Synthetic {2Fe2S}- and {2Fe3S]-Models of the [FeFe]-Hydrogenase Active Site

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[AD1] M. K. Harb, J. Windhager, A. Daraosheh, H. Görls, L. T. Lockett, N. Okumura, D. H. Evans, R. S. Glass, D. L. Lichtenberger, M. El-khateeb, W. Weigand. ***Phosphane- and Phosphite-Substituted Diiron Diselenolato Complexes as Models for [FeFe]-Hydrogenases***. *Eur. J. Inorg. Chem.* **2009**, 3414-3420.

[AD2] A. Q. Daraosheh, M. K. Harb, J. Windhager, H. Görls, M. El-khateeb, W. Weigand. ***Substitution Reactions at [FeFe] Hydrogenase Models Containing [2Fe3S] Assembly by Phosphine or Phosphite Ligands.*** *Organometallics*. **2009**, *28*, 6275-6280.

[AD3] A. Q. Daraosheh, H. Görls, M. El-khateeb, G. Mloston, W. Weigand. ***Reactions of Selected Aromatic Thioketones with Triiron Dodecarbonyl***. *Eur. J. Inorg. Chem.* **2011**, 349-355.

[AD4] A. Q. Daraosheh, U.-Peter Apfel, C. Friebe, H. Görls, M. El-khateeb, U. S. Schubert, G. Mloston, W. Weigand. ***New Approach to [FeFe]-Hydrogenase Models Using Aromatic Thioketone.*** Acceptance 201101032 / *Eur. J. Inorg. Chem*. **2011**.

Curriculum Vitae

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List of Publications

Published/accepted articles

1. A. Q. Daraosheh, U.-P Apfel, C. Friebe, H. Görls, U. S. Schubert, G. Mloston, M. El-khateeb, W. Weigand. ***New Approach to [FeFe]-hydrogenase Models Using Aromatic Thioketones***. Acceptance 201101032 / *Eur. J. Inorg. Chem*. **2011**.

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3. A. Q. Daraosheh, M. K. Harb, J. Windhager, H. Görls, M. El-khateeb, W. Weigand. ***Substitution Reactions at [FeFe]-Hydrogenase Models Containing [2Fe3S] Assembly by Phosphine or Phosphite Ligands***. *Organometallics*. **2009**, *28*, 6275-6280.

4. M. K. Harb, J. Windhager, A. Q. Daraosheh, H. Görls, L. T. Lockett, N. Okumura, D. H. Evans, R. S. Glass, D. L. Lichtenberger, M. El-khateeb, W. Weigand. ***Phosphaneand- and Phosphite-Substituted Diiron Diselenolato Complexes as Models for [FeFe]-Hydrogenases***. *Eur. J. Inorg. Chem*. **2009**, 3414-3420.

5. K. J. Asali, M. EL-Kateeb, A. Q. Daraosheh. ***Bimetallic Group 6 Tricarbonyls Containing Rigid Backbone Chelating Ligands Symmetrically Bridged by Bis(diphenylphosphino)alkane***. *Jordan Journal of Chemistry.* **2009**, *4 (3)*, 233-242.

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Ahmad Daraosheh

Declaration of authorship

I certify that the work presented here is, to the best of my knowledge and belief, original and the result of my own investigations, except as acknowledged, and has not been submitted, either in part or whole, for a degree at this or any other university.

Ich erkläre, dass ich die vorliegende Arbeit selbstständig und nur unter Verwendung der angegebenen Hilfsmittel, persönlichen Mitteilungen und Quellen angefertigt habe und dass ich nicht die gleiche, eine in wesentlichen Teilen ähnliche oder eine andere Abhandlung bei einer anderen Hochschule als Dissertation eingereicht habe.

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Ahmad Daraosheh

1. Introduction

Explanatory note: This cumulative thesis comprises four full papers. The author of this thesis is the first author of three papers and co-author of one paper. Three articles have been published in the *European Journal of Inorganic Chemistry*, and one article in *Organometallics*. All journals are peer reviewed.

All articles deal with the structural and functional analogues of the active sites of the [FeFe]-hydrogenases. Also other compounds, not closely related to the [FeFe]-hydrogenases active site have been described. The author papers are assigned as **[AD1]–[AD4]** in the text.

1.1 General considerations

Energy is one of the most fundamental parts of our universe; everything we do is connected to energy in one form or another.[1] We use many different sources to do work for us, these energy sources are classified into two groups-renewable and nonrenewable and most of our energy sources are nonrenewable.[2] Fossil fuels (coal, petroleum and natural gas) contribute about 85% of the world energy consumption. Basically, there are two main disadvantages of using fossil fuels; first, they are non-renewable resources because they are consumed at a rate much faster than they are formed, this means the supply of fossil fuels is limited and will, one day, run out. Second, the combustion of fossil fuels releases poisonous gases into the atmosphere. One of these gases is carbon dioxide, which could be the primary reason of global warming, causing the average surface temperature of the earth to rise. Thus, the industry and policy makers are increasingly being challenged to search for alternative renewable and clean energy sources.[3-12] One possible solution is the use of molecular hydrogen as alternative to fossil fuels.[10-14] However, free hydrogen is not occur naturally in quantity, and most hydrogen on Earth is bonded to oxygen in water or to hydrocarbon compounds. Therefore, the production of free Hydrogen requires the consumption of a hydrogen carrier such as a fossil fuel or water. The former consumes the fossil resource, without requiring further energy input, but it is harmful for environment. For that reason, it is particularly important to generate hydrogen by a method that dose not use fossil fuels. The electrolysis of water could be the suitable way to generate clean hydrogen, if the electrical or heat input produced from renewable, non-fossil energy.[5, 15]

The production of hydrogen from water occurs in nature by microorganisms that found in plants, algae, and cyanobacteria in oxygenic photosynthesis process.[16-18] Photosynthesis in these organisms is a complex series of reactions that use the sun light energy to drive electron transfer from water to CO_2 to yield organic compounds. Under certain conditions, however, instead of reducing CO_2, a few groups of microalgae and cyanobacteria having enzymes which can use the electrons harvested from water to reduce protons and produce hydrogen H_2. These enzymes are called hydrogenases.[19]

1.2 Hydrogenases definition

Hydrogenases are enzymes that catalyze reversible oxidation/reduction of molecular-hydrogen/protons in nature (Eq. 1). They can either oxidize H_2 to H^+ or reduce H^+ to H_2 and therefore provide a reversible sink for multi-electron transfer.[20-30].

$$H_2 \xrightleftharpoons{\text{Hydrogenase}} 2\,H^+(aq) + 2\,e^- \qquad \text{(Eq.1)}$$

Hydrogenases have been observed and characterized in many microorganisms, including some algae, trichomonads, anaerobic ciliates, and chytrid fungi.[31] Two important functions of hydrogenases are to balance the redox potential in the cell and also to provide energy by oxidation of molecular hydrogen. They may remove reducing equivalents by production of molecular hydrogen or provide electrons by splitting H_2.[9] The understanding of the biological role of the hydrogenases, and the structures of their active sites may provide a useful tool for designing an artificial electrocatalyst for large scale hydrogen production.[30, 32]

1.3 Hydrogenases classification

According to the metal composition of the active site, hydrogenases are classified into three major groups: [NiFe]-hydrogenases which are generally involved in hydrogen uptake; [FeFe]-hydrogenases which are bi-directional but usually associated with hydrogen production; [Fe]-hydrogenases or the former so-called "transition metal free hydrogenases".[30-34] A subgroup of the first class comprises the [NiFeSe] hydrogenases, in which one of the cysteine ligands of the nickel atom is replaced by selenocysteine.[35] A characteristic feature of all hydrogenases is that the

iron atoms are ligated by small inorganic ligands (CO, CN^-), which were first detected by FTIR spectroscopy.[36, 37]

1.3.1 [Fe]-Hydrogenase

The [Fe]-hydrogenase has only been recognized in methanogenic archaea, and it does not contain nickel or iron-sulfur clusters.[38,39] This enzyme can activate H_2 only in the presence of a second substrate (methenyltetrahydromethanopterin). The enzyme catalyzes the reversible reduction of methenyltetrahydromethanopterin (sub^+) with dihydrogen to methylenetetrahydromethanopterin (sub-H) and a proton (Eq. 2).[40, 41] The structure of the active enzyme has been characterized by X-ray crystallography by Shima *et al*. (Figure 1).[42] The structure shows a square pyramidial geometry of the Fe center and the pyridinol derivative binds epically to iron through the sp^2 hybridized N atom. In addition, the two *cis-carbonyl* groups with a cysteinyl thiolate and unknown ligand occupying the basal positions.[41, 32] In principle, the action of [Fe]-hydrogenase is quite different from that for the bimetallic hydrogenases. In the bimetallic hydrogenases, the electrons from the oxidation of dihydrogen flow from the active site through a set of iron-sulfur clusters to an electron acceptor protein partner. Whereas, in [Fe]-hydrogenase, electrons are not released; rather, the carboncation substrate (methenyltetrahydromethanopterin) is thought to accept directly the hydride from H_2.[32]

$$Sub^+ + H_2 \longrightarrow Sub\text{-}H + H^+ \qquad \text{(Eq. 2)}$$

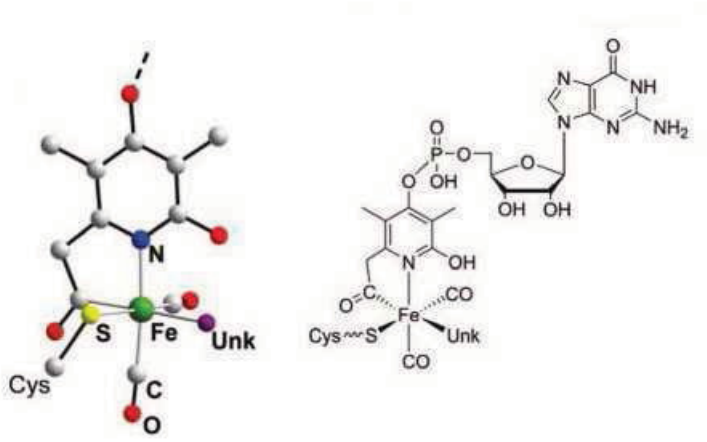


Figure 1. X-ray crystal structure and schematic representations of the active site of the [Fe]-hydrogenase. Unk = unknown ligand; this site appears to bind cyanide [Adapted from ref 32].

1.3.2 [NiFe]-Hydrogenase

[NiFe]-hydrogenase was first crystallized in 1987 from *Desulfovibrio (D.) vulgaris* Miyazaki F by Higuchi *et al*.,[43] and in the same year from *D. gigas* by Niviere *et al*.[44] After around 8 years Volbeda and co-worker reported the first crystal structure for the *D gigas* enzyme.[45, 46] Till now five crystal structures of [NiFe]-hydrogenase from closely related sulfate-reducing bacteria are known. These are the enzymes from *D. gigas*,[45-48] *D. vulgaris* Miyazaki F,[49-52] *D. desulfuricans,*[53] *D. fructosovorans*, [54, 55] *and Desulfomicrobium (Dm.) baculatum.*[35] The structure of the [NiFe]-hydrogenase of *D. gigas* (Figure 2),[46] consists of two subunits with molecular weights of about 28 and 60 kDa. The large subunit contains the active site and the geometry around this site is highly conserved throughout all [NiFe]-hydrogenases.[9] The Ni-Fe bond distance is in the range of 2.5-2.9 Å,[47] and the two metals are bridged by sulfur atoms of two cysteine groups. In addition, the nickel atom is coordinated by two more cysteines bound in a terminal position. The small subunit contains three Fe-S clusters that are involved in the electron transport to/from the active [NiFe] center. In the catalytically active hydrogenases, a proximal [4Fe-4S] cluster is located near the [NiFe] center, flanked by a [3Fe-4S] cluster. Near the protein surface a distal [4Fe-4S] cluster is present.[9] A subfamily, indicated as [NiFeSe]-hydrogenase, has a cysteine sulfur replaced by a selenium atom in the form of selenocysteine.[35, 56-58] The first crystal structure determination of a [NiFeSe]-hydrogenase isolated from *Dm. baculatum* has been published in 1999.[35] In principle, the [NiFe]-hydrogenases are more often active in H_2 oxidation rather than it is production. Extensive experimental studies and theoretical calculations have led to several proposals for the mechanism of [NiFe]-hydrogenase action. [59-61] Pardo *et al*. proposed a postulated mechanism for H_2 oxidation which is shown in Scheme 1.[62] In this mechanism it is assumed that, the iron center is the binding site for the hydrogen molecule.

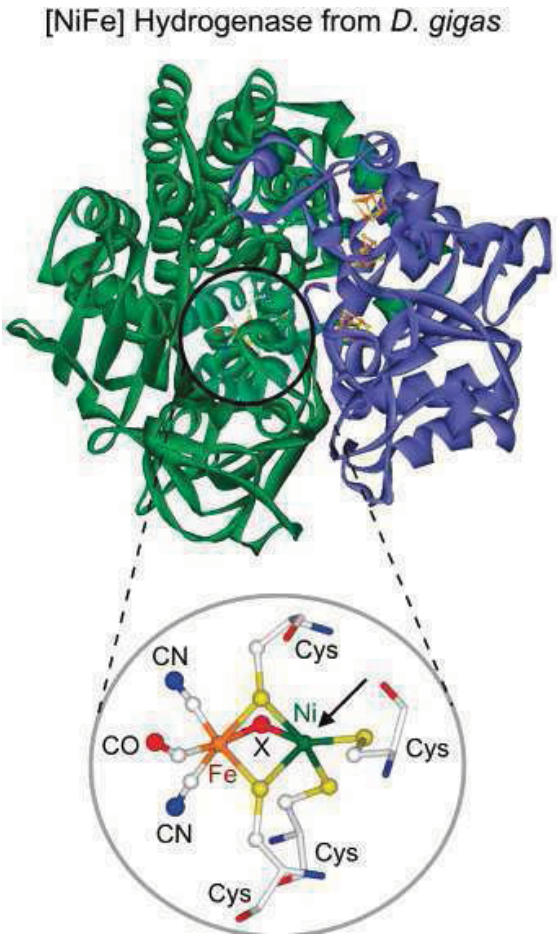
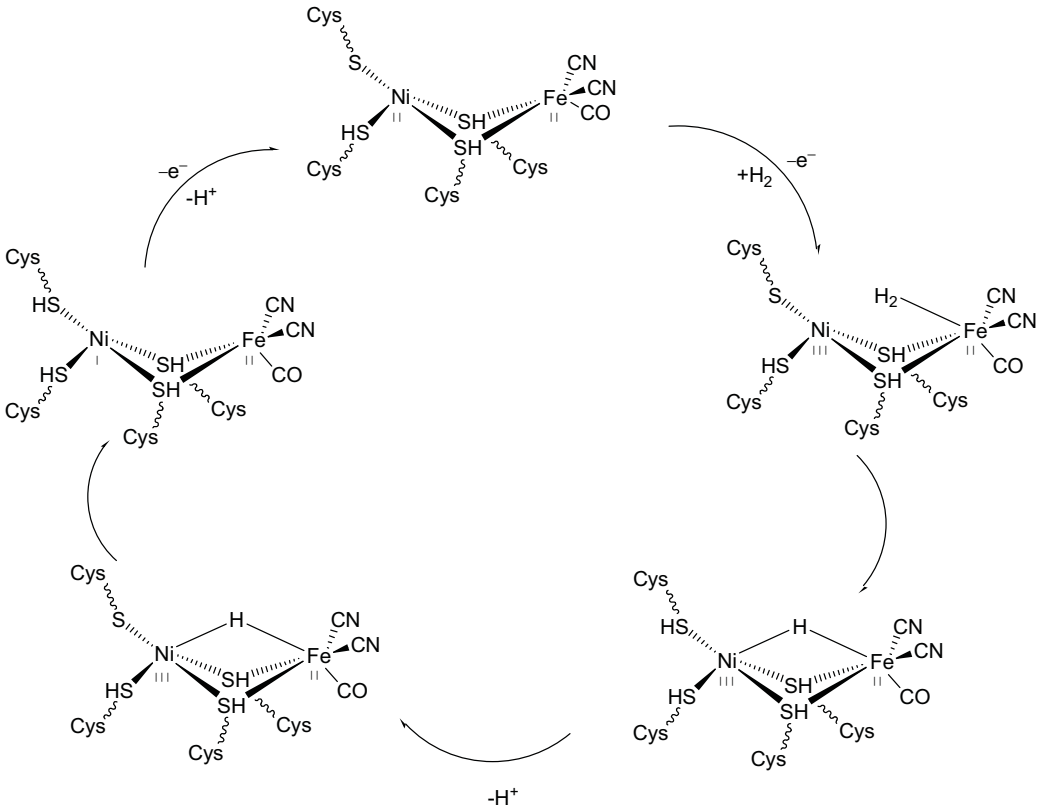


Figure 2. Structure of [NiFe] hydrogenase from *D. gigas* (PDB 1FRV) detailing the two protein subunits (small, blue; large, green), the electron-transfer chain with three Fe-S centers in the small subunit, and the active site in the large subunit. The structure of the active site is shown enlarged at the bottom (see text). The arrow indicates the sixth coordination site at Ni which is found to be unoccupied. The enzyme resided mainly in the unready state [Adapted from ref 9].



Scheme 1. Proposed catalytic cycle for H_2 oxidation by the active site of [NiFe]-hydrogenas. [After ref 62]

1.3.3 [FeFe]-Hydrogenases

Structure, Redox States, and Mechanisms of [FeFe]-Hydrogenases

The [FeFe]-hydrogenases can catalyze the consumption and production of H_2, however, these enzymes have been considered mainly to be H_2-producers.[63,64] The enzyme was first found in the gram positive bacterium *Clostridium* (*C.*) *pasteurianum*, it was the first organism that contains only iron atoms, but no nickel.[65] The location of [FeFe]-hydrogenases in the bacterial cell mirrors the enzyme's function in the generation or uptake of H_2 molecule.[32, 66] The periplasmic *Desulfovibrio desulfuricans* [FeFe]-hydrogenase (DdH) is involved in dihydrogen uptake, whereas the *Clostridium pasteurianum* [FeFe]-hydrogenase I (CpI) is a cytoplasmic enzyme that catalyzes the two-electron reduction of two protons to yield dihydrogen.[9, 32] The X-ray crystallographic structures of the monomeric [FeFe]-hydrogenases I from *C. pasteurianum*,[67] and that of the priplasmic heterodimeric [FeFe]-hydrogenases from *Desulfovibrio desulfuricans*[68, 69] are shown in Figures 3a and 3b, respectively.

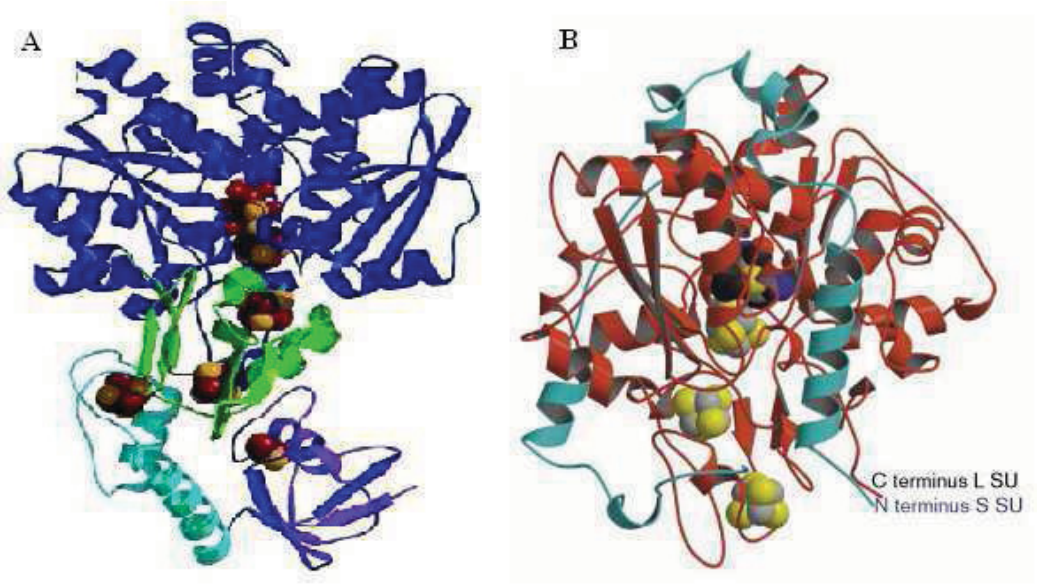


Figure 3. Three-dimensional structures of (**A**) *C. pasteurianum* I (CpI) [Adapted from ref 67] and (B) *D. desulfuricans* (DdH) [FeFe]-hydrogenases [Adapted from ref 68].

The structures determination of these two enzymes, together with spectroscopic data on [FeFe]-hydrogenase from *Desulfovibrio vulgaris*,[34, 37, 69, 70] show that the H-cluster "the active site at which protons are reduced to dihydrogen or dihydrogen oxidized to protons",[72] is composed of an $\{Fe_4S_4\}$-cubane core bridged by a cysteinyl residue to a {2Fe2S}-subsite (Figure 4).[9, 32, 67-70] The $\{Fe_4S_4\}$-cluster is linked to the protein by three cysteines from the backbone of the protein.[32] Additionally, the active sites in both enzymes are buried deeply within the protein. Furthermore, in both structures the $[2Fe]_H$ cluster is coordinated by a total of five diatomic ligands modeled as CO/CN^- and by a dithiolate ligand (SCH_2XCH_2S) not linked to the protein. Initially, some studies based on the electron density map around the active sites of the enzyme considered the X group as CH_2, but later mechanistic and stereochemical considerations led to a reinterpretation of this group, which is then assumed as to be a dithiomethylamine (DTN).[9, 69, 71] However, the nature of X is remained undecided experimentally as whether X is CH_2, NH, or O.[32, 34]

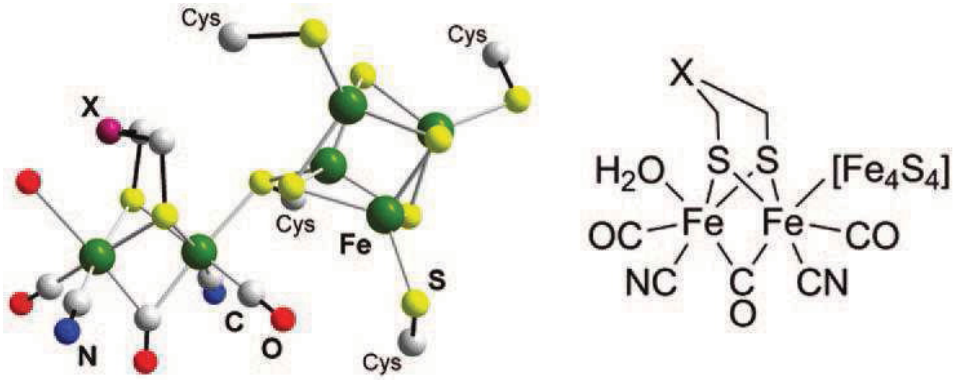
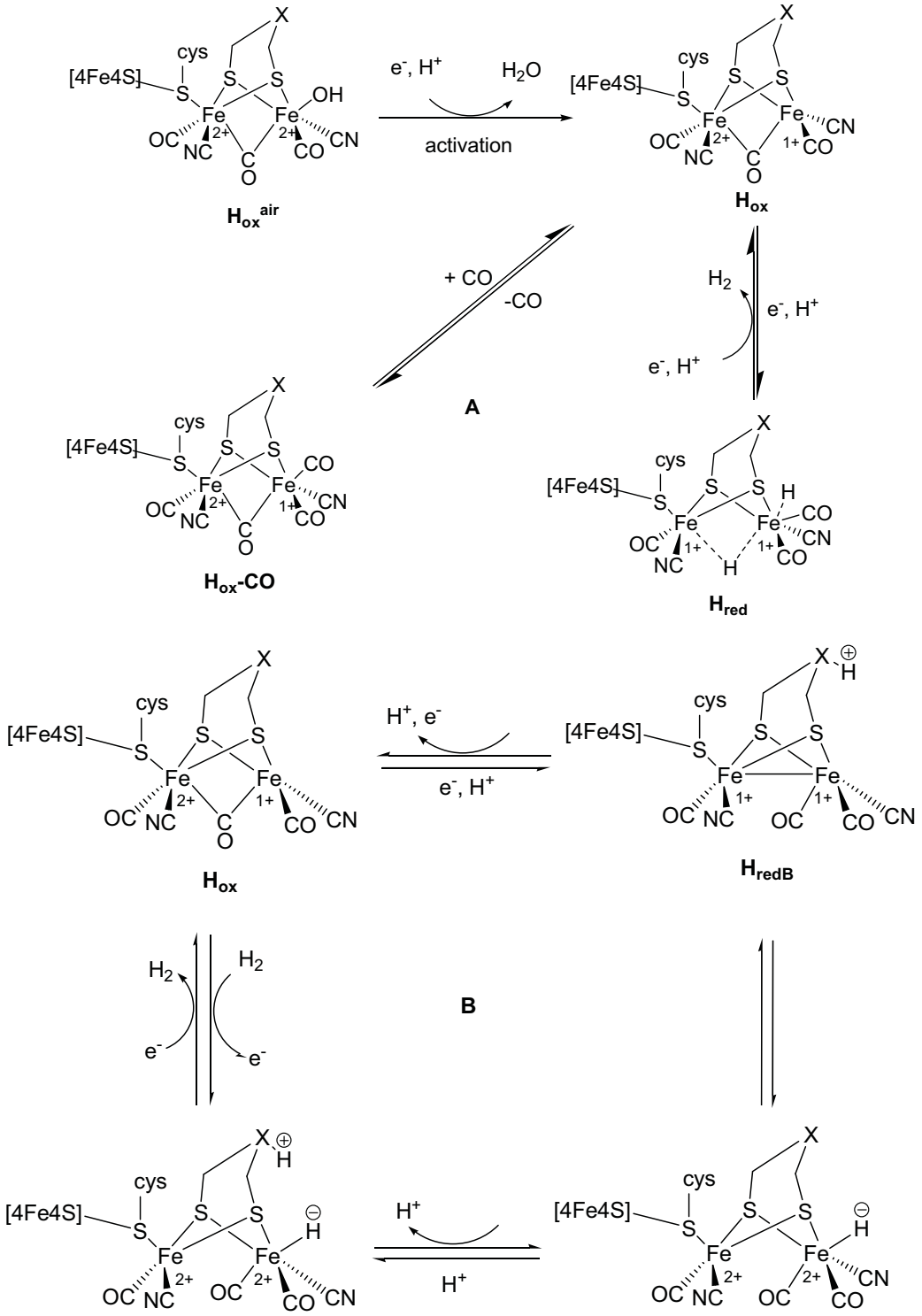


Figure 4. X-ray structure and schematic representation of the active site of the [FeFe]-hydrogenase (X = CH_2, NH, or O). [Adapted from ref 32]

The various redox states and transitions of the active site of the [FeFe] hydrogenase are shown in Scheme 2, these states have been investigated by spectroelectrochemical studies on the enzyme system and FTIR techniques.[9, 32] In the inactive and nonparamagnetic state {H_{ox}^{air}}, one CO is in a bridging position and the open coordination site at Fe_d is occupied by an oxygenic species (OH^- or H_2O) according to X-ray crystallography.[9, 32] The activation of the enzyme generates the paramagnetic oxidized state of the enzyme {H_{ox} state}, in which the Fe atom distal to the {Fe_4S_4}-cluster has a coordinated water molecule (or vacancy).[30, 72] Notably, when CO is added to this state of the enzyme at high concentration and under turnover conditions, the carbonyl group occupied the vacant site, results in a complete inhibition {H_{ox}-CO state}.[32, 73] This site is therefore thought to be where hydride/dihydrogen are likely to be bound during turnover.[30, 69, 72, 74] The addition of an electron to H_{ox} gives the H_{red} state, in which the bridged CO rearranges to terminal form. In H_{red} the formal oxidation states of the iron atom are Fe(I)-Fe(I), and this is the level at which a proton is thought to interact.[32]

More than one catalytic cycle mechanism for H_2 production by [FeFe]-hydrogenase have been proposed. Crystallographic studies and FTIR data of the active site of the enzyme, suggested that the main structural change in the active site during the catalytic cycle is the movement of the bridging CO ligand in H_{ox} toward the distal Fe of the active site, leading to terminal CO fashion in H_{red}.[55] The resulted vacant site is proposed to be the site where substrate (proton) likely to be bound during turnover (Scheme 2a).[32] Another plausible mechanism for H_2 production, including protonation at the bridgehead group X, is shown in Scheme 2b.[75-78]



Scheme 2. Possible catalytic cycle mechanisms for H_2 evolution by the active site of [FeFe]-hydrogenase. [(A) After ref 9; (B) After ref 32]

2. Synthetic models of [FeFe]-hydrogenases

2.1 {2Fe2S}-Model complexes

Since the first structure of an [FeFe]-hydrogenase was revealed by X-ray crystallography, several efforts to prepare and characterize analogous model compounds have been reported.[79, 80] The synthesis of $[Fe_2(CO)_6(\mu\text{-}SEt)_2]$ (**1**) (Figure 5) was described by Reihlen *et al*., and the structure of which was reported some 36 years later.[81, 82] The resemblance between this complex and the subsite of the H-cluster, gave evidence for the pathway synthesis of model complexes related to the active site of the [FeFe]-hydrogenase.[67, 68] The development of this chemistry by several groups Hieber, Seyferth, Poilblanc, and others,[83-117] opened the way for synthesis of model complexes possessing {2Fe2S}-core with a distorted tetrahedron butterfly fashion related to that enzyme.[32] Immediately, after publication the crystallographic data for the enzyme, three groups independently described the replacement of two CO ligands of a diiron propanedithiolate hexacarbonyl $[Fe_2(SCH_2CH_2CH_2S)(CO)_6]$ (pdt) complex (**2**)[118, 119] by cyanide, to offer the dianion $[Fe_2(SCH_2CH_2CH_2S)(CO)_4(CN)_2]^{2-}$ (**3**).[120-122] Subsequently, the replacement of bridgehead CH_2 group by NH (**4**)[123] (adt) or O (**5**) (odt)[123-126] was illustrated by Rauchfuss and Song, respectively. Recently, Weigand followed by Song and their respective co-workers, reported the synthesis of the sulfur bridgehead model complex (**6**).[127-129] Many analogues complexes of **2** and **4**, were reported based on the modification of the bridgehead group (Figure 6).[123, 124, 130-138] Very recently, Weigand and co-workers reported model complexes containing silicon-based thiolato ligands, two examples (**7**) and (**8**) are shown in Figure 5.[139]

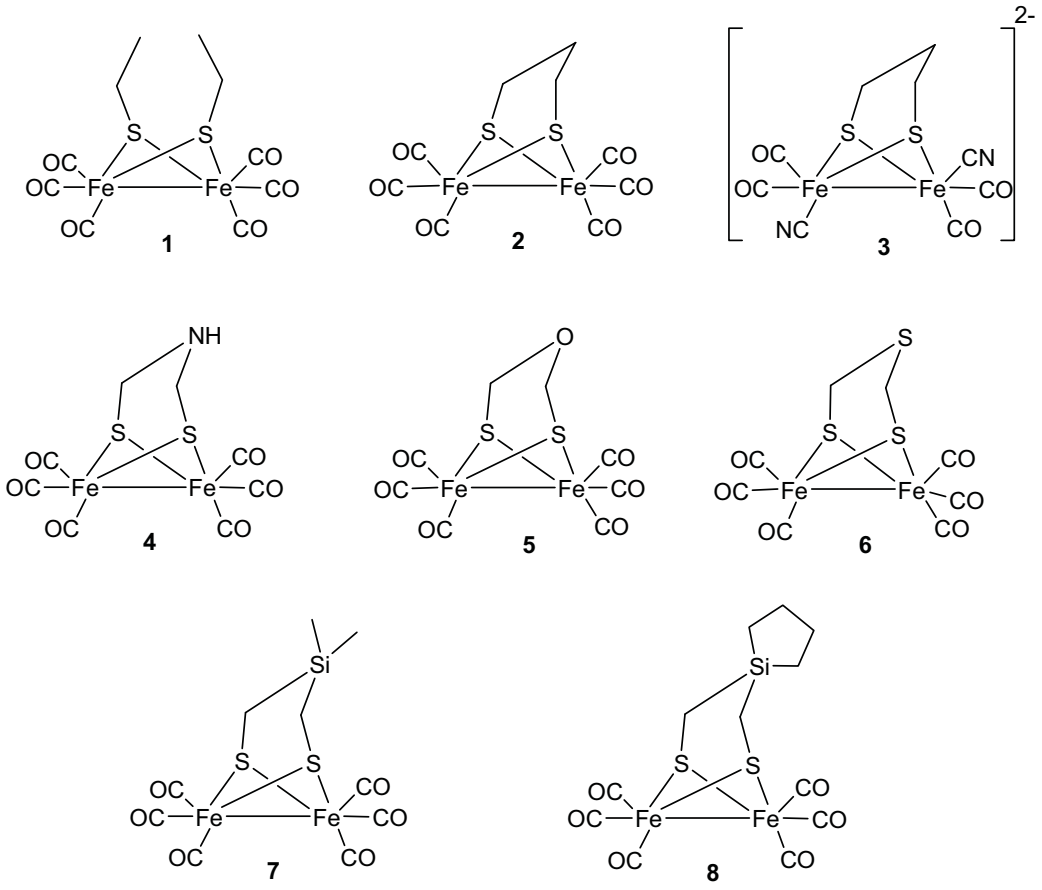


Figure 5. {2Fe2S}-Model complexes

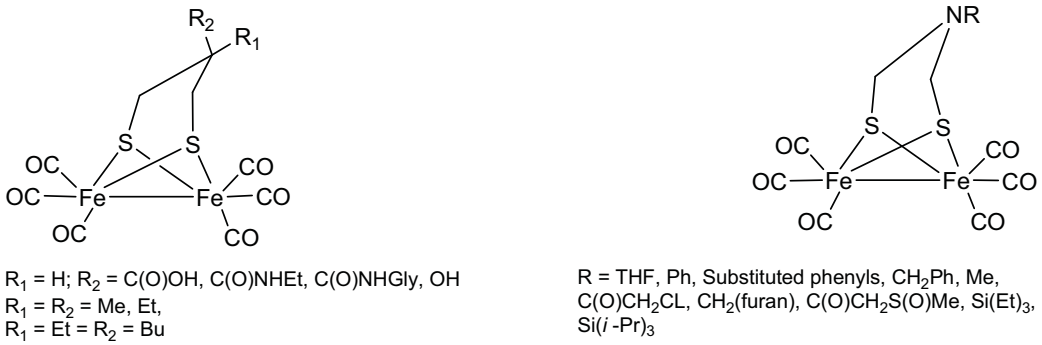


Figure 6. {2Fe2S}-Model complexes with different bridgehead moieties.

2.2 {2Fe2S}-Substituted model complexes

In order to design more efficient proton reduction catalysts, the replacement of one or more CO groups of different diiron model complexes, by strongly electron-donating ligands have been reported. Some of these substituted model complexes are discussed below.

2.2.1 Cyanide-substituted derivatives

The first dicyano dianion $[Fe_2(SCH_2CH_2CH_2S)(CO)_4(CN)_2]^{2-}$ model complex 3 was reported by three independent groups,[120-122] a schematic representation of the structure of **3** was shown in Figure 5. Elegant work by Rauchfuss and co-workers consequently, showed that the related $[Fe_2(SCH_2NRCH_2S)(CO)_4(CN)_2]^{2-}$dianions (R = H, Me) (**9**, **10**) are also accessible (Figure 7).[130] In a similar procedure, Song and co-workers also reported the synthesis of the odt dicyano dianion (**11**) $[Fe_2(SCH_2OCH_2S)(CO)_4(CN)_2]^{2-}$.[128] The 'butterfly' arrangement of the dithiolate ligands in both **3**, **9, 10** and **11** are closely similar to that in the enzymic subsite (Figure 3) and the $\{Fe(CO)_2(CN)\}$ motifs in the complexes reasonably model the distal iron of the subsite in the CO inhibited form of the enzyme $\{H_{ox}(CO)\}$.[30, 72] Furthermore, the synthesis of the monocyanide $[Fe_2(SCH_2CH_2CH_2S)(CO)_5(CN)]^-$ (**12**) was described by Darensbourg and co-workers, they showed, that **12** reacted with CN^- to offer **3.**[140] Therefore, the monocyanide **12** could be assumed as a plausible intermediate in stepwise substitution of the parent hexacarbonyl which gave the di-cyanide **3**. An alternative di-cyanation pathway was proposed by Rauchfuss and co-workers,[141] in which the proposed intermediates is an undetected bridging CO monocyanide rather than the monocyanide one. Recently, Weigand and co-workers have been reported the synthesis of the sdt dicyano dianion (**13**) $[Fe_2(SCH_2SCH_2S)(CO)_4(CN)_2]^{2-}$.[142]

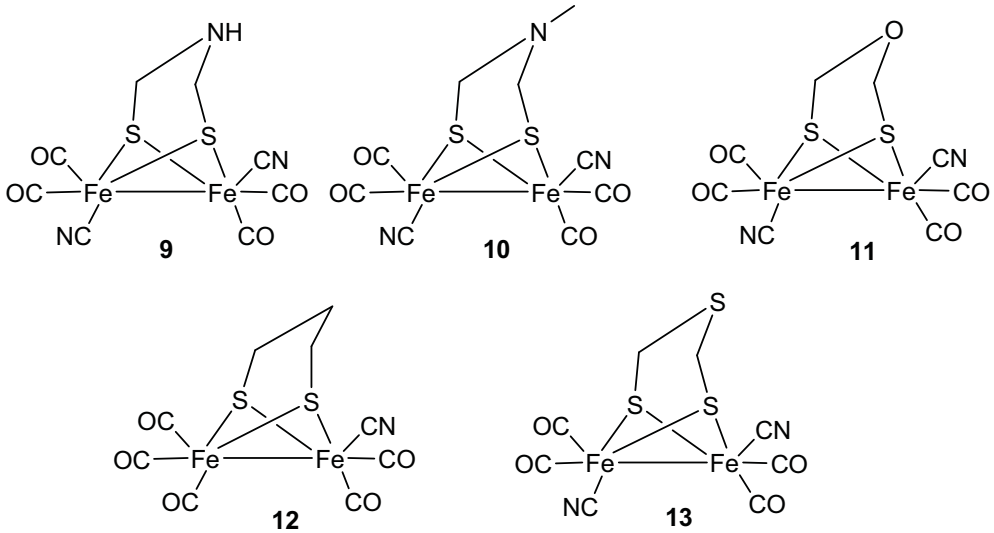
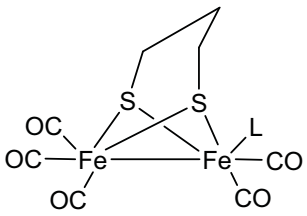
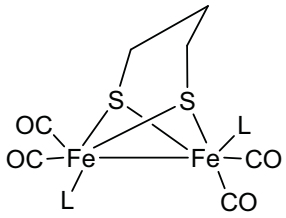


Figure 7. Dicyano (**3**, **9**, **10**, **11, 13**) and monocyano (**12**) [{2Fe2S}]$^{n-}$-model complexes (n = 1, 2).

2.2.2 Phosphine- and phosphite-substituted derivatives

The introducing of good donor ligands, such as PR_3 and $P(OR)_3$, in the $[Fe_2(SCH_2CH_2CH_2S)(CO)_6]$ complex provides the iron atoms more electron-rich and more protophilic. Model complexes of the [FeFe]-hydrogenase active site, containing tertiary phosphines are preferably synthesized for the following reasons: 1) The electronic influence of the PR_3 on the Fe atoms are comparable to that of CN^-. 2) The steric and electronic properties of PR_3 are tunable by changing the R groups. 3) The replacement of CN^- by PR_3 can avoid the complications of protonation on the cyanide nitrogen atom.[143] Therefore, a series of {2Fe2S}-model complexes enclosing PR_3 or $P(OR)_3$ groups, $[Fe_2(\mu\text{-pdt})(CO)_5L]$ [L = PMe_3 (**14**), PMe_2Ph (**15**), PPh_3 (**16**), $P(OEt)_3$ (**17**), $P(OMe)_3$ (**18**), Ph_2PH (**19**), $Ph_2PCH_2NMe_2$ (**20**), $Ph_2PFe(CO)_2Cp$ (**21**), PPh_2NH-$(CH_2)_2N(CH_3)_2$ (**22**), PPh_2NH-$(2NH_2C_6H_4)$ (**23**), $PPyr_3$ (**24**), Ph_2PPyr (**25**)] and $[Fe_2(\mu\text{-pdt})(CO)_4L_2]$ [L = PMe_2Ph (**26**), PPh_3 (**27**), $P(OEt)_3$ (**28**), Ph_2PPyr (**29**), PMe_3 (**30**), $P(OMe)_3$ (**31**), $PPyr_3$ (**32**)] have been extensively investigated (Figure 8).[137, 143-150]





14; L = PMe_3
15; L = PMe_2Ph
16; L = PPh_3
17; L = $P(OEt)_3$
18; L = $P(OMe)_3$
19; L = Ph_2PH
20; L = $Ph_2PCH_2NMe_2$
21; L = $Ph_2PFe(CO)_2$
22; L = PPh_2NH-$(CH_2)_2N(CH_3)_2$
23; L = PPh_2NH-$(2NH_2C_6H_4)$
24; L = $PPyr_3$
25; L = Ph_2PPyr

26; L = PMe_2Ph
27; L = PPh_3
28; L = $P(OEt)_3$
29; L = Ph_2PPyr
30; L = PMe_3
31; L = $P(OMe)_3$
32; L $PPyr_3$

Figure 8. Substituted model complexes of $[Fe_2(\mu\text{-pdt})(CO)_6]$.

2.2.3 Bidentate-substituted derivatives

In principle, tertiary phosphine ligands are well known to give mono- and disubstituted products, $Fe_2(SR)_2(CO)_{6-x}(PR_3)_x$ (x = 1, 2), but substitution reactions gave a trisubstituted species are rare. The degree of substitution could be controlled

by using a bidentate ligands, which could also stabilize complexes of the type $[Fe_2(SR)_2(CO)_3(chel)L]$.[151] A bidentate phosphine ligand dppf (1,1-bis(diphenylphosphino) ferrocene) has been used to give a complex of the type $[Fe_2(SR)_2(CO)_5]_2$(dppf), in which the diphosphine ligand coordinates to two {2Fe2S}-units (Figure 9A).[126] Recently, the reaction of $[Fe_2(\mu\text{-pdt})(CO)_6]$ (**2**) with dppe ($Ph_2PCH_2CH_2PPh_2$), was investigated by Sun *et el*., to deliver $[Fe_2(\mu\text{-pdt})(CO)_6]_2$(dppe) where the dppe ligand, like dppf, substitutes CO in the double monodentate manner to give a cluster of Fe_2S_2 cores antibridged by dppe (Figure 9A).[152] This was followed by the work of Taralmin and co-workers, in which they reported a complex $[Fe_2(\mu\text{-pdt})(CO)_4$(dppe)], in which dppe chelates to a single iron center (Figure 9B).[153] By contrast, treatment of **2** with dppm ($Ph_2PCH_2PPh_2$), furnished $[Fe_2(\mu\text{-pdt})(CO)_5$(dppm)], where only one phosphorus atom of dppm coordinated in a monodentate fashion to one Fe_2S_2 unit (Figure 9C).[152] Furthermore, under forcing conditions, the dppm acts as a bidentate ligand, coordinating to both iron atoms in the same molecular unit (Figure 9D).[152]

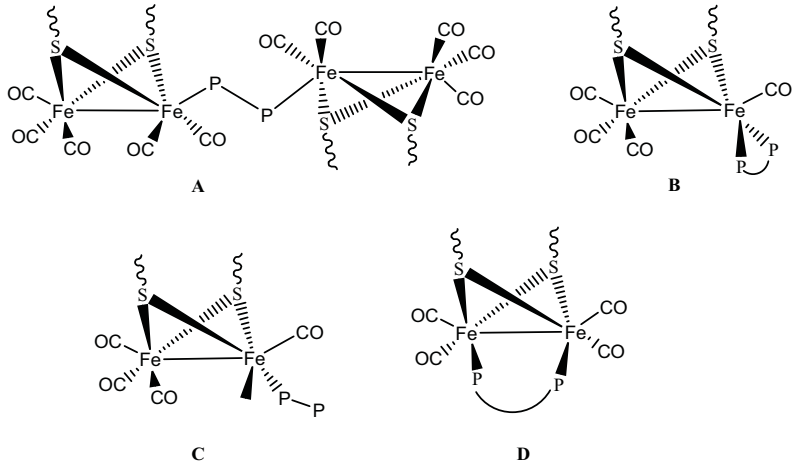


Figure 9. The possible coordination mode of bidentate phosphine ligands. [After ref 152]

2.2.4 Carbenes-substituted derivatives

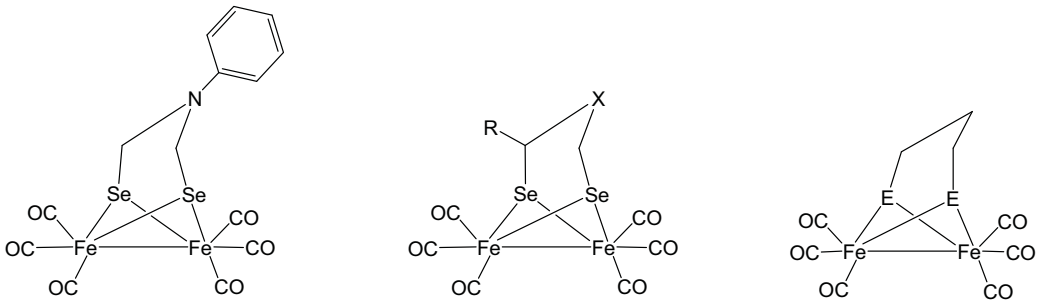
During the past decade, the synthesis of N-heterocyclic carbene (NHC) containing [FeFe]H_2ase model complexes, has received a considerable attention. The reason for this is related to the electronic properties of (NHC) ligands, which show a greater electron-donating power than those of other neutral two-electron donors such as phosphine ligands.[154-163] Capon and co-workers, reported two diiron N-

heterocyclic carbene (NHC) complexes $[Fe_2(SCH_2CH_2CH_2S)(CO)_5(L_{Me})]$ (**33**) and $[Fe_2(SCH_2CH_2CH_2S)(CO)_4(L_{Me})_2]$ (**34**) (L_{Me} = 1,3-dimethylimidazol-2-ylidene.[154] Darensbourg *et al*. subsequently prepared the N-heterocyclic carbene containing model compound, $[Fe_2(SCH_2CH_2CH_2S)(CO)_5(IMes)]$ (**35**) [IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-yldene.[157] Recently, disubstituted diiron complexes containing (NHC) have been reported.[158]

2.3 {2Fe2Se}- and {2Fe2Te}-Model complexes

The replacement of thiolates by selenlates or tellurolates in the [FeFe]-hydrogenas model complexes, which lead to an increase of the electron density at the iron atoms, and this, could enhances the reactivity and the redox properties of the biomimetic catalysts. In addition, the synthesis and studying of model complexes containing Se may be provide more information for understanding the biological function of selenium in the [NiFeSe]-hydrogenase.[164] Therefore, model complexes containing heavier chalcogens such as selenium or tellurium instead of sulfur have been recently reported by different groups. Peng and co-workers synthesized three diiron diselenolato complexes $[\{(\mu\text{-}SeCH_2)_2NC_6H_4R\}Fe_2(CO)_6]$ (R = H, **36**; R = NO_2, **37**; R = CH_3, **38**) (Figure, 10). In addition, they investigated the electrocatalytic activity for proton reduction by **38**.[165]

Recently, the analogues complexes of **2** (pdt), in which the sulfur is replaced by selenium, $Fe_2(\mu\text{-}SeC_3H_6Se)(CO)_6$ (**39**), $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_6$ (**40**) and $Fe_2[(\mu\text{-}SeCH_2)_2Se](CO)_6$ (**41**) were reported (Figure 10).[166, 16] Additionally, a comparative study on the catalytic activity of model **39** and its sulfur analog **2** proved that the Se containing complex **39** provides higher activity for proton reduction to molecular H_2 under electrochemical conditions.[167] Very recently, Weigand and co-workers described the synthesis of [FeFe]-Hydrogenase model complexes enclosing mixed dichalcogenolato ligands, $Fe_2(\mu\text{-}SC_3H_6Se)(CO)_6$ (**42**) and $Fe_2(\mu\text{-}SC_3H_6Te)(CO)_6$ (**43**).[168] Furthermore, thiolates have been also replaced by phosphide,[169-171] amide,[172, 173] and peptide groups.[174, 175]



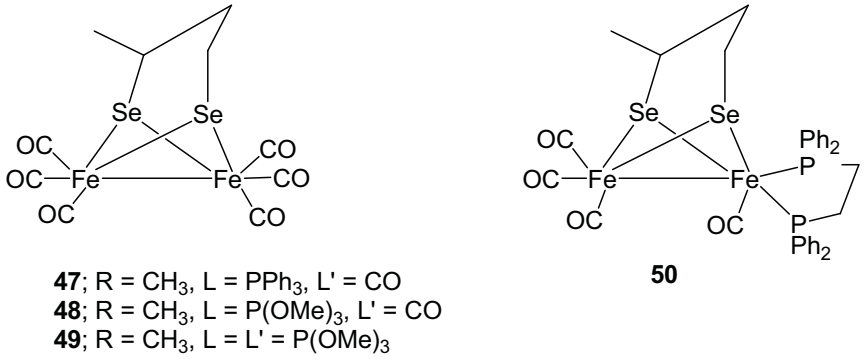
36; R = H
37; R = NO_2
38; R = CH_3

39; X = CH_2, R = H
40; X = CH_2, R = CH_3
41; X = Se, R = H

42; E = Se
43; E = Te

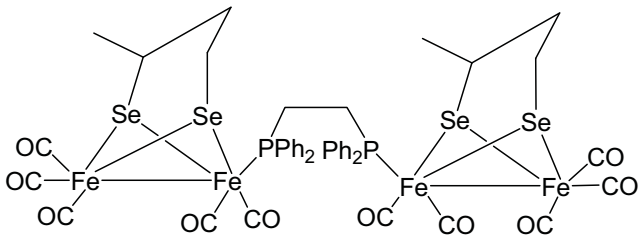
Figure 10. Models of [FeFe]-hydrogenase containing dichalcogenolato ligands. [After ref 167]

The replacement of CO ligands of diiron diselenolate model complexes, according to similar procedures as described for the sulfur analogous, by good donor ligands, substantially increases the electron density on the iron atoms.[168] Sun and coworkers reported three mono-substituted diiron complexes [Fe_2(μ-SeC_3H_6Se)$(CO)_5$L] **37** {L = PPh_3 (**44**), PPh_2H (**45**) and IMes (**46**)} changing the steric demand of the phosphine ligands.[167] In this field, we investigated the replacement of one or two carbonyl groups of [Fe_2(μ-$Se_2C_3H_5CH_3$)$(CO)_6$] **38** by PPh_3 (**47**), $P(OMe)_3$ (**48**; **49**) and dppm (**50**; **51**) as shown in Figure 11.[AD1]



47; R = CH_3, L = PPh_3, L' = CO
48; R = CH_3, L = $P(OMe)_3$, L' = CO
49; R = CH_3, L = L' = $P(OMe)_3$

50



51

Figure 11. Phosphine substituted model complexes of Fe_2(μ-$Se_2C_3H_5CH_3$)$(CO)_6$ (**40**).

2.4 {2Fe3S}-Model complexes

The X-ray crystallographic structures of [FeFe]-hydrogenases from *Desulfovibrio desulfuricans* and *Clostridium pasteurianum*, together with spectroscopic data on [FeFe]-hydrogenase from *Desulfovibrio vulgaris*, show that the active centre of the enzyme is comprised of a {2Fe3S}- rather than{2Fe2S}-core. The three sulfur atoms are trigonally capping the iron atom which is proximal to the {4Fe4S}.[37, 67, 68, 72,] During the last years, working groups of Pickett,[176-181] Rauchfuss,[182] Song[126] and Chen[183] made a considerable work on the synthesis of dithiolate thioether systems which possess the {2Fe3S}-arrangement as found in the enzyme.

Whereas the thioether ligand constitute the third leg of the sulfur bridge in Pickett (**51**) and Rauchfuss (**52**) complexes via intramolecular reaction, Song compound (**53**) is a trinuclear species where the third SR ligand is bound to two iron centers via intermolecular substitution, modeling more closely the thiolato bridge between the {2Fe2S} subunit and the proximal {4Fe4S} of the H-cluster of [FeFe]-hydrogenase. The fourth species (**54**) by Chen is also a binuclear complex where one CO of the corresponding hexacarbonyl complex was substituted by SR_2 or SRR`, respectively, as shown in Figure 12.[79 (a)]

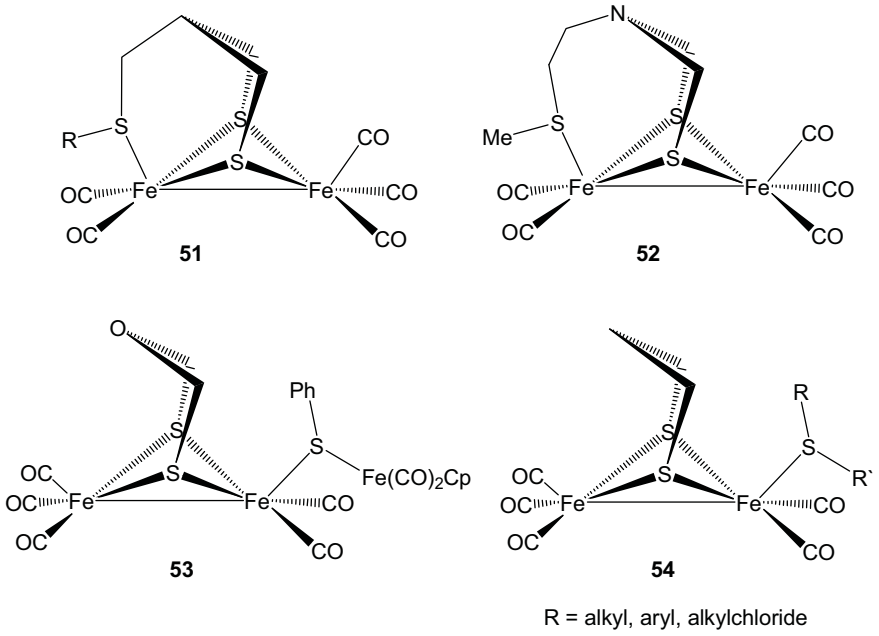
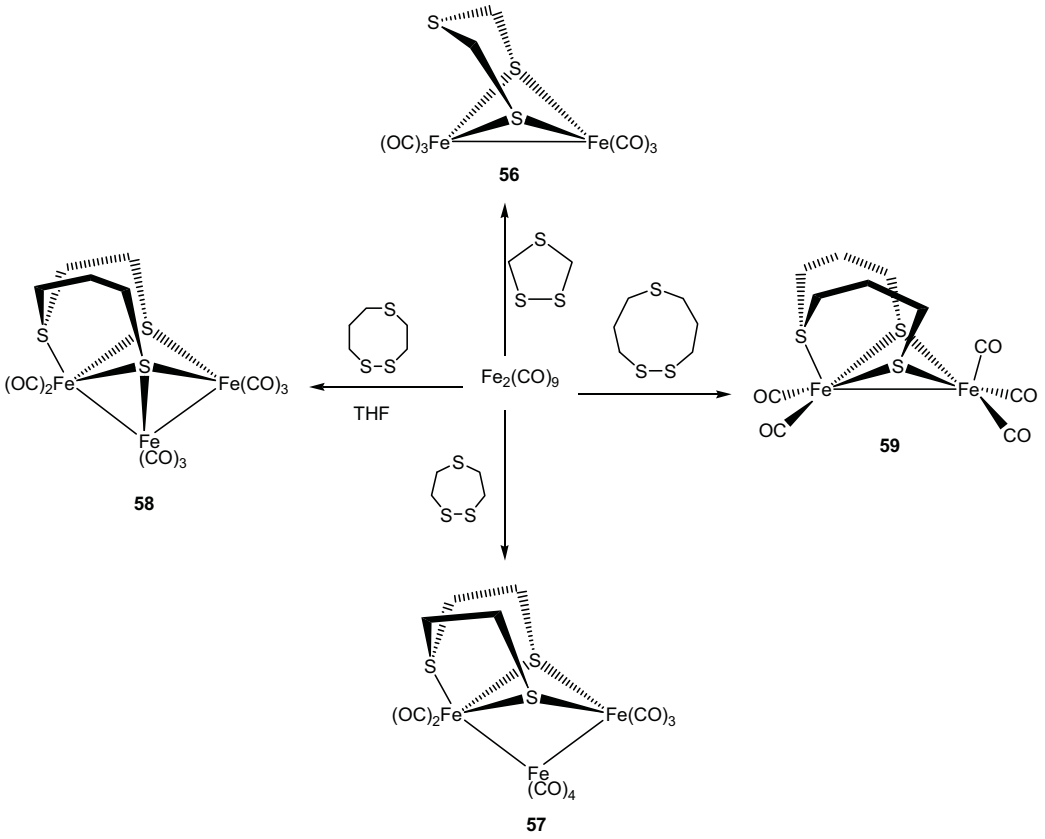


Figure 12. {2Fe3S}-Model complexes. [After ref 79 (a)]

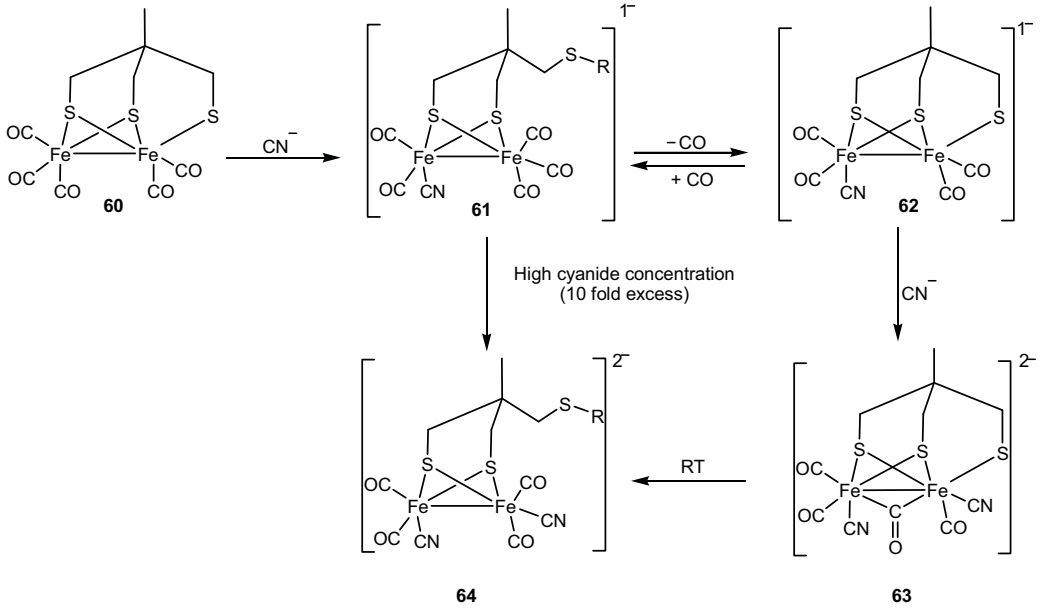
Recently, Weigand and co-workers, investigated the reactions of 1,2,4-trithiolane (**52**), 1,2,5-trithiepane (**53**), 1,2,5-trithiocane (**54**) and 1,2,6-trithionane (**55**) with ironcarbonyl complexes.[127] The ring size in these different heterocycles influenced the constitutional structure of the resultant complexes (Scheme 3). Interestingly, the nine-membered rings **55** afforded $Fe_2[\mu\text{-}S_2(C_3H_6)_2S\text{-}\mu)(CO)_5]$ (**59**), which can be seen as a model complex for the [2Fe3S] sub-site of the H-cluster. In this compound the thioether sulfur atom acts as an additional S-donor by intramolecular substitution of one carbonyl group.



Scheme 3. [FeFe]-Model complexes containing different length of dithiolato bridge ligands.

In all of these synthetic [2Fe3S]-model complexes, the thioether ligand is hemilabile and can be displaced by CO, PR_3, $P(OR)_3$, CN^-, and others. Pickett described the effect of thioether sulfur atom on the substitution of CO ligands of the complex $[Fe_2(CO)_5\{MeSCH_2C(Me)(CH_2S)_2\}]$ (**60**) and its benzyl thioether analogue by cyanide. The mechanism of the cyanation has been extensively elucidated (kinetics, stopped-flow FTIR and UV-visible spectroscopy), however the proposed

intermediate $[Fe_2(CO)_5(CN)\{RSCH_2C(Me)(CH_2S\text{-}\mu)_2\}]^-$ (**61**) has not been isolated (Scheme 4).[176-180]



Scheme 4. Synthesis of {2Fe3S}-cyanide assemblies, with R = Me or Bn. [After ref 177]

It would be of particular interest to isolate and characterize analogues intermediates. In the course of this study, we investigated the substitution reactions of [2Fe3S]-complex $Fe_2[\mu\text{-}S_2(C_3H_6)_2S\text{-}\mu)(CO)_5]$ (**59**), toward neutral nucleophiles such as $P(OMe)_3$ and PMe_3.[AD2] In this work, we were able to isolate and characterize a complex containing free thioether (**65**) $Fe_2(\mu\text{-}S_2(C_3H_6)_2S)(CO)_5P(OMe)_3$, which is believed to be the intermediate of the reaction pathway. This result could be seen as an important contribution to corroborate the mechanism for the cyanation reaction of [2Fe3S] cluster. In addition, these substitution reactions afforded the monosubstituted $Fe_2(\mu\text{-}S_2(C_3H_6)_2S\text{-}\mu)(CO)_4P(OMe)_3$ (**66**) and the disubstituted $Fe_2(\mu\text{-}S_2(C_3H_6)_2S)(CO)_4[P(OMe)_3]_2$ (**67**), and $Fe_2(\mu\text{-}S_2(C_3H_6)_2S)(CO)_4[PMe_3]_2$ (**68**) complexes (Figure 13).

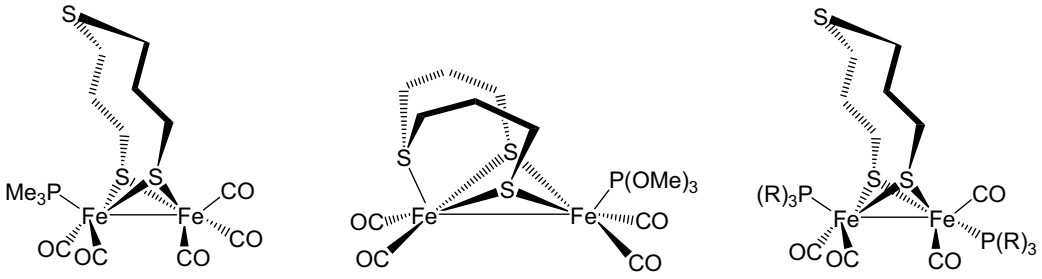
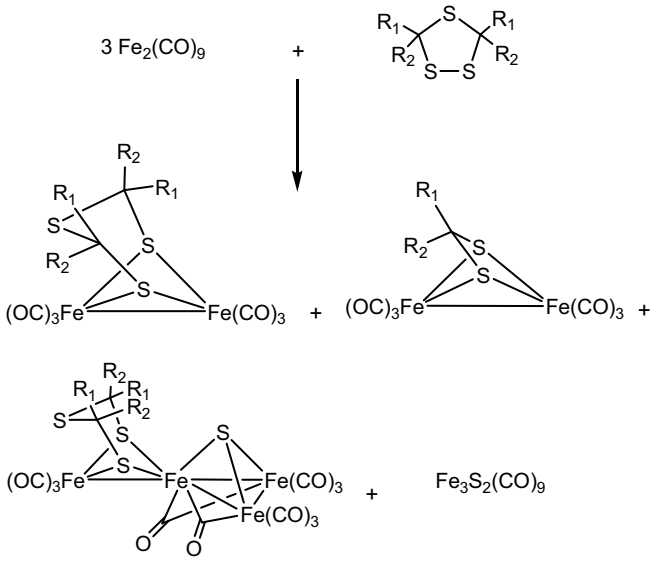


Figure 13. Substituted model complexes of $Fe_2[\mu\text{-}S_2(C_3H_6)_2S\text{-}\mu)(CO)_5]$ (**59**).

2.5 {2FeS}- and {2Fe2S}-Model complexes derived from thioketones.

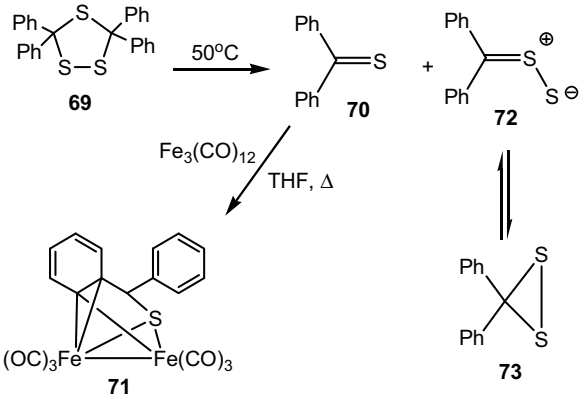
The oxidative addition of low-valent metal complexes to cyclic disulfides has received a significant attention in the recent years.[184-189] Recently, we investigated the reactions of the di- or tetra-substituted 5-memberd 1,2,4-trithiolans with $Fe_2(CO)_9$, to give model complexes as shown in Scheme 5.[142]



Scheme 5. The reaction of 1,2,4-trithiolanes with $Fe_2(CO)_9$. [After ref 142]

In continuation of our efforts on this area, we studied the reaction of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**69**) with $Fe_3(CO)_{12}$.[AD3] Interestingly, we observed a different reaction pathway compared to that of the corresponding tetralkyl substituted analogue. The later reacts with iron carbonyl complexes to give the oxidative addition

product resulted from the cleavage of the S-S bond (Scheme 5). The former, however, dissociates according to Scheme 6.[190-193] The fragments (e.g., $Ph_2C{=}S$ (**70**)) react with $Fe_3(CO)_{12}$ to yield the *ortho*-metallated complex $Fe_2(CO)_6(\kappa,\mu\text{-}S,\eta^2\text{-}C_{13}H_{10}S)$ (**71**) as the major product (Scheme 6).



Scheme 6. Thermal cycloreversion of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**69**); The reaction of thiobenzophenone (**70**) with $Fe_3(CO)_{12}$.

This result prompted us to investigate the reaction of $Fe_3(CO)_{12}$ with other selected aromatic thioketones; thiobenzophenone **70**, 4,4'-bis(dimethylamino)-thiobenzophenone (**74**), dibenzosuberenethione (**75**) and xanthione (**76**). Accordingly, four *ortho*-metallated complexes $Fe_2(CO)_6(\kappa,\mu\text{-}S,\eta^2\text{-}C_{13}H_{10}S)$ (**71**), $Fe_2(CO)_6(\kappa,\mu\text{-}S,\eta^2\text{-}C_{17}H_{20}N_2S)$ (**77**), $Fe_2(CO)_6(\kappa,\mu\text{-}S,\eta^2\text{-}C_{15}H_{12}S)$ (**78**) and $Fe_2(CO)_6(\kappa,\mu\text{-}S,\eta^2\text{-}C_{13}H_8OS)$ (**79**) were prepared and well characterized (Figure 14).[AD3] The formation of similar thiobenzophenone-iron complex **71** and **77** was described by Alper *et al*. several decades ago.[194-199] However, the structure of these compounds were suggested by Alper *et al.* based only on spectroscopic data and decomplexation reactions. In the present work, the structures of these complexes were determined by X-ray measurement in which more accurate insight into the structures is presented.

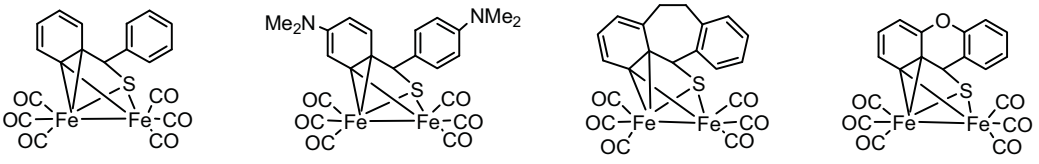
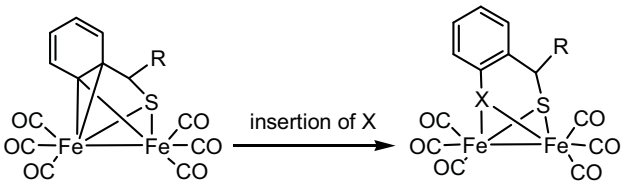


Figure 14. Schematic representation of the structures of the *ortho*-metalated complexes **71**, **77**, **78**, **79**.

Interestingly, the structures of the ortho-metallated complexes **71**, **77**, **78** and **79**, provided a hint such that, these compounds could be important intermediates in the synthesis of novel complexes that may be unattainable otherwise (Scheme 7).



R = aryl
X = S, Se, Te, CN, CO, CR_2, *etc*

Scheme 7. Insertion of X-groups into the Fe-C bonds of the *ortho*-metallated complexes.

Therefore, we investigated the reactions of triiron dodecacarbonyl with thiobenzophenone (**70**) or 9H-xanthene-9-thione (**80**), under different conditions.[AD4] In the case of 1:1 molar ratio of reactants, the ortho-metallated complexes $Fe_2(CO)_6(\kappa,\mu\text{-}S,\eta^2\text{-}C_{13}H_{10}S)$ (**71**) and $Fe_2(CO)_6(\kappa,\mu\text{-}S,\eta^2\text{-}(C_{13}H_8S_2))$ (**81**) were obtained, respectively. In contrast, treatment of triiron dodecacarbonyl with excess of **70** or **80** gave two biomimetic models for the active site of the [FeFe]-hydrogenase; $Fe_2(CO)_6(\mu\text{-}SCH(C_6H_5)C_6H_4S\text{-}\mu)$ (**82**) and $Fe_2(CO)_6(\mu\text{-}SCH(C_6H_4)\text{-}S\text{-}C_6H_3S\text{-}\mu)$ (**83**), respectively. In addition to these complexes, the two reactions also afforded $Fe_2(CO)_6(\mu\text{-}SC(C_6H_5)_2)S\text{-}\mu)$ (**84**) and $Fe_2(CO)_6(\mu\text{-}SC(C_6H_4\text{-}S\text{-}C_6H_4)S\text{-}\mu)$ (**85**), respectively. Furthermore, $[Fe_2(CO)_6(\mu\text{-}SCH(C_6H_5)_2)]_2(\mu^4\text{-}S)$ (**86**) was isolated from the reaction of $Fe_3(CO)_{12}$ with **70** (Figure 15).

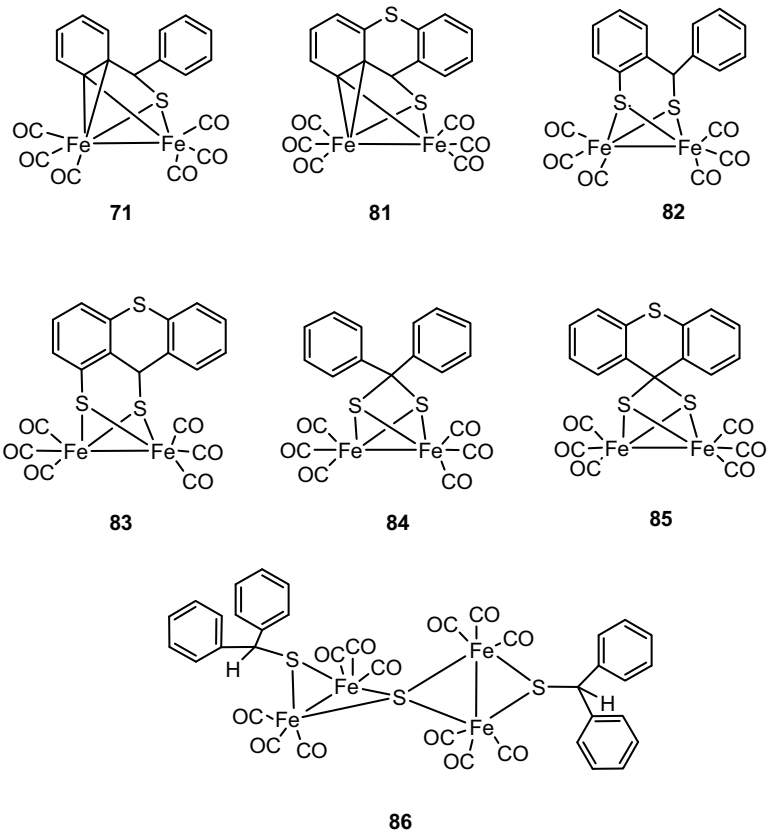


Figure 15. Schematic representation of the structures of the complexes **71** and **81**-**86**, resulted from the reaction of $Fe_3(CO)_{12}$ with thiobenzophenone (**70**) and 9H-xanthene-9-thione (**80**).

3. Electrochemistry

The evaluation of [FeFe]-hydrogenase model complexes as electrocatalysis for proton reduction or hydrogen oxidation are essentially based on three characteristics:

i) Their high turnover frequency (TOF = Molecules of H_2 produced per second and per molecule hydrogenase).[200]

ii) Their low working overpotential (the difference between the potential at which catalysis is achieved and the apparent thermodynamic potential of the H^+/H_2 couple under the operating conditions and/or it is the potential difference between the potential required by a specific compound to catalyze the reduction of protons and the potential required by platinum (the standard potential for the employed acid) under otherwise identical conditions.[200-203]

iii) Their robustness (the thermodynamic and kinetic stability of the catalyst under normal atmospheric conditions and high turnover numbers; (TON)).[200, 201]

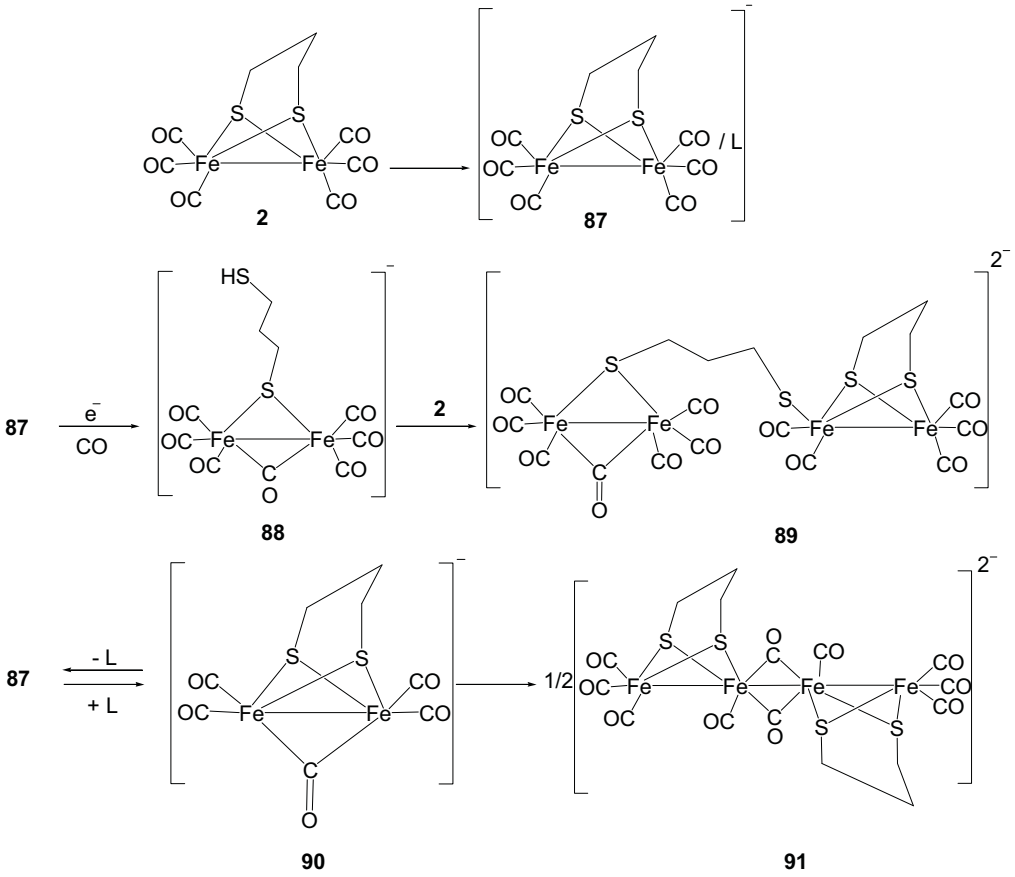
Unfortunately, no reported model complex of the [FeFe]-hydrogenase active site has so far met these characteristics satisfactorily.[32, 9, 72, 204]

Cyclic voltammetry (CV = Measurement of the intensity of current when a varying potential is applied) is the most widely used technique for the evaluation of the catalytic efficiency of [FeFe]-hydrogenase model complexes for hydrogen generation in nongaseous solvents. The catalytic activity of the synthetic model complex is estimated from their cyclic voltammogram. The increase in the height of the reduction peaks of the catalyst in the presence of proton source (acids), is a good indication for their catalytic activity. This increase is interpreted as being due to a catalytic cycle that produces hydrogen molecule and the original oxidized form of the catalyst which is in turn reduced, giving more current. The best catalysts are taken to be those that produce the largest increase in peak height in the presence of acid, and whose reduction potentials are not too negative, i.e., the catalysis happens with minimal overpotential.[202]

The reduction potential values of the synthetic [FeFe]-hydrogenase model complexes depend on the nature of the dithiolato bridge ligand. The adt complex **4** reduction potential is shifted to more positive value compared to its pdt **2** analogue. The reason for that is attributed to the possible protonation of the nitrogen atom of the co-ligand, which can lead to easier reduction. In addition, replacing one or more of the carbonyl groups of complexes **2** or **4** make their reduction potential more negative. However, increasing the donor ability of the ligands can favor protonation at the Fe-Fe bond, and this can shift the reduction potentials to more positive values.[32]

Rauchfuss and coworkers reported the first examples of electrocatalytic proton reduction by di-iron dithiolate complexes. Afterward, around 100 papers to date which examine some [FeFe]-hydrogenase model complexes as electrocatalysis for proton reduction.[32] This part of the thesis shows some examples of the electron transfer and electrocatalytic studies of some synthetic di-iron dithiolato complexes.

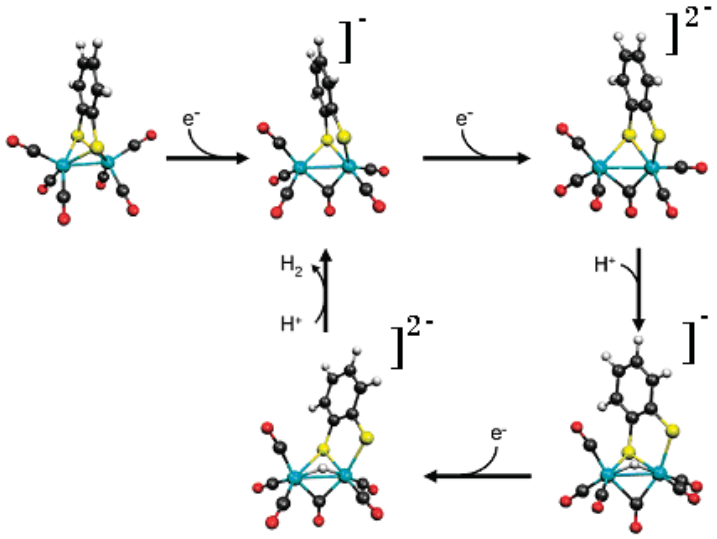
A detailed spectroelectrochemical study of $[Fe_2(CO)_6(\mu\text{-pdt})]$ (**2**) showed, that **2** is initially reduced to the unstable 19- electron anion **87** (Scheme 8). This was followed by the formulation of the CO-bridged two-electron-reduced complex **88**. This species was sufficiently nucleophilic to attack the parent compound to give a tetranuclear product **89**. Another pathway for the decay of **87** involves reversible ligand-loss to give the CO-bridge species **90** followed by formation of a symmetrical CO-bridged dimer **91**.[32, 205] In addition, electrocatalytic proton reduction in the presence of **2** in the presence of moderately strong acids, was examined by electrochemical and spectroelectrochemical techniques.[32, 205-207]



Scheme 8. The reduction pathway of PDT complex (**2**) in the absence of proton source. [After ref 32]

The electrocatalytic generation of dihydrogen by $[Fe_2(CO)_6(\mu\text{-bdt})]$ (**92**) (bdt = benzenedithiolate), using strong acid as a proton source was investigated by Capon and co-workers.[208, 209] This was followed by studies of Evans and coworkers, who investigated the electrocatalytic generation of dihydrogen using **92** in the presence of several carboxylic acids and phenols.[210] The mechanism of this process and

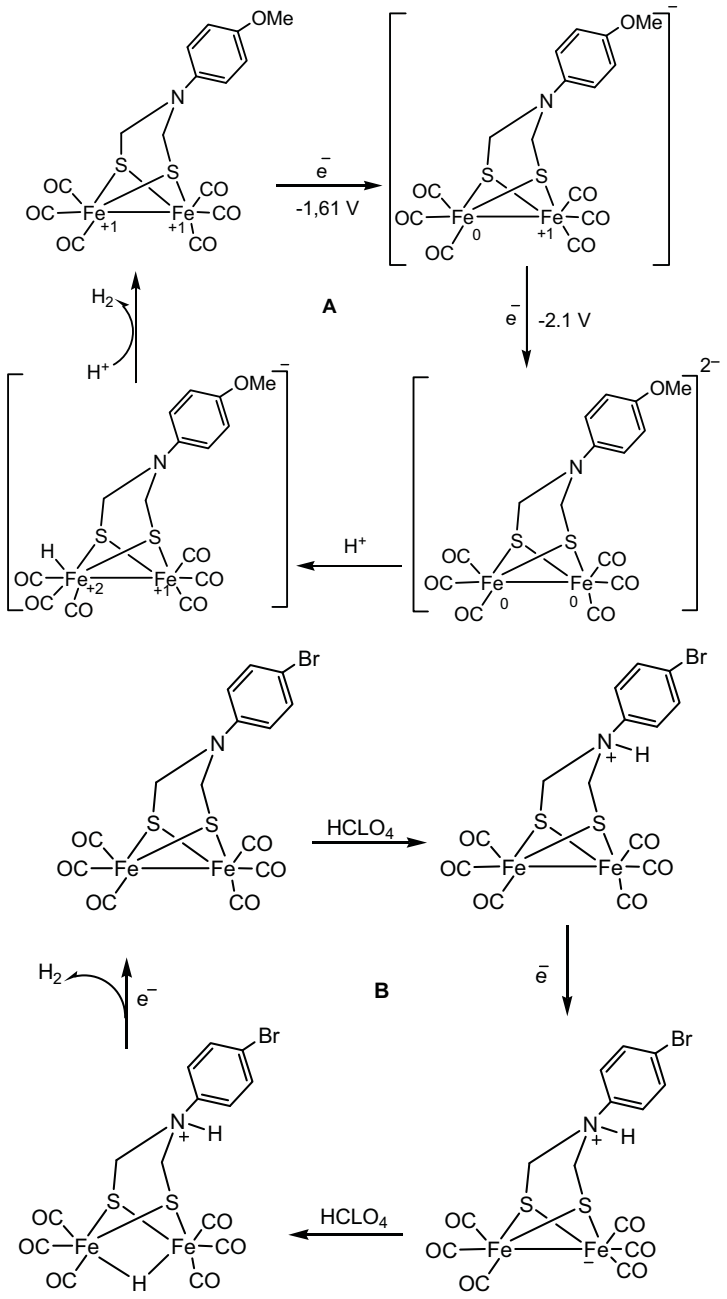
structures for the intermediates were determined by electrochemical analysis and theoretical calculations (Scheme 9).[210] The bdt system is reduced to its dianion in a reversible two-electron transfers process, with the second transfer slightly more favorable than the first. In comparison to **2**, which is similar in structure but has only a simple propanedithiolate bridge, the bdt system **92** is reduced to its dianion in a reversible two-electron transfers, whereas **2** undergoes an initial quasi-reversible one-electron reduction, followed by a second irreversible reduction. Additionally, in the pdt case **2**, a decoordination of a μ-sulfur ligand of the dithiolate bridge is observed, while in the bdt system **92**, μ_2 to μ_1 rearrangement of a bridging thiolate is suggested.[32, 210]



Scheme 9. DFT calculated structures and mechanism of the catalytic reduction of protons to H_2 by $[Fe_2(CO)_6(\mu\text{-bdt})]$ (**92**) [Adapted from ref 210].

The electrochemistry of the adt-bridged diiron model complexes differ from that of the carbon chain-bridged all-carbonyl diiron complexes. The difference is attributed to the introduction of the nitrogen atom to the dithiolato bridge of these complexes, which can be protonated in the presence of a proton.[133] The protonation of nitrogen atom depends on the acid strength. Song and co-workers investigated the electrocatalytic generation of H_2 by $[\{(\mu\text{-}SCH_2)_2N(C_6H_4OMe\text{-}p)\}Fe_2(CO)_6]$ complex (**93**) in the presence of acetic acid (HOAc), and they proposed an EECC (E = electrochemical, C = chemical) mechanism for this process as shown in Scheme 10A.[134] In contrast, Ott and co-workers, proposed ECEC mechanism for the H_2

production from $HClO_4$ catalyzed by [{(μ-SCH_2)$_2$N(C_6H_4Br-*p*)}$Fe_2(CO)_6$] complex (**94**) (Scheme 10B).[2111]



Scheme 11.Proposed mechanisms for electrocatalytic production of H_2 by A) [{(μ-SCH_2)$_2$N(C_6H_4OMe-*p*)}$Fe_2(CO)_6$] (**93**) [After ref 134]; B) [{(μ-SCH_2)$_2$N(C_6H_4Br-*p*)}$Fe_2(CO)_6$] (**94**). [After ref 211]

In the present work, we examined complex $Fe_2(CO)_6$(μ-$SCH(C_6H_5)C_6H_4S$-μ) (**82**), as electocatalysis for the H_2 generation from acetic acid, which revealed only a moderate catalytic activity. Since compound **82** reveals structural properties of

$Fe_2(CO)_6$(pdt) **2** as well as of $Fe_2(CO)_6$(bdt) **92**, a short comparison of the electrochemical behavior for these three complexes will be given here. In contrast to $Fe_2(CO)_6(\mu$-$SCH(C_6H_5)C_6H_4S$-$\mu)$ (**82**) and $Fe_2(CO)_6$(pdt) (**2**),[205-207] the $Fe_2(CO)_6$(bdt) complex,[210] shows an initial two-electron reduction to a $[Fe^0Fe^0]$ complex at –1.25 V, this reduction, however, appears at two different potentials. The one-electron reduction of complexes **2** and **82**, respectively, can be observed at –1.44 V and –1.58 V, respectively. In contrast to $Fe_2(CO)_6$(bdt), the second one-electron reduction can be found at distinctly lower potential around –2 V for both complexes. Upon adding acetic acid to the three complexes, the reduction of protons to dihydrogen can be observed for all around ~ –2 V. Based on these properties, the electrochemistry of $Fe_2(CO)_6(\mu$-$S_2C_{13}H_{10})$ **82** is comparable to those for the reported [FeFe]-hydrogenase model complexes with a propanedithiolato backbone.

4. Publications

4.1 [AD1] Phosphane- and Phosphite-Substituted Diiron Diselenolato Complexes as Models for [FeFe]-Hydrogenases.

M. K. Harb, J. Windhager, A. Daraosheh, H. Görls, L. T. Lockett, N. Okumura, D. H. Evans, R. S. Glass, D. L. Lichtenberger, M. El-khateeb, W. Weigand.

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Phosphane- and Phosphite-Substituted Diiron Diselenolato Complexes as Models for [FeFe]-Hydrogenases

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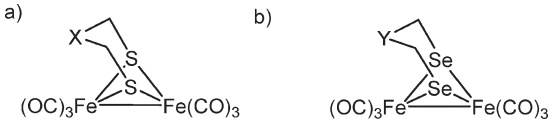
Dedicated to Professor Ingo-Peter Lorenz on the occasion of his 65th birthday

Keywords: Iron / Hydrogenases / Substitution / Electrocatalysis / Ligand effects / Enzyme catalysis / Selenium

The displacement of terminal CO ligands in $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_6$ (**1**) by triphenylphosphane, trimethyl phosphite, and bis(diphenylphosphanyl)ethane (dppe) ligands is investigated. Treatment of **1** with 1 equiv. of triphenylphosphane afforded $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5(PPh_3)$ (**2**). The mono- and disubstituted phosphite complexes $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5P(OMe)_3$(**3**)and$Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4\text{-}[P(OMe)_3]_2$ (**4**) were obtained from the reaction of **1** with excess $P(OMe)_3$ at reflux in toluene. In contrast, the reaction of **1** with 1 equiv. of dppe in the presence of $Me_3NO{\cdot}2H_2O$ gave a mixture of $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4(\kappa^2\text{-dppe})$ (**5**) and $[Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5]_2(\mu\text{-dppe})$ (**6**). The newly synthesized complexes **2**–**6** were fully characterized by IR, ^1H NMR, ^{13}C NMR, $^{77}Se\{^1H\}$ NMR, and $^{31}P\{^1H\}$ NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray diffraction analysis. Complex **2** has proved to be a catalyst for the electrochemical reduction of the weak acid, acetic acid, to give molecular hydrogen.

Introduction

The search for alternative energy sources is a challenge for mankind. Hydrogen is one of these energy sources.[1–4] Hydrogenases are enzymes that produce dihydrogen from water. An important representative example of these enzymes was isolated from *Desulfovibrio desulfuricans*.[5,6] This enzyme can produce 9000 molecules of hydrogen per second at 30 °C (hypothetically 1 mol of this enzyme could fill an airship of 13000 m^3 in about 10 min).[6] Therefore several diiron dithiolato model compounds as biomimics for the active site of this enzyme have been described (Scheme 1a).[7–24] The catalytic properties for hydrogen generation by models of [FeFe]-hydrogenases can be modified by substitution of the CO ligands. The replacement of one or two carbonyl ligands from [FeFe]-hydrogenase model complexes by CN^-, phosphanes, phosphite, carbene, and isocyanide ligands have been reported in the literature.[9–11,23–30] These complexes also serve as models of the active site of [FeFe]-hydrogenases. The substitution reactions of [FeFe]-hydrogenases with bidentate ligands such as bis(phosphanes) $[Ph_2P(CH_2)_nPPh_2]$ and diamines were also investigated.[31–36] Recently, the preparation and characterization of diiron models containing diselenolato ligands have been reported (Scheme 1b).[37–40] The ability of these complexes to act as models for the [FeFe]-hydrogenases has also been investigated. In this paper, the substitution reactions of one or two carbonyl groups of $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)\text{-}(CO)_6$ (**1**) by PPh_3 or $P(OMe)_3$ are studied in order to increase the electron density at the iron atoms and to enhance its basicity. The replacement of carbonyl ligands of **1** by bis(diphenylphosphanyl)ethane (dppe) in order to obtain dissymmetrically disubstituted diiron systems is also described. In addition, the electrochemistry of the monophosphane complex **2** was investigated by cyclic voltammetry, in order to compare its electrochemistry with **1** as well as with its sulfur analogues.



Scheme 1. (a) Models of [FeFe]-hydrogenases containing dithiolato ligands (X = CH_2, NH, O, S). (b) Models of [FeFe]-hydrogenases containing diselenolato ligands (Y = CH_2, Se, NPh).

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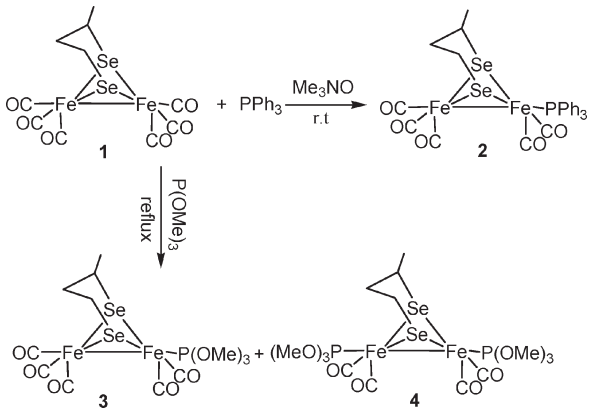
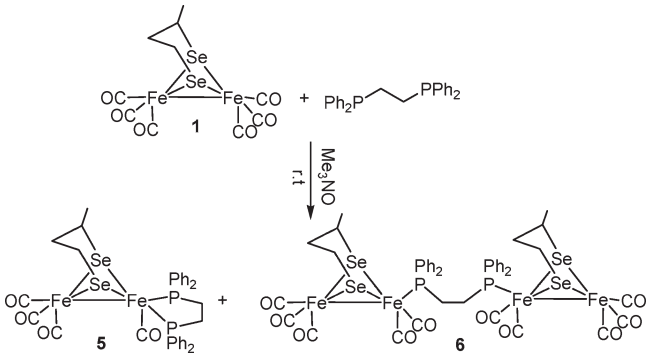
Results and Discussion

Stirring of $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_6$ (**1**) at room temperature with 1 equiv. of triphenylphosphane in the presence of trimethylamine *N*-oxide dihydrate ($Me_3NO{\cdot}2H_2O$) gives the complex $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5(PPh_3)$ (**2**) (Scheme 2). The $CH_2CH_2CH(CH_3)$ moiety bridging the selenium atoms desymmetrizes the iron atoms,[41] and the PPh_3 ligand may be *cis* or *trans* to the CH_3 group in the bridge. However, only one diastereomer has been found. In contrast, heating of **1** at reflux with an excess amount of $P(OMe)_3$ in toluene for 3 h gives two complexes, namely $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5P(OMe)_3$ (**3**) and $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4[P(OMe)_3]_2$ (**4**) (Scheme 2), in which one (**3**) or two (**4**) carbonyl ligands are substituted by $P(OMe)_3$.



Scheme 2. Models of substituted [FeFe]-hydrogenase complexes $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5(PPh_3)$ (**2**), $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5P(OMe)_3$ (**3**), and $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4[P(OMe)_3]_2$ (**4**) prepared in our laboratory.

The reaction of compound **1** with 1 equiv. of dppe in the presence of $Me_3NO{\cdot}2H_2O$ gives a mixture of the chelated diiron complex $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4(\kappa^2\text{-dppe})$ (**5**) and the bridged tetrairon complex $[Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5]_2(\mu\text{-dppe})$ (**6**), which can be separated by column chromatography (Scheme 3). Compounds **2**–**6** have been characterized by IR and multinuclear NMR spectroscopy, mass spectrometry, elemental analysis, as well as by X-ray crystallography. These complexes are air-stable in the solid state and are stable for several hours in solution. The ^1H NMR spectra for **2**–**6** exhibit a doublet at δ = 1.09, 1.28, 1.24, 1.52, and 1.03 ppm, respectively, for the methyl group of the diselenolato ligand. $^1H,^1H$ COSY, $^1H,^{13}C$ HSQC, and $^1H,^{13}C$ HMBC NMR spectroscopic experiments allowed the assignment of the other five chemically nonequivalent protons of the diselenolato ligand. These resonances are comparable to those of the unsubstituted complex **1**.[38] The $^{13}C\{^1H\}$ NMR spectra for **2**–**6** exhibit four resonances for the bridging unit. These resonances are in the same range as those observed for **1**.[38] In addition, the expected resonance for the carbonyl groups and the phosphane ligands were observed. Two signals are obtained in the $^{77}Se\{^1H\}$ NMR spectra for complexes **2**–**6** because of the presence of two different Se atoms. The ^1H-^{77}Se HMBC spectrum allows the assignment of the two different Se atoms. The $^{31}P\{^1H\}$ NMR spectra of **2** and **3** show one signal at δ = 72.1 and 193.1 ppm, respectively, whereas for **4** two resonances are observed at δ = 186.5 and 189.2 ppm from the nonequivalent iron atoms.



Scheme 3. Models of [FeFe]-hydrogenases containing a chelated dppe ligand (**5**) and bridged dppe ligand (**6**) prepared in our laboratory.

The $^{31}P\{^1H\}$ NMR spectrum of **5** displays signals at δ = 98.7 and 96.3 ppm ($^2J_{PP}$ = 20.3 Hz) representing an AB spin system, which indicates the presence of two nonequivalent phosphorus atoms. These resonances can be assigned to the basal-apical isomer of a diiron complex with a chelating dppe ligand.[32–34] Only one diastereoisomer has been observed. The mass spectra of **2**–**5** show the molecular ion peaks followed by the fragmentation of five CO groups in **2** and **3**, and four in **4** and **5**. Compound **6** exhibits two singlets in the $^{31}P\{^1H\}$ NMR spectrum at δ = 66.1 and 66.2 ppm. These resonances are shifted to higher fields compared to those reported for sulfur analogues.[31–34] The two signals (ratio 1:1) in the $^{31}P\{^1H\}$ NMR spectrum of **6** could be explained by the presence of two diastereoisomers in solution resulting from the flap pointing toward or away from the phosphane ligand. A temperature-dependent $^{31}P\{^1H\}$ NMR study (T = 273–333 K) shows that these two species are not in equilibrium. MS analysis shows the fragmentation of 10 CO groups and the molecular peak at m/z = 1330, which suggests the presence of a tetranuclear complex in which two diiron moieties are linked by a dppe ligand.

The IR spectra of **2**–**6** show three absorption bands in the regions of 1916–1955, 1972–1996, and 2033–2040 cm^{-1}. These data are within the same ranges observed for the unsubstituted[38] complex and for the sulfur analogues.[26,31–33]

The molecular structures of **2**–**6** were determined and are shown in Figures 1, 2, 3, 4, and 5, respectively. The coordination geometry around the iron cores in all complexes are similar to those in its sulfur analogues.[26,31–34] The central 2Fe2Se structures of all of the complexes are in the butterfly conformation, as was observed for the sulfur ana-

logues.[26,31–34] The displacement of one or two carbonyl groups by phosphanes or phosphite has only a small effect on the Fe–Fe distances as compared to that of **1** [2.5471(15) Å].[38] The Fe–Fe bonds in **2**–**6** are longer than those in the sulfur derivatives {**2**: 2.5573(16) Å [sulfur derivative: 2.5247(6) Å[26]], **3**: 2.5881(12) Å [sulfur derivative: 2.5142(9) Å[26]], **4**: 2.5506(6) Å, **5**: 2.6180(7) Å [sulfur derivative: 2.547(7) Å[32]], **6**: 2.5506(13) Å [sulfur derivative: 2.5108(14) Å[31]]} because of the larger size of the selenium atoms.[26,31–34] The Fe–Se bonds in **2**–**6** are slightly longer (ca. 0.017 Å) than that in the unsubstituted compound **1** due to the stronger σ-donor properties of phosphanes or phosphite ligands compared to carbonyl groups.[38] The Fe–P bond lengths [**2**: 2.246(2) Å, **3**: 2.1596(17) Å, **4**: 2.1651(8) Å and 2.1601(9) Å, **5**: 2.2323(11) Å and 2.1913(9) Å, **6**: 2.2236(18) Å] are comparable to those observed for sulfur and selenium analogues.[26,31–34,40] In compounds **2**–**4** and **6** the P atoms are coordinated to Fe in an apical position, which has been proved by $^{31}P\{^{1}H\}$ NMR spectroscopy and X-ray crystallography (Figures 1, 2, 3, and 5), whereas the apical-basal isomer is observed in **5** (Figure 4). In principle, for the monosubstituted complexes **2** and **3** the phosphane ligand may occupy an apical or basal position. The X-ray crystal structure of **2** shows that the phosphane ligand occupies an apical position. In addition, the stereochemistry of **2** is complicated by the possibility of forming diastereomers. That is, one with the CH_3 group of the bridge and P moiety on the same side (*cis*) or the other with the CH_3 group of the bridge and P moiety on opposite sides (*trans*). Furthermore, each diastereomer may adopt either of two conformations obtained by inverting the flap of the $CH_2CH_2CH(CH_3)$ moiety resulting in an equatorial or axial CH_3 group and the flap pointing toward or away from the phosphane ligand. It can be seen from the X-ray structure of **2** that the CH_3 group is equatorial and *trans* to the phosphane ligand and the flap points away from the phosphane ligand. As pointed out above, the ^{31}P NMR spectrum of **2** shows only one resonance signal suggesting that only one diastereomer is present. In **3** the P ligand is basal. There are two different basal positions owing to the dissymmetry induced by the $CH_2CH_2CH(CH_3)$ bridge. In **3** the phosphite ligand occupies the basal position *syn* to the equatorial CH_3 group, and the flap points toward the phosphane ligand. In **4** the phosphane ligands are on different Fe atoms, and both occupy apical positions with the equatorial CH_3 group. Owing to the dissymmetry of the $CH_2CH_2CH(CH_3)$ moiety the two phosphane ligands are nonequivalent as already noted above in the ^{31}P NMR spectroscopic analysis. For **5**, both P atoms of the dppe are on one Fe atom with one P atom apical and the other basal. Surprisingly, the CH_3 group is *cis* and the flap points toward the apical P atom, and the CH_3 group is *syn* to the basal P atom of the dppe ligand. In **6** both P atoms of the bridging dppe ligand occupy apical positions. The CH_3 group occupies an equatorial position and is *cis* to the phosphane ligand, and the flap points toward the phosphane ligand. The stereochemistry for the two 2Fe2Se centers is the same.

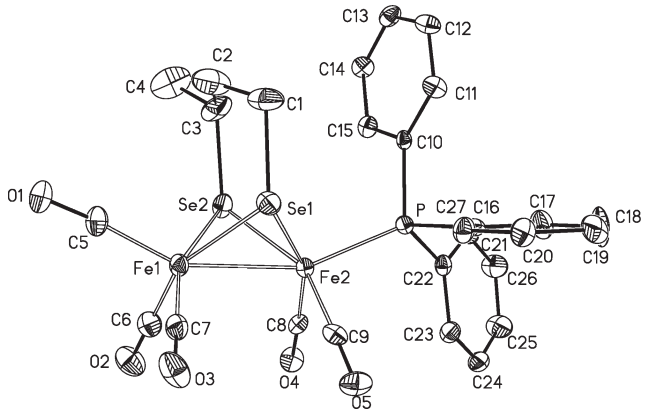


Figure 1. ORTEP drawing of $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5(PPh_3)$ (**2**). Selected distances [Å] and angles [°]: Fe1–Fe2 2.5573(16), Fe1–Se1 2.3868(16), Fe1–Se2 2.3792(15), Fe2–Se1 2.3791(15), Fe2–Se2 2.3940(14); Fe1–Se1–Fe2 64.90(5), Fe1–Se2–Fe2 64.79(5).

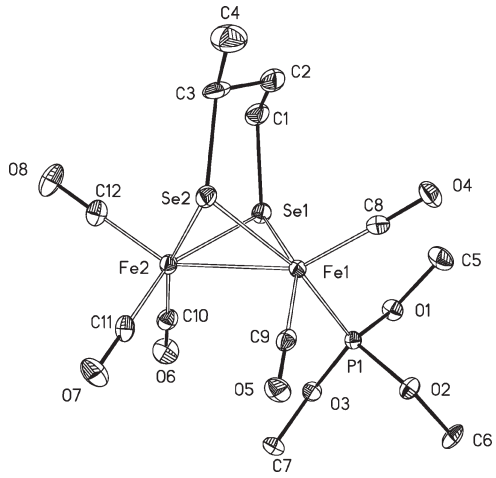


Figure 2. ORTEP drawing of $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5P(OMe)_3$ (**3**). Selected distances [Å] and angles [°]: Fe1–Fe2 2.5881(12), Fe1–Se1 2.3723(10), Fe1–Se2 2.3723(10), Fe2–Se1 2.3792(11), Fe2–Se2 2.3814(11); Fe1–Se1–Fe2 66.01(3), Fe1–Se2–Fe2 65.97(3).

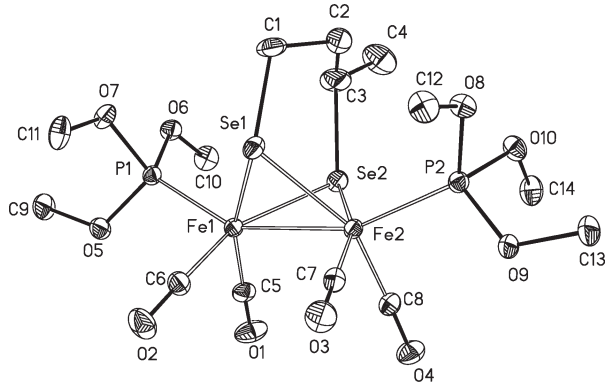


Figure 3. ORTEP drawing of $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4[P(OMe)_3]_2$ (**4**). Selected distances [Å] and angles [°]: Fe1–Fe2 2.5506(6), Fe1–Se1 2.3787(5), Fe1–Se2 2.3828(5), Fe2–Se1 2.3818(5), Fe2–Se2 2.3817(5); Fe1–Se1–Fe2 64.794(16), Fe1–Se2–Fe2 64.733(16).

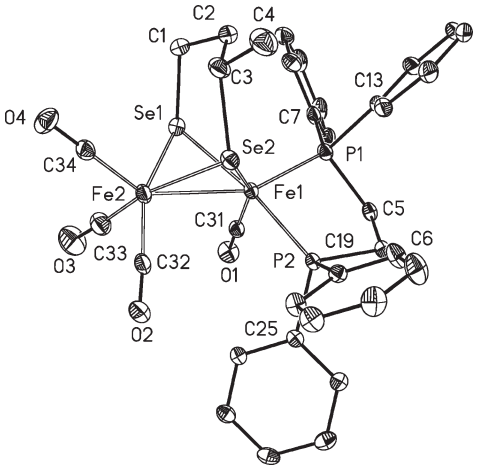


Figure 4. ORTEP drawing of $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4(\kappa^2\text{-dppe})$ (**5**). Selected distances [Å] and angles [°]: Fe1–Fe2 2.6180(7), Fe1–Se1 2.3685(6), Fe1–Se2 2.3738(6), Fe2–Se1 2.3839(6), Fe2–Se2 2.3924(6); Fe1–Se1–Fe2 66.853(19), Fe1–Se2–Fe2 66.636(19).

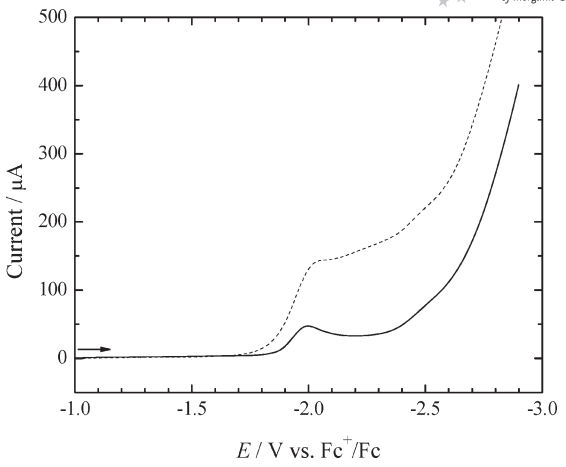


Figure 6. Cyclic voltammograms of 1.0 mM **2** in CH_2Cl_2 with 0.10 M Bu_4NPF_6 and a scan rate of 0.10 Vs^{-1}. Solid: **2** alone. Dashed: **2** + 10.5 mM CH_3COOH. Return sweeps omitted for clarity.

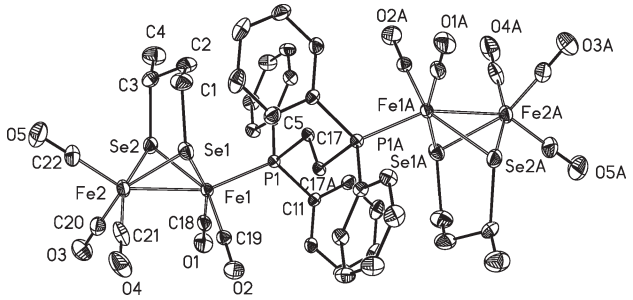


Figure 5. ORTEP drawing of $[Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5]_2(\mu\text{-dppe})$ (**6**). Selected distances [Å] and angles [°]: Fe1–Fe2 2.5506(13), Fe1–Se1 2.3871(12), Fe1–Se2 2.3743(12), Fe2–Se1 2.3904(13), Fe2–Se2 2.3774(13); Fe1–Se1–Fe2 64.54(4), Fe1–Se2–Fe2 64.93(4).

Electrochemical Investigations

Cyclic voltammograms of **2** were recorded in order to identify the electrochemical oxidation and reduction processes and to test the ability of these complexes to catalyze the reduction of weak acids to form dihydrogen. Complex **2** was studied in dichloromethane. As expected for the replacement of CO by a phosphane ligand, the phosphane complex **2** is more easily oxidized than the unsubstituted complex **1** with an anodic peak potential of +0.35 V vs. ferrocene compared to +0.76 V for **1**.[38] There is a reasonable degree of reversibility to the oxidation process. The reduction peak for **2**, whose height is also close to that expected for a one-electron process, appears at –2.00 V and is irreversible (Figure 6). As expected, the potential is more negative than that observed for **1** (–1.83 V).[38] As noted elsewhere,[42] replacement of CO by a phosphane ligand causes a shift of both the anodic and cathodic peaks in the negative direction. The shifts seen for **2**, 0.41 and 0.17 V, respectively, may be compared with shifts of 0.62 and 0.18 V seen upon replacing CO by PPh_3 in a sulfur analogue similar to **2**, $Fe_2[\mu\text{-}S(CH_2)_3S](CO)_6$.[26]

Addition of acetic acid results in catalytic reduction at the main peak rather than a separate, more negative peak as seen with **1**[38] (dashed curve, Figure 6). Thus, **2** is capable of catalyzing the production of dihydrogen by the reduction of weak acids.

Conclusions

The present study showed that the desymmetrized $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_6$ (**1**) reacts with PPh_3 and $P(OMe)_3$ producing the mono- and disubstituted complexes **2**–**4**; only one diastereoisomer has been observed in complexes **2**–**4**. By using the bidentate ligand dppe, a mixture of the chelated diiron (**5**) and the bridged tetrairon (**6**) complexes were obtained as observed for the sulfur-PDT derivatives. For $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4(\kappa^2\text{-dppe})$ (**5**) we have also obtained only one diastereoisomer with an apical-basal position of the dppe ligand, whereas two diastereoisomers have been detected for $[Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5]_2(\mu\text{-dppe})$ (**6**) as indicated by the ^{31}P NMR spectra. The results of the X-ray diffraction analysis show that the Fe–Fe distances in **2**–**6** are significantly longer than those in their sulfur analogues due to the larger size of the selenium atom. The stereochemistry is complicated by the fact that the phosphane ligand may occupy an apical or basal position (and there are two basal P diastereomers: one with the P and CH_3 group *syn* and the other *anti*), and for each of these (apical and two basal) there are two diastereomers (*cis* and *trans*), each of which can exist as two conformers with an axial or equatorial CH_3 group owing to the "flap" of the bridge, which can point toward or away from the P ligand. The electrochemical investigations of **2** showed oxidation and reduction behavior that is consistent with substitution of a CO group, as in **1** with a phosphane ligand. Catalytic reduction of acetic acid was seen at the first reduction peak of **2**.

Experimental Section

General Comments: All reactions were performed by using standard Schlenk and vacuum-line techniques under an inert gas. The ^{1}H, $^{13}C\{^{1}H\}$, $^{77}Se\{^{1}H\}$ $^{31}P\{^{1}H\}$, and 2D NMR (^{1}H,^{1}H COSY, ^{1}H,^{13}C HSQC, ^{1}H,^{13}C HMBC, ^{1}H,^{77}Se HMBC) spectra were recorded with either a Bruker Avance 200 or 400 MHz spectrometer by using the solvent residual peak or a concentrated solution of SeO_2 in D_2O as the reference. The ^{77}Se chemical shifts are reported relative to neat Me_2Se [$\delta(Me_2Se) = \delta(SeO_2) + 1302.6$ ppm].[43] External standard 85% H_3PO_4 was used as a reference for $^{31}P\{^{1}H\}$ spectral measurements. The mass spectra were recorded with a Finnigan MAT SSQ 710 instrument. The IR spectra were measured with a Perkin–Elmer System 2000 FT-IR spectrometer. Elemental analyses were performed with a Leco CHNS-932 apparatus. Silica gel 60 (0.015–0.040 mm) was used for column chromatography, and TLC was performed by using Merck TLC aluminum sheets (Silica gel 60 F_{254}). $Fe_3(CO)_{12}$ was purchased from Aldrich, solvents from Fisher Scientific, and other chemicals from Acros, and were used without further purification. All of the solvents used were dried and distilled prior to use according to standard methods. $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_6$ (**1**) was prepared according to a literature procedure.[38]

Preparation of $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5PPh_3$ (2): A solution of **1** (60 mg, 0.12 mmol) and $Me_3NO{\cdot}2H_2O$ (24 mg, 0.22 mmol) in MeCN was stirred at room temperature for 10 min. Then, triphenylphosphane (32 mg, 0.12 mmol) was added and the mixture stirred for 2 h. The resulting dark red mixture was concentrated to dryness under vacuum. The obtained solid was redissolved in a minimum amount of CH_2Cl_2 and the solution column-chromatographed (SiO_2/hexane). From the major red fraction, which was eluted with hexane/diethyl ether (2:1), **2** was obtained as a red solid, and was recrystallized from pentane at –25 °C. Yield 67 mg (77%). M.p. 193–194 °C. $C_{27}H_{23}Fe_2O_5PSe_2$ (728.05): calcd. C 44.54, H 3.18; found C 44.49, H 3.35. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.58 (m, 1 H, $SeCH_2CH_AH_B$), 1.09 (d, ^{3}J = 6.8 Hz, 3 H, CH_3), 1.27 (m, 1 H, $SeCH_2CH_AH_B$), 1.71 (m, 1 H, $SeCH_CH_D$), 2.00 (m, 1 H, SeCH), 2.03 (m, 1 H, $SeCH_CH_D$), 7.24–7.67 (m, 15 H, PPh_3) ppm. $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$): δ = 17.4 ($SeCH_2$), 25.7 (CH_3), 27.9 (SeCH), 38.5 ($SeCH_2CH_2$), 128.3, 130.1, 133.6, 136.0, 136.8 (PPh_3), 206.9, 210.3, 214.1, 214.3 (CO) ppm. $^{77}Se\{^{1}H\}$ NMR (76 MHz, $CDCl_3$): δ = 135 ($SeCH_2$), 467 (SeCH) ppm. $^{31}P\{^{1}H\}$ NMR (200 MHz, $CDCl_3$): δ = 72.1 (PPh_3) ppm. FTIR (KBr): $\tilde{\nu}$ = 2037 (vs), 1978 (vs), 1926 (w) cm^{-1}. MS (DEI = 70 eV): *m*/*z* (%) = 728 (1) [M^+], 672 (3) [M^+ – 56; 2 CO], 644 (3) [M^+ – 84; 3 CO], 588 (10) [M^+ – 140; 5 CO].

Preparation of $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5P(OMe)_3$ (3) and $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4[P(OMe)_3]_2$ (4): A solution of trimethyl phosphite [$P(OMe)_3$; 67 mg, 0.54 mmol] and **1** (90 mg, 0.18 mmol) in toluene (25 mL) was heated under reflux for 3 h. The resulting dark red mixture was concentrated to dryness under vacuum. The obtained solid was redissolved in a minimum amount of CH_2Cl_2 and the solution column-chromatographed (SiO_2/hexane). Products **3** and **4** were obtained from the first and the second fraction, respectively, by using hexane/CH_2Cl_2 (2:1) and then pure CH_2Cl_2 as eluents. Complex **3** was recrystallized from hexane at –25 °C and **4** from ethyl ether at 0 °C.

$Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5P(OMe)_3$ (3): Yield 38 mg (36%). M.p. 74–75 °C. $C_{12}H_{17}Fe_2O_8PSe_2$ (589.84): calcd. for $6C_{12}H_{17}Fe_2O_8PSe_2{\cdot}1$hexane C 25.84, H 3.24; found C 25.67, H 3.14. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.06 (m, 1 H, $SeCH_2CH_AH_B$), 1.28 (d, ^{3}J = 8.4 Hz, 3 H, CH_3), 1.68 (m, 1 H, $SeCH_2CH_AH_B$), 2.06 (m, 1 H, $SeCH_CH_D$), 2.47 (m, 1 H, SeCH), 2.57 (m, 1 H, $SeCH_CH_D$), 3.72 [s, 9 H, $P(OMe)_3$] ppm. $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$): δ = 29.4 ($SeCH_2$), 32.8 (CH_3), 37.1 (SeCH), 38.6 ($SeCH_2CH_2$), 52.0, 52.4 $P(OMe)_3$, 210.4, 210.9 (CO) ppm. $^{77}Se\{^{1}H\}$ (76 MHz, $CDCl_3$): δ = 396 ($SeCH_2$), 403 (SeCH) ppm. $^{31}P\{^{1}H\}$ NMR (200 MHz, $CDCl_3$): δ = 193.9 $P(OMe)_3$ ppm. FTIR (KBr): $\tilde{\nu}$ = 2040 (s), 1985 (vs, sh), 1931 (w) cm^{-1}. MS (DEI = 70 eV): *m*/*z* (%) = 590 (60) [M^+], 562 (9) [M^+ – 28; CO], 534 (12) [M^+ – 56; 2 CO], 506 (7) [M^+ – 84; 3 CO], 450 (23) [M^+ – 140; 5 CO].

$Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4[P(OMe)_3]_2$ (4): Yield 57 mg (46%). M.p. 155–156 °C. $C_{14}H_{26}Fe_2O_{10}P_2Se_2$ (685.91): calcd. C 24.51, H 3.82; found C 24.69, H 3.86. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.11 (m, 1 H, $SeCH_2CH_AH_B$), 1.24 (d, ^{3}J = 6.6 Hz, 3 H, CH_3), 1.53 (m, 1 H, $SeCH_2CH_AH_B$), 1.74 (m, 1 H, $SeCH_CH_D$), 1.89 (m, 1 H, SeCH), 2.39 (m, 1 H, $SeCH_CH_D$), 3.71, 3.77 [s, 18 H, 2 $P(OMe)_3$] ppm. $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$): δ = 16.1 ($SeCH_2$), 25.2 (CH_3), 26.1 (SeCH), 38.6 ($SeCH_2CH_2$), 51.4, 51.5, 51.8, 51.9 $P(OMe)_3$, 213.1, 213.4, 214.4, 214.7 (CO) ppm. $^{77}Se\{^{1}H\}$ NMR (76 MHz, $CDCl_3$): δ = 252 ($SeCH_2$), 402 (SeCH) ppm. $^{31}P\{^{1}H\}$ NMR (200 MHz, $CDCl_3$): δ = 186.5, 189.2 [$P(OMe)_3$] ppm. FTIR (KBr): $\tilde{\nu}$ = 2040 (m), 1996 (vs), 1955 (vs, sh) cm^{-1}. MS (DEI = 70 eV): *m*/*z* (%) = 686 (12) [M^+], 630 (9) [M^+ – 56; 2 CO], 602 (2) [M^+ – 84; 3 CO], 574 (16) [M^+ – 112; 4 CO].

Synthesis of $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4(\kappa^2\text{-dppe})$ (5) and $[Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5]_2(\mu\text{-dppe})$ (6): A solution of **1** (98 mg, 0.20 mmol) and $Me_3NO{\cdot}2H_2O$ (45 mg, 0.40 mmol) dissolved in MeCN was stirred at room temperature for 10 min. A solution of dppe (80 mg, 0.20 mmol) dissolved in CH_2Cl_2 (2 mL) was added and the combined solutions were stirred for 1 h. Then the solvent was evaporated under reduced pressure. The crude product was purified by chromatography on silica gel using hexane/CH_2Cl_2 (1:2) as the eluent. Complex **5** was obtained from the first red fraction and recrystallized from hexane/CH_2Cl_2 at –25 °C. A second red brownish band provided complex **6**, which was also recrystallized from hexane/CH_2Cl_2 at –25 °C.

$Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4(\kappa^2\text{-dppe})$ (5): Yield 33 mg (20%). M.p. 208–209 °C. $C_{34}H_{32}Fe_2O_4P_2Se_2$ (836.17): calcd. C 48.84, H 3.86; found C 48.45, H 3.88. ^{1}H NMR: δ = 0.91 (m, 1 H, SeCH), 1.24 (m, 1 H, $SeCH_2CH_AH_B$), 1.52 (d, ^{3}J = 6.2 Hz, 3 H, CH_3), 1.69 (m, 1 H, $SeCH_CH_D$), 1.90 (m, 1 H, $SeCH_2CH_AH_B$), 2.15 (m, 1 H, $SeCH_CH_D$), 2.52, 2.93 (m, 4 H, PCH_2CH_2P), 7.24–7.46 (m, 20 H, 2 PPh_2) ppm. $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$): δ = 21.2 (SeCH), 27.5 ($SeCH_2$), 29.2 (CH_3), 29.7 ($SeCH_2CH_2$), 45.8, 47.8 (PCH_2CH_2P) 128.6, 130.3, 132.4 (2 PPh_2), 210.2 (CO) ppm. $^{77}Se\{^{1}H\}$NMR (76 MHz, $CDCl_3$): δ = 234 ($SeCH_2$), 402 (SeCH) ppm. $^{31}P\{^{1}H\}$ NMR (200 MHz, $CDCl_3$, 25 °C): δ = 96.3 (d, $^{2}J_{PP}$ = 20.3 Hz), 98.7 (d, $^{2}J_{PP}$ = 20.3 Hz) ppm. FTIR (KBr): $\tilde{\nu}$ = 2037 (s), 1975 (vs), 1919 (w) cm^{-1}. MS (DEI = 70 eV): *m*/*z* (%) = 836 (8) [M^+], 808 (2) [M^+ – 28; CO], 752 (9) [M^+ – 84; 3 CO], 724 (38) [M^+ – 112; 4 CO].

$[Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5]_2(\mu\text{-dppe})$ (6): Yield 101 mg (76%). M.p. 193–194 °C. $C_{44}H_{40}Fe_4O_{10}P_2Se_4$ (1329.95): calcd. for $3C_{44}H_{40}Fe_4O_{10}P_2Se_4{\cdot}2$hexane C 41.22, H 3.58; found C 41.61, H 3.58. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 0.69 (m, 2 H, 2 SeCH), 0.85 (m, 2 H, 2 $SeCH_2CH_AH_B$), 1.03 (d, ^{3}J = 6.4 Hz, 6 H, 2 CH_3), 1.35 (m, 2 H, 2 $SeCH_CH_D$), 1.56 (m, 2 H, 2 $SeCH_2CH_AH_B$), 1.87 (m, 2 H, 2 $SeCH_CH_D$), 2.65, 2.81 (m, 4 H, PCH_2CH_2P), 7.03–7.51 (m, 20 H, 2 PPh_2) ppm. $^{13}C\{^{1}H\}$ NMR (50 MHz, $CDCl_3$): δ = 17.9 ($SeCH_2$), 25.5 (SeCH), 27.7 ($SeCH_2CH_2$), 30.3, 32.4 (PCH_2CH_2P), 39.1 (CH_3), 125.1, 127.9, 128.8, 137.4 (2 PPh_2), 210.8 (CO) ppm. $^{77}Se\{^{1}H\}$ NMR (76 MHz, $CDCl_3$): δ = 313 ($SeCH_2$), 409 (SeCH) ppm. $^{31}P\{^{1}H\}$ NMR

Table 1. Crystal data and refinement details for the X-ray structure determinations.

	2	**3**	**4**	**5**	**6**
Empirical formula	$C_{27}H_{23}Fe_2O_5PSe_2$	$C_{12}H_{17}Fe_2O_8PSe_2$	$C_{14}H_{26}Fe_2O_{10}P_2Se_2$	$C_{34}H_{32}Fe_2O_4P_2Se_2$	$C_{44}H_{40}Fe_4O_{10}P_2Se_4{\cdot}2CH_2Cl_2$
M_r [g mol^{-1}]	728.04	589.85	685.91	836.16	1499.79
T [°C]	–90(2)	–90(2)	–90(2)	–90(2)	–90(2)
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$Pbca$	$P2_1/n$	$P2_1/n$
a [Å]	11.5652(5)	8.4457(2)	16.3859(5)	19.2256(5)	12.5031(7)
b [Å]	15.2712(8)	23.3951(9)	16.6265(4)	9.6723(3)	16.3825(9)
c [Å]	16.5167(8)	10.0243(4)	17.8597(4)	19.5069(6)	13.5152(6)
α [°]	90	90	90	90	90
β [°]	108.486(3)	103.832(2)	90	115.157(2)	98.663(3)
γ [°]	90	90	90	90	90
V [Å^3]	2766.6(2)	1923.24(12)	4865.7(2)	3283.35(17)	2736.8(2)
Z	4	4	8	4	2
ρ [g cm^{-3}]	1.748	2.037	1.873	1.692	1.820
μ [cm^{-1}]	37.73	54.11	43.61	32.36	40.06
Measured data	18398	12801	32744	22695	18250
Data with $I > 2\sigma(I)$	3882	3307	4571	5446	3907
Unique data/R_{int}	6277/0.0819	4351/0.0701	5567/0.0585	7499/0.0638	6250/0.0755
wR_2 (all data, on F^2)[a]	0.1856	0.1259	0.0776	0.0889	0.1638
R_1 [$I > 2\sigma(I)$][a]	0.0762	0.0544	0.0335	0.0422	0.0674
s[b]	1.094	1.092	1.023	1.026	1.019
Residual density [e Å^{-3}]	2.300/–1.889	2.370/–1.633	0.684/–0.786	0.911/–0.467	2.259/–1.956
Absorption method	none	none	none	none	none
CCDC no.	705054	705055	705056	705057	705058

[a] Definition of the R indices: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$. [b] $s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

(200 MHz, $CDCl_3$): δ = 66.1, 66.2 (2 PPh_2) ppm. FTIR (KBr): $\tilde{\nu}$ = 2033 (vs), 1972 (vs), 1916 (w) cm^{-1}. MS (DEI = 70 eV): m/z (%) = 1330 (2) [M$^+$], 1176 (7) [M$^+$ – 154; 2 Ph], 1120 (5) [M$^+$ – 210; 2 Ph + 2 CO], 1064 (10) [M$^+$ – 266; 2 Ph + 4 CO], 1036 (16) [M$^+$ – 294; 2 Ph + 5 CO], 931 (88) [M$^+$ – 399; 3 Ph + 6 CO], 903 (45) [M$^+$ – 427; 3 Ph + 7 CO].

Crystal Structure Determination: The intensity data for the compounds were collected with a Nonius KappaCCD diffractometer by using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption effects.[44,45] The structures were solved by direct methods (SHELXS)[46] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).[47] All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. All non-disordered non-hydrogen atoms were refined anisotropically.[47] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations (Table 1). CCDC-705054 (for **2**), -705055 (for **3**), -705056 (for **4**), -705057 (for **5**), and -705058 (for **6**) 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.

Electrochemical Measurements: The electrochemical procedures, apparatus, and sources and treatment of solvent and electrolyte have been described.[38,48] Solutions were purged with argon, the glassy carbon disk working electrode (0.0707 cm^2) was from Bioanalytical Systems, the instrument was a Princeton Applied Research Model 2273 Parstat, and the experiments were conducted at room temperature. The laboratory reference electrode was a silver wire in contact with 0.010 M $AgNO_3$ in acetonitrile with 0.10 M tetrabutylammonium hexafluorophosphate. The potential of the ferrocenium ion/ferrocene couple was frequently measured with respect to this reference, and all potentials have been reported vs. ferrocene.

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4.2 [AD2] Substitution Reactions at [FeFe] hydrogenase Models Containing [2Fe3S] Assembly by Phosphine or Phosphite Ligands.

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Substitution Reactions at [FeFe] Hydrogenase Models Containing [2Fe3S] Assembly by Phosphine or Phosphite Ligands

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In order to elucidate the role of the "on−off" coordination mode of the thioether group in the [2Fe3S] complex **1**, which is related to the active site of [FeFe] hydrogenases, substitution studies of CO ligands by phosphite and phosphine ligands at compound $Fe_2(\mu\text{-}S_2(C_3H_6)_2S\text{-}\mu)(CO)_5$ (**1**) have been investigated. The reaction of **1** with 1 equiv of trimethylphosphite gave the kinetically controlled product $Fe_2(\mu\text{-}S_2(C_3H_6)_2S)(CO)_5P(OMe)_3$ (**2**) or the thermodynamically controlled product $Fe_2(\mu\text{-}S_2(C_3H_6)_2S\text{-}\mu)(CO)_4P(OMe)_3$ (**3**) depending on the reaction conditions. Moreover, $Fe_2(\mu\text{-}S_2(C_3H_6)_2S)(CO)_4[P(OMe)_3]_2$ (**4**) and $Fe_2(\mu\text{-}S_2(C_3H_6)_2S)(CO)_4(PMe_3)_2$ (**5**) were obtained from the reactions of **1** with excess $P(OMe)_3$ and excess PMe_3, respectively. These novel complexes have been characterized by IR, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray single-crystal structure analysis.

Introduction

In an earlier communication we reported our investigation on the reactions of 1,2,4-trithiolane, 1,2,5-trithiepane, 1,2,5-trithiocane, and 1,2,6-trithionane with nonacarbonyldiiron.[1] In that study, we found that the ring size in these different heterocycles influenced the constitutional structures of the resultant complexes. The reaction of nonacarbonyldiiron with the 1,2,6-trithionane provided $Fe_2(\mu\text{-}S_2(C_3H_6)_2S\text{-}\mu)(CO)_5$ (**1**), which can be envisioned as a model complex for the [2Fe3S] subsite of the H-cluster. In this compound the thioether sulfur atom acts as an additional S-donor by intramolecular substitution of one carbonyl group (Scheme 1).[1]

During the last several years, the research groups of Pickett,[2,3] Rauchfuss,[4] Song,[5] and Chen[6] reported the syntheses of various models for the [2Fe3S] subunit of the [FeFe] hydrogenases' active site (Scheme 2). It is generally accepted that the role of the proximal [4Fe4S] unit in the H-cluster is to shuttle electrons in and out the [2Fe2S] subunit via a cysteinato ligand.[7]

Pickett described the effect of the thioether sulfur atom on the substitution of CO ligands at the complex $[Fe_2(CO)_5\{MeSCH_2C(Me)(CH_2S)_2\}]$ and its benzyl thioether analogue by cyanide. The mechanism and the kintetics of these reactions have been extensively studied. However the proposed intermediate $[Fe_2(CO)_5(CN)\{RSCH_2C(Me)(CH_2S\text{-}\mu)_2\}]^-$ in the reaction mechanism has never been isolated.[3,8−11] Therefore, it would be of particular interest to isolate and characterize analogous intermediates that would support and verify the suggested mechanism. In the course of our present study, we investigated the substitution reactions of the carbonyl ligands at [2Fe3S] complex **1** with trimethylphosphite $[P(OMe)_3]$ and trimentylphosphine (PMe_3).

Results and Discussion

Reaction of 1 with 1 equiv of $P(OMe)_3$. Treatment of [2Fe3S] complex **1** with 1 equiv of $P(OMe)_3$ in THF at room temperature gave the first-formed kinetically controlled product $Fe_2(\mu\text{-}S_2(C_3H_6)_2S)(CO)_5P(OMe)_3$ (**2**), which upon standing at room temperature for 90 min converted to $Fe_2(\mu\text{-}S_2(C_3H_6)_2S\text{-}\mu)(CO)_4P(OMe)_3$ (**3**), the thermodynamic product. In contrast, under reflux conditions, **1** reacts with $P(OMe)_3$ to give exclusively complex **3** as the thermodynamically controlled product (Scheme 3).

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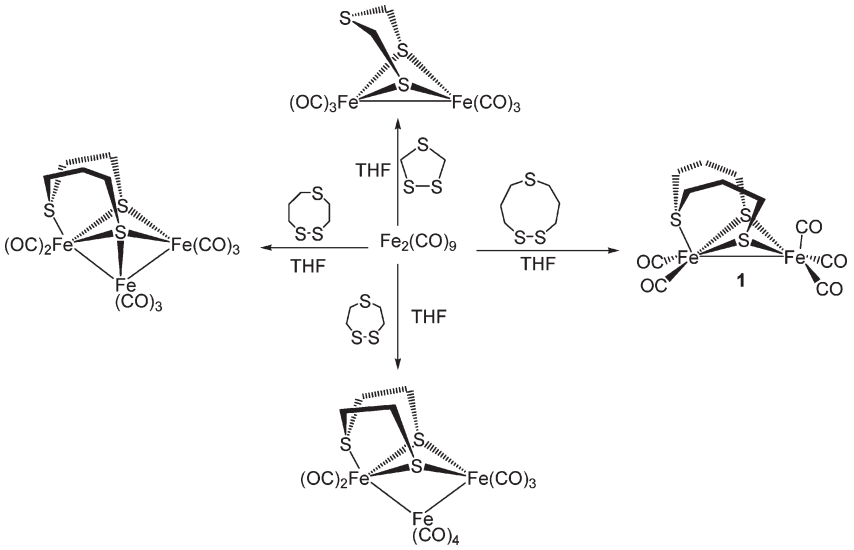
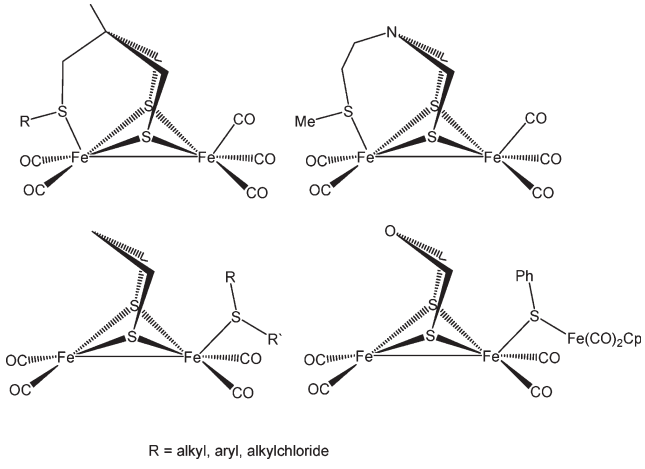
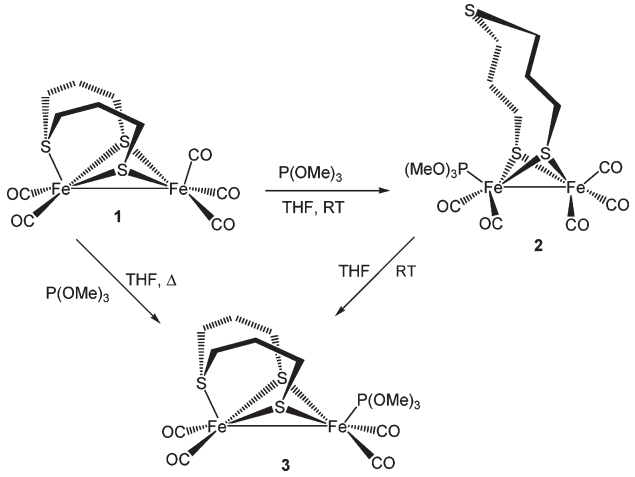
Scheme 1



Scheme 2



Scheme 3



Complexes **2** and **3** are stable in the solid state for several days. In solution, the [2Fe3S] complex **3** is stable for several hours, while **2** is unstable due to fast conversion to **3**. Compounds **2** and **3** were characterized by IR, NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray crystallography. It is noteworthy that the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **2** always contain resonance signals of **3**. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **3** exhibit a singlet at 3.74 ppm and at 52.0 ppm, respectively, corresponding to the $P(OMe)_3$ group. $^{1}H,^{1}H$ COSY, $^{1}H,^{13}C$ HSQC, and $^{1}H,^{13}C$ HMBC NMR analysis substantiated the assignments of the proton and carbon signals of the $S(CH_2)_3S(CH_2)_3S$ moiety. These resonances are in the same range as those observed for **1**.[1] The $^{31}P\{^{1}H\}$ spectrum of **3** displays two singlets at 180.1 and 183.1 ppm, indicating the presence of the basal and apical isomers in solution. The mass spectra of **2** and **3** show the molecular ion peaks followed by the fragmentation of five CO groups in **2** and four in **3**.

The X-ray diffraction analysis reveals the proposed structures of **2** and **3** as shown in Figures 1 and 2, respectively. The central [2Fe2S] moieties of these complexes are in the butterfly conformation, and the geometry around the iron atoms is distorted square pyramidal, as observed from the bond angles. This is rather similar to that of **1**[1] and to those of other analogues reported in the literature.[3,12−22] The Fe−Fe distances of **2** and **3** are 2.5049(7) and 2.5400(6) Å, respectively. The Fe−Fe bond length of **2** is comparable to that observed for the nonsubstituted complex **1**,[1] also bearing five

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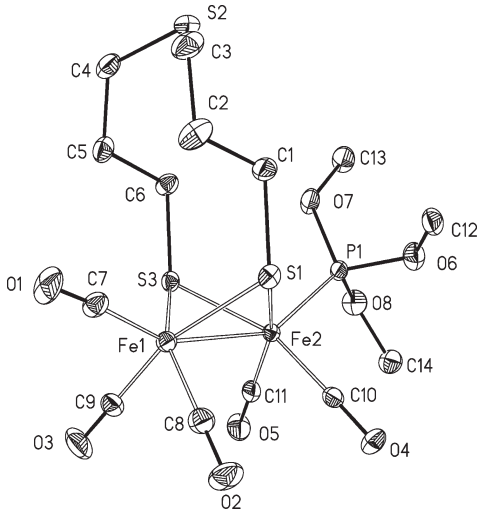

Figure 1. ORTEP drawing of $Fe_2(\mu\text{-}S_2(C_3H_6)_2S)(CO)_5P(OMe)_3$ (**2**) with thermal ellipsoids set at the 50% probability level (hydrogen atoms were omitted for clarity). Selected distances [Å] and angles [deg]: Fe1−Fe2 2.5049(7), Fe1−S1 2.2819(11), Fe1−S3 2.2849(10), Fe2−S1 2.2836(10), Fe2−S3 2.2814(10), Fe1−S1−Fe2 66.55(3), Fe1−S3−Fe2 66.54(3).

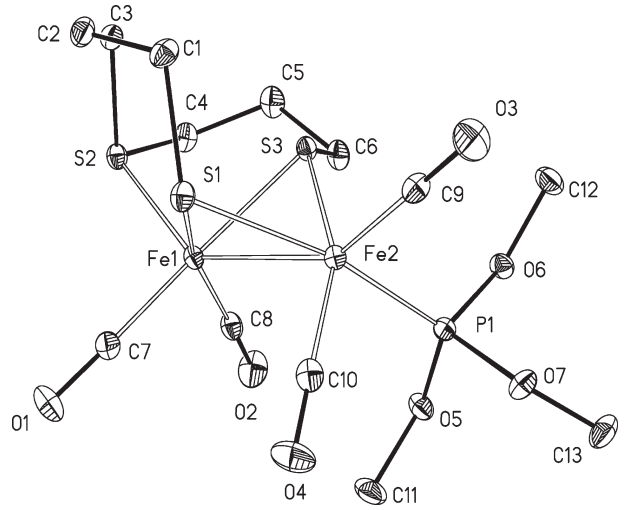

Figure 2. ORTEP drawing of $Fe_2(\mu\text{-}S_2(C_3H_6)_2S\text{-}\mu)(CO)_4P(OMe)_3$ (**3**) with thermal ellipsoids set at the 50% probability level (hydrogen atoms were omitted for clarity). Selected distances [Å] and angles [deg]: Fe1−Fe2 2.5400(6), Fe1−S1 2.2546(9), Fe1−S3 2.2554(8), Fe2−S1 2.3055(8), Fe2−S3 2.2426(8), Fe1−S2 2.2504(8), Fe1−S1−Fe2 67.69(3), Fe1−S3−Fe2 68.76(2).

CO ligands. The Fe−Fe bond length of **3** is significantly longer than that of **1**[1] due to replacement of a CO group by $P(OMe)_3$, and it is slightly longer than that observed for $[Et_4N][Fe_2\{MeSCH_2C(Me)(CH_2S)_2\}(CN)(CO)_4]$.[3] The significant increase in the Fe−Fe bond lengths of **3** compared to that in **2** could be attributed to the replacement of a carbonyl group by the thioether sulfur atom. The Fe−S (thioether sulfur atom) distance of **3** [2.2504(8) Å] is comparable to those observed for complex **1**[1] and $[Et_4N][Fe_2\{MeSCH_2C(Me)(CH_2S)_2\}(CN)(CO)_4]$.[3] The iron−thiolato bond lengths in **2** and **3** are in the same range reported for analogous complexes.[1−3,23−39]

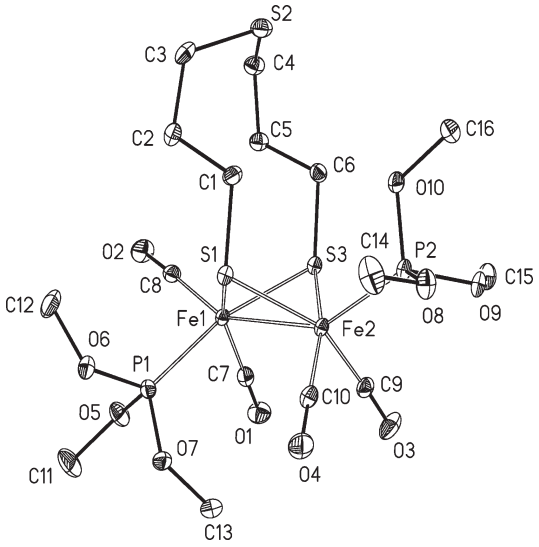

Figure 3. ORTEP drawing of $Fe_2(\mu\text{-}S_2(C_3H_6)_2S)(CO)_4[P(OMe)_3]_2$ (**4**) with thermal ellipsoids set at the 50% probability level (hydrogen atoms were omitted for clarity). Selected distances [Å] and angles [deg]: Fe1−Fe2 2.5431(5), Fe1−S1 2.2716(7), Fe1−S3 2.2845(7), Fe2−S1 2.2779(7), Fe2−S3 2.2950(7), Fe1−S1−Fe2 67.97(2), Fe1−S3−Fe2 67.47(2).

Reaction of 1 with Excess $P(OMe)_3$ or PMe_3. The reaction of **1** with excess $P(OMe)_3$ under reflux gave the disubstituted complex $Fe_2(\mu\text{-}S_2(C_3H_6)_2S)(CO)_4[P(OMe)_3]_2$ (**4**) in 85% yield (Scheme 4). Moreover, stirring of **1** with excess PMe_3

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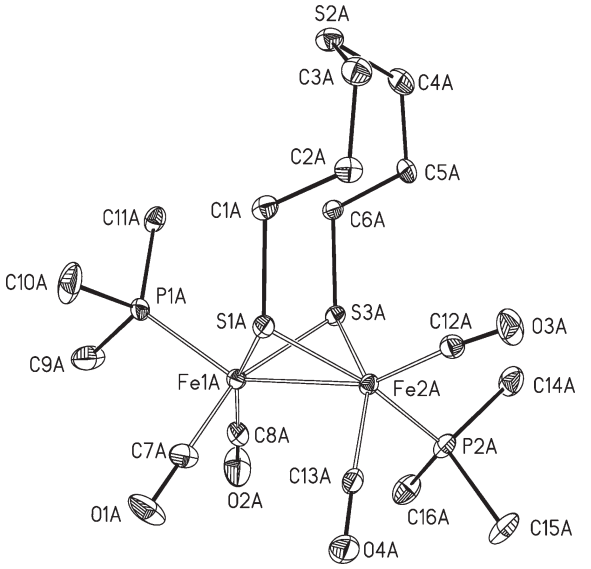


Figure 4. ORTEP drawing of $Fe_2(\mu\text{-}S_2(C_3H_6)_2S)(CO)_4[PMe_3]_2$ (**5**) with thermal ellipsoids set at the 50% probability level (hydrogen atoms were omitted for clarity). Selected distances [Å] and angles [deg]: Fe1−Fe2 2.5372(9), Fe1−S1 2.2977(13), Fe1−S3 2.2764(13), Fe2−S1 2.2829(12), Fe2−S3 2.2709(12), Fe1−S1−Fe2 67.27(4), Fe1−S3−Fe2 67.83(4).

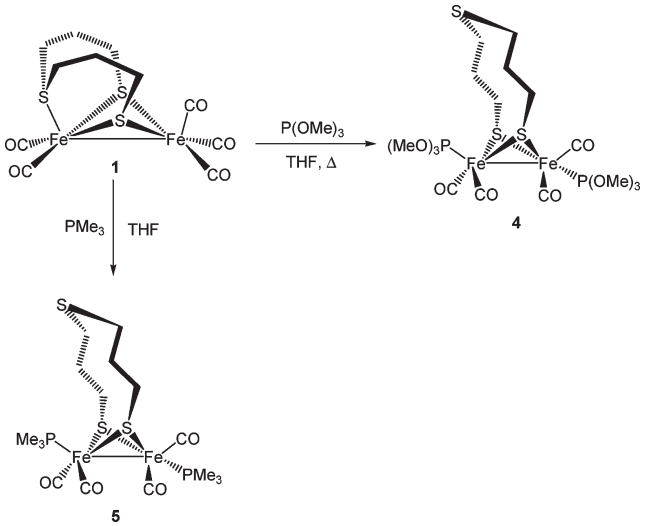
afforded the analogous disubstituted complex $Fe_2(\mu\text{-}S_2(C_3H_6)_2S)(CO)_4(PMe_3)_2$ (**5**) (Scheme 4). Compounds **4** and **5**, which are stable in the solid state and for several hours in solution, were characterized by IR, NMR spectroscopy, mass spectrometry, elemental analysis, and X-ray crystallography. The mass spectra of **4** and **5** show the molecular ion peaks followed by stepwise loss of CO groups.

The ^{1}H NMR spectra of **4** and **5** exhibit three signals at 1.83, 2.41, 2.60 ppm (**4**) and 1.98, 2.42, 2.62 ppm (**5**), corresponding to SCH_2CH_2, SCH_2CH_2, and CH_2SCH_2 moieties, respectively. Their ^{1}H,^{1}H COSY and ^{1}H,^{13}C HSQC analysis verified the assignments of the ^{13}C resonances at 26.9, 31.9, 32.6 ppm (**4**) and 28.2, 32.1, 32.4 ppm (**5**). In addition, the ^{13}C resonances for of the methyl groups of **4** (51.8 ppm), **5** (20.3 ppm) and the carbonyl groups were observed as expected. The $^{31}P\{^1H\}$ NMR spectrum of **4** displays one broad resonance at δ 180.6 ppm at 25 °C, indicative of the two phosphite ligands, which are in fast exchange on the NMR time scale. Upon cooling the sample to −40 °C, this signal splits into an AB spin system (180.6 and 183.7 ppm) with coupling constant $J_{P,P} = 38.9$ Hz, due to the apical and basal positions of the two phosphite ligands. The $^{31}P\{^1H\}$ NMR spectrum of **5** consists of a broad singlet at δ 29.2 ppm, which upon cooling to −40 °C splits into two broad signals at 22.9 and 37.2 ppm, indicating the presence of the basal and apical isomers, too.

The geometries around the Fe cores of **4** and **5** are rather similar to those observed for **2** and **3**. The Fe−Fe bond lengths of **4** (2.5431(5) Å) and **5** (2.5372(9) Å) are longer than those observed for **1** and **2** and comparable to that of **3**. These observations show that the Fe−Fe bond lengths in our model complexes depend on the number of CO ligands around the Fe atoms, which increases as the CO number decreases. The Fe−S bond lengths of **4** and **5** are within the range observed for **2** and **3**.

The IR spectra of complexes **1**−**5** (KBr disk) show three strong absorption bands at ν = 1906, 1952, 2040 cm^{-1} (**1**),[1] 1942, 1986, 2046 cm^{-1} (**2**), 1930, 1962, 2003 cm^{-1} (**3**), 1925, 1963, 2004 cm^{-1} (**4**), and 1901, 1937, 1979 cm^{-1} (**5**). The increase in the CO stretching frequencies from **1** to **2** could be attributed to the better π-acceptor property of $P(OMe)_3$ compared to that of the thioether sulfur atom. The values of ν(CO) in complexes **3**−**5** are as expected for the well-known electronic properties of the P-donor ligands.

Scheme 4



Conclusion

Substitution reactions of CO by $P(OMe)_3$ in complex **1** gave complexes **2**−**4**, as a result of the on−off coordination of a thioether ligand bound at the iron atom. These complexes were characterized by spectroscopic techniques and X-ray structure determination. Moreover, we were able to isolate and characterize the structure of complex **2**, which is believed to be the intermediate of the reaction pathway. This result could be seen as an important contribution to corroborate the mechanism for the cyanation reaction of [2Fe3S] cluster.[3,8,9] In addition, treatment of **1** with PMe_3 produced the disubstituted product **5** in a fast reaction, and the monosubstituted complex was not observed.

Experimental Section

All reactions were performed using standard Schlenk techniques under an inert atmosphere. The NMR spectra were recorded at room temperature on either a Bruker AVANCE 200 or 400 MHz spectrometer using the solvent residual peak as reference. Mass spectra were recorded on a Finnigan MAT SSQ 710 instrument. IR spectra were measured on a Perkin-Elmer System 2000 FT-IR spectrometer. Elemental analyses were performed with a LECO CHNS-932 apparatus. Silica gel 60 (0.015−0.040 mm) was used for column chromatography; TLC was done using Merck TLC aluminum sheets (silica gel 60 F_{254}). All solvents were dried and distilled prior to use according to the standard methods. $Fe_3(CO)_{12}$ was purchased from Aldrich, solvents were from Fisher Scientific, and other chemicals were from Acros; all were used without further purification. $Fe_2(\mu\text{-}S_2(C_3H_6)_2S\text{-}\mu)(CO)_5$ (**1**) was prepared according to a literature protocol.[1]

Preparation of $Fe_2(\mu\text{-}S_2(C_3H_6)_2S)(CO)_5P(OMe)_3$ (2). Trimethylphosphite (11.5 mg, 0.093 mmol) was added to a solution of **1** (40 mg, 0.093 mmol) in THF (30 mL) under argon. The reaction mixture turned immediately from brown-red to bright red and was stirred for an additional 3 min at room temperature.

Table 1. Crystal Data and Refinement Details for the X-ray Structure Determinations of Compounds 2, 3, 4, and 5

	2	3	4	5
formula	$C_{14}H_{21}Fe_2O_8PS_3$	$C_{13}H_{21}Fe_2O_7PS_3$	$C_{16}H_{30}Fe_2O_{10}P_2S_3$	$C_{16}H_{30}Fe_2O_4P_2S_3$
fw/g·mol^{-1}	556.16	528.15	652.22	556.22
T/°C	−90(2)	−90(2)	−90(2)	−90(2)
cryst syst	monoclinic	orthorhombic	triclinic	monoclinic
space group	$P2_1/n$	$P2_12_12_1$	$P\bar{1}$	$P2_1/c$
a/Å	9.3441(4)	9.4103(2)	9.4048(4)	13.2992(5)
b/Å	13.8053(3)	12.1233(3)	11.4370(5)	17.6628(7)
c/Å	17.3332(6)	17.5501(5)	13.3328(4)	20.6173(6)
α/deg	90	90	74.714(2)	90
β/deg	102.167(2)	90	84.777(2)	93.677(2)
γ/deg	90	90	72.652(2)	90
V/Å^3	2185.72(13)	2002.18(9)	1320.33(9)	4833.1(3)
Z	4	4	2	8
ρ/g·cm^{-3}	1.690	1.752	1.641	1.529
μ/cm^{-1}	17.24	18.73	15.03	16.1
measd data	15390	14338	9342	32414
data with $I > 2\sigma(I)$	3676	4155	4947	6034
unique data/R_{int}	4995/0.0558	4548/0.0429	5934/0.0382	10981/0.1303
wR_2 (all data, on F^2)[a]	0.1227	0.0560	0.0971	0.1022
R_1 ($I > 2\sigma(I)$)[a]	0.0455	0.0260	0.0388	0.0556
S[b]	1.020	0.856	1.022	0.957
res dens/e·Å^{-3}	1.800/−0.482	0.382/−0.284	0.556/−0.477	0.528/−0.449
absorpt method	NONE	NONE	NONE	NONE
CCDC no.	727151	727152	727153	727154

[a] Definition of the R indices: $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = [2F_c^2 + \mathrm{Max}(F_o^2]/3$. [b] $S = \{\sum[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

Volatiles were removed under vacuum. The bright red solid **2** was recrystallized from a mixture of CH_2Cl_2/pentane at −25 °C. Yield 48 mg (93%). Anal. Calcd for $C_{14}H_{21}Fe_2O_8S_3P$: C, 30.23; H, 3.81; S, 17.3. Found: C, 30.35; H, 3.87; S, 17.5. IR (KBr disk): $\nu_{C\equiv O}$ 2046 (s), 1986 (vs), 1944 (vs) cm^{-1}. DEI-MS (m/z): 557 [M$^+$], 528 [M$^+$ − CO], 500 [M$^+$ − 2CO], 472 [M$^+$ − 3CO], 444 [M$^+$ − 4CO], 416 [M$^+$ − 5CO].

Preparation of $Fe_2(\mu\text{-}S_2(C_3H_6)_2S\text{-}\mu)(CO)_4P(OMe)_3$ (3). Trimethylphosphite (16 mg, 0.13 mmol) was added to a brown-red solution containing **1** (56 mg, 0.13 mmol) in THF (30 mL). The reaction mixture first turned bright red then darkened to brown-red. After 90 min stirring at room temperature examination by TLC showed complete conversion to **3**. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography with diethyl ether. Crystals suitable for X-ray diffraction analysis were obtained from a solution of CH_2Cl_2/pentane at −25 °C. Yield: 53 mg (77%). Anal. Calcd for $C_{13}H_{21}Fe_2O_7S_3P\cdot 1/4\ C_5H_{12}$: C, 31.34; H, 4.43; S, 17.61. Found: C, 31.07; H, 4.13; S, 17.56. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.76, 2.83 (m, 4H, $FeSCH_2$), 2.00−2.30 (m, 4H, SCH_2CH_2), 2.63, 2.92 (m, 4H, CH_2SCH_2), 3.74 (s, 9H, $P(OMe)_3$) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 29.5, 27.5 (SCH_2CH_2), 32.2, 38.0 (CH_2SCH_2), 30.9, 36.5 ($FeSCH_2$), 52.0 ($P(OMe)_3$), 213.1 (CO) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ 180.1, 183.1 ($P(OMe)_3$) ppm. IR (KBr disk): $\nu_{C\equiv O}$ 2003 (s), 1962 (vs), 1930 (vs) cm^{-1}. DEI-MS (m/z): 528 [M$^+$], 500 [M$^+$ − CO], 472 [M$^+$ − 2CO], 444 [M$^+$ − 3CO], 416 [M$^+$ − 4CO].

Preparation of $Fe_2(\mu\text{-}S_2(C_3H_6)_2S)(CO)_4[P(OMe)_3]_2$ (4). Trimethylphosphite (49.6 mg, 0.4 mmol) was added to a solution of **1** (45 mg, 0.1 mmol) in THF (30 mL). The reaction mixture was heated at reflux for 30 min, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using diethyl ether as eluent. The orange-red fraction was collected and the solvent removed under reduced pressure. The resultant orange-red solid was recrystallized from pentane at −25 °C. Yield: 55 mg (85%). Anal. Calcd for $C_{16}H_{30}Fe_2O_{10}P_2S_2$: C, 29.46; H, 4.64; S, 14.75. Found: C, 29.46; H, 4.97; S, 15.3. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.83 (m, 4H, SCH_2CH_2), 2.41 (m, 4H, $FeSCH_2$), 2.60 (m, 4H, CH_2SCH_2), 3.74 (d, $^3J_{H,P}$ = 11.2 Hz, 18H, $P(OMe)_3$) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 26.9 ($FeSCH_2$), 31.9 (CH_2SCH_2), 32.6 (SCH_2CH_2), 51.8 ($P(OMe)_3$), 213.7 (CO) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ 180.6 (s, br, 2P-$(OMe)_3$) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, 223 K, $CDCl_3$): δ 180.6 (d, $J_{P,P}$ = 38.9 Hz, $P(OMe)_3$), 183.7 (d, $J_{P,P}$ = 38.9 Hz, $P(OMe)_3$) ppm. IR (KBr disk): $\nu_{C\equiv O}$ 2004 (s), 1963 (vs), 1925 (vs) cm^{-1}. DEI-MS (m/z): 652 [M$^+$], 624 [M$^+$ − CO], 596 [M$^+$ − 2CO], 568 [M$^+$ − 3CO], 540 [M$^+$ − 4CO].

Preparation of $Fe_2(\mu\text{-}S_2(C_3H_6)_2S)(CO)_4(PMe_3)_2$ (5). Trimethylphosphine (30.4 mg, 0.4 mmol) was added to a solution of **1** (35 mg, 0.08 mmol) in THF (30 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 30 min. The resulting dark red solution was evaporated to dryness under vacuum, and the product was purified by column chromatography with diethyl ether as eluent. A dark red fraction was collected and dried. Crystals suitable for X-ray diffraction analysis were obtained from a solution of pentane at −25 °C. Yield: 35 mg (78%). Anal. Calcd for $C_{16}H_{30}Fe_2O_4S_3P_2$: C, 34.55; H, 5.44; S, 17.29. Found: C, 34.54; H, 5.64; S, 17.35. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51 (d, $^2J_{H,P}$ = 7.6 Hz, 18H, $P(Me)_3$), 1.98 (m, 4H, SCH_2CH_2), 2.42 (m, 4H, $FeSCH_2$), 2.62 (m, 4H, CH_2SCH_2) ppm. $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 20.3 (PMe_3), 28.2 ($FeSCH_2$), 32.1 (CH_2SCH_2), 32.4 (SCH_2CH_2), 215.8 (CO) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ 29.2, (s br, 2PMe_3) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, 253 K, $CDCl_3$): δ 22.9, (s br, PMe_3), 37.2(s br, PMe_3) ppm. IR (KBr disk): $\nu_{C\equiv O}$ 1979 (s), 1937 (vs), 1901 (vs) cm^{-1}. DEI-MS (m/z): 557 [M$^+$], 528 [M$^+$ − CO], 472 [M$^+$ − 3CO], 444 [M$^+$ − 4CO].

Crystal Structure Determination. The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer, using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects, but not for absorption effects.[40,41] Crystallographic data as well as structure solution and refinement details are summarized in Table 1. The structures were solved by direct methods (SHELXS)[42] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).[42] All hydrogen atoms were included at calculated

(40) *COLLECT, Data Collection Software*; Nonius, B. V.: The Netherlands, 1998.

(41) Otwinowski, Z.; Minor, W. Processing of X-Ray Diffraction Data Collected in Oscillation Mode. In *Methods in Enzymology*; Vol. 276, *Macromolecular Crystallography, Part A*; Carter, C. W.; Sweet, R. M., Eds.; **1997**; pp 307−326.

(42) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[42] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-727151 for **2**, CCDC-727152 for **3**, CCDC-727153 for **4**, and CCDC-727154 for **5**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: deposit@ccdc.cam.ac.uk].

4.3 [AD3] Reactions of Selected Aromatic Thioketones with Triiron Dodecacarbonyl.

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Reactions of Selected Aromatic Thioketones with Dodecarbonyltriiron

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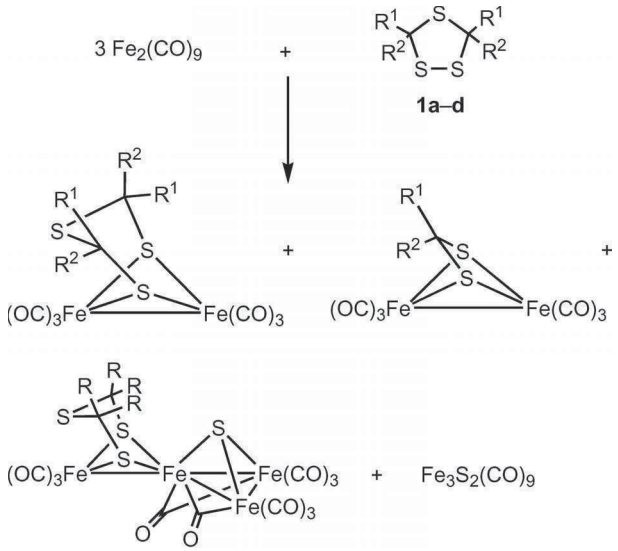
Keywords: Iron / Enzyme models / Hydrogenase / S ligands / Structure elucidation

Dodecacarbonyltriiron reacts with 3,3,5,5-tetraphenyl-1,2,4-trithiolanes (**1e**) to give the *ortho*-metalated complex $Fe_2(CO)_6$-[κ,μ-*S*,η²-($C_{13}H_{10}S$)] (**9a**), complexes of the type (Ph_2C)-$S_2Fe_2(CO)_6$ and the well known trinuclear complex $Fe_3S_2(CO)_9$ as by-products. Complex **9a** can also be obtained from the reaction of $Fe_3(CO)_{12}$ with thiobenzophenone (**2a**). In a similar way, 4,4′-bis(dimethylamino)thiobenzophenone (**2b**) reacts with $Fe_3(CO)_{12}$ to give $Fe_2(CO)_6$[κ,μ-*S*,η²-($C_{17}H_{20}N_2S$)] (**9b**). The cyclic aromatic thioketones such as dibenzosuberenethione (**2c**) and xanthione (**2d**) react with $Fe_3(CO)_{12}$ to give the cyclometalated products $Fe_2(CO)_6$[κ,μ-*S*,η²-($C_{15}H_{12}S$)] (**9c**) and $Fe_2(CO)_6$[κ,μ-*S*,η²-($C_{13}H_8OS$)] (**9d**), respectively, and a small amount of $Fe_3S_2(CO)_9$. Complexes **9a–d** have been characterized by IR and NMR spectroscopies, elemental analyses, and X-ray single crystal structure analyses.

Introduction

In two recent papers we described the oxidative addition reactions of heterocyclic trisulfides, such as 1,2,4-trithiolanes, 1,2,5-trithiepanes, 1,2,5-trithiocanes, and 1,2,6-trithionanes to carbonyliron complexes to produce [FeFe]-hydrogenase model complexes with sulfur in the bridgehead position of the dithiolato ligand.[1,2] Within the last decade, numerous model compounds with suitability as the active site of the [FeFe]-hydrogenase were prepared.[3–27] Trisulfides with different ring sizes (five- to nine-membered rings) reacted with $Fe_2(CO)_9$ to give three major products containing dithiolatodiiron complexes.[1] The structures of these three products depend on the size of the trisulfide rings. Treatment of the di- or tetra-substituted five-membered 1,2,4-trithiolans **1a–d** with $Fe_2(CO)_9$ are reported to give the complexes shown in Scheme 1.[2]

In continuation of our efforts in this field, the present work presents the reaction of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1e**) as well as the selected aromatic thioketones **2a–d** with $Fe_3(CO)_{12}$. This interest stems from the study of the formation of similar thiobenzophenone–iron complexes **4a**,**b**, **5**, and **6** described by Alper et al. several decades ago (Scheme 2).[28–30] It is also known that 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1e**) undergoes [2+3]-cycloreversion at around 50 °C and forms an equilibrium mixture of thiobenzophenone *S*-sulfide (**7**), diphenyldithiirane (**8**), and thiobenzophenone (**2a**) (Scheme 3).[31–37] Reactions of aromatic thioketones **2a**,**b** with $Fe_2(CO)_9$ yielded the *ortho*-metalated complexes **4a**,**b** as the major products, together with small amounts of complexes of the type (Ar_2C)-$S_2Fe_2(CO)_6$ (**5** and **6**) and the well-known trinuclear complex $Fe_3S_2(CO)_9$ (Scheme 2).[29,30] The structures of the main products **4a**,**b** were suggested by Alper et al. based only on spectroscopic data and decomplexation reactions. In the present report, the structures of these complexes are presented, as determined by X-ray crystallography.



Scheme 1. Reactions of 1,2,4-trithiolanes **1a–d** with $Fe_2(CO)_9$.

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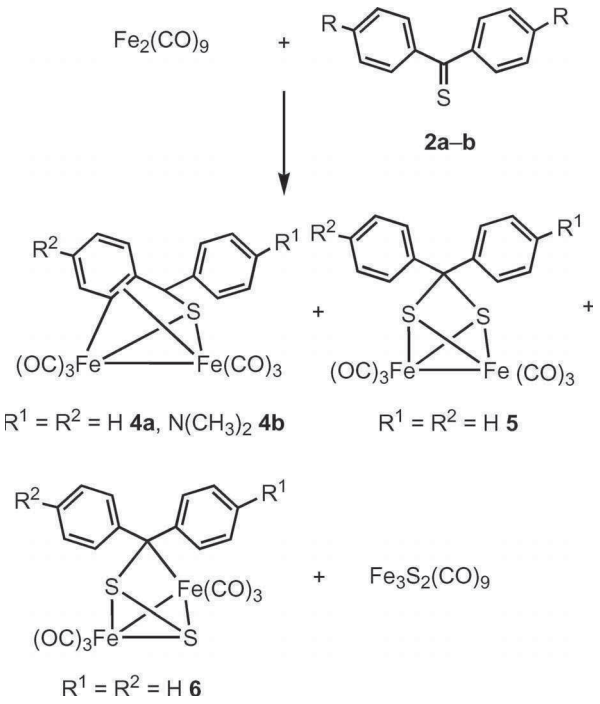
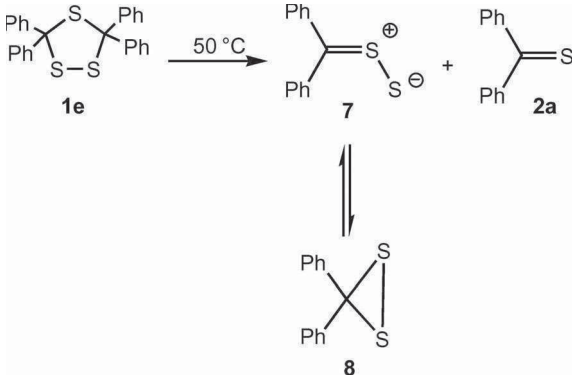


Scheme 2. Treatment of thiobenzophenone (**2a**) and 4,4′-bis-(dimethylamino)thiobenzophenone (**2b**) with $Fe_2(CO)_9$ in anhydrous benzene at room temperature.

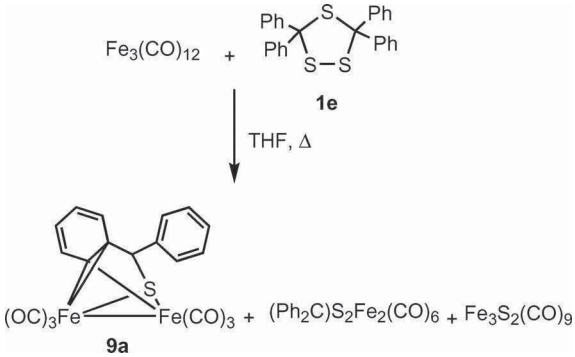


Scheme 3. Thermal cycloreversion of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1e**).

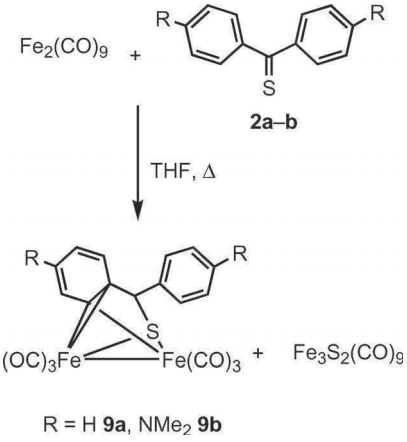
To date, reports of the reactions of aromatic thioketones with carbonyliron complexes are scarce.[28–30] Only very recently, a paper appeared in which the reactions of thiobenzophenone (**2a**) and 4,4′-bis(dimethylamino)thiobenzophenone (**2b**) with $Fe(CH_3)_2(PMe_3)_4$ were described.[38] In this case, *ortho*-metalation occurred to produce mononuclear (thiobenzophenone)iron complex with the elimination of methane. Treatment of Pt^0 complexes bearing bridged bisphosphane ligands with 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1e**) resulted in the formation of the dithiolato and η^2-thioketone complexes.[39] The latter complex was also prepared from the same Pt species and the corresponding thiobenzophenone.[39]

Results and Discussion

The reaction of **1e** with $Fe_3(CO)_{12}$ in boiling THF furnished complex **9a** as the major product, and complexes of the type $(Ph_2C)S_2Fe_2(CO)_6$ and $Fe_3S_2(CO)_9$ as by-products (Scheme 4). Complex $Fe_3(CO)_{12}$ is used for the reaction instead of $Fe_2(CO)_9$ because of its higher solubility and selectivity. Complex **9a** can also be obtained from the reaction of $Fe_3(CO)_{12}$ with **2a** as shown in Scheme 5. A conceivable explanation for this result is that in the case of **1e** the thermal dissociation of the trithiolane results in the formation of the equilibrium mixture containing some amount of thiobenzophenone (**2a**) (Scheme 3). The subsequent step may correspond to a formal [4+2] cycloaddition in which **2a** plays the role of a heterodiene; the initially formed [4+2]-cycloadduct undergoes spontaneous rearomatization through a 1,3-H shift to give the final complex **9a**.



Scheme 4. Reaction of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1e**) with $Fe_3(CO)_{12}$.

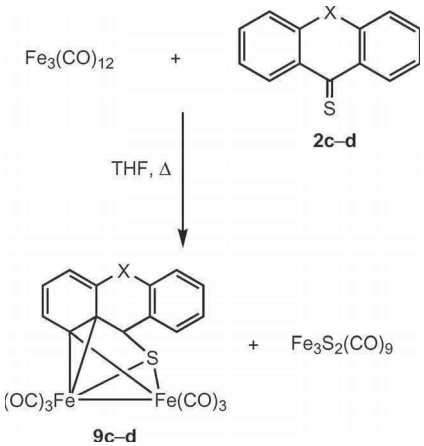


Scheme 5. Reactions of thiobenzophenone (**2a**) and 4,4′-bis-(dimethylamino)thiobenzophenone (**2b**) with $Fe_3(CO)_{12}$ to give the *ortho*-metalated complexes **9a** and **9b**, respectively.

The reaction of 4,4′-bis(dimethylamino)thiobenzophenone (**2b**) with $Fe_3(CO)_{12}$ produces the *ortho*-metalated complex **9b**, in an analogous manner to complex **9a** (Scheme 5). Similar results were obtained by Alper et al. in

the early 1970's[28–30] and based on the spectroscopic data complexes **9a** and **9b** seem to be identical to those reported by Alper et al.[29]

Refluxing a THF solution of dibenzosuberenethione (**2c**) or xanthione (**2d**) with $Fe_3(CO)_{12}$ yields, in both cases, the major product **9c** and **9d**, respectively, and the iron sulfur cluster as shown in Scheme 6. These complexes are stable for a longer time in the solid state and for several hours in solution. In addition, they are soluble in most common organic solvents, including hydrocarbons. In all reactions of the aromatic thioketones **2a**–**d** with $Fe_3(CO)_{12}$, trace amounts of a red-colored fraction (with an R_f value lower than that of the products) were obtained, however, to date we have not been able to characterize these. The IR spectra of **9c** and **9d** exhibit three strong vibration bands located in regions of 2069–2072, 2033–2037, and 1995–2001 cm^{-1}, which correspond to the terminal carbonyl groups bonded to the iron atoms. These ranges are comparable to those observed for **9a** and **9b** reported by Alper.[29] The C–S bond stretching frequency for compounds **9a**–**d** is found in the range 572–581 cm^{-1} indicating high single-bond character. The mass spectra of complexes **9a**–**d** show, in addition to the molecular ion peaks, the fragmentation of the six CO groups.



Scheme 6. Treatment of dibenzosuberenethione [**2c**, X = $(CH_2)_2$] and xanthione (**2d**, X = O) with $Fe_3(CO)_{12}$ to give the *ortho*-metallated complexes **9c** and **9d**, respectively.

The ^1H NMR spectra of **9a**–**d** show singlet resonances at δ = 5.55, 5.28, 6.12, and 4.60 ppm, respectively, corresponding to the methine protons. The ^1H NMR resonances of the methylene protons in complex **9c** appear as three sets of multiplets at δ = 2.96, 3.40, and 3.66 ppm. The ^1H NMR spectrum of **9b** consists of singlets at δ = 2.86 and 3.02 ppm assigned to the 12 protons of the two NMe_2 groups. The hydrogen atoms on the coordinated aromatic rings in compounds **9a**–**d** are generally deshielded, possibly by the tricarbonyliron group, with the protons next to the Fe–C sigma bond being the most deshielded. Their resonances appear as doublets at δ = 8.36 (**9a**; ^3J = 8.2 Hz), 7.49 ppm (**9b**; ^3J = 9.0 Hz), and 7.95 ppm (**9d**; ^3J = 8.0 Hz) and a multiplet at δ = 7.97 ppm (**9c**). The C–S sigma bonds in **9a**–**d** are evidence by the characteristic chemical shifts in the $^{13}C\{^1H\}$ NMR (δ = 63.3, 63.3, 60.2, and 52.5 ppm for **9a**–**d**, respectively). In addition, the ^{13}C NMR spectra for **9a**–**d** illustrate the resonances of the carbonyl C atoms in the range of 208–211 ppm.

Crystals suitable for the X-ray structure determinations of **9a**–**d** (Figures 1–4) were obtained from hexane solution at –25 °C. The aromatic thioketone ligand is bonded to the two iron centers through the sulfur atom, with the Fe–S

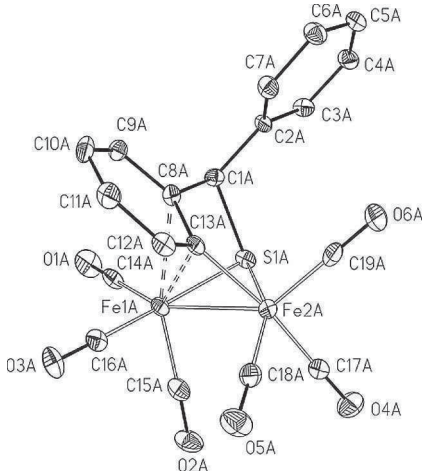


Figure 1. ORTEP drawing of $Fe_2(CO)_6[\kappa,\mu\text{-}S,\eta^2\text{-}(Ph_2CHS)]$ (**9a**) with thermal ellipsoids set at the 50% probability level (hydrogen atoms have been omitted for clarity). Selected distances [Å] and angles [°]: Fe1–Fe2 2.4986(8), Fe1–S1 2.2629(12), Fe2–S1 2.2369(13), S1–C1 1.838(4), Fe2–C13 1.996(4), Fe1–C13 2.189(4), Fe1–C8 2.290(4), F2–C13–Fe1 73.15(14), Fe1–Fe2–S1 56.77(3), Fe1–S1–Fe2 67.46(4), Fe2–Fe1–S1 55.78(3).

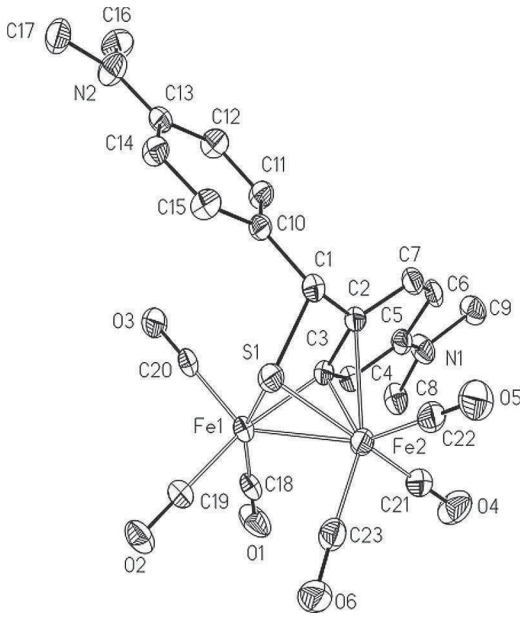


Figure 2. ORTEP drawing of $Fe_2(CO)_6[\kappa,\mu\text{-}S,\eta^2\text{-}(C_{17}H_{20}N_2S)]$ (**9b**) with thermal ellipsoids set at the 50% probability level (hydrogen atoms have been omitted for clarity). Selected distances [Å] and angles [°]: Fe1–Fe2 2.5216(10), Fe1–S1 2.2471(14), Fe2–S1 2.2467(14), S1–C1 1.840(5), Fe1–C3 1.996(4), Fe2–C3 2.211(5), Fe2–C2 2.315(5), F2–C3–Fe1 73.45(16), Fe1–Fe2–S1 55.87(4), Fe1–S1–Fe2 68.27(4), Fe2–Fe1–S1 55.86(4).

bond length in the range of 2.23–2.27 Å. It is also σ bonded to one Fe atom through the ortho carbon of one phenyl ring (1.99–2.01 Å) and is π-bonded to the other Fe atom through one C–C π-bond [*ortho*-C (2.18–2.21 Å) and the carbon atom next to C–S group (2.29–2.48 Å)]. The Fe–Fe distances in these complexes are found to be in the range of 2.495–2.521 Å, which are slightly shorter than the corresponding bond in the hydrogenase model complexes.[1–15] The Fe–S bond lengths are found to be within the same range observed for the hydrogenase model complexes.[10–18,24–26] The C–S average bond length (1.83 Å) is within the same range for a C–S single bond (1.80–1.85 Å) [40] and is significantly longer than the corresponding bond of $Fe(PMe_3)_3(Me)(\kappa,S,C–Ph_2C=S)$ [1.675(4) Å][38], which contains a C=S bond. The bite angles of the butterfly shape are within the same ranges observed for the hydrogenase model complexes indicating a distorted octahedral geometry around each iron center.[1–20]

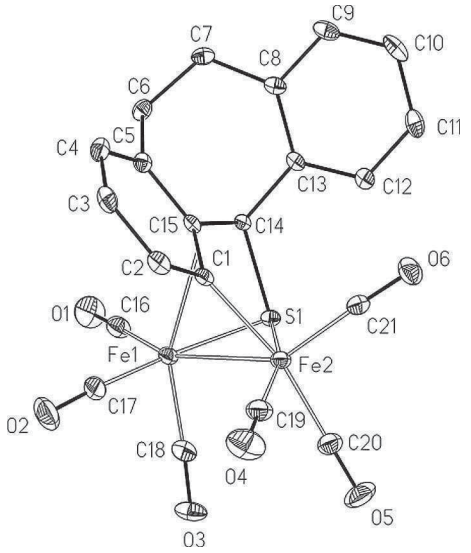


Figure 3. ORTEP drawing of $Fe_2(CO)_6[\kappa,\mu\text{-}S,\eta^2\text{-}(C_{15}H_{12}S)]$ (**9c**) with thermal ellipsoids set at the 50% probability level (hydrogen atoms have been omitted for clarity). Selected distances [Å] and angles [°]: Fe1–Fe2 2.4950(5), Fe1–S1 2.2717(7), Fe2–S1 2.2444(7), S1–C14 1.825(2), Fe2–C1 2.011(2), Fe1–C1 2.180(2), Fe1–C15 2.405(2), F2–C1–Fe1 72.95(8), Fe1–Fe2–S1 56.99(2), Fe1–S1–Fe2 67.07(2), Fe2–Fe1–S1 55.94(2).

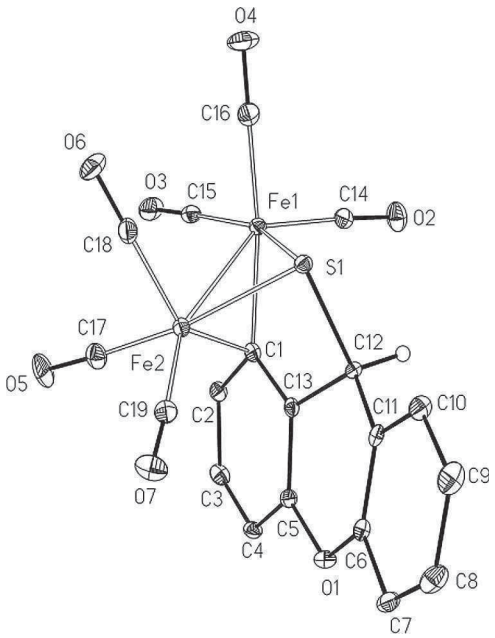


Figure 4. ORTEP drawing of $Fe_2(CO)_6[\kappa,\mu\text{-}S,\eta^2\text{-}(C_{15}H_{12}S)]$ (**9d**) with thermal ellipsoids set at the 50% probability level (hydrogen atoms have been omitted for clarity). Selected distances [Å] and angles [°]: Fe1–Fe2 2.4993(6), Fe1–S1 2.2425(9), Fe2–S1 2.2543(8), S1–C12 1.837(3), Fe1–C1 2.011(3), Fe2–C1 2.203(3), Fe2–C13 2.372(3), F1–C1–Fe2 72.60(9), Fe1–Fe2–S1 56.01(2), Fe1–S1–Fe2 67.53(2), Fe2–Fe1–S1 56.46(2).

Conclusion

The reactivity of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1e**) is different form that of the corresponding tetraalkyl-substituted analogues **1a**–**d**. The latter reacts with $Fe_3(CO)_{12}$ leading to the product of oxidative addition along the S–S bond. The former, however, dissociates according to the pathway presented in Scheme 3. The fragments (e.g., $Ph_2C=S$) react with carbonyliron compounds to yield thioketone complexes as major products. This result prompted us directly to investigate the reaction of carbonyliron compounds with thioketones. Accordingly, four *ortho*-metalated complexes $Fe_2(CO)_6[\kappa,\mu\text{-}S,\eta^2\text{-}(C_{13}H_{10}S)]$ (**9a**), $Fe_2(CO)_6[\kappa,\mu\text{-}S,\eta^2\text{-}(C_{17}H_{20}N_2S)]$ (**9b**), $Fe_2(CO)_6[\kappa,\mu\text{-}S,\eta^2\text{-}(C_{15}H_{12}S)]$ (**9c**), and $Fe_2(CO)_6[\kappa,\mu\text{-}S,\eta^2\text{-}(C_{13}H_8OS)]$ (**9d**) were prepared and characterized. The formation mechanism for these complexes can be explained by a formal [4+2] cycloaddition in which the aromatic thioketones act as heterodienes with $Fe_3(CO)_{12}$. The subsequent step may correspond to 1,3-H shift giving the final complex. Only one major product was obtained with high yield from the reactions of the cyclic aromatic thioketones **2c** and **2d** with $Fe_3(CO)_{12}$. In contrast, the reactions of **2a** and **2b** with $Fe_3(CO)_{12}$ yielded the *ortho*-metalated complexes **9a** and **9b** as major products, together with complexes of the type $(Ar_2C)S_2Fe_2(CO)_6$, as by-products. The ^1H NMR spectra of **9a**–**d** indicate that the protons at the coordinated aromatic ring are generally deshielded. Furthermore, the protons next to the Fe–C sigma bond are the most deshielded.

Experimental Section

General Comments: All reactions were carried out under inert atmosphere by using standard Schlenk techniques. The ^1H and $^{13}C\{^1H\}$ NMR and 2D NMR spectra were recorded with a Bruker AVANCE 200 or 400 MHz spectrometers at r.t. using the solvent as a standard. Mass spectra were obtained by using a FINNIGAN MAT SSQ 710 instrument. Infrared spectra were measured on a Perkin–Elmer System 2000 FT-IR spectrometer. Thiobenzophenone,[41] 4,4′-bis(dimethylamino)thiobenzophenone,[41] 3,3,5,5-tetraphenyl-1,2,4-trithiolanes,[42] dibenzosuberenethione,[43] and xanthione[43] were prepared according to literature procedures. Solvents and $Fe_3(CO)_{12}$ were purchased from Sigma–Aldrich; all sol-

vents were dried and distilled prior to use according to standard methods. Silica gel 60 (0.015–0.040 mm) was used for column chromatography. TLC was done using Merck TLC aluminum sheets Silica gel 60 F254. Elemental analyses were performed with a Vario EL III CHNS (Elementaranalyse GmbH Hanau) as single determinations.

$Fe_2(CO)_6(\kappa,\mu\text{-}S,\eta^2\text{-}Ph_2CHS)$ (9a): Thiobenzophenone (**2a**) (50 mg, 0.25 mmol) or **1e** (107 mg, 0.25 mmol) was added to a solution of $Fe_3(CO)_{12}$ (127 mg, 0.25 mmol) in THF (30 mL). The reaction mixture was heated to 65 °C with stirring for 30 min under argon. The resulting solution was cooled to r.t. and the solvent was removed under reduced pressure. The crude product was purified by column chromatography by using hexane as eluent. The dark red fraction was collected and the solvent was removed. Crystals suitable for X-ray diffraction analysis were obtained from a solution of hexane at –25 °C; yield 30 mg, 0.063 mmol (25%). $C_{19}H_{10}Fe_2O_6S$ (478): calcd. C 47.74, H 2.11, S 6.71; found C 47.33, H 2.29, S 6.39. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 5.55 (s, 1 H, 1A-H), 6.43 (m, 1 H, 4A-H), 7.05–7.21 (m, 4 H, Ar-H), 7.27 (t, ^3J = 7.6 Hz, 1 H, 10A-H), 7.32 (t, ^3J = 7.7 Hz, 1 H, 11A-H), 7.54 (d, ^3J = 7.6 Hz, 1 H, 9A-H) 8.36 (d, 1 H, ^3J = 8.2 Hz, 12A-H) ppm. ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$): δ = 63.3 (C-1A), 125.5, 126.5, 128.2, 128.5, 129.7, 129.7, 129.9, 131.6, 143.0, 149.6, 150.0, 155.2, (2Ph), 209.4, 209.6 (CO) ppm. FTIR (C_5H_{12}): $\tilde{\nu}_{C\equiv O}$ = 2071 (vs), 2035 (vs), 2001 (vs), 1981 (s, sh) ν_{C-S} 574 cm^{-1}. DEI-MS: *m*/*z* = 478 [M$^+$], 450 [M$^+$ – CO], 422 [M$^+$ – 2CO], 394 [M$^+$ – 3CO], 366 [M$^+$ – 4CO], 338 [M$^+$ – 5CO], 310 [M$^+$ – 6CO].

$Fe_2(CO)_6(\kappa,\mu\text{-}S,\eta^2\text{-}C_{17}H_{20}N_2S)$ (9b): 4,4′-Bis(dimethylamino)thiobenzophenone (**2b**) (50 mg, 0.18 mmol) was added to a solution of $Fe_3(CO)_{12}$ (90 mg, 0.18 mmol) in THF (30 mL) under argon. The reaction mixture was heated to 65 °C with stirring for 30 min. The solvent was removed under vacuum. The crude product was purified by column chromatography using hexane as eluent. From the major dark red fraction, **9b** was obtained and recrystallized from a solution of hexane at –25 °C; yield 32 mg, 0.057 mmol (31%). $C_{23}H_{20}Fe_2N_2O_6S$ (564.2): calcd. C 48.97, H 3.57, S 5.68; found calcd. C 49.38, H 3.61, S 5.26. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 2.86, 3.02 (2 s, 12 H, NMe_2), 5.28 (s, 1 H, 1-H), 6.23 (d, ^3J = 8.8 Hz, 1 H, CH), 6.45 (d, ^3J = 8.8 Hz, 1 H, CH), 6.60 (d, ^3J = 8.8 Hz, 1 H, CH), 6.81 (d, ^3J = 9.0 Hz, 1 H, CH), 7.05 (d, ^3J = 9.0 Hz, 1 H, 6-H), 7.27 (d, ^4J = 2.6 Hz, 1 H, 4-H), 7.49 (d, ^3J = 9.0 Hz, 1 H, 7-H) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 40.1, 40.5 (NMe_2), 63.3 (C-1), 111.8, 112.0, 117.9, 118.9, 124.0, 125.6, 127.2, 127.6, 131.1, 135.9, 146.6, 151.2 (Ph), 210.3, 210.9 (CO) ppm. FTIR (C_5H_{12}): $\tilde{\nu}_{C\equiv O}$ = 2062 (vs), 2026 (vs), 1986 (s), 1972 (sh) ν_{C-S} 580 cm^{-1}. DEI-MS: *m*/*z* = 565 [M$^+$], 536 [M$^+$ – CO], 508 [M$^+$ – 2CO], 480 [M$^+$ – 3CO], 452 [M$^+$ – 4CO], 424 [M$^+$ – 5CO], 396 [M$^+$ – 6CO].

$Fe_2(CO)_6(\kappa,\mu\text{-}S,\eta^2\text{-}(C_{15}H_{12}S)$ (9c): $Fe_3(CO)_{12}$ (150 mg, 0.30 mmol) was dissolved in THF (40 mL) and dibenzosuberenethione (**2c**) (67 mg, 0.30 mmol) was added. The mixture was stirred at 65 °C for 30 min under argon. The volatile components were removed in vacuo. The crude product was purified by column chromatography using hexane as eluent. The dark red fraction was collected and the solvent removed. Complex **9c** was recrystallized from a solution of hexane at –25 °C; yield 135 mg, 0.27 mmol (88%). $C_{21}H_{12}Fe_2O_6S$ (504.1): calcd. for $C_{21}H_{12}Fe_2O_6S{\cdot}1.0C_6H_{14}$ C 51.15, H 2.86 S 6.15; found C 51.21, H 2.58, S 5.85. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.96 (m, 2 H, C7H_AH_B), 3.40 (m, 1 H, C6H_CH$_D$), 3.66 (m, 1 H, C6H$_C$$H_D$), 6.12 (s, 1 H, 14-H), 6.94 (m, 1 H, 3-H), 7.25 (m, 1 H, 4-H), 7.97 (m, 1 H, 2-H), 7.0–7.20. (m, 4 H, 9–12-H) ppm. ^{13}C{^{1}H} NMR (200 MHz, $CDCl_3$): δ = 33.3 (C-7), 33.7 (C-6), 60.2 (C-14), 125.5, 126.1, 127.4, 127.8, 130.6, 131.1, 134.7, 138.5, 141.3, 145.7, 155.2 (Ph), 209.4, 209.8 (CO) ppm. FTIR (C_5H_{12}): $\tilde{\nu}_{C\equiv O}$ = 2069 (vs), 2033 (vs), 1994 (vs), 1981 (sh) ν_{C-S} 583 cm^{-1}. DEI-MS: *m*/*z* = 504 [M$^+$], 476 [M$^+$ – CO], 448 [M$^+$ – 2CO], 420 [M$^+$ – 3CO], 392 [M$^+$ – 4CO], 364 [M$^+$ – 5CO], 336 [M$^+$ – 6CO].

$Fe_2(CO)_6(\kappa,\mu\text{-}S,\eta^2\text{-}(C_{13}H_8OS)$ (9d): A mixture of $Fe_3(CO)_{12}$ (134 mg, 0.27 mmol) and xanthione (**2d**) (57 mg, 0.27 mmol) in THF (40 mL) was stirred at 45 °C for 10 min. The mixture was

Table 1. Crystal data and refinement details for the X-ray structure determinations of the compounds **9a**, **9b**, **9c**, and **9d**.

	9a	**9b**	**9c**	**9d**
Formula	$C_{19}H_{10}Fe_2O_6S$	$C_{23}H_{20}Fe_2N_2O_6S$	$C_{21}H_{12}Fe_2O_6S$	$C_{19}H_8Fe_2O_7S$
Mw [g mol^{-1}]	478.03	564.17	504.07	492.01
T [°C]	–90(2)	–90(2)	–90(2)	–140(2)
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a [Å]	15.3041(5)	9.1297(6)	9.5488(4)	8.0761(4)
b [Å]	27.7392(9)	7.9376(5)	10.0657(4)	10.3929(6)
c [Å]	8.9523(2)	33.3551(16)	11.6416(4)	11.4083(6)
α [°]	90	90	104.994(3)	87.972(3)
β [°]	96.861(2)	92.624(3)	95.791(3)	85.257(3)
γ [°]	90	90	109.866(2)	76.707(3)
V [Å^3]	3773.25(19)	2414.6(2)	994.32(7)	928.57(9)
Z	8	4	2	2
ρ [g cm^{-3}]	1.683	1.552	1.684	1.760
μ [cm^{-1}]	16.82	13.29	16	17.15
Measured data	23332	11403	6851	6525
Data with $I > 2\sigma(I)$	4517	3199	3452	3156
Unique data/R_{int}	8544/0.1009	5319/0.1058	4478/0.0281	4237/0.0333
wR_2 (all data, on F^2)[a]	0.1180	0.1802	0.0843	0.0823
R_1 [$I > 2\sigma(I)$][a]	0.0524	0.0714	0.0358	0.0414
s[b]	0.959	1.042	1.008	0.999
Residual el. density [e Å^{-3}]	0.512/–0.523	0.639/–0.479	0.339/–0.377	0.395/–0.412
Absorption correction	none	none	none	none

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

cooled to r.t. and the solvent was removed under reduced pressure. The crude product was purified by column chromatography using hexane as eluent. From the major dark red fraction, **9d** was obtained and recrystallized from a solution of hexane of at –25 °C; yield 118 mg, 0.24 mmol (84%). $C_{19}H_8Fe_2O_7S$ (491.8): calcd. C 46.38, H 1.64, S 6.52; found C 46.01, H 1.84, S 6.06. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 4.63 (s, 1 H, 12-H)), 6.81 (d, ^3J = 7.6 Hz, 1 H, 7-H), 7.00 (dd, ^3J = 7.8 Hz, 1 H, 9-H), 7.2 (d, ^3J = 8.2 Hz, 1 H, 10-H), 7.27 (dd, ^3J = 7.7 Hz, 1 H, 8-H), 7.38 (dd, ^3J = 7.7 Hz, 1 H, 3-H), 7.53 (d, ^3J = 7.6 Hz, 1 H, 4-H), 7.95 (d, ^3J = 8.0 Hz, 1 H, 2-H) ppm. ^{13}C{^{1}H} NMR (400 MHz, $CDCl_3$): δ = 52.5 (C-12), 112.3, 104.5, 116.4, 123.9, 124.7, 126.7, 128.6, 129.7, 147.6, 150.5, 152.2, 156.9, 208.7 (CO) ppm. FTIR (C_5H_{12}): $\tilde{\nu}_{C\equiv O}$ = 2072 (vs), 2037 (vs), 2001 (vs), 1985 (s, sh) ν_{C-S} 583 cm^{-1}. DEI-MS: *m*/*z* = 492 [M$^+$], 464 [M$^+$ – CO], 436 [M$^+$ – 2CO], 408 [M$^+$ – 3CO], 380 [M$^+$ – 4CO], 352 [M$^+$ – 5CO], 324 [M$^+$ – 6CO].

Crystal Structure Determination: The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects.[44,45] Crystallographic data as well as structure solution and refinement details are summarized in Table 1. The structures were solved by direct methods (SHELXS)[46] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).[47] The hydrogen at C12 for complex **9d** was located by difference Fourier synthesis and refined isotropically. All other hydrogen atom positions were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[47] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

CCDC-768287 (for **9a**), CCDC-768288 (for **9b**), CCDC-768289 (for **9c**) and CCDC-768290 (for **9d**) 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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4.4 [AD4] New Approach to [FeFe]-hydrogenase Models Using Aromatic Thioketone.

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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

Keywords: Bioinorganic chemistry / Enzyme mimics / Hydrogenase models / Electrochemistry / Sulfur heterocycles / Thioketones / Iron

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 $[Fe_2(CO)_6\{\mu,\kappa,S,SCH(C_6H_5)C_6H_4\text{-}\eta^2\}]$ (**3a**) and $[Fe_2(CO)_6\{\mu,\kappa,S,SCH(C_6H_4)\text{–}S\text{–}C_6H_3\text{-}\eta^2\}]$ (**4a**) were obtained as the major products, respectively. In contrast, the treatment of triiron dodecacarbonyl with an excess of **2a** or **2b** afforded $[Fe_2(CO)_6\{\mu\text{-}SCH(C_6H_5)C_6H_4S\text{-}\mu\}]$ (**3b**) and $[Fe_2(CO)_6\{\mu\text{-}SCH(C_6H_4)\text{–}S\text{–}C_6H_3S\text{-}\mu\}]$ (**4b**), respectively, which are both bioinspired models for the active site of [FeFe]-hydrogenase. In addition to these complexes, the two reactions afforded $[Fe_2(CO)_6\{\mu\text{-}SC(C_6H_5)_2S\text{-}\mu\}]$ (**3c**) and $[Fe_2(CO)_6\{\mu\text{-}SC(C_6H_4\text{–}S\text{–}C_6H_4)S\text{-}\mu\}]$ (**4c**). Furthermore, $[\{Fe_2(CO)_6\{\mu\text{-}SCH(C_6H_5)_2\}\}_2(\mu^4\text{-}S)]$ (**3d**) was isolated from the reaction of $Fe_3(CO)_{12}$ 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.

Introduction

Nature has developed highly efficient enzymes that regulate the generation and depletion of H_2.[1–4] 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.[5] The [FeFe]-hydrogenases have a higher hydrogen production ability compared to that of other hydrogenases.[6–8] Microorganisms 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.[9]

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.[10]

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

In an earlier investigation of the reaction of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1**) with $Fe_3(CO)_{12}$,[11b] 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[12,13a] and the fragments [e.g., $Ph_2C{=}S$ (**2a**)] react with the iron carbonyl complexes to yield the *ortho*-metallated complex **3a** as the major component of the reaction mixture.[11b–11e] 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 $Fe_3(CO)_{12}$.

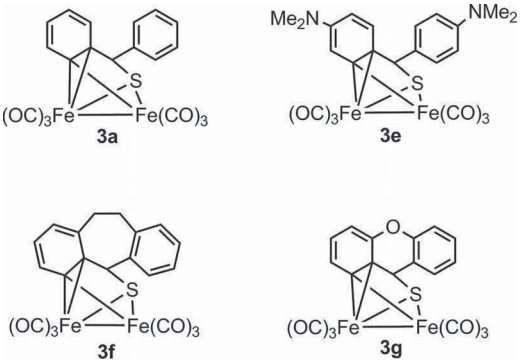


Figure 1. The *ortho*-metallated complexes **3a** and **3e**–**g**.

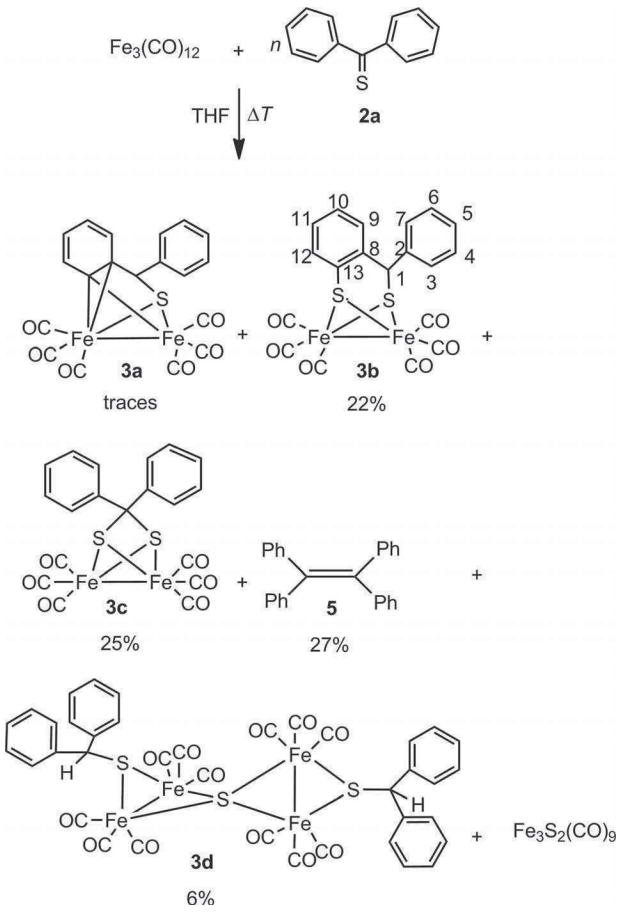
These observations prompted us to investigate the reaction of **2a** and 9H-thioxanthene-9-thione (**2b**) with $Fe_3(CO)_{12}$, and to examine the reactivity of the complexes of type **3** that were initially obtained under the applied reaction conditions. The structures of the isolated *ortho*-metallated 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.

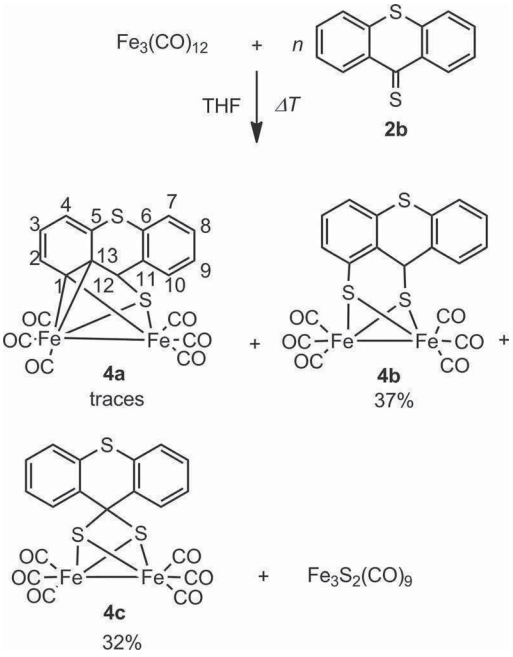
Results and Discussion

The reaction of $Fe_3(CO)_{12}$ 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, [$Fe_2(CO)_6${μ,κ,*S*,SCH(C_6H_5)C_6H_4-η^2}] (**3a**) and [$Fe_2(CO)_6${μ,κ,*S*,SCH(C_6H_4)–S–C_6H_3-η^2}] (**4a**), respectively, as the major products. In addition to **3a**, complexes [$Fe_2(CO)_6${μ-SCH(C_6H_5)C_6H_4S-μ}] (**3b**) and [$Fe_2(CO)_6${μ-SC(C_6H_5)$_2$S-μ}] (**3c**) were produced from the reaction of $Fe_3(CO)_{12}$ with **2a**. Similarly, complexes [$Fe_2(CO)_6${μ-SCH(C_6H_4)–S–C_6H_3S-μ}] (**4b**) and [$Fe_2(CO)_6$-{μ-SC(C_6H_4–S–C_6H_4)S-μ}] (**4c**) were isolated along with **4a** from the reaction of $Fe_3(CO)_{12}$ with **2b** (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 $Fe_3(CO)_{12}$ 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, [{$Fe_2(CO)_6${μ-SCH(C_6H_5)$_2$}}$_2$(μ^4-S)] (**3d**), and known tetraphenylethylene

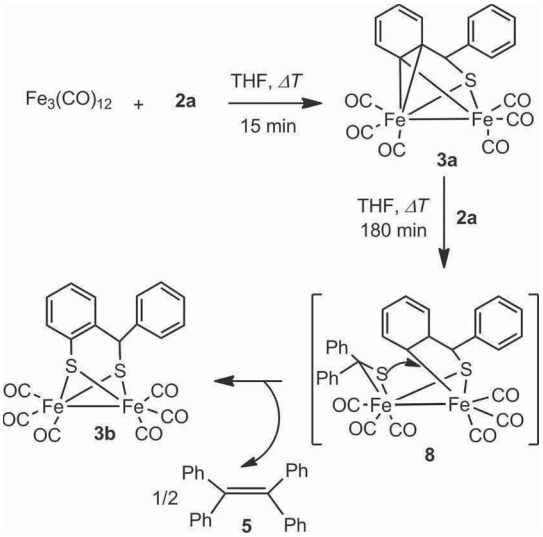


Scheme 1. The reaction of $Fe_3(CO)_{12}$ with **2a** where (a) *n* is 1, the reaction time is 20 min, **3a** (major), **3b** and **3c** (traces), and (b) *n* is 3, the reaction time is 180 min, and the main products are **3b**–**d** and **5**.



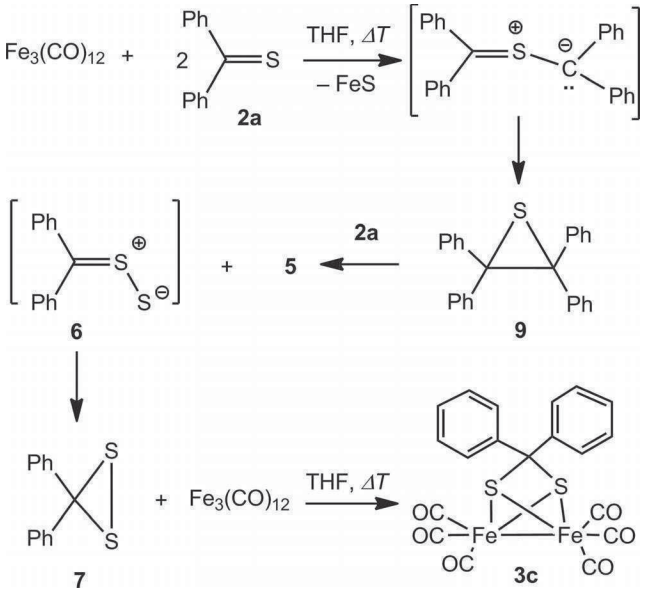
Scheme 2. The reaction of $Fe_3(CO)_{12}$ with **2b** where (a) *n* is 1, the reaction time is 20 min, **4a** (major), **4b** and **4c** (traces) and (b) *n* is 3, the reaction time is 180 min, and the main products are **4b** and **4c**.

(**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 thioketones **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 thioketones 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]

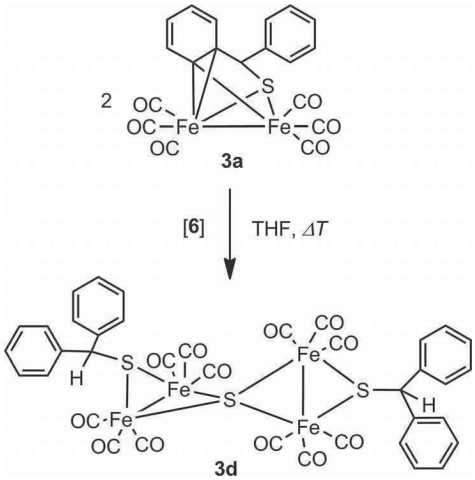


Scheme 3. The proposed mechanism for the formation of **3b** from **3a**.

Complex **3c** is believed to be produced by the oxidative addition of $Fe_3(CO)_{12}$ along the S–S bond of the in situ-generated 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.[13b] 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".[13a]



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 ^1H and $^{13}C\{^1H\}$ NMR spectra of **4a** exhibit signals at δ = 4.86 and 60.7 ppm, respectively, which were attributed to the methine group. These resonances, as well as the other signals in the ^1H and $^{13}C\{^1H\}$ NMR spectra of **4a**, are in the same range as those observed for the analogue complexes **3a** and **3e**–**g**. The ^1H NMR spectra for **3c** and **4c** show a broad signal at δ = 7.57 ppm (for **3c**) and two broad resonances at δ = 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 ^{1}H NMR spectra of **3b** and **4b** show a singlet at δ = 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 ^{1}H NMR spectrum of **3d** reveals the presence of two methine groups and the resonances for these protons are found at δ = 4.21 and 4.66 ppm, respectively. The ^{13}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^{-1}, 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 μ^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 μ^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[10i,10l,14–20] and to that of **3d** [2.5246 Å (mean)], but it is longer than the corresponding bond lengths in the analogous complexes **3e**

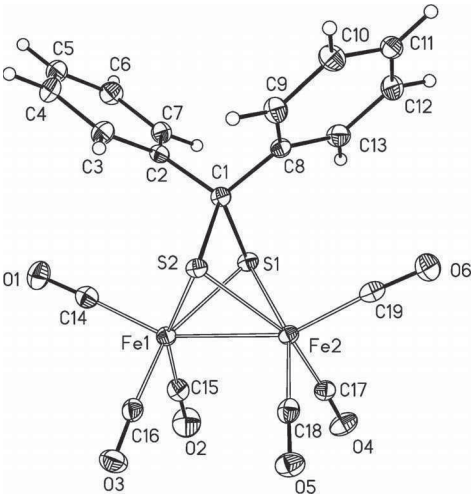


Figure 2. The ORTEP drawing of [$Fe_2(CO)_6${μ-SC(C_6H_5)$_2$S-μ}] (**3c**) with the thermal ellipsoids set at the 50% probability level. The selected distances [Å] and angles [°] are Fe(1)–Fe(2) 2.4867(4), Fe(1)–S(1) 2.2785(6), Fe(1)–S(2) 2.2625(6), Fe(2)–S(1) 2.2757(6), Fe(2)–S(2) 2.2608(6), Fe(1)–S(1)–Fe(2) 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).

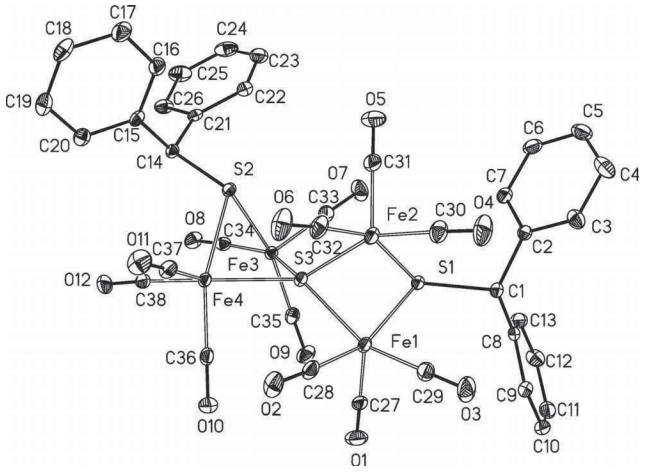


Figure 3. The ORTEP drawing of [{$Fe_2(CO)_6${μ-SCH(C_6H_5)$_2$}}$_2$-(μ^4-S)] (**3d**) with the thermal ellipsoids set at the 50% probability level. The hydrogen atoms were omitted for clarity. The selected distances [Å] and angles [°] are Fe(1)–Fe(2) 2.5195(3), Fe(3)–Fe(4) 2.5297(4), Fe(1)–S(1) 2.2555(5), 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).

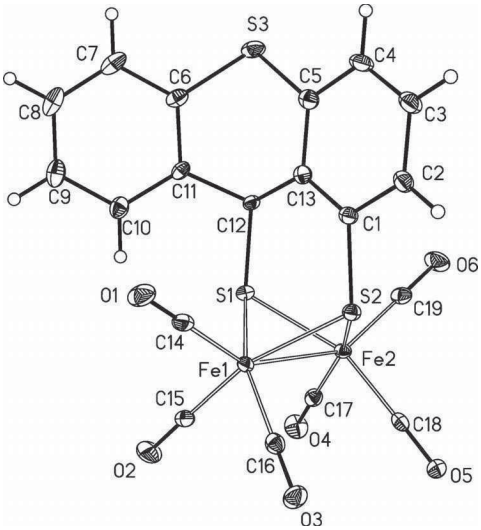


Figure 4. The ORTEP drawing of [$Fe_2(CO)_6${μ-SCH(C_6H_4)–S–C_6H_4S-μ}] (**4b**) with the thermal ellipsoids set at the 50% probability level. The selected distances [Å] and angles [°] are Fe(1)–Fe(2) 2.5218(5), Fe(1)–S(1) 2.2415(6), Fe(1)–S(2) 2.2340(6), Fe(2)–S(1) 2.2417(7), Fe(2)–S(2) 2.2412(7), 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)–Fe1 55.767(18).

[2.4993(6) Å][11b] 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[21–27] 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].[11b] The angles of S(1)–Fe(1)–S(2) [85.22(2)°] and S(1)–Fe(2)–

S(2) [85.02(2)°] in **4b** are within the same ranges as those observed for the [FeFe]-hydrogenase model complexes.[14–27] 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**.

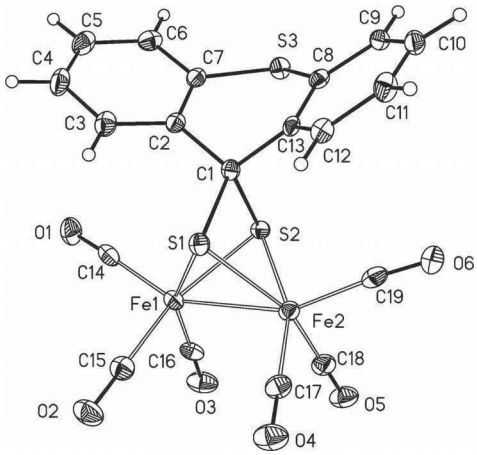


Figure 5. The ORTEP drawing of $[Fe_2(CO)_6\{\mu\text{-}SC(C_6H_4\text{–}S\text{–}C_6H_4)\text{-}S\text{-}\mu\}]$ (**4c**) with the thermal ellipsoids set at the 50% probability level. The selected distances [Å] and angles [°] are Fe(1)–Fe(2) 2.4850(5), Fe(1)–S(1) 2.2693(6), Fe(1)–S(2) 2.2629(6), Fe(2)–S(1) 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.[28] 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 $[Fe^IFe^I]\rightarrow[Fe^IFe^0]^-$ 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 $[Fe^IFe^I]$ state is transferred into $[Fe^IFe^0]^-$ 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.[29,30] 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.[29] At –2.15 V a further reduction of the chemically changed $[Fe^IFe^0]$ species was observed, which was attributed to the $[Fe^IFe^0]^-\rightarrow[Fe^0Fe^0]^{2-}$ process in accordance with $Fe_2(CO)_6(pdt)$ (pdt = propanedithiolato).[31] 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 $[Fe^IFe^I]$ species at –1.58 V. According to the literature, this might be the reoxidation of a chemically transformed $[Fe^IFe^0]$ species.[29] At ca. +1.28 V the irreversible oxidation of the $[Fe^IFe^I]$ 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 $[Fe^{II}Fe^I]$ complex as has been already described for similar reduction processes.

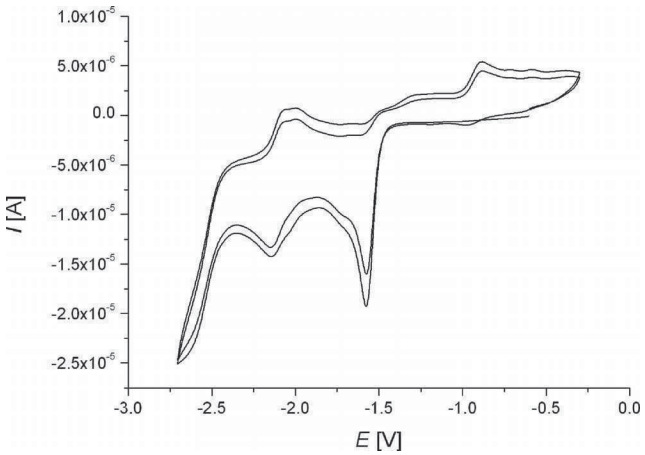


Figure 6. The cyclic voltammetric reduction of $[Fe_2(CO)_6\{\mu\text{-}SCH(C_6H_5)C_6H_4S\text{-}\mu\}]$ (**3b**) in acetonitrile (1.0 mM) on a glassy carbon electrode where Fc/Fc^+ was used as the internal standard and $[n Bu_4N][PF_6]$ (0.1 M) was used as the supporting electrolyte.

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 (pK_a = 22.3 in CH_3CN) (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

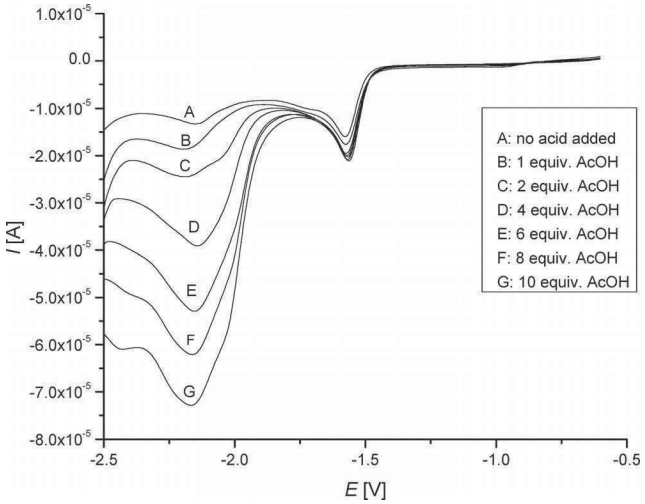


Figure 7. The cyclic voltammograms of $[Fe_2(CO)_6\{\mu\text{-}SCH(C_6H_5)\text{-}C_6H_4S\text{-}\mu\}]$ (**3b**) in acetonitrile (1 mM) in the presence of HOAc (0–10 mM), (potentials vs. Fc/Fc^+).

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**.[28] 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 $[Fe_2(CO)_6(pdt)]$,[31] $[Fe_2(CO)_6(bdt)]$[10h] shows an initial two-electron reduction to a $[Fe^0Fe^0]$ complex at –1.25 V (Table 1). This reduction, however, appears at two different potentials. The one-electron reduction of $[Fe_2(CO)_6(pdt)]$ 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**, $[\{Fe_2(CO)_6\}(pdt)]$, and $[\{Fe_2(CO)_6\}(bdt)]$.

	$E_{red\,1}$ [V]	$E_{red\,2}$ [V]	E_{ox} [V]
3b[a]	–1.58	–2.15	+1.28
$[\{Fe_2(CO)_6\}(pdt)]$[31][b]	–1.34	–1.95	+1.14
$[\{Fe_2(CO)_6\}(bdt)]$[10h][c]	–1.27	–1.23	irreversible

[a] Glassy carbon electrode (potentials given in V, ± 0.01) vs. Fc/Fc^+ (0.01 M) in $[nBu_4N][PF_6]/CH_3CN$ (0.1 M) as the supporting electrolyte. [b] CH_3CN solution (0.1 M $[nBu_4N][PF_6]$) with a glassy carbon working electrode standard vs. Fc/Fc^+. [c] First scan, v = 0.1 Vs^{-1}; solution in $[nBu_4N][PF_6]/CH_3CN$.

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 $Fe_3(CO)_{12}$ 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 σ-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-site-core 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.[32a] 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 $[Fe_2(RS)_2(CO)_6]$, sulfur, and hydrogen.[32b] 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.[32c]

Experimental Section

General Comments: All of the reactions were carried out under an argon atmosphere by using the standard Schlenk techniques. The ^1H and $^{13}C\{^1H\}$ 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**)[12d] and 9*H*-thioxanthene-9-thione (**2b**)[13a] were prepared according to the literature procedures. The solvents and $Fe_3(CO)_{12}$ 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.

$[Fe_2(CO)_6\{\mu\text{-}SCH(C_6H_5)C_6H_4S\text{-}\mu\}]$ (3b), $[Fe_2(CO)_6\{\mu\text{-}SC(C_6H_5)_2\}(S\text{-}\mu)]$ (3c), and $[\{Fe_2(CO)_6\{\mu\text{-}SCH(C_6H_5)_2S\text{-}\mu\}]$ (3d). Method A: $Fe_3(CO)_{12}$ (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 **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. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 5.90 [s, 1 H, H(1)], 7.03–7.23 (m, 5 H, Ar-H), 7.32 [dd, ^3J = 7.7 Hz, 1 H, H(10)], 7.37 [dd, ^3J = 8.1 Hz, 1 H, H(11)], 7.75 [d, ^3J = 8.0 Hz, 1 H, H(9)], 8.51 [d, ^3J = 8.2 Hz, 1 H, H(12)] ppm. $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ = 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): $\tilde{\nu}_{C\equiv O}$ = 2073 (vs), 2035 (vs), 2008 (w, sh), 1994 (s), 1979 (s) cm^{-1}. MS (DEI = 70 eV): m/z = 510 [M^+], 482 [M^+ – CO], 454 [M^+ – 2CO], 426 [M^+ – 3CO], 398 [M^+ – 4CO], 370 [M^+ – 5CO], 342 [M^+ – 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. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.57 (br. s, 10 H, 2 Ph) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ = 95.0 (SCS), 123.6, 127.7, 128.5 (2 Ph), 207.0, 208.2 (CO) ppm. FTIR (KBr): $\tilde{\nu}_{C\equiv O}$ = 2076 (vs), 2035 (vs), 1990 (vs) cm^{-1}. MS (DEI = 70 eV): *m*/*z* = 510 [M$^+$], 482 [M$^+$ – CO], 454 [M$^+$ – 2CO], 426 [M$^+$ – 3CO], 398 [M$^+$ – 4CO], 370 [M$^+$ – 5CO], 342 [M$^+$ – 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. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 4.21, 4.66 (s, 2 H, 2 SCH), 7.06, 7.44, 7.68 (br. s, 20 H, 2 Ph) ppm. $^{13}C\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ = 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): $\tilde{\nu}_{C\equiv O}$ = 2072 (vs), 2059 (w, sh), 2039 (vs), 1998 (vs) cm^{-1}. MS (DEI = 70 eV): *m*/*z* = 990 [M$^+$], 906 [M$^+$ – 3CO], 878 [M$^+$ – 4CO], 822 [M$^+$ – 6CO], 794 [M$^+$ – 7CO], 766 [M$^+$ – 8CO], 738 [M$^+$ – 9CO], 711 [M$^+$ – 10CO], 655 [M$^+$ – 12CO].

[$Fe_2(CO)_6${μ-SCH(C_6H_5)C_6H_4S-μ}] (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%).

[$Fe_2(CO)_6${μ,κ,*S*,SCH(C_6H_4)–S–C_6H_4-η^2}] (4a): $Fe_3(CO)_{12}$ (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%). $C_{19}H_8Fe_2O_6S_2$ (507.8): calcd. C 44.91, H 1.59, S 12.62; found C 44.70, H 1.92, S 12.58. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 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. $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ = 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_5H_{12}): $\tilde{\nu}_{C\equiv O}$ = 2071 (vs), 2037 (vs), 2001 (vs), 1984 (w, sh) cm^{-1}. MS (DEI = 70 eV): *m*/*z* = 508 [M$^+$], 480 [M$^+$ – CO], 452 [M$^+$ – 2CO], 424 [M$^+$ – 3CO], 396 [M$^+$ – 4CO], 368 [M$^+$ – 5CO], 340 [M$^+$ – 6CO].

[$Fe_2(CO)_6${μ-SCH(C_6H_4)–S–C_6H_4S-μ}] (4b) and [$Fe_2(CO)_6${μ-SC(C_6H_4–S–C_6H_4)S-μ}] (4c): The ligand, 9*H*-thioxanthene-9-thione (**2b**) (163 mg, 0.48 mmol), was added to a solution of $Fe_3(CO)_{12}$ (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_f = 0.6). Elution with hexane/diethyl ether (2:1, v/v) afforded a reddish solution of complex **4b** (R_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%). $C_{19}H_8Fe_2O_6S_3$ (540.1): calcd. C 42.25, H 1.49, S 17.80; found C 42.58, H 1.68, S 17.30. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, assignment analogous to **4a**): δ = 5.28 ppm. [s, 1 H, H(12)], 7.05 [dd, 1 H, ^3J = 8.0 Hz, H(8)], 7.31 [m, 1 H, H(9)], 7.43[d, 1 H, ^3J = 8.0 Hz, H(10)], 7.56 [d, 1 H, ^3J = 8.0 Hz, H(7)], 7.76 [dd, 1 H, ^3J = 8.0 Hz, H(3)], 8.03 [d, 1 H, ^3J = 8.0 Hz, H(4)], 8.62 [d, 1 H, ^3J = 8.0 Hz, H(2)] ppm. $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ = 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): $\tilde{\nu}_{C\equiv O}$ = 2075 (vs), 2038 (vs), 2017 (w, sh), 2003 (s), 1985 (s) cm^{-1}. MS (DEI = 70 eV): *m*/*z* = 540 [M$^+$], 512 [M$^+$ – CO], 484 [M$^+$ – 2CO], 456 [M$^+$ – 3CO], 428 [M$^+$ – 4CO], 400 [M$^+$ – 5CO], 372 [M$^+$ – 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. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, assignment analogous to **4a**): δ = 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	$C_{19}H_8Fe_2O_6S_3$	$C_{38}H_{22}Fe_4O_{12}S_3$	$C_{19}H_7Fe_2O_6S_3$	$C_{19}H_{10}Fe_2O_6S_2$
fw [g mol^{-1}]	540.13	990.14	539.13	510.09
T [°C]	–140(2)	–140(2)	–140(2)	–140(2)
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$C2/c$
a [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)
α [°]	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
ρ [g cm^{-3}]	1.832	1.644	1.762	1.754
μ [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)[a]	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 [e Å^{-3}]	0.475/–0.409	0.485/–0.368	1.765/–0.534	0.466/–0.349
Absorption correction	none	none	none	none

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

Ph) ppm. $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$): δ = 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): $\tilde{\nu}_{C\equiv O}$ = 2075 (vs), 2037 (vs), 2001 (vs) cm^{-1}. MS (DEI = 70 eV): *m*/*z* = 540 [M^+], 512 [M^+ – CO], 484 [M^+ – 2CO], 456 [M^+ – 3CO], 428 [M^+ – 4CO], 400 [M^+ – 5CO], 372 [M^+ – 6CO].

Characterization of 1,1,2,2-Tetraphenylethene (5): Colorless crystals, m.p. 222–224 °C (ref.[33] m.p. 222 °C). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 7.05–7.21 (m, 20 H, Ar-H) ppm. MS (DEI = 70 eV): *m*/*z* = 332 [M^+].

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_3CN as the reference electrode. The solvent contained [nBu$_4$N][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^+ couple as an internal standard ($E_{1/2}$ = 503 mV vs. Ag/AgCl in CH_3CN).

Crystal Structure Determination: The intensity data for the compounds were collected with a Nonius KappaCCD diffractometer by using graphite-monochromated Mo-K_α radiation. The data were corrected for Lorentz and polarization effects but not for absorption effects.[34,35] 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)[36] and were refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97).[36] 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.[36] XP (SIEMENS 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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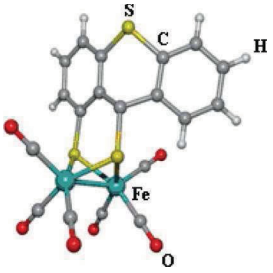
[FeFe]-Hydrogenase Models

The generation of the [FeFe]-hydrogenase model complexes $[Fe_2(CO)_6\{\mu\text{-}SCH(C_6H_5)C_6H_4S\text{-}\mu\}]$ (**3b**) and $[Fe_2(CO)_6\{\mu\text{-}SCH(C_6H_4)\text{–}S\text{–}C_6H_3S\text{-}\mu\}]$ (**4b**) is reported. A plausible mechanism for the formation of **3b** is described, in which thiobenzophenone (**2a**) acts as a sulfur transfer reagent, while the *ortho*-metallated complex $[Fe_2(CO)_6\{\mu,\kappa,S,SCH(C_6H_5)C_6H_4\text{-}\eta^2\}]$ (**3a**) is the reaction pathway intermediate.



A. Q. Daraosheh, U.-P. Apfel, H. Görls, C. Friebe, U. S. Schubert, M. El-khateeb, G. Mloston,* W. Weigand* **1–10**

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

Keywords: Bioinorganic chemistry / Enzyme mimics / Hydrogenase models / Electrochemistry / Sulfur heterocycles / Thioketones / Iron

5. Documentation of authorship

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- M. K. Harb: Synthesis and characterization of all complexes
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- J. Windhager: Assistance in manuscript preparation
- A. Q. Daraosheh: Assistance in complex preparation
- H. Görls: X-Ray structures analyses
- L. Lockett/N. Okumura Assistance in electrochemical investigations
- D. H. Evans: Electrochemical investigations
- R. S. Glass: Electrochemical investigations
- D. L. Lichtenberger: Electrochemical investigations
- M. El-khateeb: Co-Adviser, Preparation of the manuscript
- W. Weigand: Supervision, Preparation of the manuscript

[AD2] A. Q. Daraosheh, M. K. Harb, J. Windhager, H. Görls, M. El-khateeb, W. Weigand. ***Substitution Reactions at [FeFe] Hydrogenase Models Containing [2Fe3S] Assembly by Phosphine or Phosphite Ligands.*** *Organometallics* **2009**, *28*, 6275-6280.

- A. Q. Daraosheh: Synthesis and characterization of all complexes
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- M. K. Harb: Assistance in complex preparation
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- H. Görls: X-Ray structures analyses
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- W. Weigand: Supervision, Preparation of the manuscript

[AD3] A. Q. Daraosheh, H. Görls, M. El-khateeb, G. Mloston, W. Weigand. ***Reactions of Selected Aromatic Thioketones with Triiron Dodecarbonyl***. *Eur. J. Inorg. Chem.* **2011**, 349-355.

- A. Q. Daraosheh: Synthesis and characterization of all complexes
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- H. Görls: X-Ray structures analyses
- M. El-khateeb: Co-Adviser, Preparation of the manuscript
- G. Mloston: Discussion of the manuscript
- W. Weigand: Supervision, Preparation of the manuscript

[AD4] A. Q. Daraosheh, U.-P Apfel, C. Friebe, H. Görls, U. S. Schubert, G. Mloston, M. El-khateeb, W. Weigand. ***New Approach to [FeFe]-hydrogenase Models Using Aromatic Thioketone***. Acceptance 201101032 / *Eur. J. Inorg. Chem*. **2011**.

A. Q. Daraosheh: Synthesis and characterization of all complexes
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- C. Friebe: Assistance in electrochemical investigations
- H. Görls: X-Ray structures analyses
- U. S. Shubert: Electrochemical investigations
- M. El-khateeb: Co-Adviser, Preparation of the manuscript
- G. Mloston: Discussion of the manuscript
- W. Weigand: Supervision, Preparation of the manuscript

6. Summary

Explanatory note: All bold numbers give the compounds presented in the respective articles.

In this work, our efforts was concentrated on the synthesis of model complexes related to the active site of the [FeFe]-hydrogenase. In general, all articles [AD1]-[AD4] deal with the structural investigations of new synthesized models. Moreover, [AD4] investigated, the electrocatalytic generation of dihydrogen by one synthesized complex, using acetic acid as proton source.

[AD1]: In this article, the substitution of CO ligands from $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_6$ (**1**) by PPh_3, $P(OMe)_3$, and bis(diphenylphosphanyl)ethane (dppe) has been investigated. The reaction of **1** with 1 equiv. of PPh_3 in acetonitrile at room temperature gave $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5PPh_3$ (**2**). Whereas treatment of **1** with excess $P(OMe)_3$ in refluxing toluene offered, the mono- and disubstituted phosphite complexes $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5P(OMe)_3$ (**3**) and $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4[P(OMe)_3]_2$ (**4**). In addition, the reaction of **1** with 1 equiv. of dppe in the presence of $Me_3NO{\cdot}2H_2O$ yielded two complexes $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4(\kappa_2\text{-dppe})$ (**5**), wherein the dppe ligand is chelated to a single iron atom, and $[Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5]_2(\mu\text{-dppe})$ (**6**), where two {2Fe2S} units are linked by the dppe. The newly prepared model complexes **1-6** were characterized by spectroscopic techniques and X-ray structure determination. Moreover, complex **2** has been proved to be a catalyst for electrochemical reduction of protons from the weak acids, acetic acid, to give hydrogen.

[AD2]: In this article, we investigated the role of the hemilabile thioether ligand in the substitution of CO ligands at the complex $Fe_2(\mu\text{-}S_2(C_3H_6)_2S\text{-}\mu)(CO)_5$ (**1**), By $P(OMe)_3$ and PMe_3. The reaction of **1** with 1 equiv. of $P(OMe)_3$ in THF at room temperature afforded the first-formed kinetically controlled product $Fe_2(\mu\text{-}S_2(C_3H6)_2S)(CO)_5P(OMe)_3$ (**2**), which upon standing at room temperature for 90 min converted to $Fe_2(\mu\text{-}S_2(C_3H_6)_2S\text{-}\mu)(CO)_4P(OMe)_3$ (**3**) the thermodynamic product. In contrast, complex **3** is directly produced from the reaction of **1** with $P(OMe)_3$ under reflux conditions. Additionally, refluxing a THF solution of **1** with

excess of $P(OMe)_3$ or PMe_3 gave exclusively the disubstituted complexs $Fe_2(\mu$-$S_2(C_3H6)_2S)(CO)_4[P(OMe)_3]_2$ (**4**) and $Fe_2(\mu$-S_2-$(C_3H_6)_2S)(CO)_4(PMe_3)_2$ (**5**), respectively. Interestingly, we were able to isolate complex **2**, which is believed to be the intermediate of the reaction pathway from **1** to **3**. Complexes **1-4** have been characterized by IR, NMR spectroscopy, elemental analysis and X-ray single crystal structure analysis.

[AD3]: The article, described the reaction of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1e**) as well as the selected aromatic thioketones thiobenzophenone (**2a**), 4,4-bis(dimethylamino)thiobenzophenone (**2b**), dibenzosuberenethione (**2c**) and xanthione (**2d**) with $Fe_3(CO)_{12}$. The *ortho*-metalated complex $Fe_2(CO)_6$-[κ,μ-*S*,η^2-$(C_{13}H_{10}S)$] (**9a**) was obtained by refluxing $Fe_3(CO)_{12}$ with **1e** or **2a** in THF. The heterocyclic trisulfides **1e** first, undergoes [2+3]-cycloreversion at around 50 °C and the fragments (e.g., **2a**) react with $Fe_3(CO)_{12}$ to yield **9a** complex as the major product. In addition, treatment of $Fe_3(CO)_{12}$ with **2b**, **2c** and **2d** gave $Fe_2(CO)_6$[κ,μ-*S*,η^2-$(C_{17}H_2ON_2S)$] **9b**, $Fe_2(CO)_6$[κ,μ-*S*,η^2-$(C_{15}H_{12}S)$] **9c** and $Fe_2(CO)_6$[κ,μ-*S*,η^2-$(C_{13}H_8OS)$] **9d**, respectively. A conceivable formation mechanism for these complexes can be explained by a formal [4+2] cycloaddition in which the aromatic thioketones act as heterodienes with $Fe_3(CO)_{12}$. The initially formed [4+2]-cycloadduct undergoes spontaneous rearomatization through a 1,3-H shift to give the final *ortho*-metalated complex. Compounds **9a-d** were characterized by spectroscopic techniques (NMR, IR, photoelectron spectroscopy), mass spectrometry, and single-crystal X-ray analysis.

[AD4]: Herein we extended our effort to study the chemistry of the *ortho*-metallated complexes **9a-d**, which were prepared in the previous article [AD3]. The structures of these complexes provided a hint such that, these compounds could be important intermediates in the synthesis of novel [FeFe]-hydrogenase model complexes. For that reason, reactions of triiron $Fe_3(CO)_{12}$ with thiobenzophenone (**2a**) or 9H-xanthene-9-thione (**2e**) have been investigated under different conditions. In the case of 1:1 molar ratio of reactants, the *ortho*-metallated complexes $Fe_2(CO)_6(\mu, \kappa;$ *S*, $SCH(C_6H_5)C_6H_4$-η^2) (**3a**) and $Fe_2(CO)_6(\mu, \kappa;$ *S*, $SCH[(C_6H_4)$-S-C_6H_4-$\eta^2)]$ (**4a**) were obtained, respectively. Whereas treatment of triiron dodecacarbonyl with

excess of **2a** or **2e** gave two biomimetic models for the active site of the [FeFe]-hydrogenase; $Fe_2(CO)_6(\mu\text{-}SCH(C_6H_5)C_6H_4S\text{-}\mu)$ (**3b**) and $Fe_2(CO)_6(\mu\text{-}SCH(C_6H_4)\text{-}S\text{-}C_6H_4S\text{-}\mu)$ (**4b**), respectively**.** In addition to these complexes, the two reactions also afforded $Fe_2(CO)_6(\mu\text{-}SC(C_6H_5)_2)S\text{-}\mu)$ (**3c**) and $Fe_2(CO)_6(\mu\text{-}SC(C_6H_4\text{-}S\text{-}C_6H_4)S\text{-}\mu)$ (**4c**)**,** respectively. Furthermore, $[Fe_2(CO)_6(\mu\text{-}SCH(C_6H_5)_2]_2(\mu^4\text{-}S)]$ (**3d**) was isolated from the reaction of $Fe_3(CO)_{12}$ with **2a**. Additionally, a plausible formation mechanism of complexes **3b** and **3c** is described. Moreover, the electrocatalytic production of H_2 by **3b** from acetic acid has been investigated by cyclic voltammetry, which revealed a moderate catalytic activity.

Zusammenfassung

Anmerkungen: Alle in fettgedruckten Nummern gekennzeichneten Verbindungen sind in den betreffenden Veröffentlichung vorgestellt.

In dieser Arbeit konzentrierten sich unsere Bestrebungen auf die Synthesen von Modellkomplexen, welche sich auf das aktive Zentrum der [FeFe]-Hydrogenase beziehen. Im Allgemeinen behandeln alle Artikel [AD1]-[AD4] die strukturelle Untersuchung der neu synthetisierten Modellverbindungen. Außerdem wurde in [AD4] die elektrokatalytische Wasserstoffgenerierung durch einen der synthetisierten Komplex unter Nutzung von Essigsäure als Protonenquelle erforscht.

[AD1]: In diesem Artikel wurde die Substitution von CO-Liganden in $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_6$ (**1**) durch PPh_3, $P(OMe)_3$ und Bis(diphenylphosphanyl)ethane (dppe) getestet. Die Reaktion von **1** mit 1 eq. PPh_3 ergab in Acetonitril bei Raumtemperatur den Komplex $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5PPh_3$ (**2**), wohingegen die Behandlung von **1** mit einem Überschuss an $P(OMe)_3$ unter Rückfluss in Toluen die mono- und disubstituierten Phosphitkomplexe $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5P(OMe)_3$ (**3**) und $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4[P(OMe)_3]_2$ (**4**) ergab. Darüber hinaus lieferte die Reaktion von **1** mit 1 eq. dppe in Gegenwart von $Me_3NO{\cdot}2H_2O$ zwei Kompelexe: $Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_4(\kappa_2\text{-dppe})$ (**5**), worin der dppe-Ligand mit einem Eisenatom chelatisiert, und $[Fe_2(\mu\text{-}Se_2C_3H_5CH_3)(CO)_5]_2(\mu\text{-dppe})$ (**6**), in dem zwei {2Fe2S}-Einheiten durch den dppe-Liganden verbunden sind. Die neu hergestellten Modellkomplexe **1**-**6** wurden spektroskopisch und durch Röntgenstrukturanalyse charakterisiert. Ferner konnte die elektrochemische Reduktion von Protonen zu Wasserstoff in Anwesenheit einer schwachen Säure (Essigsäure) mit Komplex **2** als Katalysator nachgewiesen werden.

[AD2]: In diesem Artikel haben wir die hemilabile Eigenschaft eines Thioetherliganden im Komplex $Fe_2(\mu\text{-}S_2(C_3H_6)_2S\text{-}\mu)(CO)_5$ (**1**) untersucht, bei dem anstelle der CO-Liganden $P(OMe)_3$ und PMe_3 koordiniert sind. Die Reaktion von **1** mit 1 eq. $P(OMe)_3$ in THF lieferte bei Raumtemperatur unter kinetischer Kontrolle zunächst Produkt $Fe_2(\mu\text{-}S_2(C_3H6)_2S)(CO)_5P(OMe)_3$ (**2**), welches nach Lagern bei Raumtemperatur innerhalb von 90 Minuten in das thermodynamisch kontrollierte

Produkt $Fe_2(\mu\text{-}S_2(C_3H_6)_2S\text{-}\mu)(CO)_4P(OMe)_3$ (**3**) überging. Im Gegensatz dazu wird Komplex **3** direkt aus der Reaktion von **1** mit $P(OMe)_3$ unter Rückfluss gebildet. Weiterhin lieferte eine THF-Lösung von **1** mit einem Überschuss an $P(OMe)_3$ oder PMe_3 unter Rückfluss die disubstituierten Komplexe $Fe_2(\mu\text{-}S_2(C_3H6)_2S)(CO)_4[P(OMe)_3]_2$ (**4**) beziehungsweise $Fe_2(\mu\text{-}S_2\text{-}(C_3H_6)_2S)(CO)_4(PMe_3)_2$ (**5**). Interessanterweise waren wir in der Lage, Komplex **2** zu isolieren, welcher als Intermediat des Reaktionspfades von Komplex **1** zu **3** angenommen wird. Die Komplexe **1**-**4** wurden durch IR-, NMR-Spektroskopie, Elementaranalyse und Röntgenkristallstrukturanalyse charakterisiert.

[AD3]: In diesem Artikel sind die Reaktionen von 3,3,5,5-Tetraphenyl-1,2,4-trithiolane (**1e**) ebenso wie von ausgewählten aromatischen Thioketonen (Thiobenzophenon) (**2a**), 4,4-Bis(dimethylamino)-thiobenzophenon (**2b**), Bibenzosuberenethion (**2c**) und Xanthion (**2d**) mit $Fe_3(CO)_{12}$ beschrieben. Der *ortho*-metallierte Komplex $Fe_2(CO)_6\text{-}[\kappa,\mu\text{-}S,\eta^2\text{-}(C_{13}H_{10}S)]$ (**9a**) entstand bei der Reaktion von $Fe_3(CO)_{12}$ mit **1e** oder **2a** in siedendem THF. Die heterozyklischen Trisulfide **1e** durchlaufen zuerst eine [2+3]-Cycloaddition bei etwa 50°C und die Fragmente (z.B. **2a**) reagieren mit $Fe_3(CO)_{12}$ zu Komplex **9a** als Hauptprodukt. Weiterhin ergibt die Umsetzung von $Fe_3(CO)_{12}$ mit **2b**, **2c** und **2d** die Verbindungen $Fe_2(CO)_6[\kappa,\mu\text{-}S,\eta^2\text{-}(C_{17}H_2ON_2S)]$ **9b**, $Fe_2(CO)_6[\kappa,\mu\text{-}S,\eta^2\text{-}(C_{15}H_{12}S)]$ **9c** beziehungsweise $Fe_2(CO)_6[\kappa,\mu\text{-}S,\eta^2\text{-}(C_{13}H_8OS)]$ **9d**. Ein denkbarer Mechanismus für die Bildung dieser Komplexe kann mit einer [4+2]-Cycloaddition erklärt werden, bei der die aromatischen Thioketone als Heterodiene mit $Fe_3(CO)_{12}$ agieren. Das zunächst gebildete [4+2]-Cycloaddukt unterliegt einer spontanen Rearomatisierung durch eine 1,3-H-Verschiebung, welche zum *ortho*-metallierten Komplex führt. Die Verbindungen **9a-d** wurden durch spektroskopische Methoden (NMR, IR, Photoelektronenspektroskopie), Massenspektrometrie und Röntgenkristallstrukturanalyse charakterisiert.

[AD4]: Hierin haben wir unserer Bemühungen zum Verständnis der Natur der *ortho*-metallierten Komplexe **9a-d** ausgeweitet, deren Präparation in dem vorangegangen Artikel [AD3] beschrieben wurde. Die Strukturen dieser Komplexe lieferten einen Hinweis, dass solche Verbindungen wichtige Intermediate in der Synthese neuartiger [FeFe]-Hydrogenase Modelle seien können. Aus diesem Grund

wurden Reaktionen von $Fe_3(CO)_{12}$ mit Thiobenzophenon (**2a**) oder 9H-Xanthen-9-thion (**2e**) bei verschiedenen Reaktionsbedingungen untersucht. Im Fall eines 1:1 Verhältnisses der Reaktanden wurden die *ortho*-metallierten Komplexe $Fe_2(CO)_6(\mu,\kappa; S, SCH(C_6H_5)C_6H_4\text{-}\eta^2)$ (**3a**) beziehungsweise $Fe_2(CO)_6(\mu,\kappa; S, SCH[(C_6H_4)\text{-}S\text{-}C_6H_4\text{-}\eta^2)]$ (**4a**) erhalten. Im Gegensatz dazu ergab die Umsetzung von $Fe_3(CO)_{12}$ mit einem Überschuss an **2a** oder **2e** zwei biomimetische Modellverbindungen für das aktive Zentrum der [FeFe]-Hydrogenase: $Fe_2(CO)_6(\mu\text{-}SCH(C_6H_5)C_6H_4S\text{-}\mu)$ (**3b**) bzw. $Fe_2(CO)_6(\mu\text{-}SCH(C_6H_4)\text{-}S\text{-}C_6H_4S\text{-}\mu)$ (**4b**). Zudem lieferten die Reaktionen $Fe_2(CO)_6(\mu\text{-}SC(C_6H_5)_2)S\text{-}\mu)$ (**3c**) sowie $Fe_2(CO)_6(\mu\text{-}SC(C_6H_4\text{-}S\text{-}C_6H_4)S\text{-}\mu)$ (**4c**). Weiterhin entstand $[Fe_2(CO)_6(\mu\text{-}SCH(C_6H_5)_2]_2(\mu^4\text{-}S)]$ (**3d**) bei der Reaktion von $Fe_3(CO)_{12}$ mit **2a**. Zusätzlich wurde ein plausibler Bildungsmechanismus von Komplex **3b** und **3c** beschrieben und die elektrokatalytische Wasserstoffproduktion durch **3b** aus Essigsäure mittels Cyclovoltammetrie untersucht. Es zeigte sich eine moderate katalytische Aktivität.

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