Ferrous Carbonyl Dithiolates as Precursors to FeFe, FeCo, and FeMn Carbonyl Dithiolates

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ABSTRACT: Reported are complexes of the formula Fe(dithiolate)-(CO)2(diphos) and their use to prepare homo- and heterobimetallic dithiolato derivatives. The starting iron dithiolates were prepared by a one-pot reaction of FeCl2 and CO with chelating diphosphines and dithiolates, where dithiolate = S2(CH2)nS2 (n = 1−8) and diphos = C5H4(SR)2 (dppb), C6H4(SR)2 (dppe), C5H4(PPh2)2 (dpbbz), C6H4[P(C6H11)2]2 (dcpe). The incorporation of 57Fe into such building block complexes commenced with the conversion of 57Fe into 57FeFe(S2(SR)2(CO)6), which then was treated with K2pdt, CO, and dppe to give 57Fe2I4(FiLaPrOH)4, which exists as mixtures of all-cis and trans-CO isomers, edt2− favoring the former and pdt2− the latter. Treatment of Fe(dithiolate)-(CO)2(diphos) with the Fe(0) reagent (benzylideneacetone)Fe(CO)3 gave Fe2(dithiolate)(CO)2(diphos), thereby defining a route from simple ferrous salts to models for hydrogenase active sites. Extending the building block route to heterobimetallic complexes, treatment of Fe(pdt)(CO)2(dppe) with [(acenaphthene)Mn(CO) 3]+ gave [(CO)3Mn(pdt)Fe(CO)2(dppe)]+. Reduction of [(3d(CO)]2 (H)Fe(CO)(dfpe)3d with BH4− gave the C3-symmetric μ-hydride (CO)3Mn(pdt)Fe(CO)2(dppe)3d. Complex H3d is reversibly protonated by strong acids, the proposed site of protonation being sulfur. Treatment of Fe(dithiolate)(CO)2(diphos) with CpCoI2(CO)2 followed by reduction by Cp2Co affords CpCo(dithiolate)Fe(CO)(dfpe)4, which can be prepared from Fe(dithiolate)(CO)2(diphos) and CpCo(CO)2. Like the electronically related (CO)Fe(pdt)(Fe(CO)(diphos)), these complexes undergo protonation to afford the μ-hydrido complexes [CpCo(dithiolate)-HFe(CO)(diphos)]+. Low-temperature NMR studies indicate that Co is the kinetic site of protonation.

INTRODUCTION

Compounds of the type Fe2(SR)2(CO)6−Lx are topical because of their relationship to the active sites of the [FeFe]-hydrogenases (H2ases).1 The quest for a deeper understanding of the enzyme mechanism, as well as interest in base metal H2-processing catalysts,2 has led chemists to prepare many organosulfur ligands.7 Diiron dithiolato carbonyls can also be prepared from more oxidized iron sources, as exemplified by the reductive carbonylation of ferrous halides in the presence of dithiolates (Scheme 1).8 The method, which proceeds in at least modest yields, is suited for generating 57Fe-labeled derivatives, which are of interest for nuclear resonance vibrational spectroscopy (NRVS)9 and Mössbauer measurements.10

Scheme 1. Illustrative Routes to Fe2(SR)2(CO)6−Lx

Fe2(CO)3 + 3 RSH → 2/3 Fe2(SR)3(OH) + 1/2 H2 + 3 CO
2 FeCl2 + 6 CO + 2 NaSR + Zn → Fe2(SR)2(CO)6 + 2 NaCl + ZnCl2
Fe2(SL)2(OH) + 2 RX → Fe2(SR)2(OH) + 2 LiX
Fe2(SH2)2(CO)4 + 2 CH3O + H2X → Fe2(SCH2)2X2(CO)6 + 2 H2O

Promising precursors to diimetal dithiolato complexes are monoiron complexes of the type Fe(0)(dithiolate)(CO)2(PR3)2. These compounds should be obtainable from complexes of the form FeX2(CO)2(PR3)2,12−14 which in turn are accessed by mild carbonylation of ferrous halides in the presence of phosphine ligands. Ferrous bis(thiolato) complexes appear especially amenable to carbonylation15,16 (eq 1). Routes to ferrous dithiolato carbonyls have been established in the case of Fe(11)2(CO)2(PR3)2 (edt2− = ethanedithiolate)17 and related complexes containing bidentate phosphine ligands (Scheme 2).18 The benzenedithiolates Fe(S6C6H3X2)(CO)2(PMe3)2 (X = H, Cl) are formed from diiron dithiolato precursors,19 which undergo cleavage upon treatment with PMe3. With regard to structure, complexes of the type FeX2(CO)2(chel) exist in...
Various isomeric forms, as the all-cis isomer. Complexes of formula FeX2(CO)2(PR3)2, in which all the ligands are monodentate, exhibit two or three bands in the νCO region. The pair of bands at ~2000 and 1960 cm⁻¹ is assigned to the symmetrical isomer, and one band at 1970 cm⁻¹ is assigned to the asymmetrical trans-dicarbonyl isomer. The complex Fe(pdt)(CO)(dppe) (1f) was also prepared. As with the other pdt⁻ complexes, it exists as a mixture of symmetrical and unsymmetrical isomers. Relative to the dppe analogue 1b, the νCO bands for 1f are shifted to lower energy. Unlike complexes 1a–g, Fe(edt)(CO)2(PMe3)₂ is present in solution as a single isomer with mutually trans PMe₃ ligands. The IR spectrum of solid 1d indicates that the trans isomer dominates, which is also the predominant isomer in THF solution.

Diffraction-quality crystals of 1a and 1c were obtained, and the molecular structures were determined by X-ray crystallography (Figures 1 and 2). In both cases, the major solution isomer crystallized.

Starting from ⁵⁷Fe₂I₄(iPrOH)₄, which can be derived from metallic ⁵⁷Fe, the isotopically labeled complex ⁵⁷Fe(pdt)(CO)(dppe) (⁵⁷¹d) was prepared (eqs 3 and 4).

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2⁵⁷Fe + 2I₂ + 4PrOH ⇌ ⁵⁷²FeI₄(PrOH)₄

(3)

⁵⁷²FeI₄(PrOH)₄ + 2dppe + 2K₂pdt + 4CO → ²⁵⁷Fe(pdt)(CO)₂(dppe) + 4KI + 4PrOH

(4)
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Diiron Dithiolato Carbonyl Complexes via Comproportionation. A comproportionation reaction was applied to the synthesis of unsymmetrically disubstituted subferrous diiron dithiolates (eq 5; xdt = edt, pdt; diphos = diphenylphosphino). The reaction occurred over the course of several hours at room temperature, giving 83% isolated yield. The complex Fe₂(pdt)(CO)₄(dppe) (2d) was prepared analogously in about 60% yield. This species can be obtained in modest yields under very specific conditions by substitution of Fe₂(pdt)(CO)₄. The synthesis of unsymmetrically disubstituted subferrous diiron dithiolates (eq 5; xdt = edt, pdt; diphos = diphenylphosphino)
Table 1. Spectroscopic Data for Ferrous Carbonyl Complexes

| complex                          | isomer ratio unsym:sym (20 °C) | νCO (cm⁻¹) (THF) | 31P{1H} NMR (δ) unsym isomer | J(31P-1H) (Hz) | 31P{1H} NMR (δ) sym isomer |
|---------------------------------|---------------------------------|------------------|-------------------------------|----------------|-----------------------------|
| Fe(edt)(CO)₃(dpvv) (1a)         | 2:1                             | 2013 (s), 1978 (s), 1960 (s) | 89.4 (d)                     | 21.1           | 87.7 (s)                    |
| Fe(edt)(CO)₃(dppe) (1b)         | 3:1                             | 2009 (s), 1973 (s), 1959 (s) | 78.3 (d)                     | 29.1           | 77.5 (s)                    |
| Fe(pdt)(CO)₂(dpvv) (1c)         | 1:4                             | 2010 (m), 1975 (s) | 87.3 (d)                     | 22.0           | 81.2 (s)                    |
| Fe(pdt)(CO)₂(dppe) (1d)         | 2:3                             | 2004 (m), 1969 (s), 1958 (sh) | 78.0 (d)                     | 30.9           | 73.7 (s)                    |
| Fe(pdt)(CO)₂(dpbbx) (1e)        | 1:7                             | 2012 (m), 1970 (s) | 78.5 (d)                     | 38.6           | 80.8 (s)                    |
| Fe(pdt)(CO)₂(dcpp) (1f)         | 1:2                             | 1990 (m), 1940 (s) | 79.19 (δ)                    | 32.9           | 81.34 (s)                   |
| Fe(Me₂pdt)(CO)₂(dppe) (1g)      | 1:3                             | 2006 (m), 1969 (s) | 78.3 (d)                     | 30.5           | 73.8 (s)                    |

*IR spectra are reported for THF, wherein signals are better resolved. 31P{1H} NMR spectra were recorded in CD₂Cl₂ solution, but isomer ratios were similar in THF solution.

Figure 1. Structure of the unsymmetrical isomer of Fe(edt)-(CO)₃(dpvv) (1a). Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Key distances (Å) and angles (deg): Fe1–C1, 1.777(3); Fe1–C2, 1.790(3); Fe1–P2, 2.2304(8); Fe1–P1, 2.2648(7); Fe1–Si1, 2.3313(8); Fe1–Si2, 2.3471(7); C1–Fe1–C2, 93.60(12); C1–Fe1–P2, 94.43(8); C2–Fe1–P2, 95.80(9); C1–Fe1–P1, 95.90(8); C2–Fe1–P1, 170.41(9); P1–Fe1–P2, 84.80(3); C1–Fe1–Si1, 85.78(8); C2–Fe1–Si1, 89.16(9); P2–Fe1–Si1, 175.01(3); P1–Fe1–Si1, 90.23(3); C1–Fe1–Si2, 174.68(8); C2–Fe1–Si2, 85.05(9); P2–Fe1–Si2, 90.80(3); P1–Fe1–Si2, 85.32(3); S1–Fe1–Si2, 89.07(3).

Figure 2. Structure of the symmetrical isomer of Fe(pdt)(CO)₂(dpvv) (1e). Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Key distances (Å) and angles (deg): Fe1–C1, 1.808(2); Fe1–C2, 1.799(2); Fe1–P2, 2.2204(1); Fe1–P1, 2.214(1); Fe1–Si1, 2.3441(6); Fe1–Si2, 2.3462(6); C1–Fe1–C2, 169.3(1); C1–Fe1–P2, 91.07(7); C2–Fe1–P2, 95.25(7); C1–Fe1–P1, 93.85(7); C2–Fe1–P1, 91.80(7); P2–Fe1–P1, 86.76(2); C1–Fe1–Si1, 87.82(7); C2–Fe1–Si1, 82.97(7); P2–Fe1–Si1, 177.54(2); P1–Fe1–Si1, 91.58(2); C1–Fe1–Si2, 83.20(7); C2–Fe1–Si2, 91.74(6); P2–Fe1–Si2, 89.50(2); P1–Fe1–Si2, 175.07(2); S1–Fe1–Si2, 92.25(2).

The reaction of the dppe complex 1f with (bda)Fe(CO)₃ afforded Fe₂(pdt)(CO)₄(dppe) (2f) in 81% yield. As with the analogous dppe complex 2d, 2f exists in solution as a 3:1 mixture of apical–basal and dibasal isomers. The reaction of Fe₂(pdt)(CO)₄ and dppe gives only a low yield of 2f, highlighting the advantage of the building block method. When, however, Fe(pdt)(CO)₂(PMe₃)₂ was treated with (bda)Fe(CO)₃, the product is the known complex Fe(pdt)-(CO)₄(PMe₃)₂ where the phosphine ligands are bound to different iron centers.

Synthesis of MnFe⁺² Complexes. The salt [(acenaphthene)Mn(CO)₃]BF₄ with the ethanedithiolate 1b afforded a mixture of isomers even after extended time for equilibration. The result is not surprising, since edt²⁻ vs pdt²⁻ affects the isomer ratio in 1b and 1d. The complexes [(CO)₃Mn(pdt)Fe(CO)₄(dpbbx)]BF₄, [(CO)₃Mn(pdt)Fe(CO)₄(dppe)]BF₄, and [(CO)₃Mn(Me₂pdt)Fe(CO)₄(dppe)]-

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BF$_4$ form in a manner analogous to that for [3(CO)]BF$_4$, and their spectroscopic data were similar.

**Synthesis of MnFe$^{II}$ Hydride.** Reaction of [3d(CO)]BF$_4$ with [Bu$_4$N]BH$_4$ results in loss of one CO ligand and formation of the neutral hydride complex (CO)$_3$Mn(pdt)(μ-H)Fe(CO)-(dppe) (H3d) (eq 6). The $^1$H NMR spectrum of H3d consists of a triplet at δ −12.3, indicating coupling to two equivalent phosphorus centers. The $^{31}$P{$^1$H} NMR spectrum exhibits a singlet at δ 80.8, which confirms that the two phosphorus centers are equivalent, both occupying basal positions.

The structure of H3d was confirmed by X-ray crystallography, and the details are consistent with the NMR data (Figure 5). The phosphorus centers on the dppe ligand both occupy basal positions. The bridging hydrido ligand, whose location was identified on the difference map, refined to a position slightly closer to Fe (1.62(2) Å) than to MnH (1.75(2) Å). The $d^6$$d^6$ 36e-complex (H3d is 34e-) FeMn(μ-SPh)$_4$(CO)$_4$ has been described.$^{32}$ The cyclic voltammogram of H3d consists of a reversible oxidation event at 0.125 V vs Fe$^{+/0}$, characterized by the linear dependence of $i_P$ on (scan rate)$^{1/2}$ (Supporting Information).

The acid–base behavior of H3d was investigated. Upon treatment of H3d with [H(Et$_2$O)$_2$]BAr$_4$ the ν$_{CO}$ bands shifted by 20−50 cm$^{-1}$ to higher energy. Protonation of H3d was anticipated to give H$_2$ or a dihydrogen complex (see [(H$_2$)Mn(CO)$_3$(dppe)]$^+$).$^{33}$ Treatment of the acidified reaction mixture with Et$_3$N gave back H3d (Figure 6). The reversible protonation of H3 is proposed to occur at sulfur. Similar S-protonations have been proposed for related charge-neutral diiron dithiolate complexes.$^{34}$ In contrast to the behavior of H3d, the closely related complex [(μ-H)Fe$_2$(pdt)-(CO)$_4$(dppe)]$^+$ is unreactive toward [H(Et$_2$O)$_2$]BAr$_4$, illustrating the effect of charge on the basicity of the thiolate S centers.

$^{31}$P{$^1$H} and $^1$H NMR (hydride region) resonances for H3d were broadened upon protonation of this complex (Supporting Information). In the presence of 2 equiv of acid, a pair of doublets appears at 79.6 and 78.5 in the $^{31}$P{$^1$H} NMR spectrum, assigned to the nonequivalent phosphorus centers in [H$_3$dH]$^+$. In view of the electrochemical and chemical reduction results, the initial reduction is proposed to induce decarbonylation, generating (CO)$_3$Mn(pdt)Fe(CO)-(dppe) ([3d(CO)]$^0$). Analytically pure [3d(CO)]$^0$ was obtained once it was determined that its stability was greater in THF than in CH$_2$Cl$_2$ solution. Cyclic voltammetry of this salt exhibits the quasi-reversible couple at −1.3 V.

**Scheme 4. Routes to Fe$_2$(pdt)(CO)$_4$(dppe) and Related Complexes**
Cobalt–Iron Dithiolates. Treatment of the ferrous dithiolato carbonyls with CpCo(CO)₂ in refluxing toluene or THF gave complexes of the type CpCo(pdt)Fe(CO)(dppx) (4a, d). The yields for these preparations were inconsistent, however, varying from 50% to almost nothing. A related but more reliable route to the same compounds involved the reactions of the ferrous dithiolates with CpCoI₂(CO) followed by reduction. For example, 1d and CpCoI₂(CO) react rapidly to give an isomeric mixture of the intermediate [CpCoI(pdt)Fe(CO)(dppe)]⁺ (νₐ CO 1952 cm⁻¹). When this reaction is monitored by ³¹P{¹H} NMR spectroscopy, two isomeric Co–Fe complexes are observed. Akin to the MnFe systems, the ³¹P{¹H} NMR spectrum showed that one isomer is unsymmetrical (doublets at δ 47 and 90) and the second isomer is characterized by a singlet at δ 59. In these isomers the phosphine ligands occupy apical−basal and dibasal sites, respectively. Reduction of [CpCoI(pdt)Fe(CO)(dppe)]⁺ with 2 equiv of Cp₂Co gave 4d in good yield (eqs 7 and 8).

Figure 4. ³¹P{¹H} NMR spectra of a CD₂Cl₂ solution of (a) Fe(pdt)(CO)₂(dppe) (triangle, unsym isomer; circle, sym isomer), (b) the same solution 30 min after addition of [(acenaphthene)Mn(CO)₂]BF₄ (diamond, unsym isomer; star, sym isomer), and (c) the same solution after 12 h.

Figure 5. Structure of (CO)₃Mn(pdt)(μ-H)Fe(CO)(dppe) (H₃d) with thermal ellipsoids drawn at the 50% probability level. Selected distances (Å): Fe₁–Mn₁, 2.6433(4); Fe₁–C₂₇, 1.753(2); Fe₁–P₁, 2.2139(5); Fe₁–P₂, 2.2086(5); Fe₁–S₁, 2.2759(5); Fe₁–S₂, 2.2648(5); Fe₁–H₁, 1.62(2); Mn₁–C₃₁, 1.813(2); Mn₁–C₃₃, 1.799(2); Mn₁–S₁, 2.3361(6); Mn₁–S₂, 2.3042(5); Mn₁–H₁, 1.75(2).

Figure 6. IR spectra in CH₂Cl₂ of (a) (CO)₃Mn(pdt)(μ-H)Fe(CO)(dppe) and this solution (b) after addition of 1 equiv of H(Et₂O)₂BArF₄, (c) after addition of 0.5 equiv of Et₃N, and (d) after addition of 1 equiv total of Et₃N.

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Scheme 5. Synthesis of [(CO)₃Mn(pdt)Fe(CO)₂(dppe)]BF₄ from Isomers of 1d

\[
\text{Fe(pdt)(CO)₂} + \text{CpCoI(CO)} \rightarrow \text{[CpCoI(pdt)Fe(CO)(dppe)]I} + 2\text{CO} \\
\text{[CpCoI(pdt)Fe(CO)(dppe)]I} + 2\text{Cp}_2\text{Co} \\
\rightarrow \text{CpCo(dpdt)Fe(CO)(dppe)} + 2\text{Cp}_2\text{CoI}
\]
Like the corresponding diiron complexes, 4d oxidizes reversibly, at a potential (−0.6 V vs Fe⁷⁰⁰) between those for Fe₂(pdt)(CO)₄(dppe)₂ (−0.19 V) and Fe₂(pdt)(CO)₄(dppe) (−0.94 V). Crystallographic and spectroscopic characterization of the ethanedithiolate 4a proved mutually consistent (Figure 7). The complex can be described as a pair of five-coordinate metal centers linked by a Co−Fe bond (2.5038(5) Å). A distinctive feature of the structure is the acute angle for the FeP₂ plane relative to the FeS₂ plane.

The $^{31}$P{¹H} NMR spectrum of 4d established the presence of only one isomer, even at low temperatures. Below −60 °C, the spectrum consists of a pair of singlets with ∼4:1 intensities, attributed to conformational isomers arising from the pdt⁻ backbone. Using an internal integration standard, >90% of the sample was verified to be in solution at −90 °C.

Co⁸FeⅤ Hydrides. At room temperature, the Co−Fe complexes protonate to give the corresponding μ-hydrido derivatives. Protonation shifts the νCO band from 1890 to 1975 cm⁻¹. The $^{31}$P{¹H} and ¹H NMR spectra indicate that the hydride complex is Cs-symmetric. On the basis of its chemical shift and J($^{31}$P,¹H) value of 25 Hz, the hydride ligand is bridging the Fe and Co centers.

NMR studies on the protonation at low temperatures revealed at least two intermediates. The initial product of protonation, formed quantitatively at −85 °C, is characterized by singlets at δ = −9.0 and δ = 70.7 in the ¹H and $^{31}$P{¹H} NMR spectra, respectively (Figures 8 and 9). These signals are assigned to a terminal hydride complex with the hydride ligand on the CpCo center (Scheme 6). When the temperature is raised to −50 °C, this terminal hydride converts to approximately equal amounts of two species characterized by a doublet at δ = −14.7 (J = 30 Hz) and triplet at δ = −15.5 (J = 25 Hz). These species correspond to the bridging hydrides with apical−basal and dibasal phosphines. Bridging hydrides typically exhibit a ∼25 Hz coupling to the cis phosphine, whereas coupling to the trans phosphine is often weak or is not observed. At room temperature, the unsymmetrical isomer, labeled a,b for apical−basal, converts to the dibasal isomer. Comparable isomerizations have been observed for diiron complexes.

DISCUSSION

Ferrous dicarbonyl dithiolato diphosphine complexes are versatile precursors to dimetallic complexes, as illustrated by their conversion to FeFe₂, MnFe, and CoFe dithiolate complexes described above. The new synthesis of Fe₂(pdt)⁻(CO)₄(dppe) avoids side reactions that hamper the installation of flexible chelating ligands. Related complexes can be prepared via Fe₄(CO)₁₄. The new routes are potentially appealing because the iron complexes are derived from FeCl₂. Conveniently available sources of Fe₁⁻ are easily converted to the dichloride and Fe₂I₄(iPrOH). Although the preparations reported herein proceed in modest yields, the precursors are readily available and the product workup is relatively simple. The methods lend themselves to the incorporation of Fe₁⁻ into ferrous carbonyl building blocks, as illustrated by the synthesis of Fe₂(pdt)(CO)₄(dppe). Interest in Fe₁⁻ labeling

Figure 7. Structure of CpCo(edt)Fe(CO)(dpv) (4a) with thermal ellipsoids drawn at the 50% probability level. Selected distances (Å): Fe1−Co1, 2.5038(5); Fe1−C1, 1.754(3); Fe1−P1, 2.2318(5); Fe1−S4, 2.1748(6); Co1−S1, 1.6727(3).

Figure 8. $^{31}$P{¹H} NMR spectra of a CD₂Cl₂ solution of 4d and 1 equiv of [H(OEt₂)₂]BArF. The solution was prepared at −85 °C and then warmed to the indicated temperatures.

Figure 9. ¹H NMR spectra of a CD₂Cl₂ solution of 4d and 1 equiv of [H(OEt₂)₂]BArF. The solution was prepared at −85 °C and then warmed to the indicated temperatures.

Scheme 6. Protonation of 4d and Isomerization of Resulting Hydride Complexes

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stems from the wealth of information available from, among other techniques, Mössbauer and NRVs spectroscopy.

This building block approach allowed the synthesis of the first dithiolato-bridged MnFe complexes. Related dimanganese dithiolate complexes had been reported by Treichel. The most curious property of [(CO)₃Mn(pdt)(Fe(CO)₂(dppe))]⁺ is its tendency to decarbonylate upon 1e-reduction. The resulting complex, (CO)(dppe), which was characterized crystallographically, is isoelectronic with [HFe(dpdt)(CO)₄(dppe)]⁺. Similarly, the hydride (CO)₃Mn(dpdt)HFe(CO)(dppe), which was characterized crystallographically, is isoelectronic with [HFe(dpdt)(CO)₄(dppe)]⁺. The MnFe complex is sufficiently electron rich that it undergoes a mild one-electron oxidation (~0.1 V vs Fe+/0), whereas oxidations of analogous dif erent hydrides occur only at very positive potentials.

This building block approach also allowed the synthesis of dithiolato-bridged iron—cobalt complexes. Two complementary routes to these CoFe complexes were devised: a direct Co(I) + Fe(II) pathway and an less direct but more reliable route via Co(III) + Fe(II), followed by 2e-reduction. The latter method is modeled after the route to (CO)₃Fe(dpdt)Ni(dppe) from Fe(CO)(dppe) + Ni(dpdt) following by reduction. The complexes CpCo(dithiolate)Fe(CO)(dppe) are electronically related to Fe₃(pdt)(CO)₄(dppe), both being of d⁹ configuration. Like FeFe dithiolates, the CoFe species undergo protonation and redox reactions.

**EXPERIMENTAL SECTION**

Methods used in this work have been recently described. Chromatography was performed using silica gel (40–63 µm, 230–400 mesh) as the stationary phase. K pdt. and [acenaphthene]Mn(CO)₅BF₄ were prepared according to the literature methods. ESI-MS data were recorded on a Waters Micromass Quadrupole II spectrometer. ATR data were collected on a PerkinElmer Spectrum 100 FT-IR instrument. NMR spectra were recorded at 500 MHz and ³¹P[¹H] NMR spectra at 202 MHz. Coupling constants are reported in Hz. IR measurements, reported in cm⁻¹, were recorded only in the ν(CO) region.

**Illustrative Preparation:** Fe(dpdt)(CO)₂(dppe) (1d). Under a CO atmosphere, a solution of 1.9 g of FeCl₂ (15.0 mmol) in 250 mL of acetone was treated with a solution of 5.98 g (15.0 mmol) of dppe in 6 mL of 1/1 iPrOH/THF. After it was stirred for 24 h in the absence of light, the mixture was filtered through Celite, and the solvent was evaporated from the filtrate. The residue was extracted into 50 mL of CH₂Cl₂. The product was recrystallized by addition of hexanes to a concentrated CH₂Cl₂ solution. Yield: 400 mg (20%). ¹H NMR (CD₂Cl₂): δ 7.4–7.6 (m, 24H, C₆H₁₆), 1.94 (s, 2H, CH₂(C₆H₁₂)). IR (CH₂Cl₂): 2012, 1970. Anal. Calcd for C₅₃H₄₆FeO₂P₂S₂: C, 56.94 (56.50); H, 4.40 (4.40).

Fe(dpdt)(CO)₃(dppe) (1f). Under a CO atmosphere, a solution of 0.50 g of FeCl₃ (3.94 mmol) in 100 mL of acetone was treated with a solution of 1.76 g (15.0 mmol) of dppe in 40 mL of THF. The solution changed from pale orange to dark orange, indicating formation of Fe₃Cl₃(CO)₄(dppe). Separately, 1.71 mL (17.0 mmol) of C₃H₆(SH)₂ and 0.72 g (30.0 mmol) of K₂pdt in 3 mL of iPrOH. After it was stirred for 24 h in the absence of light, the mixture was allowed to stand fi ltered through Celite, and the solvent was evaporated from the filtrate. The title compound as a pink powder (23.6 mg, 38.2%). ¹H NMR (CD₂Cl₂): δ 7.3 (m, 20H, C₆H₁₂), 2.18 and 0.21 (t each, 1:1 H, C₆H₁₂), 2.53 (s, 2H, C₆H₁₂), 0.34 (s, 1H, SH₂, sym). IR (THF): 2009 (s), 1973 (w), 1959 (s). Anal. Calcd for C₃₁H₂₈FeO₅P₂S₂: C, 60.28 (60.0); H, 5.24 (5.4).
product was chromatographed on silica gel in air, with toluene as eluent. The first brown-red band was collected and dried in vacuo. Yield: 123 mg (83%). The IR, 1H NMR, and 31P{1H} NMR spectra of the product match reported data.

Fe(pdtd)(CO)3(dppe) (2d) from 1d. An orange mixture of 1d (250 mg, 0.40 mmol) and (bda)Fe(CO)3 (115 mg, 0.40 mmol) in 70 mL of toluene gradually darkened over the course of several hours to a deep red solution. The reaction was monitored by IR spectroscopy. After 24 h, the reaction solution was concentrated, and the crude product was chromatographed on silica gel in air, with toluene as eluent. The first brown-red band was collected. Yield: 150 mg (60%). The IR, 1H NMR, and 31P{1H} NMR spectra of the product match reported data.

Fe(pdtd)(CO)3(dppe) (2f) from 1f. A 5 mL solution of (bda)Fe(CO)3 (48 mg, 0.17 mmol) and (bda)Fe(CO)3 (48 mg, 0.17 mmol) in 50 mL of CH2Cl2 was treated with a solution of 810 mg (1.32 mmol) of Fe2(pdt)(CO)4(dcpe) (2f) from 1f.

Yield: 123 mg (83%). The IR, 1H NMR, and 31P{1H} NMR spectra of the product match reported data.

Fe(pdtd)(CO)3(dppe) (2e) from 1e. 1H NMR (CD2Cl2; δ 89.27 (s), apical–basal; 74.90 (s), dibasal. IR (CH2Cl2): 1905 (br). Anal. Calcd for C34H30BF4FeMnO5P2S2 (found): C, 48.48 (48.66); H, 3.59 (3.61). IR band shifted to 1879 cm−1 upon standing overnight. 31P{1H} NMR (CD2Cl2, δ 93.56 (s). IR (CH2Cl2): 1890.

CpCo(pdtd)(Fe(CO)3(dppe)) (3f) from CpCo(CO)3. A mixture of 1a (200 mg, 0.34 mmol) and CpCo(CO)3 (92 μL, 0.68 mmol) was stirred in toluene (100 mL) at reflux for 2.0 h to give a dark brown solution containing a small amount of red-brown solid. The IR spectrum at this stage revealed a new band at 1896 cm−1. The solution was filtered, and the brown filtrate was evaporated. The brown residue was washed with ~10 mL each of hexanes and EtO. The brown residue was extracted into ~4 mL of CH2Cl2, and the extract was layered with 10 mL of hexane. Dark brown crystals of 3a formed overnight. Yields were variable. Anal. Calc. for C28H19CoFe5O6P2S2 (found): C, 54.41 (54.50); H, 4.49 (4.55). IR (CH2Cl2): 1885.

CpCo(pdtd)(Fe(CO)3(dppe)) (4d) from CpCo(CO)3. A solution of Fe(pdtd)(CO)3(dppe) (50 mg, 0.08 mmol) and CpCo(CO)3 (31 mg, 0.08 mmol) in CH2Cl2 (20 mL) was stirred overnight. Formation of a new product was detected by an IR band at 1952 cm−1. The reaction solution was treated with a solution of CpCo (38 mg, 0.20 mmol) in CH2Cl2 (5 mL). After the solution was stirred for 5 min, the dominant IR band shifted to 1879 cm−1. The solution was filtered through Celite, and the product was purified by column chromatography on silica gel, initially with 1/1 CH2Cl2/pentane as eluent, which produced a green band. Evuting with CH2Cl2 gave the product as a brown solid, which was evaporated to leave a brown solid. Yield: 23 mg (40%). 1H NMR (CD2Cl2, δ 7.82–7.29 (m, 20 H, C6H5), 3.84 (s, 5 H, C5H4), 1.51 (m, 2 H, C6H5), 2.98 (m, 2 H, PCH3), 2.58 and 2.26 (m each, 2 H, CH2), 1.87 and 1.89 (m each, 1 H each, PCH3), 1.47 (m, 2 H, S(CH2)4CH2). 31P{1H} NMR (CD2Cl2, δ 83.48 (s). IR (CH2Cl2): 1880.

CpCo(pdtd)(Fe(CO)3(dppe)) (4d) from CpCo(CO)3. A mixture of 1d (200 mg, 0.32 mmol) and CpCo(CO)3 (67 μL, 0.65 mmol) was stirred in toluene (100 mL) at reflux temperature for 7 h to give a dark brown solution. The IR spectrum at this stage revealed a new band at 1883 cm−1. The solution was filtered, and the brown filtrate was evaporated. The brown residue was washed with ~15 mL of hexane and then extracted into ~5 mL of CH2Cl2. This extract was layered with 10 mL of hexane to yield dark brown crystals of 4d upon standing overnight. 1H NMR (CD2Cl2; δ 8.17–7.30 (m, 20 H, C6H5), 3.51 (s, 5 H, C5H4), 2.30 and 2.20 (m each, 2 H, CH2), 1.87 (m, 2 H, S(CH2)4CH2). 31P{1H} NMR (CD2Cl2, δ 90.17 (s). IR (CH2Cl2): 1885.

CpCo(pdtd)(Fe(CO)3(dppe)) (4d) from CpCo(CO)3. A mixture of 1d (200 mg, 0.32 mmol) and CpCo(CO)3 (67 μL, 0.65 mmol) was stirred in toluene (100 mL) at reflux temperature for 2.0 h to give a dark brown solution containing a small amount of red-brown solid. The IR spectrum at this stage revealed a new band at 1892 cm−1. The solution was filtered, and the brown filtrate was evaporated. The brown residue was washed with ~10 mL of hexanes and then extracted into ~5 mL of CH2Cl2. This extract was layered with 10 mL of hexane to yield dark brown crystals of 4f upon standing overnight. 1H NMR (CD2Cl2; δ 8.17–7.30 (m, 20 H, C6H5), 3.51 (s, 5 H, C5H4), 2.30 and 2.20 (m each, 2 H, CH2), 1.87 (m, 2 H, S(CH2)4CH2). 31P{1H} NMR (CD2Cl2, δ 90.17 (s). IR (CH2Cl2): 1885.

CpCo(pdtd)(Fe(CO)3(dppe)) (4d) from CpCo(CO)3. A mixture of 1d (200 mg, 0.32 mmol) and CpCo(CO)3 (67 μL, 0.65 mmol) was stirred in toluene (100 mL) at reflux temperature for 7 h to give a dark brown solution. The IR spectrum at this stage revealed a new band at 1883 cm−1. The solution was filtered, and the brown filtrate was evaporated. The brown residue was washed with ~10 mL of hexanes and then extracted into ~5 mL of CH2Cl2. This extract was layered with 10 mL of hexane to yield dark brown crystals of 4f upon standing overnight. Yields were variable. 1H NMR (CD2Cl2, δ 7.82–7.29 (m, 20 H, C6H5), 3.84 (s, 5 H, C5H4), 1.51 (m, 2 H, C6H5), 2.98 (m, 2 H, PCH3), 2.58 and 2.26 (m each, 2 H, CH2), 1.87 and 1.89 (m each, 1 H each, PCH3), 1.47 (m, 2 H, S(CH2)4CH2). 31P{1H} NMR (CD2Cl2, δ 85.54 (s). Anal. Calc. for Cp2H6CoFeMoOP3S2 (found): C, 59.00 (58.89); H, 4.85 (4.83). IR (CH2Cl2, cm−1): ν(CO) 1879. Data for the low-temperature intermediate, terminal hydride are as follows. 1H NMR (CD2Cl2, δ 7.73–7.35 (m, 20 H, C6H5), 3.61 (s, 5 H, C5H4), 2.98 (m, 2 H, PCH3), 2.56 and 2.25 (m each, 2 H each, SCH2), 1.87 and 1.89 (m each, 1 H each, PCH3), 1.51 (m, 2 H, S(CH2)4CH2).
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