ORGANOMETALLICS

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

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Supporting Information

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 = $S_2(CH_2)_2^{2-}$ (edt²⁻), $S_2(CH_2)_3^{2-}$ (pdt²⁻), $S_2(CH_2)_2(C(CH_3)_2)^{2-}$ (Me₂pdt²⁻) and diphos = *cis*-C₂H₂(PPh₂)₂ (dppv), C₂H₄(PPh₂)₂ (dppe), C₆H₄(PPh₂)₂ (dppbz), $C_2H_4[P(C_6H_{11})_2]_2$ (dcpe). The incorporation of ⁵⁷Fe into such building block complexes commenced with the conversion of ⁵⁷Fe into ⁵⁷Fe₂I₄(^{*i*}PrOH)₄, which then was treated with K₂pdt, CO, and dppe to give ⁵⁷Fe(pdt)(CO)₂(dppe). NMR and IR analyses show that these complexes exist



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)₄(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)]⁺ $([3d(CO)]^+)$. Reduction of $[3d(CO)]^+$ with BH_4^- gave the C₅-symmetric μ -hydride $(CO)_3Mn(pdt)(H)Fe(CO)(dppe)$ (H3d). Complex H3d is reversibly protonated by strong acids, the proposed site of protonation being sulfur. Treatment of $Fe(dithiolate)(CO)_2(diphos)$ with $CpCoI_2(CO)$ followed by reduction by Cp_2Co affords CpCo(dithiolate)Fe(CO)(diphos)(4), which can also be prepared from $Fe(dithiolate)(CO)_2(diphos)$ and $CpCo(CO)_2$. Like the electronically related $(CO)_{3}$ 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 $Fe_2(SR)_2(CO)_{6-x}L_x$ 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 H₂processing catalysts,² has led chemists to prepare many examples of these dithiolates.³ Since the [NiFe]-H₂ases feature related $Ni(SR)_2Fe(CO)L_2$ 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 $Fe_2(SR)_2(CO)_{6-x}L_x$ are prepared by ligand (L) substitution of hexacarbonyls $Fe_2(SR)_2(CO)_{60}^4$ which in turn are obtained by treating $Fe_3(CO)_{12}$ with thiols. Complementarily, $Fe_2(S_2)(CO)_6^5$ 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 57Fe-labeled derivatives, which are of interest for nuclear resonance vibrational spectroscopy (NRVS)⁹ and Mössbauer measurements.¹⁰

Scheme 1. Illustrative Routes to $Fe_2(SR)_2(CO)_6^{4,8,11}$

 $Fe_3(CO)_{12}$ + 3 RSH \rightarrow 3/2 $Fe_2(SR)_2(CO)_6$ + 3/2 H_2 + 3 CO $2 \operatorname{FeCl}_2 + 6 \operatorname{CO} + 2 \operatorname{NaSR} + \operatorname{Zn} \rightarrow \operatorname{Fe}_2(\operatorname{SR})_2(\operatorname{CO})_6 + 2 \operatorname{NaCl} + \operatorname{ZnCl}_2$ $Fe_2(SLi)_2(CO)_6 + 2 RX \rightarrow Fe_2(SR)_2(CO)_6 + 2 LiX$ $Fe_2(SH)_2(CO)_6 + 2 CH_2O + H_2X \rightarrow Fe_2[(SCH_2)_2X](CO)_6 + 2 H_2O$

Promising precursors to *di*metallic dithiolato complexes are monoiron complexes of the type $Fe(dithiolate)(CO)_2(PR_3)_2$. These compounds should be obtainable from complexes of the form $FeX_2(CO)_2(PR_3)_{2,}^{12-14}$ 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 *di*thiolato carbonyls have been established in the case of $Fe(edt)(CO)_2(PMe_3)_2$ (edt²⁻ = ethanedithiolate)¹⁷ and related complexes containing bidentate phosphine ligands (Scheme 2).¹⁸ The benzenedithiolates $Fe(S_2C_6H_2X_2)(CO)_2(PMe_3)_2$ (X = H, Cl) are formed from *di*iron dithiolato precursors, ¹⁹ which undergo cleavage upon treatment with PMe₃. With regard to structure, complexes of the type $FeX_2(CO)_2(chel)$ exist in

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$$2FeSO_4 + 2CO + 2RSNa + chel$$

$$\rightarrow Fe(SR)_2(CO)_2(chel) + Na_2SO_4$$

(chel = dppe, en, phen, bipy) (1)

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

 $\begin{aligned} & \operatorname{FeCl}_2 + 2\operatorname{CO} + \operatorname{Na}_2(\operatorname{edt}) + 2\operatorname{PMe}_3 \xrightarrow{} \operatorname{Fe}(\operatorname{edt})(\operatorname{CO})_2(\operatorname{PMe}_3)_2 + 2\operatorname{NaCl} \\ & \operatorname{Fe}_2(\operatorname{S}_2\operatorname{C}_6\operatorname{R}_4)(\operatorname{CO})_6 + 2\operatorname{PMe}_3 \xrightarrow{} \operatorname{Fe}(\operatorname{S}_2\operatorname{C}_6\operatorname{R}_4)(\operatorname{CO})_2(\operatorname{PMe}_3)_2 + \dots \end{aligned}$

various isomeric forms.^{13,20} Fe(SPh)₂(CO)₂(dppe) crystallizes as the all-cis isomer.¹⁵ Complexes of formula $FeX_2(CO)_2(PR_3)_2$, 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 metalloligands, 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

$$Fe(pdt)(CO)_{2}(dppe) + NiCl_{2}(dppe)$$

$$\rightarrow [(dppe)(CO)FeCl(pdt)Ni(dppe)]Cl (2)$$

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 $FeCl_2$ and the diphosphine ligand, followed by the addition of the sodium dithiolate (Scheme 3). The reaction affords a mixture of the two isomers





possible for an octahedral complex of type $M(chel)(chel')L_2$. The complex $FeCl_2(CO)_2(dppe)^{13}$ 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 $pdtH_2$ did not proceed.

Spectroscopic measurements on the new compounds indicate the presence of two isomers, with the ${}^{31}P{}^{1}H$ 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 (edt^{2-}) complexes 1a.b. the unsymmetrical isomer is the major species, whereas the symmetrical isomers predominate for complexes of 1,3-propanedithiolate (pdt^{2-}) and 2-dimethyl-1,3-propanedithiolate (Me₂pdt²⁻), 1c-f. (Table 1, Scheme 3). The IR spectra of the edt^{2-} complexes **1***a*,**b** exhibit two or three bands in the $\nu_{\rm CO}$ 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 $\nu_{\rm CO}$ bands for 1f are shifted by 20 cm^{-1} to lower energy. Unlike complexes 1a-g, Fe(edt)- $(CO)_2(PMe_3)_2$ 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 crystallog-raphy (Figures 1 and 2). In both cases, the major solution isomer crystallized.

Starting from ${}^{57}\text{Fe}_2\text{I}_4({}^{1}\text{PrOH})_4$, which can be derived from metallic ${}^{57}\text{Fe}$, the isotopically labeled complex ${}^{57}\text{Fe}(\text{pdt})$ -(CO)₂(dppe) (${}^{57}\text{1d}$) was prepared (eqs 3 and 4). Character-

$$2^{57}\text{Fe} + 2I_2 + 4^{i}\text{PrOH} \rightarrow {}^{57}\text{Fe}_2I_4({}^{i}\text{PrOH})_4$$
(3)

$${}^{57}\text{Fe}_{2}I_{4}(^{i}\text{PrOH})_{4} + 2\text{dppe} + 2K_{2}\text{pdt} + 4\text{CO} \rightarrow$$

$${}^{2^{57}\text{Fe}(\text{pdt})(\text{CO})_{2}(\text{dppe}) + 4\text{KI} + 4^{i}\text{PrOH}}$$

$${}^{57}\text{Id} \qquad (4)$$

ization of *cis/trans*-⁵⁷**1d** included the observation of ⁵⁷Fe-³¹P coupling in the ³¹P{¹H} NMR spectrum (${}^{1}J_{PFe} = 35$ 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 =

$$Fe(xdt)(CO)_{2}(diphos) + (bda)Fe(CO)_{3}$$

$$\rightarrow Fe_{2}(xdt)(CO)_{4}(diphos) + bda + CO$$
(5)

benzylideneacetone). Thus, the reaction $1a + (bda)Fe(CO)_3$ gave the known complex $Fe_2(edt)(CO)_4(dppv)$ (2a).²⁶ The reaction occurred over the course of several hours at room temperature, giving 83% isolated yield. The complex $Fe_2(pdt)$ -(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 $Fe_2(pdt)(CO)_6.^{27,28}$ The

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complex	isomer ratio unsym:sym (20 °C)	$ u_{\rm CO} \ ({\rm cm}^{-1}) \ ({\rm THF}) $	$^{31}P{^{1}H} NMR (\delta) unsym$ isomer	J_{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)	21.1	87.7 (s)
			59.9 (d)	21.1	
$Fe(edt)(CO)_2(dppe)$ (1b)	3:1	2009 (s), 1973 (s), 1959 (s)	78.3 (d)	29.1	77.5 (s)
			48.1 (d)	29.1	
Fe(pdt)(CO) ₂ (dppv) (1c)	1:4	2010 (m), 1975 (s)	87.3 (d)	22.0	81.2 (s)
			60.4 (d)	22.1	
Fe(pdt)(CO) ₂ (dppe) (1d)	2:3	2004 (m), 1969 (s), 1958 (sh)	78.0 (d)	30.9	73.7 (s)
			51.2 (d)	30.6	
Fe(pdt)(CO) ₂ (dppbz) (1e)	1:7	2012 (m), 1970 (s)	78.5 (d)	38.6	80.8 (s)
			68.2 (d)	39.3	
Fe(pdt)(CO) ₂ (dcpe) (1f)	1:2	1990 (m), 1940 (s)	79.19 (d)	32.9	81.34 (s)
			55.8 (d)	32.9	
Fe(Me ₂ pdt)(CO) ₂ (dppe) (1g)	1:3	2006 (m), 1969 (s)	78.3 (d)	30.5	73.8 (s)
			52.6 (d)	30.8	

^{*a*}IR spectra are reported for THF, wherein signals are better resolved. ${}^{31}P{}^{1}H$ NMR spectra were recorded in CD_2Cl_2 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 $Fe_2(pdt)(CO)_4(dcpe)$ (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 $Fe_2(pdt)(CO)_6$ and dcpe gives only a low yield of 2f, highlighting the advantage of the building block method. When, however, $Fe(pdt)(CO)_2(PMe_3)_2$ was treated with $(bda)Fe(CO)_3$, the product is the known complex Fe(pdt)- $(CO)_4(PMe_3)_2$,²⁹ where the phosphine ligands are bound to different iron centers.

Synthesis of $Mn^{I}Fe^{II}$ Complexes. The salt $[(CO)_{3}Mn(pdt)Fe(CO)_{2}(dppe)]BF_{4}$ ($[3d(CO)]BF_{4}$) forms upon treatment of 1d with $[(acenaphthene)Mn(CO)_{3}]BF_{4}$, a well-known source of $Mn(CO)_{3}^{+}$ (Scheme 5).³⁰ When monitored by ${}^{31}P{}^{1}H$ 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 $[(acenaphthene)Mn(CO)_3]BF_4$ 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 $[(CO)_3Mn(pdt)Fe(CO)_2(dppbz)]BF_4$, $[(CO)_3Mn(pdt)Fe(CO)_2(dppb)]$ -

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Figure 3. ³¹P{¹H} NMR spectrum of a mixture of the two isomers of ${}^{57}\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppe})$ (CD₂Cl₂ solution). Expanded regions show the additional coupling to ${}^{57}\text{Fe}$.

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

Synthesis of Mn^IFe^{II} Hydride. Reaction of $[3d(CO)]BF_4$ with $[Bu_4N]BH_4$ results in loss of one CO ligand and formation of the neutral hydride complex $(CO)_3Mn(pdt)(\mu-H)Fe(CO)$ -(dppe) (H3d) (eq 6). The ¹H NMR spectrum of H3d consists



of a triplet at δ –12.3, indicating coupling to two equivalent phosphorus centers. The ³¹P{¹H} 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^6d^6 36e-complex (H3d is 34e-) FeMn(μ -SPh)₃(CO)₆ has been described.³² The cyclic voltammogram of H3d consists of a reversible oxidation event at 0.125 V vs Fc^{+/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 $[H(Et_2O)_2]BAr^F_4$, the ν_{CO} bands shifted by 20–50 cm⁻¹ to higher energy. Protonation of H3d was anticipated to give H₂ or a dihydrogen complex (see $[(H_2)Mn(CO)_3(dppe)]^+$).³³ Treatment of the acidified reaction mixture with Et₃N 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 complexe.³⁴ In contrast to the behavior of H3d, the closely related complex $[(\mu-H)Fe_2(pdt)-(CO)_4(dppv)]^+$ is unreactive toward $[H(Et_2O)_2]BAr^F_4$, 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 $[H3dH]^{+}$.

Reduction of Mn^IFe^{II} Complexes. The electrochemical behavior of $[3d(CO)]BF_4$ 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 $[3d(CO)]BF_4$ was treated with 1 equiv of cobaltocene, producing a new species characterized by $\nu_{\rm CO}$ 1997 and 1902 cm⁻¹. In view of the electrochemical and chemical reduction results, the initial reduction is proposed to induce decarbonylation, generating (CO)₃Mn(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 CH₂Cl₂ 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





Figure 4. ${}^{31}P{}^{1}H{}$ NMR spectra of a CD_2Cl_2 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)₃]BF₄ (diamond, unsym isomer; star, sym isomer), and (c) the same solution after 12 h.



Figure 5. Structure of $(CO)_3Mn(pdt)(\mu-H)Fe(CO)(dppe)$ (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, 1.789(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 $CpCo(CO)_2$ 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

Figure 6. IR spectra in CH_2Cl_2 of (a) $(CO)_3Mn(pdt)(\mu-H)Fe(CO)-(dppe)$ and this solution (b) after addition of 1 equiv of $H(Et_2O)_2BAr_{4}^F$, (c) after addition of 0.5 equiv of Et_3N , and (d) after addition of 1 equiv total of Et_3N .

cm⁻¹

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)]⁺ (ν_{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).

$$CpCoI_{2}(CO) + Fe(pdt)(CO)_{2}(dppe)$$

$$\rightarrow [CpCoI(pdt)Fe(CO)(dppe)]I + 2CO$$
(7)

$$[CpCoI(pdt)Fe(CO)(dppe)]I + 2Cp_2Co$$

$$\rightarrow CpCo(pdt)Fe(CO)(dppe) + 2Cp_2CoI$$
4d
(8)

These CoFe complexes are analogues of $Fe_2(S_2C_nH_{2n})$ -(CO)₄(dppx), in which CpCo replaces the Fe(CO)₃ center.

Like the corresponding diiron complexes, **4d** oxidizes reversibly, at a potential $(-0.6 \text{ V vs Fc}^{+/0})$ between those for $Fe_2(pdt)(CO)_2(dppv)_2$ (-0.19 V) and $Fe_2(pdt)(CO)_4(dppv)$ $(-0.94 \text{ V}).^{26,35}$ 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 CpCo(edt)Fe(CO)(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 FeP₂ plane relative to the FeS₂ plane.

The ³¹P{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 pdt²⁻ backbone. Using an internal integration standard, >90% of the sample was verified to be in solution at -90 °C.

Co^{III}Fe^{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 ³¹P{¹H} and ¹H NMR spectra indicate that the hydride complex is C_s -symmetric. On the basis of its chemical shift and $J(^{31}P,^{1}H)$ 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 δ -9.0 and δ 70.7 in the ¹H and ³¹P{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.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. $^{31}P\{^{1}H\}$ NMR spectra of a CD₂Cl₂ solution of 4d and 1 equiv of $[H(OEt_2)_2]BAr^F_4$. The solution was prepared at $-85\ ^\circ C$ and then warmed to the indicated temperatures.



Figure 9. ¹H NMR spectra of a CD_2Cl_2 solution of 4d and 1 equiv of $[H(OEt_2)_2]BAr^F_4$. 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 dithiolate complexes described above. The new synthesis of Fe₂(pdt)-(CO)₄(dppe) avoids side reactions that hamper the installation of flexible chelating ligands.^{27,28} Related complexes can be prepared via FeX₂(CO)₄.^{14,37} The new routes are potentially appealing because the iron complexes are derived from FeCl₂.⁸ Conveniently available sources of ⁵⁷Fe are easily converted to the dichloride and ⁵⁷Fe₂I₄(ⁱPrOH)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 ⁵⁷Fe (*I* = $-^{1}/_{2}$) into ferrous carbonyl building blocks, as illustrated by the synthesis of ⁵⁷Fe(pdt)(CO)₂(dppe). Interest in ⁵⁷Fe 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 $[(CO)_3Mn(pdt)Fe(CO)_2(dpe)]^+$ is its tendency to decarbonylate upon 1e-reduction. The resulting complex, $(CO)_3Mn(pdt)Fe(CO)(dppe)$, is electronically related to the mixed-valence "H_{ox}-models" $[Fe_2(pdt)-(CO)_{6-x}L_x]^+$.³⁹ Similarly, the hydride $(CO)_3Mn(pdt)HFe(CO)(dppe)$, which was characterized crystallographically, is isoelectronic with $[HFe_2(pdt)(CO)_4(dppe)]^+$.²⁸ The MnFe complex is sufficiently electron rich that it undergoes a mild one-electron oxidation (~0.1 V vs 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 $(CO)_3Fe(pdt)Ni(dppe)$ from $FeI_2(CO)_4$ + Ni(pdt)(dppe) followed by reduction.⁴¹ The complexes CpCo(dithiolate)Fe(CO)(diphos) are electronically related to $Fe_2(dithiolate)(CO)_4(diphos)$, both being of d^7d^7 configuration. Like $Fe^{I}Fe^{I}$ dithiolates, the Co^{II}Fe^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 μ m, 230–400 mesh) as the stationary phase. K₂pdt,⁴² [(acenaphthene)Mn(CO)₃]BF4,³⁰ ⁵⁷Fe₂I₄(ⁱPrOH)4,⁴³ and CpCo(CO)I₂⁴⁴ were prepared according to the literature methods. ESI-MS data were recorded on dilute CH₂Cl₂ 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 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(pdt)(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 60 mL of THF. The solution changed from pale orange to green and then to dark orange, signaling formation of $FeCl_2(CO)_2(dppe)$. Separately, 1.71 mL (17.0 mmol) of C₃H₆(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 Na2S2C3H6 was added to the solution of $FeCl_2(CO)_2(dppe)$. 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 CH₂Cl₂ and purified by flash column chromatography on a 4×50 cm column of silica gel. After a yellow band eluted with CH2Cl2, the red band containing the product eluted with 5/1 CH₂Cl₂/Et₂O. Evaporation of solvent from this band afforded 1d as a red solid. Yield: 3.34 g (36%). ¹H NMR (CD₂Cl₂): δ 7.89–7.32 (m, 20H, C₆H₅), 2.63 (m, 4H, PCH₂), 2.50 (d, 4H, SCH₂), 1.97 (m, 2H, SCH₂CH₂). IR (CH₂Cl₂): 2010, 1968. Anal. Calcd for C31H30FeO2P2S2.0.3CH2Cl2 (found): C, 58.56 (58.24); H, 4.80 (4.7).

Fe(edt)(CO)₂(dppv) (1a). Conducted as for 1d. Yield: 12-50%. ¹H NMR (CD₂Cl₂): δ 8.14–7.32 (m, 20H, C₆H₅), 2.53 (s, 2H, CH₂), 2.46 and 2.02 (d each, 1:1 H, CH₂), 2.18 and 0.21 (t each, 1:1 H, CH). IR (CH₂Cl₂): 2013 (s), 1978 (s), 1960 (s). Anal. Calcd for C₃₀H₂₆FeO₂P₂S₂·0.5CH₂Cl₂ (found): C, 56.98 (57.35); H, 4.23 (4.17). **Fe(edt)(CO)₂(dppe) (1b).** Conducted as for 1d. Yield: 50%. ¹H NMR (CD₂Cl₂): δ 7.87–7.27 (m, C₆H₅), 2.62 (s, 4H, S CH₂, sym), 2.50 (s, 4H, PCH₂, sym), 2.78 (d 2H PCH₂, unsym), 2.16 (d 2H PCH₂, unsym), 1.22 (s, 3H, SCH₂, unsym), 0.34 (s, 1H, SCH₂, unsym). IR (THF): 2009 (s), 1973 (s), 1959 (s). Anal. Calcd for C₃₀H₂₈FeO₂P₂S₂ (found): C, 59.81 (59.78); H, 4.68 (5.0).

Fe(pdt)(CO)₂(dppv) (1c). Conducted as for 1d, but the column was eluted with 10/1 CH₂Cl₂/Et₂O. Yield: 78%. ¹H NMR (CD₂Cl₂): δ 7.94–7.32 (m, 20H, C₆H₃), 2.44 (d, 4H, CH₂), 1.96 (d, 2H, SCH₂). IR (CH₂Cl₂): 2014, 1975. Anal. Calcd for C₃₁H₂₈FeO₂P₂S₂·0.7CH₂Cl₂ (found): C, 56.49 (56.50); H, 4.40 (4.40).

Fe(pdt)(CO)₂(dppbz) (1e). Under a CO atmosphere, a solution of 0.50 g of FeCl₂ (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 FeCl₂(CO)₂(dppbz). Separately, 181 µL (4.33 mmol) of $C_{3}H_{6}(SH)_{2}$ and 188 mg (7.88 mmol) of NaH were combined in 15 mL of THF. After 1 h, the resulting solution of Na₂S₂C₃H₆ was added to the solution of FeCl₂(CO)₂(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 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, C₆H₅ and C₆H₄), 2.39 (s, 4H, SCH₂CH₂), 1.94 (s, 2H, SCH₂CH₂). IR (CH₂Cl₂): 2012, 1970. Anal. Calcd for C35H30FeO2P2S2.0.2CH2Cl2 (found): C, 62.03 (62.22); H, 4.5 (4.83).

Fe(pdt)(CO)₂(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 °C, resulting in the formation of dark red crystals. Yield: 430 mg (35%). IR (CH₂Cl₂): 1997 (w), 1945 (s). Anal. Calcd for $C_{31}H_{54}FeO_2P_2S_2\cdot0.2CH_2Cl_2$ (found): C, 56.98 (56.94); H, 8.34 (8.71).

 57 Fe₂I₄(ⁱPrOH)₄. This complex was obtained as a green powder in 95% yield analogously to the published method for Fe₂I₄(ⁱPrOH)₄,⁴³ using 57 Fe as the precursor. ESI-MS: m/z 674.8 [M - ⁱPrOH - I⁻]⁺, 364.1 [M - ⁱPrOH - 57 Fe²⁺ - 3I⁻]⁺. Anal. Calcd for C₁₂H₃₂O₄I₄ 57 Fe₂ (found): C, 16.72 (16.16); H, 3.74 (3.44); N, 0.00 (0.00).

 57 Fe(pdt)(CO)₂(dppe) (57 1d). A mixture of 86.2 mg (100 μ mol) of $^{57}\mathrm{Fe_2I_4(^iPrOH)_4}$ and 79.7 mg (200 $\mu\mathrm{mol})$ of dppe in 6 mL of 1/1 ⁱPrOH/THF was stirred under 1 atm of CO. The suspension, which had developed a red color, was treated with 36.8 mg (200 μ mol) of K₃pdt in 3 mL of ⁱPrOH. 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 \times 5 mL of CH₂Cl₂, and these extracts were concentrated to ~0.5 mL and chromatographed on a ~5 cm column of silica gel, with CH₂Cl₂ as eluent. The second band, deep red, was collected, concentrated to ~ 2 mL, and treated with 10 mL of Et₂O. 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 °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 μ mol, 19%). ³¹P{¹H} NMR (CH₂Cl₂): δ 76.2 (dd, ¹J_{PFe} = 35, ²J_{PP} = 32, cis isomer), 71.8 (d, ${}^{1}J_{PFe}$ = 38, trans isomer), 49.2 (dd, ${}^{1}J_{PFe}$ = 35, ${}^{2}J_{PP}$ = 32, cis isomer). FTIR (CH₂Cl₂): 2010 (cis), 1969 (overlapping cis/trans). ESI-MS: m/z 618.2 $[M + H^+]^+$ (similar analysis for the unlabeled complex gave m/z 617.1).

Fe(Me₂pdt)(CO)₂(dppe) (1g). Conducted as for 1d. Yield: 1.03 g (40%). ¹H NMR (CD₂Cl₂): δ 7.4–7.8 (m, 20H, C₆H₅), 2.65 (dd, 4H, P₂CH₂CH₂), 2.23 (s, 4H, SCH₂), 1.01 (s, 6H, CCH₃). IR (CH₂Cl₂): 2006 (w), 1969 (s). Anal. Calcd for C₃₃H₃₄FeO₂P₂S₂·0.2CH₂Cl₂ (found): C, 60.28 (60.0); H, 5.24 (5.41).

Fe₂(edt)(CO)₄(dppv) (2a) from 1a. A mixture of **1a** (125 mg, 0.208 mmol) and 50 mg (0.208 mmol) of (bda)Fe(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 $\nu_{\rm CO}$ bands for (bda)Fe(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 ³¹P{¹H} NMR spectra of the product match reported data.²⁶

 $Fe_2(pdt)(CO)_4(dppe)$ (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.²⁸

Fe₂(pdt)(CO)₄(dcpe) (2f) from 1f. A 5 mL solution of (bda)Fe(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%). ³¹P{¹H} NMR (CD₂Cl₂): δ 89.27 (s), apical–basal; 74.90 (s), dibasal. IR (CH₂Cl₂): 2013 (s), 1939 (br), 1882 (br).

[(CO)₃Mn(pdt)Fe(CO)₂(dppe)]BF₄ ([3(CO)]BF₄). A solution of 500 mg (1.32 mmol) of [(acenaphthene)Mn(CO)₃]BF₄ in 125 mL of CH_2Cl_2 was treated with a solution of 810 mg (1.32 mmol) of 1b in 50 mL of CH₂Cl₂. 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 CH₂Cl₂, 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 CH₂Cl₂ solution with pentane. ¹H NMR (CD₂Cl₂): δ 7.41-7.80 (m, 20H, C₆H₅), 3.50 (m, 2H, PCH₂), 3.28 (m, 2H, PCH₂), 3.08 (m, 2H, SCH₂), 2.84 (m, 3H, SCH₂CH₂), 2.03 (m, 1H, SCH₂CH₂). ³¹P{¹H} NMR (CD₂Cl₂): δ 58 (s). IR (CH₂Cl₂): 2053 (w), 2027 (s), 1992 (s), 1974 (s), 1905 (br). Anal. Calcd for C₃₄H₃₀BF₄FeMnO₅P₂S₂ (found): C, 48.48 (48.66); H, 3.59 (3.81)

(CO)₃Mn(pdt)(µ-H)Fe(CO)(dppe) (H3). A solution of 590 mg (0.70 mmol) of $[3(CO)]BF_4$ 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 [Bu₄N]BH₄ in 60 mL of CH₂Cl₂ 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 (CD₂Cl₂): δ 7.38-7.84 (m, 20H, C₆H₅), 2.76 (m, 4H, PCH₂), 2.58 (m, 2H, SCH₂), 2.41 (m, 3H, SCH₂CH₂), 1.91 (m, 1H, SCH₂CH₂), -12.26 (t, 1H, Mn-H-Fe). ³¹P{¹H} NMR (CD₂Cl₂): δ 80.80 (s). IR (CH₂Cl₂): 2002 (s), 1935 (br), 1905 (br). Anal. Calcd for C₃₃H₃₁FeMnO₄P₂S₂ (found): C, 54.41 (54.35); H, 4.29 (4.49).

(CO)₃Mn(pdt)Fe(CO)(dppe). A solution of $[4d(CO)]BF_4$ (71 mg, 84 μ mol) in THF (10 mL) was treated with a THF solution of Cp₂Co (16 mg, 84 μ mol). The solution was filtered through Celite, and then the solvent was removed under vacuum to yield a red solid. Yield: 46 mg (75%). IR (CH₂Cl₂): 1997 (s), 1902 (s). Anal. Calcd for C₃₃H₃₀FeMnO₄P₂S₂ (found): C, 54.49 (54.54); H, 4.16 (4.55).

CpCo(edt)Fe(CO)(dppv) (4a) from CpCol₂(CO). A mixture of **1a** (100 mg, 0.17 mmol) and CpCo(CO)I₂ (68 mg, 0.17 mmol) was

stirred in CH₂Cl₂ (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 Cp₂Co (68 mg, 0.36 mmol) in 20 mL of CH₂Cl₂. 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 CH₂Cl₂ and pentane as eluent and gradually increasing the CH₂Cl₂ content. After an initial green band, the product eluted as a brown band using CH₂Cl₂. Evaporation of the solution gave the brown product. Yield: 45 mg (39%). ¹H NMR (CD₂Cl₂, 23 °C): δ 8.30–7.12 (m, 20 H, C₆H₅), 4.75 (s, 2 H, PCH), 3.36 (s, 5 H, C₅H₅), 2.26 and 1.84 (d each, 2 H each, SCH₂). ³¹P{¹H} NMR (CD₂Cl₂, 23 °C): δ 93.56 (s). IR (CH₂Cl₂): 1890.

CpCo(edt)Fe(CO)(dppv) from CpCo(CO)₂. A mixture of **1a** (200 mg, 0.34 mmol) and CpCo(CO)₂ (92 μ L, 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 Et₂O. The brown residue was extracted into ~4 mL of CH₂Cl₂, and the extract was layered with 10 mL of hexane. Dark brown crystals of **4a** formed overnight. Yields were variable. Anal. Calcd for C₃₄H₃₁CoFeOP₂S₂ (found): C, 58.63 (58.12); H, 4.49 (4.37). IR (CH₂Cl₂): 1890.

CpCo(pdt)Fe(CO)(dppv) (4c). A mixture of 1c (200 mg, 0.32 mmol) and CpCo(CO)₂ (67 μ L, 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 4b upon standing overnight. ¹H NMR (CD₂Cl₂, 23 °C): δ 8.17–7.30 (m, 20 H, C₆H₅), 3.51 (s, 5 H, C₅H₅), 2.30 and 2.20 (d each, 2 H each, SCH₂), 1.87 (m, 2 H, SCH₂CH₂). ³¹P{¹H} NMR (CD₂Cl₂, 23 °C): δ 90.17 (s). IR (CH₂Cl₂): 1885.

CpCo(pdt)Fe(CO)(dppe) (4d) from CpCol₂(CO). A solution of Fe(pdt)(CO)₂(dppe) (50 mg, 0.08 mmol) and CpCo(CO)I₂ (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 Cp₂Co (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 gave the product as a brown band, which was evaporated to leave a brown solid. Yield: 23 mg (40%). ¹H NMR (CD₂Cl₂, 23 °C): δ 7.82–7.29 (m, 20 H, C₆H₅), 3.84 (s, 5 H, C₅H₅), 2.98 (m, 2 H, PCH₂), 2.58 and 2.26 (m each, 2 H each, SCH₂), 2.17 and 1.89 (m each, 1 H each, PCH₂), 1.47 (m, 2 H, S(CH₂)₂CH₂). ³¹P{¹H</sup> NMR (CD₂Cl₂, 23 °C): δ 83.48 (s). IR (CH₂Cl₂): 1880.

CpCo(pdt)Fe(CO)(dppe) (4d) from CpCo(CO)₂. A mixture of 1d (200 mg, 0.32 mmol) and $CpCo(CO)_2$ (67 μ L, 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 CH₂Cl₂. This extract was layered with 10 mL of hexane to yield dark brown crystals of 4d upon standing overnight. Yields were variable. ¹H NMR (CD₂Cl₂, 23 °C): δ 7.82-7.29 (m, 20 H, C₆H₅), 3.84 (s, 5 H, C₅H₅), 2.98 (m, 2 H, PCH₂), 2.56 and 2.25 (m each, 2 H each, SCH₂), 2.18 and 1.87 (m each, 1 H each, PCH₂), 1.51 (m, 2 H, CH₂SCH₂). ³¹P{¹H} NMR (CD₂Cl₂, 23 °C): δ 85.54 (s). Anal. Calcd for C₃₅H₃₅CoFeOP₂S₂ (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 (CD₂Cl₂, 23 °C): δ 7.73–7.35 (m, 20 H, C₆H₅), 3.61 (s, 5 H, C₅H₅), 2.98 (m, 2 H, PCH₂), 2.56 and 2.25 (m each, 2 H each, SCH₂), 2.18 and 1.87 (m each, 1 H each, PCH₂), 1.51 (m, 2 H, S(CH₂)₂CH₂).

³¹P{¹H} NMR (CD₂Cl₂, 23 °C): δ 85.54 (s). Data for the low-temperature intermediate, apical-basal μ -hydride are as follows. ¹H NMR (CD₂Cl₂, 23 °C): δ 7.82–7.29 (m, 20 H, C₆H₅), 3.84 (s, 5 H, C₅H₅), 2.98 (m, 2 H, PCH₂), 2.56 and 2.25 (m each, 2 H each, SCH₂), 2.18 and 1.87 (m each, 1 H each, PCH₂), 1.51 (m, 2 H, CH₂SCH₂). ³¹P{¹H} NMR (CD₂Cl₂, 23 °C): δ 85.54 (s).

Low-Temperature Protonation of CpCo(pdt)Fe(CO)(dppe) (4d). In a J. Young NMR tube, $\sim 1 \text{ mL}$ of CD_2Cl_2 was distilled and frozen onto 4d (5 mg, 0.007 mmol) and [H(OEt₂)₂]BAr^F₂₄ (8.5 mg, 0.008 mmol) in a liquid-N2 bath. The sample was then thawed, placed in an NMR spectrometer (probe precooled to -85 °C), and analyzed by NMR spectroscopy. ¹H NMR (CD₂Cl₂, -85 °C): δ 3.61 (s, C₅H₅, [term-H4d]⁺); -9.0 (s, Co-H, [term-H4d]⁺). ³¹P{¹H} NMR (CD₂Cl₂, -85 °C): δ 70.65 (s, [term-H4d]⁺). When the sample was warmed to -50 °C, the NMR spectra indicated the presence of two new species. ¹H NMR (CD₂Cl₂, -50 °C): δ 3.61 (s, C_5H_5 , [term-H4d]⁺); -9.0 (s, Co-H, $[term-H4d]^+$; 5.29 (s, C₅H₅, a,b- $[\mu-H4d]^+$); -14.68 (d, $J_{P-H} =$ 30, Co-H-Fe, a,b- $[\mu$ -H4d]⁺); 4.69 (s, C₅H₅, b,b- $[\mu$ -H4d]⁺); -15.48 (t, $J_{P-H} = 25$, Co-H-Fe, b,b- $[\mu$ -H4d]⁺). ³¹P{¹H} NMR (CD₂Cl₂, -50 °C): δ 70.65 (s, [term-H4d]⁺); 88.17, 85.58 (d, a,b-[μ-H4d]⁺); 85.3 (s, b,b-[μ -H4d]⁺). When the sample was warmed above -20 °C, the signals for $[term-H4d]^+$ in the ¹H and ³¹P{¹H} NMR spectra disappeared. At room temperature, a,b- $[\mu$ -H4d]⁺ converts entirely to b,b-[µ-H4d]⁺

[CpCo(edt)(H)Fe(CO)(dppv)]BF₄ **([H4a]BF**₄**).** A solution of 4a (20 mg, 0.03 mmol) in CH₂Cl₂ (10 mL) was treated with 2 equiv of HBF₄·Et₂O. The mixture was stirred for 15 min. The volume was then reduced under vacuum, and Et₂O was added to precipitate a brown powder. ¹H NMR (400 MHz, CD₂Cl₂, 25 °C): δ 8.50–7.26 (m, 20 H, C₆H₅), 4.31 (s, 5 H, C₅H₅), 3.06 and 2.70 (d each, 2 H each, SCH₂), -18.14 (t, *J*_{PH} = 26.8, 1H, Co-*H*-Fe). ³¹P{¹H} NMR (CD₂Cl₂, 23 °C): δ 89.72 (d). IR (CH₂Cl₂): 1975.

[CpCo(pdt)(H)Fe(CO)(dppe)]BF₄ ([H4d]BF₄). A solution of 4d (20 mg, 0.03 mmol) in CH₂Cl₂ (10 mL) was treated with 2 equiv of HBF₄·Et₂O. After it was stirred for 15 min, the solution was concentrated and then diluted with Et₂O to precipitate a brown powder. ¹H NMR (CD₂Cl₂, 25 °C): δ 7.66–7.30 (m, 20H, C₆H₅), 4.79 (s, 5H, C₅H₅), 3.30 (m, 2H, PCH₂), 3.01 and 2.71 (m each, 2H each, SCH₂), 2.61 (m, 1H, PCH₂), 2.15 (m, 3H, PCH₂ and CH₂SCH₂), -15.19 (t, J_{PH} = 27, 1H, Co-H-Fe). ³¹P{¹H} NMR (CD₂Cl₂, 25 °C): δ 82.91 (d). Anal. Calcd for C₃₅H₃₆BCoF₄FeOP₂S₂. 0.2CH₂Cl₂ (found): C, 51.73 (51.90); H, 4.49 (4.61). IR (CH₂Cl₂): 1962.

ASSOCIATED CONTENT

Supporting Information

Figures giving ¹H NMR, ³¹P{¹H} 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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