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# New Approach to [FeFe]-Hydrogenase Models Using Aromatic Thioketones

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Dedicated to Professor Heinz Heimgartner on the occasion of his 70th birthday

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The reactions of triiron dodecacarbonyl with thiobenzophenone (2a) and 9*H*-thioxanthene-9-thione (2b) were investigated under different conditions. In the case of a 1:1 molar ratio of triiron dodecacarbonyl and 2a or 2b, the *ortho*-metallated complexes  $[Fe_2(CO)_6\{\mu,\kappa,S,SCH(C_6H_5)C_6H_4-\eta^2\}]$  (3a) and  $[Fe_2(CO)_6\{\mu,\kappa,S,SCH(C_6H_4)-S-C_6H_3-\eta^2\}]$  (4a) were obtained as the major products, respectively. In contrast, the treatment of triiron dodecacarbonyl with an excess of 2a or 2b afforded  $[Fe_2(CO)_6\{\mu-SCH(C_6H_5)C_6H_4S-\mu\}]$  (3b) and  $[Fe_2(CO)_6\{\mu-SCH(C_6H_3)-K_6H_4S-\mu\}]$  (3b) and  $[Fe_2(CO)_6\{\mu-SCH(C_6H_3)-K_6H_4S-\mu\}]$  (3b) and  $[Fe_2(CO)_6\{\mu-SCH(C_6H_3)-K_6H_4S-\mu\}]$  (3c) and  $[Fe_2(CO)_6\{\mu-SC(C_6H_5)_2S-\mu\}]$  (3c) and

## Introduction

Nature has developed highly efficient enzymes that regulate the generation and depletion of  $H_2$ .<sup>[1–4]</sup> These enzymes are called hydrogenases and can be classified into three major groups according to the metal content of their active sites, namely, [FeFe]-, [NiFe]-, and [Fe]-hydrogenases.<sup>[5]</sup> The [FeFe]-hydrogenases have a higher hydrogen production ability compared to that of other hydrogenases.<sup>[6–8]</sup> Micro-

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 $[Fe_2(CO)_6[\mu-SC(C_6H_4-S-C_6H_4)S-\mu]]$  (4c). Furthermore,  $[\{Fe_2-(CO)_6[\mu-SCH(C_6H_5)_2]\}_2(\mu^4-S)]$  (3d) was isolated from the reaction of Fe<sub>3</sub>(CO)<sub>12</sub> with 2a. The molecular structures of all of the new complexes were determined from the spectroscopic and analytical data and the crystal structures for 3c, 3d, 4b, and 4c were obtained. A plausible mechanism for the formation of the isolated complexes that involves dithiirane derivatives as the key intermediates is proposed. Herein, thioketones 2a and 2b act as sulfur transfer reagents. The electrochemical experiments showed that complex 3b behaves as a catalyst for the electrochemical reduction of protons from acetic acid.

organisms have used  $H_2$  as a primary fuel source for billions of years and consume an enormous amount of  $H_2$  in different forms as an energy source and as a transporter.<sup>[9]</sup>

Inspired by the rapid and reversible proton reduction that is catalyzed by these hydrogenase enzymes, considerable research has been devoted to the design and synthesis of model species that mimic the active sites of the hydrogenases.<sup>[10]</sup>

Recently, we investigated the oxidative addition of the dior tetra-substituted 1,2,4-trithiolans to iron carbonyl compounds in an attempt to produce [FeFe]-hydrogenase model complexes.<sup>[11a]</sup>

In an earlier investigation of the reaction of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (1) with Fe<sub>3</sub>(CO)<sub>12</sub>,<sup>[11b]</sup> we observed a different reaction pathway to that of the corresponding tetra-alkyl-substituted analogues. The latter react with iron carbonyl complexes to yield the oxidative addition products that result from the cleavage of the S–S bond. In contrast, the former undergoes a [2+3]-cycloreversion reaction<sup>[12,13a]</sup> and the fragments [e.g., Ph<sub>2</sub>C=S (**2a**)] react with the iron carbonyl complexes to yield the *ortho*-metallated complex **3a** as the major component of the reaction mixture.<sup>[11b-11e]</sup> In the same paper, the *ortho*-metallated complexes **3e**, **3f**, and **3g** (Figure 1) were obtained after the aro-

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matic thioketones 4,4'-bis(dimethylamino)-thiobenzophenone, dibenzosuberenethione, and xanthione, respectively, were treated with  $Fe_3(CO)_{12}$ .



Figure 1. The ortho-metallated complexes 3a and 3e-g.

These observations prompted us to investigate the reaction of 2a and 9H-thioxanthene-9-thione (2b) with Fe<sub>3</sub>-(CO)<sub>12</sub>, and to examine the reactivity of the complexes of type 3 that were initially obtained under the applied reaction conditions. The structures of the isolated *ortho*-metallated complexes 3a and 3e–g (Figure 1) suggested that these compounds can play the role of key intermediates in the synthesis of new iron complexes that may be unattainable otherwise.

In the present work we demonstrate the role of the *ortho*metallated complexes as precursors for the synthesis of the new [FeFe]-hydrogenase model complexes. In addition, the synthesis and the structural characterization of the two synthetic targets **3b** and **4b**, as well as the proposed mechanism (Scheme 3) of their formation, are described. To the best of our knowledge, this is the first study to illustrate the synthesis of the 1,3-dithiolato-diiron complexes from the symmetrical aromatic thioketones.

### **Results and Discussion**

The reaction of Fe<sub>3</sub>(CO)<sub>12</sub> with one equivalent of thiobenzophenone (**2a**) or 9H-thioxanthene-9-thione (**2b**) in thf at reflux for 20 min resulted in the formation of the *ortho*-metallated complexes, [Fe<sub>2</sub>(CO)<sub>6</sub>{ $\mu,\kappa,S,SCH(C_6H_5)C_6H_4-\eta^2$ }] (**3a**) and [Fe<sub>2</sub>(CO)<sub>6</sub>{ $\mu,\kappa,S,SCH(C_6H_4)-S-C_6H_3-\eta^2$ }] (**4a**), respectively, as the major products. In addition to **3a**, complexes [Fe<sub>2</sub>(CO)<sub>6</sub>{ $\mu-SCH(C_6H_5)C_6H_4S-\mu$ }] (**3b**) and [Fe<sub>2</sub>(CO)<sub>6</sub>{ $\mu-SC(C_6H_5)2S-\mu$ }] (**3c**) were produced from the reaction of Fe<sub>3</sub>(CO)<sub>12</sub> with **2a**. Similarly, complexes [Fe<sub>2</sub>(CO)<sub>6</sub>{ $\mu-SCH(C_6H_4)-S-C_6H_3S-\mu$ }] (**4b**) and [Fe<sub>2</sub>(CO)<sub>6</sub>{ $\mu-SC(C_6H_4)-S-C_6H_3S-\mu$ }] (**4b**) and [Fe<sub>2</sub>(CO)<sub>6</sub>{ $\mu-SC(C_6H_4)-S-C_6H_4S-\mu$ ]] (**4b**) and [Fe<sub>2</sub>(CO)<sub>6</sub>{ $\mu-SC(C_6H_4-S-C_6H_4)-S-C_6H_4S-\mu$ }] (**4b**) and [Fe<sub>2</sub>(CO)<sub>6</sub>{ $\mu-SC(C_6H_4-S-C_6H_4)-S-L_6H_4S-\mu$ }] (**4b**) (Schemes 1 and 2).

It must be noted, however, that products **3b**, **3c**, **4b**, and **4c** were obtained in trace amounts in these reactions. In contrast, the treatment of Fe<sub>3</sub>(CO)<sub>12</sub> with an excess of **2a** or **2b** in thf at reflux for ca. 3 h gave the [2Fe2S]-model complexes, **3b–c** and **4b–c**, respectively, in moderate yields. Unexpectedly, the tetranuclear complex, [{Fe<sub>2</sub>(CO)<sub>6</sub>{ $\mu$ -SCH(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>}<sub>2</sub>( $\mu$ <sup>4</sup>-S)] (**3d**), and known tetraphenylethylene



Scheme 1. The reaction of  $Fe_3(CO)_{12}$  with **2a** where (a) *n* is 1, the reaction time is 20 min, **3a** (major), **3b** and **3c** (traces), and (b) *n* is 3, the reaction time is 180 min, and the main products are **3b–d** and **5**.



Scheme 2. The reaction of  $Fe_3(CO)_{12}$  with **2b** where (a) *n* is 1, the reaction time is 20 min, **4a** (major), **4b** and **4c** (traces) and (b) *n* is 3, the reaction time is 180 min, and the main products are **4b** and **4c**.

(5) were obtained from the reaction of 2a with  $Fe_3(CO)_{12}$ . Complexes 3b-d and 4a-c are air-stable in the solid state for months and for several hours in solution. It is worth noting that these complexes are fairly soluble in common organic solvents including the hydrocarbons. It is interesting to note that there is only one sulfur atom in the structures of starting thicketones 2a and 2b. The reaction of these compounds with  $Fe_3(CO)_{12}$ , however, furnished the [2Fe2S] complexes, 3b, 3c, 4b, and 4c, and the [4Fe3S] complex, 3d. Thus, an important question arose about the source of the additional sulfur atom in these complexes. A possible explanation is based on the assumption that these thioketones act as sulfur transfer reagents. If this assumption is true, then the question arises as to whether or not these thicketones can be used as efficient precursors for [FeFe]-hydrogenase model synthesis. In order to find convincing answers for these questions, we investigated the reaction of 3a with 2a. This reaction led to the formation of complex 3b in a moderate yield, which suggests that 2a is acting as a sulfur transfer reagent, while 3a is an important intermediate in the multistep synthesis of the [FeFe]-hydrogenase model complexes of the type **3b**. A plausible mechanism for the formation of complex 3b from 3a is shown in Scheme 3. The postulated reactive intermediate 8 plays a key role in the formation of **3b**. A similar reaction pathway has already been described by Eisch et al.[13c]



Scheme 3. The proposed mechanism for the formation of 3b from 3a.

Complex 3c is believed to be produced by the oxidative addition of  $Fe_3(CO)_{12}$  along the S–S bond of the in situgenerated diphenyldithiirane (7). The latter could be formed from 2a by means of a stepwise mechanism (Scheme 4) under the catalytic influence of the carbonyliron complex that is present in the reaction mixture. Thiobenzophenone *S*sulfide (thiosulfine) (6) is believed to be a reactive intermediate in the formation of 7. On the other hand, compound 6 could play the role of a sulfur transfer reagent in the process that leads to the formation of complex 3d (Scheme 5). Saito et al. described the conversion of a special type of thioketone to dithiiranes by means of heating the corresponding thioketone with  $S_8$ .<sup>[13b]</sup> In addition, Huisgen and Rapp have also suggested that "the thioketone itself can be converted to a sulfur donor that is capable of generating the thione *S*-sulfide in an unidentified pathway".<sup>[13a]</sup>



Scheme 4. The reaction pathway for the formation of 3c via the intermediate diphenyldithiirane (7).



Scheme 5. The proposed mechanism for the conversion of the initially formed 3a into the dinuclear complex 3d by means of a sulfur transfer mechanism.

The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **4a** exhibit signals at  $\delta = 4.86$  and 60.7 ppm, respectively, which were attributed to the methine group. These resonances, as well as the other signals in the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of **4a**, are in the same range as those observed for the analogue complexes **3a** and **3e–g**. The <sup>1</sup>H NMR spectra for **3c** and **4c** show a broad signal at  $\delta = 7.57$  ppm (for **3c**) and two broad resonances at  $\delta = 7.42$  and 7.74 ppm (for **4c**), which were attributed to the aromatic protons. In addition, there are no signals at  $\delta < 6.2$  ppm to indicate the presence of methine protons in these complexes. The <sup>1</sup>H NMR spectra of **3b** and **4b** show a singlet at  $\delta = 5.90$  and 5.28 ppm, respectively, which corresponds to the methine protons. These values are shifted downfield compared to those of the analogues **3a** and **4a**, respectively. The <sup>1</sup>H NMR spectrum of **3d** reveals the presence of two methine groups and the resonances for these protons are found at  $\delta = 4.21$  and 4.66 ppm, respectively. The <sup>13</sup>C NMR spectra of **3b–d** and **4a–c** display the resonances of the C=O groups in the range of 207 to 210 ppm. Finally, the IR spectra of complexes **3b– d** and **4a–c** display three major absorption bands in the region of 2075 to 1985 cm<sup>-1</sup>, which are typical for carbonyl groups that are bonded to iron atoms.

The molecular structures of complexes 3c, 3d, 4b, and 4c were confirmed by X-ray diffraction analysis and are shown in Figures 2, 3, 4, and 5, respectively. The central [2Fe2S] moieties of these complexes are in the "butterfly" arrangement and have a distorted octahedral geometry around the iron center. The thiolato sulfur atoms S(1) and S(2) are  $\mu^2$ coordinated to Fe(1) and Fe(2) in the structures of 3c, 4b, and 4c. However, the two sulfur atoms of the bridging dithiolato ligand of complex 4b are connected to different carbon atoms. One of the sulfur atoms is bonded to an aliphatic carbon while the other one is bonded to an aromatic carbon. In complexes 3c and 4c, on the other hand, the sulfur atoms are both bonded to the same aliphatic carbon. All of the iron atoms in tetranuclear complex 3d are bonded to the same sulfur atom (S3) and, in addition, the thiolato sulfur atoms S(1) and S(2) are  $\mu^2$ -coordinated to Fe(1), Fe(2) and Fe(3), Fe(4), respectively. The Fe-Fe bond length of 4b [2.5218(5) Å] is comparable to those reported for the [FeFe]-hydrogenase model complexes<sup>[10i,10l,14-20]</sup> and to that of 3d [2.5246 Å (mean)], but it is longer than the corresponding bond lengths in the analogous complexes 3e



Figure 2. The ORTEP drawing of  $[Fe_2(CO)_6{\mu-SC(C_6H_5)_2S-\mu}]$ (3c) with the thermal ellipsoids set at the 50% probability level. The selected distances [Å] and angles [°] are Fe(1)–Fe(2) 2.4867(4), Fe(1)–S(1) 2.2785(6), Fe(1)–S(2) 2.2625(6), Fe(2)–S(1) 2.2757(6), Fe(2)–S(2) 2.2608(6), Fe(1)–S(1)–Fe(2) 66.190(19), Fe(1)–S(2)– Fe(2) 66.699(19), S(1)–Fe(1)–S(2) 72.21(2), and S(1)–Fe(2)–Fe(1) 56.618(17).



Figure 3. The ORTEP drawing of  $[\{Fe_2(CO)_6\{\mu-SCH(C_6H_5)_2\}\}_2 - (\mu^4-S)]$  (3d) with the thermal ellipsoids set at the 50% probability level. The hydrogen atoms were omitted for clarity. The selected distances [Å] and angles [°] are Fe(1)–Fe(2) 2.5195(3), Fe(3)–Fe(4) 2.5297(4), Fe(1)–S(1) 2.2555(5), Fe(2)–S(1) 2.2625(5), Fe(1)–S(3) 2.2321(5), Fe(2)–S(3) 2.2443(4), Fe(3)–S(2) 2.2701(5), Fe(4)–S(2) 2.2637(5), Fe(3)–S(3) 2.2344(5), Fe(4)–S(3) 2.2379(5), Fe(1)–S(1)–Fe(2) 67.789(16), Fe(1)–S(3)–Fe(2) 68.505(15), Fe(3)–S(2)–Fe(4) 67.831(14), Fe(3)–S(3)–Fe(4) 68.849(15), Fe(1)–S(3)–Fe(3) 136(74), S(2)–Fe(4)–S(3) 76.324(17), and S(1)–Fe(2)–Fe(1) 55.974(13).



Figure 4. The ORTEP drawing of  $[Fe_2(CO)_6 \{\mu$ -SCH(C<sub>6</sub>H<sub>4</sub>)–S–C<sub>6</sub>H<sub>4</sub>S- $\mu$ }] (**4b**) with the thermal ellipsoids set at the 50% probability level. The selected distances [Å] and angles [°] are Fe(1)–Fe(2) 2.5218(5), Fe(1)–S(1) 2.2415(6), Fe(1)–S(2) 2.2340(6), Fe(2)–S(1) 2.2417(7), Fe(2)–S(2) 2.2412(7), Fe(1)–S(1)–Fe(2) 68.46(2), Fe(1)–S(2)–Fe(2) 66.60(2), S(1)–Fe(2)–S(2) 85.05(2), and S(1)–Fe(2)–Fe(2)–Fe1 55.767(18).

[2.4993(6) Å]<sup>[11b]</sup> and **4c** [2.4867(4) Å]. In addition, the Fe–S bond lengths of **4b** [2.2396 Å (mean)] are significantly shorter than those reported for the [FeFe]-hydrogenase model complexes<sup>[21–27]</sup> and are about 0.02 Å shorter than those of **4c** [2.2694 Å (mean)] and of **3c** [2.2673 Å (mean)]. The Fe–Fe bond length of **3c** [2.4850(5) Å] is similar to that of the reported analogous complex **3a** [2.4986(6) Å].<sup>[11b]</sup> The angles of S(1)–Fe(1)–S(2) [85.22(2)°] and S(1)–Fe(2)–

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S(2) [85.02(2)°] in **4b** are within the same ranges as those observed for the [FeFe]-hydrogenase model complexes.<sup>[14–27]</sup> However, these angles are wider than the corresponding angles of S(1)–Fe(1)–S(2) [72.21(2)°] and S(1)–Fe(2)–S(2) [72.29(2)°] in **4c**, and of S(1)–Fe(1)–S(2) [72.26(2)°] and S(1)–Fe(2)–S(2) [72.17(2)°] in **3c**, which is attributed to the bonding of the two sulfur atoms of the dithiolato ligand to the same carbon in **3c** or **4c**.



Figure 5. The ORTEP drawing of  $[Fe_2(CO)_6{\mu-SC(C_6H_4-S-C_6H_4)-S-\mu}]$  (4c) with the thermal ellipsoids set at the 50% probability level. The selected distances [Å] and angles [°] are Fe(1)–Fe(2) 2.4850(5), Fe(1)–S(1) 2.2693(6), Fe(1)–S(2) 2.2629(6), Fe(2)–S(1) 2.2643(6), Fe(2)–S(2) 2.2728(7), Fe(1)–S(1)–Fe(2) 66.478(19), Fe(1)–S(2)–Fe(2) 66.44(2), S(1)–Fe(1)–S(2) 72.26(2), and S(1)–Fe(1)–Fe(2) 56.666(18).

#### **Electrochemical Investigations**

The electrocatalytic dihydrogen formation of the [FeFe]hydrogenase model compounds has been well established.<sup>[28]</sup> In order to show the ability of the new complexes to act as catalyst for dihydrogen formation, cyclic voltammetry was performed for compound 3b in the presence and absence of acetic acid. The cathodic scan of complex 3b (Figure 6) reveals an irreversible reduction peak at  $E_{p,red}$  = -1.58 V. In comparison to the internal standard ferrocene, this signal is most likely a one-electron reduction and was therefore attributed to the  $[Fe^{I}Fe^{I}] \rightarrow [Fe^{I}Fe^{0}]^{-}$  process. The signal remained completely irreversible at the different scan rates (1.5, 1.0, 0.8, 0.1, and 0.05 V/s). This behavior suggests an EC mechanism where the [Fe<sup>I</sup>Fe<sup>I</sup>] state is transferred into [Fe<sup>I</sup>Fe<sup>0</sup>]- by a one-electron reduction, followed by a fast change in the bonding properties within the molecule, which is in good agreement with the literature results.<sup>[29,30]</sup> This change in the bonding properties can be best described by the cleavage of the Fe-Fe bond and/or the appearance of a bridging carbonyl molecule.<sup>[29]</sup> At -2.15 V a further reduction of the chemically changed [Fe<sup>I</sup>Fe<sup>0</sup>] species was observed, which was attributed to the  $[Fe^{I}Fe^{0}] \rightarrow$  $[Fe^{0}Fe^{0}]^{2-}$  process in accordance with  $Fe_{2}(CO)_{6}(pdt)$  (pdt = propanedithiolato).<sup>[31]</sup> Two sparsely separated reoxidation signals were observed at -2.07 and -2.00 V. An additional

oxidation peak appears at -0.80 V. This signal was only observed upon the initial one-electron reduction of the initial [Fe<sup>I</sup>Fe<sup>I</sup>] species at -1.58 V. According to the literature, this might be the reoxidation of a chemically transformed [Fe<sup>I</sup>Fe<sup>0</sup>] species.<sup>[29]</sup> At ca. +1.28 V the irreversible oxidation of the [Fe<sup>I</sup>Fe<sup>I</sup>] cluster can be observed. A corresponding reduction signal appeared at -0.67 mV, which suggests that there was structural reorganization after the oxidation and that it was not solely a simple reduction of the obtained [Fe<sup>II</sup>Fe<sup>I</sup>] complex as has been already described for similar reduction processes.



Figure 6. The cyclic voltammetric reduction of  $[Fe_2(CO)_6{\mu-SCH(C_6H_5)C_6H_4S-\mu}]$  (**3b**) in acetonitrile (1.0 mM) on a glassy carbon electrode where Fc/Fc<sup>+</sup> was used as the internal standard and  $[nBu_4N][PF_6]$  (0.1 M) was used as the supporting electrolyte.

The influence of compound **3b** towards the electrochemical reduction of protons to dihydrogen was investigated between 0.0 and -2.5 V by the addition of acetic acid (p $K_a$  = 22.3 in CH<sub>3</sub>CN) (Figure 7). In the presence of acid, the initial one-electron reduction signal remains unchanged. Neither a significant increase nor a shift of the signal was observed. An acid-dependent increase in the peak current



Figure 7. The cyclic voltammograms of  $[Fe_2(CO)_6{\mu-SCH(C_6H_5)-C_6H_4S-\mu}]$  (3b) in acetonitrile (1 mM) in the presence of HOAc (0–10 mM), (potentials vs. Fc/Fc<sup>+</sup>).

around -2.0 V was observed when the cathodic scan included more negative potentials. According to the literature, this behavior could be explained by the catalytic reduction of acetic acid by a reduced **3b**<sup>[28]</sup> However, a comparison of the peak currents at around -2.0 V and in pure acetic acid reveals only moderate catalytic activity for compound **3b**.

Since compound **3b** revealed the structural properties of  $[Fe_2(CO)_6(pdt)]$  (pdt = propanedithiolato) (Fe-S-alkyl bond) and  $[Fe_2(CO)_6(bdt)]$  (bdt = benzenedithiolato) (Fe-S-phenyl bond), and since both of the complexes revealed different electrochemical properties, a short comparison between the three complexes will be given here. In contrast to **3b** and  $[Fe_2(CO)_6(pdt)]$ ,<sup>[31]</sup>  $[Fe_2(CO)_6(bdt)]^{[10h]}$  shows an initial two-electron reduction to a [Fe<sup>0</sup>Fe<sup>0</sup>] complex at -1.25 V (Table 1). This reduction, however, appears at two different potentials. The one-electron reduction of [Fe<sub>2</sub>- $(CO)_6(pdt)$ ] and **3b** is observed at -1.34 and -1.58 V, respectively. In contrast to  $[Fe_2(CO)_6(bdt)]$ , the second one-electron reduction is found at a distinctly lower potential around -2 V for both of the complexes. When acetic acid was added to the complexes, the reduction of the protons to dihydrogen was observed for all of the complexes at around -2 V. Based on these results, complex **3b** should be considered to be a comparable model to the [FeFe]-hydrogenase model complexes with a propanedithiolato backbone.

Table 1. The electrochemical data of the iron complexes 3b, [{Fe<sub>2</sub>(CO)<sub>6</sub>}(pdt)], and [{Fe<sub>2</sub>(CO)<sub>6</sub>}(bdt)].

	$E_{\text{red 1}}$ [V]	$E_{\text{red 2}}$ [V]	$E_{\rm ox}$ [V]
$3b^{[a]}$ [{Fe <sub>2</sub> (CO) <sub>6</sub> }(pdt)] <sup>[31][b]</sup>	-1.58 -1.34	-2.15 -1.95	+1.28 +1.14
$[{Fe_2(CO)_6}(bdt)]^{[10h][c]}$	-1.27	-1.23	irreversible

[a] Glassy carbon electrode (potentials given in V,  $\pm 0.01$ ) vs. Fc/ Fc<sup>+</sup> (0.01 M) in [*n*Bu<sub>4</sub>N][PF<sub>6</sub>]/CH<sub>3</sub>CN (0.1 M) as the supporting electrolyte. [b] CH<sub>3</sub>CN solution (0.1 M [*n*Bu<sub>4</sub>N][PF<sub>6</sub>]) with a glassy carbon working electrode standard vs. Fc/Fc<sup>+</sup>. [c] First scan, v =0.1 Vs<sup>-1</sup>; solution in [*n*Bu<sub>4</sub>N][PF<sub>6</sub>]/CH<sub>3</sub>CN.

### Conclusions

In summary, we have succeeded in synthesizing two new complexes, **3b** and **4b**, that are bioinspired models for the active site of the [FeFe]-hydrogenases by using the aromatic thioketones, **2a** and **2b**, as the starting materials. The synthesis of **3b** was accomplished by a multistep reaction. A possible mechanism for the formation of **3b** has been proposed. Firstly, thioketone **2a** reacts with Fe<sub>3</sub>(CO)<sub>12</sub> to give the *ortho*-metallated complex, **3a**. Secondly, a further equivalent of **2a**, which is activated by a side-on coordination to an iron atom, serves as a sulfur transfer reagent. Thirdly, complex **3b** is formed by the insertion of sulfur into the Fe-C  $\sigma$ -bond of **3a**. It was found that complex **3b** behaves as a catalyst for the electrochemical production of hydrogen in the presence of a weak acid, for example acetic acid, at a moderate potential.



The most remarkable feature of this investigation, however, is the assembly of a [FeFe]-hydrogenase active-sitecore analogue from simple aromatic thioketones. This is of particular interest to prebiotic chemistry since one can envision that in a hydrothermal vent environment that has a higher CO concentration, where reduced hydrothermal fluids pass through the iron-/sulfide-containing crust, significant concentrations of iron carbonyls and thioketones might be formed.<sup>[32a]</sup> In a slightly different prebiotic reaction that was reported by Cody et al., iron sulfide is consumed in the presence of CO and alkylthiol to produce [Fe<sub>2</sub>(RS)<sub>2</sub>(CO)<sub>6</sub>], sulfur, and hydrogen.<sup>[32b]</sup> These possible prebiotic reactions that are emerging for the [FeFe]-hydrogenase model systems are of great importance in the context of the iron-sulfur world hypothesis.<sup>[32c]</sup>

## **Experimental Section**

General Comments: All of the reactions were carried out under an argon atmosphere by using the standard Schlenk techniques. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR and 2D NMR spectra were recorded with a Bruker AVANCE 200 or 400 MHz spectrometer at room temperature and the solvent was used as the standard. The Mass spectra were obtained with a FINNIGAN MAT SSQ 710 instrument. The infrared spectra were measured with a Perkin-Elmer System 2000 FTIR spectrometer. Thiobenzophenone (2a)<sup>[12d]</sup> and 9Hthioxanthene-9-thione (2b)<sup>[13a]</sup> were prepared according to the literature procedures. The solvents and Fe<sub>3</sub>(CO)<sub>12</sub> were purchased from Sigma-Aldrich. All of the solvents were dried and distilled prior to use according to the standard methods. Silica gel 60 (0.015–0.040 mm) was used for the column chromatography. TLC was done with Merck TLC aluminum sheets, silica gel 60  $F_{254}$ . The elemental analyses were performed with a Vario EL III CHNS (Elementaranalysen GmbH Hanau) as single determinations.

**[Fe<sub>2</sub>(CO)<sub>6</sub>{μ-SCH(C<sub>6</sub>H<sub>5</sub>)C<sub>6</sub>H<sub>4</sub>S-μ}] (3b), [Fe<sub>2</sub>(CO)<sub>6</sub>{μ-SC(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>}-(S-μ)] (3c), and [{Fe<sub>2</sub>(CO)<sub>6</sub>{μ-SCH(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>S-μ}] (3d). Method A: Fe<sub>3</sub>(CO)<sub>12</sub> (100 mg, 0.2 mmol) and thiobenzophenone (2a) (118 mg, 0.4 mmol) in thf (30 mL) were stirred at 65 °C under argon for a period of 3 to 4 h. The reaction mixture was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by column chromatography. Elution with hexane gave an orange solution of complex <b>3c** ( $R_f = 0.7$ ), elution with hexane/diethyl ether (1:1, v/v) afforded a reddish solution of complex **3b** ( $R_f = 0.5$ ) and elution with diethyl ether gave a red solution of **3d** ( $R_f = 0.5$ ). The solutions were evaporated under vacuum. Suitable crystals of **3c** and **3d** for X-ray analysis were obtained by the slow evaporation of a concentrated pentane solution at -25 °C.

**3b:** Yield 22 mg (22%).  $C_{19}H_{10}Fe_2O_6S_2$  (509.9): calcd. C 44.74, H 1.98, S 12.57; found C 45.18, H 1.83, S 12.1. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 5.90 [s, 1 H, H(1)], 7.03–7.23 (m, 5 H, Ar-H), 7.32 [dd, <sup>3</sup>J = 7.7 Hz, 1 H, H(10)], 7.37 [dd, <sup>3</sup>J = 8.1 Hz, 1 H, H(11)], 7.75 [d, <sup>3</sup>J = 8.0 Hz, 1 H, H(9)], 8.51 [d, <sup>3</sup>J = 8.2 Hz, 1 H, H(12)] ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 70.7 (C1), 123.8, 125.9, 126.7, 127.1, 128.2, 130.8, 138.3, 141.8, 143.7, 144.6, 152.5, 157.8 (2 Ph), 207.3, 208.9, 210.5 (CO) ppm. FTIR (KBr):  $\tilde{v}_{C=0}$  = 2073 (vs), 2035 (vs), 2008 (w, sh), 1994 (s), 1979 (s) cm<sup>-1</sup>. MS (DEI = 70 eV): m/z = 510 [M<sup>+</sup>], 482 [M<sup>+</sup> – CO], 454 [M<sup>+</sup> – 2CO], 426 [M<sup>+</sup> – 3CO], 398 [M<sup>+</sup> – 4CO], 370 [M<sup>+</sup> – 5CO], 342 [M<sup>+</sup> – 6CO].

**3c:** Yield 25 mg (25%).  $C_{19}H_{10}Fe_2O_6S_2$  (509.9): calcd. C 44.74, H 1.98, S 12.57; found C 44.96, H 1.72, S 12.23. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 7.57 (br. s, 10 H, 2 Ph) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 95.0 (SCS), 123.6, 127.7, 128.5 (2 Ph), 207.0, 208.2 (CO) ppm. FTIR (KBr):  $\tilde{v}_{C=O}$  = 2076 (vs), 2035 (vs), 1990 (vs) cm<sup>-1</sup>. MS (DEI = 70 eV): *m*/*z* = 510 [M<sup>+</sup>], 482 [M<sup>+</sup> - CO], 454 [M<sup>+</sup> - 2CO], 426 [M<sup>+</sup> - 3CO], 398 [M<sup>+</sup> - 4CO], 370 [M<sup>+</sup> - 5CO], 342 [M<sup>+</sup> - 6CO].

**3d:** Yield 21 mg (10%).  $C_{38}H_{22}Fe_4O_{12}S_3$  (989.8): calcd. C 46.09, H 2.24, S 9.72; found C 46.52, H 2.47, S 9.39. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 4.21, 4.66 (s, 2 H, 2 SCH), 7.06, 7.44, 7.68 (br. s, 20 H, 2 Ph) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  = 38.1, 38.9 (2 CS), 121.3, 125.2, 126.5, 127.3 (2 Ph), 206.6, 207.8, 208.1 (CO) ppm. FTIR (KBr):  $\tilde{v}_{C=O}$  = 2072 (vs), 2059 (w, sh), 2039 (vs), 1998 (vs) cm<sup>-1</sup>. MS (DEI = 70 eV): *m*/*z* = 990 [M<sup>+</sup>], 906 [M<sup>+</sup> – 3CO], 878 [M<sup>+</sup> – 4CO], 822 [M<sup>+</sup> – 6CO], 794 [M<sup>+</sup> – 7CO], 766 [M<sup>+</sup> – 8CO], 738 [M<sup>+</sup> – 9CO], 711 [M<sup>+</sup> – 10CO], 655 [M<sup>+</sup> – 12CO].

[Fe<sub>2</sub>(CO)<sub>6</sub>{ $\mu$ -SCH(C<sub>6</sub>H<sub>5</sub>)C<sub>6</sub>H<sub>4</sub>S- $\mu$ }] (3b). Method B: Thioketone 2a (18 mg, 0.1 mmol) was added to a solution of 3a (46 mg, 0.1 mmol) in thf (30 mL) under argon and the mixture was stirred at 65 °C for 3 h. The solvent was removed under vacuum and the crude product was purified by column chromatography. Elution with hexane/diethyl ether (1:1, v/v) gave a reddish solution ( $R_f = 0.5$ ), which was identified as complex 3b. Yield 21 mg (41%).

**[Fe<sub>2</sub>(CO)<sub>6</sub>{μ,κ,***S***,SCH(C<sub>6</sub>H<sub>4</sub>)–S–C<sub>6</sub>H<sub>4</sub>-η<sup>2</sup>}]** (4a): Fe<sub>3</sub>(CO)<sub>12</sub> (140 mg, 0.28 mmol) was dissolved in thf (40 mL) and 9*H*-thioxanthene-9-thione (**2b**) (64 mg, 0.28 mmol) was added to the solution. The mixture was stirred at 65 °C for 20 min under argon. The solvent was removed in vacuo. The crude product was purified by column chromatography by using hexane as the eluent. The major dark red band ( $R_f = 0.5$ ) was collected and the solvent was removed. The product was identified as complex **4a**. Yield 92 mg (65%). C<sub>19</sub>H<sub>8</sub>Fe<sub>2</sub>O<sub>6</sub>S<sub>2</sub> (507.8): calcd. C 44.91, H 1.59, S 12.62; found C 44.70, H 1.92, S 12.58. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta = 4.82$  [s, 1 H, H(12)], 6.94 [m, 1 H, H(8)] 7.26 [m, 1 H, H(9)], 7.36 [m, 1 H, H(10)], 7.39 [m, 1 H, H(7)], 7.62 [m, 1 H, H(3)], 7.92 [m, 1 H, H(4)], 8.04 [m, 1 H, H(2)] ppm.  $^{13}C\{^{1}H\}$  NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 60.7$  (CS), 125.0, 125.8, 126.6, 127.2, 127.5, 128.2, 128.5, 131.0, 135.9, 136.8, 141.8, 154.8 (2Ph), 208.6, 209.4 (CO) ppm. FTIR (C<sub>5</sub>H<sub>12</sub>):  $\tilde{v}_{C=O} = 2071$  (vs), 2037 (vs), 2001 (vs), 1984 (w, sh) cm<sup>-1</sup>. MS (DEI = 70 eV): m/z = 508 [M<sup>+</sup>], 480 [M<sup>+</sup> - CO], 452 [M<sup>+</sup> - 2CO], 424 [M<sup>+</sup> - 3CO], 396 [M<sup>+</sup> - 4CO], 368 [M<sup>+</sup> - 5CO], 340 [M<sup>+</sup> - 6CO].

 $[Fe_2(CO)_6{\mu-SCH(C_6H_4)-S-C_6H_4S-\mu}]$  (4b) and  $[Fe_2(CO)_6{\mu-SCH(C_6H_4)-S-C_6H_4S-\mu}]$  $SC(C_6H_4-S-C_6H_4)S-\mu$ ] (4c): The ligand, 9*H*-thioxanthene-9thione (2b) (163 mg, 0.48 mmol), was added to a solution of Fe<sub>3</sub>(CO)<sub>12</sub> (120 mg, 0.24 mmol) in thf (40 mL) under argon. The reaction mixture was stirred at 65 °C for a period of 3 to 4 h. After evaporation of the solvent, the residue was purified by coloum chromatography on a silica gel column. Elution with hexane gave an orange-reddish solution of complex 4c ( $R_{\rm f} = 0.6$ ). Elution with hexane/diethyl ether (2:1, v/v) afforded a reddish solution of complex 4b ( $R_{\rm f} = 0.3$ ). The two solutions were evaporated under vacuum. Suitable crystals of 4b and 4c for X-ray analysis were obtained by the slow evaporation of a concentrated pentane solution at -25 °C. 4b. Yield 48 mg (37%). C<sub>19</sub>H<sub>8</sub>Fe<sub>2</sub>O<sub>6</sub>S<sub>3</sub> (540.1): calcd. C 42.25, H 1.49, S 17.80; found C 42.58, H 1.68, S 17.30. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, assignment analogous to 4a):  $\delta$  = 5.28 ppm. [s, 1 H, H(12)], 7.05 [dd, 1 H,  ${}^{3}J$  = 8.0 Hz, H(8)], 7.31 [m, 1 H, H(9)], 7.43[d, 1 H,  ${}^{3}J$  = 8.0 Hz, H(10)], 7.56 [d, 1 H,  ${}^{3}J$  = 8.0 Hz, H(7)], 7.76 [dd, 1 H,  ${}^{3}J$  = 8.0 Hz, H(3)], 8.03 [d, 1 H,  ${}^{3}J$  = 8.0 Hz, H(4)], 8.62 [d, 1 H,  ${}^{3}J$  = 8.0 Hz, H(2)] ppm.  ${}^{13}C{}^{1}H$  NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 69.9 (C12), 125.3, 126.4, 126.5, 126.8, 126.9, 127.1, 127.8, 128.05, 129.3, 132.8, 142.1 158.2 (2 Ph), 207.0, 208.5, 209.2, 212.2 (CO) ppm. FTIR (KBr):  $\tilde{v}_{C=O} = 2075$  (vs), 2038 (vs), 2017 (w, sh), 2003 (s), 1985 (s) cm<sup>-1</sup>. MS (DEI = 70 eV): m/z= 540 [M<sup>+</sup>], 512 [M<sup>+</sup> - CO], 484 [M<sup>+</sup> - 2CO], 456 [M<sup>+</sup> - 3CO], 428 [M<sup>+</sup> - 4CO], 400 [M<sup>+</sup> - 5CO], 372 [M<sup>+</sup> - 6CO]. 4c: Yield 41 mg (32%).  $C_{19}H_8Fe_2O_6S_3$  (540.1): calcd. C 42.25, H 1.49, S 17.80; found C 42.73, H 1.58, S 17.62. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C, assignment analogous to 4a):  $\delta$  = 7.42, 7.74 (br. s, 8 H, 2

Table 2. The crystal data and refinement details for the X-ray structure determinations of the compounds 3c, 3d, 4b, and 4c.

	3c	3d	4b	4c
Formula	$C_{19}H_8Fe_2O_6S_3$	C <sub>38</sub> H <sub>22</sub> Fe <sub>4</sub> O <sub>12</sub> S <sub>3</sub>	C <sub>19</sub> H <sub>7</sub> Fe <sub>2</sub> O <sub>6</sub> S <sub>3</sub>	$C_{19}H_{10}Fe_2O_6S_2$
$fw [gmol^{-1}]$	540.13	990.14	539.13	510.09
	-140(2)	-140(2)	-140(2)	-140(2)
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P\overline{1}$	$P2_1/c$	C2/c
<i>a</i> [Å]	10.3982(3)	9.1211(2)	7.8592(2)	20.4829(12)
b [Å]	9.6800(2)	13.7459(2)	14.9765(3)	6.4767(5)
c [Å]	19.7021(5)	16.5123(3)	17.2733(3)	30.4653(17)
	90	89.164(1)	90	90
β [°]	99.020(2)	83.405(1)	92.011(1)	107.121(3)
γ [°]	90	76.626(1)	90	90
$V[Å^3]$	1958.58(9)	2000.65(6)	2031.87(7)	3862.5(4)
Z	4	2	4	8
$\rho \left[ \text{g cm}^{-3} \right]$	1.832	1.644	1.762	1.754
$\mu  [\mathrm{cm}^{-1}]$	18.37	16.39	17.71	17.53
Measured data	12241	21290	12476	6437
Data with $I > 2\sigma(I)$	3895	8546	4262	3780
Unique data/ $R_{int}$	4480/0.0313	10330/0.0197	4595/0.0231	4106/0.0218
$wR_2$ (all data, on $F^2$ ) <sup>[a]</sup>	0.0727	0.0701	0.0865	0.0733
$R_1 [I > 2\sigma(I)]^{[a]}$	0.0306	0.0294	0.0341	0.0311
s[b]	1.027	1.042	1.011	1.065
Residual electron density [eÅ <sup>-3</sup> ]	0.475/-0.409	0.485/-0.368	1.765/-0.534	0.466/-0.349
Absorption correction	none	none	none	none

[a]  $R_1 = (\Sigma ||F_o| - |F_c||) / \Sigma |F_o|$ ;  $wR_2 = \{\Sigma [w(\overline{F_o^2 - F_c^2})^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$ ;  $w^{-1} = \sigma^2 (F_o^2) + (aP)^2 + bP$ ;  $P = [2F_c^2 + \max(F_o^2)] / 3$ . [b]  $s = \{\Sigma [w(F_o^2 - F_c^2)^2] / (N_o - N_p) \}^{1/2}$ .

Ph) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 93.9 (SCS), 123.8, 126.3, 127.0,129.3, 132.9, 134.3, 137.0 (2 Ph), 207.0, 208.1 (CO) ppm. FTIR (KBr):  $\tilde{v}_{C=O}$  = 2075 (vs), 2037 (vs), 2001 (vs) cm<sup>-1</sup>. MS (DEI = 70 eV): m/z = 540 [M<sup>+</sup>], 512 [M<sup>+</sup> – CO], 484 [M<sup>+</sup> – 2CO], 456 [M<sup>+</sup> – 3CO], 428 [M<sup>+</sup> – 4CO], 400 [M<sup>+</sup> – 5CO], 372 [M<sup>+</sup> – 6CO].

**Characterization of 1,1,2,2-Tetraphenylethene (5):** Colorless crystals, m.p. 222–224 °C (ref.<sup>[33]</sup> m.p. 222 °C). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  = 7.05–7.21 (m, 20 H, Ar-H) ppm. MS (DEI = 70 eV): *m*/*z* = 332 [M<sup>+</sup>].

**Electrochemistry:** The cyclic voltammograms were measured in a three electrode cell with a 1.0 mm diameter glassy carbon disc working electrode, a platinum auxiliary electrode, and Ag/AgCl in CH<sub>3</sub>CN as the reference electrode. The solvent contained  $[nBu_4N][PF_6]$  (0.1 M) as the supporting electrolyte. The measurements were performed at room temperature with a Metrohm 663 VA Standard galvanostat. Deaeration of the sample solutions was accomplished by passing a stream of nitrogen through the solutions for 5 min prior to the measurements, and the solutions were kept under nitrogen for the duration of the measurements. All of the data obtained were corrected against the Fc/Fc<sup>+</sup> couple as an internal standard ( $E_{1/2} = 503$  mV vs. Ag/AgCl in CH<sub>3</sub>CN).

**Crystal Structure Determination:** The intensity data for the compounds were collected with a Nonius KappaCCD diffractometer by using graphite-monochromated Mo- $K_{\alpha}$  radiation. The data were corrected for Lorentz and polarization effects but not for absorption effects.<sup>[34,35]</sup> The crystallographic data, as well as the structure solutions and refinement details, are summarized in Table 2. The structures were solved by direct methods (SHELXS)<sup>[36]</sup> and were refined by full-matrix least-squares techniques against  $F_{o}^2$  (SHELXL-97).<sup>[36]</sup> All of the hydrogen atom positions were included at the calculated positions with fixed thermal parameters. All of the non-hydrogen atoms were refined anisotropically.<sup>[36]</sup> XP (SIE-MENS Analytical X-ray Instruments, Inc.) was used for the structure representations.

CCDC-803654 (for **3c**), -803655 (for **3d**), -803656 (for **4b**) and -803657 (for **4c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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