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Synthesis of Diiron(I) Dithiolato Carbonyl Complexes

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Abstract

Virtually all organosulfur compounds react with Fe(0) carbonyls to give the title complexes. These reactions are reviewed in light of major advances over the past few decades, spurred by interest in $Fe_2(\mu\text{-}SR)_2(CO)_x$ centers at the active sites of the [FeFe]-hydrogenase enzymes. The most useful synthetic route to $Fe_2(\mu\text{-}SR)_2(CO)_6$ involves the reaction of thiols with $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$. Such reactions can proceed via mono-, di-, and triiron intermediates. The reactivity of Fe(0) carbonyls toward thiols is highly chemoselective, and the resulting dithiolato complexes are fairly rugged. Thus, many complexes tolerate further synthetic elaboration directed at the organic substituents. A second major route involves alkylation of $Fe_2(\mu\text{-}S_2)(CO)_6$, $Fe_2(\mu\text{-}SH)_2(CO)_6$, and $Li_2Fe_2(\mu\text{-}S)_2(CO)_6$. This approach is especially useful for azadithiolates $Fe_2[(\mu\text{-}SCH_2)_2NR](CO)_6$. Elaborate complexes arise via addition of the Fe*SH* group to electrophilic alkenes, alkynes, and carbonyls. Although the first example of $Fe_2(\mu\text{-}SR)_2(CO)_6$ was prepared from ferrous reagents, ferrous compounds are infrequently used, although the $Fe(II)(SR)_2$ + Fe(0) condensation reaction is promising. Almost invariably low-yielding, the reaction of $Fe_3(CO)_{12}$, S_8, and a variety of unsaturated substrates results in C–H activation, affording otherwise inaccessible derivatives. Thiones and related C═S-containing reagents are highly reactive toward Fe(0), often giving complexes derived from substituted methanedithiolates and C–H activation.

Graphical abstract

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Notes
The authors declare no competing financial interest.

Supporting Information
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Known diiron(I) dithiolato hexacarbonyls are shown (PDF)

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1. INTRODUCTION

1.1. Scope of Review

This Review summarizes the syntheses of compounds of the type $Fe_2(\mu\text{-}SR)_2(CO)_6$. Such compounds have come under intense scrutiny because of their structural similarity to the active site of [FeFe]-hydrogenases, which are some of the fastest catalysts for oxidation and production of H_2 (Figure 1, right).[1] Crystallographic analyses of the [FeFe]-hydrogenase enzymes were reported in 1998–1999,[2,3] and the biosynthesis of the diiron dithiolate active site has been partially elucidated in the past few years.[4,5]

The chemistry of synthetic high-spin Fe–S clusters has been reviewed extensively, e.g., by Holm and co-workers.[6,7] In contrast, low-spin species rich derivatives exhibit acid (μ-SR)$_2$(CO)$_{6-x}$L$_x$ have not been reviewed, although they have been the subject of hundreds of publications.[8] Because the literature is so scattered and in view of the intensity of work on these compounds, a review is timely. These complexes are chemically versatile for many reasons. First, these complexes are so easy to make that they are almost unavoidable in organoiron chemistry. A huge number of thiolates can be installed (see Supporting Information). The hexacarbonyl complexes readily undergo stepwise substitution by many ligands, thus multiplying the range of possible complexes well into the thousands. The resulting electron-rich derivatives exhibit acid–base and redox properties, forming hydrides and many oxidized derivatives both by chemical and electrochemical means.[9]

Reviews on the preparation of models for the [FeFe]-hydrogenases have been published,[10–12] but the basic organometallic chemistry behind these models has never been emphasized. The chemistry of iron carbonyls with chalcogen ligands has an extensive history,[13–15] as do the reactions of organosulfur compounds with iron and other metal carbonyls.[16]

1.2. Physical Properties of Diiron(I) Dithiolato Carbonyls

The diiron dithiolato hexacarbonyls are bright red–brown diamagnetic solids (Figure 2).[17] They are stable in air and often sublimable, and some even survive steam distillation.[18]

Thermogravimetric analysis[19] shows that, in the presence of atmospheric oxygen, $Fe_2(\mu\text{-}SEt)_2(CO)_6$ decomposes around 100 °C with loss of CO and formation of FeS and Fe.[18] In an early report, $Fe_2(\mu\text{-}SEt)_2(CO)_6$ and $Fe_2(\mu\text{-}SPh)_2(CO)_6$ were purified by boiling for 1 h in dilute aqueous NaOH.[20] Further illustrating the robustness of these compounds, $Fe_2(\mu\text{-}SMe)_2(CO)_6$ is prepared at 120–30 °C and 65 atm of CO (see Section 2.2.1). Most derivatives are soluble in organic solvents, although water solubility can be achieved[21] through the use of hydrophilic substituents, e.g., the tetraol $Fe_2[\mu\text{-}SCH_2CH(OH)CH_2OH]_2(CO)_6$[22] and the sodium sulfonate $Fe_2[\mu\text{-}S_2C_2H_3(CH_2SO_3Na)](CO)_6$.[23] Because of their convenient stability and solubility, $Fe_2(\mu\text{-}SR)_2(CO)_6$ complexes are usually purified by chromatography, as illustrated by separation of two isomers of $Fe_2(\mu\text{-}SMe)_2(CO)_6$.[24] Although these compounds are probably toxic, they have been considered in the pharmaceutical context.[21]

1.3. Chemical Properties of Diiron(I) Dithiolato Carbonyls

A vast literature describes the reactions of the diiron dithiolato hexacarbonyls. The diiron dithiolato hexacarbonyls are electrochemically silent over a wide potential range. The $[Fe_2(\mu\text{-}SMe)_2(CO)_6]^{+/0}$ couple is ~0.8 V vs $[Fe(C_5H_5)_2]^{+/0}$, and the reduction $[Fe_2(\mu\text{-}SPh)_2(CO)_6]^{0/-}$ is −1.4 V vs the same reference.[9] The oxidation potential shifts by >1 V up to replacement of CO with donor ligands,[25] and the reduction can be adjusted by as much as 0.5 V through judicious selection of the dithiolates.[26] The hexacarbonyls are stable to all but the strongest nonoxidizing acids.[27]

The most commonly studied reactions of the diiron dithiolato hexacarbonyls involve substitution of CO by Lewis bases. Substituting ligands include phosphines, isocyanides, carbenes, cyanide, phosphites, thioethers, and others.[11] For highly nucleophilic ligands, disubstitution occurs often near room temperature. Installing less basic ligands requires more forcing thermal or photochemical activation, as well as the use of decarbonylation agents such as Me_3NO.[28] The substituted derivatives are often rather basic and oxidizable,[29] whereas the hexacarbonyls are typically air-stable.

The $Fe_2(\mu\text{-}SR)_2(CO)_6$ center is relatively immune to reactions directed at the organic substituents on the thiolates. In this way, the $Fe_2(\mu\text{-}SR)_2(CO)_6$ center serves as a platform for the development of elaborate, multifunctional structures. Although Fe(0) reagents are highly reactive toward thiols, once formed, the $Fe_2(\mu\text{-}SR)_2(CO)_6$ complexes are essentially unreactive toward thiols and thiolates (see section 3.7). Reactions tolerated by the Fe_2S_2 core in these hexacarbonyls are listed in Table 1. The functional group tolerance also applies to solvents used in syntheses. As is discussed in greater detail below, the most common iron carbonyl reagents are $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$, typically employing tetrahydrofuran (THF) and toluene as solvent, respectively. However, for highly polar organosulfur reagents, methanol or aqueous methanol has been employed.[23,30]

Although $Fe_2(\mu\text{-}SR)_2(CO)_6$ centers are fairly chemical resilient, they are attacked by strong electrophiles and strong nucleophiles. The sulfur centers are oxidized with peracid and dioxiranes.[63,69,70] S-Alkylation by the strongly electrophilic EtOTf occurs with $Fe_2(\mu\text{-}SR)_2(CO)_4(PMe_3)_2$, but probably less readily with the parent hexacarbonyl.[71] The hexacarbonyls decompose upon treatment with aqueous base, although this reaction has not been described. Some alkylthiolate derivatives undergo deprotonation with strong non-nucleophilic bases (see section 3.7). Strong reducing agents such as $Co(C_5Me_5)_2$ reduce the hexacarbonyls.[72]

1.4. Structures of Diiron(I) Dithiolato Carbonyls

Although this Review focuses on synthetic methods, it is useful to review general structural trends. The structure proposed by Reihlen et al. in 1928 is presented in Figure 3.[73] Early organometallic chemists, including Hieber, were very confused about the structures of the metal carbonyls. The crystallographic analysis of $Fe_2(\mu\text{-SEt})_2(CO)_6$ in 1962[74] was the first of hundreds of subsequent structural studies. These studies reveal that diiron(I) dithiolato hexacarbonyls adopt very similar structures. The Fe_2S_2 butterfiy core has idealized C_{2v} symmetry, with the Fe–Fe bond and two apical CO ligands defining one plane of symmetry. With the bulky thiolate SC_6H_2-2,4,6-(*i*-Pr)$_3$, the Fe–Fe distance contracts to 2.466 Å,[75] substantially shorter than that observed in the SEt species (2.537 Å)[74] and SPh species (2.516 Å).[76]

1.4.1. Bis(monothiolate) Derivatives—Depending on the orientation of the R substituents, the compounds $Fe_2(\mu\text{-SR})_2(CO)_6$ can adopt three structures: equatorial–equatorial (*ee*), axial–equatorial (*ae*), and axial–axial (*aa*), as depicted in Figure 4.[77] The *aa* isomer is only observed with chelating dithiolates and as a component of $Fe_2(\mu\text{-SH})_2(CO)_6$.[78] Typical nonchelating organic thiolates give a mixture of the *ae* and *ee* isomers. In the case of $Fe_2(\mu\text{-SMe})_2(CO)_6$, the interconversion of these isomers is so slow that the major (92%) ae isomer can be separated chromatographically from the minor (8%) *ee* isomer.[24,79] The *ee* isomer is observed in the solid $Fe_2[\mu\text{-SC}_6H_2\text{-2,4,6-}(i\text{-Pr})_3]_2(CO)_6$ (Figure 5), but the solution structure was not described.[75] The *ae* and *ee* isomers of compounds $Fe_2(\mu\text{-SMe})_2(CO)_6$ and $Fe_2(\mu\text{-SBn})_2(CO)_6$ undergo carbonyl substitution reactions by phosphine ligands at different rates.[77] The isomerization of *ee*-$Fe_2(\mu\text{-SMe})_2(CO)_6$ to *ae*-$Fe_2(\mu\text{-SMe})_2(CO)_6$ is intramolecular.[80,81] The barrier for isomerization is higher for small alkyl groups, such as Me, Et, and Bn. For *t*-Bu, the barrier is sufficiently low (17 kcal/mol) that the dynamic interconversion of the *ae* and *ee* isomers can be observed by NMR at 100 °C.[79] For aryl groups, the *ae* isomer predominates, and isomerization of *ae* to *ee* isomer is 10 times faster than that for small alkyl groups.[79]

1.4.2. Chelating Dithiolate Derivatives—In the methane-, 1,2-ethane-, 1,3-propane-, and 1,4-butanedithiolates[82–84] $Fe_2[\mu\text{-S}_2(CH_2)_n](CO)_6$, the organic substituents are constrained to the *aa* conformation. An additional degree of freedom applies to the compounds $Fe_2[(\mu\text{-SCH}_2)_2X](CO)_6$ ($X = CH_2$, NH, O, etc.), where the dithiolate backbone is nonplanar,[17,85–87] being analogous to cyclohexane. In these complexes, the conformational equilibration is fast at room temperature on the NMR time scale, but individual conformers are sometimes observed by low-temperature NMR measurements. For 2-substituted propanedithiolates, $Fe_2[(\mu\text{-SCH}_2)_2CHR](CO)_6$, the flippamers are not of equal energy, and the R substituent tends to adopt the equatorial orientation. In such cases, “equatorial” refers to the orientation of the R substituent relative to the conformation of the ring, in analogy to the nomenclature used for substituted cyclohexanes.

The azadithiolate derivatives $Fe_2[(\mu\text{-}SCH_2)_2NR](CO)_6$ have additional degrees of freedom (Figure 6).[87] When the R substituent is small (R = H,[33] Me,[88] CH_2CH_2OH,[89] etc.), the substituent tends to be axial (i.e., projects nearly parallel with the Fe–Fe bond). This geometry is predicted by the anomeric effect, i.e., favorable overlap of the two C–S σ* orbitals and the lone pair on nitrogen.[88] For larger R groups (R = furanylmethyl,[90] cycloalkyl,[91] etc.), the substituent tends to adopt equatorial orientations. When the substituent is aryl[41,92,93] or is unsaturated (e.g., alkynyl[42]), the amine is planar. In these cases pi-conjugation with the *p*-orbital of the nitrogen is reflected by short N–C distances.

Interesting structural trends emerge for diiron dithiolates obtained from long-chain alkane dithiols. This theme has been systematically examined with dithiols derived from polyethylene glycols (Table 2).[84] Shorter chains favor bis(diiron dithiolate)s, whereas dithiols with 14 spacer atoms give 20–30% yields of diiron dithiolates. These derivatives exist as *ae* isomers (Figure 7).[94–96]

2. SYNTHESIS OF DIIRON(I) DITHIOLATO CARBONYLS FROM IRON(0) REAGENTS

2.1. Reactions of Iron(0) Reagents and Thiols

2.1.1. Monothiols—The reactions of iron(0) carbonyls with thiols are the most common route to diiron dithiolato carbonyls. This route is also the best understood. As summarized in the Supporting Information, a large number of compounds have been prepared from monothiols. The first example of this reaction was reported in 1929 by Reihlen et al., who obtained $Fe_2(\mu\text{-}SEt)_2(CO)_6$ in good yield by photolysis of a boiling solution of $Fe(CO)_5$ in EtSH.[100] These authors demonstrated the evolution of the 1 equiv of H_2 and 2 equiv of CO per iron precursor (eq 1).

$$2\mathrm{Fe(CO)}_5+2\mathrm{EtSH}\rightarrow \mathrm{Fe}_2(\mu\text{- SEt})_2(\mathrm{CO})_6+\mathrm{H}_2+4\mathrm{CO} \quad (1)$$

In a series of papers beginning in the 1930s, Hieber, Reihlen's colleague, refined these findings, beginning a multidecade program focused on the reactions of sulfur compounds with iron carbonyls, especially $Fe_3(CO)_{12}$ (which Hieber referred to as "$Fe(CO)_4$").[101] Early reactions were conducted in neat thiol, although subsequently Hieber conducted related reactions, e.g., using naphthalene-1-thiol, using conventional hydrocarbon solvents.[102] He often quantified the evolved gases, with some results being represented in eq 2.

$$2\mathrm{Fe}_3(\mathrm{CO})_{12}+6\mathrm{RSH}\rightarrow \underset{(\mathrm{R=Et,Ph,1-C_{10}H_7,2-C_{10}H_7})}{3\mathrm{Fe}_2(\mu\text{- SR})_2(\mathrm{CO})_6}+3\mathrm{H}_2+6\mathrm{CO} \quad (2)$$

In the 1970s, Nametkin and colleagues began a multiyear study on organosulfur derivatives of iron carbonyls.[18] They examined the reaction of octylthiol with $Fe_3(CO)_{12}$ in heptane solution at room temperature. Under these conditions the diiron complex is produced in 70%

yield. The reaction also produces a substantial amount of dioctyl disulfide, the mechanistic significance of which is unexplained. Because disulfides also react with iron carbonyls to give the same dithiolates, their involvement in typical syntheses would not be noticed in many preparations. The RSH/$Fe_3(CO)_{12}$ reaction is currently the most popular route for diiron dithiolato carbonyls.[20,61,99,103–116] The RSH/$Fe_2(CO)_9$ route to $Fe_2(\mu\text{-}SR)_2(CO)_6$ is also widely employed; these reactions proceed typically at slightly lower efficiency than the $Fe_3(CO)_{12}$ route.

Because iron(0) carbonyls are specifically reactive toward the SH group, a variety of functionalities can be tolerated on the thiol side chain. Thus, many diiron dithiolato carbonyls have been prepared with reactive functional groups attached to the thiol group. Illustrative of the functional group tolerance is the attachment of an O/N-protected derivative of cysteine (see Table 1). When two such multifunctional thiolates are adjacent on the diiron framework, they undergo an intramolecular condensation to afford an ethanedithiol-derived amino acid (Scheme 1).[117] A further example is the efficient preparation of $Fe_2(\mu\text{-}SC_6H_4NH_2)_2(CO)_6$ from 4-$H_2NC_6H_4SH$[118] (as well as by hydrogenation of $Fe_2(\mu\text{-}SC_6H_4NO_2)_2(CO)_6$[38]). Iron(0) carbonyls are proposed to survive boiling water in their reaction with thiol-containing peptides to give diiron hexacarbonyl dithiolates.[119]

2.1.2. Mechanism of Conversion of Iron Carbonyls and Thiols to $Fe_2(\mu\text{-}SR)_2(CO)_6$—

The formation of $Fe_2(\mu\text{-}SR)_2(CO)_6$ from thiols and $Fe(CO)_5$ (and probably $Fe_2(CO)_9$, which is a source of $Fe(CO)_4$) proceeds via complexes of the type $Fe(CO)_4(RSH)$ and $HFe(CO)_4(SR)$ (R = H, Me, Et, Ph). Thiol complexes of other metals have been well-characterized, for example, $[Ru(NH_3)_5(EtSH)]^{2+}$.[120] The intermediacy of $Fe(CO)_4(RSH)$ may also arise by the reaction of $H_2Fe(CO)_4$ with thiols, which affords $Fe_2(\mu\text{-}SR)_2(CO)_6$ quantitatively at 0°C (R = Ph, C_6F_5, *i*-Pr).[121] The $Fe(CO)_4(RSH)$ complexes can be generated by protonation of the thiolato anions $[Fe\text{-}(CO)_4(SR)]^-$ (R = Me, Et), which can be obtained by reaction of $Fe_2(CO)_9$ and thiolate salts (Scheme 2).[122] These alkyl thiol complexes have been characterized by NMR and IR spectroscopy at low temperatures. Upon warming to near room temperature, these $Fe(CO)_4(RSH)$ complexes convert to $Fe_2(\mu\text{-}SR)_2(CO)_6$ with loss of CO and H_2.[122] Protonation of PPN[$(PhS)Fe(CO)_4$] gives $Fe_2(\mu\text{-}SPh)_2(CO)_6$ even at −78 °C, showing that the acidic thiol complexes convert more rapidly. The facility of the protonation-induced reactions is consistent with the efficiency of the $Fe_2(CO)_9$/RSH route to $Fe_2(\mu\text{-}SR)_2(CO)_6$ (R = Et, *i*-Pr, *s*-Bu). [123]

Toluene- and 1,3-propanedithiol react with THF solutions of $Na_2[Fe(CO)_4]$ to produce diiron dithiolato carbonyls in moderate yields.[124] This counterintuitive approach probably involves protonation of $[Fe(CO)_4]^{2-}$ by the thiol.

In contrast to the lability of the $HFe(SPh)(CO)_4$/$Fe\text{-}(CO)_4(PhSH)$ system, the disubstituted complex $HFe(SPh)\text{-}(CO)_2[P(OPh)_3]_2$ has been isolated at room temperature and characterized crystallographically.[125] This phosphite complex shows, however, no tendency to convert to diiron(I) dithiolates. No such hydride intermediate is observed in the conversion of the Fe(0) phosphine complex $Fe\text{-}(R_2PCH_2CH_2SH)(CO)_4$, which contains a pendant thiol. No hydride intermediates were observed in the photochemical conversion to the diiron derivatives $Fe_2\ (\mu\text{-}SCH_2CH_2PR_2)_2(CO)_4$ (Scheme 3).[126]

Insight into the pathway connecting $Fe(HSR)(CO)_4$ to the diiron(I) dithiolates is provided by studies on related HX substrates. Sources of $Fe(CO)_4$, generated by photolysis of $Fe(CO)_5$ or dissociation of $Fe_2(CO)_9$, react with HX (X = Br,I) to give $Fe_2(\mu\text{-}X)_2(CO)_6$.[127] The secondary phosphine $HP(CF_3)_2$ reacts with $Fe_2(CO)_9$ to give the adduct $Fe(CO)_4[HP(CF_3)_2]$, which is analogous to $Fe(CO)_4(RSH)$. This *mono*iron phosph*ine* complex converts thermally and photochemically to the *di*iron phosph*ide* $Fe_2[\mu\text{-}P\text{-}(CF_3)_2]_2(CO)_6$. Using ^1H and ^{19}F NMR spectroscopy, *cis*- and *trans*-$H_2Fe_2[\mu\text{-}P(CF_3)_2]_2(CO)_6$ were characterized as intermediates (Scheme 4).[128] Similar intermediates can be envisioned for the formation of dithiolates from RSH. Such dihydrides are poised to eliminate H_2 concomitant with formation of the Fe–Fe bond, perhaps after migration of one hydride to a bridging position. Diferrous dithiolato dihydrides are rarely observed.[129]

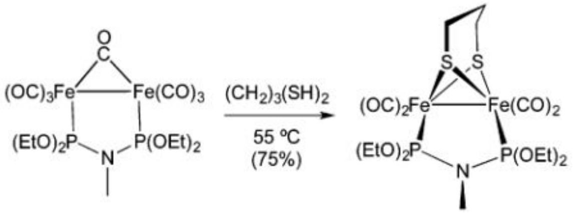
The reaction of thiols with the triiron cluster $Fe_3(CO)_{12}$ is an important route to $Fe_2(\mu\text{-}SR)_2(CO)_6$ complexes. This conversion differs mechanistically from the pathways starting with $Fe(CO)_4$ sources, although again H_2 is produced. In the case of bulky thiols, the reaction of $Fe_3(CO)_{12}$ gives the triiron clusters $Fe_3(\mu\text{-}SR)(\mu\text{-}H)(CO)_9$ as the first detectable intermediate (R = R = *i*-Pr, *s*-Bu, *t*-Bu, Scheme 5).[123,130] The species $Fe_3(\mu\text{-}S\text{-}t\text{-}Bu)(\mu\text{-}H)(CO)_9$ reacts with additional *t*-BuSH to give the triiron dithiolate $Fe_3(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_9$, which retains two Fe–Fe bonds.[131] This triiron species appears to be an intermediate connecting $Fe_3(\mu\text{-}S\text{-}t\text{-}Bu)(H)(CO)_9$ and $Fe_2(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_6$.[123] Access to $Fe_3(\mu\text{-}SR)(\mu\text{-}SR')(CO)_9$ for non-bulky R groups is gained by reaction of $Et_3NH[Fe_3(\mu\text{-}SR)(CO)_9]$ (R = *t*-Bu, C_6H_{11}) with sulfenyl chlorides (R′SCl, R′ = Me, Ph). The $Fe_3(\mu\text{-}SR)(\mu\text{-}SR')(CO)_9$ clusters convert to the diiron derivatives upon heating (Scheme 5)[131] Complementary to the $Fe_3(CO)_{12}$/RSH reactions are reactions of $Fe_3(CO)_{12}$ with thiolate *anions* (section 2.1.6).

The salt $Et_3NH[HFe_3(CO)_{11}]$, which is produced readily from Et_3N, $Fe(CO)_5$, and protic solvent,[132] reacts efficiently with thiols according to the stoichiometry in eq 3.[18,133,134]

$$2Et_3NH^+[HFe_3(CO)_{11}]^- + 6RSH \rightarrow 3Fe_2(\mu\text{- }SR)_2(CO)_6 + 2Et_3N + 5H_2 + 4CO \quad (3)$$

2.1.3. Derivatives of Alkanedithiols and Alkenedi-thiols—

Methane-, 1,2-ethane-, and 1,3-propanedithiols react with $Fe_3(CO)_{12}$ to give good yields of $Fe_2[\mu\text{-}S_2(CH_2)_n](CO)_6$.[17,28,82] For H_2edt and H_2pdt, the reactions are accompanied by the formation of ~5% triiron species of the formula $Fe_3(\mu\text{-}xdt)_2(CO)_7$ (xdt = edt, pdt). In the case of $Fe_2(\mu\text{-}pdt)(CO)_6$, yields of 33% and 92% are observed from the reactions of H_2pdt with $Fe(CO)_5$ and $Fe_3(CO)_{12}$, respectively.[17,28,135,136] King observed that, although H_2edt barely reacts with $Fe(CO)_5$,[137] it reacts with $Fe_3(CO)_{12}$ to give $Fe_2(\mu\text{-}edt)(CO)_6$ in 65% yield.[17] The reactions of substituted iron(0) carbonyls, e.g., $Fe(CO)_4(PPh_3)$, with thiols have been investigated only lightly, so this approach may be fertile.[126,138] In one example, H_2pdt reacts efficiently with substituted derivatives of $Fe_2(CO)_9$ (eq 4).[136]

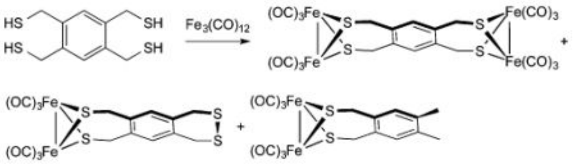


(4)

Because they are nearly isosteric with the azadithiolate cofactor in the [FeFe]-hydrogenase, propanedithiolate derivatives have been the subject of careful study. Bulky analogues of H_2pdt, i.e., $R_2C(CH_2SH)_2$ (R = Me, Et, *i*-Pr, and Ph), react with $Fe_3(CO)_{12}$ less efficiently than H_2pdt but still produce good yields of the diiron dithiolates.[139–141] The diiron complex $Fe_2[(\mu\text{-}SCHPh)_2SiPh_2](CO)_6$ was obtained by the reaction of *meso*-$Ph_2Si(CH(Ph)SH)_2$ with $Fe_3(CO)_{12}$.[142] This and related sterically crowded complexes are of interest as precursors to diiron ditholates that adopt unsymmetrical, “rotated” structures (Figure 8).[140,141,143]

2-Benzoyldithioacetic acids, as their ene-dithiol tautomers $ArC(O)CH{=}C(SH)_2$, feature geminal dithiol groups and thus represent precursors to diiron dithiolato carbonyls. These dithiols react under mild conditions with $Fe_2(CO)_9$ to give the methanedithiolates.[144] The same dithiols also react reasonably efficiently with $Fe_3(CO)_{12}$ to produce the C_s-symmetrical alkylidene-1,1-dithiolate complexes. The selectivity for the alkene- vs alkanedithiolate is sensitive to the reactant ratio.[145] The differing products in these relatively similar reactions indicate, but do not explain, the involvement of iron hydride intermediates that in turn depend on the Fe(0) precursor (Scheme 6).[145]

Reactions of $Fe_3(CO)_{12}$ with the tetrathiol 1,2,4,5-$(HSCH_2)_4C_6H_2$ illustrate the range of reactions for benzylic thiols with Fe(0): formation of dithiolates, dehydrogenation, and desulfurization (eq 5).[84] The formation of disulfide-containing products is consistent with Nametkin’s study of the organosulfur byproducts from the reaction of thiols and $Fe_3(CO)_{12}$.[18]



(5)

2.1.4. Derivatives of Aryldi- and Arylpolythiols, Including Heterocycles—

Aromatic dithiols such as 1,2-benzene-, 3,4-toluene, and 1,8-naphthalenedithiols react efficiently with $Fe_3(CO)_{12}$ and related Fe(0) reagents to give the expected diiron derivatives[146] In the reaction of dichlorobenzenedithiol with $Fe_3(CO)_{12}$ to give $Fe_2(\mu$-

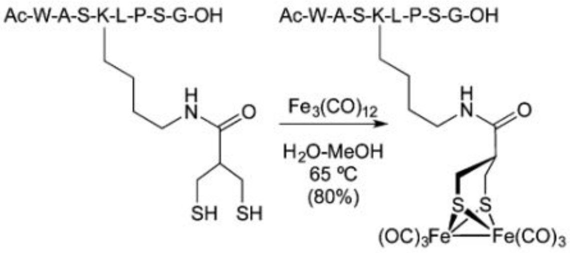
$S_2C_6Cl_2H_2)(CO)_6$,[147] an intermediate mixed valence species $Fe_3(\mu\text{-}S_2C_6Cl_2H_2)_2(CO)_7$ is produced.[148] The structure proposed for this intermediate (Scheme 7) is isomeric with the $Fe_3(\mu\text{-pdt})_2(CO)_7$ species obtained as a minor product in the reaction of $pdtH_2$ and $Fe_3(CO)_{12}$.[17] Benzenehexathiol and $Fe_3(CO)_{12}$ react to give a 17% yield of the tris(diiron) derivative of benzenehexathiolate, $(\mu\text{-}C_6S_6)[Fe_2(CO)_6]_3$.[149] This species features an inorganic $C_6S_6Fe_6$ core that should display interesting substitution reactions (Figure 9).

An interesting carboxylate-functionalized diiron complex is $Fe_2[\mu\text{-}S_2C_6H_2\text{-}3,6\text{-}(CO_2H)_2](CO)_6$, derived from 1,2-dimer-captobenzene-3,6-dicarboxylic acid. The resulting dicarboxylate forms an organometallic metal–organic framework (MOF) upon condensation with a Zr_6 oxide cluster (Figure 10).$_{65,66}$ The synthesis was achieved in water by displacement of a fraction of benzenedicarboxylate groups in the preformed MOF UiO-66.

Heterocyclic dithiols also form diiron dithiolate carbonyls. The diiron hexacarbonyl derivative of dicarboranedithiol $1,2\text{-}C_2B_{10}H_{10}(SH)_2$ exhibits particularly low reduction potential, reflecting the electron-withdrawing character of the carborane backbone.[150] Dithiolato complexes derived from quinoxaline-dithiols are of interest because the heterocyclic backbone sustains reversible protonation, thereby affecting the redox properties of the diiron center.[151,152]

2.1.5. Derivatives of Elaborated Alkanedithiols (Mainly Propanedithiolates)—

By reactions of functional groups on the thiolate ligands, many derivatives have been prepared employing standard organic synthetic manipulations. This approach has been enabled by the resilience of many organic substituents to substitution reactions at iron, e.g., by phosphines,[153–156] cyanide,[27] and NHC's.[157] Propanedithiolate complexes bearing functionality at C2 are versatile precursors. One such complex is $Fe_2[(\mu\text{-}SCH_2)_2CHCO_2H](CO)_6$, derived from commercially available dihydroasparagusic acid $((HSCH_2)_2CHCO_2H)$.[55] The carboxylic acid group in $Fe_2[(\mu\text{-}SCH_2)_2CHCO_2H](CO)_6$ has been converted to amides, including peptides,[158] and esters without affecting the diiron core, which remains susceptible to ligand substitution (Scheme 8, see Table 1).[55,58,64,159–161] The dihydroasparagusic acid also can be attached to lysine side chains, allowing anchoring of the diiron center to peptides (eq 6).[30]

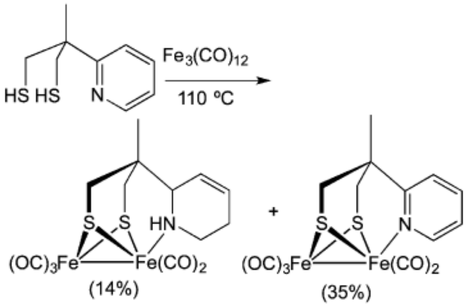


(6)

A hydroxy-functionalized diiron dithiolate is readily prepared from 2-hydroxy-1,3-propanedithiol.[17,98] The alcohol group in the resulting complex $Fe_2[(\mu\text{-}SCH_2)_2C(H)OH]$

$(CO)_6$ can be modified in interesting ways, including conversion to a pendant phosphonite ligand (Scheme 9).[53] Complementarily, the hydroxy-1,3-propanedithiol can be modified before the dithiol is installed on the diiron center. In this way, water-soluble diiron dithiolate complexes were produced bearing a sugar residue.[60]

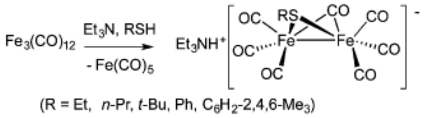
Propanedithiols functionalized with ligands at the 2-position have been fruitfully pursued en route to biomimetic catalysts.[11] Examples of $Fe_2[(\mu\text{-}SCH_2)_2C(Me)CH_2R](CO)_6$ have been prepared where R = SMe,[109] NH_2, 2-pyridyl, and SAc.[110] The hydroxy derivatives $Fe_2[(\mu\text{-}SCH_2)_2C(Me)CH_2OH](CO)_6$ shows no tendency to decarbonylate, consistent with the weak coordinating tendency of the hydroxyl group.[110] The reaction of $Fe_3(CO)_{12}$ with the pyridine-containing dithiol $(HSCH_2)_2C(Me)CH_2$-2-py results in partial hydrogenation of the ring.[162] This unexpected result implicates the intermediacy of iron hydrides that are capable of hydrogenation of the pyridine ring, which normally resists hydrogenation (eq 7). The pendant thioacetate group in $Fe_2[(\mu\text{-}SCH_2)_2C(Me)CH_2SAc]\text{-}(CO)_6$ reacts with 4Fe-4S cubane clusters to give an Fe_6S_6 ensemble. This cluster coupling reaction proceeds via elimination of AcSEt, followed by displacement of one CO ligand by the pendant 4Fe-4S cluster ligand (Scheme 10).[163,164]



(7)

The reaction of the trithiol $(HSCH_2)_3C(Me)H$ with $Fe_3(CO)_{12}$ is, not surprisingly, complicated. High Fe(0)/thiol ratios give dendritic derivatives containing three diiron dithiolate subunits.[165] When the Fe(0) is the limiting reagent, one obtains the mixed valence species $\{Fe_2[(\mu\text{-}SCH_2)_3CMe]\text{-}(CO)_4\}_2$ (Scheme 11).[166,167] Implicit in these results, but unproven, is the reaction of Fe_4 species with additional Fe(0) reagent to give the Fe_6 product.

2.1.6. Routes to $Fe_2(\mu\text{-}SR)_2(CO)_6$ via $[Fe_2(\mu\text{-}SR)(CO)_7]^-$—In addition to the diiron(I) dithiolato carbonyls, diiron(0) *mono*thiolato carbonyls are well-established. With the formula $[Fe_2(\mu\text{-}SR)(CO)_7]^-$, these species are classified as $[Fe(0)]_2$ derivatives. These anions are prepared by the reaction of $Fe_3(CO)_{12}$ with thiolate anions, often in the form of the mixture RSH/Et_3N (eq 8). [168–171] The formulas for these monothiolato diiron(0) species are sometimes more explicitly written as $[Fe_2(\mu\text{-}SR)(\mu\text{-}CO)(CO)_6]^-$, which highlights their structural similarity to $Fe_2(\mu\text{-}SR)_2(CO)_6$. The salts $Et_3NH\text{-}[Fe_2(\mu\text{-}SR)(CO)_7]$ convert to the diiron(I) dithiolates, usually in low yields, upon heating[172–174] and with weak oxidants and electrophiles.[175–177] These diiron(0) anions are oxidized by S_8 to give what are proposed to be diiron(I) anions. Thus, treatment of $[Fe_2(\mu\text{-SEt})(CO)_7]^-$ with sulfur followed by methylation with MeI gave both $Fe_2(\mu\text{-SEt})_2(CO)_6$ and $Fe_2(\mu\text{-SMe})(\mu\text{-SEt})(CO)_6$ (Scheme 12).[178] These results point to unexplored pathways for thiolate exchange.[175,177]



(8)

The diiron(0) complexes $[Fe_2(\mu\text{-SR})(CO)_7]^-$ react with sulfenyl chlorides to give the mixed dithiolate in high yields (eq 9).[178] The method is, however, limited by the poor availability and instability of most sulfenyl chlorides. Complementary to this route to mixed thiolato diiron complexes is the more reliable reaction of $Fe_2(\mu\text{-}S_2)(CO)_6$ with RLi followed by alkylation with alkyl halides (see section 3.1.1).

$$\mathrm{Et_3NH^+[Fe_2(\mu\text{- S- t- Bu})(CO)_7]^- + EtSCl \rightarrow Fe_2(\mu\text{- S- t- Bu})(\mu\text{- SEt})(CO)_6 + CO + Et_3NH^+Cl^-}$$

(9)

The reaction of Fe(0) with di- and trithiols in the presence of base has been developed. Dithiols gives linked pairs of $[Fe_2(\mu\text{-SR})(CO)_7]^-$ centers, which react with bis(sulfenyl chloride)s to give macrocyclic bisdiiron dithiolates (Scheme 13).[179,180] The trithiol $MeC(CH_2SH)_3$ gives triiron species containing both $Fe_2(\mu\text{-SR})_2(CO)_6$ and $[Fe(\mu\text{-SR})(CO)_7]^-$ centers.[181] Such compounds could undergo degenerate intra- or intermolecular exchange between the Fe(0) and Fe(I) sites, but such experiments have not been reported. The course of the reactions of $MeC(CH_2SH)_3/Et_3N$ with $Fe_3(CO)_{12}$ contrasts with the related reaction conducted in the absence of Et_3N, which afford $Fe_2(\mu\text{-SR})_2(CO)_6$ derivatives exclusively (Scheme 11).[165–167]

Related to the anionic diiron thiolates, anionic *tri*iron clusters $[Fe_3(\mu\text{-SR})(CO)_9]^-$ are also claimed to arise from the reaction of $Fe_3(CO)_{12}$ with NaSR (R = Et, Ph, Bu, etc.) in hot THF.[182] Other work implies that some of these proposed $Fe_3(\mu\text{-SR})$ cluster anions may in fact be $[Fe_2(\mu\text{-SR})(CO)_7]^-$.[169] In general, many of these studies implicate the series $[Fe(SR)(CO)_4]^- \rightarrow [Fe_2(\mu\text{-SR})(CO)_7]^- \rightarrow [Fe_3(\mu\text{-SR})(CO)_9]^-$. This “aufbau” sequence remains to be tested under well-defined conditions.

2.2. Reactions of Iron(0) Reagents and Organic Di- and Polysulfides

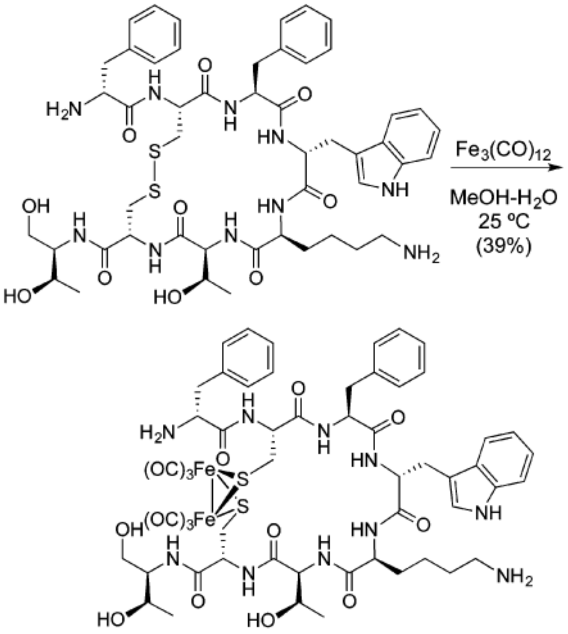
2.2.1. Ordinary Disulfides—Compounds containing RS–SR bonds oxidatively add to iron(0) carbonyls to give diiron dithiolato hexacarbonyls.[183–187] The method was first demonstrated by Hieber and Scharfenberg using diphenyldisulfide and $Fe_3(CO)_{12}$.[102] The route is typically less efficient than routes from thiols. The photoreaction of $Fe(CO)_5$ with Ph_2S_2 was originally thought to give an adduct with a Ph_2S_2 ligand;[188] a subsequent crystallographic study confirmed that the product is $Fe_3(\mu\text{-SPh})_6(CO)_6$, i.e., the ferrous species $(CO)_3Fe(\mu\text{-SPh})_3Fe(\mu\text{-SPh})_3Fe(CO)_3$.[189] The conversion of this green paramagnetic complex to or from $Fe_2(\mu\text{-SPh})_2(CO)_6$ has not been reported.

The preparation of $Fe_2(\mu\text{-SMe})_2(CO)_6$ using Me_2S_2 is instructive. Using the disulfide is more convenient than the thiol route because Me_2S_2 is a liquid whereas MeSH is a gas. Starting from $Fe(CO)_5$ in neat Me_2S_2, the yield of $Fe_2(\mu\text{-SMe})_2(CO)_6$ is 60% when the preparation is conducted under 65 atm of CO (Scheme 14). Without an atmosphere of CO, this reaction affords the red insoluble polymer $[Fe(\mu\text{-SMe})_2(CO)_2]_n$.[190] This and related polymeric ferrous dithiolato carbonyls[191] have not been investigated further. The hexacarbonyl $Fe_2(\mu\text{-SMe})_2(CO)_6$ was found not to react with Me_2S_2, suggesting that the ferrous product arises via an alternative pathway. The reaction of $Fe_3(CO)_{12}$ with Me_2S_2 in refluxing benzene gives $Fe_2(\mu\text{-SMe})_2(CO)_6$ in 27% yield.[24]

The disulfide route has been employed to prepare diiron complexes with relatively exotic thiolates. Oxidative addition of the disilyl disulfide to $Fe(CO)_5$ under UV irradiation gives the silylthiolate $Fe_2[\mu\text{-SSi}(t\text{-Bu})_3]_2(CO)_6$.[192] The volatile $Fe_2(\mu\text{-SCF}_3)_2(CO)_6$ was obtained by addition of $(SCF_3)_2$ to $Fe_2(CO)_9$.[193] The related reactions of $Fe(CO)_5$ with $XSCF_3$ (X= SMe, SCF_3) give trace amounts of "$Fe_2(\mu\text{-S})(\mu\text{-SCF}_3)_2(CO)_6$", which, as mentioned elsewhere, could be a perthiolate $Fe_2(\mu\text{-SCF}_3)(\mu\text{-S}_2CF_3)_2(CO)_6$. Sulfido-bridged diferrous carbonyls is an unusual motif,[194] although trithiolate related species of the type $[Fe_2(\mu\text{-SR})_3(CO)_6]^+$ are well-known.[195]

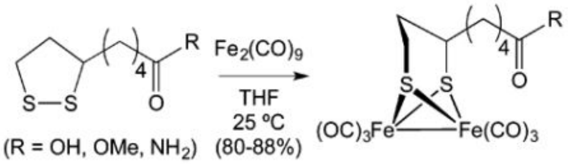
2.2.2. Functionalized Disulfides—

The reaction of Fe(0) carbonyls with organic disulfides tolerates many functional groups. For example, treatment of $Fe_3(CO)_{12}$ with bis(2-acylaminophenyl)disulfides in toluene at 70 °C affords diiron dithiolates in moderate yields.[183] A peptide was conjugated to $Fe_2(CO)_6$ by reaction of the cyclic disulfide sandostatin with $Fe_3(CO)_{12}$ (eq 10).[196]



(10)

Lipoamide and related derivatives also react efficiently with $Fe_2(CO)_9$ to give the corresponding dithiolates, which are chiral (eq 11).[197]



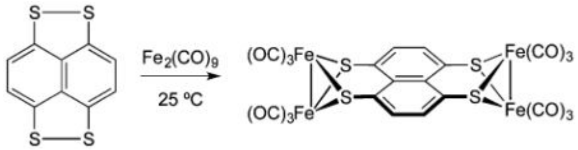
(11)

Because both disulfides and thioethers are reactive toward iron(0) carbonyls, thioether disulfides are expected to give complex product distributions. For example 7-, 8-, and 9-membered cyclic thioether disulfides oxidatively add to $Fe_2(CO)_9$. The nature of the products depends on the ring size of the precursor. Larger rings appear to favor triiron dithiolates, which are formally related to the diiron dithiolates by the addition of an $Fe(CO)_4$ unit across the Fe–Fe bond (Scheme 15).[198,199] Characteristically, these reactions are accompanied by the formation of other products of C–S bond scission such as $Fe_3(\mu\text{-}S)_2(CO)_9$, $Fe_2(\mu\text{-}S_2CH_2)(CO)_6$, and $Fe_2(\mu\text{-edt})(CO)_6$. The formation of Fe_2 vs Fe_3 product is subtly based on the flexibility of the thioether backbone.[199,200] The $Fe_3(CO)_8$ cluster is related to $Fe_3(\mu\text{-S-}t\text{-Bu})_2(CO)_9$ described earlier.

Tetraalkyl-1,2,4-trithiolanes react with $Fe_2(CO)_9$ to give ~3:1 mixtures of the thiadithiolates[160] and the 1,1-dithiolates, with formula $Fe_2[(\mu\text{-}SCR_2)_2S](CO)_6$ and $Fe_2(\mu\text{-}$

$S_2CR_2)(CO)_6$, respectively[199,200] The thiadithiolates arise via oxidative addition across the S–S bond. The pathway to the 1,1-dithiolates is less clear, but they do not result from the thiadithiolates. The reactivity of 1,2,4-trithiolanes is discussed further in section 2.4 in the context of thione substrates. Thiosulfinates, a rare class of organosulfur compounds with the functionality RS(O)SR′, also oxidatively add to Fe(0) carbonyls to give $Fe_2(\mu\text{-}SR)_2(CO)_6$ as well as the mono-oxygenated derivative.[201]

2.2.3. Peri-naphthalene Disulfides—Peri-naphthalene disulfides are particularly popular precursors to diiron(I) dithiolates starting from Fe(0) reagents.[146,202,203] The peri-naphthalene disulfides, which feature a strained 5-membered C_3S_2 ring, are readily prepared in one pot by dilithiation of 1-bromonaphthalene.[202] The resulting $Fe_2(\mu\text{-}S_2C_{10}H_{6-x}R_x)$-$(CO)_6$ derivatives have simplified stereochemistry relative to the more floppy propanedithiolates. These naphthalene disulfides can be fitted with diverse functional groups, which remain untouched in the oxidative addition of the disulfide by the Fe(0) reagent. Functional groups include Schiff bases,[204] porphyrins,[29,205] carboxylic acid anhydrides, imides,[206] and formyl groups.[48] A selection of these products are shown in Figure 11. Naphthalene bis(disulfide) reacts with $Fe_2(CO)_9$ in benzene at room temperature to give the bis(diiron) complex $[Fe_2(CO)_6]_2(\mu\text{-}S_4C_{10}H_4)$ (eq 12).[207]



(12)

2.2.4. Perthioesters—The perthioesters (RC(O)SSR′, RC(S)SSR′) derived from thiosalicylic acids give diiron dithiolates with planar dithiolate bridges.[208] The complex $Fe_2[\mu\text{-}SC_6H_4C(O)S](CO)_6$ is one of the few μ-acylthiolate complexes confirmed by X-ray crystallography. Its reactivity toward nucleophiles would be of interest, because it would appear to be an activated ester. The corresponding reaction of the trithio ester results in a more complicated product resulting from the binding of the thione functionality to a second $Fe_2(CO)_6$ subunit (Scheme 16).[208,209] This complication arises from the high reactivity of iron carbonyls toward the C═S functionality, as is discussed in section 2.4.[210–213]

2.2.5. From Polysulfides—Organic polysulfides have often been examined as precursors to metal thiolates.[214] As applied to the synthesis of diiron dithiolates, the use of organic polysulfides always cogenerates significant amounts of $Fe_3(\mu\text{-}S)_2(CO)_9$.[215] This cluster and the diiron dithiolates are readily separated by chromatography so that, in cases where the polysulfide is readily available, there is usually no point in converting it to the dithiol prior to reaction with the iron carbonyl. The cyclic tetrasulfide derived from tetrafluoroethylene reacts with $Fe_3(CO)_{12}$ carbonyls to afford the volatile $Fe_2(\mu\text{-}S_2C_2F_4)$ $(CO)_6$, a rare example of a diiron perfluoroalkyldithiolate complex. The related reaction, but using the mixed disulfide thioether $(C_2F_4)_2S_3$, is far less efficient, highlighting the greater reactivity of S–S bonds.[137] Similar reactions have been mentioned for $Me_3SiC_2H_3S_x$,[216] 1,1′-ferrocenetrisulfide,[217] norbornanetrisulfide,[135] and trisulfide of cycloheptadiene[218] (Table 3).

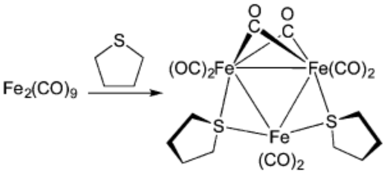
2.3. Reactions of Iron(0) Reagents and Thioethers

2.3.1. Unstrained Thioethers—Usually thioethers are less reactive toward diiron carbonyls than disulfides and thiols.[219] In 1940, Hieber and Scharfenberg reported, without mentioning yields, that Me_2S and Et_2S react with $Fe_3(CO)_{12}$ to afford $Fe_2(\mu\text{-}SR)_2(CO)_6$ (R = Me, Et).[102] Many years later, Nametkin conducted thorough comparison of various organosulfur precursors (Table 4). Only a modest effect on the rate and efficiency of the reaction: The key determinants of yield and rate were the organosulfur and iron(0) reagents. Thiols are the best substrates, and thioethers were the slowest. These results clearly show that the $Fe_3(CO)_{12}$ + RSH route is highest yielding and fastest. Slowest and lowest yielding is the reaction of thioethers with $Fe(CO)_5$.[18]

The now famous $Fe_2(\mu\text{-pdt})(CO)_6$ was first prepared by degradation of a tetrathiacyclophane with a refluxing methyl-cyclohexane solution of $Fe(CO)_5$(Scheme 17).[220] The reaction conceivably proceeds via radical pathway, which would be facilitated by the benzylic substituents. Cyclic di- and polythioethers appear to more readily degraded to diiron dithiolates, perhaps suggesting that they more readily form adducts, which are poised to degrade via Fe-induced C–S bond scission.[221] Rings with several heteroatoms, e.g., the groups $–S–CH_2–S–C$ and $C–S–CH_2–CH_2–S–$, appear especially susceptible to activation by Fe(0).[222–224] The methane- and ethanedithiolate $Fe_2(\mu\text{-}S_2(CH_2)_2)(CO)_6$ arise (no yields being mentioned) from the reaction of $Fe_3(CO)_{12}$ with 1,4-dithiane and 1,3,5-trithiane $(SCH_2)_3$, respectively.[225] The thiol route ($CH_2(SH)_2$ + Fe_3 $(CO)_{12}$) is far more efficient (Scheme 18).[82,225,226] Another degradative route to $Fe_2(\mu\text{-pdt})(CO)_6$ involves the combined thermal-photochemical reaction of $Fe(CO)_5$ and 1,3-dithiane.[227] Further study is required to reconcile these results, specifically the relationship between the formation of $Fe_2(\mu\text{-pdt})(CO)_6$ and the product of oxidative addition of the C–S bond.

More so than saturated thioethers, usaturated sulfur compounds are activated toward cleavage by Fe(0) carbonyls. The first indication of this reactivity was the finding that vinylthioethers, including thiophenes, oxidatively add to iron carbonyls to give $Fe_2(\mu\text{-}SR)(\mu\text{-}CHCHR)(CO)_6$ (R = alkyl, vinyl).[224,228,229] 1,4-Dithiins, six-membered rings of the formula $C_4R_4S_2$, are activated by $Fe_2(CO)_9$ as well as $Fe_3(CO)_{12}$ to give dithiolenes $Fe_2(\mu\text{-}S_2C_2R_2)(CO)_6$, but the yields are low.[230]

2.3.2. Mechanistic Aspects of Thioether Activation by Iron(0) Carbonyls—C–S bonds typically are strong (~73 kcal/mol) and kinetically stable. It is therefore surprising that iron thiolates are often readily obtained in good yields by the reaction of iron carbonyls with unstrained thioethers. The mechanism of this process has not been widely discussed. The simple adducts $(R_2S)Fe(CO)_4$ exhibit no unusual structural or spectroscopic features.[203,204] It is conceivable that C–S bond activation requires coordination of the thioether as a bridging ligand. It is reported that organosulfur ligands bridged to several Fe centers are labile toward C–S bond scission.[182] Indeed, iron carbonyl clusters with bridging thioether ligands are known.[231,232] For example, the complex $Fe_3(\mu\text{-}SC_4H_8)_2(CO)_8$ is obtained in 30% yield by the reaction of tetrahydrothiophene (THT) with $Fe_2(CO)_9$ at room temperature (eq 13).[153] The reaction of THT with $Fe_3(CO)_{12}$ at elevated temperatures gives moderate to good yields of $Fe_3(\mu\text{-}S)_2(CO)_9$ and $Fe_2(\mu\text{-}S_2)(CO)_6$, together with butane and butenes.[233]

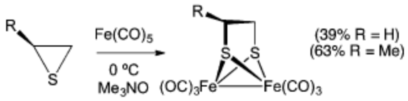


(13)

The photochemical reaction of 1,3-dithiane and Fe(0) can proceed with formal oxidative addition of a C–S bond. (Scheme 19).[227,234,235]

2.3.3. Strained Thioethers: Thiiranes and Thietes—Strained cyclic thioethers can be effective precursors to diiron dithiolato carbonyls, although the route is rarely used. It has long been known that iron carbonyls desulfurize thiiranes (episulfides).[236–238] In fact, a good synthesis of $Fe_3(\mu\text{-}S)_2(CO)_9$ involves the reaction of $Fe_3(CO)_{12}$ and ethylene sulfide.[239] Propylene sulfide reacts with $Fe(CO)_5$ in the presence of the decarbonylating agent Me_3NO to give good yields of the simplest chiral dithiolato complex (eq 14).[240] $Fe_2(\mu\text{-}edt)(CO)_6$ can be obtained less efficiently by reaction of thiirane-S-oxide and $Fe_3(CO)_{12}$ in hot THF.[241] The fate of the oxo group in this obscure reaction was not determined. The deoxygenation of sulfur ligands is observed in other reactions of $Fe_3(CO)_{12}$.[201] Reactions of thietanes, e.g., $(CH_2)_3S$, and iron carbonyls have not been reported.

Thietes, unsaturated four-membered C_3S rings, are valence isomers related to the highly reactive species thioacrolein ($CH_2{=}CHCH{=}S$). These strained heterocycles ring-open upon treatment with iron carbonyls. The resulting thioacrolein complex (η^4-$CH_2{=}CHCH{=}S$)$Fe(CO)_3$ represents an analogue of (η^4-butadiene)$Fe(CO)_3$. It undergoes decarbonylation to give the corresponding $36e^-$ tetracarbonyl diiron dithiolate (Scheme 20).[242]



(14)

2.4. Reactions of Iron(0) Reagents and C═S-Containing Reagents

Iron carbonyls are highly reactive toward the C═S functionality[221] (thioketones,[243–245] dithioesters,[209,246,247] and di- and trithiocarbonates[248–250]), giving a variety of products. Although this approach often suffers from low yields, it produces diiron dithiolates of distinctive structures.

2.4.1. Thiones—The case of diphenylcyclopropenethione is an instructive starting point for the discussion. Upon treatment with $Fe_2(CO)_9$, it forms a simple 1:1 adduct $Fe(CO)_4(SC_3Ph_2)$ in high yield. The efficiency of the reaction reflects the almost unique ability of this thione to serve as a unidentate Lewis base, a consequence of the aromatic character of the cyclopropenium cation.[251] Otherwise thioketones typically attach to metals as η^2-ligands, as in $Pt(\eta^2\text{-}SCPh_2)(PPh_3)_2$.[252]

The reactions of thiobenzophenones toward Fe(0) can often be rationalized by invoking the degradation of the thione to the thiosulfine $Ar_2C{=}S{=}S$. The thiosulfine is a dipole that adds Ph_2CS to give tetraphenyl-1,2,4-trithiolane.[253,254] This trithiolane exists in equilibrium, rapid near 50 °C, with Ph_2CS and, possibly, the thione-sulfide/dithiirane isomers of Ph_2CS_2 (Scheme 21).[245]

Thus, the formation of $Fe_2(\mu\text{-}S_2CPh_2)(CO)_6$ from Ph_2CS and Fe(0) carbonyls can be rationalized by invoking the oxidative addition of the dithiirane Ph_2CS_2.[243,245,255,256] C–H activation occurs in these, as illustrated by one of the products in Scheme 22.[243]

Bulky aliphatic thiones (nonbulky dialkyl thiones are unstable with respect to oligomerization[257]) generally react with Fe(0) reagents to give diiron 1,1-dithiolates. These reactions have been proposed to proceed via 1,1-dithiolatodiiron complexes with two bridging CO ligands.[255] Diiron dithiolates with a single bridging CO have rarely been observed,[142] much less two bridging CO groups. Thus, these assignments should be viewed with caution.

Potentially relevant to the pathway leading to $Fe_2(\mu\text{-}S_2CR_2)(CO)_6$ from thioketones are studies on the reactions of a bulky thioketene with $Fe_2(CO)_9$. This reaction affords the $Fe_2(CO)_6$ adduct.[258] This species reacts further with thioketene to give the 1,1-dithiolate with perfect stoichiometry (Scheme 23).[213]

2.4.2. Derivatives of CS_2—In its reactions with metal carbonyls, carbon disulfide is often a source of esoteric products, which can inspire rational syntheses.[259,260] A tetrairon derivative of methanetetrathiolate arises via the reaction of $Fe_3(CO)_{12}$ with a mixture of CS_2 and PEt_3 (Scheme 24).[261] No yield was published, but it is probably very low. The structure was determined by X-ray crystallography. The related reaction of CS_2 with $Fe_3(CO)_{12}$ gives a complex derived from C_2S_4, again in very low yield. A number of complexes are known with ligands derived from tetrathiooxalate,[262,263] but this FeC_2S_4 species remains unique. As established by X-ray crystallography, it is a rare complex of an ethylenetetrathiolate ($C_2S_4^{4-}$) vs a tetrathiooxalate ($C_2S_4^{2-}$), featuring the unprecedented 1,1-dithiolene bonding mode.[264]

2.4.3. Dithioesters and Related Di- and Trithiocarbonates—Upon treatment with $PhCS_2Me$ and related dithioester substrates, iron carbonyls give diiron adducts, not thiolates.[265] As summarized in Linford and Raubenheimer's review,[221] the reactions of Fe(0) reagents with many acyclic trithiocarbonates (i.e., $(RS)_2CS$) and xanthates (i.e., (RS)-(RO)CS) proceed similarly.[221] Ethylenetrithiocarbonate ($SCS_2C_2H_4$) reacts with $Fe_2 (CO)_9$ to give adducts of $Fe_2(CO)_6$ similar to those obtained from dithioesters. This initial species undergoes a complicated but efficient transformation to the diiron 1,1-dithiolate.[266,267] These results are reminiscent of Behrens's report on thioketenes serving as S-donors and alkylidene precursor (Scheme 23). This parallel supported the notion that at least some diiron 1,1-dithiolato complexes arise by S-abstraction from $R_2C{=}S$ functionality, not from dithiiranes.

Dithiocarbonates ($OC(SR)_2$) react with $Fe_2(CO)_9$ to give modest yields of the dithiolate complexes including those of edt, pdt, and ethylenedithiolates. An idealized equation for this transformation is given in eq 15.

$$2\mathrm{Fe}_2(\mathrm{CO})_9+(\mathrm{RS})_2\mathrm{CO} \rightarrow \mathrm{Fe}_2(\mathrm{SR})_2(\mathrm{CO})_6+2\mathrm{Fe}(\mathrm{CO})_5+3\mathrm{CO} \qquad (15)$$

These reactions proceed via oxidative addition leading to the intermediate $Fe_2(\mu\text{-}SR)(\mu\text{-}C(O)SR)(CO)_6$.[268] The latter was proposed to feature a μ-R*SC*(O) group. This intermediate should probably be reformulated with the acyl bridge μ-RS*C*(*O*) related to acyl thiolates $Fe_2(\mu\text{-}SR)(\mu\text{-}C(O)R)(CO)_6$ derived from acylation of $[Fe_2(\mu\text{-}SR)(CO)_7]^-$ (section 3.7).[169] From unsymmetrical dithiocarbonates (OC(SR)(SR′)), one can obtain the mixed thiolate complexes, sometimes selectively.[268,269] A more efficient route to mixed dithiolates starts, however, with $Fe_2(\mu\text{-}S_2)(CO)_6$ (section 3.2).

2.4.4. Thioamides—Thioamides generally have not proven to be useful precursors to diiron(I) dithiolato carbonyls. Mercaptopyrimidine, which can be viewed as a tautomer of a thioamide, undergoes desulfurization by Fe(0).[270] Tetramethylthiourea gives an adduct $Fe(CO)_4(SC(NMe_2)_2)$,[255] analogous to Weiss's cyclopropenethione $Fe(CO)_4(S{=}CC_2Ph_2)$ described earlier.

Dithiooxamides (DTAs) are a family of potentially chelating organic thiocarbonyls.[272] At room temperature in THF solution, they react with $Fe_2(CO)_9$ to initially give complexes of the type $Fe(CO)_3(\kappa^2\text{-DTA})$, wherein the DTA is proposed to function as a $4e^-$ donor, *S,S*-chelated to Fe. Although not examined crystallographically, these deeply colored $Fe(CO)_3(\kappa^2\text{-DTA})$ complexes were well characterized spectroscopically and, in one case, obtained in analytical purity. These monomeric intermediates react further with $Fe_2(CO)_9$ to form, depending on the substituents, three types of diiron hexacarbonyl complexes, often in high yield (Scheme 25).[271]

2.4.5. Miscellaneous Thiocarbonyl Derivatives—Thiocarbonyl complexes are known for Fe(0), e.g., $Fe(CO)_4CS$, although derivatives of the type $Fe_2(\mu\text{-}SR)_2(CO)_{6-x}(CS)_x$ have not been reported. Reaction of $Fe(CO)_4CS$ with $P(NMe_2)_3$ results in complicated mixtures reflecting the multiple roles served by this very basic phosphine, which is an S-abstractor ligand and forms phosphoranes. One of the products, confirmed by X-ray crystallography, is $Fe_2[\mu\text{-}S_2C_2(O)(P\text{-}(NMe_2)_3)](CO)_6$,[273] which is related to the diiron dithiooxamide species shown above.[271] *N*-Sulfinylphenylhydrazine (PhNHNSO) is degraded by $Fe_2(CO)_9$ to give traces of $Fe_2(\mu\text{-}SPh)_2(CO)_6$.[274]

2.5. Reactions of Iron(0) Reagents and Thioesters and Thioamides

Thioesters, compounds with the functionality RC(O)SR′, are intriguing substrates for reactions with iron carbonyls. Iron sulfide minerals are proposed to catalyze the formation of thioesters by a carbonylation pathway according to Wächter-shäuser's Iron–Sulfur Theory for the origin of life.[275,276] Reactions of iron carbonyls with thioesters, however, have been examined only lightly.

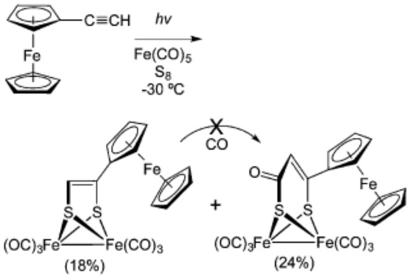
When $Fe_2(CO)_9$ is treated with chelating phosphine thioesters, one obtains diiron(II) dithiolates.[277] The process appears to proceed via the chelate-assisted oxidative addition of the thioester to a single iron(0) center (Scheme 26).[278] A pair of the resulting acyliron thiolates condense concomitant with their decarbonylation, a reaction that can be reversed under high pressures of CO.[277] The decarbonylation is consistent with the usual instability of ferrous tricarbonyl complexes. Pyridine-containing thioesters react with Fe(0) carbonyls to give thiolate/pyridyl-bridged diiron hexacarbonyl complexes.[279]

2.6. Reactions of Iron(0) Reagents, Elemental Sulfur, and Alkenes

One might expect that iron carbonyls, being zerovalent, would react readily with elemental sulfur to afford Fe–S–CO complexes and clusters. Such transformations, however, have not been demonstrated to be synthetically useful. This same reaction, however, affords the fundamental Fe–S–CO species $Fe_2(\mu\text{-}S_2CO)(CO)_6$, albeit in only 1% yield.[280] This dithiocarbonate can be prepared in 45% yield by UV photolysis of a solution of $Fe_2(\mu\text{-}S_2)(CO)_6$ and CO.[69]

2.6.1. Alkene, Alkyne, and Imine Trapping Reactions—Although often proceeding in very low yields, the reaction of $Fe(CO)_5$ (or $Fe_3(CO)_{12}$[281]) with sulfur in the presence of alkenes gives diiron dithiolate complexes, often unusual ones (Scheme 27).[282] No reaction is expected between the alkene and the sulfur in the absence of the iron carbonyl. The reaction of trimethylvinylsilane with sulfur in the presence of $Fe_3(CO)_{12}$ gives a few percent of dithiolate diiron hexacarbonyl complex.[283] The related reaction of $Fe_3(CO)_{12}$, S_8, and 1-hexene (60 °C, 2 h) gives $Fe_4(\mu\text{-}S)(\mu\text{-}S_2X)(CO)_{11}$ ($(HS)_2X$ = 1,2-hexylenedithiol) in 2% yield.[284–286] Mixtures of $Fe_3(CO)_{12}$ and S_8 even activate THF to produce traces of diiron complex derived from *cis*-tetrahydrofuran-2,3-dithiol.[287,288] Further illustrative of this theme (and the diligence of these workers) is the reaction of $Fe_3(CO)_{12}$, S_8, and cyclohexene, which again gives a variety of products in low yields.[289] Thus, starting from 50 g of $Fe_3(CO)_{12}$, one obtains a variety of cyclohexyl/cyclohexenyl–thiolato complexes.[290–292] $Fe_3(CO)_{12}$ reacts with excess styrene and S_8 at 60 °C to give the perthiolate complex $Fe_2(\mu\text{-}S_3CH_2)(CO)_6$ (Scheme 27), in addition to the usual mixture of minor products ($Fe_2(\mu\text{-}S_2)(CO)_6$, $Fe_3(\mu\text{-}S)_2(CO)_9$, $Fe_2(\mu\text{-}S_2CO)(CO)_6$, and $Fe_2(\mu\text{-}S_2C_2H_3Ph)(CO)_6$).[293–295] The related perthiolate $Fe_2(\mu\text{-}S_3CPh_2)(CO)_6$ can be prepared by photoaddition of $Fe_2(\mu\text{-}S_2)(CO)_6$ (section 3.6). The formation of $Fe_2(\mu\text{-}S_3CH_2)(CO)_6$ implies the scission of the C═C bond in styrene. This unusual product is obtained only in low yields, unfortunately. The complex $Fe_2(\mu\text{-}S_3CH_2)(CO)_6$ is a rare example of a perthiolate derivative of an diiron dithiolato carbonyl; other examples of μ-perthiolato diiron complexes include $[Fe_2(\mu\text{-}S_2\text{-}t\text{-}Bu)(\mu\text{-}S)(CO)_6]^-$ and possibly $[Fe_2(\mu\text{-}S_2CF_3)(\mu\text{-}SCF_3)(CO)_6]$.[194,296] Reaction of $Fe_3(CO)_{12}$ with S_8 and benzalaniline (PhCH═NPh) gives low yields of the 1,1-dithiolate $Fe_2(\mu\text{-}S_2CHPh)(CO)_6$.[297] This complex is more efficiently prepared (22%) by the reaction of $PhCH(SH)_2$ with $Fe_3(CO)_{12}$.[82]

Photochemical reactions of $Fe(CO)_5$, FcC≡CH, and S_8 at low temperatures afford dithiolene complexes $Fe_2(\mu\text{-}S_2C_2HFc)\text{-}(CO)_6$ and the thioester $Fe_2(\mu\text{-}S_2C(O)C_2HFc)(CO)_6$ (eq 16).[298] The complex $Fe_2(\mu\text{-}S_2C_2HFc)(CO)_6$ can also be obtained by microwave irradiation of toluene solution of $Fe_3(\mu\text{-}S_2)(CO)_9$ with FcC≡CH and $Me_3NO{\cdot}2H_2O$.[299]



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2.6.2. Diene-Trapping Reactions

Diverse complexes are generated by the thermal reaction of dienes with iron carbonyls in the presence of S_8, although again the yields are low. In the case of 1,3-cyclohexadiene, one obtains the expected 3-cyclohexene-1,2-dithiolato complex. Also formed in this reaction is the trinuclear complex $Fe_3(\eta^4\text{-}C_6H_8)(\mu\text{-}S)(CO)_8$, a substituted derivative of $Fe_3(\mu\text{-}S)(CO)_{10}$.[300,301] Analogously, $Fe_3(CO)_{12}$, S_8, and 1,5-cyclooctadiene gave the adduct $Fe_2(\mu\text{-}S_2C_8H_{12})(CO)_6$ as well as the usual collection of iron carbonyls, $Fe_2(\mu\text{-}S_2)(CO)_6$, $Fe_3(\mu\text{-}S)_2(CO)_9$, and $Fe_3(\mu\text{-}S)\text{-}(CO)_{10}$ (Scheme 27). In addition to various Fe–S–CO clusters, the reaction of $Fe_3(CO)_{12}$, S_8, and norbornadiene gives four isomers of $Fe_2(\mu\text{-}S_2C_7H_8)(CO)_6$ (Figure 12).[302–307] Two of these species are chiral owing to the low symmetry of their dithiolate backbones.

2.7. Transmetalation of Heterometal Dithiolates by Iron(0) Carbonyls

Diiron(I) dithiolates form upon treatment of diverse metal thiolates with iron carbonyls.[308,309] The complex Ni(pdt)-(dppe) reacts with iron(0) carbonyls to give $Fe_2(\mu\text{-}pdt)(CO)_6$. The conversion proceeds via the intermediacy of a NiFe intermediate according to eqs 17 and 18.[308]

$$\mathrm{Ni(pdt)(dppe)+Fe_2(CO)_9 \rightarrow (OC)_3Fe(\mu\text{- } pdt)Ni(dppe)+Fe(CO)_5+CO} \quad (17)$$

$$\mathrm{(OC)_3Fe(\mu\text{- }pdt)Ni(dppe)+2Fe_2(CO)_9 \rightarrow Fe_2(\mu\text{- }pdt)(CO)_6+Ni(dppe)(CO)_2+2Fe(CO)_5+CO} \tag{18}$$

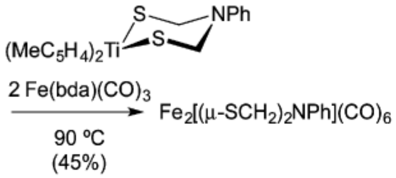
The reaction of the bis(dithiolene) complexes $M(S_2C_2R_2)_2$ (M = Fe, Co, Ni) with $Fe(CO)_5$ affords $Fe_2(\mu\text{-}S_2C_2R_2)(CO)_6$ (R = H, Me, Ph, 4-$MeOC_6H_4$) in unstated yield.[310,311] The pathway of related reactions has been investigated,[312] and the coordination of a $Fe(CO)_n$ unit to the $MS_2C_2R_2$ ring can be reasonably assumed to be an early step.

A related thiolate transfer process is implicated in the reaction of $CpFe(CO)_2SPh$ with $Fe_2(CO)_9$ to give $Fe_2(\mu\text{-}SPh)_2(CO)_6$. The transmetalation reaction occurs with transfer of the Cp ligand in the case of the reaction $CpFe(CO)_2SPh$ + $M(CO)_5(THF)$ (M = Mo, W).[313] The heterometallic intermediate was crystallized for the W–Fe case. The presumed transformations are summarized in eqs 19 and 20.[215]

$$\mathrm{CpFe(CO)_2SPh+W(CO)_5(THF) \rightarrow CpFe(CO)_2(\mu\text{- }SPh)W(CO)_5+THF} \tag{19}$$

$$\mathrm{2CpFe(CO)_2(\mu\text{- }SPh)W(CO)_5 \rightarrow Cp_2W_2(CO)_6+Fe_2(\mu\text{- }SPh)_2(CO)_6+2CO} \tag{20}$$

A related transmetalation reaction involves the titanocenedithiolates $(MeC_5H_4)_2Ti(SCH_2)_2NR$, which react with Fe(bda)-$(CO)_3$ to give the corresponding diiron thiolates (eq 21).[314] Treatment of $[Mn_2(\mu\text{-}S\text{-imidazole})_2(CO)_6]$, wherein S-imidazole is a N,S-chelating mercaptoimidazole ligand, with $Fe_3(CO)_{12}$ is proposed to result in transmetalation to give the bis(perthiolate) species $[Fe_2(\mu\text{-}S_2\text{-imidazole})_2(CO)_3]_2$,[315] which would contain a pair of 19e Fe centers. Reformulation of this species as $[Mn_2(\mu\text{-}S_2\text{-imidazole})_2(CO)_3]_2$ would also be consistent with the published elemental analysis and X-ray crystallography.



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2.8. Reactions of Iron(0) Reagents with Miscellaneous N–S Compounds

The preparation of diiron dithiolato carbonyls from organic thiocyanates (RSCN) could be of value because they are often more readily prepared from alkyl halides than thiols. Nonetheless, the route is rarely employed and early work was plagued by low yields. The reaction of MeSCN and $Fe_3(CO)_{12}$ gives only ca. 20% $Fe_2(\mu\text{-SMe})_2(CO)_6$ as well as $(\mu^4\text{-S})[Fe_2(\mu\text{-SMe})\text{-}(CO)_6]_2$.[316] In a more promising finding, the dithiocyanate in Scheme 28, however, afforded 47% of the diiron dithiolato derivative, comparable to the yield obtained when starting from the polysulfide.[317]

Photolysis of $Fe_3(CO)_{12}$ and $N(SCF_3)_3$ gives good yields of $Fe_2(\mu\text{-SCF}_3)_2(CO)_6$. This reaction is proposed to proceed via SCF_3 radicals.[318] Trace amounts of $Fe_2(\mu\text{-SPh})_2(CO)_6$ arise from the reaction of PhNHNSO and $Fe_3(CO)_{12}$.[274]

Although the yield is very low (ca. 6%), the C_s-symmetric complex $Fe_2(\mu\text{-SC}_6H_4\text{-2-CH}_2S)(CO)_6$ can be obtained by reaction of $Fe_2(C_6H_4\text{-2-CH}_2NPh)(CO)_6$ with S_8.[319] The process gives only low yields and is of little interest except to suggest that the product is potentially versatile. The chelating dithiol $HSCH_2C_6H_4\text{-2-SH}$ is well-known[320,321] and would be expected to react with $Fe_3(CO)_{12}$ to efficiently afford the same product. Related arylbenzyl thiolate derivatives are obtained in modest yields by treating $Fe_3(CO)_{12}$ with excess thiobenzophenone (see Scheme 21).[243]

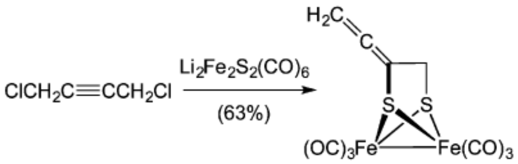
3. SYNTHESIS OF DIIRON(I) DITHIOLATO CARBONYLS FROM IRON(I) PRECURSORS

3.1. Alkylation of $Li_2Fe_2(\mu\text{-S})_2(CO)_6$

3.1.1. Reaction of $Li_2Fe_2(\mu\text{-S})_2(CO)_6$ with Organic Halides—The discovery and use of alkali metal salts of “$[Fe_2(\mu\text{-S})_2(CO)_6]^{2-}$” marked a major innovation in the chemistry of $Fe_2(\mu\text{-SR})_2(CO)_6$.[322] Of particular interest is $Li_2Fe_2(\mu\text{-S})_2(CO)_6$, which is produced by reduction of $Fe_2(\mu\text{-S}_2)(CO)_6$ by 2 equiv of $LiHBEt_3$ (“Super Hydride”). The reduction is typically conducted at −78 °C. One equivalent of the hydride agent cleaves the S–S bond, and the second equivalent causes release of H_2 (Scheme 29).[83] On rare occasions, an Et group transfers from the boron reagent to give $Fe_2(\mu\text{-SEt})(\mu\text{-SR})(CO)_6$ derivatives.[323] $LiHBEt_3$ reacts similarly with substituted derivatives of the diiron complex such as $Fe_2(\mu\text{-S}_2)(CO)_5(PPh_3)$.[324] Although $Li_2Fe_2(\mu\text{-S})_2(CO)_6$ has not been crystallographically characterized, the structure of $Li_2Fe_2(\mu\text{-Se})_2(CO)_6$ has been assessed by both Fe and Se extended X-ray absorption fine structure (EXAFS), which confirms that the Fe–Fe bond is retained but the Se–Se bond is cleaved.[325] A multistep synthesis of $Li_2\,{}^{57}Fe_2(\mu\text{-S})_2(CO)_6$ from ${}^{57}Fe$ metal has also been reported.[326]

The alkylation of $Li_2Fe_2(\mu\text{-S})_2(CO)_6$ is efficient for primary alkyl halides (RCl, RBr) and tosylates.[46,323,327–330] Except for some vinyl and aromatic iodides, aryl halides are usually not effective electrophiles.[331,332] The use of $Li_2Fe_2(\mu\text{-S})_2(CO)_6$ for the preparation of diiron dithiolates is mainly reserved for cases where the corresponding organosulfur compounds are not readily available.[333] Otherwise the methods described in sections 2.1 and 2.2 are easier. This situation is illustrated by the case of $Fe_2[(\mu\text{-SCH}_2)_2CHOH](CO)_6$, which can be prepared by alkylation of $Li_2Fe_2(\mu\text{-}S)_2(CO)_6$ with $(BrCH_2)_2CHOH$ (42% yield from $Fe_2(\mu\text{-}S_2)(CO)_6)$[17] or, more expediently, by the reaction of $Fe_3(CO)_{12}$ with the dithiol (Scheme 30).[53]

The preparation of the 1,4-butanedithiolate $Fe_2(\mu\text{-}S_2C_4H_8)\text{-}(CO)_6$ highlights an advantage to the use of $Li_2Fe_2(\mu\text{-}S)_2(CO)_6$. This molecule is obtained in excellent yield by dialkylation of $Li_2Fe_2(\mu\text{-}S)_2(CO)_6$ with 1,4-dibromobutane.[83] In contrast, the reaction of $Fe_3(CO)_{12}$ with 1,4-butanedithiol affords only traces of the *bis*(diiron(I)) species (Scheme 31).[97] Treatment of $Li_2Fe_2(\mu\text{-}S)_2(CO)_6$ with 1,4-dichloro-2-butyne affords the allenyldithiolate diiron complex $Fe_2(\mu\text{-}S_2CH_2C{=}C{=}CH_2)(CO)_6$ (eq 22).[334]



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Preparation of Diiron Azadithiolates: The alkylation of $Li_2Fe_2(\mu\text{-}S)_2(CO)_6$ is especially valuable for the preparation of azadithiolate complexes of the type $Fe_2[(\mu\text{-}SCH_2)_2NR](CO)_6$. The required dihalides are obtained by chloromethylation of primary amines with a mixture of CH_2O and $SOCl_2$.[335] These dichlorides alkylate $Li_2Fe_2(\mu\text{-}S)_2(CO)_6$ to give complexes $Fe_2[(\mu\text{-}SCH_2)_2NR](CO)_6$ in yields of 30–58% (Scheme 32).[23] Many derivatives of $(ClCH_2)_2NR$ have been prepared as precursors to azadithiolate complexes, as summarized in the Supporting Information. The substituent on the amine is amenable to further elaboration; thus, the range of azadithiolates is fairly extensive (see Table A11). For example, the N-functionalized adt complexes have been exploited for the covalent attachment of diverse groups to the diiron center. This approach is illustrated by the reaction of the iodophenyl $Fe_2[(\mu\text{-}SCH_2)_2NC_6H_4\text{-}4\text{-}I](CO)_6$ with 4′-ethynyl-2,2′:6′,2″-terpyridine under the cross-coupling conditions, followed by treatment with $Ru(terpy)(DMSO)Cl_2$ (DMSO = dimethyl sulfoxide) (Scheme 33).[39–41] Similarly, the benzaldehyde derivative $Fe_2[(\mu\text{-}SCH_2)_2NC_6H_4CHO](CO)_6$ converts to diiron dithiolate-containing porphyrins.[49,336] Exploiting the reactivity of the NH group, the parent adt complex $Fe_2[(\mu\text{-}SCH_2)_2NH](CO)_6$ has been converted to a wide range of N-acylated diiron azadithiolate complexes.[31,34–36]

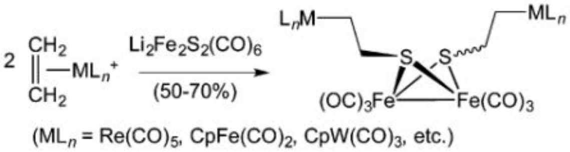
In addition to the azadithiolates, other heteroatom-substituted analogues of pdt_2^- have been prepared from $Li_2Fe_2(\mu\text{-}S)_2(CO)_6$. These other derivatives include $Fe_2[(\mu\text{-}SCH_2)_2X](CO)_6$ for X = P(O)Ph, O, and S, derived from the alkylating agents $PhP(O)(CH_2Cl)_2$,[337] $O(CH_2Cl)_2$,[275] and $S(CH_2Br)_2$,[338] respectively. A similar synthetic route gave a series of diiron complexes containing bulky Si-heteroaromatic systems. In this way, the geometry of the $Fe_2(\mu\text{-}SR)_2(CO)_6$ species are being engineered.[142,339,340]

Thioester-bridged diiron hexacarbonyls are readily prepared by acylation of $Li_2Fe_2(\mu\text{-}S)_2(CO)_6$ and $Fe_2(\mu\text{-}SR)(\mu\text{-}SCOR')\text{-}(CO)_6$.[341] Related reactions with the imidoyl chloride

PhC-(Cl)═NPh give $Fe_2(\mu\text{-}SC(Ph){=}NPh)_2(CO)_6$ and $Fe_2(\mu\text{-}SC(Ph){=}NPh)(\mu\text{-}SR)(CO)_6$.[342] Diacid chlorides (*o*-phthaloyl, succinoyl, glutaryl) react with $Li_2Fe_2(\mu\text{-}S)_2(CO)_6$ to give the dithioesters (Scheme 34).[341] Treatment of $LiFe_2(\mu\text{-}SR)(\mu\text{-}S)(CO)_6$ with diacid halides gives thermally labile derivatives in which two Fe_2 units are linked. The resulting $[Fe_2(\mu\text{-}SR)(\mu\text{-}SCOR')(CO)_6]_2$ compounds efficiently degrade near room temperature to give $(\mu_4\text{-}S)[Fe_2(\mu\text{-}SR)(CO)_6]_2$ [343] and presumably the diacylsulfide.

3.1.2. Reaction of $Li_2Fe_2(\mu\text{-}S)_2(CO)_6$ with Organometallic Electrophiles

The nucleophilic sulfido centers in $Li_2Fe_2(\mu\text{-}S)_2(CO)_6$ can also be alkylated with cationic ethylene complexes such as $[(C_2H_4)ML_n]^+$ (ML_n = CpW(CO)$_3$, CpFe(CO)$_2$, Re(CO)$_5$; eq 23).[344] The scope of this reaction extends to cationic cycloheptatrienyl and cyclohexadienyl complexes as well as the alkylidyne complexes $[Cp(CO)_2M{\equiv}CPh]^+$ (eq 24).[175,345,346]



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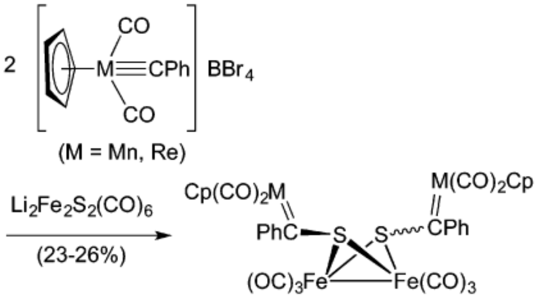

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3.2. Alkylation of $Fe_2(\mu\text{-}S_2)(CO)_6$

Complementary to the alkylation of $Li_2Fe_2(\mu\text{-}S)_2(CO)_6$ is the sequential reaction of carbanionic reagents with $Fe_2(\mu\text{-}S_2)\text{-}(CO)_6$ followed by alkylation by organic electrophiles (Scheme 34).[322,347–353] This conversion proceeds via thiolato sulfido intermediates of the type $Fe_2(\mu\text{-}SR)(\mu\text{-}SM)(CO)_6$ (M = Li, MgX). Such species are usually alkylated in situ to give unsymmetrical derivatives. Alkyl iodides are far more reactive than the bromides and chlorides.[348] The intermediates $Fe_2(\mu\text{-}SR)(\mu\text{-}SM)(CO)_6$ also add well to electrophilic alkenes and epoxides to afford, after protonation, the mixed thiolates $Fe_2(\mu\text{-}SR)(\mu\text{-}SR')(CO)_6$.[354–371] Organometallic electrophiles such as $[Cp(CO)_2M{\equiv}CPh]^+$ (M = Mn, Re) can also be employed as alkylating agents.[175,345,346,372] The intermediate $Fe_2(\mu\text{-}SR)(\mu\text{-}SM)(CO)_6$ can be protonated and oxidatively coupled, affording $Fe_2(\mu\text{-}SR)(\mu\text{-}SH)(CO)_6$ and

$[Fe_2(\mu\text{-}SR)(CO)_6]_2(\mu\text{-}S_2)$, respectively. The oxidatively coupled species, which contains an S–S bond, is again susceptible to attack by carbanionic reagents to afford mixed thiolates.[169]

Lithium acetylides and the related bromomagnesium compounds add to $Fe_2(\mu\text{-}S_2)(CO)_6$, cleaving the S–S bonds. This intermediate species can be quenched with a range of electrophiles to afford good yields of diverse diiron dithiolate complexes.[363,364] Concerning the mechanism of the reaction, only one species, thought to be $Fe_2(\mu\text{-}SC_2R)(\mu\text{-}SLi)(CO)_6$, is observed in solution. This alkynyl thiolate complex is proposed to exist in equilibrium with two ring-closed derivatives featuring carbanions (Scheme 35). Evidence for this equilibrium is provided by the products obtained upon quenching the reaction with electrophiles. Three types of products are obtained: 1,1-alkenedithiolates, 1,2-alkenedithiolates,[373,374] and alkynylthiolate/alkylthiolates.[375] For the dithiolates, the ratio of 1,1- and 1,2-dithiolenes correlates with the ability of the substituent on the alkyne to stabilize the carbanion. These closed products may arise via SH-containing intermediates. Illustrative is the reaction of $HC{\equiv}CMgBr$ and $Fe_2(\mu\text{-}S_2)(CO)_6$ followed by protonation of CF_3CO_2H, which represents the best route to the 1,2-ethylenedithiolate $Fe_2(\mu\text{-}S_2C_2H_2)\text{-}(CO)_6$.[373,374] The reaction of $Fe_2(\mu\text{-}S_2)(CO)_6$ and thiophenyl alkyne ($C_4H_3S\text{-}2\text{-}C_2H$) is induced even with sodium acetate in methanol to give the 1,2-dithiolene.[376]

3.3. Addition of Alkenes and Alkynes to $Fe_2(\mu\text{-}SH)_2(CO)_6$

The species $Fe_2(\mu\text{-}SH)_2(CO)_6$ is a versatile precursor to diiron(I) dithiolates. It is generated by protonation of $Li_2Fe_2(\mu\text{-}S)_2(CO)_6$,[83,338] and its structure has been verified crystallographically.[78] It behaves as a dithiol: in the presence of a basic catalyst, such as piperidine, the dithiol adds 2 equiv of Michael acceptors, e.g., methylvinyl ketone and cyclohexenones, to give the dithiolato complexes.[377–379] When the alkene is substituted appropriately, the 1:1 adduct cyclizes (Scheme 36). Electrophilic alkynes give alkane-1,1-dithiolates.

1,4-Benzoquinone and related compounds react with $Fe_2(\mu\text{-}SH)_2(CO)_6$ to give the quinol-2,3-dithiolates (Scheme 37). The conversion is proposed to proceed via a Michael-like addition followed by dehydrogenation of an initial dihydro-intermediate by unreacted benzoquinone. Derivatives of 1,4-naphthoquinone and 1,4-anthroquinone can be obtained by the same synthetic route.[59,380] These diiron quinonedithiolates can be prepared from the UV-induced reaction of $Fe_2(\mu\text{-}S_2)(CO)_6$ with alkenes that is described in section 3.6.

3.4. Reactions of $Fe_2(\mu\text{-}SH)_2(CO)_6$ with Aldehydes and Ketones

$Fe_2(\mu\text{-}SH)_2(CO)_6$ reacts with 2 equiv of formaldehyde to give the hydroxymethylthiolate $Fe_2(\mu\text{-}SCH_2OH)_2(CO)_6$, which has been crystallographically characterized as the *ae* isomer.[31] The adducts $Fe_2[\mu\text{-}S_2C_2(OH)_2R_2](CO)_6$, which features a chelating dithiolate, is obtained by the addition of glyoxal ($(CHO)_2$) benzil derivatives to $Fe_2(\mu\text{-}SH)_2(CO)_6$.[31] These chelating species were exclusively obtained as the chiral, C_2-symmetric isomers.

This parent azadithiolate $Fe_2[(\mu\text{-}SCH_2)_2NH](CO)_6$ has received particular attention because of its relevance to the active site of all [FeFe]-hydrogenases.[1,326,381,382] Furthermore, mechanistic studies show that this azadithiolate with a secondary amine behaves differently from the related adt complexes with tertiary amines.[383,384]

The complex $Fe_2[(\mu\text{-}SCH_2)_2NH](CO)_6$ can be prepared in ~28% yield by reaction of $Fe_2(\mu\text{-}SH)_2(CO)_6$ with a mixture of paraformaldehyde and $(NH_4)_2CO_3$ (Scheme 38).[92] The $Fe_2(\mu\text{-}SH)_2(CO)_6/CH_2O/RNH_2$ condensation is an organometallic version of organic "thioalkylations" involving the condensation of RSH, CH_2O, and R'_2NH,[385] which affords $RSCH_2NR'_2$. The sequence of steps from $Fe_2(\mu\text{-}SH)_2(CO)_6/CH_2O/RNH_2$ to $Fe_2[(\mu\text{-}SCH_2)_2NH](CO)_6$ is unclear: the reactions $Fe_2(\mu\text{-}SCH_2OH)_2(CO)_6 + RNH_2$ and $Fe_2(\mu\text{-}SH)_2(CO)_6 + RN\text{-}(CH_2OH)_2$ are both realistic. Consistent with the latter pathway, $R_3SiN(CH_2OH)_2$ condenses with $Fe_2(\mu\text{-}SH)_2(CO)_6$ to give $Fe_2[(\mu\text{-}SCH_2)_2NSiR_3](CO)_6$ (R_3 = Et_3, Me_2(*t*-Bu), (*i*-Pr)$_3$), which are not isolated but converted directly into $Fe_2[(\mu\text{-}SCH_2)_2NH](CO)_6$ (Scheme 38).[33] Complementary to the alkylation of $Li_2Fe_2(\mu\text{-}S)_2(CO)_6$ by $RN(CH_2Cl)_2$, the reaction of $Fe_2(\mu\text{-}SH)_2(CO)_6$ with formaldehyde in the presence of amines gives azadithiolato complexes.[31,90,91,93,386–388]

The condensation of $Fe_2(\mu\text{-}SH)_2(CO)_6$ with acetaldehyde and $(NH_4)_2CO_3$ gives $Fe_2[(\mu\text{-}SCHMe)_2NH](CO)_6$ (Scheme 39).[389] The meso (*R,S*) isomer (C_s symmetry group) predominates and was characterized crystallographically. The methyl groups are equatorial with respect to the bicyclic $Fe_2(\mu\text{-}S_2C_2N)$ core. The *S,S*-isomer is also observed in the ^1H NMR spectrum.

3.5. Reactions of $Fe_2(\mu\text{-}SH)_2(CO)_6$ with Cyclic Imines

$Fe_2(\mu\text{-}SH)_2(CO)_6$ is also reactive toward imine equivalents. The cyclic imine trimers $(RNCH_2)_3$ (R = Me, Ph) react to give the N-substituted azadithiolates in moderate yields (Scheme 40). Hexamethylenetetramine, which can be viewed as a derivative of $CH_2{=}NH$, reacts similarly with $Fe_2(\mu\text{-}SH)_2(CO)_6$ to give $Fe_2[(\mu\text{-}SCH_2)_2NH](CO)_6$ with yields comparable to the $(NH_4)_2CO_3/CH_2O$ method.[92]

Aminoalkylation of Fe–S–CO compounds is important because most azadithiols ($RN(CH_2SH)_2$) are unstable, thus precluding $RN(CH_2SH)_2$ + Fe(0) routes.[390] The instability of the normal azadithiols is related to the basicity of the amine. Azadithiols with nonbasic amines are stable. For example, the tosylamide $TsN(CH_2SH)_2$ is a crystalline solid that reacts with $Fe_3(CO)_{12}$ to give $Fe_2[(\mu\text{-}SCH_2)_2NTs](CO)_6$ in 35% yield (Ts = $MeC_6H_4SO_2$).[390]

The aminoalkylations can also be effected using diverse Fe–S–CO clusters, using not only $Fe_2(\mu\text{-}SH)_2(CO)_6$ but also the unreduced $Fe_2(\mu\text{-}S_2)(CO)_6$ and the rugged $Fe_3(\mu\text{-}S)_2(CO)_9$. One CO ligand in Fe_3 is known to undergo substitution by Me_2NH. Thus, converstion of $Fe_3(\mu\text{-}S)_2(CO)_9$ to $Fe_2(\mu\text{-}adt)(CO)_6$ conceivably proceeds by binding of the imine trimer to Fe.[239]

3.6. Photoaddition of Unsaturated Compounds to $Fe_2(\mu\text{-}S_2)(CO)_6$

UV irradiation of $Fe_2(\mu\text{-}S_2)(CO)_6$ in the presence of alkenes generates the corresponding diiron 1,2-dithiolates. Implicated as an intermediate in these conversions is the diferrous species $Fe_2(\mu\text{-}S)_2(CO)_6$, which has been detected by low-temperature IR spectroscopy.[391] In the absence of substrate, photolysis converts $Fe_2(\mu\text{-}S_2)(CO)_6$ to the cuboidal cluster $Fe_4(\mu\text{-}S)_4(CO)_{12}$.[392]

For the di- and triolefins, only one double bond participates. Thus, 1,3-butadiene and other dienes undergo 1,2-addition (Scheme 41).[69,393,394] Generally, the yields of these photoadditions are low (9–15%), but these experiments were conducted with only 2× excess of the alkene. Indeed, the photoreaction of Fe_2S_2 with a C_2H_4-purged solution gave 65% of $Fe_2(\mu\text{-edt})(CO)_6$. The 1,2-dithiolato complex derived from cycloheptatriene is chiral.[394] With the formula $Fe_2(\mu\text{-}S_2C_7H_8)\text{-}(CO)_6$, it is also isomeric with the cycloheptadiene-1,3-dithiolato complex obtained from trisulfidocycloheptadiene (Table 3).[225] The photoaddition route provides access to the fullerene-derived dithiolates $Fe_2(\mu\text{-}S_2C_{60})(CO)_6$ and $Fe_2(\mu\text{-}S_2C_{70})(CO)_6$ (Figure 13).[395] Substituted diiron reagents, e.g., $Fe_2(\mu\text{-}S_2)(CO)_5(PPh_3)$, also participate in this reaction. These fullerenedithiolates are thermally unstable, reverting to $Fe_2(\mu\text{-}S_2)(CO)_6$ and fullerene upon heating in toluene.

As seen for other metal di- and polysulfido complexes,[396] electrophilic alkynes react with $Fe_2(\mu\text{-}S_2)(CO)_6$.[397] When conducted under photochemical conditions, these reactions give to the dithiolene complexes $Fe_2(\mu\text{-}S_2C_2R_2)(CO)_6$ (R = CF_3, CO_2Me).[398] The parent dithiolene complex $Fe_2(\mu\text{-}S_2C_2H_2)(CO)_6$ is more efficiently generated by the reaction of HC≡CMgBr with $Fe_2(\mu\text{-}S_2)(CO)_6$ followed by protonation with CF_3CO_2H (section 3.2).[373]

The simple photoaddition of nonfunctional alkenes and fullerenes contrasts with the photoaddition of $Fe_2(\mu\text{-}S_2)(CO)_6$ to 1,4-benzoquinone. This reaction gives the hydroquinone complex $Fe_2(\mu\text{-}S_2C_6H_2\text{-}3,5\text{-}(OH)_2)(CO)_6$, which proceeds with scission of C–H bonds (see Scheme 37).[399]

Other unsaturated species add to $Fe_2(\mu\text{-}S_2)(CO)_6$ under photochemical conditions. In this way the dithiocarbonate $Fe_2(\mu\text{-}S_2CO)(CO)_6$ was prepared in 47% yield via insertion of CO.[69] The CO is readiy lost thermally from this species. UV irradiation of $Fe_2(\mu\text{-}S_2CO)(CO)_6$ and thiobenzophenone gives the perthiolate complex $Fe_2(\mu\text{-}S_3CPh_2)(CO)_6$ in good yield.[400]

One might expect that diazomethane would convert $Fe_2(\mu\text{-}S_2)(CO)_6$ to the methanedithiolate, but this reaction, effected thermally, gives only low yields.[401] Under UV irradiation, diazoethane adds to $Fe_2(\mu\text{-}S_2)(CO)_6$ to afford the thioacetaldehyde derivative $Fe_2(\mu\text{-}SCHMe)_2(CO)_6$.[402]

3.7. Conversions of Other Diiron(I) Compounds

In principle complexes of the type $Fe_2(\mu\text{-}SR)_2(CO)_6$ could be prepared by thiol exchange with other precursors, i.e., $Fe_2(\mu\text{-}SR)_2(CO)_6 + R'SH \rightarrow Fe_2(\mu\text{-}SR)(SR')(CO)_6 + RSH$. Such reactions, however, are so slow that they are disregarded. $Fe_2(\mu\text{-}SPh)_2(CO)_6$ exchanges with dodecylthiol over the course of 6 h at 65 °C.[403] Using ^{35}S-labeled thiol, exchange between $Fe_2(\mu\text{-}SC_8H_{17})_2(CO)_6$ and PhSH was shown to involve scission of Fe–S, not C–S, bonds, as expected on the basis of likely strengths of Fe–SR vs S–C bonds.[403] Similarly slow (incomplete at 90 °C even after several hours), the reaction of dodecylthiol with $Fe_3(\mu\text{-}S)_2(CO)_9$ gives $Fe_2(\mu\text{-}SC_{12}H_{25})_2(CO)_6$, $Fe_2(\mu\text{-}S_2)(CO)_6$, and the disulfide $(SC_{12}H_{25})_2$ as well as H_2S.[404] In general, bridging thiolate ligands in low spin, coordinatively saturated complexes resists exchange.

Although $Fe_2(\mu\text{-}SMe)_2(CO)_6$ is unreactive toward thiols, it exchanges stepwise with Et_2S_2. Similarly, heating a mixture of $Fe_2(\mu\text{-}SPh)_2(CO)_6$ and $(C_6F_5)_2S_2$ gives $Fe_2(\mu\text{-}SPh)(\mu\text{-}SC_6F_5)\text{-}(CO)_6$ (eq 25).[405] Conceivably this reaction proceeds via oxidative addition of R_2S_2 followed by reductive elimination of RSSR′. The slowness of these exchange reactions is relevant to the isolability of the individual components of a mixture of $Fe_2(\mu\text{-}SPh)_2(CO)_6$, $Fe_2(\mu\text{-}SPh)(\mu\text{-}SC_6F_5)(CO)_6$, and $Fe_2(\mu\text{-}SC_6F_5)_2(CO)_6$ from the reaction of $Fe_3(CO)_{12}$ with a 1:1 mixture of Ph_2S_2 and $(C_6F_5)_2S_2$.[405] Thiolate exchange between $Fe_2(\mu\text{-}SMe)_2(CO)_6$ and $Fe_2(\mu\text{-}SEt)_2(CO)_6$ to give $Fe_2(\mu\text{-}SMe)(\mu\text{-}SEt)(CO)_6$ is also very slow.[406]

$$\mathrm{Fe_2(\mu\text{- }SAr)_2(CO)_6+Ar'_2S_2 \rightarrow Fe_2(\mu\text{- }SAr)(\mu\text{- }SAr')(CO)_6+ArSSAr'} \qquad (25)$$

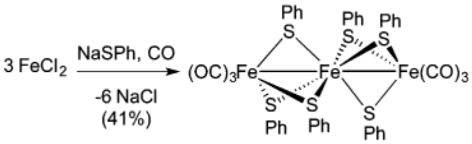
The diiron(I) precursors $Fe_2(\mu\text{-}halide)_2(CO)_6$ are known (X = Br, I),[127] but their reactions with thiolates have apparently been overlooked. Diacyl diiron(I) hexacarbonyls, prepared by oxidation of the monometallic derivatives $[Fe(C(O)R)\text{-}(CO)_4]^-$, react with thiols at room temperature to give the dithiolato hexacarbonyls with elimination of the aldehyde (established in the case of PhCHO).[407] These transformations implicate the intermediacy of the mixed acylthiolate $Fe_2(\mu\text{-}acyl)(\mu\text{-}SR)(CO)_6$. Diiron acylthiolates have been obtained in low yields by other methods, including the oxidative addition of ethylthioacetate to Fe(0) and acylation of $[Fe_2(\mu\text{-}SEt)(CO)_7]^-$ (Scheme 42, hypothesized transformations shown with broken arrow).[169]

The alkyl substituents in the diiron(I) dithiolates are susceptible to deprotonation by strong bases.[82] Deprotonation of $Fe_2(edt)(CO)_6$ gives complexes of vinylthiolate, the conjugate base of thioacetaldehyde (Scheme 43). The resulting diiron vinylthiolate is amenable to alkylation of the sulfido ligand.[82] The same vinyl thiolates can be generated by the addition of vinyl Grignard reagents to $Fe_2(\mu\text{-}S_2)(CO)_6$.[347] The diiron methanedithiolate, 1,3-propanedithiolate, and xylenedithiolate complexes also undergo deprotonation, concomitant with rearrangement to anionic complexes.[82] For example, deprotonation of $Fe_2(\mu\text{-}S_2CH_2)(CO)_6$ gives the anionic dithioformate derivative, which undergoes S-alkylation.[82,408]

4. SYNTHESIS OF DIIRON(I) DITHIOLATO CARBONYLS FROM IRON(II) PRECURSORS

4.1. Abiological Pathways

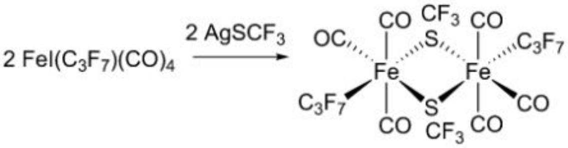
Diiron dithiolato carbonyls were originally prepared by reaction of ferrous sulfate, thiols, and strong aqueous base under an atmosphere of CO. The yield was low: from 10 g of ferrous sulfate, ~0.8 g of product was obtained.[73] The synthetic method was inspired by the earlier finding that “$Fe(SEt)_2$” reacts with NO to give $Fe_2(\mu\text{-}SEt)_2(NO)_4$, the ethyl “ester” of Roussin’s Red Salt ($Na_2Fe_2(\mu\text{-}S)_2(NO)_4$). The pathway for the conversion of Fe(II) to Fe(I) derivatives remains unclear. One possible mechanism, related to the Hieber base reaction,[409] involves hydroxide attack at a ferrous carbonyl, resulting in ferrous hydrides that are susceptible to deprotonation to give reduced iron species. Another possibility is the CO-induced reductive elimination of Et_2S_2, as observed in the reaction of $FeI_2(CO)_4$ with thiolates.[410] Heating mixtures of iron sulfides (“FeS”) under an atmosphere of CO in the presence of alkyl thiol (RSH) inevitably affords some $Fe_2(\mu\text{-}SR)_2(CO)_6$. Such compounds also arise by treatment of $Fe_3(\mu\text{-}S)_2(CO)_9$ with thiols.[411]



(26)

Ferrous salts react with 3 equiv of benzenethiolate under CO to give anionic ferrous thiolato carbonyls. One product is $[Fe(SPh)_3(CO)_3]^-$,[412] which forms a complex with a ferrous ion to give $Fe_3(\mu\text{-}SPh)_6(CO)_6$ (eq 26).[189,413] Similar reactions involve ferrous salts with propanedithiolate in the presence of CO. In these cases, two triion complexes were isolated, $Fe_3(\mu\text{-}pdt)_3(CO)_4(PEt_3)_2$ and the mixed-valent $[Fe_3(\mu\text{-}pdt)_4(CO)_4]^-$.[414]

Charge-neutral $18e^-$ ferrous tetracarbonyldithiolates of the type $Fe(SR)_2(CO)_4$ are unknown. Reactions of $FeI_2(CO)_4$ with thiolates result in complex mixtures. The case of isopropylthiolate gives $Fe_2(\mu\text{-}S\text{-}i\text{-}Pr)_3I(CO)_5$.[415] A subsequent study showed that the $FeI_2(CO)_4$ reacts with 1 equiv of RSH (R = Me, Et) in the presence of Et_3N to give moderate yields of $Fe_2(\mu\text{-}SR)_3I(CO)_5$. The $FeI_2(CO)_4$/RSH/Et_3N reactions are accompanied by formation of $Fe_2(\mu\text{-}SR)_2(CO)_6$, especially for chelating dithiols.[410] Diferrous dithiolato carbonyls can be produced from $FeI(C_3F_7)(CO)_4$ (eq 27).[137]

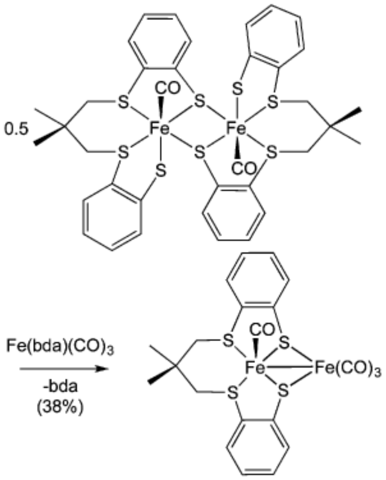


(27)

Although ferrous tetracarbonyldithiolates remain elusive, substituted ones are well-known. Already in the 1920s and 1930s, it was observed that 1:2 ferrous cysteinate complexes absorb 2 equiv of CO to give air-stable complexes.[416–418] Since that time, many $Fe(SR)_2(CO)_2L_2$ complexes have been prepared by treating ferrous salts with CO and thiolates in the presence of donor ligands.[419–424] Examples include $Fe(SPh)_2(CO)_2$(chel) where chel = dppe, ethylenediamine, and phenanthroline. This family of ferrous building blocks has been expanded to include dithiolates such as Fe(pdt)-$(CO)_2$(dppv) and many others. These ferrous dithiolates “condense” with iron(0) reagents to give substituted diiron complexes. For example, treatment of Fe(pdt)$(CO)_2$(diphos) (diphos = dppe, dcpe, etc.) with $Fe(bda)(CO)_3$ at room temperature affords $Fe_2(\mu\text{-}pdt)(CO)_4$(diphos) in 60–83% yields (eq 28).[425]

$$\mathrm{Fe(pdt)(CO)_2(diphos){+}Fe(bda)(CO)_3 \rightarrow Fe_2(\mu\text{- }pdt)(CO)_4(diphos){+}bda{+}CO} \quad (28)$$

The Fe(0) + Fe(II) $(SR)_2$ route was demonstrated by Sellmann et al. The charge-neutral ferrous complex $[Fe\text{-}(\text{'}S_4C_3Me_2\text{'})(CO)]_2$ reacts with the iron(0) source $Fe(bda)\text{-}(CO)_3$ to give, ostensibly, a diiron(I) dithiolate (eq 29).[309]



(29)

Comproportionation reactions are also relevant to the formation of diiron(I) dithiolenes from the cyclic disulfide $(CF_3)_2C_2S_2$.[137] This electrophilic strained ring is highly reactive toward iron(0) carbonyls, ultimately giving $Fe_2[\mu\text{-}S_2C_2(CF_3)_2]\text{-}(CO)_6$. The oxidative addition affords a green species with the formula $Fe[S_2C_2(CF_3)_2](CO)_3$.[426] Crystallographic and Mössbauer measurements revealed that this ferrous species is a dimer.[427] The conversion of this diferrous species to the diiron(I) dithiolate proceeds via the comproportionation of ferrous dithiolene and Fe(0) carbonyl (Scheme 44).

4.2. Biological Pathways

Diiron(I) dithiolates are produced from ferrous precursors in the biosynthesis of the active site of the [FeFe]-hydrogenase enzymes. Although many details of this process remain unresolved, the iron source has been identified as an Fe(II) center attached to a 4Fe-4S cluster scaffold within a bifunctional maturase enzyme called HydG. This “dangler” Fe(II) center contains one CN^- and two CO ligands, which are derived by degradation of tyrosine.[4] The $Fe(CO)_2CN$ center is temporarily protected by a tridentate cysteinate ligand.[5,428] The pathway for installing the azadithiolate is unknown but is probably mediated by the radical SAM enzyme HydE. After the $[Fe_2(\mu\text{-adt})(CN)_2(CO)_4]^{2-}$ entity is assembled within the scaffold protein called HydF, it is transferred to the apohydrogenase protein HydA. In this transformation, one CO is displaced, and the geometry of the $Fe_2(\mu\text{-adt})(CO)_3(CN)_2$ center is reorganized. The uptake of synthetic $[Fe_2(\mu\text{-adt})(CO)_4(CN)_2]^{2-}$ by HydF and by apo-HydA has been demonstrated (Scheme 45).[326,381,382]

5. CONCLUSIONS

In recent years, the diiron(I) dithiolato carbonyls have been the subject of intense study. This work is mainly motivated by the structural similarity of these complexes to the active site of [FeFe]-hydrogenases, which are some of the fastest catalysts for oxidation and production of H^2. The synthetic advances have established the versatility of the hexacarbonyls, both as a platform in their own right and as the precursor to their substituted derivatives, which are more reactive.

Important synthetic routes include (i) reaction of thiols with $Fe_3(CO)_{12}$ and $Fe_2(CO)_9$, which is currently the most popular method; (ii) treatment of di- and polysulfides with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$, which is usually applied when these organosulfur compounds are more available than the thiols; (iii) alkylation of $Fe_2(\mu\text{-}S)_2(CO)_6$, which is the preferred precursor to the mixed dithiolates and azadithiolates. Generally hexacarbonyls are often obtainable in good yields from inexpensive, even primitive reagents. Furthermore, they are rather air-stable and exhibit convenient solubility. Through substitution of some of the CO ligands, rich acid–base and redox chemistries are enabled.[8,10,29] Given the versatility of the $Fe_2(\mu\text{-}SR)_2(CO)_6$ motif, this type of complex is likely to be developed further, not only for its relevance to biology but also as platforms for new organometallic and perhaps catalytic chemistry.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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ABBREVIATIONS

AIBN	azobis(isobutyronitrile)
Bda	benzylideneacetone (MeC(O)CH═CHPh)
BOP	(benzotriazol-1-yloxy)tris(dimethylamino)-phosphonium hexafluorophosphate
COD	1,5-cyclooctadiene
Cp	cyclopentadienyl
DCC	*N*,*N*-dicyclohexylcarbodiimide
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone

DMAP	4-dimethylaminopyridine
DMF	dimethylformamide
dcpe	1,2-bis(dicyclohexylphophino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
$edtH_2$	1,2-ethanedithiol
Fc	ferrocenyl ($(C_5H_5)Fe(C_5H_4)$); note: in some cited literature, Fc refers to $Fe(C_5H_4)_2$ as well as ferrocene Itself
LDA	lithium diisopropylamide
$nbdtH_2$	norbornyldithiol ($C_7H_{10}(SH)_2$)
NMI	naphthalene monoimide
NHC	N-heterocyclic carbene
$pdtH_2$	1,3-pronedithiol (also R_2pdtH_2 = 2,2-disubstituted propane-1,3-dithiol; R = Me, Et, etc.)
PPN^+	bis(triphenylphosphine)iminium
Py	pyridyl
terpy	2,2′:6,2″-terpyridine
TFA	CF_3CO_2H
H_2TPP	tetraphenylporphyrin
ZnP	zinc porphyrinate

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Biographies

Yu-Long Li was born in 1983 in Suining, China. He received his B.S. degree in chemistry and Ph.D. degree in organic chemistry from Nankai University in Tianjin, China. He started his independent career at the Sichuan University of Science & Engineering, where he is an Associate Professor. He was a visiting scholar in the group of Professor Rauchfuss during the preparation of this review. His research interests are in the synthesis of Fe_2S_2 complexes and hydrogenase models.

Thomas B. Rauchfuss was born in 1949 in Baltimore, MD. He received his undergraduate degree from the University of Puget Sound (1971) and his Ph.D. from Washington State University (1976). After a postdoc with David Buckingham at the Australian National University, he started his independent career at the University of Illinois at Urbana–Champaign in 1978, where he has remained. He has also studied at the following institutions: the University of Auckland, University of Louis Pasteur, and the Technical University of Karlsruhe. His research focuses on synthetic inorganic and organometallic chemistry, with an emphasis on environmentally motivated themes. For the past decade, his group has conducted research on synthetic modeling of the active sites of hydrogenase enzymes.

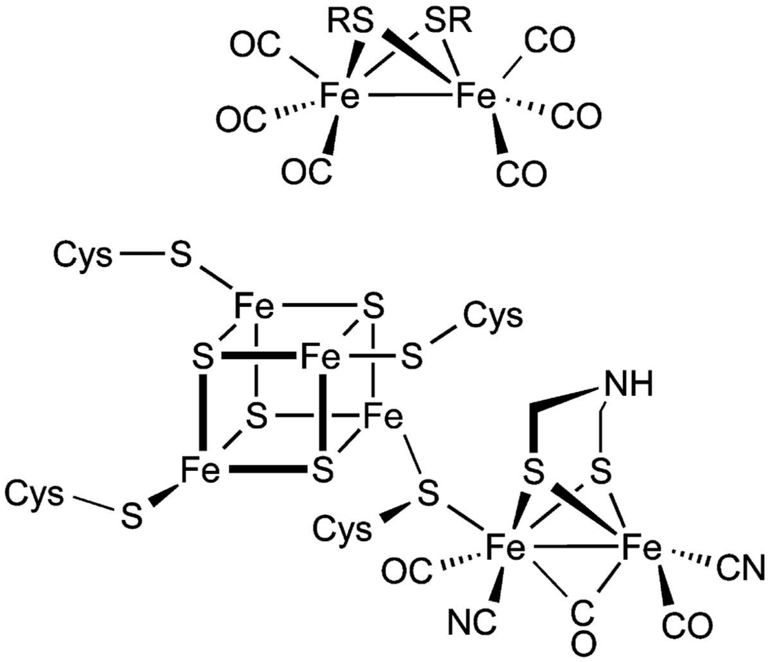


Figure 1.

Structure of $Fe_2(\mu\text{-}SR)_2(CO)_6$ and the H-cluster.

Figure 2.
Sample (20 g) of crystalline $Fe_2(\mu\text{-pdt})(CO)_6$.

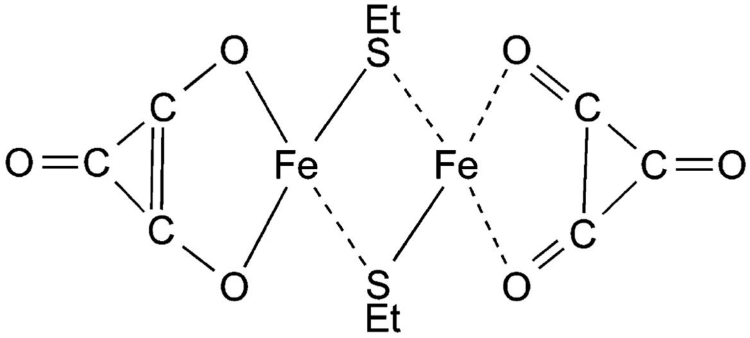


Figure 3.

Structure of $Fe_2(\mu\text{-}SEt)_2(CO)_6$ proposed by Reihlen et al. in 1928.[73] Notice the careful attention to depicting each carbon with four bonds.

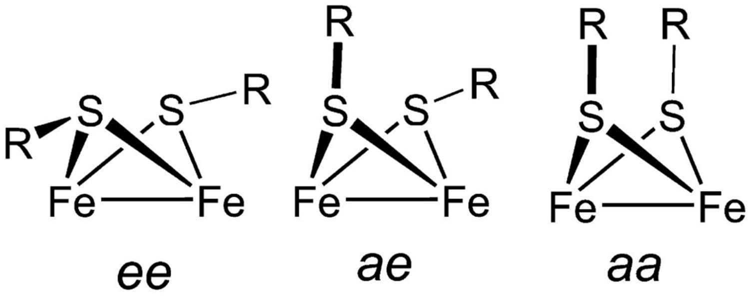


Figure 4.

Three isomers of diiron dithiolato carbonyls with CO ligands omitted. The *ee*, *ae*, and *aa* isomers are sometimes referred to as syn eq, anti, and syn ax, respectively.

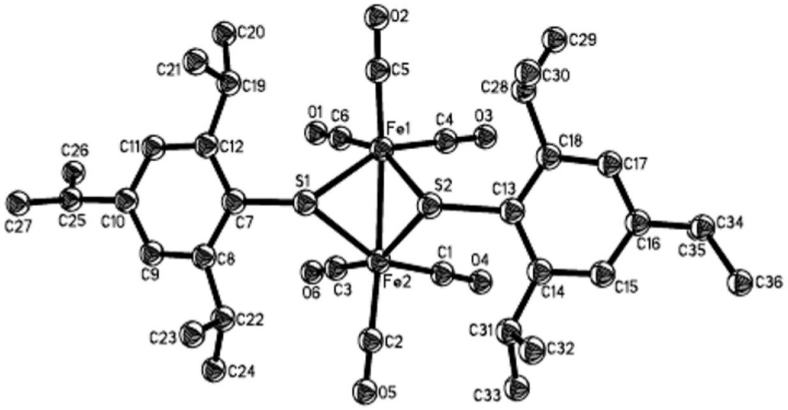


Figure 5.

Structure of $Fe_2[\mu\text{-}SC_6H_2\text{-}2,4,6\text{-}(i\text{-}Pr)_3]_2(CO)_6$. With its very bulky thiolates, the Fe–Fe distance is 0.06 Å shorter than that typically observed. Reproduced from ref 75. Copyright 1999 Elsevier.

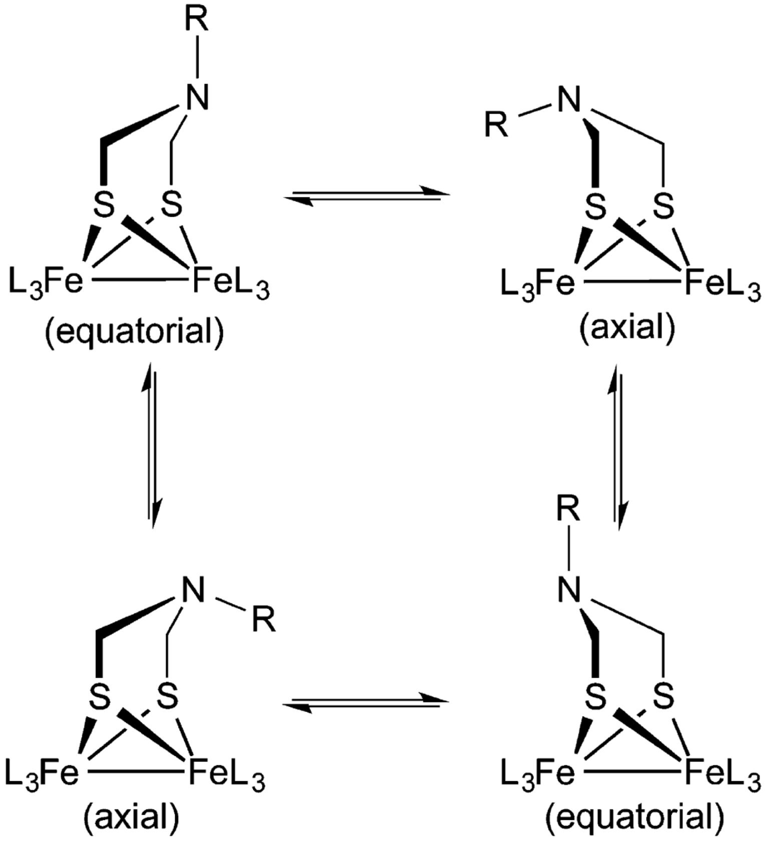


Figure 6.

Conformational equilibria for the azadithiolates $Fe_2(\mu\text{-adt}^R)L_6$.

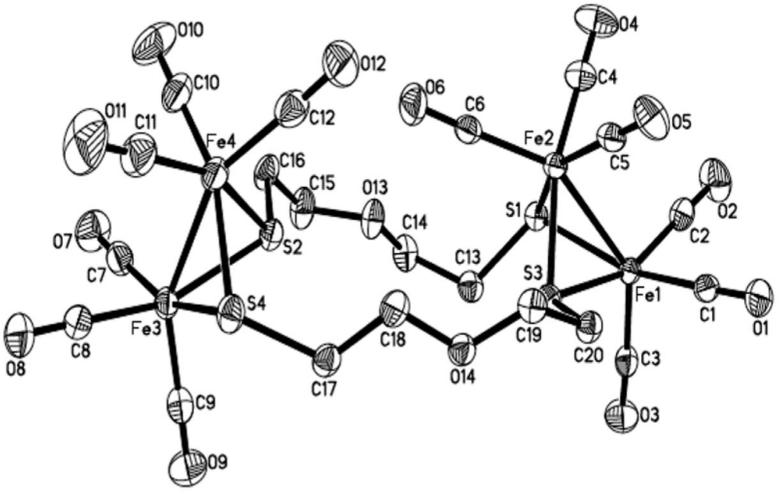


Figure 7.

Structure of $[Fe_2(\mu\text{-}SC_2H_4OC_2H_4S)(CO)_6]_2$. Notice that the organic substituents on sulfur adopt the *ae* stereochemistry. Reproduced from ref 94. Copyright 2006 American Chemical Society.

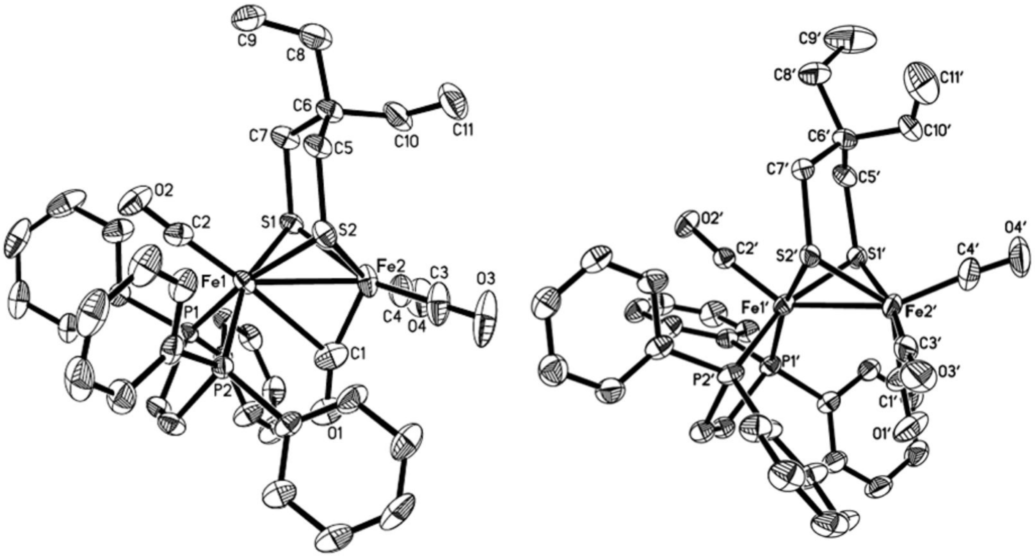


Figure 8.

Structures of rotated (left) and normal (right) isomers of $Fe_2[(\mu\text{-}SCH_2)_2CEt_2](CO)_4(dppv)$. Reproduced from ref 141. Copy-right 2013 John Wiley and Sons.

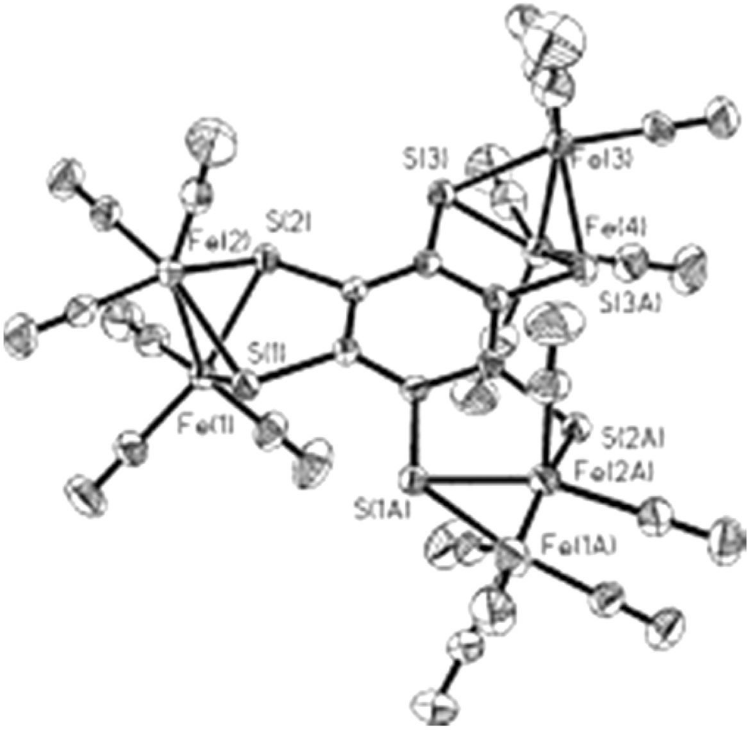


Figure 9.

Structure of $C_6S_6[Fe_2(CO)_6]_3$. Reproduced from ref 149. Copyright 2012 John Wiley and Sons.

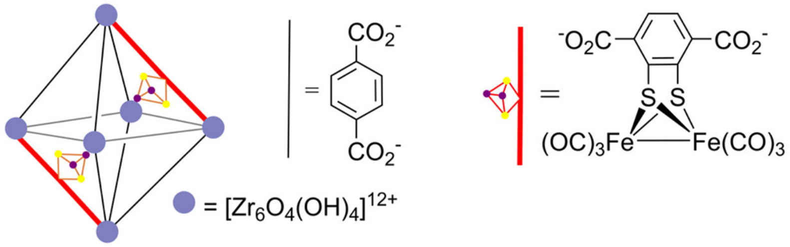


Figure 10.

Schematic illustration of the role of the dicarboxylic acid $Fe_2[\mu\text{-}S_2C_6H_2\text{-}3,6\text{-}(CO_2H)_2](CO)_6$ as part of a metal–organic framework.[65]

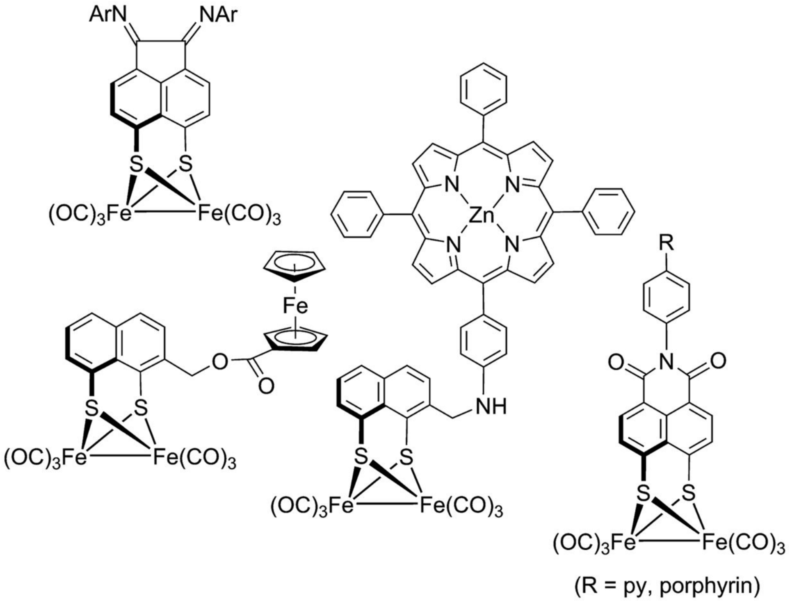


Figure 11.

Peri-naphthalenedithiolatodiiron complexes with functional substituents.[202,203]

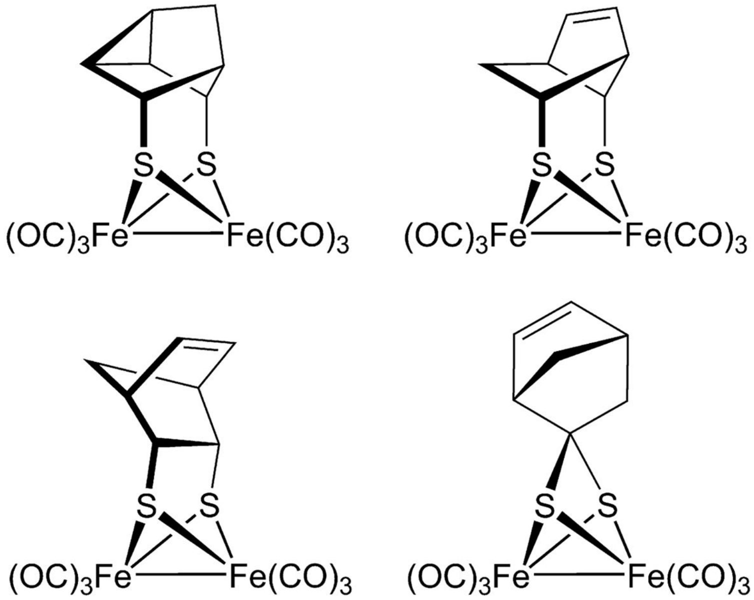


Figure 12.

Four isomers of $Fe_2(\mu\text{-}S_2C_7H_8)(CO)_6$.[302–307]

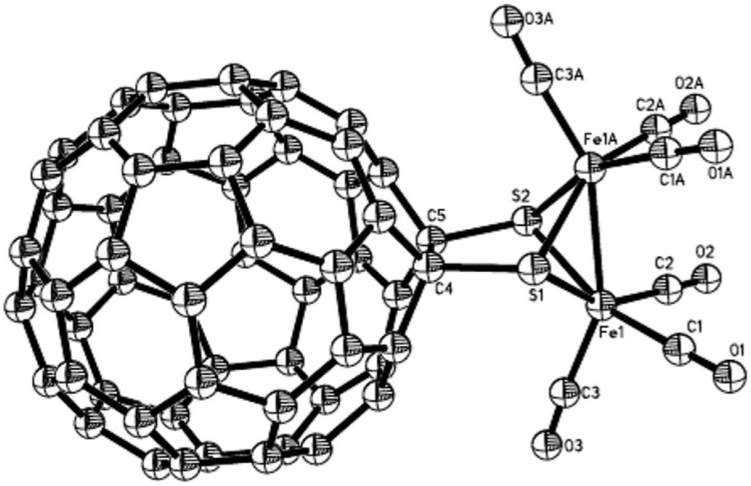
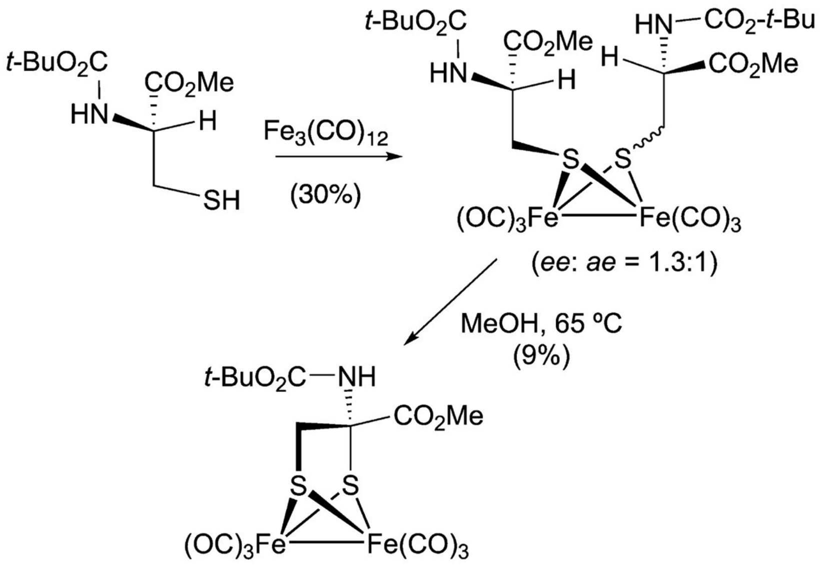


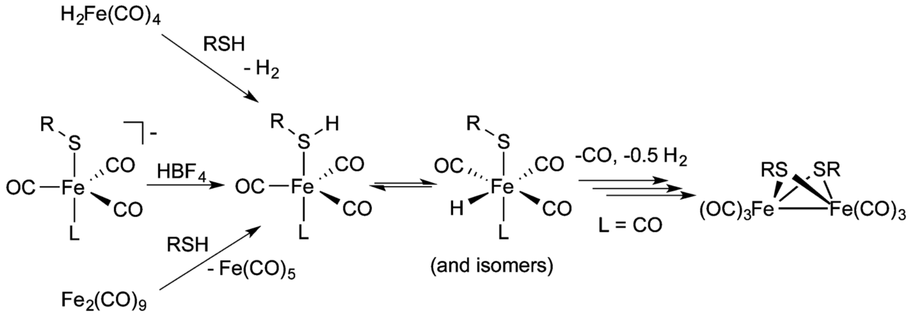
Figure 13.

Structure of $Fe_2(\mu\text{-}S_2C_{60})(CO)_6$. Reproduced from ref 395. Copyright 2009 American Chemical Society.



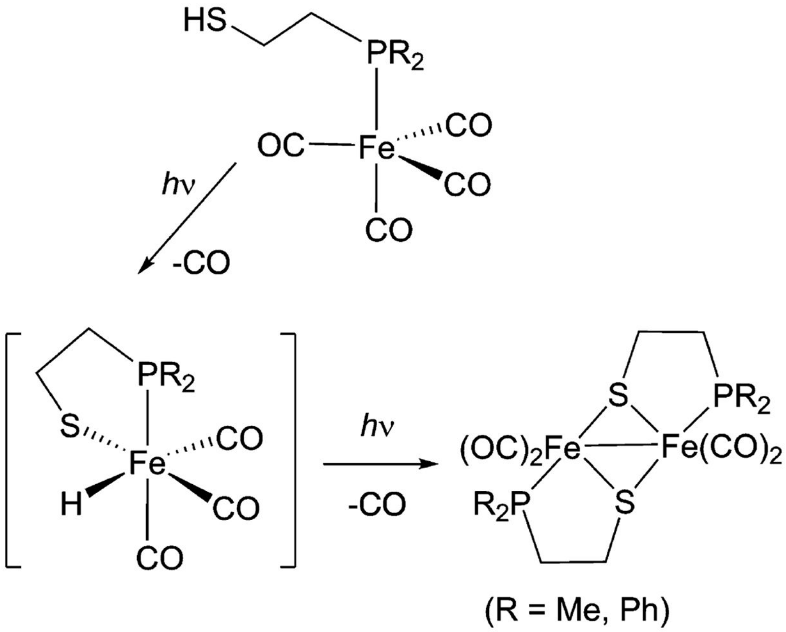
Scheme 1.

Formation of Fe_2(3-L-cysOMe–*N*–C(O)O–*t*-Bu$)_2$(CO$)_6$ and Its Intramolecular Condensation[117]



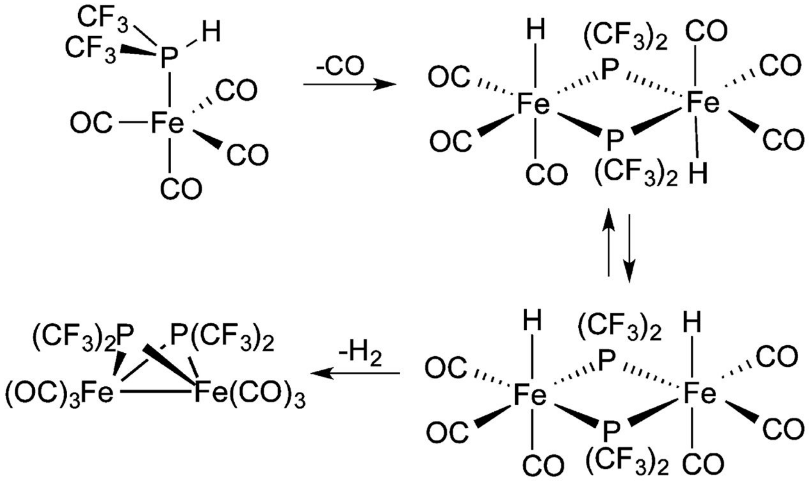
Scheme 2.

Protonation of $[Fe(SR)(CO)_4]^-$ Gives $Fe(HSR)(CO)_4$, the Probable Intermediate in the Reaction of $Fe(CO)_4$ Sources with Thiols



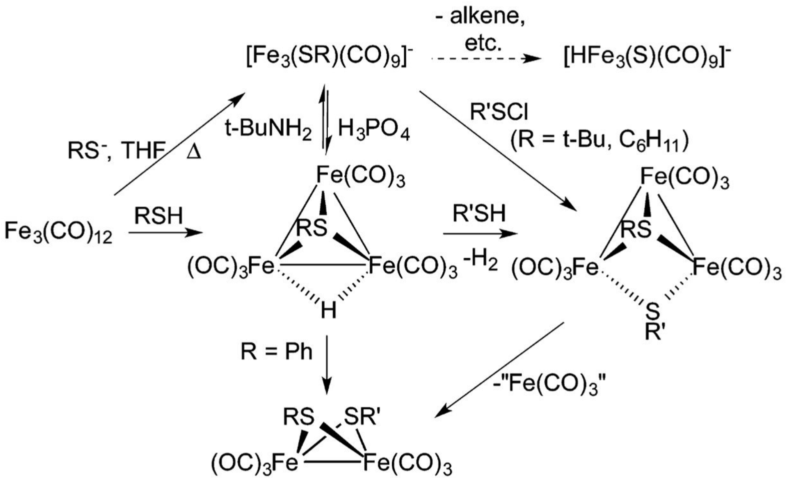
Scheme 3.

Proposed Oxidative Addition Step in the Conversion of Fe(0) Complex with Pendant Thiol to Diiron Dithiolate[126]



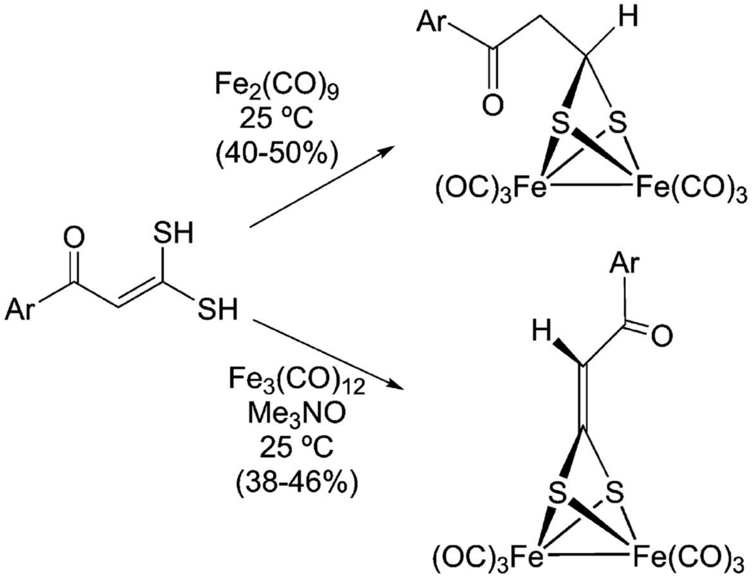
Scheme 4.

Role of Diiron(II) Dihydrides in the Formation of Diiron(I) Diphosphides[128]



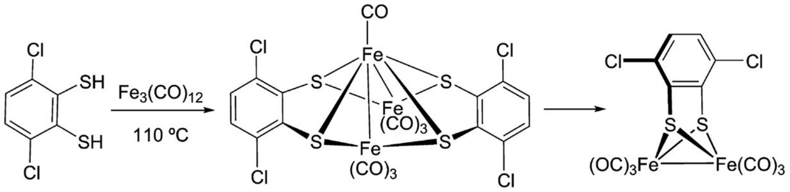
Scheme 5.

$Fe_3(\mu\text{-}SR)$ Intermediates Derived from the Reaction of $Fe_3(CO)_{12}$ with Thiols and Related Reactions[123,130,131]



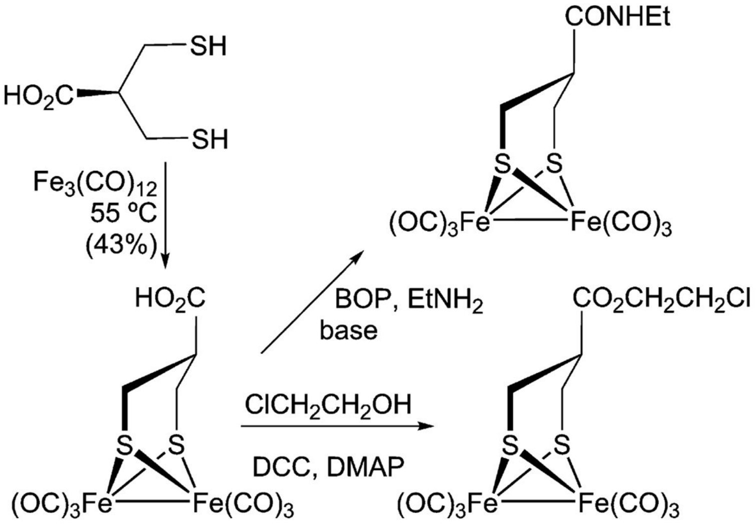
Scheme 6.

Conversion of Geminal Enedithiols to Two Kinds of 1,1-Dithiolato Complexes[145]



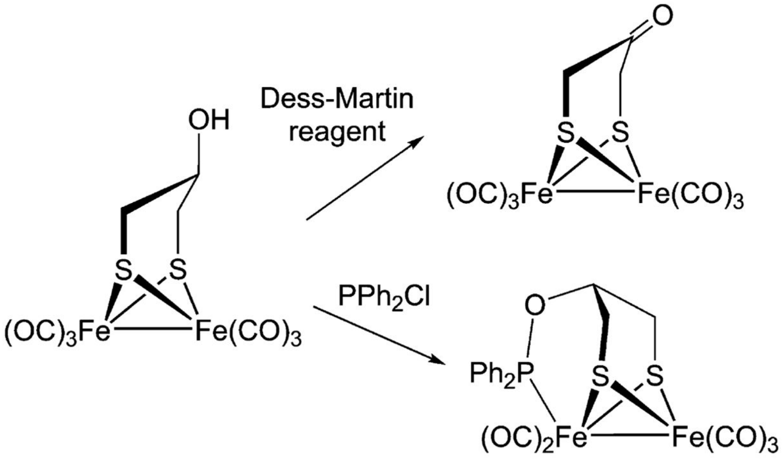
Scheme 7.

Fe_3 Intermediate in the Reaction of $Fe_3(CO)_{12}$ with a Substituted Benzenedithiol[148]



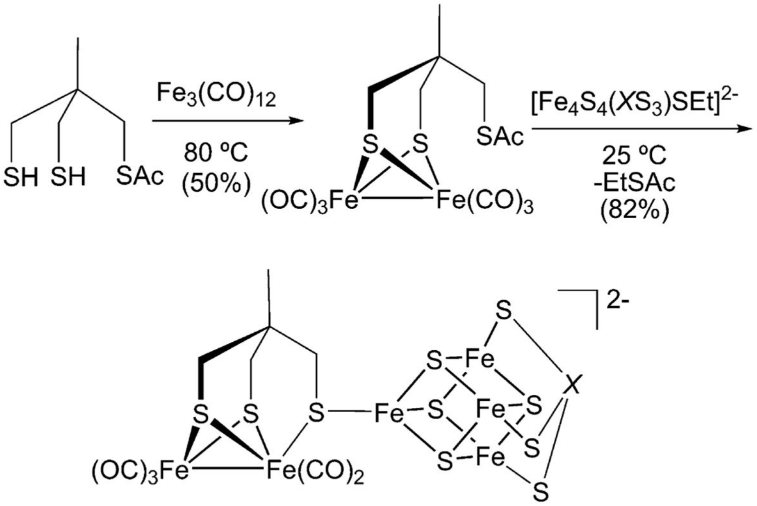
Scheme 8.

Synthesis and Derivatization of Diiron Asparagusic Acid Complex[55]



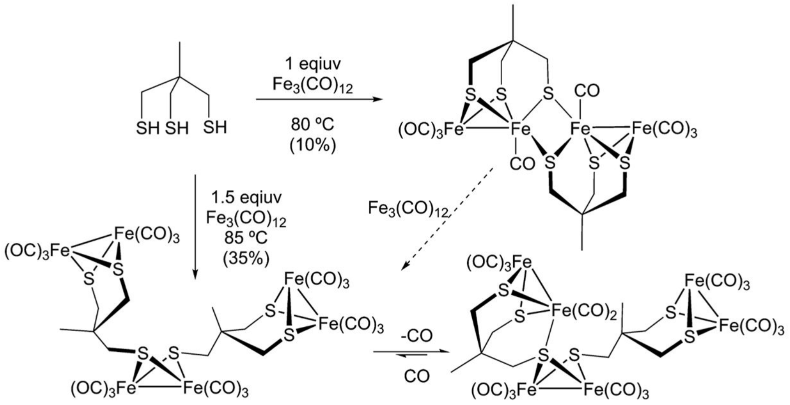
Scheme 9.

Derivatization of Diiron Complexes of 2-Hydroxy-1,3-propanedithiolate[53]



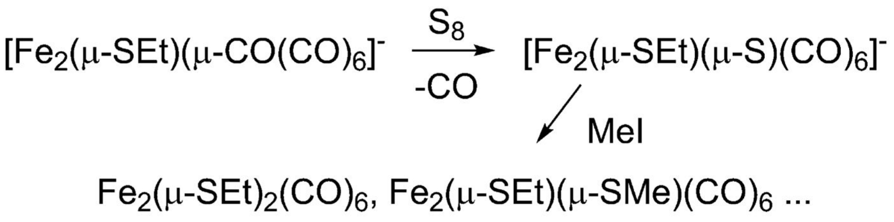
Scheme 10.

Stepwise Assembly of a Biomimetic Diiron Dithiolate Complex Containing an Appended 4Fe-4S Cluster (*X* Is a Trithiolate)[163]



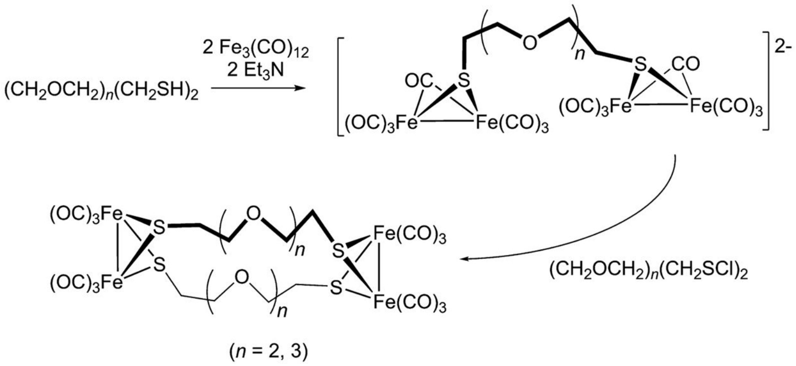
Scheme 11.

Tetra- and Hexairon Products from the Reaction of $Fe_3(CO)_{12}$ and $MeC(CH_2SH)_3$[165–167]



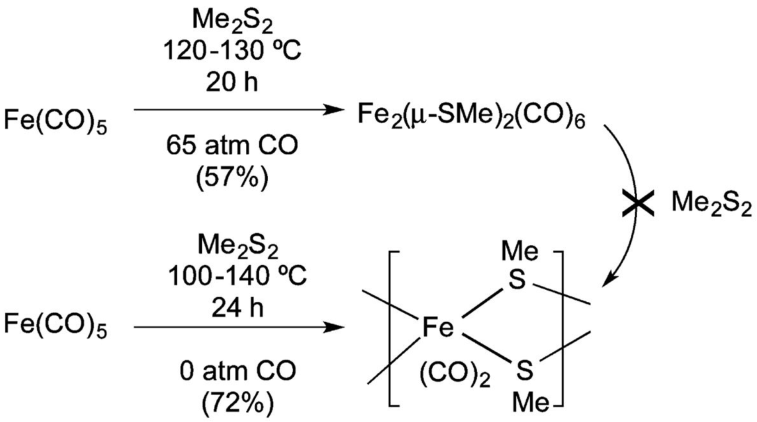
Scheme 12.

Generation and Alkylation of "$[Fe_2(\mu\text{-}SEt)S(CO)_6]$" as the Et_3NH^+ Salt



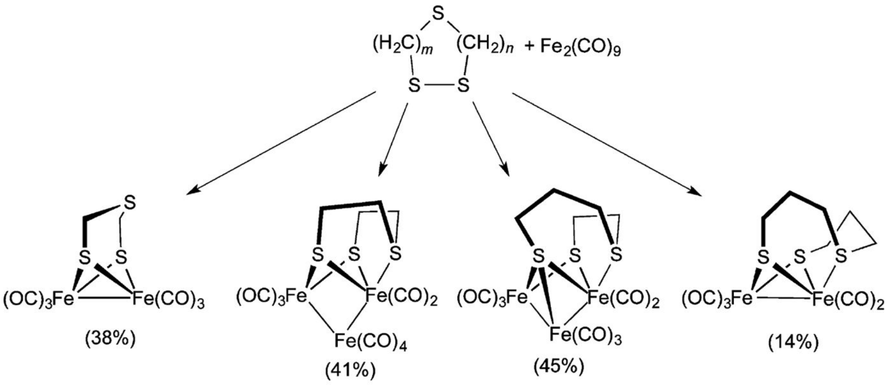
Scheme 13.

Illustrative Synthesis of Macrocyclic Bis(diiron) Dithiolates (Countercation Not Shown)[179,180]



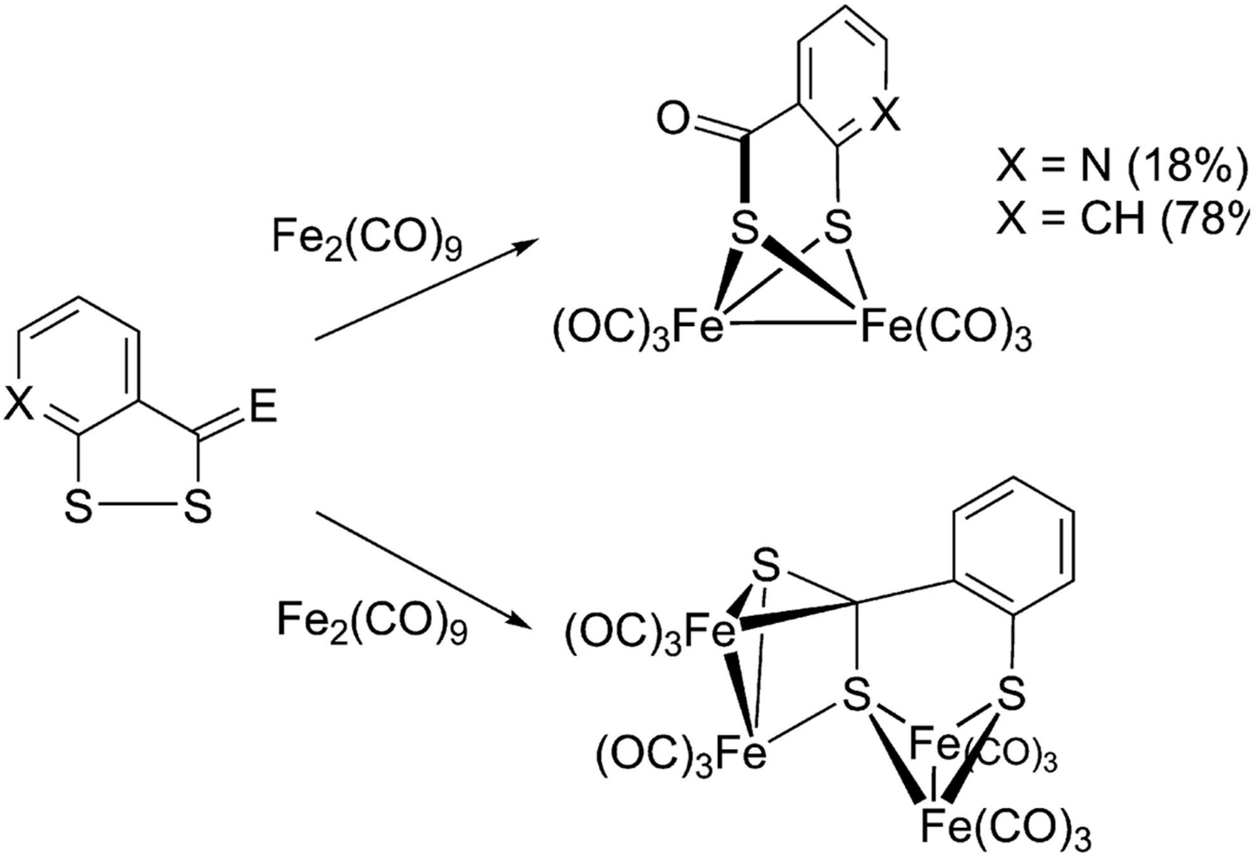
Scheme 14.

Effect of CO Pressure on the Reaction of $Fe(CO)_5$ and Me_2S_2 190



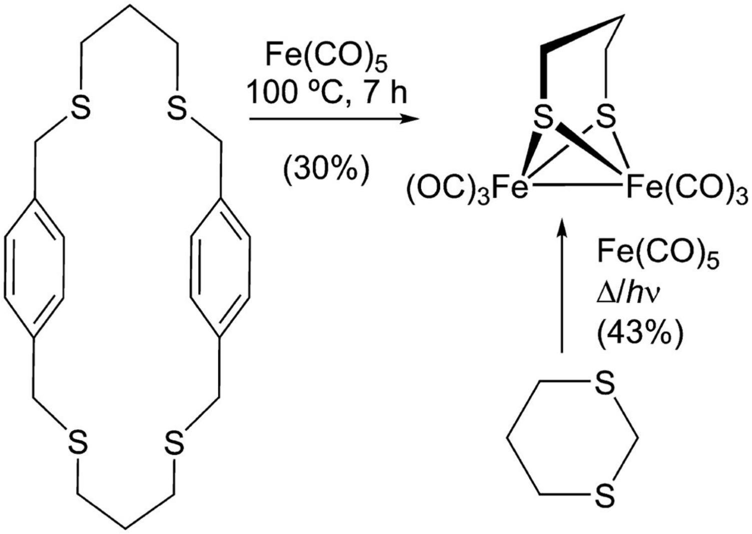
Scheme 15.

Reactions of Cyclic Thioether Disulfides with $Fe_2(CO)_9$ [198–200]



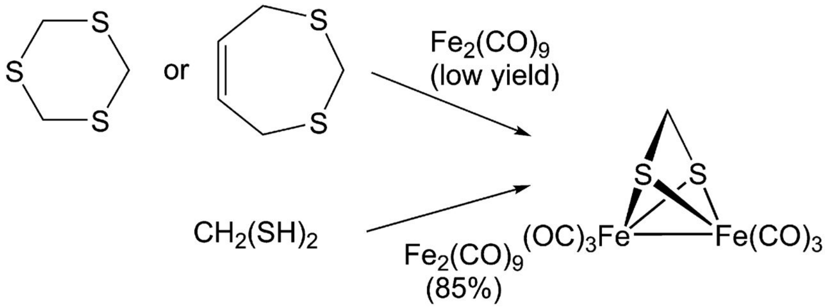
Scheme 16.

Oxidative Addition of Perthioesters to Fe(0)[208,209]



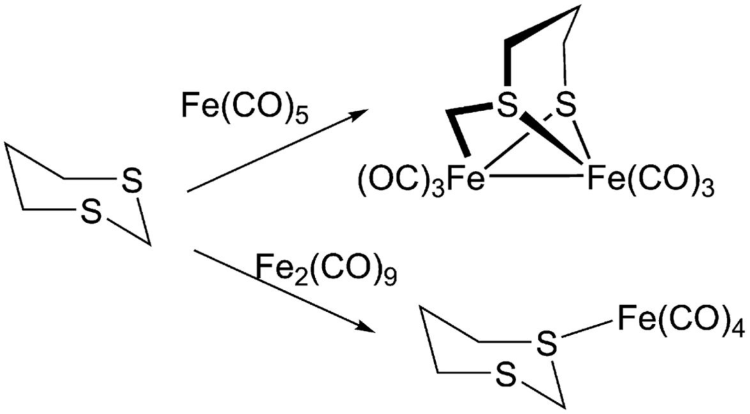
Scheme 17.

Degradative Routes from Thioethers and $Fe(CO)_5$ to $Fe_2(\mu\text{-pdt})(CO)_6$ [220,227]

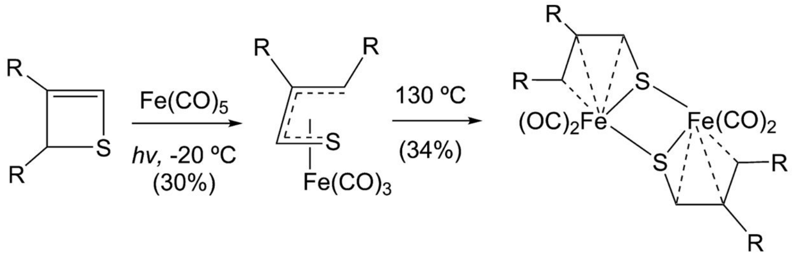


Scheme 18.

Routes to the Diiron Methanedithiolate by Fe(0)-Induced Degradation of Methylene Bisthioethers,[225,226] Contrasted with the Efficient Thiol Method[82]

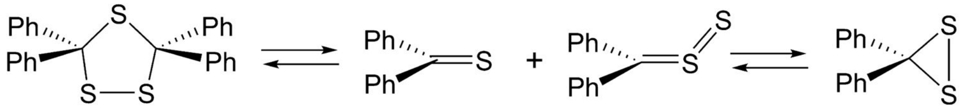


Scheme 19.
Activation of $CH_2(SR)_2$ Substrates by Fe(0)[227,234,235]



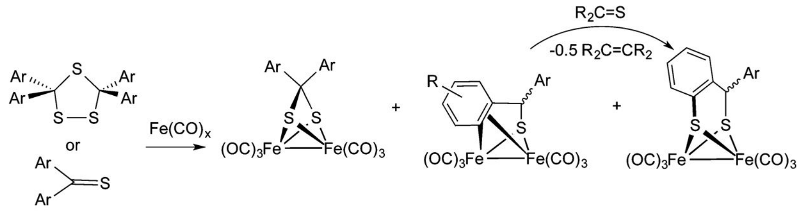
Scheme 20.

C–S Bond Scission by Fe(0) To Give Thioacrolein Complexes[242]



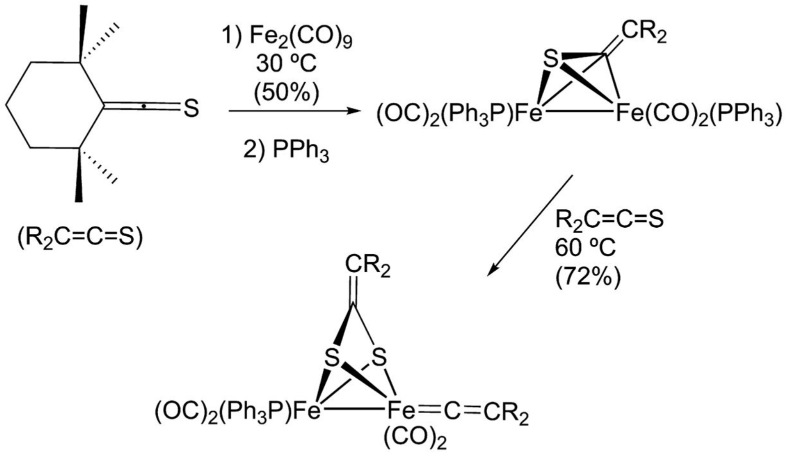
Scheme 21.

Equilibria Relating Thiobenzophenone, Its Thiosulfine and Dithiirane Derivatives, and the Corresponding 1,2,4-Trithiolane[253,254]



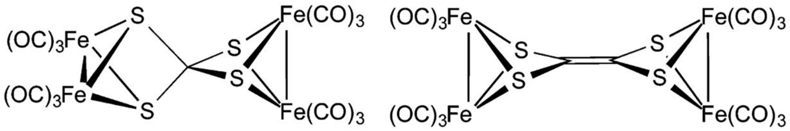
Scheme 22.

General Pattern for Reactions of Diarylthiones and the Tetraaryl 1,2,4-Trithiolanes with Iron Carbonyls[243,255]



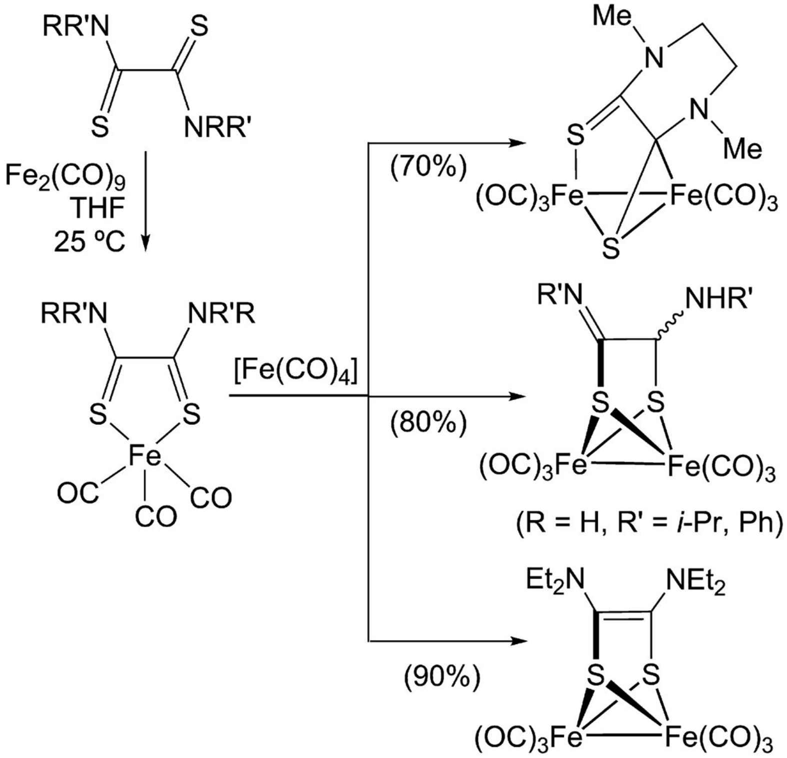
Scheme 23.

Efficient Pathway Connecting a Thioketene and a Diiron 1,1-Dithiolate[258,213]



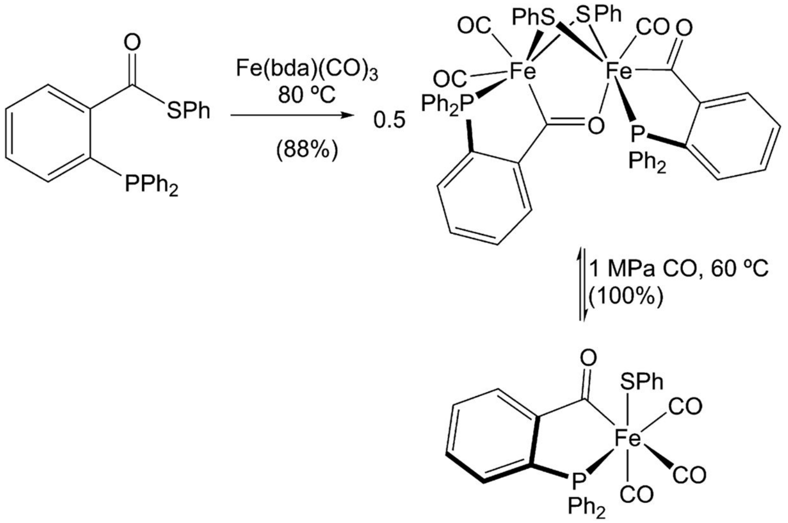
Scheme 24.

Unusual Products Obtained from the Reactions of $Fe_3(CO)_{12}$ with CS_2 [264,261]



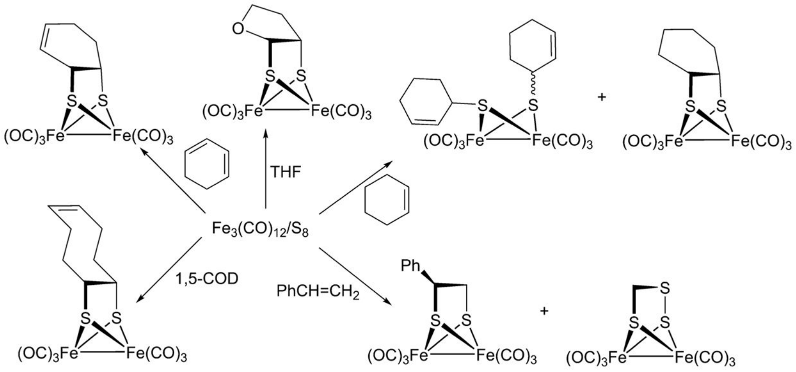
Scheme 25.

Products Generated by Reaction of $Fe_2(CO)_9$ with Dithiooxamide[271]



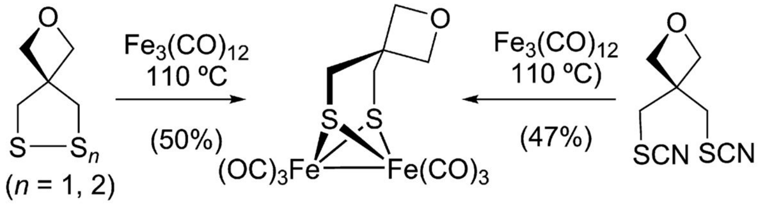
Scheme 26.

Oxidative Addition of a Thioester by Fe(0)[277]



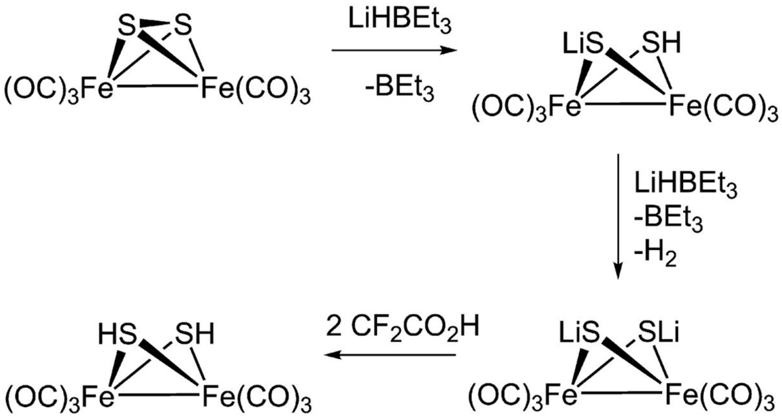
Scheme 27.

Illustrative Diiron Dithiolates Obtained by the Reaction of Alkenes with $Fe_3(CO)_{12}$ and S_8 (See Text for References); The Yields for These Reactions Are Typically <10%



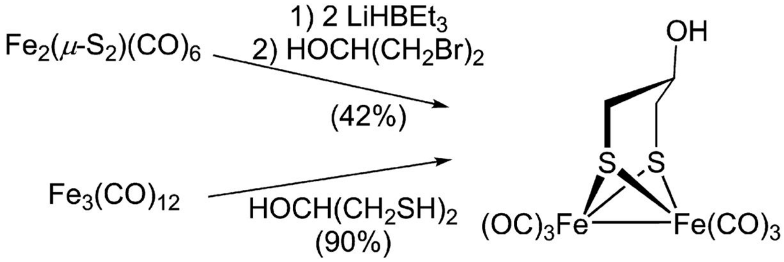
Scheme 28.

Routes to Oxetane Dithiolato Complexes, Illustrating the Reactivity of Polysulfides and Thiocyanates toward Fe(0)[317]



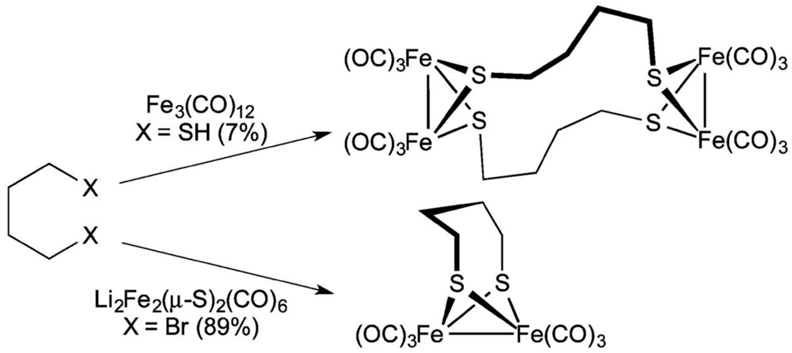
Scheme 29.

Preparation of $Li_2Fe_2(\mu\text{-}S)_2(CO)_6$ and $Fe_2(\mu\text{-}SH)_2(CO)_6$ from $Fe_2(\mu\text{-}S_2)(CO)_6$ Using $LiBHEt_3$ [322]



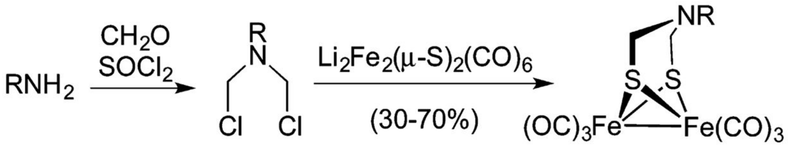
Scheme 30.

Two Routes to $Fe_2(\mu\text{-}S_2C_3H_5OH)(CO)_6$ [17,53]



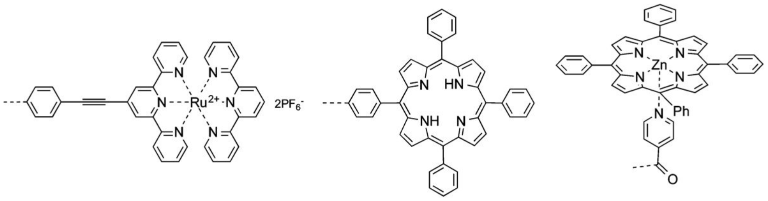
Scheme 31.

Preparation of Di- and Tetrairon Butanedithiolates



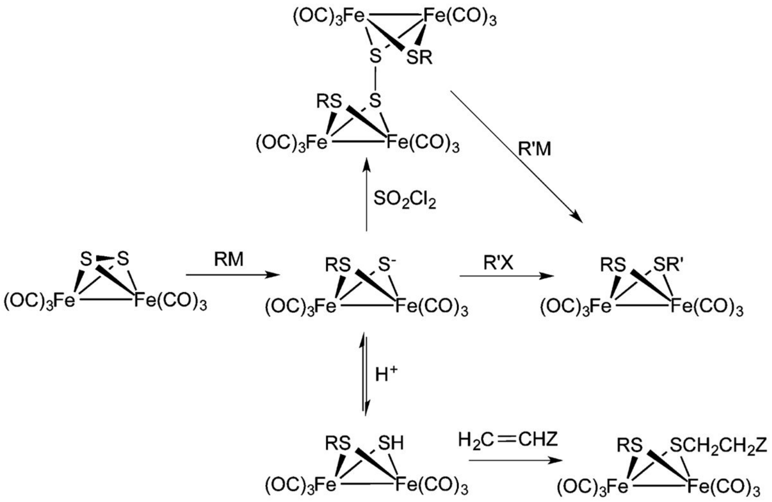
Scheme 32.

Route to Diiron Azadithiolates from Bis(chloromethyl)amines



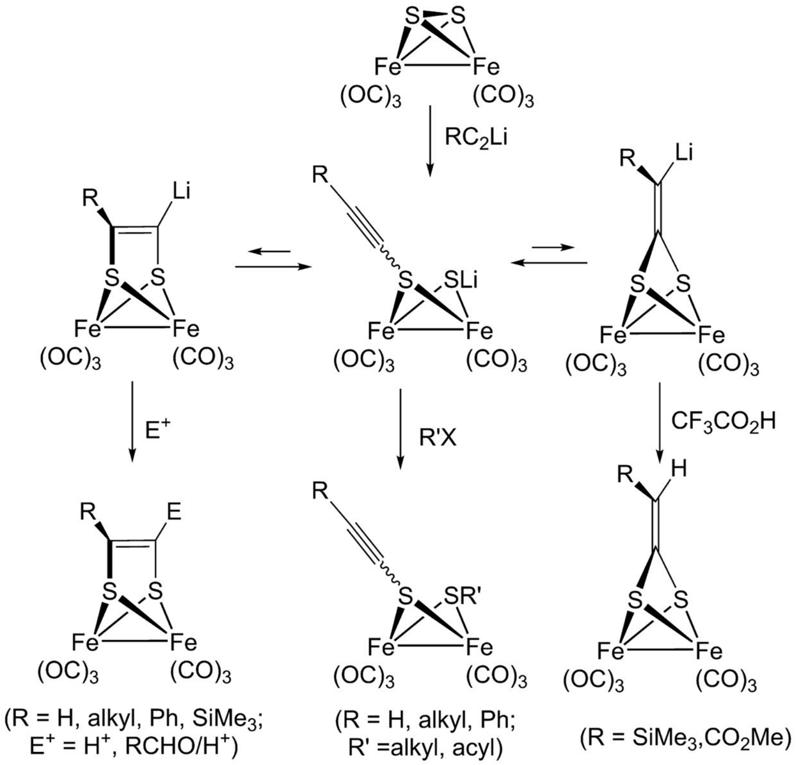
Scheme 33.

Photosensitizing Substituents That Have Been Installed on Diiron Azadithiolates



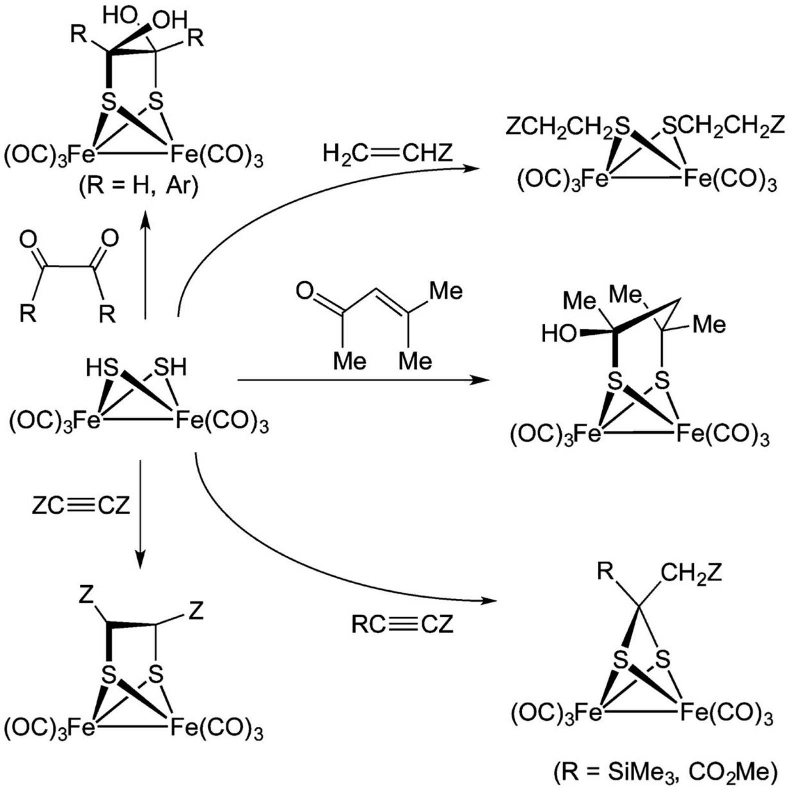
Scheme 34.

Routes to Unsymmetrical Diiron Dithiolates from $Fe_2(\mu\text{-}S_2)(CO)_6$



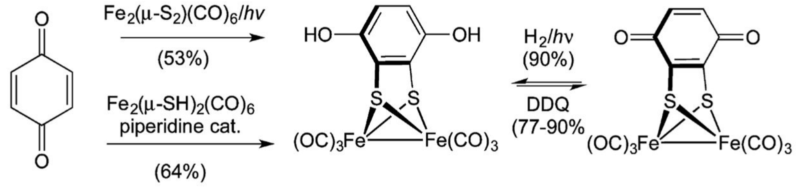
Scheme 35.

Reactions of Acetylides with $Fe_2(\mu\text{-}S_2)(CO)_6$ and Related Reactions[374]



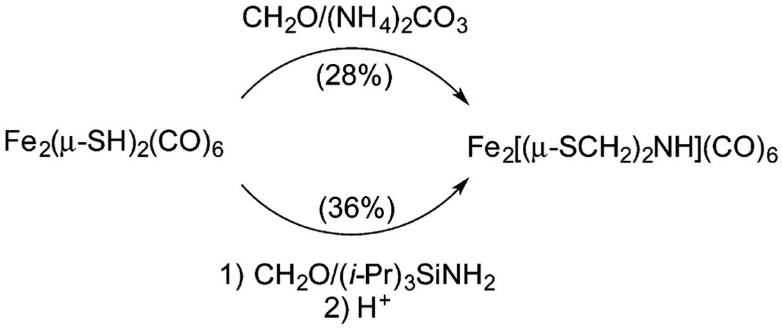
Scheme 36.

Reactions of $Fe_2(\mu\text{-}SH)_2(CO)_6$ with Unsaturated Organic Electrophiles: Dicarbonyls, Alkenes, and Alkynes ($Z = CO_2Me$, CN)[31,50]



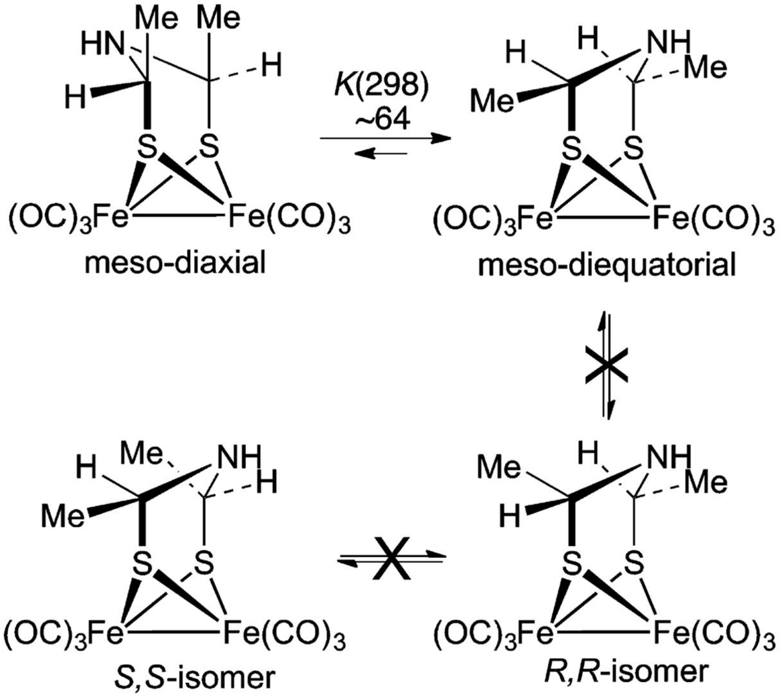
Scheme 37.

Synthesis and Reactions of Diiron Quinoldithiolates; Similar Reactions Occur with Naphtho- And Anthroquinones



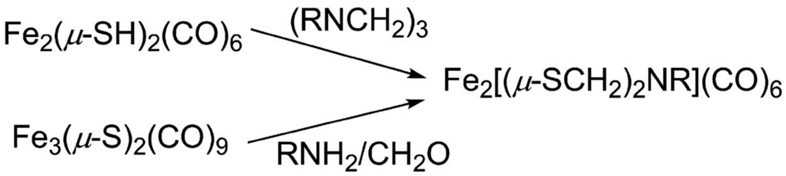
Scheme 38.

Routes to $Fe_2[(\mu\text{-}SCH_2)_2NH](CO)_6$ [92,33]

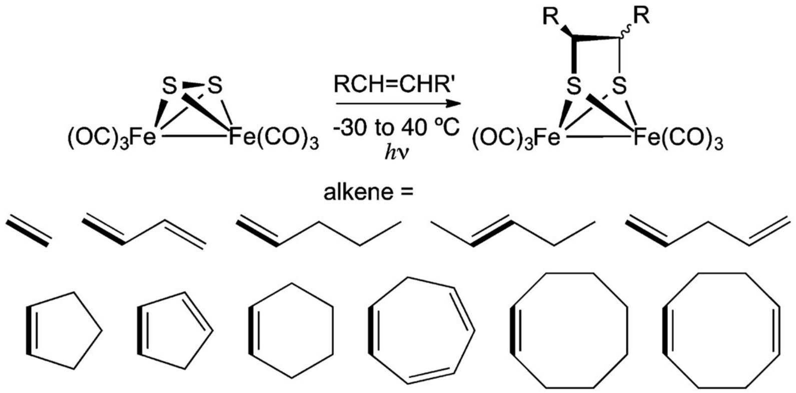


Scheme 39.

Stereoisomers of $Fe_2[(\mu\text{-}SCHMe)_2NH](CO)_6$ [389]

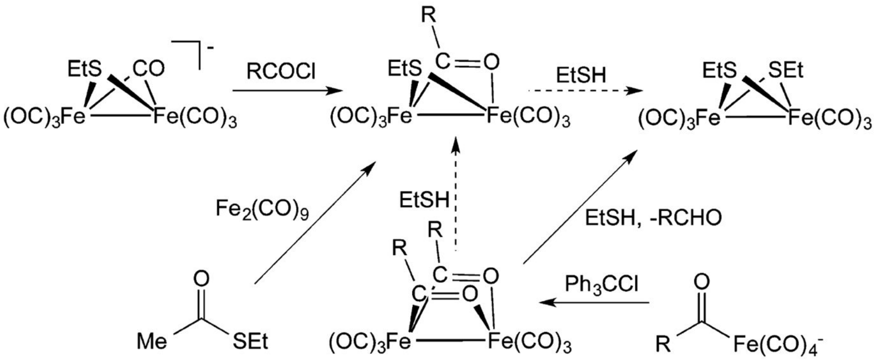


Scheme 40.
Condensation of Fe–S–CO Compounds with Formaldehyde, Imines, and Their Derivatives[92]



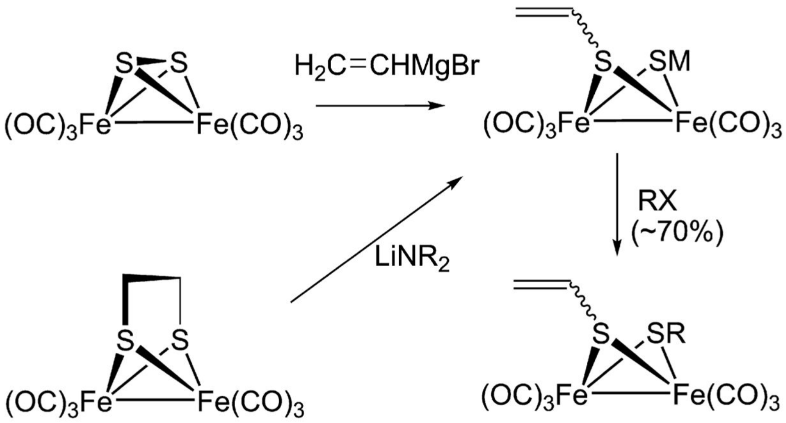
Scheme 41.

Photoaddition of Alkenes to $Fe_2(\mu\text{-}S_2)(CO)_6$ [69,393,394]

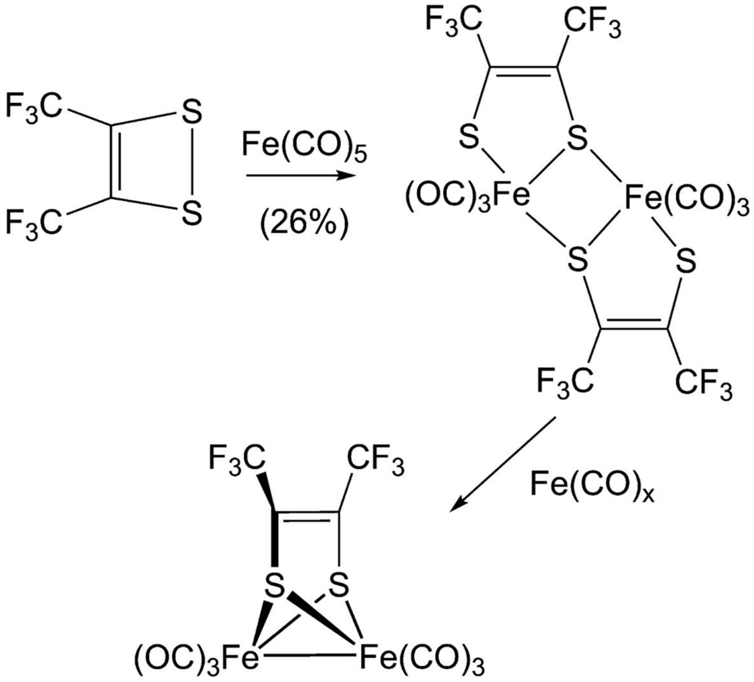


Scheme 42.

Synthesis and Reactions of *μ*-Acyl Diiron Thiolate Complexes[169,407]

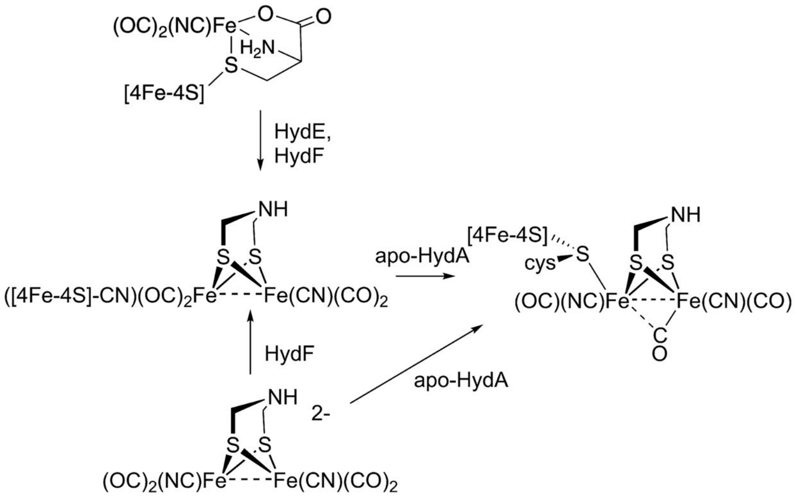


Scheme 43.
Two Routes to Diiron Vinylthiolato Carbonyls[347,82]



Scheme 44.

Formation of Diiron(I) Dithiolate Via a Diiron(II) Bis(dithiolate)[426,427]



Scheme 45.

Biosynthetic and Semisynthetic Routes to the [FeFe]-hydrogenase Active Site

Table 1

Reactions of Thiolate Substituents in $Fe_2(\mu\text{-}SR)_2(CO)_6$ Complexes

transformation	reagent	description
$R_2NC(O)R' \rightarrow R_2NC(S)R'$	$(MeOC_6H_4PS_2)_2$ (Lawesson's reagent)	thioamide formation[31]
$RN(H)C(O)OBu\text{-}t \rightarrow RNH_2$	CF_3CO_2H	*t*-Boc deprotection[32]
$R_2NSiR_3 \rightarrow R_2NH$	CF_3CO_2H	N-desilylation[33]
$RNH_2 \rightarrow RNHC(O)R'$	$R'COCl$	N-acylations[34–36]
$RNH_2 \rightarrow RNHC(O)R'$	*N*-hydroxysuccinimide, RNH_2	ester amination[37]
$ArNO_2 \rightarrow ArNH_2$	$H_2/Pd/C$	hydrogenation of nitro group[38]
$ArI/Br \rightarrow ArC_2\text{–}Ar$	ArC_2H $PdCl_2(PPh_3)_2$, CuI, Et_3N,	Sonogashira coupling[39–44]
$RC_2H \rightarrow RC_2(H)N_3R'$	$R'N_3$, CuI	azide click reaction[45]
$n\,RCH{=}CH_2 \rightarrow (RCH\text{–}CH_2)_n$	azobis(isobutyronitrile) (AIBN)	polymerization of alkenes[46]
$n\,RC{\equiv}CH \rightarrow (RCCH)_n$	[Rh(norbornadiene)Cl]$_2$	Rh-catalyzed polymerization of alkynes[47]
$RCHO \rightarrow RCH_2OH$	$NaBH_4$	aldehydes reduction[48]
ArCHO $\rightarrow$ porphyrin	pyrrole, HOAc, PhCHO, chloranil ($C_6O_2Cl_4$), $BF_3{\cdot}Et_2O$	Rothemund condensation, aromatization[35,49]
$ROH \rightarrow ROSiMe_3$	Me_3SiCl	O-silylation[50]
$ROH \rightarrow RO_2CR'$	$R'COCl/Et_3N$	O-acylations[34,48,51–53]
$ROH \rightarrow ROPX_2$	$ClPX_2$ (X = Ph, Cl)	phosphinite formation[53,54]
$ROH \rightarrow RCO_2R'$	$R'CO_2H$, DCC, DMAP	esterification[55–58]
$R_2CHOH \rightarrow R_2CO$	Dess–Martin reagent	alcohol oxidation[53]
quinol $\rightarrow$ quinone	DDQ	quinol oxidation[59]
$ROH \rightarrow RBr$	CBr_4/PPh_3	Appel halogenation[51]
$AcOR \rightarrow NaOR$	NaOMe	ester cleavage[60]
$R_2O \rightarrow RBr$	BBr_3	ether cleavage[61]
$RSH \rightarrow RS\text{–}Au$	Au	chemisorption[62]
$R_2S \rightarrow R_2SO, R_2SO_2$	dimethyldioxirane	sulfoxidation[63]
$RSH \rightarrow RS(Z)(H)C_2H_2Z$	maleimide	S-alkylation[64]
$RCl \rightarrow RS(CO)R'$	AcSM (M = Na, K)	thioester formation[35,51]
$RCO_2H \rightarrow RCO_2M$	$Zr_6O_4(OH)_4(C_6H_4(CO_2)_2)_6$ MOF	formation[65,66]
$RCO_2H \rightarrow RCO_2H\text{–}ZnS$	ZnS	chemisorption[67]
porph $\rightarrow$ Zn(porph)	$Zn(OAc)_2$	porphyrin (porph) metalation[68]
Zn(porph) $\rightarrow$ py-Zn(porph)	Zn(TPP)	complexation[36]

Table 2

Yields of $Fe_2(\mu\text{-}SR)_2$ vs $[Fe_2(\mu\text{-}SR)_2]_2$ Complexes Derived from Long-Chain Dithiols

dithiol	**$Fe_2(\mu\text{-}SR)_2$ yield (size of FeS_2X_n ring)[a]**	**$[Fe_2(\mu\text{-}SR)_2]_2$ yield (size of $(FeS_2X_n)_2$ ring)[a]**
1,2-$C_6H_4(CH_2SH)_2$ [85]	85 (7)	0[b] (16)
$(CH_2CH_2SH)_2$ [97]	0[b,c] (7)	7 (16)
d,l-$[CH(OH)]_2CH_2SH)_2$ [98]	0[b] (7)	8 (16)
2,2′-$[C_6Cl_2H_2SH]_2$ [99]	34 (7)	0[b] (16)
$CH_2(CH_2CH_2SH)_2$ [95]	0[b] (8)	5 (18)
n and *i*-$PrN(CH_2CH_2SH)_2$ [95,96]	0[b] (8)	16–17 (18)
$O(CH_2CH_2SH)_2$ [94]	19 (8)	11 (18)
$HSCH_2(CH_2OCH_2)_2CH_2SH$[94]	17 (12)	0[b] (24)
$HSCH_2(CH_2OCH_2)_3CH_2SH$[94]	21 (15)	0[b] (30)
$HSCH_2(CH_2OCH_2)_4CH_2SH$[94]	33 (18)	0[b] (36)

[a] X = CH^2, NR, O.

[b] 0% yield is inferred when no product was claimed.

[c] 89% of the monomer is obtained by alkylation of $Li_2Fe_2(\mu\text{-}S)_2(CO)_6$ with 1,4-dibromobutane.[83]

Table 3

Diiron Dithiolates Obtained by Degradation of Organic Polysulfides

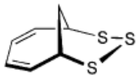
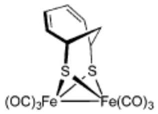
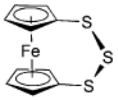
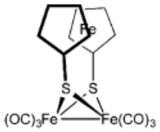
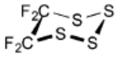
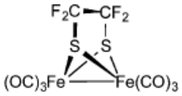
Conditions	**Polysulfide**	**Diiron Dithiolate Product**
$Fe_2(CO)_9$, 20°C (17–25%)[248]		
$Fe_3(CO)_{12}$, 80°C (24%)[217]		
$Fe_3(CO)_{12}$, 80°C (21%)[137]		

Table 4

Synthetic Results for Reactions of Thiols, Disulfides, and Thioethers with Fe(0) Carbonyls to Give $Fe_2(\mu\text{-}SR)_2(CO)_6$; (Reactions Were Conducted with 0.02 mol of Fe(0) Reagent in 100 mL of Decane at 80 °C)[18]

	$Fe_3(CO)_{12}$			$Fe_2(CO)_9$			$Fe(CO)_5$		
organosulfur compound	**equiv of S cmpd/equiv of $Fe_3(CO)_{12}$**	**time (h)**	**% yield[a]**	**equiv of S cmpd/equiv of $Fe_2(CO)_9$**	**time (h)**	**% yield**	**equiv of S cmpd/equiv of $Fe(CO)_5$**	**time (h)**	**% yield**
RSH[b]	3:1	1	92	2:1	11	91	1:1	22	60
RSSR[c]	3:2	5	74	1:1	19	66	1:2	34	56
RSR[d]	3:1	18	62	2:1	24	52	1:1	36	24

[a] Yields are averages for $Fe_2(\mu\text{-}SR)_2(CO)_6$ isolated after chromatographic purification.

[b] R = alkyl, benzyl, phenyl.

[c] R = alkyl.

[d] R = alkyl, phenyl.