

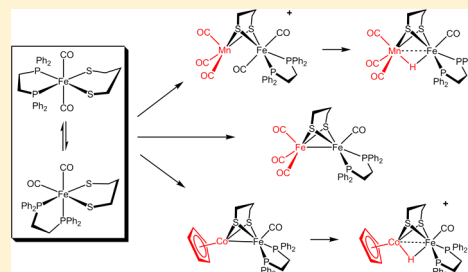
Ferrous Carbonyl Dithiolates as Precursors to FeFe, FeCo, and FeMn Carbonyl Dithiolates

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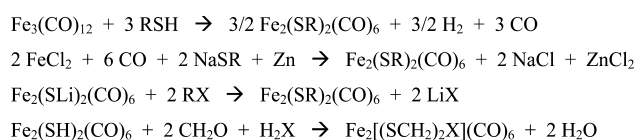
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Supporting Information

ABSTRACT: Reported are complexes of the formula $\text{Fe}(\text{dithiolate})(\text{CO})_2(\text{diphos})$ and their use to prepare homo- and heterobimetallic dithiolato derivatives. The starting iron dithiolates were prepared by a one-pot reaction of FeCl_2 and CO with chelating diphosphines and dithiolates, where dithiolate = $\text{S}_2(\text{CH}_2)_2^{2-}$ (edt^{2-}), $\text{S}_2(\text{CH}_2)_3^{2-}$ (pdt^{2-}), $\text{S}_2(\text{CH}_2)_2(\text{C}(\text{CH}_3)_2)^{2-}$ ($\text{Me}_2\text{pdt}^{2-}$) and diphos = *cis*- $\text{C}_2\text{H}_2(\text{PPh}_2)_2$ (dppv), $\text{C}_2\text{H}_4(\text{PPh}_2)_2$ (dppe), $\text{C}_6\text{H}_4(\text{PPh}_2)_2$ (dppbz), $\text{C}_2\text{H}_4[\text{P}(\text{C}_6\text{H}_{11})_2]_2$ (dcpe). The incorporation of ^{57}Fe into such building block complexes commenced with the conversion of ^{57}Fe into $^{57}\text{Fe}_2\text{I}_4(\text{PrOH})_4$, which then was treated with K_2pdt , CO, and dppe to give $^{57}\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppe})$. NMR and IR analyses show that these complexes exist as mixtures of all-*cis* and *trans*-CO isomers, edt^{2-} favoring the former and pdt^{2-} the latter. Treatment of $\text{Fe}(\text{dithiolate})(\text{CO})_2(\text{diphos})$ with the $\text{Fe}(0)$ reagent (benzylideneacetone) $\text{Fe}(\text{CO})_3$ gave $\text{Fe}_2(\text{dithiolate})(\text{CO})_4(\text{diphos})$, thereby defining a route from simple ferrous salts to models for hydrogenase active sites. Extending the building block route to heterobimetallic complexes, treatment of $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppe})$ with $[(\text{acenaphthene})\text{Mn}(\text{CO})_3]^+$ gave $[(\text{CO})_3\text{Mn}(\text{pdt})\text{Fe}(\text{CO})_2(\text{dppe})]^+$ ($[\mathbf{3d}(\text{CO})]^+$). Reduction of $[\mathbf{3d}(\text{CO})]^+$ with BH_4^- gave the C_s -symmetric μ -hydride $(\text{CO})_3\text{Mn}(\text{pdt})(\text{H})\text{Fe}(\text{CO})_2(\text{dppe})$ (H3d). Complex H3d is reversibly protonated by strong acids, the proposed site of protonation being sulfur. Treatment of $\text{Fe}(\text{dithiolate})(\text{CO})_2(\text{diphos})$ with $\text{CpCoI}_2(\text{CO})$ followed by reduction by Cp_2Co affords $\text{CpCo}(\text{dithiolate})\text{Fe}(\text{CO})_2(\text{diphos})$ ($\mathbf{4}$), which can also be prepared from $\text{Fe}(\text{dithiolate})(\text{CO})_2(\text{diphos})$ and $\text{CpCo}(\text{CO})_2$. Like the electronically related $(\text{CO})_3\text{Fe}(\text{pdt})\text{Fe}(\text{CO})_2(\text{diphos})$, these complexes undergo protonation to afford the μ -hydrido complexes $[\text{CpCo}(\text{dithiolate})\text{HFe}(\text{CO})_2(\text{diphos})]^+$. Low-temperature NMR studies indicate that Co is the kinetic site of protonation.



Scheme 1. Illustrative Routes to $\text{Fe}_2(\text{SR})_2(\text{CO})_6$ ^{4,8,11}



INTRODUCTION

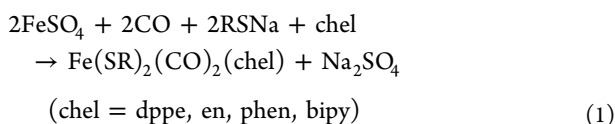
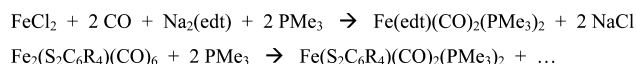
Compounds of the type $\text{Fe}_2(\text{SR})_2(\text{CO})_{6-x}\text{L}_x$ are topical because of their relationship to the active sites of the $[\text{FeFe}]$ -hydrogenases (H_2 ases).¹ The quest for a deeper understanding of the enzyme mechanism, as well as interest in base metal H_2 -processing catalysts,² has led chemists to prepare many examples of these dithiolates.³ Since the $[\text{NiFe}]\text{-H}_2$ ases feature related $\text{Ni}(\text{SR})_2\text{Fe}(\text{CO})\text{L}_2$ centers, a new methodology addresses both families of enzymes. This paper describes a new route to models of these two families of enzyme active sites.

Traditionally, compounds of the type $\text{Fe}_2(\text{SR})_2(\text{CO})_{6-x}\text{L}_x$ are prepared by ligand (L) substitution of hexacarbonyls $\text{Fe}_2(\text{SR})_2(\text{CO})_6$,⁴ which in turn are obtained by treating $\text{Fe}_3(\text{CO})_{12}$ with thiols. Complementarily, $\text{Fe}_2(\text{S}_2)(\text{CO})_6$ ⁵ is an ideal precursor to diiron complexes⁶ of more elaborate 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 ^{57}Fe -labeled derivatives, which are of interest for nuclear resonance vibrational spectroscopy (NRVS)⁹ and Mössbauer measurements.¹⁰

Promising precursors to *dimetallic* dithiolato complexes are *monoiron* complexes of the type $\text{Fe}(\text{dithiolate})(\text{CO})_2(\text{PR}_3)_2$. These compounds should be obtainable from complexes of the form $\text{FeX}_2(\text{CO})_2(\text{PR}_3)_2$,^{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 carbonylation^{15,16} (eq 1). Routes to ferrous dithiolato carbonyls have been established in the case of $\text{Fe}(\text{edt})(\text{CO})_2(\text{PMe}_3)_2$ (edt^{2-} = ethanedithiolate)¹⁷ and related complexes containing bidentate phosphine ligands (Scheme 2).¹⁸ The benzenedithiolates $\text{Fe}(\text{S}_2\text{C}_6\text{H}_4\text{X}_2)(\text{CO})_2(\text{PMe}_3)_2$ (X = H, Cl) are formed from diiron dithiolato precursors,¹⁹ which undergo cleavage upon treatment with PMe_3 . With regard to structure, complexes of the type $\text{FeX}_2(\text{CO})_2(\text{chel})$ exist in

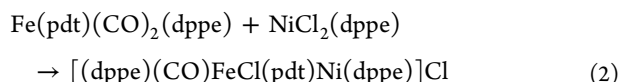
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Scheme 2. Synthetic Routes to Fe(dithiolate)(CO)₂L₂


various isomeric forms.^{13,20} Fe(SPh)₂(CO)₂(dppe) crystallizes as the all-cis isomer.¹⁵ Complexes of formula FeX₂(CO)₂(PR₃)₂, in which all the ligands are monodentate, exist as both the cis,cis,trans and all-trans isomers, depending on the phosphine ligand.²¹

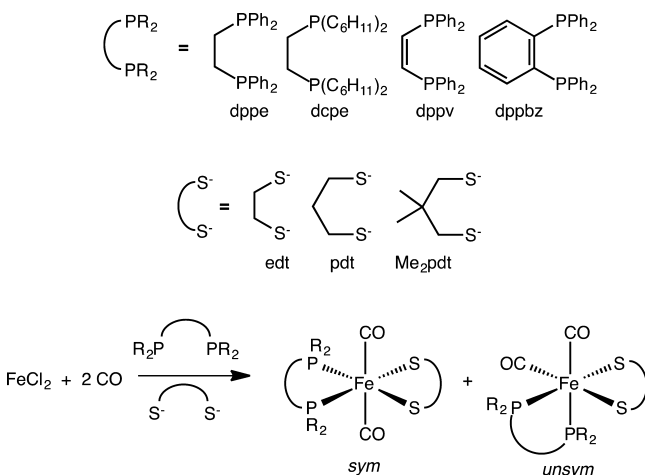
Ferrous carbonyl thiolates have been examined as metal-ligands, analogous to the use of metal dithiolates to prepare diverse dithiolato-bridged dimetallic complexes.²² Thiolates retain significant basicity even when bound to a metal, as evidenced by the formation of adducts of Fe-(SPh)₂(CO)₂(dppe) with HgCl₂.¹⁵ Similarly, the bis(chelate) complex Fe(pdt)(CO)₂(dppe) is a useful precursor to bimetallic species, including Ni–Fe dithiolates (eq 2).²³



Presented here is a general route to monoiron precursors. Reactions of these monoiron precursors with iron, manganese, and cobalt carbonyl complexes afford the respective FeFe, MnFe, and CoFe complexes. In the course of this work, one of the authors (J.C.) published some of these results without the knowledge of the other authors.²⁴ The new compounds and new synthetic routes demonstrate the broad scope for first-row analogues of the active sites of the [FeFe]- and [NiFe]-H₂ases.

RESULTS

Ferrous Dithiolato Carbonyls. New diphosphine-substituted ferrous carbonyl dithiolates were prepared by carbonylation of a slurry of anhydrous FeCl₂ and the diphosphine ligand, followed by the addition of the sodium dithiolate (Scheme 3). The reaction affords a mixture of the two isomers

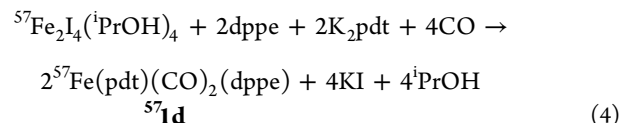
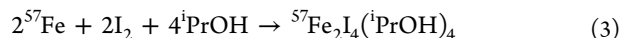
Scheme 3. Main Route to Fe(dithiolate)(CO)₂(diphosphine)


possible for an octahedral complex of type M(chel)(chel')L₂. The complex FeCl₂(CO)₂(dppe)¹³ was observed spectroscopically as an intermediate in the preparation of **1d**. Although yields ranged from 10 to 50%, the necessary reagents are readily available. A complementary route to **1d** involving the reaction of Fe(CO)₃(dppe) and pdtH₂ did not proceed.

Spectroscopic measurements on the new compounds indicate the presence of two isomers, with the ³¹P{¹H} NMR spectra exhibiting three signals: a singlet corresponding to the symmetrical isomer and a pair of doublets corresponding to the unsymmetrical isomer (Table 1). For 1,2-ethanedithiolate (edt²⁻) complexes **1a,b**, the unsymmetrical isomer is the major species, whereas the symmetrical isomers predominate for complexes of 1,3-propanedithiolate (pdt²⁻) and 2-dimethyl-1,3-propanedithiolate (Me₂pdt²⁻), **1c–f**. (Table 1, Scheme 3). The IR spectra of the edt²⁻ complexes **1a,b** exhibit two or three bands in the ν_{CO} region. The pair of bands at ~2000 and 1960 cm⁻¹ is assigned to the unsymmetrical isomer, and one band at 1970 cm⁻¹ is assigned to the symmetrical *trans*-dicarbonyl isomer. The complex Fe(pdt)(CO)₂(dcpe) (**1f**) was also prepared. As with the other pdt²⁻ complexes, it exists as a mixture of symmetrical and unsymmetrical isomers. Relative to the dppe analogue **1b**, the ν_{CO} bands for **1f** are shifted by 20 cm⁻¹ 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.¹⁷ The IR spectrum of solid **1d** indicates that the *trans* isomer dominates, which is also the predominant isomer in THF solution.

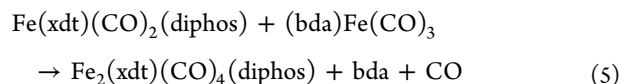
Diffraction-quality crystals of **1a** and **1c** were obtained, and the molecular structures were determined by X-ray crystallography (Figures 1 and 2). In both cases, the major solution isomer crystallized.

Starting from ⁵⁷Fe₂I₄(ⁱPrOH)₄, which can be derived from metallic ⁵⁷Fe, the isotopically labeled complex ⁵⁷Fe(pdt)-(CO)₂(dppe) (**571d**) was prepared (eqs 3 and 4). Character-



ization of *cis/trans*-**571d** included the observation of ⁵⁷Fe–³¹P coupling in the ³¹P{¹H} NMR spectrum (¹J_{PF} = 35 and 38 Hz for *cis* and *trans* isomers, respectively, Figure 3).²⁵

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 = diphosphine; bda =



benzylideneacetone). Thus, the reaction **1a** + (bda)Fe(CO)₃ gave the known complex Fe₂(edt)(CO)₄(dppv) (**2a**).²⁶ 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)₆.^{27,28} The

Table 1. Spectroscopic Data for Ferrous Carbonyl Complexes^a

complex	isomer ratio unsym:sym (20 °C)	ν_{CO} (cm ⁻¹) (THF)	³¹ P{ ¹ H} NMR (δ) unsym isomer	$J_{\text{P-P}}$ (Hz)	³¹ P{ ¹ H} NMR (δ) sym isomer
Fe(edt)(CO) ₂ (dppv) (1a)	2:1	2013 (s), 1978 (s), 1960 (s)	89.4 (d) 59.9 (d)	21.1 21.1	87.7 (s)
Fe(edt)(CO) ₂ (dppe) (1b)	3:1	2009 (s), 1973 (s), 1959 (s)	78.3 (d) 48.1 (d)	29.1 29.1	77.5 (s)
Fe(pdt)(CO) ₂ (dppv) (1c)	1:4	2010 (m), 1975 (s)	87.3 (d) 60.4 (d)	22.0 22.1	81.2 (s)
Fe(pdt)(CO) ₂ (dppe) (1d)	2:3	2004 (m), 1969 (s), 1958 (sh)	78.0 (d) 51.2 (d)	30.9 30.6	73.7 (s)
Fe(pdt)(CO) ₂ (dppbz) (1e)	1:7	2012 (m), 1970 (s)	78.5 (d) 68.2 (d)	38.6 39.3	80.8 (s)
Fe(pdt)(CO) ₂ (dcpe) (1f)	1:2	1990 (m), 1940 (s)	79.19 (d) 55.8 (d)	32.9 32.9	81.34 (s)
Fe(Me ₂ pdt)(CO) ₂ (dppe) (1g)	1:3	2006 (m), 1969 (s)	78.3 (d) 52.6 (d)	30.5 30.8	73.8 (s)

^aIR 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.

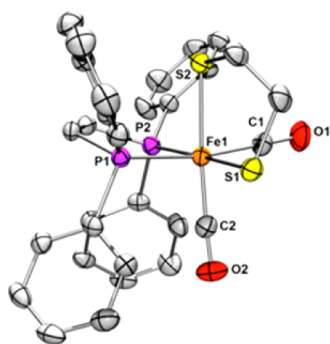


Figure 1. Structure of the unsymmetrical isomer of Fe(edt)(CO)₂(dppv) (**1a**). Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Key distances (Å) and angles (deg): Fe1–C1, 1.777(3); Fe1–C2, 1.790(3); Fe1–P2, 2.2304(8); Fe1–P1, 2.2648(7); Fe1–S1, 2.3313(8); Fe1–S2, 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); P2–Fe1–P1, 84.80(3); C1–Fe1–S1, 85.78(8); C2–Fe1–S1, 89.16(9); P2–Fe1–S1, 175.01(3); P1–Fe1–S1, 90.23(3); C1–Fe1–S2, 174.68(8); C2–Fe1–S2, 85.05(9); P2–Fe1–S2, 90.80(3); P1–Fe1–S2, 85.32(3); S1–Fe1–S2, 89.07(3).

low yields result from complications arising from the flexibility of the dppe ligand, which allows other intra- and intermolecular processes (Scheme 4).^{27,28}

The reaction of the dcpe complex **1f** with (bda)Fe(CO)₃ afforded Fe₂(pdt)(CO)₄(dcpe) (**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)₆ and dcpe 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)₂,²⁹ where the phosphine ligands are bound to different iron centers.

Synthesis of Mn/Fe^{II} Complexes. The salt [(CO)₃Mn(pdt)Fe(CO)₂(dppe)]BF₄ (**3d**(CO)]BF₄) forms upon treatment of **1d** with [(acenaphthene)Mn(CO)₃]BF₄, a well-known source of Mn(CO)₃⁺ (Scheme 5).³⁰ When monitored by ³¹P{¹H} NMR spectroscopy, the reaction was found to produce two isomeric MnFe compounds: an unsymmetrical species

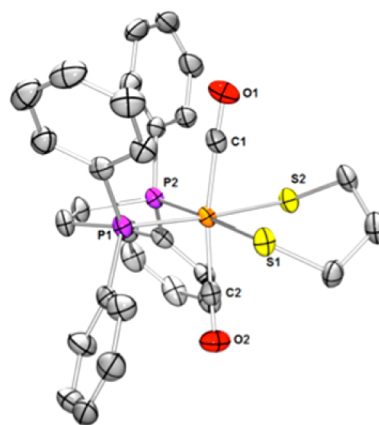


Figure 2. Structure of the symmetrical isomer of Fe(pdt)(CO)₂(dppv) (**1c**). Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Key distances (Å) and angles (deg): Fe1–C1, 1.808(2); Fe1–C2, 1.799(2); Fe1–P2, 2.2204(1); Fe1–P1, 2.214(1); Fe1–S1, 2.3441(6); Fe1–S2, 2.3462(6); C1–Fe1–C2, 169.3(1); C1–Fe1–P2, 91.10(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–S1, 87.82(7); C2–Fe1–S1, 82.97(7); P2–Fe1–S1, 177.54(2); P1–Fe1–S1, 91.58(2); C1–Fe1–S2, 83.20(7); C2–Fe1–S2, 91.74(6); P2–Fe1–S2, 89.50(2); P1–Fe1–S2, 175.07(2); S1–Fe1–S2, 92.25(2).

(doublets at δ 48 and 76) and a symmetrical species (singlet at δ 58). In these species the diphosphine ligands occupy apical–basal and dibasal sites on the Fe centers (Scheme 5). The initial isomer ratio matches that of the starting iron complex. The unsymmetrical isomer was found to convert to the symmetrical isomer over the course of 24 h (Figure 4). Comparably slow isomerism is observed in related diiron(II) dithiolates.³¹

Analogous complexes featuring different dithiolate and diphosphine ligands were also examined. Reaction of [(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)₂(dppbz)]BF₄, [(CO)₃Mn(pdt)Fe(CO)₂(dcpe)]BF₄, and [(CO)₃Mn(Me₂pdt)Fe(CO)₂(dppe)]-

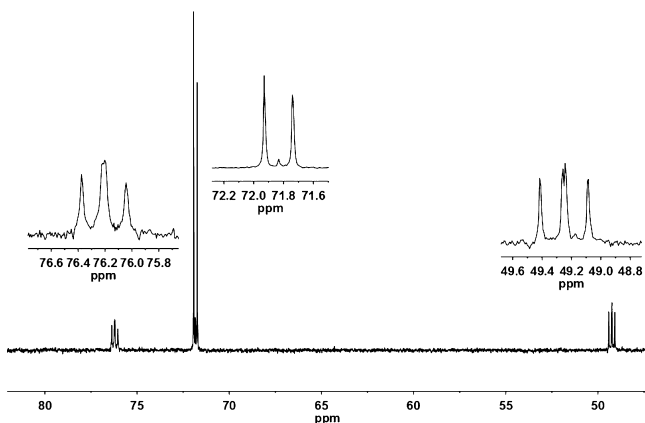
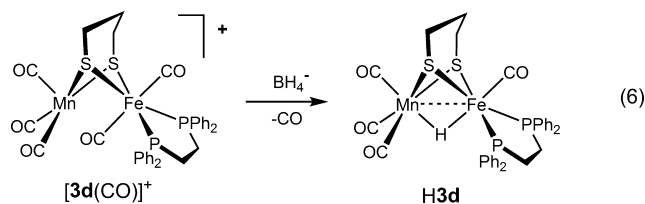


Figure 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of a mixture of the two isomers of $^{57}\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppe})$ (CD_2Cl_2 solution). Expanded regions show the additional coupling to ^{57}Fe .

BF_4 form in a manner analogous to that for $[\text{3}(\text{CO})]\text{BF}_4$, and their spectroscopic data were similar.

Synthesis of $\text{Mn}'\text{Fe}^{\text{II}}$ Hydride. Reaction of $[\text{3d}(\text{CO})]\text{BF}_4$ with $[\text{Bu}_4\text{N}]\text{BH}_4$ results in loss of one CO ligand and formation of the neutral hydride complex $(\text{CO})_3\text{Mn}(\text{pdt})(\mu\text{-H})\text{Fe}(\text{CO})(\text{dppe})$ (**H3d**) (eq 6). The ^1H NMR spectrum of **H3d** consists



of a triplet at $\delta -12.3$, indicating coupling to two equivalent phosphorus centers. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum exhibits a singlet at $\delta 80.8$, 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 hydride ligand, whose location was identified on the difference map, refined to a position

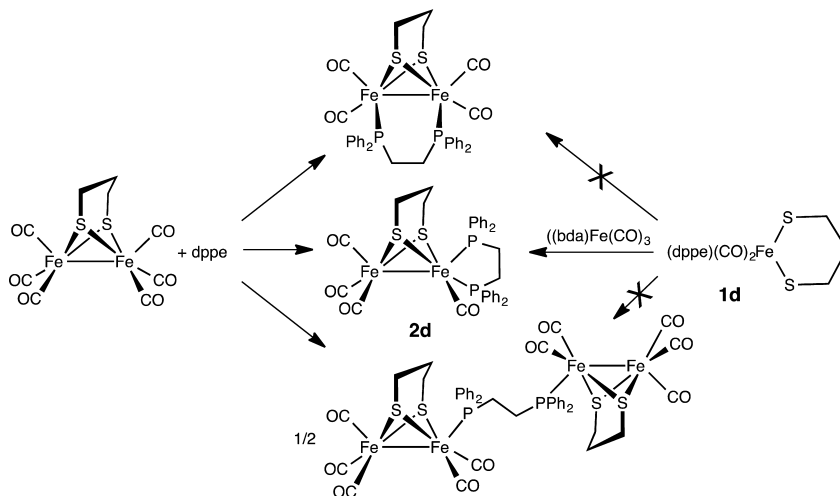
slightly closer to Fe (1.62(2) Å) than to Mn (1.75(2) Å). The d^6d^6 36e-complex (**H3d** is 34e-) $\text{FeMn}(\mu\text{-SPh})_3(\text{CO})_6$ has been described.³² The cyclic voltammogram of **H3d** consists of a reversible oxidation event at 0.125 V vs $\text{Fc}^{+/0}$, characterized by the linear dependence of i_p on $(\text{scan rate})^{1/2}$ (Supporting Information).

The acid–base behavior of **H3d** was investigated. Upon treatment of **H3d** with $[\text{H}(\text{Et}_2\text{O})_2]\text{BAR}^{\text{F}}_4$, 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 $[(\text{H}_2)\text{Mn}(\text{CO})_3(\text{dppe})]^+$).³³ Treatment of the acidified reaction mixture with Et_3N 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 $[(\mu\text{-H})\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{dppv})]^+$ is unreactive toward $[\text{H}(\text{Et}_2\text{O})_2]\text{BAR}^{\text{F}}_4$, illustrating the effect of charge on the basicity of the thiolate S centers.

$^{31}\text{P}\{^1\text{H}\}$ and ^1H 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, assigned to the nonequivalent phosphorus centers in $[\text{H3dH}]^+$.

Reduction of $\text{Mn}'\text{Fe}^{\text{II}}$ Complexes. The electrochemical behavior of $[\text{3d}(\text{CO})]\text{BF}_4$ was investigated by cyclic voltammetry. At -1.0 V, an irreversible reduction is observed, followed by a reversible event centered at -1.3 V. Consistent with its being reductive decarbonylation, the irreversible event at -1.0 V diminishes upon further electrochemical cycling (i.e., as decarbonylation proceeds to completion) but is less irreversible at low temperatures. To probe this irreversible chemical process, a solution of $[\text{3d}(\text{CO})]\text{BF}_4$ was treated with 1 equiv of cobaltocene, producing a new species characterized by ν_{CO} 1997 and 1902 cm^{-1} . In view of the electrochemical and chemical reduction results, the initial reduction is proposed to induce decarbonylation, generating $(\text{CO})_3\text{Mn}(\text{pdt})\text{Fe}(\text{CO})(\text{dppe})$ ($[\text{3d}(\text{CO})]^0$). Analytically pure $[\text{3d}(\text{CO})]^0$ was obtained once it was determined that its stability was greater in THF than in CH_2Cl_2 solution. Cyclic voltammetry of this salt exhibits the quasi-reversible couple at -1.3 V.

Scheme 4. Routes to $\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{dppe})$ and Related Complexes



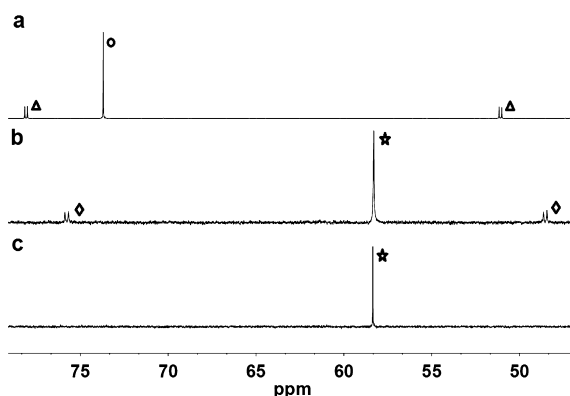
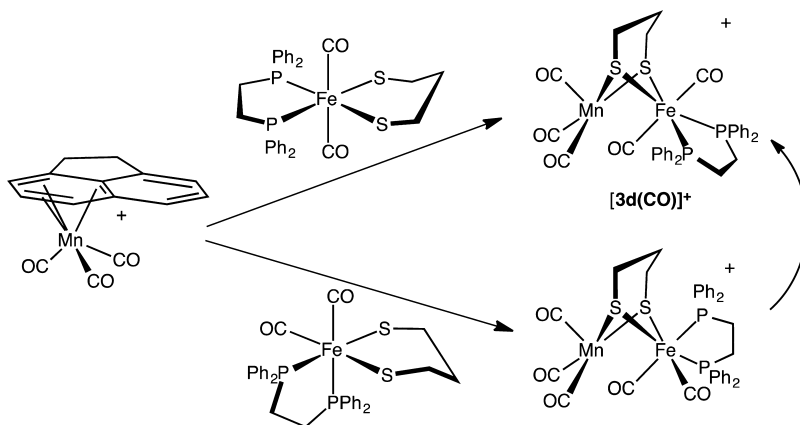
Scheme 5. Synthesis of $[(\text{CO})_3\text{Mn}(\text{pdt})\text{Fe}(\text{CO})_2(\text{dppe})]\text{BF}_4$ from Isomers of **1d**

Figure 4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of a CD_2Cl_2 solution of (a) $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppe})$ (triangle, unsym isomer; circle, sym isomer), (b) the same solution 30 min after addition of $[(\text{acenaphthene})\text{Mn}(\text{CO})_3]\text{BF}_4$ (diamond, unsym isomer; star, sym isomer), and (c) the same solution after 12 h.

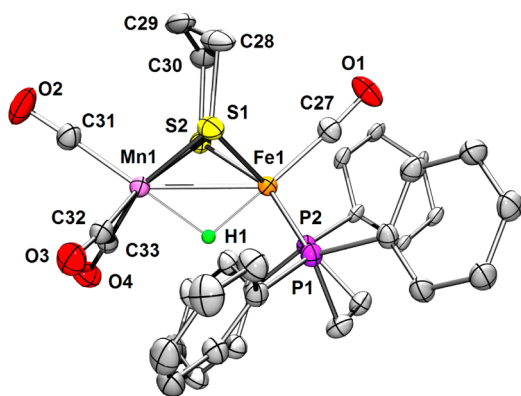


Figure 5. Structure of $(\text{CO})_3\text{Mn}(\text{pdt})(\mu\text{-H})\text{Fe}(\text{CO})(\text{dppe})$ (**H3d**) with thermal ellipsoids drawn at the 50% probability level. Selected distances (Å): Fe1–Mn1, 2.6433(4); Fe1–C27, 1.753(2); Fe1–P1, 2.2139(5); Fe1–P2, 2.2086(5); Fe1–S1, 2.2759(5); Fe1–S2, 2.2648(5); Fe1–H1, 1.62(2); Mn1–C31, 1.789(2); Mn1–C32, 1.813(2); Mn1–C33, 1.799(2); Mn1–S1, 2.3361(6); Mn1–S2, 2.3042(5); Mn1–H1, 1.75(2).

Cobalt–Iron Dithiolates. Treatment of the ferrous dithiolato carbonyls with $\text{CpCo}(\text{CO})_2$ in refluxing toluene or THF gave complexes of the type $\text{CpCo}(\text{pdt})\text{Fe}(\text{CO})(\text{dppx})$ (**4a,d**). The yields for these preparations were inconsistent, however, varying from 50% to almost nothing. A related but

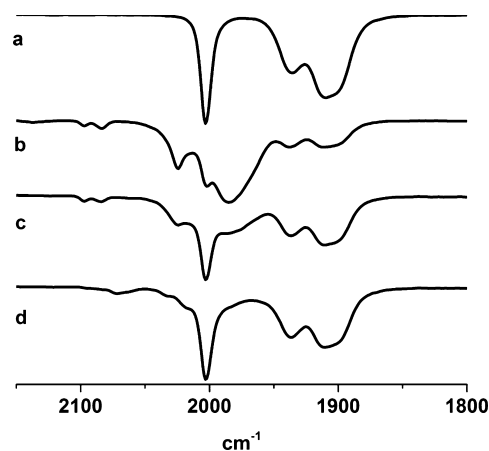
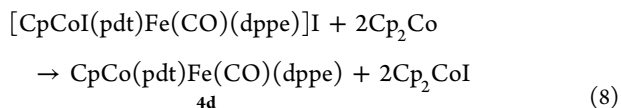
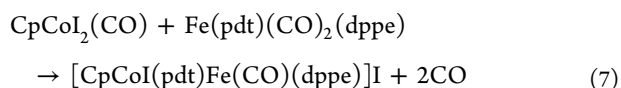


Figure 6. IR spectra in CH_2Cl_2 of (a) $(\text{CO})_3\text{Mn}(\text{pdt})(\mu\text{-H})\text{Fe}(\text{CO})(\text{dppe})$ and this solution (b) after addition of 1 equiv of $\text{H}(\text{Et}_2\text{O})_2\text{BARF}_4$, (c) after addition of 0.5 equiv of Et_3N , and (d) after addition of 1 equiv total of Et_3N .

more reliable route to the same compounds involved the reactions of the ferrous dithiolates with $\text{CpCoI}_2(\text{CO})$ followed by reduction. For example, **1d** and $\text{CpCoI}_2(\text{CO})$ react rapidly to give an isomeric mixture of the intermediate $[\text{CpCoI}(\text{pdt})\text{Fe}(\text{CO})(\text{dppe})]^+$ (ν_{CO} 1952 cm^{-1}). When this reaction is monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, two isomeric Co–Fe complexes are observed. Akin to the MnFe systems, the $^{31}\text{P}\{^1\text{H}\}$ 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 $[\text{CpCoI}(\text{pdt})\text{Fe}(\text{CO})(\text{dppe})]^+$ with 2 equiv of Cp_2Co gave **4d** in good yield (eqs 7 and 8).



These CoFe complexes are analogues of $\text{Fe}_2(\text{S}_2\text{C}_n\text{H}_{2n})-(\text{CO})_4(\text{dppx})$, in which CpCo replaces the $\text{Fe}(\text{CO})_3$ center.

Like the corresponding diiron complexes, **4d** oxidizes reversibly, at a potential (-0.6 V vs $\text{Fc}^{+/0}$) between those for $\text{Fe}_2(\text{pdt})(\text{CO})_2(\text{dppv})_2$ (-0.19 V) and $\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{dppv})$ (-0.94 V).^{26,35} Crystallographic and spectroscopic characterization of the ethanedithiolate **4a** proved mutually consistent (Figure 7). The complex can be described as a pair of five-

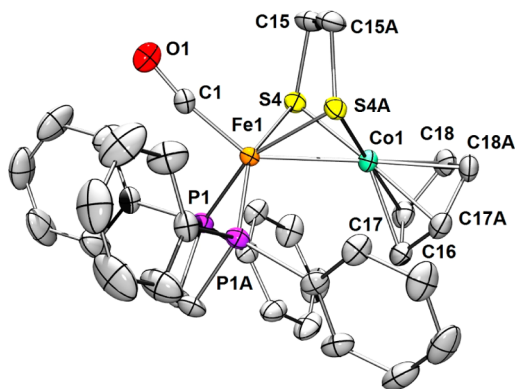


Figure 7. Structure of $\text{CpCo}(\text{edt})\text{Fe}(\text{CO})(\text{dppv})$ (**4a**) with thermal ellipsoids drawn at the 50% probability level. Selected distances (Å): Fe1–Co1 , 2.5038(5); Fe1–C1 , 1.754(3); Fe1–P1 , 2.2038(5); Fe1–S4 , 2.2318(5); Co1–S1 , 2.1748(6); Co–Cp centroid , 1.6727(3).

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 FeP_2 plane relative to the FeS_2 plane.

The $^{31}\text{P}\{^1\text{H}\}$ 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 $\sim 4:1$ intensities, attributed to conformational isomers arising from the pdt^{2-} backbone. Using an internal integration standard, $>90\%$ of the sample was verified to be in solution at -90 °C.

$\text{Co}^{\text{III}}\text{Fe}^{\text{II}}$ Hydrides. At room temperature, the Co–Fe complexes protonate to give the corresponding μ -hydrido derivatives. Protonation shifts the ν_{CO} band from 1890 to 1975 cm^{-1} . The $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra indicate that the hydride complex is C_s -symmetric. On the basis of its chemical shift and $J(^{31}\text{P}, ^1\text{H})$ 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 $\delta -9.0$ and $\delta 70.7$ in the ^1H and $^{31}\text{P}\{^1\text{H}\}$ 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 $\delta -14.7$ ($J = 30$ Hz) and triplet at $\delta -15.5$ ($J = 25$ 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.³⁶ 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.

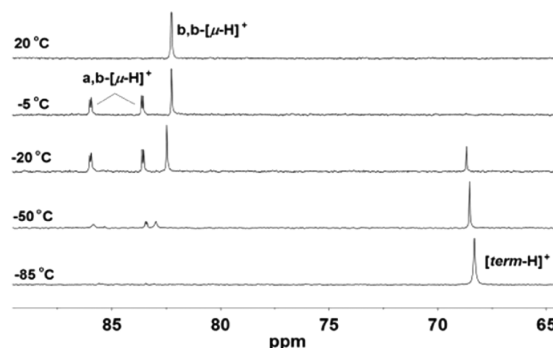


Figure 8. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of a CD_2Cl_2 solution of **4d** and 1 equiv of $[\text{H}(\text{OEt}_2)_2]\text{BAr}^{\text{F}}_4$. The solution was prepared at -85 °C and then warmed to the indicated temperatures.

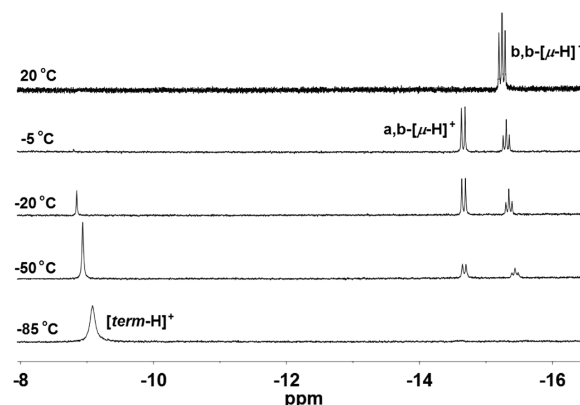
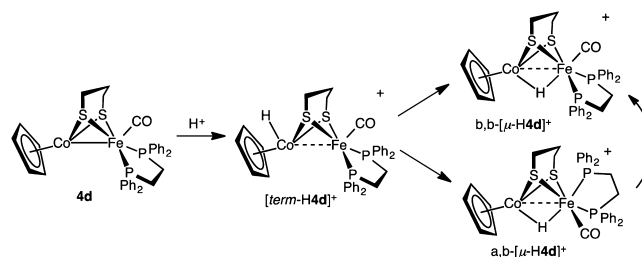


Figure 9. ^1H NMR spectra of a CD_2Cl_2 solution of **4d** and 1 equiv of $[\text{H}(\text{OEt}_2)_2]\text{BAr}^{\text{F}}_4$. The solution was prepared at -85 °C and then warmed to the indicated temperatures.

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



DISCUSSION

Ferrous dicarbonyl dithiolato diphosphine complexes are versatile precursors to dimetallic complexes, as illustrated by their conversion to FeFe , MnFe , and CoFe dithiolato complexes described above. The new synthesis of $\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{dppe})$ avoids side reactions that hamper the installation of flexible chelating ligands.^{27,28} Related complexes can be prepared via $\text{FeX}_2(\text{CO})_4$.^{14,37} The new routes are potentially appealing because the iron complexes are derived from FeCl_2 .⁸ Conveniently available sources of ^{57}Fe are easily converted to the dichloride and $^{57}\text{Fe}_2\text{I}_4(\text{PrOH})_4$. 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 ^{57}Fe ($I = -1/2$) into ferrous carbonyl building blocks, as illustrated by the synthesis of $^{57}\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppe})$. Interest in ^{57}Fe labeling

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.³⁸ The most curious property of $[(\text{CO})_3\text{Mn}(\text{pdt})\text{Fe}(\text{CO})_2(\text{dppe})]^+$ is its tendency to decarbonylate upon 1e-reduction. The resulting complex, $(\text{CO})_3\text{Mn}(\text{pdt})\text{Fe}(\text{CO})(\text{dppe})$, is electronically related to the mixed-valence “ H_{ox} -models” $[\text{Fe}_2(\text{pdt})(\text{CO})_{6-x}\text{L}_x]^+$.³⁹ Similarly, the hydride $(\text{CO})_3\text{Mn}(\text{pdt})\text{HFe}(\text{CO})(\text{dppe})$, which was characterized crystallographically, is isoelectronic with $[\text{HFe}_2(\text{pdt})(\text{CO})_4(\text{dppe})]^+$.²⁸ The MnFe complex is sufficiently electron rich that it undergoes a mild one-electron oxidation (~ 0.1 V vs $\text{Fc}^{+/0}$), whereas oxidations of analogous diferrous hydrides occur only at very positive potentials.⁴⁰

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 $(\text{CO})_3\text{Fe}(\text{pdt})\text{Ni}(\text{dppe})$ from $\text{FeI}_2(\text{CO})_4$ + $\text{Ni}(\text{pdt})(\text{dppe})$ followed by reduction.⁴¹ The complexes $\text{CpCo}(\text{dithiolate})\text{Fe}(\text{CO})(\text{diphos})$ are electronically related to $\text{Fe}_2(\text{dithiolate})(\text{CO})_4(\text{diphos})$, both being of d^7d^7 configuration. Like $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}$ dithiolates, the $\text{Co}^{\text{II}}\text{Fe}^{\text{I}}$ species undergo protonation and redox reactions.

EXPERIMENTAL SECTION

Methods used in this work have been recently described.³⁵ Chromatography was performed using silica gel (40–63 μm , 230–400 mesh) as the stationary phase. K_2pdt ,⁴² [(acenaphthene)Mn(CO)₃] BF_4 ,³⁰ $^{57}\text{Fe}_2\text{I}_4(\text{PrOH})_4$,⁴³ and $\text{CpCo}(\text{CO})\text{I}_2$ ⁴⁴ were prepared according to the literature methods. ESI-MS data were recorded on dilute CH_2Cl_2 solutions on a Waters Micromass Quattro II spectrometer. ATR data were collected on a PerkinElmer Spectrum 100 FT-IR instrument. ^1H NMR spectra were recorded at 500 MHz and $^{31}\text{P}\{^1\text{H}\}$ 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: $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppe})$ (1d). Under a CO atmosphere, a solution of 1.9 g of FeCl_2 (15.0 mmol) in 250 mL of acetone was treated with a solution of 5.98 g (15.0 mmol) of dppe in 60 mL of THF. The solution changed from pale orange to green and then to dark orange, signaling formation of $\text{FeCl}_2(\text{CO})_2(\text{dppe})$. Separately, 1.71 mL (17.0 mmol) of $\text{C}_3\text{H}_6(\text{SH})_2$ and 0.72 g (30.0 mmol) of NaH were combined in 50 mL of THF. After 1 h, the resulting solution of $\text{Na}_2\text{S}_2\text{C}_3\text{H}_6$ was added to the solution of $\text{FeCl}_2(\text{CO})_2(\text{dppe})$. After being allowed to react for 16 h, the mixture was filtered through Celite, and the solvent was evaporated from the filtrate. The residue was extracted into 15 mL of CH_2Cl_2 and purified by flash column chromatography on a 4×50 cm column of silica gel. After a yellow band eluted with CH_2Cl_2 , the red band containing the product eluted with 5/1 $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. Evaporation of solvent from this band afforded **1d** as a red solid. Yield: 3.34 g (36%). ^1H NMR (CD_2Cl_2): δ 7.89–7.32 (m, 20H, C_6H_5), 2.63 (m, 4H, PCH_2), 2.50 (d, 4H, SCH_2), 1.97 (m, 2H, SCH_2CH_2). IR (CH_2Cl_2): 2010, 1968. Anal. Calcd for $\text{C}_{31}\text{H}_{30}\text{FeO}_2\text{P}_2\text{S}_2 \cdot 0.3\text{CH}_2\text{Cl}_2$ (found): C, 58.56 (58.24); H, 4.80 (4.7).

$\text{Fe}(\text{edt})(\text{CO})_2(\text{dppv})$ (1a). Conducted as for **1d**. Yield: 12–50%. ^1H NMR (CD_2Cl_2): δ 8.14–7.32 (m, 20H, C_6H_5), 2.53 (s, 2H, CH_2), 2.46 and 2.02 (d each, 1:1 H, CH_2), 2.18 and 0.21 (t each, 1:1 H, CH). IR (CH_2Cl_2): 2013 (s), 1978 (s), 1960 (s). Anal. Calcd for $\text{C}_{30}\text{H}_{26}\text{FeO}_2\text{P}_2\text{S}_2 \cdot 0.5\text{CH}_2\text{Cl}_2$ (found): C, 56.98 (57.35); H, 4.23 (4.17).

$\text{Fe}(\text{edt})(\text{CO})_2(\text{dppe})$ (1b). Conducted as for **1d**. Yield: 50%. ^1H NMR (CD_2Cl_2): δ 7.87–7.27 (m, C_6H_5), 2.62 (s, 4H, S CH_2 , sym), 2.50 (s, 4H, PCH_2 , sym), 2.78 (d 2H PCH_2 , unsym), 2.16 (d 2H PCH_2 , unsym), 1.22 (s, 3H, SCH_2 , unsym), 0.34 (s, 1H, SCH_2 , unsym). IR (THF): 2009 (s), 1973 (s), 1959 (s). Anal. Calcd for $\text{C}_{30}\text{H}_{28}\text{FeO}_2\text{P}_2\text{S}_2$ (found): C, 59.81 (59.78); H, 4.68 (5.0).

$\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppv})$ (1c). Conducted as for **1d**, but the column was eluted with 10/1 $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. Yield: 78%. ^1H NMR (CD_2Cl_2): δ 7.94–7.32 (m, 20H, C_6H_5), 2.44 (d, 4H, CH_2), 1.96 (d, 2H, SCH_2). IR (CH_2Cl_2): 2014, 1975. Anal. Calcd for $\text{C}_{31}\text{H}_{28}\text{FeO}_2\text{P}_2\text{S}_2 \cdot 0.7\text{CH}_2\text{Cl}_2$ (found): C, 56.49 (56.50); H, 4.40 (4.40).

$\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppbz})$ (1e). Under a CO atmosphere, a solution of 0.50 g of FeCl_2 (3.94 mmol) in 100 mL of acetone was treated with a solution of 1.76 g (15.0 mmol) of dppbz in 40 mL of THF. The solution changed from pale orange to dark orange, signaling formation of $\text{FeCl}_2(\text{CO})_2(\text{dppbz})$. Separately, 181 μL (4.33 mmol) of $\text{C}_3\text{H}_6(\text{SH})_2$ and 188 mg (7.88 mmol) of NaH were combined in 15 mL of THF. After 1 h, the resulting solution of $\text{Na}_2\text{S}_2\text{C}_3\text{H}_6$ was added to the solution of $\text{FeCl}_2(\text{CO})_2(\text{dppbz})$. A large amount of red precipitate had formed after 15 h. The solution was filtered, the filtrate was discarded, and the red solid was extracted into 50 mL of CH_2Cl_2 . The product was recrystallized by addition of hexanes to a concentrated CH_2Cl_2 solution. Yield: 400 mg (20%). ^1H NMR (CD_2Cl_2): δ 7.4–7.6 (m, 24H, C_6H_5 and C_6H_4), 2.39 (s, 4H, SCH_2CH_2), 1.94 (s, 2H, SCH_2CH_2). IR (CH_2Cl_2): 2012, 1970. Anal. Calcd for $\text{C}_{35}\text{H}_{30}\text{FeO}_2\text{P}_2\text{S}_2 \cdot 0.2\text{CH}_2\text{Cl}_2$ (found): C, 62.03 (62.22); H, 4.5 (4.83).

$\text{Fe}(\text{pdt})(\text{CO})_2(\text{dcpe})$ (1f). Conducted as for **1d**, but instead of chromatography, the product was extracted into ~ 100 mL of hexanes. The solution volume was reduced to ~ 20 mL and the solution cooled to 0 $^\circ\text{C}$, resulting in the formation of dark red crystals. Yield: 430 mg (35%). IR (CH_2Cl_2): 1997 (w), 1945 (s). Anal. Calcd for $\text{C}_{31}\text{H}_{54}\text{FeO}_2\text{P}_2\text{S}_2 \cdot 0.2\text{CH}_2\text{Cl}_2$ (found): C, 56.98 (56.94); H, 8.34 (8.71).

$^{57}\text{Fe}_2\text{I}_4(\text{PrOH})_4$. This complex was obtained as a green powder in 95% yield analogously to the published method for $\text{Fe}_2\text{I}_4(\text{PrOH})_4$,⁴³ using ^{57}Fe as the precursor. ESI-MS: m/z 674.8 $[\text{M} - ^1\text{PrOH} - \text{I}]^+$, 364.1 $[\text{M} - ^1\text{PrOH} - ^{57}\text{Fe}^{2+} - 3\text{I}]^+$. Anal. Calcd for $\text{C}_{12}\text{H}_{32}\text{O}_4\text{I}_4^{57}\text{Fe}_2$ (found): C, 16.72 (16.16); H, 3.74 (3.44); N, 0.00 (0.00).

$^{57}\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppe})$ ($^{57}\text{1d}$). A mixture of 86.2 mg (100 μmol) of $^{57}\text{Fe}_2\text{I}_4(\text{PrOH})_4$ and 79.7 mg (200 μmol) of dppe in 6 mL of 1/1 $^1\text{PrOH}/\text{THF}$ was stirred under 1 atm of CO. The suspension, which had developed a red color, was treated with 36.8 mg (200 μmol) of K_2pdt in 3 mL of $^1\text{PrOH}$. After it was stirred for 24 h in the absence of light, the mixture was evaporated to dryness. The dark residue was extracted with 2×5 mL of CH_2Cl_2 , and these extracts were concentrated to ~ 0.5 mL and chromatographed on a ~ 5 cm column of silica gel, with CH_2Cl_2 as eluent. The second band, deep red, was collected, concentrated to ~ 2 mL, and treated with 10 mL of Et_2O . Any dark solids that formed were removed by filtration, and the filtrate was treated with 15 mL of pentane. The mixture was allowed to stand at -28 $^\circ\text{C}$ for 1 h, after which the solid that formed was isolated by filtration, washed with additional pentane, and dried briefly to afford the title compound as a pink powder (23.6 mg, 38.2 μmol , 19%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CH_2Cl_2): δ 76.2 (dd, $^1J_{\text{PFe}} = 35$, $^2J_{\text{PP}} = 32$, cis isomer), 71.8 (d, $^1J_{\text{PFe}} = 38$, trans isomer), 49.2 (dd, $^1J_{\text{PFe}} = 35$, $^2J_{\text{PP}} = 32$, cis isomer). FTIR (CH_2Cl_2): 2010 (cis), 1969 (overlapping cis/trans). ESI-MS: m/z 618.2 $[\text{M} + \text{H}]^+$ (similar analysis for the unlabeled complex gave m/z 617.1).

$\text{Fe}(\text{Me}_2\text{pdt})(\text{CO})_2(\text{dppe})$ (1g). Conducted as for **1d**. Yield: 1.03 g (40%). ^1H NMR (CD_2Cl_2): δ 7.4–7.8 (m, 20H, C_6H_5), 2.65 (dd, 4H, $\text{P}_2\text{CH}_2\text{CH}_2$), 2.23 (s, 4H, SCH_2), 1.01 (s, 6H, CCH_3). IR (CH_2Cl_2): 2006 (w), 1969 (s). Anal. Calcd for $\text{C}_{33}\text{H}_{34}\text{FeO}_2\text{P}_2\text{S}_2 \cdot 0.2\text{CH}_2\text{Cl}_2$ (found): C, 60.28 (60.0); H, 5.24 (5.41).

$\text{Fe}_2(\text{edt})(\text{CO})_4(\text{dppv})$ (2a) from 1a. A mixture of **1a** (125 mg, 0.208 mmol) and 50 mg (0.208 mmol) of (bda) $\text{Fe}(\text{CO})_3$ in 20 mL of toluene gradually darkened over the course of several hours to a deep red solution. The reaction was monitored by IR for the disappearance of ν_{CO} bands for (bda) $\text{Fe}(\text{CO})_3$ and **1a** and the appearance of **2a**. 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 and dried in vacuo. Yield: 123 mg (83%). The IR, ^1H NMR, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the product match reported data.²⁶

$\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{dppe})$ (2d) from 1d. An orange mixture of **1d** (250 mg, 0.40 mmol) and $(\text{bda})\text{Fe}(\text{CO})_3$ (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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the product match reported data.²⁸

$\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{dcpe})$ (2f) from 1f. A 5 mL solution of $(\text{bda})\text{Fe}(\text{CO})_3$ (48 mg, 0.17 mmol) was added to a red solution of **1f** (107 mg, 0.17 mmol) in 20 mL of toluene. The solution gradually darkened over the course of several hours to a deep red-brown 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 a glovebox, with toluene as eluent. The first brown-red band was collected. Yield: 101 mg (81%). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 89.27 (s), apical-basal; 74.90 (s), dibasal. IR (CH_2Cl_2): 2013 (s), 1939 (br), 1882 (br).

$[(\text{CO})_3\text{Mn}(\text{pdt})\text{Fe}(\text{CO})_2(\text{dppe})]\text{BF}_4$ (3(CO)**) BF_4 .** A solution of 500 mg (1.32 mmol) of $[(\text{acenaphthene})\text{Mn}(\text{CO})_3]\text{BF}_4$ in 125 mL of CH_2Cl_2 was treated with a solution of 810 mg (1.32 mmol) of **1b** in 50 mL of CH_2Cl_2 . The solution was stirred for 20 h and gradually became dark brown. The IR spectrum of the solution showed bands for the product. The solution was evaporated to dryness. The resulting brown residue was extracted into ~ 30 mL of CH_2Cl_2 , and the extract was filtered through a pad of Celite. The brown solution was concentrated to ~ 10 mL and then diluted with 100 mL of hexanes. Upon storage of the solution at 0°C , brown microcrystals formed. Yield: 1.00 g (90%). Crystals were obtained by layering a CH_2Cl_2 solution with pentane. ^1H NMR (CD_2Cl_2): δ 7.41–7.80 (m, 20H, C_6H_5), 3.50 (m, 2H, PCH_2), 3.28 (m, 2H, PCH_2), 3.08 (m, 2H, SCH_2), 2.84 (m, 3H, SCH_2CH_2), 2.03 (m, 1H, SCH_2CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 58 (s). IR (CH_2Cl_2): 2053 (w), 2027 (s), 1992 (s), 1974 (s), 1905 (br). Anal. Calcd for $\text{C}_{34}\text{H}_{30}\text{BF}_4\text{FeMnO}_5\text{P}_2\text{S}_2$ (found): C, 48.48 (48.66); H, 3.59 (3.81).

$(\text{CO})_3\text{Mn}(\text{pdt})(\mu\text{-H})\text{Fe}(\text{CO})(\text{dppe})$ (H3**).** A solution of 590 mg (0.70 mmol) of $[\text{3(CO)}]\text{BF}_4$ in 100 mL of CH_2Cl_2 was cooled to -78°C and treated with a precooled solution of 257 mg (0.70 mmol) of $[\text{Bu}_4\text{N}]\text{BH}_4$ in 60 mL of CH_2Cl_2 over the course of 90 min, during which time the solution changed from brown to dark red. The reaction progress was monitored by IR spectroscopy. The solution was warmed to room temperature and stirred at room temperature for 15 h before being evaporated to dryness. An extract of the red residue in ~ 20 mL of toluene was chromatographed on silica gel with a 3/1 toluene/hexanes mixture as eluent. The product (an orange band) eluted first, followed by a brown band. The orange band was evaporated under vacuum, and the resulting orange residue was extracted into ~ 25 mL of toluene. This extract was filtered through Celite, concentrated to half volume, and then diluted with 60 mL of hexanes. After storage of the solution at 0°C , orange crystals formed. Yield: 98 mg (20%). Diffraction-quality crystals were grown at 0°C by layering a toluene solution with hexanes. ^1H NMR (CD_2Cl_2): δ 7.38–7.84 (m, 20H, C_6H_5), 2.76 (m, 4H, PCH_2), 2.58 (m, 2H, SCH_2), 2.41 (m, 3H, SCH_2CH_2), 1.91 (m, 1H, SCH_2CH_2), -12.26 (t, 1H, Mn–H–Fe). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 80.80 (s). IR (CH_2Cl_2): 2002 (s), 1935 (br), 1905 (br). Anal. Calcd for $\text{C}_{33}\text{H}_{31}\text{FeMnO}_4\text{P}_2\text{S}_2$ (found): C, 54.41 (54.35); H, 4.29 (4.49).

$(\text{CO})_3\text{Mn}(\text{pdt})\text{Fe}(\text{CO})(\text{dppe})$. A solution of $[\text{4d(CO)}]\text{BF}_4$ (71 mg, 84 μmol) in THF (10 mL) was treated with a THF solution of Cp_2Co (16 mg, 84 μmol). The solution was filtered through Celite, and then the solvent was removed under vacuum to yield a red solid. Yield: 46 mg (75%). IR (CH_2Cl_2): 1997 (s), 1902 (s). Anal. Calcd for $\text{C}_{33}\text{H}_{30}\text{FeMnO}_4\text{P}_2\text{S}_2$ (found): C, 54.49 (54.54); H, 4.16 (4.55).

$\text{CpCo}(\text{edt})\text{Fe}(\text{CO})(\text{dppv})$ (4a**) from $\text{CpCoI}_2(\text{CO})$.** A mixture of **1a** (100 mg, 0.17 mmol) and $\text{CpCo}(\text{CO})\text{I}_2$ (68 mg, 0.17 mmol) was

stirred in CH_2Cl_2 (20 mL) at room temperature for 2 h to give a dark brown solution with a predominant IR band at 1978 cm^{-1} . To this solution was added a solution of Cp_2Co (68 mg, 0.36 mmol) in 20 mL of CH_2Cl_2 . The IR spectrum of the resulting solution revealed a prominent band at 1890 cm^{-1} . After the mixture was stirred for 30 min, solvent was removed, and the residue was purified by column chromatography, initially with a 1/1 mixture of CH_2Cl_2 and pentane as eluent and gradually increasing the CH_2Cl_2 content. After an initial green band, the product eluted as a brown band using CH_2Cl_2 . Evaporation of the solution gave the brown product. Yield: 45 mg (39%). ^1H NMR (CD_2Cl_2 , 23°C): δ 8.30–7.12 (m, 20 H, C_6H_5), 4.75 (s, 2 H, PCH), 3.36 (s, 5 H, C_5H_5), 2.26 and 1.84 (d each, 2 H each, SCH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 23°C): δ 93.56 (s). IR (CH_2Cl_2): 1890.

$\text{CpCo}(\text{edt})\text{Fe}(\text{CO})(\text{dppv})$ from $\text{CpCo}(\text{CO})_2$. A mixture of **1a** (200 mg, 0.34 mmol) and $\text{CpCo}(\text{CO})_2$ (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 Et_2O . The brown residue was extracted into ~ 4 mL of CH_2Cl_2 , and the extract was layered with 10 mL of hexane. Dark brown crystals of **4a** formed overnight. Yields were variable. Anal. Calcd for $\text{C}_{34}\text{H}_{31}\text{CoFeO}_2\text{P}_2\text{S}_2$ (found): C, 58.63 (58.12); H, 4.49 (4.37). IR (CH_2Cl_2): 1890.

$\text{CpCo}(\text{pdt})\text{Fe}(\text{CO})(\text{dppv})$ (4c**).** A mixture of **1c** (200 mg, 0.32 mmol) and $\text{CpCo}(\text{CO})_2$ (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 CH_2Cl_2 . This extract was layered with 10 mL of hexane to yield dark brown crystals of **4b** upon standing overnight. ^1H NMR (CD_2Cl_2 , 23°C): δ 8.17–7.30 (m, 20 H, C_6H_5), 3.51 (s, 5 H, C_5H_5), 2.30 and 2.20 (d each, 2 H each, SCH_2), 1.87 (m, 2 H, SCH_2CH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 23°C): δ 90.17 (s). IR (CH_2Cl_2): 1885.

$\text{CpCo}(\text{pdt})\text{Fe}(\text{CO})(\text{dppe})$ (4d**) from $\text{CpCoI}_2(\text{CO})$.** A solution of $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppe})$ (50 mg, 0.08 mmol) and $\text{CpCo}(\text{CO})\text{I}_2$ (31 mg, 0.08 mmol) in CH_2Cl_2 (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 Cp_2Co (38 mg, 0.20 mmol) in CH_2Cl_2 (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 CH_2Cl_2 /pentane as eluent, which produced a green band. Eluting with CH_2Cl_2 gave the product as a brown band, which was evaporated to leave a brown solid. Yield: 23 mg (40%). ^1H NMR (CD_2Cl_2 , 23°C): δ 7.82–7.29 (m, 20 H, C_6H_5), 3.84 (s, 5 H, C_5H_5), 2.98 (m, 2 H, PCH_2), 2.58 and 2.26 (m each, 2 H each, SCH_2), 2.17 and 1.89 (m each, 1 H each, PCH_2), 1.47 (m, 2 H, $\text{S}(\text{CH}_2)_2\text{CH}_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 23°C): δ 83.48 (s). IR (CH_2Cl_2): 1880.

$\text{CpCo}(\text{pdt})\text{Fe}(\text{CO})(\text{dppe})$ (4d**) from $\text{CpCo}(\text{CO})_2$.** A mixture of **1d** (200 mg, 0.32 mmol) and $\text{CpCo}(\text{CO})_2$ (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 toluene and then extracted into ~ 4 mL of CH_2Cl_2 . This extract was layered with 10 mL of hexane to yield dark brown crystals of **4d** upon standing overnight. Yields were variable. ^1H NMR (CD_2Cl_2 , 23°C): δ 7.82–7.29 (m, 20 H, C_6H_5), 3.84 (s, 5 H, C_5H_5), 2.98 (m, 2 H, PCH_2), 2.56 and 2.25 (m each, 2 H each, SCH_2), 2.18 and 1.87 (m each, 1 H each, PCH_2), 1.51 (m, 2 H, $\text{S}(\text{CH}_2)_2\text{CH}_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 23°C): δ 85.54 (s). Anal. Calcd for $\text{C}_{33}\text{H}_{33}\text{CoFeO}_2\text{P}_2\text{S}_2$ (found): C, 59.00 (58.89); H, 4.95 (4.83). IR (CH_2Cl_2 , cm^{-1}): ν_{CO} 1879. Data for the low-temperature intermediate, terminal hydride are as follows. ^1H NMR (CD_2Cl_2 , 23°C): δ 7.73–7.35 (m, 20 H, C_6H_5), 3.61 (s, 5 H, C_5H_5), 2.98 (m, 2 H, PCH_2), 2.56 and 2.25 (m each, 2 H each, SCH_2), 2.18 and 1.87 (m each, 1 H each, PCH_2), 1.51 (m, 2 H, $\text{S}(\text{CH}_2)_2\text{CH}_2$).

$^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 23 °C): δ 85.54 (s). Data for the low-temperature intermediate, apical–basal μ -hydride are as follows. ^1H NMR (CD_2Cl_2 , 23 °C): δ 7.82–7.29 (m, 20 H, C_6H_5), 3.84 (s, 5 H, C_5H_5), 2.98 (m, 2 H, PCH_2), 2.56 and 2.25 (m each, 2 H each, SCH_2), 2.18 and 1.87 (m each, 1 H each, PCH_2), 1.51 (m, 2 H, CH_2SCH_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 23 °C): δ 85.54 (s).

Low-Temperature Protonation of $\text{CpCo}(\text{pdt})\text{Fe}(\text{CO})(\text{dppe})$ (4d). In a J. Young NMR tube, ~ 1 mL of CD_2Cl_2 was distilled and frozen onto **4d** (5 mg, 0.007 mmol) and $[\text{H}(\text{OEt}_2)_2]\text{BAR}^{\text{F}}_{24}$ (8.5 mg, 0.008 mmol) in a liquid- N_2 bath. The sample was then thawed, placed in an NMR spectrometer (probe precooled to -85 °C), and analyzed by NMR spectroscopy. ^1H NMR (CD_2Cl_2 , -85 °C): δ 3.61 (s, C_5H_5 , $[\text{term-H4d}]^+$); -9.0 (s, Co-H, $[\text{term-H4d}]^+$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -85 °C): δ 70.65 (s, $[\text{term-H4d}]^+$). When the sample was warmed to -50 °C, the NMR spectra indicated the presence of two new species. ^1H NMR (CD_2Cl_2 , -50 °C): δ 3.61 (s, C_5H_5 , $[\text{term-H4d}]^+$); -9.0 (s, Co-H, $[\text{term-H4d}]^+$); 5.29 (s, C_5H_5 , a,b- $[\mu\text{-H4d}]^+$); -14.68 (d, $J_{\text{P-H}} = 30$, Co-H-Fe, a,b- $[\mu\text{-H4d}]^+$); 4.69 (s, C_5H_5 , b,b- $[\mu\text{-H4d}]^+$); -15.48 (t, $J_{\text{P-H}} = 25$, Co-H-Fe, b,b- $[\mu\text{-H4d}]^+$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -50 °C): δ 70.65 (s, $[\text{term-H4d}]^+$); 88.17, 85.58 (d, a,b- $[\mu\text{-H4d}]^+$); 85.3 (s, b,b- $[\mu\text{-H4d}]^+$). When the sample was warmed above -20 °C, the signals for $[\text{term-H4d}]^+$ in the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra disappeared. At room temperature, a,b- $[\mu\text{-H4d}]^+$ converts entirely to b,b- $[\mu\text{-H4d}]^+$.

$[\text{CpCo}(\text{edt})(\text{H})\text{Fe}(\text{CO})(\text{dppv})]\text{BF}_4$ ([H4a] BF_4). A solution of **4a** (20 mg, 0.03 mmol) in CH_2Cl_2 (10 mL) was treated with 2 equiv of $\text{HBF}_4\cdot\text{Et}_2\text{O}$. The mixture was stirred for 15 min. The volume was then reduced under vacuum, and Et_2O was added to precipitate a brown powder. ^1H NMR (400 MHz, CD_2Cl_2 , 25 °C): δ 8.50–7.26 (m, 20 H, C_6H_5), 4.31 (s, 5 H, C_5H_5), 3.06 and 2.70 (d each, 2 H each, SCH_2), -18.14 (t, $J_{\text{PH}} = 26.8$, 1H, Co-H-Fe). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 23 °C): δ 89.72 (d). IR (CH_2Cl_2): 1975.

$[\text{CpCo}(\text{pdt})(\text{H})\text{Fe}(\text{CO})(\text{dppe})]\text{BF}_4$ ([H4d] BF_4). A solution of **4d** (20 mg, 0.03 mmol) in CH_2Cl_2 (10 mL) was treated with 2 equiv of $\text{HBF}_4\cdot\text{Et}_2\text{O}$. After it was stirred for 15 min, the solution was concentrated and then diluted with Et_2O to precipitate a brown powder. ^1H NMR (CD_2Cl_2 , 25 °C): δ 7.66–7.30 (m, 20H, C_6H_5), 4.79 (s, 5H, C_5H_5), 3.30 (m, 2H, PCH_2), 3.01 and 2.71 (m each, 2H each, SCH_2), 2.61 (m, 1H, PCH_2), 2.15 (m, 3H, PCH_2 and CH_2SCH_2), -15.19 (t, $J_{\text{PH}} = 27$, 1H, Co-H-Fe). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C): δ 82.91 (d). Anal. Calcd for $\text{C}_{35}\text{H}_{36}\text{BCoF}_4\text{FeOP}_2\text{S}_2$: 0.2 CH_2Cl_2 (found): C, 51.73 (51.90); H, 4.49 (4.61). IR (CH_2Cl_2): 1962.

■ ASSOCIATED CONTENT

■ Supporting Information

Figures giving ^1H NMR, $^{31}\text{P}\{^1\text{H}\}$ NMR, and IR spectra for new complexes and CIF files giving X-ray crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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