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Article

Precursors to [FeFe]-Hydrogenase Models: Syntheses of $Fe_2(SR)_2(CO)_6$ from CO-Free Iron Sources

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This report describes routes to iron dithiolato carbonyls that do not require preformed iron carbonyls. The reaction of $FeCl_2$, Zn, and $Q_2S_2C_nH_{2n}$ ($Q^+ = Na^+$, Et_3NH^+) under an atmosphere of CO affords $Fe_2(S_2C_nH_{2n})(CO)_6$ ($n = 2, 3$) in yields >70%. The method was employed to prepare $Fe_2(S_2C_2H_4)(^{13}CO)_6$. Treatment of these carbonylated mixtures with tertiary phosphines, instead of Zn, gave the ferrous species $Fe_3(S_2C_3H_6)_3(CO)_4(PR_3)_2$, for R = Et, Bu, and Ph. Like the related complex $Fe_3(SPh)_6(CO)_6$, these compounds consist of a linear arrangement of three conjoined face-shared octahedral centers. Omitting the phosphine but with an excess of dithiolate, we obtained the related mixed-valence triiron species $[Fe_3(S_2C_nH_{2n})_4(CO)_4]^-$. The highly reducing all-ferrous species $[Fe_3(S_2C_nH_{2n})_4(CO)_4]^{2-}$ is implicated as an intermediate in this transformation. Reactive forms of iron, prepared by the method of Rieke, also combined with dithiols under a CO atmosphere to give $Fe_2(S_2C_nH_{2n})(CO)_6$ in modest yields under mild conditions. Studies on the order of addition indicate that ferrous thiolates are formed prior to the onset of carbonylation. Crystallographic characterization demonstrated that the complexes $Fe_3(S_2C_3H_6)_3(CO)_4(PEt_3)_2$ and $PBnPh_3[Fe_3(S_2C_3H_6)_4(CO)_4]$ feature high-spin ferrous and low-spin ferric as the central metal, respectively.

Introduction

Compounds of the type $Fe_2(SR)_2(CO)_6$ have become topical because of their similarity to the active site of the [FeFe]-hydrogenases (Figure 1).[1–3] Modern syntheses of such diiron(I) dithiolates rely on the reactions of thiols with iron carbonyls, typically $Fe_3(CO)_{12}$, as first described by Hieber.[4–6] This paper, which was motivated for reasons explained below, discloses routes to such diiron(I) species without use of preformed iron carbonyls.

Two routes to $Fe_2(SR)_2(CO)_6$ that utilize CO-free ferrous sources have been described. Compounds of the type $Fe_2(SR)_2(CO)_6$ were first prepared by treating a mixture of ferrous sulfate, ethanethiol, and KOH with an atmosphere of CO.[7] This transformation, which is possibly biosynthetically significant, is proposed by us to proceed via hydrido intermediates that form by attack of hydroxide on CO ligands.[8] Cody et al. reported that FeS, CO (via the decomposition of formic acid), and nonylthiol react at high temperatures and high pressures to afford $Fe_2(SC_9H_{19})_2(CO)_6$.[9,10] Routes remain unknown, however, to $Fe_2(SR)_2(CO)_6$ from ferrous salts that utilize practical laboratory conditions and produce reasonable yields.

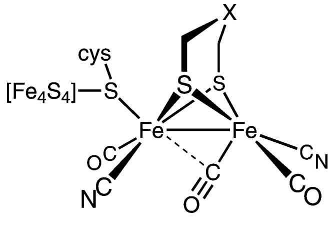

Figure 1. Structure of the diiron active site of the [FeFe]-hydrogenases. X is CH_2, NH, or O.

One could consider other CO-free ferrous sources to access $Fe^I(SR)(CO)_x$ species via reduction of ferrous carbonyls. A

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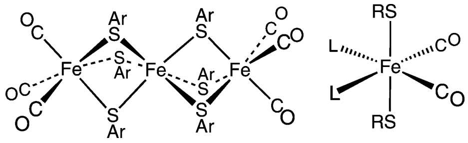
Scheme 1. Ferrous Carbonyls Prepared from Ferrous Salts (L = amine)



relevant precedent is the preparation of $Ru_2(SR)_2(CO)_6$ derivatives that arise from the reaction of $RuCl_3(H_2O)_x$ with CO, followed by addition of thiolate and reduction by Zn.[11,12] Whereas ruthenium chlorides carbonylate readily,[13] ferrous halides do not. Furthermore, ferrous carbonyl halides are metastable—they arise via halogenation of $Fe(CO)_5$, not carbonylation of the halides.[14]

In contrast to ferrous halides, ferrous thiolates have long been known to carbonylate readily. The reversible carbonylation of ferrous complexes of cysteine was first described in the 1920s.[15–18] Several monomeric dithiolato dicarbonyls prepared by carbonylation of ferrous thiolates have been subsequently characterized.[19–22] Ferrous arylthiolato carbonyl derivatives are conveniently accessed via treatment of ferrous chloride with aryl thiolate salts under an atmosphere of CO to give the all-ferrous species $Fe_3(SAr)_6(CO)_6$ (Ar = Ph, C_6H_4Me, C_6H_4OMe; see Scheme 1).[20,23–28] Such compounds represent potential precursors to subferrous carbonyl thiolates. Furthermore, more complex FeS clusters, which can be prepared from simple precursors,[29] are susceptible to reductive carbonylation.[30,31]

Routes to $Fe_2(SR)_2(CO)_6$ derivatives involving ferrous iron are likely relevant to the biosynthesis of the active site of the hydrogenases.[32,33] New routes to these diiron dithiolate complexes could also provide useful building blocks to more elaborate synthetic models. The further motivation for this effort was our search for methods to isotopically label $Fe_2(SR)_2(CO)_6$ with ^{57}Fe and ^{13}CO for Mössbauer spectroscopy,[34] nuclear resonance vibrational spectroscopy,[35] and vibrational spectroscopy. The need for scarce $^{57}Fe_x(CO)_y$ precursors could be obviated if efficient routes from ^{57}Fe metal to $Fe_2(SR)_2(CO)_6$ were available. These spectroscopic techniques complement experimental and theoretical[36] investigations into the mechanism of biological hydrogenesis.

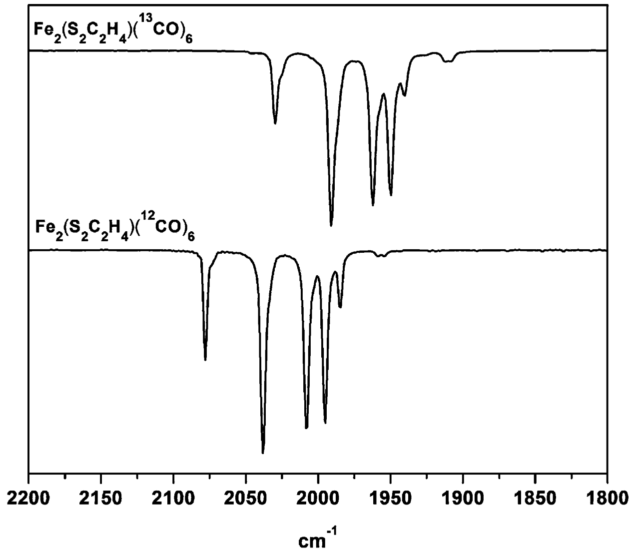


Figure 2. IR spectra (hexane solution) of $Fe_2(S_2C_2H_4)(^{13}CO)_6$ (top) and the same compound prepared from natural abundance CO (bottom).

Results and Discussion

Synthesis of $Fe_2(S_2C_nH_{2n})(CO)_6$ from $FeCl_2$. An efficient synthesis of $Fe_2(S_2C_2H_4)(CO)_6$ was achieved by treatment of an acetone solution of $FeCl_2$ with $Na_2S_2C_2H_4$ (and equivalent sources such as $(Et_3NH)_2S_2C_2H_4$) under an atmosphere of CO, followed by reduction with zinc (eq 1).

$$2FeCl_2 + 6CO + Na_2S_2C_3H_6 + Zn \rightarrow Fe_2(S_2C_3H_6)(CO)_6 + ZnCl_2 + 2NaCl \qquad (1)$$

The ethanedithiolate $Fe_2(S_2C_2H_4)(CO)_6$ was prepared in >70% yield. The yields for the propanedithiolate $Fe_2(S_2C_3H_6)(CO)_6$ were only about 40−50%, a major side product being an insoluble reddish solid with an IR spectrum indistinguishable from the hexacarbonyl, which we propose is the polymer *catena*-$\{Fe_2(S_2C_3H_6)(CO)_6\}_n$. When the reaction of $FeCl_2$ with $Na_2S_2C_2H_4$ and Zn was conducted under an atmosphere of ^{13}CO, we obtained the corresponding $Fe_2(S_2C_2H_4)(^{13}CO)_6$ as verified by IR spectroscopy (Figure 2). The ν^{13}_{CO} bands match the shift predicted by the effect of reduced mass ratio of 0.9771.

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We examined the conversion by stepwise addition of reagents. Under an atmosphere of CO, the solution of $FeCl_2$ was found to react with 0.5 equiv $Na_2S_2C_nH_{2n}$ ($n = 2, 3$) to produce red-brown suspensions that dissolved only upon the addition of zinc. If, instead of zinc, the slurry was treated with tertiary phosphines, homogeneous green solutions were obtained. These green compounds have the formula $Fe_3(S_2C_nH_{2n})_3(CO)_4(PR_3)_2$ (eq 2). Products were characterized for $PR_3 = PBu_3$ for $n = 2$ and for $PR_3 = PEt_3$, PBu_3, and PPh_3 for $n = 3$. These phosphine complexes displayed two ν_{CO} bands in their IR spectra near 2000 and 1945 cm^{-1}. Like $Fe_3(SAr)_6(CO)_6$,[20,24–28,37] these complexes feature a single high-spin ferrous center, as indicated by the ^1H NMR spectrum and crystallography (see below).

$$3FeCl_2 + 4CO + 3Na_2S_2C_3H_6 + 2PR_3 \rightarrow Fe_3(S_2C_3H_6)_3(CO)_4(PR_3)_2 + 6NaCl \quad (2)$$

The order of addition is important in the synthesis of these triiron complexes: treatment of preformed iron(II) phosphine chlorides with CO *followed by* the dithiolate gave monomeric complexes, such as $Fe(S_2C_2H_4)(CO)_2(PMe_3)_2$.[38]

If, instead of adding two phosphine ligands, additional equivs of dithiolate are added to THF slurries of $FeCl_2/C_nH_{2n}S_2$ a jade-green product is obtained. The new species absorbs CO rapidly and dissolves to give a dark red solution that, after 12 h, exhibits an IR spectrum consisting of ν_{CO} bands at 1993 (s) and 1943 (m). This reaction produces neither $Fe_2(S_2C_nH_{2n})(CO)_6$, nor the anion $[Fe(S_2C_nH_{2n})_2(CO)_2]^{2-}$.[12] Instead, we obtained a triiron species that is somewhat analogous to the above-mentioned triiron phosphine adducts. ESI-MS analysis of the reaction mixture indicated $[Fe_3(dithiolate)_4(CO)_4]^-$. Analytically pure complexes were obtained upon addition of 18-crown-6 to give salts of the formula $M[Fe_3(S_2C_nH_{2n})_4(CO)_4]$ ($n = 2, 3$; $M^+ = PBnPh_3^+$, $[Na(18\text{-crown-}6)]^+$). Low-temperature EPR spectra of a THF glass of the mixed-valence $[Na(18\text{-crown-}6)][Fe_3(S_2C_3H_6)_4(CO)_4]$ exhibited an axial signal with g-values of 2.102 and 2.001, consistent with the central Fe atom being low-spin ferric in a noncubic environment.[39,40]

One of the striking aspects of $[Fe_3(S_2C_2H_4)_4(CO)_4]^-$ is the presence of a ferric center that must arise from oxidation of an all-ferrous species. The cyclic voltammogram of $[Na(18\text{-crown-}6)][Fe_3(S_2C_3H_6)_4(CO)_4]$ revealed that it is irreversibly reduced at −1.76 V versus Ag/AgCl in MeCN solution. This highly negative reduction potential is consistent with the ease of oxidation of an all-ferrous dianion. Whereas the presumed $[Fe_3(dithiolate)_4(CO)_4]^{2-}$ readily oxidizes by one electron to give the isolated monoanion, no evidence of one-electron oxidation of $Fe_3(dithiolate)_3(CO)_4(PR_3)_2$ was observed in its cyclic voltammetry. The differing redox properties are attributed to the effects of charge and the π-donor nature of the terminal thiolates.

Synthesis of $Fe_2(S_2C_nH_{2n})(CO)_6$ from Rieke Iron. In analogy to the reactivity of $Fe^0_x(CO)_y$ species,[5,41,42] we anticipated that metallic Fe would be oxidized by dithiols in the presence of CO to yield $Fe_2(S_2C_nH_{2n})(CO)_6$. Commercial 300-mesh iron powder appeared unreactive with a CO-saturated THF solution of propanedithiol. Experiments starting from *activated* iron powder, prepared according to the methods of Rieke,[43] were more successful. This form of iron was prepared by reduction of THF solutions of $FeCl_2$ with Li in the presence of naphthalene.[44] Treatment of the resulting black-brown mixture with 0.5 equiv of ethanedithiol under CO atmosphere produced $Fe_2(S_2C_2H_4)(CO)_6$ in ~40% yield over the course of several hours at room temperature (eq 3).

$$2Fe(\text{“Rieke”}) + 6CO + H_2S_2C_nH_{2n} \rightarrow Fe_2(S_2C_nH_{2n})(CO)_6 + H_2 \quad (3)$$

The conversion was mildly exothermic and rapidly evolved gas, assumed to be H_2. The method proceeded equally well with propanedithiol to generate $Fe_2(S_2C_3H_6)(CO)_6$, and, although not further pursued, ethanethiol likewise afforded $Fe_2(SC_2H_5)_2(CO)_6$.

The pathway by which Rieke-Fe converts to $Fe_2(S_2C_nH_{2n})(CO)_6$ was partially illuminated through experiments that probed order of addition. Rieke-Fe was unreactive toward CO in the absence of dithiol, even after 24 h in refluxing THF. This finding suggests that carbonylation depends on the formation of a ferrous thiolate. Even in the absence of CO, Rieke Fe was found to react rapidly upon addition of 1 equiv ethanedithiol with evolution of gas. The resulting dark red mixture was found to absorb CO to afford $Fe_2(S_2C_2H_4)(CO)_6$ in about 40% yield. When the solution resulting from the reaction of Rieke Fe and ethane- or propanedithiol was filtered *prior to carbonylation*, we did *not* observe formation of $Fe_2(S_2C_nH_{2n})(CO)_6$. Instead, these filtered, carbonylated solutions afforded mixed-valence $[Fe_3(S_2C_nH_{2n})_4(CO)_4]^-$ described above. These experiments are consistent with a pathway to $Fe_2(SR)_2(CO)_6$ that entails a rapidly formed ferrous dithiolate that undergoes reduction by Fe only in the presence of CO.

We also generated Rieke iron using dimethoxyethane as a solvent,[43] which, as reported, gave a more granular form of iron that could be washed. This material also was found to react with ethanedithiol to give $Fe_2(S_2C_2H_4)(CO)_6$, although in diminished yields, attributed to the lower surface area of the iron particles.

Structural Characterization of Triiron Compounds. The complex $Fe_3(S_2C_3H_6)_3(CO)_4(PEt_3)_2$ consists of a confacial trioctahedral species (Figure 3). The first coordination sphere of the iron centers resembles that in $Fe_3(SPh)_6(CO)_6$.[24]

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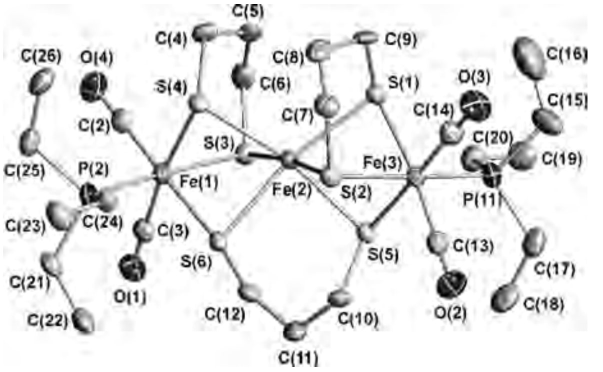

Figure 3. Structure of $Fe_3(S_2C_3H_6)_3(CO)_4(PEt_3)_2$. Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity.

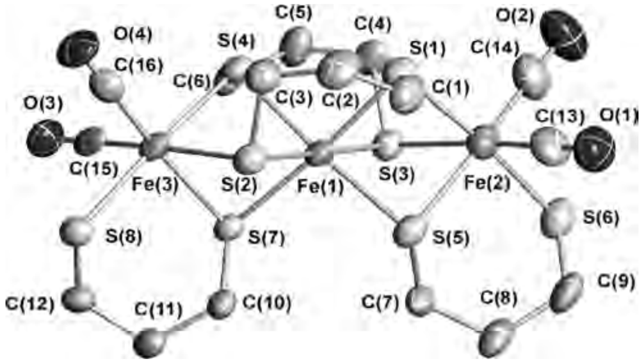

Figure 4. Structure of the anion in $PBnPh_3[Fe_3(S_2C_3H_6)_4(CO)_4]$, with hydrogen atoms omitted for clarity. Thermal ellipsoids are set at the 50% probability level.

Whereas the arylthiolato complexes are linear, the FeFeFe angle in the triiron dithiolates is 167°.

The Fe—S distances in $Fe_3(S_2C_3H_6)_3(CO)_4(PEt_3)_2$ provide insight into the spin state of the central Fe atom (Table 1). The $(CO)_2PS_3$ coordination spheres of the terminal Fe centers feature Fe—ligand distances (see below) consistent with low-spin Fe^{II}, as expected. The $(CO)_2PS_3$ coordination spheres of the terminal Fe centers feature Fe-ligand distances (2.34–2.35 Å) consistent with low-spin Fe^{II}, as expected. For the central iron the Fe—S distances (2.49–2.56 Å) are about 0.2 Å longer, indicating that this central iron is high-spin. The correlation between Fe—S bond lengths and spin state for FeS_6 systems is supported by several precedents. For $[Fe(9\text{-ane-}S_3)_2]^{2+}$, which is low-spin, the Fe—S distances are 2.24—2.26 Å.[45,46] The related low-spin ferric species, $[Fe(9\text{-ane-}S_3)_2]^{3+}$, has Fe—S distances of 2.28 Å, thereby illustrating that Fe—S bond lengths are more sensitive to spin state than oxidation state. Also, the $Mo(\mu\text{-}SC_2H_5)_3Fe(\mu\text{-}SC_2H_5)_3Mo$ core in $[Mo_2Fe_7S_8(SC_2H_5)_{12}]^{3-}$ features a low-spin ferric center with Fe—S distances of 2.31 Å, whereas the unique FeS_6 center in the tetraanion $[Mo_2Fe_7S_8(SCH_2Ph)_{12}]^{4-}$ features high-spin ferrous with Fe—S distances of 2.52 Å.[47] In general, Fe—S bond lengths are about 2.2—2.3 Å for low-spin complexes and about 2.5—2.6 Å for high-spin complexes, regardless of oxidation state. The Fe—S bond lengths in $Fe_3(S_2C_3H_6)_3(CO)_4(PEt_3)_2$ and $Fe_3(SPh)_6(CO)_6$are similar, thereby further supporting our assignment of ls/hs/ls in our triferrous structure.

By virtue of the three chelating dithiolate ligands, $Fe_3(S_2C_3H_6)_3(CO)_4(PEt_3)_2$ exists as Δ and Λ configurations at the central Fe. In D_3-symmetric $Mn_3(S_2C_3H_6)_3(CO)_6$, the dithiolates adopt an alternative connectivity, being ligated in a κ^2-μ, μ' fashion.[48] The Mn(I)–S distances in this Mn_3 species are comparable to the terminal Fe(II)–S distances, consistent with the assignment of these ferrous sites as low-spin.

X-ray crystallographic analysis of $PBnPh_3[Fe_3(S_2C_3H_6)_4(CO)_4]$ (Figure 4, Table 2) revealed a roughly linear ($\angle(FeFeFe) = 173°$) triiron ensemble bound by eight thiolato ligands and four terminal CO ligands. In terms of the first coordination sphere, the anion $[Fe_3(S_2C_3H_6)_4(CO)_4]^-$ resembles $Fe_3(S_2C_3H_6)_3(CO)_4(PEt_3)_2$ by the interchange of two terminal thiolato and two phosphine ligands. For this anion, the Fe—S distances for the central iron center are 2.283—2.311 Å, about 0.2 Å shorter than the Fe—S distances of the central high-spin ferrous site in $Fe_3(S_2C_3H_6)_3(CO)_4(PEt_3)_2$. In the monoanion, the Fe—S distances for the central iron center are *also* shorter than the Fe—S bonds of the terminal Fe centers, which range from 2.297 to 2.354 Å, consistent with a central iron that is low-spin ferric. The bond distances and the charge clearly indicate that the species is a mixed-valence $Fe^{II}Fe^{III}Fe^{II}$ compound.[49] Species featuring $Fe(SR)_4(CO)_x$ coordination have not been previously well characterized.[19] The closest analogue is a mixed-spin diferrous complex of the type $(diamineFe)(SR)(\mu\text{-}SR)_3Fe(SR_2)(CO)_2$.[50] In the latter, the high-spin Fe—S distances average 0.15 Å longer than the corresponding bonds to low-spin Fe.

Conclusions and Summary

In this work, we elucidated new routes to the versatile $Fe_2(SR)_2(CO)_6$ species from ferrous chloride via reductive carbonylation under mild conditions (Scheme 2). The reductive carbonylation method enables the preparation of these compounds in reasonable yield without requiring preformed iron carbonyls.

Our experiments underscore the ability of thiolates to enhance the affinity of ferrous complexes for CO, a theme dating back to early experiments on iron-cysteine complexes.[15–17] Hieber noted that the carbonylation of iron metal is catalyzed by sulfur,[51] implicating the role of Fe(II)—S species in the formation of iron(0) carbonyls. The literature on ferrous thiolates and even ferric thiolates is substantial.[52,53]

Triiron thiolato complexes were found to arise when polymeric ferrous dithiolates were generated in the presence

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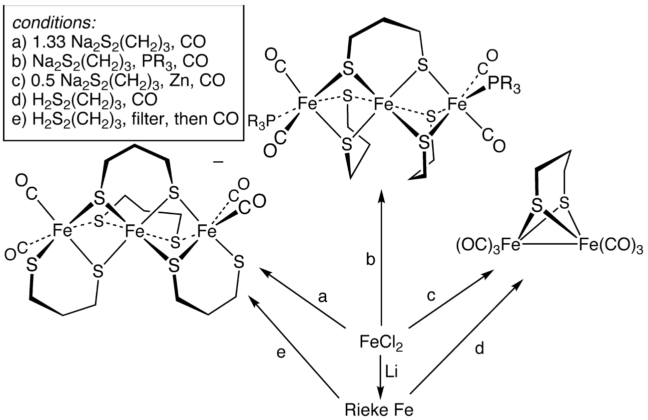
Table 1. Selected Bond Lengths (Å) and Angles (°) for $Fe_3(SPh)_6(CO)_6$,[24] $Fe_3(S_2C_3H_6)_3(CO)_4(PEt_3)_2$, and $PBnPh_3[Fe_3(S_2C_3H_6)_4(CO)_4]$

$Fe_3(SPh)_6(CO)_6$		$Fe_3(S_2C_3H_6)_3(CO)_4(PEt_3)_2$		$PBnPh_3[Fe_3(S_2C_3H_6)_4(CO)_4]$	
Fe(1)—S	2.346(1)	Fe(1)—S(3)	2.3424(15)	Fe(1)—S(1)	2.285(2)
Fe(1)—S	2.348(1)	Fe(1)—S(4)	2.3422(13)	Fe(2)—S(1)	2.309(2)
Fe(1)—S	2.348(1)	Fe(1)—S(6)	2.3504(13)	Fe(2)—S(3)	2.352(2)
Fe(1)—C	1.811(1)	Fe(1)—P(2)	2.2659(15)	Fe(2)—S(5)	2.354(2)
Fe(1)—C	1.796(1)	Fe(1)—C(2)	1.764(5)	Fe(2)—S(6)	2.319(2)
Fe—C	1.793(4)	Fe(1)—C(3)	1.752(5)	Fe(1)—S(7)	2.311(2)
Fe(1)—Fe(2)	3.188(1)	Fe(1)—Fe(2)	3.201	Fe(1)—Fe(3)	2.9473(16)
Fe(2)—S	2.513(1)	Fe(2)—S(1)	2.5144(14)	Fe(1)—S(2)	2.284(2)
Fe(2)—S	2.473(1)	Fe(2)—S(2)	2.5403(14)	Fe(1)—S(3)	2.288(2)
Fe(2)—S	2.519(1)	Fe(2)—S(3)	2.5646(14)	Fe(1)—S(4)	2.283(2)
Fe(2)—S	2.513(1)	Fe(2)—S(4)	2.5184(14)	Fe(1)—S(5)	2.296(2)
Fe(2)—S	2.473(1)	Fe(2)—S(5)	2.4926(14)	Fe(2)—C(13)	1.739(8)
Fe(2)—S	2.519(1)	Fe(2)—S(6)	2.4866(14)	Fe(2)—C(14)	1.750(9)
Fe(1)—Fe(2)	3.170(1)	Fe(2)—Fe(3)	3.185	Fe(1)—Fe(2)	2.9259(17)
Fe—Fe—Fe	180.0(0)	Fe(1)—Fe(2)—Fe(3)	167.36	Fe(2)—Fe(1)—Fe(3)	173.50(5)
C—Fe—C	94.27(6)	C(3)—Fe(1)—C(2)	92.8(2)	C(13)—Fe(2)—C(14)	92.7(4)
C—Fe(1)—C	94.801(3)	C(2)—Fe(1)—P(2)	91.26(16)	C(13)—Fe(2)—S(6)	87.9(3)
C—Fe(1)—C	96.131(3)	C(3)—Fe(1)—P(2)	92.69(16)	C(14)—Fe(2)—S(6)	86.3(3)
S—Fe(1)—S	79.28(2)	S(3)—Fe(2)—S(4)	76.44(4)	S(4)—Fe(1)—S(2)	85.37(7)
S—Fe(1)—S	85.33(3)	S(3)—Fe(1)—S(4)	84.35(5)	S(4)—Fe(3)—S(2)	83.49(7)

Scheme 2. Fe—Thiolate—CO Complexes Prepared From $FeCl_2$, Thiolate, and CO



of additional donor ligands, such as phosphines and thiolates. The complexes $Fe_3(S_2C_3H_6)_3(CO)_4(PEt_3)_2$ and $[Fe_2(S_2C_nH_{2n})_4(CO)_4]^-$ resemble the previously reported arylthiolato complexes $Fe_3(\mu\text{-SAr})_3(CO)_6$.[20,23–28] Other oligomeric Fe—SR—CO species[54] feature the following connectivities: $(CO)_3Fe(\mu\text{-RS})_2Fe(CO)(\mu\text{-RS})_2Fe(CO)(\mu\text{-SR})_2Fe(CO)_3]^{2-}$,[55,56] $(CO)_3Fe(\mu\text{-SR})_2Fe(CO)(\mu\text{-SR})_2Fe(CO)_3$[4] (and substituted analogues),[57] and $\{[Fe_2(\mu\text{-SR})_2(CO)_5(SR)][Fe_2(\mu\text{-SR})(CO)_7]\}^{2-}$.[58,59]

The results using Rieke iron highlight the potential of such highly reactive metals as precursors to new clusters. These conversions, which are heterogeneous and probably highly complex mechanistically, illustrate again the robustness of iron thiolato carbonyls. Our experiments indicate that, in addition to being a source of iron, the Rieke iron serves as a reducing agent that converts initially formed ferrous thiolates to iron(I) derivatives. Altogether, the newly elucidated routes to $Fe_2(SR)_2(CO)_6$ complexes via the CO-free iron sources are promising pathways for efficiently generating isotopically labeled models for the FeFe-hydrogenases.

Experimental Section

General Protocols. Methods used in the laboratory have been described recently.[60] Fe powder (Aldrich, 300 mesh) was stored in a glovebox under N_2 atmosphere. NaH was rinsed free of mineral oil with hexane before use. Reactions were conducted using standard Schlenk techniques, but work ups of the $Fe_2(S_2C_nH_{2n})(CO)_6$ species were conducted in air. NMR data are reported in ppm and IR data in cm^{-1}. The EPR instrumentation and simulations were recently described.[61]

For preparations using $FeCl_2$, this reagent was also generated by combining iron powder (2.23 g, 40 mmol) with 12 M HCl (15 mL, 180 mmol) in MeOH (15 mL).[62,63] After stirring the mixture for 16 h, solvent was removed in vacuum, leaving a pale gray powder of $[Fe(MeOH)_x]Cl_2$. Heating this powder at 100−110 °C in a vacuum for 5 h gave an off-white solid.

$Fe_2(S_2C_2H_4)(CO)_6$ from $FeCl_2$ with NaH. A solution of 0.507 g (4.00 mmol) of $FeCl_2$ in 45 mL of acetone was saturated with CO for 30 min. In a separate flask, $Na_2S_2C_2H_4$ was prepared from 0.39 mL (4.70 mmol) of $C_2H_4(SH)_2$ and 0.144 g (4.90 mmol) of NaH in 4 mL of THF for 1 h. The THF suspension was added over a 20 min period to the $FeCl_2$, causing an immediate color change from a pale green solution to a red-brown suspension (this solid became black and less reactive upon removal of solvent). The red-brown suspension was stirred for 1 h before the addition of 0.265 g (4.05 mmol) of Zn. The reaction was monitored via IR

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spectroscopy until conversion to $Fe_2(S_2C_2H_4)(CO)_6$ was complete. The reaction mixture was passed through a plug of Celite in air to remove the Zn. The solvent from the filtrate was removed in vacuum to dryness. The red residue was extracted into 15 mL of CH_2Cl_2 and passed through a 3 cm plug of silica gel, washing with CH_2Cl_2. Evaporation of the solvent gave a red oil. A hexane extract of this oil was then passed through a second 3 cm plug of silica gel, washing with hexane. Evaporation of the eluate gave an orange-red solid. Yield: 0.553−0.47 g (74−63%).

$Fe_2(S_2C_2H_4)(CO)_6$ from $FeCl_2$ with Et_3N. A solution of 0.495 g (3.90 mmol) $FeCl_2$ in 45 mL of acetone was saturated with CO for 30 min. This solution was treated with 0.56 mL (4.0 mmol) Et_3N, immediately giving a blue-gray slurry. Addition of 0.17 mL (2.0 mmol) of $C_2H_4(SH)_2$ to the slurry caused an immediate color change to dark red-brown. Zn powder, 0.264 g (4.04 mmol), was added to the slurry, resulting in no observable, immediate change. The reaction was monitored via IR spectroscopy until conversion to $Fe_2(S_2C_2H_4)(CO)_6$ was complete. The reaction mixture was passed through a plug of Celite in air to remove the Zn. The filtrate was taken to dryness under vacuum. The red residue was extracted into about 15 mL CH_2Cl_2 and passed through 3 cm of silica gel, washing with CH_2Cl_2. Evaporation of the solvent gave a red oil. A hexane extract of this oil was then passed through a second plug of 3 cm of silica gel, washing with hexane. Evaporation of the eluate gave an orange-red solid. Yield: 0.50 g (68%).

$Fe_2(S_2C_3H_6)(CO)_6$ from $FeCl_2$. A solution of 0.507 g (4.00 mmol) of $FeCl_2$ in 45 mL of acetone was saturated with CO for 30 min. In a separate flask, $Na_2S_2C_3H_6$ was prepared from 0.47 mL (4.70 mmol) of $C_3H_6(SH)_2$ and 0.144 g (4.90 mmol) of NaH in 4 mL of THF for 1 h. The THF suspension was added over a 20 min period to the $FeCl_2$, causing an immediate color change from pale green to a red-brown suspension. The red-brown suspension was stirred for 1 h before the addition of 0.265 g (4.05 mmol) of Zn. The reaction was monitored via IR spectroscopy until conversion to $Fe_2(S_2C_3H_6)(CO)_6$ was complete. The reaction mixture was passed through a plug of Celite in air to remove the Zn. The solvent from the filtrate was removed in vacuum to dryness. The red residue was extracted into 15 mL of CH_2Cl_2 and passed through a 3 cm plug of silica gel, washing with CH_2Cl_2. A glassy red residue remained on the filter: ν_{CO} (KBr) = 2070 (m), 2030 (s), 1986 (br s) (proposed to be *catena*-$\{Fe_2(S_2C_3H_6)(CO)_6\}_n$). Evaporation of the solvent gave a red oil. A hexane extract of this oil was then passed through a second 3 cm plug of silica gel, washing with hexane. Evaporation of the eluate gave an orange-red solid. Yield: 0.408 g (53%).

$Fe_2(S_2C_2H_4)(CO)_6$ from Rieke-Fe. A mixture of 1.221 g (9.633 mmol) of $FeCl_2$, 0.187 g (1.46 mmol) naphthalene, and 0.154 g (22.2 mmol) Li was suspended in 20 mL of THF. Within 5 min, the suspension began darkening to gray and then black. Up to this stage, the procedure follows exactly that of Rieke et al. After about 18 h, the resulting black mixture was saturated with CO and then 404 μL (4.82 mmol) of $C_2H_4(SH)_2$ was added by syringe. Vigorous bubbling ensued for 30 s. from the slightly exothermic reaction, and the black mixture gradually developed a red tint. After 18 h, the mixture was filtered through Celite in air. The red-black filtrate was chromatographed on silica gel; eluting with CH_2Cl_2 gave an impure red product band. Further silica gel chromatography with hexane produced orange-red oil contaminated with naphthalene. Drying in vacuo afforded red crystals. Yield: 0.76 g (42%).

$Fe_2(SC_2H_5)_2(CO)_6$ from Rieke-Fe. A mixture of 0.611 g (4.821 mmol) of $FeCl_2$, 0.094 g (0.73 mmol) of naphthalene, and 0.077 g (11 mmol) of Li was suspended in 10 mL of THF. Within 5 min, the suspension began darkening to gray and then black. After 16 h, the resulting black oily mixture of Rieke-Fe was saturated with CO and then treated with 357 μL (4.82 mmol) of C_2H_5SH. Gas evolution was not observed, but the black mixture gradually developed a red tint over hours. After 24 h, the mixture was filtered through Celite in air. The orange-red filtrate was chromatographed on silica gel with hexane, eluting a red-orange major product band (the anti or a/e isomer) and a yellow-orange minor product band (the syn or e/e isomer). Combined yield: 0.190 g (20%).

$Li[Fe_3(S_2C_2H_4)_4(CO)_4]$ from Rieke-Fe. A mixture of 1.221 g (9.633 mmol) of $FeCl_2$, 0.187 g (1.46 mmol) of naphthalene, and 0.150 g (22.2 mmol) Li was suspended in 20 mL of THF. Within 5 min, the suspension began darkening to gray and then black. After 12 h, the resulting black oily mixture of Rieke-Fe was treated with 808 μL (9.63 mmol) of $C_2H_4(SH)_2$. Vigorous bubbling ensued for 30 s from the slightly exothermic reaction. After 1.5 h, the mixture was filtered through Celite, and the dark reddish-black filtrate was saturated with CO. After 2 h, the resulting deep red-black solution was filtered and dried under vacuum. IR (THF): 1995 (vs) and 1943 (s).

$[Na(18\text{-crown-}6)][Fe_3(S_2C_2H_4)_4(CO)_4]$. A suspension of $Na_2S_2C_2H_4$ was prepared from 298 μL (3.56 mmol) of $C_2H_4(SH)_2$ and 0.170 g (7.11 mmol) of NaH in 10 mL of THF for 1 h. This slurry was added to a suspension of 0.300 g (2.37 mmol) of $FeCl_2$ in 10 mL of THF. The resulting mixture darkened immediately. After 10 min, the dark red slurry was saturated with CO. After 3 h, the red-brown solution contained a small amount of red-brown solid in suspension. The IR spectrum at this stage revealed bands at 1994 and 1944 cm^{-1}. The reaction mixture was filtered through Celite, and the filtrate was treated with a solution of 418 mg (1.58 mmol) of 18-crown-6 in 5 mL of THF. Over 4 h, a brown-red powder precipitated, which is proposed to be $[Na(18\text{-crown-}6)][Fe_3(S_2C_2H_4)_4(CO)_4]$. The product was purified by extraction into ~8 mL of MeCN, followed by the addition of ~15 mL of Et_2O to precipitate a dark red-brown powder. Yield: 554 mg (75%). IR (MeCN, cm^{-1}): 1998 (s), 1947 (m). Anal. Calcd for $C_{24}H_{40}Fe_3NaO_{10}S_8$ (found): C, 30.81 (30.74); H, 4.31 (4.23).

$[Na(18\text{-crown-}6)][Fe_3(S_2C_3H_6)_4(CO)_4]\cdot THF$. A suspension of $Na_2S_2C_3H_6$ was prepared from 450 μL (4.48 mmol) of $C_3H_6(SH)_2$ and 0.230 g (9.50 mmol) of NaH in 10 mL of THF for 1 h. This slurry was added to a suspension of 0.286 g (2.25 mmol) of $FeCl_2$ in 10 mL of THF. The resulting mixture darkened immediately. After 10 min, the dark red slurry was saturated with CO. After 3 h, the red-brown solution contained a small amount of red-brown solid in suspension. The IR spectrum showed bands at 1994 and 1944 cm^{-1}. The reaction mixture was filtered through Celite, and the filtrate was treated with a solution of 870 mg (3.30 mmol) of 18-crown-6 in 5 mL of THF. The solution was stirred for 4 h, but no precipitation was observed. The solution was concentrated to approximately 5 mL, and the product was precipitated as a dark red oil by addition of ~50 mL of hexanes. The supernatant was decanted, and ~50 mL of more hexanes was added to the flask. The oil was triturated overnight, giving a red-brown powder. Yield: 554 mg (75%). IR (THF, cm^{-1}): 1993 (s), 1943 (m). Anal. Calcd for $C_{32}H_{56}Fe_3NaO_{11}S_8$ (found): C, 35.97 (36.13); H, 5.23 (5.31).

$PBnPh_3[Fe_3(S_2C_2H_4)_4(CO)_4]$. A suspension of $Na_2S_2C_2H_4$ was prepared from 397 μL (4.73 mmol) of $C_2H_4(SH)_2$ and 0.378 g (9.47 mmol) of a 60% NaH-mineral oil suspension in 10 mL THF for 1 h. In a separate flask, a suspension of 0.300 g (2.37 mmol) of $FeCl_2$ in 10 mL of THF was prepared. The $FeCl_2$ suspension was treated with the $Na_2S_2C_2H_4$ mixture, and the resulting mixture immediately began darkening. After 10 min, the dark red-black slurry was saturated with CO. After 2 h, the reaction mixture was filtered through Celite, and volatiles were removed in vacuo. A

Table 2. Selected Crystallographic Data for $PBnPh_3[Fe_3(S_2C_3H_6)_4(CO)_4]\cdot 3THF$ and $Fe_3(S_2C_3H_6)_3(CO)_4(PEt_3)_2$

empirical formula	$C_{94}H_{116}Fe_6O_{11}P_2S_{16}$	$C_{25}H_{48}Fe_3O_4P_2S_6$
formula weight	2331.87	834.48
temperature (K)	193(2)	193(2)
wavelength (Å)	0.71073	0.71073
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P21/c$
a (Å)	12.409(5)	17.243(3)
b (Å)	14.658(5)	11.4089(18)
c (Å)	16.276(6)	18.414(3)
α (°)	72.961(6)	90
β (°)	80.745(7)	92.939(4)
γ (°)	65.861(6)	90
volume (Å^3)	2580.2(16)	3617.8(10)
Z	1	4
ρ (calculated) (g/cm^3)	1.501	1.532
μ (Mo-Ka) (mm^{-1})	1.232	1.232
$F(000)$	1210	1736
crystal size (mm^3)	0.44 × 0.16 × 0.03	0.08 × 0.04 × 0.04
theta range (°)	1.57 to 25.45	1.18 to 25.72
reflections collected	24749	30460
independent reflections	9454 [R(int) = 0.1772]	6884
absorption correction	integration	integration
max. and min. transmission	0.9647 and 0.6910	0.94207 and 0.87607
goodness-of-fit on F^2	0.853	0.815
final R indices [$I > 2\sigma(I)$]	R1 = 0.0624 wR2 = 0.0925	R1 = 0.0442 R2 = 0.0644
R indices (all data)	R1 = 0.2241 wR2 = 0.1245	R1 = 0.1043 wR2 = 0.0743
largest diff. peak/hole (e·Å^{-3})	0.548 and −0.373	0.654 and −0.513

solution of the product in 10 mL of H_2O was treated with a solution of 920 mg (2.37 mmol) of $PBnPh_3Cl$ in 10 mL of H_2O. The resulting red-brown precipitate was collected on a frit, rinsed with 15 mL of H_2O, and dried in vacuo. The product was eluted with THF, reprecipitated three times from THF/hexanes, and triturated under C_6H_{14} to afford dark red-brown powder. Yield: 684 mg (87%). IR (MeCN, cm^{-1}): 1997 (s), 1945 (m). ESI-MS (m/z): 647.8 (M^-), 591.2 ($[M - 2CO]^-$), 535.9 ($[M - 4CO]^-$), 443.9 ($[M - Fe(S_2C_2H_4)(CO)_2]^-$), 388.0 ($[M - Fe(S_2C_2H_4)(CO)_4]^-$), 239.9 ($[M - Fe_2(S_2C_2H_4)_2(CO)_4]^-$). The propanedithiolate analog, synthesized analogously, afforded X-ray diffraction quality crystals from a THF solution layered with hexane and then cooled to −20 °C.

$Fe_3(S_2C_3H_6)_3(CO)_4(PBu_3)_2$. A CO-saturated solution of 1.00 g (7.89 mmol) of $FeCl_2$ in 150 mL of acetone was treated with 2.2 mL (15.8 mmol) of Et_3N, resulting in an immediate change from clear yellow to blue-gray and cloudy. To this suspension was added 0.80 mL (8.0 mmol) of $C_3H_6(SH)_2$. Immediately, the suspension became red-brown, and weak IR bands were observed at 2012 and 1960 cm^{-1}. After the addition of 1.3 mL (5.3 mmol) of PBu_3, the suspended solid redissolved to give a dark red solution. The IR spectrum at this stage revealed bands at 1996, 1941, and 1915 cm^{-1}. After stirring for 10 h under CO, the mixture was filtered from the insoluble material. The solvent was concentrated to about 5 mL, and a byproduct was precipitated by addition of 100 mL of hexane. The supernatant was filtered from the green precipitate and concentrated to about 5 mL. Addition of 100 mL of EtOH precipitated a hexane-soluble green solid. Pure compound was obtained by recrystallization from hexane at −20 °C. Yield: 0.89 g (34%). IR (hexane, cm^{-1}): 2000 (vs), 1946 (s). ^1H NMR for PBu_3 signals (CD_2Cl_2): δ 18.991 (5.50H), 18.250 (5.50H), 11.579 (6.2H), 10.128 (6.2H), 3.4727 (6H), 3.275 (6H), 0.527 (17.73H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 50.06. FD-MS (m/z): 1002 $\{[Fe_3(S_2C_3H_6)_3(CO)_4(PBu_3)_2]^+\}$. Anal. Calcd for $C_{37}H_{72}Fe_3O_4P_2S_6$ (found): C, 44.31 (44.09); H, 7.24 (7.23). Substituting PEt_3 for the above procedure gave the corresponding adduct, which provided X-ray quality crystals. Substituting PPh_3 gave $[Fe_3(S_2C_3H_6)_3(CO)_4(PPh_3)_2]$. IR (MeCN): $\nu_{CO} = 2025$, 1981 cm^{-1}. ESI-MS (m/z): 1122 (M^+).

Crystal Structure Analysis. Crystals were mounted to thin glass fibers using Paratone-N oil (Exxon). Data, collected at 198 K on a Siemens CCD diffractometer, were filtered to remove statistical outliers. The integration software (*SAINT*) was used to test for crystal decay as a bilinear function of X-ray exposure time and $\sin(\theta)$. The data were solved using *SHELXTL* (Table 2) by direct methods for $Fe_3(S_2C_3H_6)_3(CO)_4(PEt_3)_2$ and by Patterson methods for $PBnPh_3[Fe_3(S_2C_3H_6)_4(CO)_4\cdot 3THF$; atomic positions were deduced from an E map or by an unweighted difference Fourier synthesis. Hydrogen atom U's were assigned as 1.2 U_{eq} for adjacent carbon atoms. Non-hydrogen atoms were refined anisotropically. Successful convergence of the full-matrix least-squares refinement of F^2 was indicated by the maximum shift/error for the final cycle.

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Supporting Information Available: Crystallographic data for two compounds (CIF), selected EPR and NMR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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