlorosilyl anion. A reaction of dianion V with 0.5 molar equiv of $SeCl_4$ resulted in the usual color change from green to red, and an air-sensitive, dark red liquid could be isolated in 78% yield. The IR spectrum of the product was in agreement with the presence of the usual $Fe_2(CO)_6$ unit. However, this material was so extremely malodorous (much more so than the malodorous $(\mu\text{-}RSe)_2Fe_2(CO)_6$ complexes[45]) that further characterization data were not sought. We assume that the product is the Se(IV) analogue of X.

When dianion V prepared by reaction of 2 equiv of $LiBEt_3H$ with $(\mu\text{-}S_2)Fe_2(CO)_6$ was treated with various transition-metal dihalides in THF at −78 °C, no reaction usually was observed. However, reaction did occur when a small amount of acetone was added to the mixture with subsequent slow warming to room temperature. The reactions carried out are outlined in Scheme IV. The product yields in most cases were excellent. Reactions of dianion V with ligand-free metal dihalides also were studied, using an excess of the dianion (eq 4). The anions

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(41) Pawlenko, S. "Houben-Weyl Methoden der Organischen Chemie", 4th ed.; Georg-Thieme Verlag: Stuttgart, 1980; Vol. XIII/5, pp 212–225.

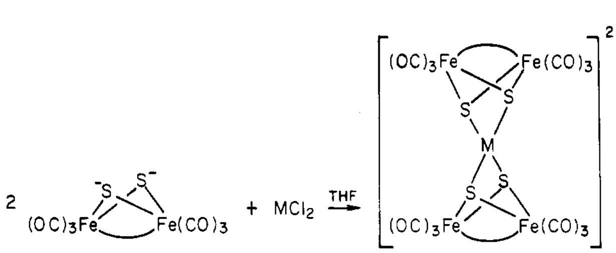
(42) Bähr, G.; Pawlenko, S. "Houben-Weyl Methoden der Organischen Chemie", 4th ed.; Georg-Thieme Verlag: Stuttgart, 1978; Vol. XIII/6, pp 335–353.

(43) The mechanism of formation of IX by reaction of $(\mu\text{-}S_2)Fe_2(CO)_6$ with $HGeCl_3{\cdot}2Et_2O$ and of X by reaction of the S_2–iron complex with $HGeCl_3{\cdot}Et_3N$ is by no means clear. In both cases, the $HGeCl_3$–Lewis base adduct is a source first of the $GeCl_3{}^-$ anion en route to $GeCl_2$. $GeCl_2$ insertion into the S–S bond of $(\mu\text{-}S_2)Fe_2(CO)_6$ certainly is a possibility in either case. However, an alternative mechanism, one involving initial nucleophilic cleavage of the S–S bond by $GeCl_3{}^-$ to give $[(\mu\text{-}S)(\mu\text{-}Cl_3GeS)Fe_2(CO)_6]^-$ and subsequent intramolecular displacement of Cl from the $SGeCl_3$ group by the bridging S^- ligand to give IX, also is a possibility. This question requires further experimental study.

(44) Nametkin, N. S.; Tyurin, V. D.; Aleksandrov, G. G.; Kuz'min, O. V.; Nekhaev, A. I.; Andrianov, V. G.; Mavlonov, M.; Struchkov, Yu. T. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 1353.

(45) Seyferth, D.; Henderson, R. S. *J. Organomet. Chem.* **1981**, *204*, 333.

XII were isolated as the stable tetraethylammonium salts.[46]



(4)

XII, M = Ni, Pd, Pt

Very likely, many other main group and transition element halides will react with dianion V to produce products of type VIII. During the course of this work, however, unexpected results were obtained in some cases. In view of the readiness with which $[(\mu\text{-S})_2Fe_2(CO)_6]^{2-}$ reacts with Me_2SnCl_2 and the stability of the $(\mu\text{-}Me_2SnS)Fe_2(CO)_6$ which results, one might expect that dianion V will also react with Me_3SnCl to give $(\mu\text{-}Me_3SnS)_2Fe_2(CO)_6$ and that this compound also will be stable. This was not the case. Addition of 2 equiv of Me_3SnCl to a solution of dianion V at −78 °C did result in the usual color change from green to red, but no stable products could be isolated. Similar attempts to prepare $(\mu\text{-}Ph_3MS)_2Fe_2(CO)_6$ (M = Sn, Pb) complexes also were unsuccessful. However, it was possible to prepare $(\mu\text{-RHgS})_2Fe_2(CO)_6$ (R = Me and Et) by the dianion route, albeit in only low yield.[40] This suggests that complexes of type $(\mu\text{-}R_3MS)_2Fe_2(CO)_6$ may be unstable because of steric problems.

We also were interested in preparing complexes in which the two $Fe(CO)_3$ units were bridged by a longer sulfur chain, e.g., $(S_3)Fe_2(CO)_6$ and $(S_4)Fe_2(CO)_6$, by appropriate reactions of $[(\mu\text{-S})_2Fe_2(CO)_6]^{2-}$. When SCl_2 or S_2Cl_2 was added to a solution of this dianion at −78 °C, a green-to-red color change again took place, but the only product which could be isolated was $(\mu\text{-}S_2)Fe_2(CO)_6$ (in >90% yield). Examination by mass spectrometry of the crude product, an oily red solid, obtained from such a reaction of dianion V with SCl_2 by careful evaporation of solvent, showed only the presence of the S_2 ligand complex. Similar results were obtained when $SOCl_2$ or SO_2Cl_2 was added to the dianion solution. These observed reactions find their counterparts in organosulfur chemistry. Sulfur extrusion from organic polysulfides (e.g., RSSSR → RSSR + S) is a known[21c] process, and the coupling of organic thiols by the action of sulfuryl[47] and thionyl chloride[47a,48] is a known prepartion of organic disulfides.

In summary, the results reported here show a marked similarity between the chemistry of $(\mu\text{-}S_2)Fe_2(CO)_6$ and organic disulfides: both are reduced by alkali metals; both undergo nucleophilic S–S cleavage on reaction with simple and complex metal hydrides. Subsequent papers in this series will bring details of other reactions of $(\mu\text{-}S_2)Fe_2(CO)_6$, some of which provide further examples of a striking similarity to those of organic disulfides.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified tank nitrogen unless otherwise indicated. Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl. Reagent grade acetone, pentane, dichloromethane, and hexane were deoxygenated by bubbling nitrogen through them for 15 min prior to use. The progress of the reactions was monitored by thin-layer chromatography (TLC) (J. T. Baker silica gel 1B). Since reactions yielded only a single product, full-scale column chromatography was not required. Instead, filtration chromatography, in which the reaction products were dissolved in a suitable solvent and poured on top of a bed of Mallinckrodt 100-mesh silicic acid (ca. 200 mL) in a 350-mL glass-frit filter funnel, was used in most cases. The eluting solvent then was passed through with suction filtration.

Infrared spectra were obtained with a Perkin-Elmer Model 457A double-beam grating infrared spectrophotometer. Proton NMR spectra were recorded on either a Varian Associates T60 or a Hitachi-Perkin-Elmer R-20B spectrometer, both operating at 60 MHz. Chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane. Chloroform or dichloromethane generally was used as an internal standard. Mass spectra were obtained with a Varian MAT-44 instrument operating at 70 eV. Molecular ions were assigned on the basis of the most abundant natural isotope(s) (^{56}Fe, ^{117}Sn and ^{119}Sn, etc.). Melting points were determined on analytically pure samples using a Büchi capillary melting point apparatus and are uncorrected. Microanalyses were performed by Scandinavian Microanalytic Laboratory, Herlev, Denmark.

All of the reported data were determined on recrystallized samples. The reported isomer ratios are of these recrystallized samples because the solids collected after filtration chromatography were not quite pure enough to obtain excellent NMR spectra in most cases. However, because these samples were recrystallized from only a small amount of pentane (5–15 mL), they do closely indicate the true isomer ratio. There may be a slight discrepancy between the actual and the recrystallized isomer ratios because of the varying solubilities of the individual isomers.

Preparation of μ-Dithio-bis(tricarbonyliron). $(\mu\text{-}S_2)Fe_2(CO)_6$ was prepared as described by Brendel[3] and by Hieber and Gruber[4] with some modification. All solvents and solutions were purged with nitrogen before use. A 3-L, three-necked, round-bottomed flask equipped with a serum cap, a mechanical stirrer, and a nitrogen inlet tube was flushed with nitrogen and charged with 200 mL of reagent grade methanol and 35 mL (250 mmol) of iron pentacarbonyl (Alfa). After the mixture had been cooled to 0 °C, 80 mL of 50% aqueous KOH (w/v) was added. A solution equivalent to 416 mmol of Na_2S_5 was prepared by combining 100 g (416 mmol) of $Na_2S\cdot 9H_2O$ (Alfa), 55 g (1.72 mol) of sublimed sulfur, 10 mL of 50% aqueous KOH, and 400 mL of distilled water in a 1-L beaker. After it had been stirred on a hot plate, the deep red Na_2S_5 solution was transferred to a 1-L flask, degassed, and cooled to 0 °C. The Na_2S_5 solution then was poured into the vigorously stirred reaction solution through a funnel against a countercurrent flow of nitrogen. A mildly exothermic reaction resulted, with brisk CO evolution and formation of a dark red solution. The reaction mixture was stirred at 0 °C for 2 h. The serum cap then was replaced by an addition funnel containing a degassed solution of HCl (200 mL of 37% HCl and 200 mL of distilled H_2O). *Cautious* acidification of the reaction mixture resulted in the evolution of H_2S and formation of a brown precipitate and a colorless solution. The brown solid was collected on a 350-mL coarse frit in air, washed with 300 mL of distilled H_2O, and dried under vacuum overnight. It then was divided into three portions. Each portion was extracted twice by stirring for 15 min in 600 mL of pentane. After combining the extracts, solvent was removed on a rotary evaporator, leaving a red-brown solid which was dried on the vacuum line. This solid was a mixture of $(\mu\text{-}S_2)Fe_2(CO)_6$ and $S_2Fe_3(CO)_9$. Sublimation at 40 °C (0.1 mm) for 10 h yielded 10.33 g (30 mmol, 24% based on $Fe(CO)_5$) of μ-dithio-bis(tricarbonyliron) as ruby-red, air-stable crystals, mp 46–47 °C (lit.[3,4] mp 46.5 °C), whose infrared spectrum (in CCl_4)

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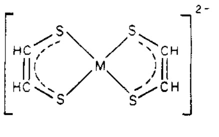
[46] If $(\mu\text{-}S_2)Fe_2(CO)_6$ is considered to be an inorganic analogue of organic disulfides, then the anions XII could be considered to be "inorganic" analogues of 1,2-dithiolene complexes, e.g.



Heber, R.; Hoyer, E. *J. Prakt. Chem.* **1973**, *315*, 106. Hoyer, E.; Dietzsch, W.; Hennig, H.; Schroth, W. *Chem. Ber.* **1969**, *102*, 603.

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(48) (a) Holmberg, B. *Justus Liebigs Ann. Chem.* **1908**, *359*, 81. (b) Holmberg, B. *Ber.* **1910**, *43*, 226.

showed bands at 2085 s, 2044 vs, and 2006 vs cm^{-1} in the terminal CO region. Mass spectrum, *m/z* (rel intensity) 344 (M$^+$), 316 (M$^+$ − CO), 288 (M$^+$ − 2CO), 260 (M$^+$ − 3CO), 232 (M$^+$ − 4CO), 204 (M$^+$ − 5CO), 176 (S_2Fe_2), 144 (SFe_2), 112 (Fe_2), 88 (SFe), and 56 (Fe).

Reaction between μ-Dithio-bis(tricarbonyliron), Sodium, and Iodomethane. A 200-mL, three-necked, round-bottomed flask fitted with a stir-bar, a nitrogen inlet tube, and two serum caps was flushed with nitrogen and charged with 0.31 g (6.74 mmol) of a 50% sodium/paraffin dispersion. The paraffin was removed by washing with three 20-mL portions of degassed pentane; then 40 mL of THF was added. To this was added, via cannula, a solution of 1.00 g (2.91 mmol) of (μ-S_2)$Fe_2(CO)_6$ in 20 mL of THF. The resulting deep red reaction mixture was stirred for 4 h at room temperature while being monitored by TLC. The dark, red-brown solution was filtered under nitrogen into a Schlenk flask and then was treated with 0.9 mL (14.4 mmol) of MeI (Aldrich). No significant color change was observed. After the mixture had been stirred overnight, solvent was removed on a rotary evaporator, leaving a brown solid which was chromatographed (silicic acid–pentane) to yield 0.339 g (0.91 mmol, 31%) of (μ-MeS)$_2Fe_2(CO)_6$ as a red, air-stable solid which was a mixture of two isomers. The product was recrystallized from pentane: IR (CCl_4) 2930 m, 2855 w, 1427 m, 1316 m, 1304 w, 1259 w, 950 m, 690 w, 615 m, 560 m, cm^{-1}; terminal carbonyl region: 2074 s, 2037 vs, 2000 vs, 1990 vs cm^{-1}; NMR (CCl_4) δ 1.62 and 2.13 (s, 2.74 H, a,e isomer, CH_3) and δ 2.07 ppm (s, 1 H, e,e isomer, CH_3); mass spectrum, *m/z* (rel intensity) 374 (M$^+$, 2.3), 346 (M$^+$ − CO, 9.4), 318 (M$^+$ − 2CO, 5.7), 290 (M$^+$ − 3CO, 8.5), 262 (M$^+$ − 4CO, 5.5), 234 (M$^+$ − 5CO, 8.3), 206 (M$^+$ − 6CO, 38.6), 191 (MeS_2Fe_2, 35.5), 176 (S_2Fe_2, 49.1), 144 (SFe_2, 34.2), 112 (Fe_2, 12.9), 88 (SFe, 15.1), and 56 (Fe, 100).

When (μ-MeS)$_2Fe_2(CO)_6$ was rechromatographed by using a longer column, the two isomers were separated. Pentane eluted a red band (a,e isomer) and then an orange band (e,e isomer). Each was recrystallized from pentane.

a,e Isomer: red, air-stable crystals, mp 65–67 °C (lit.[30] 65–67.5 °C); IR (CCl_4) terminal carbonyl region: 2080 s, 2050 vs, 1990 vs cm^{-1}; NMR (CCl_4) δ 1.62 and 2.13 ppm (s, CH_3).

e,e Isomer: orange-red, air-stable crystals, mp 101.5–102.5 °C (lit.[30] 101.5–103.5 °C); IR (CCl_4) terminal carbonyl region: 2070 s, 2040 vs, 1990 vs cm^{-1}; NMR (CCl_4) δ 2.07 ppm (s, CH_3).

A similar reaction in which iodoethane was added to the reagent solution gave (μ-EtS)$_2Fe_2(CO)_6$, a dark red, air-stable solid which was a mixture of isomers, in 29% yield. After recrystallization from pentane the isomer ratio was a,e:e,e = 2. The melting point was 69–74 °C (lit.[49] mp (a,e isomer) 75–76 °C); 250-MHz ^{1}H NMR ($CDCl_3$) δ 1.087, 1.303, 1.355 (three t, J = 7.5 Hz, 3 H, CH_3) and 2.115, 2.418, 2.426 ppm (three q, 2 H, CH_2).

When sodium sand[50] was used to generate dianion V instead of sodium dispersion, the yield of (μ-MeS)$_2Fe_2(CO)_6$ was 34% (a,e/e,e = 3.1) when the reagent solution was quenched with iodomethane.

Reactions of (μ-KS)$_2$Fe$_2$(CO)$_6$. (a) With Alkyl Iodides. In a glovebox a 100-mL, three-necked, round-bottomed flask was charged with 0.274 g (6.85 mmol) of KH (Alfa) and then equipped with a stir-bar, two serum caps, and a nitrogen inlet tube. THF (20 mL) was added by syringe, and the reaction mixture was stirred to effect solution. A solution of 0.943 g (2.74 mmol) of (μ-S_2)$Fe_2(CO)_6$ in 30 mL of THF was cannulated into the reaction flask. Immediately, a dark red solution was formed and slight gas evolution was observed. The reaction mixture was stirred for 4 h at room temperature with monitoring by TLC. The dark, red-brown solution was filtered under nitrogen into a Schlenk flask. The filtrate was quenched with 0.90 mL (14.4 mmol) of MeI and stirred overnight. Solvent was removed on a rotary evaporator, leaving a brown solid which was chromatographed (silicic acid–pentane) to yield 0.540 g (1.44 mmol, 53% yield) of (μ-MeS)$_2Fe_2(CO)_6$ (a,e/e,e = 1.4).

A similar reaction in which iodoethane was added to the dianion solution gave (μ-EtS)$_2Fe_2(CO)_6$ in 45% yield (a,e/e,e = 3.7).

(b) With Other Substrates. Addition of 3.66 mmol of dimethyltin dichloride to a filtered solution of (μ-KS)$_2Fe_2(CO)_6$ (from 3.66 mmol of (μ-S_2)$Fe_2(CO)_6$ and 9.15 mmol of KH) gave (μ-Me_2SnS_2)$Fe_2(CO)_6$ in 45% yield. A similar reaction of (μ-KS)$_2Fe_2(CO)_6$ with Me_2GeCl_2 led to the isolation of (μ-Me_2GeS_2)$Fe_2(CO)_6$ in 53% yield. The addition of 2.8 mmol of $GeCl_4$ to a dianion solution prepared from 2.8 mmol of (μ-S_2)$Fe_2(CO)_6$ and 7.6 mmol of KH gave Ge[$S_2Fe_2(CO)_6$]$_2$ in 32% yield, while the addition of a THF solution of (μ-KS)$_2Fe_2(CO_6)$ (from 3.35 mmol of (μ-S_2)$Fe_2(CO)_6$ and 8.4 mmol of KH) to 23.5 mmol of $GeCl_4$ produced (μ-Cl_2GeS_2)$Fe_2(CO)_6$ in 51% yield.

Characterizing data for these products are given in the following sections.

Reactions of (μ-LiS)$_2$Fe$_2$(CO)$_6$ Prepared by the Lithium Triethylborohydride Procedure. (a) With Alkyl Halides. A 200-mL Schlenk flask equipped with serum cap and a stir-bar was charged with 1.00 g (2.91 mmol) of (μ-S_2)$Fe_2(CO)_6$ and then was flushed with nitrogen. THF (75 mL) was added and the reaction solution was cooled to −78 °C (dry ice/acetone). By syringe, 6.0 mL of 1 M $LiEt_3BH$ in THF (Aldrich) was added in 0.5-mL aliquots every 5 min. At the midpoint of the addition the reaction solution turned from red to a dark emerald green; for the rest of the addition it remained green. To this was added (at −78 °C) 0.90 mL (14.4 mmol) of MeI (Aldrich). The dry ice/acetone bath was removed and the reaction mixture was stirred for 1 h. The color changed back to red. Solvent was removed on a rotary evaporator, leaving a dark red solid which was chromatographed (silicic acid–10% CH_2Cl_2/pentane) to give 1.00 g (2.67 mmol, 92% yield) of (μ-MeS)$_2Fe_2(CO)_6$ (a,e/e,e = 4.4).

Similar reactions were carried out in which other alkyl halides or dihalides were added to a solution of (μ-LiS)$_2Fe_2(CO)_6$ prepared in this manner.

Reaction with iodoethane (12.5 mmol) with the dianion prepared from 2.91 mmol of (μ-S_2)$Fe_2(CO)_6$ and 6 mmol of $LiBEt_3H$ in 85 mL of THF at −78 °C gave 1.125 g (96%) of (μ-EtS)$_2Fe_2(CO)_6$ (a,e/e,e = 2.7).

When 8.0 mmol of $PhCH_2Cl$ was added to a solution of dianion V (from 2.91 mmol of (μ-S_2)$Fe_2(CO)_6$) at −78 °C, the green color was not discharged within 5 min. The reaction mixture was still green after 1 h at −78 °C; it was stirred at −78 °C for another 3 h and then was allowed to warm slowly to room temperature overnight. A red reaction mixture resulted. Removal of solvent at reduced pressure left a red-brown oil which was subjected twice to filtration chromatography (silicic acid–10% CH_2Cl_2/pentane) and cooled in the refrigerator until crystallization occurred. The red solid (1.71 g, 83%) was recrystallized from pentane to give red crystals of (μ-$PhCH_2S$)$_2Fe_2(CO)_6$: mp 92–92.5 °C (lit.[49] mp 91–92 °C); IR (CCl_4) (terminal CO region) 2074 s, 2039 vs, 2003 vs, 1991 vs cm^{-1}; 250-MHz ^{1}H NMR ($CDCl_3$) δ 3.240, 3.600, 3.668 (s, CH_2), and 7.333–7.814 (m, Ph). The 3.240- and 3.668-ppm signals were of equal intensity and are assigned to the axial and equatorial CH_2 groups, respectively, of the a,e isomer. The 3,600-ppm signal is assigned to the e,e isomer CH_2 group. The integrated intensities of these signals give an a,e/e,e ratio of 7.1.

The reaction of dianion V (2.91 mmol) and 8 mmol of allyl bromide, carried out as described above, did not appear to occur at −78 °C since the color change to red took place only at −15 °C while the reaction mixture was allowed to warm slowly to room temperature. The reaction mixture was evaporated at reduced pressure, and the residue was taken up in hexane and filtered. The hexane solution was distilled (short path) to give a red, air-sensitive oil, (μ-$CH_2{=}CHCH_2S$)$_2Fe_2(CO)_6$, bp 103–105 °C (0.2 mmHg); IR (CCl_4) (terminal CO region) 2075 s, 2040 vs, 2003 vs, 1992 vs cm^{-1}; 60-MHz ^{1}H NMR (CCl_4) δ 2.74 and 3.06 (doublets, J = 6.6 Hz, CH_2) and 4.92–6.04 ppm (complex m, $CH{=}CH_2$). The CH_2 signals are assignable to the a,e isomer, but since the integrated intensities of the doublets were not quite equal (I(3.06 ppm) > I(2.74 ppm) signal), we conclude that a small quantity of the e,e, isomer must also be present.

(b) With Diodomethane. The dianion solution was prepared by the addition of 6.0 mL of a 1 M solution of $LiEt_3BH$ to a solution of 2.91 mmol of (μ-S_2)$Fe_2(CO)_6$ in 75 mL of THF at −78 °C. To the reagent solution was added 8.1 mmol of CH_2I_2 (Aldrich). After the mixture had been stirred for 1 h at −78 °C, TLC monitoring showed no reaction. The reaction mixture was warmed to room temperature while being stirred an additional

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(50) Jolly, W. L. "The Synthesis and Characterization of Inorganic Compounds"; Prentice-Hall: Englewood Cliffs, NJ, 1970; p 476.

2 h. Solvent was removed from the red-black solution on a rotary evaporator, leaving a black oil which was chromatographed (silicic acid–pentane) to give 0.259 g (0.723 mmol, 25% yield) of (μ-$CH_2S_2)Fe_2(CO)_6$ as a dark red, air-stable solid, mp 73–75 °C (known compound;[29] melting point not given). After recrystallization from pentane it was identified by comparison of its IR and NMR spectra to those of an authentic sample (prepared by $Et_3N/(\mu\text{-}HS)_2Fe_2(CO)_6/CH_2I_2$ method in a previous experiment).[51]

(c) With 1,2-Dibromoethane. The dianion solution was prepared as above. To the reagent solution was added 8.1 mmol of $BrCH_2CH_2Br$ (Aldrich). After the mixture had been stirred for 1 h at −78 °C, TLC monitoring showed that no reaction had occurred. The reaction mixture was warmed to room temperature while being stirred an additional 2 h. Solvent was removed from the red-black solution on a rotary evaporator, leaving a black oil which was chromatographed (silicic acid–20% CH_2Cl_2/pentane) to give 0.510 g (1.37 mmol, 47% yield) of $(\mu\text{-}SCH_2CH_2S)Fe_2(CO)_6$ as a dark red, air-stable solid. After recrystallization from pentane, mp 75–77 °C (lit.[52] 76–77 °C), it was identified by comparison of its IR and NMR spectra with those of an authentic sample (prepared by $Et_3N/(\mu\text{-}HS)_2Fe_2(CO)_6/BrCH_2CH_2Br$ method in a previous experiment.[51]

(d) With Diorganotin Dichlorides. To 2.91 mmol of $(\mu\text{-}LiS)_2Fe_2(CO)_6$ in 75 mL of THF at −78 °C was added 3.18 mmol of Me_2SnCl_2 as a solid against a counterflow of nitrogen. After it had been stirred for 30 min. at −78 °C, the solution had turned red. After warming to room temperature, the solvent was removed on a rotary evaporator, leaving a brown solid which was chromatographed (silicic acid–CH_2Cl_2) to give 1.317 g (2.67 mmol, 92% yield) of $(\mu\text{-}Me_2SnS_2)Fe_2(CO)_6$ as a red-purple, air-stable solid, mp 95 °C dec: IR (CH_2Cl_2) 770 m, 610 m, 560 m cm^{-1}; terminal carbonyl region: 2085 s, 2045 vs, 1997 vs cm^{-1}; NMR (acetone-d_6) δ 1.02 ppm (s with Sn satellites, ${}^2J_{({}^{117/119}\mathrm{Sn-H})} = 60/64$ Hz); ${}^{13}C$ NMR (acetone-d_6) δ_C 12.37 [s with Sn satellites, ${}^1J_{({}^{117/119}\mathrm{Sn}CH_3)} = 383/400$ Hz] and 211.24 ppm (s, CO); mass spectrum, molecular ions at m/e 492, 494 (${}^{117}Sn$ and ${}^{119}Sn$, respectively) with fragment ions corresponding to $M^+ - (CO)_x$ for x = 1–6, $MeSnS_2Fe_2$, $SnFe_2S_2$, S_2Fe_2, SFe_2, Fe_2, SFe, and Fe. Anal. Calcd for $C_8H_6Fe_2O_6S_2Sn$: C, 19.50; H, 1.23. Found: C, 19.67; H, 1.63.

A similar reaction of 2.91 mmol of dianion V in THF at −78 °C with 0.743 g (3 mmol) of Et_2SnCl_2 (0.5 h at −78 °C, 1 h at room temperature) was carried out. After the solvent had been removed at reduced pressure, the residue was chromatographed (silicic acid–CH_2Cl_2), and the product thus obtained was recrystallized from CH_2Cl_2 to give 1.08 g (71%) of $(\mu\text{-}Et_2SnS_2)Fe_2(CO)_6$, orange crystals, mp 118 °C dec. The mass spectrum showed the molecular ion and fragment ions corresponding to the successive loss of the six CO ligands. The IR spectrum (in Me_2CO) in the terminal carbonyl region showed bands at 2053 s, 2010 vs, 1975 vs, and 1965 vs cm^{-1}. Anal. Calcd for $C_{10}H_{10}O_6S_2Fe_2Sn$: C, 23.07; H, 1.94. Found: C, 22.99; H, 1.95.

A reaction was also carried out between 2.91 mmol of dianion V in THF at −78 °C with 3 mmol of di-*n*-butyltin dichloride (30 min at −78 °C and 1 h at room temperature). The reaction mixture was evaporated at reduced pressure. The residue was extracted with pentane; the pentane extracts were evaporated, and the crude product was recrystallized from pentane to give 1.30 g (77%) of a dark red, air-sensitive solid, mp 85 °C. The mass spectrum showed the molecular ion and fragment ions corresponding to loss of the six CO ligands. The IR spectrum ($CHCl_3$) showed bands at 2074 s, 2034 vs, 2003 vs, and 1991 vs cm^{-1} in the terminal CO region. The analysis supported the formulation as $(\mu\text{-}(n\text{-}C_4H_9)_2SnS_2)Fe_2(CO)_6$. Anal. Calcd for $C_{14}H_{18}O_6S_2Fe_2Sn$: C, 29.09; H, 3.36. Found: C, 28.76; H, 3.23.

(e) With Diorganogermanium Dichlorides. Dianion V was prepared on a 2.91-mmol scale as described above, and then 0.34 mL (2.91 mmol) of Me_2GeCl_2 (Alfa) was added at −78 °C. The solution immediately turned red. It then was warmed to room temperature. Solvent was removed on a rotary evaporator, leaving a dark red solid which was chromatographed (silicic acid–CH_2Cl_2) to yield 1.275 g (2.855 mmol, 98% yield) of $(\mu\text{-}Me_2GeS_2)Fe_2(CO)_6$ as a red-black solid. Recrystallization from pentane gave material with mp 113 °C dec; IR ($CHCl_3$) 2910 w, 1400 w, 1235 m, 843 m, 610 m, 563 m cm^{-1}; terminal carbonyl region: 2077 s, 2037 vs, 2003 s, 1995 s cm^{-1}; NMR ($CDCl_3$) δ 1.20 ppm (s, CH_3); mass spectrum, m/z (rel intensity) 447 (M^+, 7), 419 (M^+ − CO, 6), 391 (M^+ − 2CO, 11), 363 (M^+ − 3CO, 6), 335 (M^+ − 4CO, 11), 307 (M^+ − 5CO, 17), 279 (M^+ − 6CO, 29), 249 (S_2Fe_2Ge, 36), 176 (S_2Fe_2, 12), 144 (SFe_2, 61), 112 (Fe_2, 17), 88 (SFe, 29), and 56 (Fe, 100). Anal. Calcd for $C_8H_6Fe_2GeO_6S_2$: C, 21.52; H, 1.35. Found: C, 21.46; H, 1.40.

A similar reaction of the dianion prepared from 2.91 mmol of $(\mu\text{-}S_2)Fe_2(CO)_6$ by the $LiBEt_3H$ procedure with 0.893 g (3 mmol) of diphenylgermanium dichloride (5 h at −78 °C, overnight at room temperature) gave, after chromatography on silicic acid–pentane and recrystallization from pentane, $(\mu\text{-}Ph_2GeS_2)Fe_2(CO)_6$, deep red solid, mp 131–132 °C. The mass spectrum of the product showed the molecular ion and fragment loss corresponding to successive loss of the six CO ligands; IR ($CHCl_3$) 2079 s, 2040 vs, 2004 vs, 1999 vs cm^{-1} in the terminal carbonyl region. Anal. Calcd for $C_{18}H_{10}O_6S_2GeFe_2$: C, 37.88; H, 1.77. Found: C, 37.90; H, 1.82.

(f) With Germanium Tetrachloride. (i) One-half Equivalent of $GeCl_4$. To a solution of 2.91 mmol of $(\mu\text{-}LiS)_2Fe_2(CO)_6$ in 75 mL of THF at −78 °C was added 0.17 mL (1.5 mmol) of $GeCl_4$ which caused a color change to deep red. After it had been stirred 15 min at −78 °C and then warmed to room temperature, solvent was removed from the reaction mixture on a rotary evaporator. The residue was applied in CH_2Cl_2 to a silicic acid–CH_2Cl_2 filtration chromatography column. Diethyl ether eluted a dark red band which gave 0.795 g (1.04 mmol, 72% yield) of $Ge[S_2Fe_2(CO)_6]_2$ as dark, ruby-red crystals, mp 143 °C dec[53] (lit.[12] mp 150 °C dec). Recrystallization of the air-stable product from dichloromethane gave pure material: IR (CH_2Cl_2) terminal carbonyl region: 2078 s, 2050 vs, 2013 vs cm^{-1}; mass spectrum, molecular ion at m/e 761 with fragment ions corresponding to $M^+ - (CO)_x$ for x = 1–12, S_2Fe_2, SFe_2, Fe_2, FeS, and Fe. Anal. Calcd for $C_{12}Fe_4GeO_{12}S_4$: C, 18.96; H, 0.00. Found: C, 19.09; H, 0.14.

(ii) With an Excess of $GeCl_4$. A THF solution of dianion V was prepared from 2.91 mmol of $(\mu\text{-}S_2)Fe_2(CO)_6$ by using the $LiBEt_3H$ procedure. To the solution was added 2.33 mL (20.4 mmol) of $GeCl_4$, which caused an immediate color change to red. The mixture was warmed to room temperature. Then solvent was removed on a rotary evaporator, leaving a red solid which was extracted with CH_2Cl_2. The extracts were filtered through a Celite pad on a medium-porosity fritted funnel. Removal of solvent on a rotary evaporator gave 1.103 g (2.26 mmol, 78% yield) of $(\mu\text{-}Cl_2GeS_2)Fe_2(CO)_6$ as an orange-red solid. The product was recrystallized from dichloromethane/pentane to give material with mp 120–122 °C (darkens, then melts) (lit.[12] mp 100 °C dec); IR (CH_2Cl_2) terminal carbonyl region: 2089 m, 2056 vs, 2018 s cm^{-1} (bands due to a trace amount of $Ge[S_2Fe_2(CO)_6]_2$ also are always visible); mass spectrum, m/z (rel intensity) 487 (M^+, 0.8), 459 (M^+ − CO, 0.8), 431 (M^+ − 2CO, 1), 403 (M^+ − 3CO, 0.6), 375 (M^+ − 4CO, 2.2), 347 (M^+ − 5CO, 2.6), 319 (M^+ − 6CO, 9), 284 (S_2Fe_2GeCl, 0.7), 249 (S_2Fe_2Ge, 0.6), 176 (S_2Fe_2, 16), 144 (SFe_2, 19), 112 (Fe_2, 11), 88 (SFe, 44) and 56 (Fe, 100).

A side reaction occurred when $(Cl_2GeS_2)Fe_2(CO)_6$ was chromatographed or when its solutions were exposed to air for a prolonged period of time. When it was chromatographed with a silicic acid column, there was considerable conversion to $Ge[S_2Fe_2(CO)_6]_2$. Similarly, when a THF solution was exposed to air for several hours, this same reaction also occurred. In this case, however, degradation to a brown insoluble product also accompanied this process. Analytically pure samples of $(\mu\text{-}Cl_2GeS_2)Fe_2(CO)_6$ were never obtained.

Reaction between μ-Dithio-bis(tricarbonyliron) and the Trichlorogermane–Triethylamine Adduct.[12,44] A 200-mL flask equipped with a stir-bar, serum cap, and a nitrogen inlet needle was charged with 1.00 (2.91 mmol) of $(\mu\text{-}S_2)Fe_2(CO)_6$ and flushed with nitrogen. After 70 mL of THF was added, 1.14 g (4.07 mmol) of $HGeCl_3{\cdot}NEt_3$[54] was added by syringe. The reaction solution darkened slightly overnight at room temperature. Solvent was removed on a rotary evaporator, leaving a red-brown solid which was chromatographed (silicic acid–CH_2Cl_2). Dichloromethane

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[51] Seyferth, D.; Henderson, R. S., *J. Organomet. Chem.*, in press.

[52] King, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 1584.

[53] The melting point capillary was inserted into a preheated bath at 110 °C and a heating rate of 10 °C per min was used.

[54] Nametkin, N. S.; Kuz'min, O. V.; Korolev, V. K.; Kobrakov, K. I.; Patrikeev, A. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 676.

eluted a trace of (μ-S_2)$Fe_2(CO)_6$. Ether eluted a deep red band which yielded 0.564 g (0.74 mmol, 51% yield) of a deep ruby-red solid, mp ~135 °C dec, which was identified as $Ge[S_2Fe_2(CO)_6]_2$ by comparison of its IR and mass spectra with those of $Ge[S_2Fe_2(CO)_6]_2$ prepared by the KH and $LiBEt_3H$ procedures.

Reaction between μ-Dithio-bis(tricarbonyliron) and Trichlorogermane Diethyl Etherate.[12,44] A 200-mL three-necked flask equipped with a stir-bar, two serum caps, and a nitrogen inlet tube was flushed with nitrogen, and then charged with 2.91 mmol of (μ-S_2)$Fe_2(CO)_6$ and 75 mL of THF. An excess of (1.0 mL, 3.63 mmol) of $HGeCl_3{\cdot}2Et_2O$[55] was added in four portions over 1 h. The reaction mixture was stirred overnight with monitoring of the reaction progress by TLC. After 18 h, a small amount of (μ-S_2)$Fe_2(CO)_6$ remained, so another 0.5 mL of $HGeCl_3{\cdot}2Et_2O$ was added. After 4 additional h the reaction was complete. Solvent was removed on a rotary evaporator, leaving a red solid which was extracted with CH_2Cl_2 and then filtered through a bed of Celite supported on a medium-porosity fritted fuunnel. The filtrate was evaporated to give 0.699 g (1.44 mmol, 49% yield) of (μ-Cl_2GeS_2)$Fe_2(CO)_6$ as an orange-red solid which was identical in all respects with the product of the reaction of (μ-MS)$_2Fe_2(CO)_6$ (M = Li or K) with an excess of $GeCl_4$ (melting point and IR and mass spectra).

(g) With One-half Equivalent of Silicon Tetrachloride. To 2.91 mmol of (μ-LiS)$_2Fe_2(CO)_6$ in 75 mL of THF at −78 °C was added 1.5 mmol of $SiCl_4$ (Alfa) by syringe over 3 min. An immediate color change to red was observed. The reaction mixture was warmed to room temperature, and volatiles then were removed in vacuo, leaving a dark red solid which was extracted with 4 × 25 mL of CH_2Cl_2. The combined extracts were filtered under nitrogen through a Celite pad supported on a medium-porosity fritted funnel. Removal of solvent in vacuo yielded 1.03 g (1.44 mmol, 99% yield) of $Si[S_2Fe_2(CO)_6]_2$ as ruby-red crystals.[44] Recrystallization of the air-sensitive product from dichloromethane (under nitrogen) gave pure material: mp 175 °C dec (sealed capillary) (ref 44 gives no melting point); IR (CH_2Cl_2) 1085 br, 610 m, 565 m, cm^{-1}; terminal carbonyl region: 2080 s, 2048 vs, 2012 vs, cm^{-1}; mass spectrum, *m/z* (rel intensity) 716 (M^+, 1.5), 688 (M^+ − CO, 1), 660 (M^+ − 2CO, 5), 632 (M^+ − 3CO, 2), 604 (m^+ − 4CO, 4), 576 (M^+ − 5CO, 1), 548 (M^+ − 6CO, 4), 520 (M^+ − 7CO, 6), 492 (M^+ − 8CO, 18), 464 (M^+ − 9CO, 15), 436 (M^+ − 10CO, 10), 408 (M^+ − 11CO, 17), 380 (M^+ − 12CO, 47), 320 (S_3Fe_4, 72), 264 (S_3Fe_3, 29), 232 (S_2Fe_3, 11), 176 (S_2Fe_2, 33), 144 (SFe_2, 31), 112 (Fe_2, 11), 88 (SFe, 7) and 56 (Fe, 100). Anal. Calcd for $C_{12}Fe_4O_{12}S_4Si$: C, 20.13; H, 0.00; S, 17.91. Found: C, 20.31; H, 0.25; S, 16.80.

(h) With Diorganodichlorosilanes. Dianion V was prepared as usual on a 2.91-mmol scale. To the reagent solution was added 0.70 mL (5.82 mmol) of Me_2SiCl_2 (Petrarch) dropwise by syringe over a 10-min period which caused a green-to-red color change. The reaction solution was warmed to room temperature. Volatiles were removed in vacuo, leaving an oily, dark-red solid which was extracted with 3 × 30 mL of pentane. The combined extracts were filtered under nitrogen through a Celite pad supported on a medium-porosity fritted funnel. Removal of the solvent in vacuo yielded 0.660 g (1.64 mmol, 56% yield) of (μ-Me_2SiS_2)$Fe_2(CO)_6$ as an air-sensitive, purple-red solid. This product was recrystallized from pentane under nitrogen to give pure material: mp 104–106 °C; IR (CH_2Cl_2) 2960 w, 1395 w, 1250 m (Si–Me), 1050 br, 850 m, 625 m, 575 m cm^{-1}; terminal carbonyl region: 2083 sh, 2077 s, 2046 vs, 2004 vs (cm^{-1}); NMR ($CDCl_3$) δ 0.91 ppm [s, $Si(CH_3)_2$]; mass spectrum, *m/z* (rel intensity) 402 (M^+, 13), 374 (M^+ − CO, 10), 346 (M^+ − 2CO, 23), 318 (M^+ − 3CO, 14), 290 (M^+ − 4CO, 23), 262 (M^+ − 5CO, 40), 234 (M^+ − 6CO, 100), 219 ($MeSiS_2Fe_2$, 34), 204 (SiS_2Fe_2, 33), 176 (S_2Fe_2, 16), 144 (SFe_2, 88), 112 (Fe_2, 28), 88 (SFe, 21), and 56 (Fe, 93). Anal. Calcd for $C_8H_6Fe_2O_6S_2Si$: C, 23.90; H, 1.50. Found: C, 23.76; H, 1.66.

Similar reactions of dianion V were carried out on the same scale with diethyl-, diphenyl-, and phenylmethyldichlorosilane. Because of the air and moisture sensitivity of these organosilicon derivatives, column chromatography could not be used. Instead, in each case, the reaction mixture was evaporated at reduced pressure and the residue was extracted (under nitrogen) with hexane. The hexane extracts were evaporated, and the solid which remained was recrystallized from hexane. Thus prepared were the following:

(μ-Et_2SiS_2)$Fe_2(CO)_6$, dark red, air-sensitive crystals, mp 78–79 °C, in 80% yield (before recrystallization): IR (CCl_4) terminal CO region: 2093 sh, 2079 s, 2046 vs, 2041 vs, 2007 s cm^{-1}. Anal. Calcd for $C_{10}H_{10}O_6S_2SiFe_2$: C, 27.93; H, 2.34. Found: C, 27.46; H, 2.48.

(μ-Ph_2SiS_2)$Fe_2(CO)_6$, dark red, air-sensitive crystals, mp 142–143 °C, in 82% yield (before recrystallization): IR (CCl_4) (terminal CO region) 2081 s, 2045 vs, 2005 vs, 1993 sh cm^{-1}. Anal. Calcd for $C_{18}H_{10}O_6S_2SiFe_2$: C, 41.09; H, 1.92. Found: C, 41.10; H, 2.04.

(μ-$PhMeSiS_2$)$Fe_2(CO)_6$, dark red, air-sensitive crystals, mp 94–95 °C, in 93% yield (before recrystallization): IR ($CHCl_3$) terminal CO region: 2082 s, 2046 vs, 2005 vs cm^{-1}; NMR ($CDCl_3$) 0.96 (s, 3 H, CH_3) and 7.44 ppm (s, 5 H, Ph). Anal. Calcd for $C_{13}H_8O_6S_2SiFe_2$: C, 33.64; H, 1.74. Found: C, 33.61; H, 1.90.

(i) With Selenium Tetrachloride. Dianion V was prepared on a 2.91-mmol scale in THF via $LiBEt_3H$ by the usual procedure. To this solution was added 0.30 g (1.36 mmol) of $SeCl_4$ (Alfa). After it had been stirred for 30 min at −78 °C and then for 1 h at room temperature, the color had changed from green to deep red. Solvent was removed on a rotary evaporator, leaving a red-black oil which was chromatographed (silicic acid–pentane) to give 0.816 g (1.06 mmol, 78% yield based on $SeCl_4$) of $Se[S_2Fe_2(CO)_6]_2$ as an extremely malodorous, air-sensitive dark red oil. This material could be short path distilled, bp 85 °C (2 mmHg); IR (pentane) terminal carbonyl region: 2086 s, 2048 vs, 2010 vs, 1995 m cm^{-1}. In view of the vile odor of this product, no further attempts were made to characterize it.

(j) With Bis(1,2-diphenylphosphino)ethane–Nickel Dichloride. A THF solution of dianion V was prepared on the 2.91-mmol scale as usual. To this solution was added 1.584 g (3 mmol) of (diphos)$NiCl_2$[56] as a solid against a counterflow of nitrogen. Acetone (15 mL) was added to solubilize it. However, after 6 h at −78 °C no reaction had taken place. The reaction mixture was warmed to room temperature while being stirred an additional hour. Solvent was removed on a rotary evaporator, leaving a black solid which was chromatographed (silicic acid–CH_2Cl_2) to give 2.161 g (2.70 mmol, 93% yield) of [μ-(diphos)-NiS_2]$Fe_2(CO)_6$ as a black solid. After recrystallization from CH_2Cl_2, mp 160–162 °C, it was identified by comparison of its IR and mass spectra with those of an authentic sample obtained by insertion of (diphos)Ni(0) (via (diphos)$Ni(CO)_2$) into the S–S bond of (μ-S_2)$Fe_2(CO)_6$.[57]

(k) With *cis*-Bis(triphenylphosphine)platinum Dichloride. A THF solution of dianion V was prepared by the $LiBEt_3H$ procedure from 0.64 mmol of (μ-S_2)$Fe_2(CO)_6$ at −78 °C. To this solution was added 0.50 g (0.632 mmol) of solid *cis*-$(Ph_3P)_2PtCl_2$ (Strem) against a counterflow of nitrogen. Acetone (15 mL) was added to solubilize it. However, after 4.5 h at −78 °C no reaction had taken place. The reaction mixture was warmed to room temperature while being stirred an additional hour. Solvent was removed from the red solution on a rotary evaporator, leaving a red solid which was chromatographed (silicic acid–CH_2Cl_2) to give 0.534 g (0.502 mmol, 80% yield, based on $(Ph_3P)_2PtCl_2$) of [μ-$(Ph_3P)_2PtS_2$]$Fe_2(CO)_6$ as an orange-red, air-stable crystalline solid. After recrystallization from CH_2Cl_2–pentane, mp 200 °C dec, it was identified by comparison of its IR and NMR spectra with those of an authentic sample prepared by the insertion of $(Ph_3P)_2Pt(0)$ (via $(Ph_3P)_4Pt$) into the S–S bond of (μ-S_2)$Fe_2(CO)_6$.[57]

(l) With Bis(triphenylphosphine)palladium Dichloride. A THF solution of dianion V was prepared by the $LiBEt_3H$ procedure from 1.45 mmol of (μ-S_2)$Fe_2(CO)_6$ at −78 °C. To this solution was added 1.00 g (1.42 mmol) of *cis*-$(Ph_3P)_2PdCl_2$ (Strem) as a solid against a counterflow of nitrogen. Acetone (15 mL) was added to solubilize it. However, after 1.5 h at −78 °C no reaction had occurred. The reaction mixture was warmed to room temperature while being stirred an additional hour. Solvent was removed from the deep red solution on a rotary evaporator, leaving a purple solid which was chromatographed (silicic acid–CH_2Cl_2)

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to give 1.276 g (1.31 mmol, 92% yield, based on $(Ph_3P)_2PdCl_2$) of $[\mu\text{-}(Ph_3P)_2PdS_2]Fe_2(CO)_6$ as an air-stable, purple-brown solid. Recrystallization from a mixture of CH_2Cl_2 and pentane gave pure material, mp 165 °C dec: IR (CH_2Cl_2) terminal carbonyl region: 2049 s, 2008 vs, 1971 s, 1959 sh cm^{-1}; NMR ($CDCl_3$) δ 7.03–7.50 ppm (complex m, P*Ph*). Anal. Calcd for $C_{42}H_{30}Fe_2O_6PdP_2S_2$: C, 51.75; H, 3.10. Found: C, 51.75; H, 3.11.

(m) With (η^5-Cyclopentadienyl)carbonylcobalt Diiodide. To 2.91 mmol of $(\mu\text{-}LiS)_2Fe_2(CO)_6$ in 75 mL of THF at −78 °C was added 1.34 g (3.3 mmol) of solid $\eta^5\text{-}C_5H_5Co(CO)I_2$[58] against a counterflow of nitrogen. The reaction mixture was stirred for 1 h at −78 °C and then 2 h at room temperature, during which time a green-to-purple color change occurred. Solvent was removed on a rotary evaporator, leaving a black solid which was chromatographed (silicic acid–pentane) to give 0.680 g (1.45 mmol, 50% yield) of $(\mu\text{-}\eta^5\text{-}C_5H_5CoS_2)Fe_2(CO)_6$ as a black, air-stable crystalline solid. After recrystallization from pentane, mp 135 °C dec, it was identified by comparison of its IR, NMR, and mass spectra with those of an authentic sample prepared by the reaction of $\eta^5\text{-}C_5H_5CO(CO)_2$ with $(\mu\text{-}S_2)Fe_2(CO)_6$.[57]

(n) With Sulfur Chlorides. To 2.91 mmol of $(\mu\text{-}LiS)_2Fe_2(CO)_6$ in 75 mL of THF at −78 °C was added 0.20 mL (3 mmol) of SCl_2 (Alfa), which caused an immediate green-to-red color change. Volatiles were removed in vacuo. A cold finger was inserted into the Schlenk flask, and the oily residue was sublimed at 45 °C (0.3 mm) for 1 h to give 0.900 g (2.62 mmol, 90% yield) of $(\mu\text{-}S_2)Fe_2(CO)_6$ as ruby-red crystals, mp 43.5–45 °C, which was identified by comparison of its IR and mass spectra with those of an authentic sample. (A mass spectrum of the oily residue before sublimination showed only the presence of $(\mu\text{-}S_2)Fe_2(CO)_6$.) Anal. Calcd for $C_6Fe_2O_6S_2$: C, 20.96; H, 0.00. Found: C, 20.92; H, 0.06.

A similar reaction of dianion V (from 2.91 mmol of $(\mu\text{-}S_2)Fe_2(CO)_6$) with 0.24 mL (3 mmol) of S_2Cl_2 at −78 °C also resulted in an immediate green-to-red color change. After volatiles had been removed under reduced pressure, a cold finger was inserted into the Schlenk flask, and the residue was sublimed at 45 °C (0.3 mm) for 1 h to give 0.915 g (2.66 mmol, 91% yield) of $(\mu\text{-}S_2)Fe_2(CO)_6$ as ruby-red crystals, mp 43–45 °C, which was identified by comparison of its IR and mass spectra with those of an authentic sample. Anal. Calcd for $C_6Fe_2O_6S_2$: C, 20.96; H, 0.00. Found: C, 20.89; H, 0.07.

A reaction of 2.91 mmol of dianion V with 3 mmol of $SOCl_2$ proceeded in the same manner and gave $(\mu\text{-}S_2)Fe_2(CO)_6$ in 94% yield.

(o) With Ligand-Free Metal Dichlorides. The dianion solution was prepared as usual from 2.91 mmol of $(\mu\text{-}S_2)Fe_2(CO)_6$. To this solution was added, at −78 °C with stirring, slowly by syringe, a solution of 0.2 g (1.54 mmol) of anhydrous $NiCl_2$ in 50 mL of anhydrous ethanol. A color change from dark green to brown-red was observed. The reaction mixture was stirred at −78 °C for 30 min, and then 0.45 g (2.14 mmol) of solid tetraethylammonium bromide was added to the mixture against a countercurrent of nitrogen. The reaction mixture was allowed to warm to room temperature and was stirred overnight. Filtration left 0.62 g (42%) of a black-red powder. Recrystallization from 1:1 $CH_2Cl_2/EtOH$ gave 0.45 g of black crystalline solid, mp 162 °C dec; $[Et_4N]_2\,[Ni(S_2Fe_2(CO)_6)_2]$: IR ($Me_2CO$) terminal Co region: 2037 sh, 2021 m, 1998 s, 1944 s cm^{-1}. Anal. Calcd for $C_{28}H_{40}O_{12}N_2S_4NiFe_4$: C, 33.40; H, 4.00. Found: C, 33.98; H, 4.28.

A similar procedure was followed in the reaction of 0.27 g (1.50 mmol) of palladium(II) chloride (in 50 mL of EtOH) with dianion V prepared from 2.91 mmol of $(\mu\text{-}S_2)Fe_2(CO)_6$. Subsequently, 1.365 g (6.50 mmol) of tetraethylammonium bromide in 10 mL of EtOH was added, and the reaction mixture was allowed to warm slowly from −78 °C to room temperature (overnight). The black-red precipitate was filtered, washed with ethanol, and dried in vacuo, giving 1.101 g (72%) of $[Et_4N]_2[Pd(S_2Fe_2(CO)_6)_2]$. The product was purified by precipitating it from hot acetone solution by slow addition of pentane to give a black solid, mp ca. 175 °C dec: IR (Me_2CO) terminal CO region: 2024 s, 1999 vs, 1940 s cm^{-1}. Anal. Calcd for $C_{28}H_{40}O_{12}N_2S_4PdFe_4$: C, 31.89; H, 3.82. Found: C, 30.96; H, 3.91.

The platinum derivative, $[Et_4N]_2[Pt(S_2Fe_2(CO)_6)_2]$, mp ca. 185 °C dec, a dark red, air-stable solid, was prepared and purified in the same way; IR (in Me_2CO) terminal CO region: 2025 s, 2000 vs, 1942 vs cm^{-1}. Anal. Calcd for $C_{28}H_{40}O_{12}N_2S_4PtFe_4$: C, 29.41; H, 3.53. Found: C, 28.98; H, 3.68.

Acknowledgment. We are grateful to the National Science Foundation for support of this work, to Cincinnati Milacron Co., M&T Chemicals, Inc., and Eagle Picher Co. for gifts of chemicals, to M. K. Gallagher for some mass spectra, and to R. M. Weinstein for some NMR spectra.

Registry No. $(\mu\text{-}S_2)Fe_2(CO)_6$, 14243-23-3; $(\mu\text{-}KS)_2Fe_2(CO)_6$, 79255-02-0; $(\mu\text{-}LiS)_2Fe_2(CO)_6$, 74438-48-5; $(\mu\text{-}MeS)_2Fe_2(CO)_6$ (a,e isomer), 19976-88-6; $(\mu\text{-}MeS)_2Fe_2(CO)_6$ (e,e isomer), 19976-87-5; $(\mu\text{-}EtS)_2Fe_2(CO)_6$ (a,e isomer), 18771-06-7; $(\mu\text{-}EtS)_2Fe_2(CO)_6$ (e,e isomer), 18771-07-8; $(\mu\text{-}PhCH_2S)_2Fe_2(CO)_6$ (a,e isomer), 18771-08-9; $(\mu\text{-}PhCH_2S)_2Fe_2(CO)_6$ (e,e isomer), 18771-09-0; $(\mu\text{-}CH_2{=}CH{-}CH_2S)_2Fe(CO)_6$ (a,e isomer), 79298-99-0; $(\mu\text{-}CH_2{=}CH{-}CH_2S)_2Fe_2(CO)_6$ (e,e isomer), 79299-00-6; $(\mu\text{-}Me_2SnS_2)Fe_2(CO)_6$, 69718-37-2; $(\mu\text{-}Me_2GeS_2)Fe_2(CO)_6$, 74438-41-8; $Ge[S_2Fe_2(CO)_6]_2$, 71560-38-8; $(\mu\text{-}Cl_2GeS_2)Fe_2(CO)_6$, 71560-36-6; $(\mu\text{-}CH_2S_2)Fe_2(CO)_6$, 69878-86-0; $(\mu\text{-}SCH_2CH_2S(Fe_2(CO)_6$, 15492-14-5; $(\mu\text{-}Et_2SnS_2)Fe_2(CO)_6$, 74438-39-4; $(\mu\text{-}(n\text{-}C_4H_9)_2SnS_2)Fe_2(CO)_6$, 74438-40-7; $(\mu\text{-}Ph_2GeS_2)Fe_2(CO)_6$, 74438-42-9; $Si[S_2Fe_2(CO)_6]_2$, 71592-21-7; $(\mu\text{-}Me_2SiS_2)Fe_2(CO)_6$, 79255-03-1; $(\mu\text{-}Et_2SiS_2)Fe_2(CO)_6$, 74452-95-2; $(\mu\text{-}Ph_2SiS_2)Fe_2(CO)_6$, 74438-44-1; $(\mu\text{-}PhMeSiS_2)Fe_2(CO)_6$, 74438-43-0; $Se[S_2Fe_2(CO)_6]_2$, 79255-04-2; $[\mu\text{-}(diphos)NiS_2]Fe_2(CO)_6$, 74438-45-2; $[\mu\text{-}(Ph_3P)_2PtS_2]Fe_2(CO)_6$, 75249-93-3; $[\mu\text{-}(Ph_3P)_2PdS_2]Fe_2(CO)_6$, 75249-92-2; $(\mu\text{-}(\eta^5\text{-}C_5H_5)CoS_2)Fe_2(CO)_6$, 79391-48-3; $[Et_4N]_2[Ni(S_2Fe_2(CO)_6)_2]$, 79255-06-4; $[Et_4N]_2[Pd(S_2Fe_2(CO)_6)_2]$, 79255-08-6; $[Et_4N]_2[Pt(S_2Fe_2(CO)_6)_2]$, 79255-10-0; $Fe(CO)_5$, 13463-40-6; Na_2S_5, 12034-40-1; MeI, 74-88-4; EtI, 75-03-6; Me_2SnCl_2, 753-73-1; $GeCl_4$, 10038-98-9; Me_2GeCl_2, 1529-48-2; $PhCH_2Cl$, 100-44-7; $H_2C{=}CH{-}CH_2{-}Br$, 106-95-6; CH_2I_2, 75-11-6; $BrCH_2CH_2Br$, 106-93-4; Et_2SnCl_2, 866-55-7; Bu_2SnCl_2, 683-18-1; Ph_2GeCl_2, 1613-66-7; $HGeCl_3{\cdot}NEt_3$, 37501-42-1; $HGeCl_3{\cdot}2Et_2O$, 3237-20-5; $SiCl_4$, 10026-04-7; Me_2SiCl_2, 75-78-5; Et_2SiCl_2, 1719-53-5; Ph_2SiCl_2, 80-10-4; $PhMeSiCl_2$, 149-74-6; $SeCl_4$, 10026-03-6; $(diphos)NiCl_2$, 38754-20-0; *cis*-$(Ph_3P)_2PtCl_2$, 15604-36-1; *cis*-$(Ph_3P)_2PdCl_2$, 15604-37-2; $(\eta^5\text{-}C_5H_5)CO(CO)I_2$, 12012-77-0; SCl_2, 10545-99-0; S_2Cl_2, 10025-67-9; $SOCl_2$, 7719-09-7; $NiCl_2$, 7718-54-9; $PdCl_2$, 7647-10-1.

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