

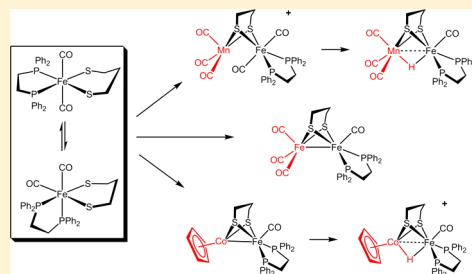
# Ferrous Carbonyl Dithiolates as Precursors to FeFe, FeCo, and FeMn Carbonyl Dithiolates

Maria E. Carroll, Jinzhu Chen, Danielle E. Gray, James C. Lansing, Thomas B. Rauchfuss,\* David Schilter, Phillip I. Volkers, and Scott R. Wilson

Department of Chemistry, University of Illinois, Urbana, Illinois 61801, United States

## S Supporting Information

**ABSTRACT:** Reported are complexes of the formula Fe(dithiolate)(CO)<sub>2</sub>(diphos) and their use to prepare homo- and heterobimetallic dithiolato derivatives. The starting iron dithiolates were prepared by a one-pot reaction of FeCl<sub>2</sub> and CO with chelating diphosphines and dithiolates, where dithiolate = S<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub><sup>2-</sup> (edt<sup>2-</sup>), S<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub><sup>2-</sup> (pdt<sup>2-</sup>), S<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>(C(CH<sub>3</sub>)<sub>2</sub>)<sup>2-</sup> (Me<sub>2</sub>pdt<sup>2-</sup>) and diphos = *cis*-C<sub>2</sub>H<sub>2</sub>(PPh<sub>2</sub>)<sub>2</sub> (dppv), C<sub>2</sub>H<sub>4</sub>(PPh<sub>2</sub>)<sub>2</sub> (dppe), C<sub>6</sub>H<sub>4</sub>(PPh<sub>2</sub>)<sub>2</sub> (dppbz), C<sub>2</sub>H<sub>4</sub>[P(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>]<sub>2</sub> (dcpe). The incorporation of <sup>57</sup>Fe into such building block complexes commenced with the conversion of <sup>57</sup>Fe into <sup>57</sup>Fe<sub>2</sub>I<sub>4</sub>(<sup>1</sup>PrOH)<sub>4</sub>, which then was treated with K<sub>2</sub>pdt, CO, and dppe to give <sup>57</sup>Fe(pdt)(CO)<sub>2</sub>(dppe). NMR and IR analyses show that these complexes exist as mixtures of all-*cis* and trans-CO isomers, edt<sup>2-</sup> favoring the former and pdt<sup>2-</sup> the latter. Treatment of Fe(dithiolate)(CO)<sub>2</sub>(diphos) with the Fe(0) reagent (benzylideneacetone)Fe(CO)<sub>3</sub> gave Fe<sub>2</sub>(dithiolate)(CO)<sub>4</sub>(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)<sub>2</sub>(dppe) with [(acenaphthene)Mn(CO)<sub>3</sub>]<sup>+</sup> gave [(CO)<sub>3</sub>Mn(pdt)Fe(CO)<sub>2</sub>(dppe)]<sup>+</sup> ([3d(CO)]<sup>+</sup>). Reduction of [3d(CO)]<sup>+</sup> with BH<sub>4</sub><sup>-</sup> gave the C<sub>s</sub>-symmetric μ-hydride (CO)<sub>3</sub>Mn(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)<sub>2</sub>(diphos) with CpCoI<sub>2</sub>(CO) followed by reduction by Cp<sub>2</sub>Co affords CpCo(dithiolate)Fe(CO)(diphos) (4), which can also be prepared from Fe(dithiolate)(CO)<sub>2</sub>(diphos) and CpCo(CO)<sub>2</sub>. Like the electronically related (CO)<sub>3</sub>Fe(pdt)Fe(CO)(diphos), these complexes undergo protonation to afford the μ-hydrido complexes [CpCo(dithiolate)-HFe(CO)(diphos)]<sup>+</sup>. Low-temperature NMR studies indicate that Co is the kinetic site of protonation.

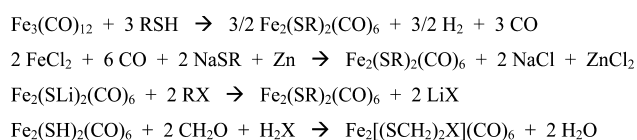


## INTRODUCTION

Compounds of the type Fe<sub>2</sub>(SR)<sub>2</sub>(CO)<sub>6-x</sub>L<sub>x</sub> are topical because of their relationship to the active sites of the [FeFe]-hydrogenases (H<sub>2</sub>ases).<sup>1</sup> The quest for a deeper understanding of the enzyme mechanism, as well as interest in base metal H<sub>2</sub>-processing catalysts,<sup>2</sup> has led chemists to prepare many examples of these dithiolates.<sup>3</sup> Since the [NiFe]-H<sub>2</sub>ases feature related Ni(SR)<sub>2</sub>Fe(CO)L<sub>2</sub> 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<sub>2</sub>(SR)<sub>2</sub>(CO)<sub>6-x</sub>L<sub>x</sub> are prepared by ligand (L) substitution of hexacarbonyls Fe<sub>2</sub>(SR)<sub>2</sub>(CO)<sub>6</sub>,<sup>4</sup> which in turn are obtained by treating Fe<sub>3</sub>(CO)<sub>12</sub> with thiols. Complementarily, Fe<sub>2</sub>(S<sub>2</sub>)(CO)<sub>6</sub><sup>5</sup> is an ideal precursor to diiron complexes<sup>6</sup> of more elaborate organosulfur ligands.<sup>7</sup> 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).<sup>8</sup> The method, which proceeds in at least modest yields, is suited for generating <sup>57</sup>Fe-labeled derivatives, which are of interest for nuclear resonance vibrational spectroscopy (NRVS)<sup>9</sup> and Mössbauer measurements.<sup>10</sup>

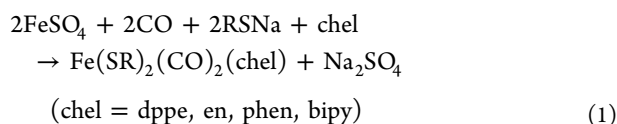
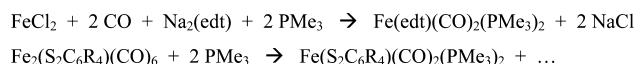
## Scheme 1. Illustrative Routes to Fe<sub>2</sub>(SR)<sub>2</sub>(CO)<sub>6</sub><sup>4,8,11</sup>



Promising precursors to dimetallic dithiolato complexes are monoiron complexes of the type Fe(dithiolate)(CO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>. These compounds should be obtainable from complexes of the form FeX<sub>2</sub>(CO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>,<sup>12–14</sup> 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<sup>15,16</sup> (eq 1). Routes to ferrous dithiolato carbonyls have been established in the case of Fe(edt)(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (edt<sup>2-</sup> = ethanedithiolate)<sup>17</sup> and related complexes containing bidentate phosphine ligands (Scheme 2).<sup>18</sup> The benzenedithiolates Fe(S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>X<sub>2</sub>)(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> (X = H, Cl) are formed from diiron dithiolato precursors,<sup>19</sup> which undergo cleavage upon treatment with PMe<sub>3</sub>. With regard to structure, complexes of the type FeX<sub>2</sub>(CO)<sub>2</sub>(chel) exist in

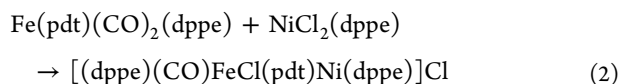
Received: July 28, 2013

Published: February 3, 2014


**Scheme 2. Synthetic Routes to Fe(dithiolate)(CO)<sub>2</sub>L<sub>2</sub>**


various isomeric forms.<sup>13,20</sup> Fe(SPh)<sub>2</sub>(CO)<sub>2</sub>(dppe) crystallizes as the all-*cis* isomer.<sup>15</sup> Complexes of formula FeX<sub>2</sub>(CO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>, in which all the ligands are monodentate, exist as both the *cis,cis,trans* and all-*trans* isomers, depending on the phosphine ligand.<sup>21</sup>

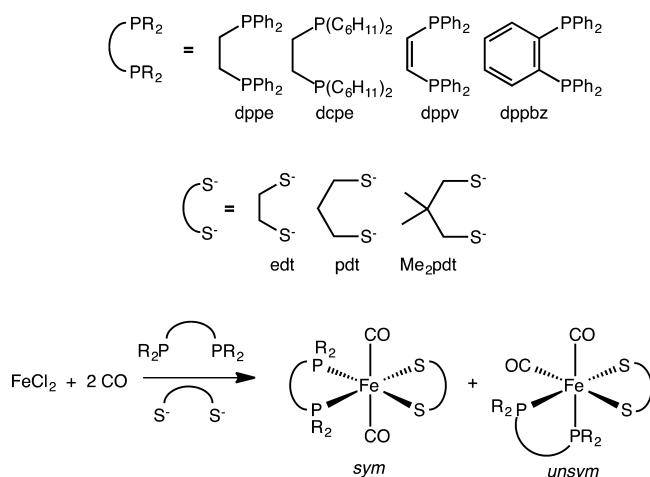
Ferrous carbonyl thiolates have been examined as metal-ligands, analogous to the use of metal dithiolates to prepare diverse dithiolato-bridged dimetallic complexes.<sup>22</sup> Thiolates retain significant basicity even when bound to a metal, as evidenced by the formation of adducts of Fe-(SPh)<sub>2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



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.<sup>24</sup> The new compounds and new synthetic routes demonstrate the broad scope for first-row analogues of the active sites of the [FeFe]- and [NiFe]-H<sub>2</sub>ases.

## RESULTS

**Ferrous Dithiolato Carbonyls.** New diphosphine-substituted ferrous carbonyl dithiolates were prepared by carbonylation of a slurry of anhydrous FeCl<sub>2</sub> and the diphosphine ligand, followed by the addition of the sodium dithiolate (Scheme 3). The reaction affords a mixture of the two isomers

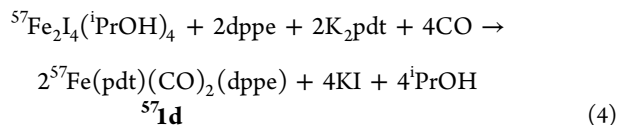
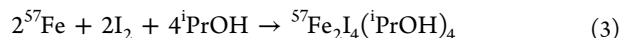
**Scheme 3. Main Route to Fe(dithiolate)(CO)<sub>2</sub>(diphosphine)**


possible for an octahedral complex of type M(chel)(chel')L<sub>2</sub>. The complex FeCl<sub>2</sub>(CO)<sub>2</sub>(dppe)<sup>13</sup> 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)<sub>3</sub>(dppe) and pdtH<sub>2</sub> did not proceed.

Spectroscopic measurements on the new compounds indicate the presence of two isomers, with the <sup>31</sup>P{<sup>1</sup>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<sup>2-</sup>) complexes **1a,b**, the unsymmetrical isomer is the major species, whereas the symmetrical isomers predominate for complexes of 1,3-propanedithiolate (pdt<sup>2-</sup>) and 2-dimethyl-1,3-propanedithiolate (Me<sub>2</sub>pdt<sup>2-</sup>), **1c–f**. (Table 1, Scheme 3). The IR spectra of the edt<sup>2-</sup> complexes **1a,b** exhibit two or three bands in the ν<sub>CO</sub> region. The pair of bands at ~2000 and 1960 cm<sup>-1</sup> is assigned to the unsymmetrical isomer, and one band at 1970 cm<sup>-1</sup> is assigned to the symmetrical *trans*-dicarbonyl isomer. The complex Fe(pdt)(CO)<sub>2</sub>(dcpe) (**1f**) was also prepared. As with the other pdt<sup>2-</sup> complexes, it exists as a mixture of symmetrical and unsymmetrical isomers. Relative to the dppe analogue **1b**, the ν<sub>CO</sub> bands for **1f** are shifted by 20 cm<sup>-1</sup> to lower energy. Unlike complexes **1a–g**, Fe(edt)-(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> is present in solution as a single isomer with mutually *trans* PMe<sub>3</sub> ligands.<sup>17</sup> The IR spectrum of solid **1d** indicates that the *trans* isomer dominates, which is also the predominant isomer in THF solution.

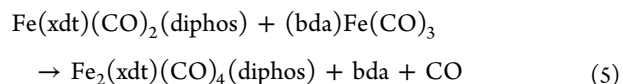
Diffraction-quality crystals of **1a** and **1c** were obtained, and the molecular structures were determined by X-ray crystallography (Figures 1 and 2). In both cases, the major solution isomer crystallized.

Starting from <sup>57</sup>Fe<sub>2</sub>I<sub>4</sub>(<sup>i</sup>PrOH)<sub>4</sub>, which can be derived from metallic <sup>57</sup>Fe, the isotopically labeled complex <sup>57</sup>Fe(pdt)-(CO)<sub>2</sub>(dppe) (**571d**) was prepared (eqs 3 and 4). Character-



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

**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 =

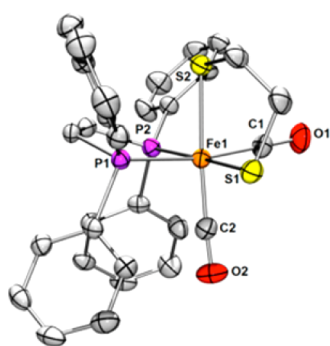


benzylideneacetone). Thus, the reaction **1a** + (bda)Fe(CO)<sub>3</sub> gave the known complex Fe<sub>2</sub>(edt)(CO)<sub>4</sub>(dppv) (**2a**).<sup>26</sup> The reaction occurred over the course of several hours at room temperature, giving 83% isolated yield. The complex Fe<sub>2</sub>(pdt)-(CO)<sub>4</sub>(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<sub>2</sub>(pdt)(CO)<sub>6</sub>.<sup>27,28</sup> The

Table 1. Spectroscopic Data for Ferrous Carbonyl Complexes<sup>a</sup>

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

<sup>a</sup>IR spectra are reported for THF, wherein signals are better resolved. <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded in CD<sub>2</sub>Cl<sub>2</sub> solution, but isomer ratios were similar in THF solution.

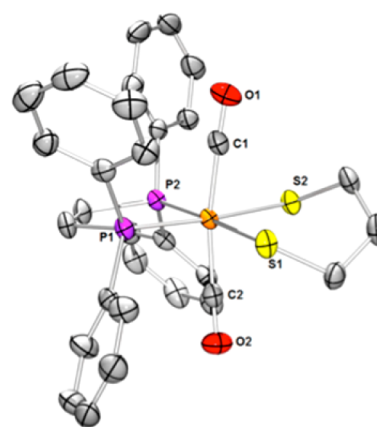


**Figure 1.** Structure of the unsymmetrical isomer of Fe(edt)(CO)<sub>2</sub>(dppv) (**1a**). Thermal ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted for clarity. Key distances (Å) and angles (deg): Fe1–C1, 1.777(3); Fe1–C2, 1.790(3); Fe1–P2, 2.2304(8); Fe1–P1, 2.2648(7); 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).<sup>27,28</sup>

The reaction of the dcpe complex **1f** with (bda)Fe(CO)<sub>3</sub> afforded Fe<sub>2</sub>(pdt)(CO)<sub>4</sub>(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<sub>2</sub>(pdt)(CO)<sub>6</sub> and dcpe gives only a low yield of **2f**, highlighting the advantage of the building block method. When, however, Fe(pdt)(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> was treated with (bda)Fe(CO)<sub>3</sub>, the product is the known complex Fe(pdt)(CO)<sub>4</sub>(PMe<sub>3</sub>)<sub>2</sub>,<sup>29</sup> where the phosphine ligands are bound to different iron centers.

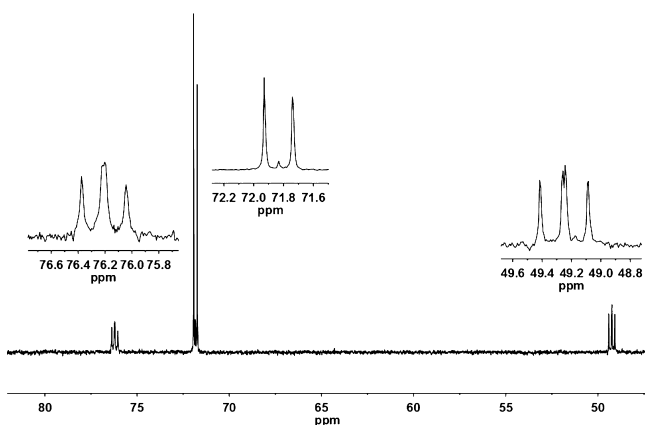
**Synthesis of Mn<sup>II</sup>Fe<sup>II</sup> Complexes.** The salt [(CO)<sub>3</sub>Mn(pdt)Fe(CO)<sub>2</sub>(dppe)]BF<sub>4</sub> (**3d**(CO)]BF<sub>4</sub>) forms upon treatment of **1d** with [(acenaphthene)Mn(CO)<sub>3</sub>]BF<sub>4</sub>, a well-known source of Mn(CO)<sub>3</sub><sup>+</sup> (Scheme 5).<sup>30</sup> When monitored by <sup>31</sup>P{<sup>1</sup>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)<sub>2</sub>(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  $\delta$  48 and 76) and a symmetrical species (singlet at  $\delta$  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.<sup>31</sup>

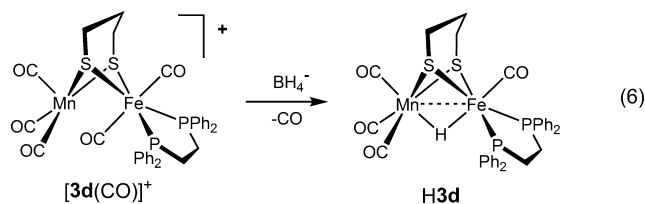
Analogous complexes featuring different dithiolate and diphosphine ligands were also examined. Reaction of [(acenaphthene)Mn(CO)<sub>3</sub>]BF<sub>4</sub> with the ethanedithiolate **1b** afforded a mixture of isomers even after extended time for equilibration. The result is not surprising, since edt<sup>2-</sup> vs pdt<sup>2-</sup> affects the isomer ratio in **1b** and **1d**. The complexes [(CO)<sub>3</sub>Mn(pdt)Fe(CO)<sub>2</sub>(dppbz)]BF<sub>4</sub>, [(CO)<sub>3</sub>Mn(pdt)Fe(CO)<sub>2</sub>(dcpe)]BF<sub>4</sub>, and [(CO)<sub>3</sub>Mn(Me<sub>2</sub>pdt)Fe(CO)<sub>2</sub>(dppe)]-



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

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

**Synthesis of  $\text{Mn}^{\text{I}}\text{Fe}^{\text{II}}$  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  $^1\text{H}$  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

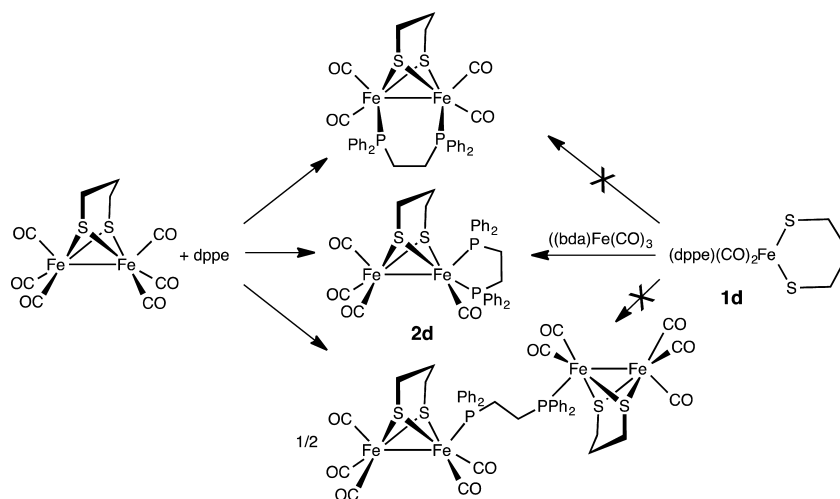
slightly closer to Fe (1.62(2) Å) than to Mn (1.75(2) Å). The  $d^6d^6$  36e-complex (**H3d** is 34e-)  $\text{FeMn}(\mu\text{-SPh})_3(\text{CO})_6$  has been described.<sup>32</sup> The cyclic voltammogram of **H3d** consists of a reversible oxidation event at 0.125 V vs  $\text{Fc}^{+/0}$ , characterized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

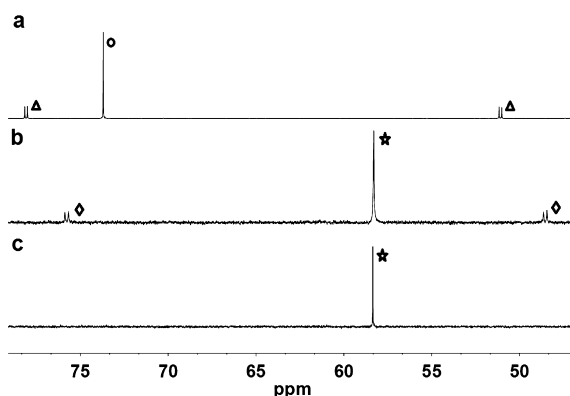
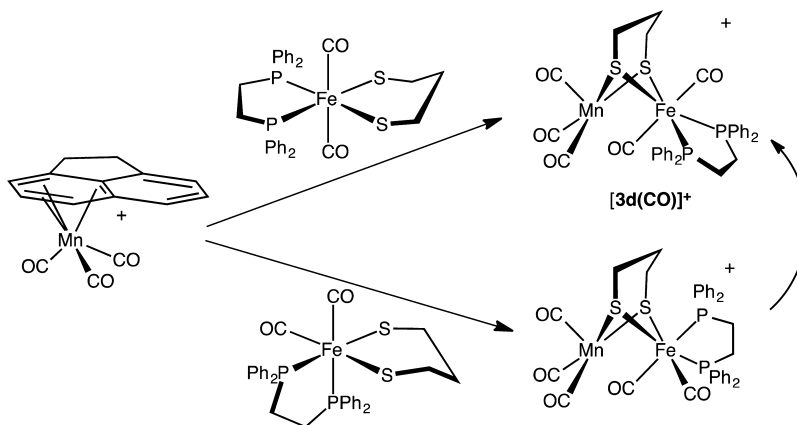
The acid–base behavior of **H3d** was investigated. Upon treatment of **H3d** with  $[\text{H}(\text{Et}_2\text{O})_2]\text{BAR}^{\text{F}}_4$  the  $\nu_{\text{CO}}$  bands shifted by 20–50  $\text{cm}^{-1}$  to higher energy. Protonation of **H3d** was anticipated to give  $\text{H}_2$  or a dihydrogen complex (see  $[(\text{H}_2)\text{Mn}(\text{CO})_3(\text{dppe})]^+$ ).<sup>33</sup> Treatment of the acidified reaction mixture with  $\text{Et}_3\text{N}$  gave back **H3d** (Figure 6). The reversible protonation of **H3** is proposed to occur at sulfur. Similar S-protonations have been proposed for related charge-neutral diiron dithiolate complexes.<sup>34</sup> 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  $^1\text{H}$  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  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, assigned to the nonequivalent phosphorus centers in  $[\text{H3dH}]^+$ .

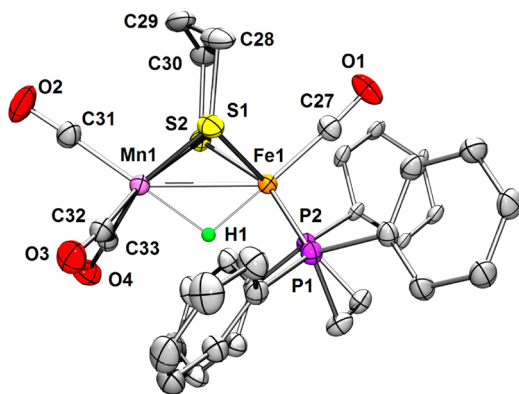
**Reduction of  $\text{Mn}^{\text{I}}\text{Fe}^{\text{II}}$  Complexes.** The electrochemical behavior of  $[\text{3d}(\text{CO})]\text{BF}_4$  was investigated by cyclic voltammetry. At  $-1.0$  V, an irreversible reduction is observed, followed by a reversible event centered at  $-1.3$  V. Consistent 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  $\nu_{\text{CO}}$  1997 and 1902  $\text{cm}^{-1}$ . 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  $\text{CH}_2\text{Cl}_2$  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



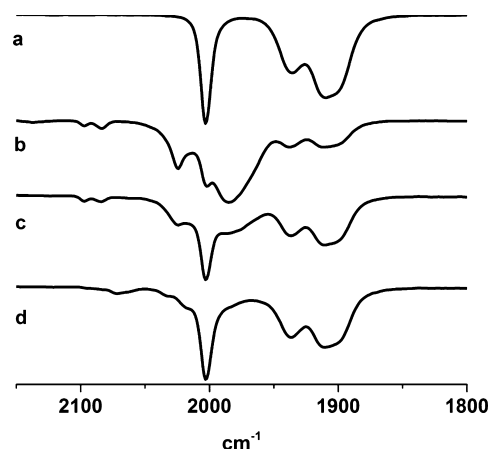
Scheme 5. Synthesis of  $[(\text{CO})_3\text{Mn}(\text{pdt})\text{Fe}(\text{CO})_2(\text{dppe})]\text{BF}_4$  from Isomers of **1d**

**Figure 4.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of a  $\text{CD}_2\text{Cl}_2$  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.



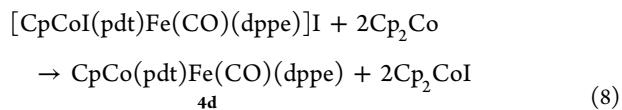
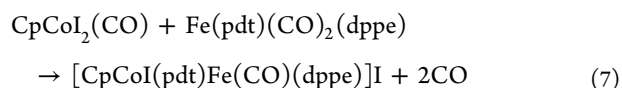
**Figure 5.** Structure of  $(\text{CO})_3\text{Mn}(\text{pdt})(\mu\text{-H})\text{Fe}(\text{CO})(\text{dppe})$  (**H3d**) with thermal ellipsoids drawn at the 50% probability level. Selected distances (Å): Fe1–Mn1, 2.6433(4); Fe1–C27, 1.753(2); Fe1–P1, 2.2139(5); Fe1–P2, 2.2086(5); Fe1–S1, 2.2759(5); 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



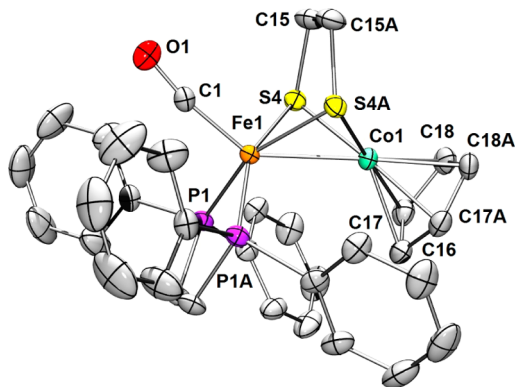
**Figure 6.** IR spectra in  $\text{CH}_2\text{Cl}_2$  of (a)  $(\text{CO})_3\text{Mn}(\text{pdt})(\mu\text{-H})\text{Fe}(\text{CO})(\text{dppe})$  and this solution (b) after addition of 1 equiv of  $\text{H}(\text{Et}_2\text{O})_2\text{BARF}_4$ , (c) after addition of 0.5 equiv of  $\text{Et}_3\text{N}$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

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  $[\text{CpCoI}(\text{pdt})\text{Fe}(\text{CO})(\text{dppe})]^+$  ( $\nu_{\text{CO}}$  1952  $\text{cm}^{-1}$ ). 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  $\delta$  47 and 90) and the second isomer is characterized by a singlet at  $\delta$  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  $\text{Cp}_2\text{Co}$  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  $\text{CpCo}$  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).<sup>26,35</sup> Crystallographic and spectroscopic characterization of the ethanedithiolate **4a** proved mutually consistent (Figure 7). The complex can be described as a pair of five-



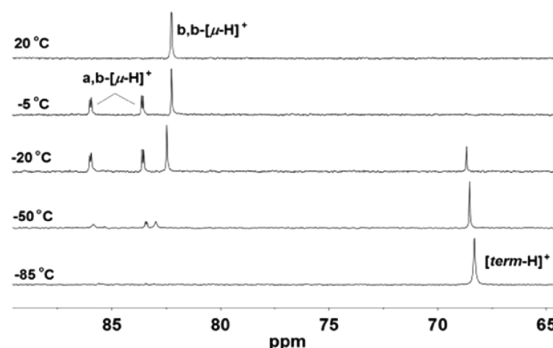
**Figure 7.** Structure of  $\text{CpCo}(\text{edt})\text{Fe}(\text{CO})(\text{dppv})$  (**4a**) with thermal ellipsoids drawn at the 50% probability level. Selected distances ( $\text{\AA}$ ):  $\text{Fe1-Co1}$ , 2.5038(5);  $\text{Fe1-C1}$ , 1.754(3);  $\text{Fe1-P1}$ , 2.2038(5);  $\text{Fe1-S4}$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

coordinate metal centers linked by a  $\text{Co-Fe}$  bond (2.5038(5)  $\text{\AA}$ ). A distinctive feature of the structure is the acute angle for the  $\text{FeP}_2$  plane relative to the  $\text{FeS}_2$  plane.

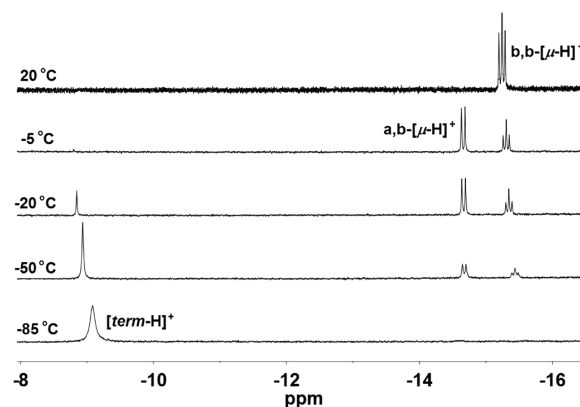
The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **4d** established the presence of only one isomer, even at low temperatures. Below  $-60$   $^\circ\text{C}$ , the spectrum consists of a pair of singlets with  $\sim 4:1$  intensities, attributed to conformational isomers arising from the  $\text{pdt}^{2-}$  backbone. Using an internal integration standard,  $>90\%$  of the sample was verified to be in solution at  $-90$   $^\circ\text{C}$ .

**Co<sup>III</sup>Fe<sup>II</sup> Hydrides.** At room temperature, the  $\text{Co-Fe}$  complexes protonate to give the corresponding  $\mu$ -hydrido derivatives. Protonation shifts the  $\nu_{\text{CO}}$  band from 1890 to 1975  $\text{cm}^{-1}$ . The  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  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 (Scheme 6).

NMR studies on the protonation at low temperatures revealed at least two intermediates. The initial product of protonation, formed quantitatively at  $-85$   $^\circ\text{C}$ , is characterized by singlets at  $\delta -9.0$  and  $\delta 70.7$  in the  $^1\text{H}$  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  $\text{CpCo}$  center (Scheme 6). When the temperature is raised to  $-50$   $^\circ\text{C}$ , 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  $\sim 25$  Hz coupling to the cis phosphine, whereas coupling to the trans phosphine is often weak or is not observed.<sup>36</sup> 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.

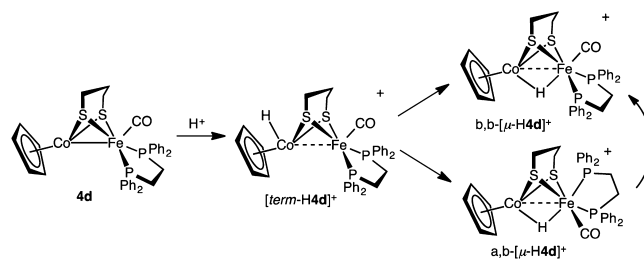


**Figure 8.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of a  $\text{CD}_2\text{Cl}_2$  solution of **4d** and 1 equiv of  $[\text{H}(\text{OEt}_2)_2]\text{BAr}^{\text{F}}_4$ . The solution was prepared at  $-85$   $^\circ\text{C}$  and then warmed to the indicated temperatures.



**Figure 9.**  $^1\text{H}$  NMR spectra of a  $\text{CD}_2\text{Cl}_2$  solution of **4d** and 1 equiv of  $[\text{H}(\text{OEt}_2)_2]\text{BAr}^{\text{F}}_4$ . The solution was prepared at  $-85$   $^\circ\text{C}$  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  $\text{FeFe}$ ,  $\text{MnFe}$ , and  $\text{CoFe}$  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.<sup>27,28</sup> Related complexes can be prepared via  $\text{FeX}_2(\text{CO})_4$ .<sup>14,37</sup> The new routes are potentially appealing because the iron complexes are derived from  $\text{FeCl}_2$ .<sup>8</sup> Conveniently available sources of  $^{57}\text{Fe}$  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  $^{57}\text{Fe}$  ( $I = -1/2$ ) into ferrous carbonyl building blocks, as illustrated by the synthesis of  $^{57}\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppe})$ . Interest in  $^{57}\text{Fe}$  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.<sup>38</sup> 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<sub>ox</sub>-models”  $[\text{Fe}_2(\text{pdt})(\text{CO})_{6-x}\text{L}_x]^+$ .<sup>39</sup> Similarly, the hydride  $(\text{CO})_3\text{Mn}(\text{pdt})\text{HFe}(\text{CO})(\text{dppe})$ , which was characterized crystallographically, is isoelectronic with  $[\text{HFe}_2(\text{pdt})(\text{CO})_4(\text{dppe})]^+$ .<sup>28</sup> The MnFe complex is sufficiently electron rich that it undergoes a mild one-electron oxidation ( $\sim 0.1$  V vs  $\text{Fc}^{+/0}$ ), whereas oxidations of analogous diferrous hydrides occur only at very positive potentials.<sup>40</sup>

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.<sup>41</sup> 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.<sup>35</sup> Chromatography was performed using silica gel (40–63  $\mu\text{m}$ , 230–400 mesh) as the stationary phase.  $\text{K}_2\text{pdt}$ ,<sup>42</sup> [(acenaphthene)Mn(CO)<sub>3</sub>] $\text{BF}_4$ ,<sup>30</sup>  $^{57}\text{Fe}_2\text{I}_4(\text{PrOH})_4$ ,<sup>43</sup> and  $\text{CpCo}(\text{CO})\text{I}_2$ <sup>44</sup> were prepared according to the literature methods. ESI-MS data were recorded on dilute  $\text{CH}_2\text{Cl}_2$  solutions on a Waters Micromass Quattro II spectrometer. ATR data were collected on a PerkinElmer Spectrum 100 FT-IR instrument.  $^1\text{H}$  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  $\text{cm}^{-1}$ , were recorded only in the  $\nu_{\text{CO}}$  region.

**Illustrative Preparation:  $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppe})$  (1d).** Under a CO atmosphere, a solution of 1.9 g of  $\text{FeCl}_2$  (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  $\text{CH}_2\text{Cl}_2$  and purified by flash column chromatography on a 4 × 50 cm column of silica gel. After a yellow band eluted with  $\text{CH}_2\text{Cl}_2$ , 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%).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.89–7.32 (m, 20H,  $\text{C}_6\text{H}_5$ ), 2.63 (m, 4H,  $\text{PCH}_2$ ), 2.50 (d, 4H,  $\text{SCH}_2$ ), 1.97 (m, 2H,  $\text{SCH}_2\text{CH}_2$ ). IR ( $\text{CH}_2\text{Cl}_2$ ): 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%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.14–7.32 (m, 20H,  $\text{C}_6\text{H}_5$ ), 2.53 (s, 2H,  $\text{CH}_2$ ), 2.46 and 2.02 (d each, 1:1 H,  $\text{CH}_2$ ), 2.18 and 0.21 (t each, 1:1 H, CH). IR ( $\text{CH}_2\text{Cl}_2$ ): 2013 (s), 1978 (s), 1960 (s). Anal. Calcd for  $\text{C}_{30}\text{H}_{26}\text{FeO}_2\text{P}_2\text{S}_2 \cdot 0.5\text{SCH}_2\text{Cl}_2$  (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%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.87–7.27 (m,  $\text{C}_6\text{H}_5$ ), 2.62 (s, 4H, S  $\text{CH}_2$ , sym), 2.50 (s, 4H,  $\text{PCH}_2$ , sym), 2.78 (d 2H  $\text{PCH}_2$ , unsym), 2.16 (d 2H  $\text{PCH}_2$ , unsym), 1.22 (s, 3H,  $\text{SCH}_2$ , unsym), 0.34 (s, 1H,  $\text{SCH}_2$ , 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%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.94–7.32 (m, 20H,  $\text{C}_6\text{H}_5$ ), 2.44 (d, 4H,  $\text{CH}_2$ ), 1.96 (d, 2H,  $\text{SCH}_2$ ). IR ( $\text{CH}_2\text{Cl}_2$ ): 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  $\text{FeCl}_2$  (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  $\mu\text{L}$  (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  $\text{CH}_2\text{Cl}_2$ . The product was recrystallized by addition of hexanes to a concentrated  $\text{CH}_2\text{Cl}_2$  solution. Yield: 400 mg (20%).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.4–7.6 (m, 24H,  $\text{C}_6\text{H}_5$  and  $\text{C}_6\text{H}_4$ ), 2.39 (s, 4H,  $\text{SCH}_2\text{CH}_2$ ), 1.94 (s, 2H,  $\text{SCH}_2\text{CH}_2$ ). IR ( $\text{CH}_2\text{Cl}_2$ ): 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  $\sim 100$  mL of hexanes. The solution volume was reduced to  $\sim 20$  mL and the solution cooled to 0 °C, resulting in the formation of dark red crystals. Yield: 430 mg (35%). IR ( $\text{CH}_2\text{Cl}_2$ ): 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  $\text{Fe}_2\text{I}_4(\text{PrOH})_4$ ,<sup>43</sup> using  $^{57}\text{Fe}$  as the precursor. ESI-MS:  $m/z$  674.8  $[\text{M} - \text{PrOH} - \text{I}]^+$ , 364.1  $[\text{M} - \text{PrOH} - ^{57}\text{Fe}^{2+} - 3\text{I}]^+$ . 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  $\mu\text{mol}$ ) of  $^{57}\text{Fe}_2\text{I}_4(\text{PrOH})_4$  and 79.7 mg (200  $\mu\text{mol}$ ) of dppe in 6 mL of 1/1  $^i\text{PrOH}/\text{THF}$  was stirred under 1 atm of CO. The suspension, which had developed a red color, was treated with 36.8 mg (200  $\mu\text{mol}$ ) of  $\text{K}_2\text{pdt}$  in 3 mL of  $^i\text{PrOH}$ . 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  $\text{CH}_2\text{Cl}_2$ , and these extracts were concentrated to  $\sim 0.5$  mL and chromatographed on a  $\sim 5$  cm column of silica gel, with  $\text{CH}_2\text{Cl}_2$  as eluent. The second band, deep red, was collected, concentrated to  $\sim 2$  mL, and treated with 10 mL of  $\text{Et}_2\text{O}$ . 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  $\mu\text{mol}$ , 19%).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CH}_2\text{Cl}_2$ ):  $\delta$  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 ( $\text{CH}_2\text{Cl}_2$ ): 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%).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.4–7.8 (m, 20H,  $\text{C}_6\text{H}_5$ ), 2.65 (dd, 4H,  $\text{P}_2\text{CH}_2\text{CH}_2$ ), 2.23 (s, 4H,  $\text{SCH}_2$ ), 1.01 (s, 6H,  $\text{CCH}_3$ ). IR ( $\text{CH}_2\text{Cl}_2$ ): 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  $\nu_{\text{CO}}$  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,  $^1\text{H}$  NMR, and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the product match reported data.<sup>26</sup>

**$\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{dppe})$  (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,  $^1\text{H}$  NMR, and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the product match reported data.<sup>28</sup>

**$\text{Fe}_2(\text{pdt})(\text{CO})_4(\text{dcpe})$  (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 ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  89.27 (s), apical-basal; 74.90 (s), dibasal. IR ( $\text{CH}_2\text{Cl}_2$ ): 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<sub>4</sub>**).** A solution of 500 mg (1.32 mmol) of  $[(\text{acenaphthene})\text{Mn}(\text{CO})_3]\text{BF}_4$  in 125 mL of  $\text{CH}_2\text{Cl}_2$  was treated with a solution of 810 mg (1.32 mmol) of **1b** in 50 mL of  $\text{CH}_2\text{Cl}_2$ . 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  $\sim 30$  mL of  $\text{CH}_2\text{Cl}_2$ , and the extract was filtered through a pad of Celite. The brown solution was concentrated to  $\sim 10$  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  $\text{CH}_2\text{Cl}_2$  solution with pentane.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.41–7.80 (m, 20H,  $\text{C}_6\text{H}_5$ ), 3.50 (m, 2H,  $\text{PCH}_2$ ), 3.28 (m, 2H,  $\text{PCH}_2$ ), 3.08 (m, 2H,  $\text{SCH}_2$ ), 2.84 (m, 3H,  $\text{SCH}_2\text{CH}_2$ ), 2.03 (m, 1H,  $\text{SCH}_2\text{CH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  58 (s). IR ( $\text{CH}_2\text{Cl}_2$ ): 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  $[\text{3(CO)BF}_4]$  in 100 mL of  $\text{CH}_2\text{Cl}_2$  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  $\text{CH}_2\text{Cl}_2$  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  $\sim 20$  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  $\sim 25$  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.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.38–7.84 (m, 20H,  $\text{C}_6\text{H}_5$ ), 2.76 (m, 4H,  $\text{PCH}_2$ ), 2.58 (m, 2H,  $\text{SCH}_2$ ), 2.41 (m, 3H,  $\text{SCH}_2\text{CH}_2$ ), 1.91 (m, 1H,  $\text{SCH}_2\text{CH}_2$ ),  $-12.26$  (t, 1H, Mn–H–Fe).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  80.80 (s). IR ( $\text{CH}_2\text{Cl}_2$ ): 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  $[\text{4d(CO)BF}_4]$  (71 mg, 84  $\mu\text{mol}$ ) in THF (10 mL) was treated with a THF solution of  $\text{CpCo}$  (16 mg, 84  $\mu\text{mol}$ ). The solution was filtered through Celite, and then the solvent was removed under vacuum to yield a red solid. Yield: 46 mg (75%). IR ( $\text{CH}_2\text{Cl}_2$ ): 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  $\text{CpCo}(\text{CO})_2$ .** A mixture of **1a** (100 mg, 0.17 mmol) and  $\text{CpCo}(\text{CO})_2$  (68 mg, 0.17 mmol) was

stirred in  $\text{CH}_2\text{Cl}_2$  (20 mL) at room temperature for 2 h to give a dark brown solution with a predominant IR band at  $1978\text{ cm}^{-1}$ . To this solution was added a solution of  $\text{CpCo}$  (68 mg, 0.36 mmol) in 20 mL of  $\text{CH}_2\text{Cl}_2$ . The IR spectrum of the resulting solution revealed a prominent band at  $1890\text{ cm}^{-1}$ . 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  $\text{CH}_2\text{Cl}_2$  and pentane as eluent and gradually increasing the  $\text{CH}_2\text{Cl}_2$  content. After an initial green band, the product eluted as a brown band using  $\text{CH}_2\text{Cl}_2$ . Evaporation of the solution gave the brown product. Yield: 45 mg (39%).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 23 °C):  $\delta$  8.30–7.12 (m, 20 H,  $\text{C}_6\text{H}_5$ ), 4.75 (s, 2 H,  $\text{PCH}$ ), 3.36 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 2.26 and 1.84 (d each, 2 H each,  $\text{SCH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 23 °C):  $\delta$  93.56 (s). IR ( $\text{CH}_2\text{Cl}_2$ ): 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  $\mu\text{L}$ , 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  $1896\text{ cm}^{-1}$ . The solution was filtered, and the brown filtrate was evaporated. The brown residue was washed with  $\sim 10$  mL each of hexanes and  $\text{Et}_2\text{O}$ . The brown residue was extracted into  $\sim 4$  mL of  $\text{CH}_2\text{Cl}_2$ , and the extract was layered with 10 mL of hexane. Dark brown crystals of **4a** formed overnight. Yields were variable. Anal. Calcd for  $\text{C}_{34}\text{H}_{31}\text{CoFeOP}_2\text{S}_2$  (found): C, 58.63 (58.12); H, 4.49 (4.37). IR ( $\text{CH}_2\text{Cl}_2$ ): 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  $\mu\text{L}$ , 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  $1892\text{ cm}^{-1}$ . The solution was filtered, and the brown filtrate was evaporated. The brown residue was washed with  $\sim 10$  mL of hexanes and then extracted into  $\sim 5$  mL of  $\text{CH}_2\text{Cl}_2$ . This extract was layered with 10 mL of hexane to yield dark brown crystals of **4b** upon standing overnight.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 23 °C):  $\delta$  8.17–7.30 (m, 20 H,  $\text{C}_6\text{H}_5$ ), 3.51 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 2.30 and 2.20 (d each, 2 H each,  $\text{SCH}_2$ ), 1.87 (m, 2 H,  $\text{SCH}_2\text{CH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 23 °C):  $\delta$  90.17 (s). IR ( $\text{CH}_2\text{Cl}_2$ ): 1885.

**$\text{CpCo}(\text{pdt})\text{Fe}(\text{CO})(\text{dppe})$  (4d) from  $\text{CpCo}(\text{CO})_2$ .** A solution of  $\text{Fe}(\text{pdt})(\text{CO})_2(\text{dppe})$  (50 mg, 0.08 mmol) and  $\text{CpCo}(\text{CO})_2$  (31 mg, 0.08 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 mL) was stirred overnight. Formation of a new product was detected by an IR band at  $1952\text{ cm}^{-1}$ . The reaction solution was treated with a solution of  $\text{CpCo}$  (38 mg, 0.20 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL). After the solution was stirred for 5 min, the dominant IR band shifted to  $1879\text{ cm}^{-1}$ . The solution was filtered through Celite, and the product was purified by column chromatography on silica gel, initially with 1/1  $\text{CH}_2\text{Cl}_2$ /pentane as eluent, which produced a green band. Eluting with  $\text{CH}_2\text{Cl}_2$  gave the product as a brown band, which was evaporated to leave a brown solid. Yield: 23 mg (40%).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 23 °C):  $\delta$  7.82–7.29 (m, 20 H,  $\text{C}_6\text{H}_5$ ), 3.84 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 2.98 (m, 2 H,  $\text{PCH}_2$ ), 2.58 and 2.26 (m each, 2 H each,  $\text{SCH}_2$ ), 2.17 and 1.89 (m each, 1 H each,  $\text{PCH}_2$ ), 1.47 (m, 2 H,  $\text{S}(\text{CH}_2)_2\text{CH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 23 °C):  $\delta$  83.48 (s). IR ( $\text{CH}_2\text{Cl}_2$ ): 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  $\mu\text{L}$ , 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  $1883\text{ cm}^{-1}$ . The solution was filtered, and the brown filtrate was evaporated. The brown residue was washed with  $\sim 15$  mL of toluene and then extracted into  $\sim 4$  mL of  $\text{CH}_2\text{Cl}_2$ . This extract was layered with 10 mL of hexane to yield dark brown crystals of **4d** upon standing overnight. Yields were variable.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 23 °C):  $\delta$  7.82–7.29 (m, 20 H,  $\text{C}_6\text{H}_5$ ), 3.84 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 2.98 (m, 2 H,  $\text{PCH}_2$ ), 2.56 and 2.25 (m each, 2 H each,  $\text{SCH}_2$ ), 2.18 and 1.87 (m each, 1 H each,  $\text{PCH}_2$ ), 1.51 (m, 2 H,  $\text{CH}_2\text{SCH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 23 °C):  $\delta$  85.54 (s). Anal. Calcd for  $\text{C}_{33}\text{H}_{33}\text{CoFeOP}_2\text{S}_2$  (found): C, 59.00 (58.89); H, 4.95 (4.83). IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu_{\text{CO}}$  1879. Data for the low-temperature intermediate, terminal hydride are as follows.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 23 °C):  $\delta$  7.73–7.35 (m, 20 H,  $\text{C}_6\text{H}_5$ ), 3.61 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 2.98 (m, 2 H,  $\text{PCH}_2$ ), 2.56 and 2.25 (m each, 2 H each,  $\text{SCH}_2$ ), 2.18 and 1.87 (m each, 1 H each,  $\text{PCH}_2$ ), 1.51 (m, 2 H,  $\text{S}(\text{CH}_2)_2\text{CH}_2$ ).



$^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 23 °C):  $\delta$  85.54 (s). Data for the low-temperature intermediate, apical–basal  $\mu$ -hydride are as follows.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 23 °C):  $\delta$  7.82–7.29 (m, 20 H,  $\text{C}_6\text{H}_5$ ), 3.84 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 2.98 (m, 2 H,  $\text{PCH}_2$ ), 2.56 and 2.25 (m each, 2 H each,  $\text{SCH}_2$ ), 2.18 and 1.87 (m each, 1 H each,  $\text{PCH}_2$ ), 1.51 (m, 2 H,  $\text{CH}_2\text{SCH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 23 °C):  $\delta$  85.54 (s).

**Low-Temperature Protonation of  $\text{CpCo}(\text{pdt})\text{Fe}(\text{CO})(\text{dppe})$  (4d).** In a J. Young NMR tube,  $\sim 1$  mL of  $\text{CD}_2\text{Cl}_2$  was distilled and frozen onto **4d** (5 mg, 0.007 mmol) and  $[\text{H}(\text{OEt}_2)_2]\text{BARF}_{24}$  (8.5 mg, 0.008 mmol) in a liquid- $\text{N}_2$  bath. The sample was then thawed, placed in an NMR spectrometer (probe precooled to  $-85$  °C), and analyzed by NMR spectroscopy.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-85$  °C):  $\delta$  3.61 (s,  $\text{C}_5\text{H}_5$ ,  $[\text{term-H4d}]^+$ );  $-9.0$  (s, Co-H,  $[\text{term-H4d}]^+$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-85$  °C):  $\delta$  70.65 (s,  $[\text{term-H4d}]^+$ ). When the sample was warmed to  $-50$  °C, the NMR spectra indicated the presence of two new species.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-50$  °C):  $\delta$  3.61 (s,  $\text{C}_5\text{H}_5$ ,  $[\text{term-H4d}]^+$ );  $-9.0$  (s, Co-H,  $[\text{term-H4d}]^+$ ); 5.29 (s,  $\text{C}_5\text{H}_5$ , a,b- $[\mu\text{-H4d}]^+$ );  $-14.68$  (d,  $J_{\text{P-H}} = 30$ , Co-H-Fe, a,b- $[\mu\text{-H4d}]^+$ ); 4.69 (s,  $\text{C}_5\text{H}_5$ , 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 ( $\text{CD}_2\text{Cl}_2$ ,  $-50$  °C):  $\delta$  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  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra disappeared. At room temperature, a,b- $[\mu\text{-H4d}]^+$  converts entirely to b,b- $[\mu\text{-H4d}]^+$ .

**$[\text{CpCo}(\text{edt})(\text{H})\text{Fe}(\text{CO})(\text{dppv})\text{BF}_4$  ( $[\text{H4a}]\text{BF}_4$ ).** A solution of **4a** (20 mg, 0.03 mmol) in  $\text{CH}_2\text{Cl}_2$  (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  $\text{Et}_2\text{O}$  was added to precipitate a brown powder.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 25 °C):  $\delta$  8.50–7.26 (m, 20 H,  $\text{C}_6\text{H}_5$ ), 4.31 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 3.06 and 2.70 (d each, 2 H each,  $\text{SCH}_2$ ),  $-18.14$  (t,  $J_{\text{PH}} = 26.8$ , 1H, Co-H-Fe).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 23 °C):  $\delta$  89.72 (d). IR ( $\text{CH}_2\text{Cl}_2$ ): 1975.

**$[\text{CpCo}(\text{pdt})(\text{H})\text{Fe}(\text{CO})(\text{dppe})\text{BF}_4$  ( $[\text{H4d}]\text{BF}_4$ ).** A solution of **4d** (20 mg, 0.03 mmol) in  $\text{CH}_2\text{Cl}_2$  (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  $\text{Et}_2\text{O}$  to precipitate a brown powder.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25 °C):  $\delta$  7.66–7.30 (m, 20H,  $\text{C}_6\text{H}_5$ ), 4.79 (s, 5H,  $\text{C}_5\text{H}_5$ ), 3.30 (m, 2H,  $\text{PCH}_2$ ), 3.01 and 2.71 (m each, 2H each,  $\text{SCH}_2$ ), 2.61 (m, 1H,  $\text{PCH}_2$ ), 2.15 (m, 3H,  $\text{PCH}_2$  and  $\text{CH}_2\text{SCH}_2$ ),  $-15.19$  (t,  $J_{\text{PH}} = 27$ , 1H, Co-H-Fe).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 25 °C):  $\delta$  82.91 (d). Anal. Calcd for  $\text{C}_{35}\text{H}_{36}\text{BCoF}_4\text{FeOP}_2\text{S}_2 \cdot 0.2\text{CH}_2\text{Cl}_2$  (found): C, 51.73 (51.90); H, 4.49 (4.61). IR ( $\text{CH}_2\text{Cl}_2$ ): 1962.

## ■ ASSOCIATED CONTENT

### Supporting Information

Figures giving  $^1\text{H}$  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>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail for T.B.R.: [rauchfuz@illinois.edu](mailto:rauchfuz@illinois.edu).

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the National Institutes of Health (Grant GM61153). We thank Teresa Wieckowska for help with collection of the X-ray diffraction data. Also acknowledged is support from the International Institute for Carbon Neutral Energy Research (WPI-I<sup>2</sup>CNER), sponsored by the World Premier International Research Center Initiative (WPI), MEXT, Japan.

## ■ REFERENCES

- (1) Tard, C.; Pickett, C. J. *Chem. Rev.* **2009**, *109*, 2245.
- (2) *Catalysis without Precious Metals*; Bullock, R. M., Ed.; Wiley-VCH: Weinheim, Germany, 2010.
- (3) Wang, M.; Chen, L.; Sun, L. *Energy Environ. Sci.* **2012**, *5*, 6763.
- (4) Mack, A. E.; Rauchfuss, T. B. *Inorg. Synth.* **2011**, *35*, 142.
- (5) Seyferth, D.; Henderson, R. S.; Song, L. C. *Organometallics* **1982**, *1*, 125. Seyferth, D.; Henderson, R. S.; Song, L.-C.; Womack, G. B. *J. Organomet. Chem.* **1985**, *292*, 9.
- (6) Brandt, P. F.; Lesch, D. A.; Stafford, P. R.; Rauchfuss, T. B. *Inorg. Synth.* **1997**, *31*, 112.
- (7) Lawrence, J. D.; Li, H.; Rauchfuss, T. B. *Chem. Commun.* **2001**, 1482. Lawrence, J. D.; Li, H.; Rauchfuss, T. B.; Bénard, M.; Rohmer, M.-M. *Angew. Chem., Int. Ed.* **2001**, *40*, 1768.
- (8) Volkers, P. I.; Boyke, C. A.; Chen, J.; Rauchfuss, T. B.; Whaley, C. M.; Wilson, S. R.; Yao, H. *Inorg. Chem.* **2008**, *47*, 7002.
- (9) Kamali, S.; Wang, H.; Mitra, D.; Ogata, H.; Lubitz, W.; Manor, B. C.; Rauchfuss, T. B.; Byrne, D.; Bonnefoy, V.; Jenney, F. E.; Adams, M. W. W.; Yoda, Y.; Alp, E.; Zhao, J.; Cramer, S. P. *Angew. Chem., Int. Ed.* **2013**, *52*, 724.
- (10) Silakov, A.; Olsen, M. T.; Sproules, S.; Reijerse, E. J.; Rauchfuss, T. B.; Lubitz, W. *Inorg. Chem.* **2012**, *51*, 8617.
- (11) Li, H.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2002**, *124*, 726.
- (12) Booth, G.; Chatt, J. *J. Chem. Soc.* **1962**, 2099. Battaglia, L. P.; Chiusoli, G. P.; Delledonne, D.; Nardelli, M.; Pelizzi, C.; Predieri, G. *Gazz. Chim. Ital.* **1989**, *119*, 345.
- (13) Manuel, T. A. *Inorg. Chem.* **1963**, *2*, 854.
- (14) Zhang, Z.-Z.; Zhang, J.-K.; Zhang, W.-D.; Xi, H.-P.; Cheng, H.; Wang, H.-G. *J. Organomet. Chem.* **1996**, *515*, 1.
- (15) Takács, J.; Markó, L.; Párkányi, L. *J. Organomet. Chem.* **1989**, *361*, 109.
- (16) Takács, J.; Soós, E.; Nagy-Magos, Z.; Markó, L.; Gervasio, G.; Hoffmann, T. *Inorg. Chim. Acta* **1989**, *166*, 39. Wang, X.; Li, Z.; Zeng, X.; Luo, Q.; Evans, D. J.; Pickett, C. J.; Liu, X. *Chem. Commun.* **2008**, 3555.
- (17) Guo, Y.; Wang, H.; Xiao, Y.; Vogt, S.; Thauer, R. K.; Shima, S.; Volkers, P. I.; Rauchfuss, T. B.; Pelmenshikov, V.; Case, D. A.; Alp, E. E.; Sturhahn, W.; Yoda, Y.; Cramer, S. P. *Inorg. Chem.* **2008**, *47*, 3969.
- (18) Beyler, M.; Ezzaher, S.; Karnahl, M.; Santoni, M.-P.; Lomoth, R.; Ott, S. *Chem. Commun.* **2011**, *47*, 11662.
- (19) Schwartz, L.; Singh, P. S.; Eriksson, L.; Lomoth, R.; Ott, S. C. R. *Chim. Acta* **2008**, *11*, 875. Kaur-Ghumaan, S.; Schwartz, L.; Lomoth, R.; Stein, M.; Ott, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 8033.
- (20) Breuer, J.; Frühauf, H.-W.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chim. Acta* **1999**, *291*, 438. Benito-Garagorri, D.; Lagoja, I.; Vieros, L. F.; Kirchner, K. A. *Dalton Trans.* **2011**, *40*, 4778.
- (21) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Venturi, C.; Zuccaccia, C. *J. Organomet. Chem.* **2006**, *691*, 3881.
- (22) Cai, S.; Hou, X.-F.; Chen, Y.-Q.; Jin, G.-X. *Dalton Trans.* **2006**, *0*, 3736. Murata, M.; Habe, S.; Araki, S.; Namiki, K.; Yamada, T.; Nakagawa, N.; Nankawa, T.; Nihei, M.; Mizutani, J.; Kurihara, M.; Nishihara, H. *Inorg. Chem.* **2006**, *45*, 1108. Ohki, Y.; Tatsumi, K. *Eur. J. Inorg. Chem.* **2011**, *2011*, 973. Song, L.-C.; Li, J.-P.; Xie, Z.-J.; Song, H.-B. *Inorg. Chem.* **2013**, *52*, 11618.
- (23) Barton, B. E.; Whaley, C. M.; Rauchfuss, T. B.; Gray, D. L. *J. Am. Chem. Soc.* **2009**, *131*, 6942.
- (24) Gao, H.; Huang, J.; Chen, L.; Liu, R.; Chen, J. *RSC Adv.* **2013**, *3*, 3557.
- (25) Ninoreille, S.; Broussier, R.; Amardeil, R.; Kubicki, M. M.; Gautheron, B. *Bull. Soc. Chim. Fr.* **1995**, *132*, 128.
- (26) Justice, A. K.; Zampella, G.; De Gioia, L.; Rauchfuss, T. B.; van der Vlugt, J. I.; Wilson, S. R. *Inorg. Chem.* **2007**, *46*, 1655.
- (27) Adam, F. I.; Hogarth, G.; Kabir, S. E.; Richards, I. C. R. *Chim.* **2008**, *11*, 890.
- (28) Ezzaher, S.; Capon, J.-F.; Gloaguen, F.; Pétilion, F. Y.; Schollhammer, P.; Talarmin, J.; Pichon, R.; Kervarec, N. *Inorg. Chem.* **2007**, *46*, 3426.
- (29) Zhao, X.; Georgakaki, I. P.; Miller, M. L.; Yarbrough, J. C.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2001**, *123*, 9710.

- (30) Kim, S. B.; Lotz, S.; Sun, S.; Chung, Y. K.; Pike, R. D.; Sweigart, D. A. *Inorg. Synth.* **2010**, *35*, 114.
- (31) Boyke, C. A.; van der Vlugt, J. I.; Rauchfuss, T. B.; Wilson, S. R.; Zampella, G.; De Gioia, L. *J. Am. Chem. Soc.* **2005**, *127*, 11010.
- (32) Walters, M. A.; Dewan, J. C. *Inorg. Chim. Acta* **1991**, *187*, 123.
- (33) Orchin, M.; Mandal, S. K.; Feldman, J. *Inorg. Synth.* **1998**, *32*, 298.
- (34) Zaffaroni, R.; Rauchfuss, T. B.; Gray, D. L.; De Gioia, L.; Zampella, G. *J. Am. Chem. Soc.* **2012**, *134*, 19260. Apfel, U.-P.; Troegel, D.; Halpin, Y.; Tschierlei, S.; Uhlemann, U.; Görls, H.; Schmitt, M.; Popp, J.; Dunne, P.; Venkatesan, M.; Coey, M.; Rudolph, M.; Vos, J. G.; Tacke, R.; Weigand, W. *Inorg. Chem.* **2010**, *49*, 10117. Dong, W.; Wang, M.; Liu, X.; Jin, K.; Li, G.; Wang, F.; Sun, L. *Chem. Commun.* **2006**, 305. Ezzaher, S.; Gogoll, A.; Bruhn, C.; Ott, S. *Chem. Commun.* **2010**, *46*, 5775.
- (35) Carroll, M. E.; Barton, B. E.; Rauchfuss, T. B.; Carroll, P. J. *J. Am. Chem. Soc.* **2012**, *134*, 18843.
- (36) Barton, B. E.; Zampella, G.; Justice, A. K.; De Gioia, L.; Rauchfuss, T. B.; Wilson, S. R. *Dalton Trans.* **2010**, *39*, 3011.
- (37) Cohen, I. A.; Basolo, F. *J. Inorg. Nucl. Chem.* **1966**, *28*, 511. Li, B.; Liu, T.; Popescu, C. V.; Bilko, A.; Darensbourg, M. Y. *Inorg. Chem.* **2009**, *48*, 11283.
- (38) Lyons, L. J.; Tegen, M. H.; Haller, K. J.; Evans, D. H.; Treichel, P. M. *Organometallics* **1988**, *7*, 357. Adams, R. D.; Kwon, O. S.; Smith, M. D. *Inorg. Chem.* **2001**, *40*, 5322. Reyes-Lezama, M.; Höpfl, H.; Zúñiga-Villareal, N. *J. Organomet. Chem.* **2008**, *693*, 987.
- (39) Justice, A. K.; De Gioia, L.; Nilges, M. J.; Rauchfuss, T. B.; Wilson, S. R.; Zampella, G. *Inorg. Chem.* **2008**, *47*, 7405. Liu, T.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **2007**, *129*, 7008.
- (40) Ezzaher, S.; Capon, J.-F.; Dumontet, N.; Gloaguen, F.; Pétilion, F. Y.; Schollhammer, P.; Talarmin, J. *J. Electroanal. Chem.* **2009**, *626*, 161.
- (41) Carroll, M. E.; Barton, B. E.; Gray, D. L.; Mack, A. E.; Rauchfuss, T. B. *Inorg. Chem.* **2011**, *50*, 9554.
- (42) Ohki, Y.; Yasumura, K.; Kuge, K.; Tanino, S.; Ando, M.; Li, Z.; Tatsumi, K. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105*, 7652.
- (43) Nunes, G. G.; Bottini, R. C. R.; Reis, D. M.; Camargo, P. H. C.; Evans, D. J.; Hitchcock, P. B.; Leigh, G. J.; Sá, E. L.; Soares, J. F. *Inorg. Chim. Acta* **2004**, *357*, 1219.
- (44) Contakes, S. M.; Klausmeyer, K. K.; Rauchfuss, T. B. *Inorg. Synth.* **2004**, *34*, 166.