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

Dissertation

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List of Publications

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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.

________________________________
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.\textsuperscript{[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\textsubscript{2} to yield organic compounds. Under certain conditions, however, instead of reducing CO\textsubscript{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\textsubscript{2}. These enzymes are called hydrogenases.\textsuperscript{[19]}

\subsection*{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\textsubscript{2} to H\textsuperscript{+} or reduce H\textsuperscript{+} to H\textsubscript{2} and therefore provide a reversible sink for multi-electron transfer.\textsuperscript{[20-30]}

\begin{equation}
\begin{aligned}
\text{H}_2 & \quad \leftrightarrow \quad 2 \text{H}^+(aq) + 2 \text{e}^- \\
\text{Hydrogenase} & 
\end{aligned}
\end{equation}

Hydrogenases have been observed and characterized in many microorganisms, including some algae, trichomonads, anaerobic ciliates, and chytrid fungi.\textsuperscript{[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\textsubscript{2}.\textsuperscript{[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.\textsuperscript{[30,32]}

\subsection*{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”.\textsuperscript{[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.\textsuperscript{[35]} A characteristic feature of all hydrogenases is that the
iron atoms are ligated by small inorganic ligands (CO, CN\textsuperscript{−}), which were first detected by FTIR spectroscopy.\textsuperscript{[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.\textsuperscript{[38,39]} This enzyme can activate \( \text{H}_2 \) only in the presence of a second substrate (methenyltetrahydromethanopterin). The enzyme catalyzes the reversible reduction of methenyltetrahydromethanopterin (\( \text{sub}^+ \)) with dihydrogen to methylenetetrahydromethanopterin (\( \text{sub-H} \)) and a proton (Eq. 2).\textsuperscript{[40, 41]} The structure of the active enzyme has been characterized by X-ray crystallography by Shima \textit{et al.} (Figure 1).\textsuperscript{[42]} The structure shows a square pyramidal geometry of the Fe center and the pyridinol derivative binds epically to iron through the \( \text{sp}^2 \) hybridized N atom. In addition, the two \textit{cis-carbonyl} groups with a cysteinyl thiolate and unknown ligand occupying the basal positions.\textsuperscript{[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 \( \text{H}_2 \).\textsuperscript{[32]}

\[
\text{Sub}^+ + \text{H}_2 \rightarrow \text{Sub-H} + \text{H}^+ \quad \text{(Eq. 2)}
\]

![Figure 1](image_url)

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 H2 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 H2 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].
1.3.3 [FeFe]-Hydrogenases

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

The [FeFe]-hydrogenases can catalyze the consumption and production of H₂, however, these enzymes have been considered mainly to be H₂-producers. 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. The location of [FeFe]-hydrogenases in the bacterial cell mirrors the enzyme’s function in the generation or uptake of H₂ molecule. 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. The X-ray crystallographic structures of the monomeric [FeFe]-hydrogenases I from *C. pasteurianum* and that of the priplasmic heterodimeric [FeFe]-hydrogenases from *Desulfovibrio desulfuricans* 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*, 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 {Fe₄S₄}-cubane core bridged by a cysteinyl residue to a {2Fe2S}-subsite (Figure 4).[9, 32, 67-70] The {Fe₄S₄}-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 [2Fe₃]₄ cluster is coordinated by a total of five diatomic ligands modeled as CO/CN⁻ and by a dithiolate ligand (SCH₂XCH₂S) 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 CH₂, 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 CH₂, NH, or O.[32, 34]
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 \(\{\text{H}_{\text{ox}}^\text{air}\}\), one CO is in a bridging position and the open coordination site at Fe\(_d\) is occupied by an oxygenic species (OH\(^-\) or H\(_2\)O) according to X-ray crystallography.\(^{9, 32}\) The activation of the enzyme generates the paramagnetic oxidized state of the enzyme \(\{\text{H}_{\text{ox}}\}\), in which the Fe atom distal to the \{Fe\(_4\)S\(_4\)\}-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 \(\{\text{H}_{\text{ox}}^\text{CO state}\}\).\(^{32, 73}\) 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 \(\text{H}_{\text{ox}}\) gives the \(\text{H}_{\text{red}}\) state, in which the bridged CO rearranges to terminal form. In \(\text{H}_{\text{red}}\) 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 \(\text{H}_2\) 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 \(\text{H}_{\text{ox}}\) toward the distal Fe of the active site, leading to terminal CO fashion in \(\text{H}_{\text{red}}\).\(^{55}\) 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 \(\text{H}_2\) production, including protonation at the bridgehead group X, is shown in Scheme 2b.\(^{73-78}\)
Scheme 2. Possible catalytic cycle mechanisms for H\textsubscript{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 \([\text{Fe}_2(\text{CO})_6(\mu-\text{SEt})_2]\) (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 \(\{2\text{Fe2S}\}\)-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 \([\text{Fe}_2(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})(\text{CO})_6]\) (pdt) complex (2)\(^{118, 119}\) by cyanide, to offer the dianion \([\text{Fe}_2(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})(\text{CO})_4(\text{CN})_2]^{2-}\) (3).\(^{120-122}\) Subsequently, the replacement of bridgehead \(\text{CH}_2\) 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.\(^{139}\)
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 \([\text{Fe}_2(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})(\text{CO})_4(\text{CN})_2]^{2-}\) model complex 3 was reported by three independent groups,\cite{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 \([\text{Fe}_2(\text{SCH}_2\text{NRCH}_2\text{S})(\text{CO})_4(\text{CN})_2]^{2-}\) dianions (R = H, Me) (9, 10) are also accessible (Figure 7).\cite{130} In a similar procedure, Song and co-workers also reported the synthesis of the odt dicyano dianion (11) \([\text{Fe}_2(\text{SCH}_2\text{OCH}_2\text{S})(\text{CO})_4(\text{CN})_2]^{2-}\).\cite{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 \{\text{Fe}(\text{CO})_2(\text{CN})\} motifs in the complexes reasonably model the distal iron of the subsite in the CO inhibited form of the enzyme \{\text{Hox}(\text{CO})\}.\cite{30, 72} Furthermore, the synthesis of the monocyanide \([\text{Fe}_2(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})(\text{CO})_5(\text{CN})]^{-}\) (12) was described by Darensbourg and co-workers, they showed, that 12 reacted with \text{CN}^{-} to offer 3.\cite{140} Therefore, the monocyanide 12 could be assumed as a plausible intermediate in stepwise substitution of the parent hexacarbonyl which gave the dicyanide 3. An alternative di-cyanation pathway was proposed by Rauchfuss and co-workers,\cite{141} in which the proposed intermediates is an undetected bridging CO monocyani de one. Recently, Weigand and co-workers have been reported the synthesis of the sdt dicyano dianion (13) \([\text{Fe}_2(\text{SCH}_2\text{SCH}_2\text{S})(\text{CO})_4(\text{CN})_2]^{2-}\).\cite{142}

Figure 7. Dicyano (3, 9, 10, 11, 13) and monocyano (12) \([\{2\text{FeS}_2\}]^{n-}\)-model complexes (n = 1, 2).
2.2.2 Phosphine- and phosphite-substituted derivatives

The introducing of good donor ligands, such as PR₃ and P(OR)₃, in the [Fe₂(SCH₂CH₂CH₂S)(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 PR₃ on the Fe atoms are comparable to that of CN⁻. 2) The steric and electronic properties of PR₃ are tunable by changing the R groups. 3) The replacement of CN⁻ by PR₃ can avoid the complications of protonation on the cyanide nitrogen atom.[143] Therefore, a series of {2Fe2S}-model complexes enclosing PR₃ or P(OR)₃ groups, [Fe₂(μ-pdt)(CO)₃L] [L = PMe₃ (14), PMe₂Ph (15), PPh₃ (16), P(OEt)₃ (17), P(OMe)₃ (18), Ph₂PH (19), Ph₂PCH₂NMe₂ (20), Ph₂PFe(CO)₂Cp (21), PPh₂NH-(CH₂)₂N(CH₃)₂ (22), PPh₂NH-(2NH₂C₆H₄) (23), PPy₃ (24), Ph₂PPyr (25)] and [Fe₂(μ-pdt)(CO)₃L₂] [L = PMe₂Ph (26), PPh₃ (27), P(OEt)₃ (28), Ph₂PPyr (29), PMe₃ (30), P(OMe)₃ (31), PPy₃ (32)] have been extensively investigated (Figure 8).[137, 143-150]

![Figure 8. Substituted model complexes of [Fe₂(μ-pdt)(CO)₆].](image)

2.2.3 Bidentate-substituted derivatives

In principle, tertiary phosphine ligands are well known to give mono- and disubstituted products, Fe₂(SR)₂(CO)₆₋ₓ(PR₃)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 [Fe₂(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 [Fe₂(SR)₂(CO)₃]₂(dppe), in which the diphosphine ligand coordinates to two {2Fe₂S}-units (Figure 9A).[126] Recently, the reaction of [Fe₆(μ-pdt)(CO)₆] (2) with dppe (Ph₂PCH₂CH₂PPh₂), was investigated by Sun et al., to deliver [Fe₆(μ-pdt)(CO)₆]₂(dppe) where the dppe ligand, like dppf, substitutes CO in the double monodentate manner to give a cluster of Fe₂S₂ cores antibridged by dppe (Figure 9A).[152] This was followed by the work of Taralmin and co-workers, in which they reported a complex [Fe₆(μ-pdt)(CO)₆(dppe)], in which dppe chelates to a single iron center (Figure 9B).[153] By contrast, treatment of 2 with dppm (Ph₂PCH₂PPh₂), furnished [Fe₆(μ-pdt)(CO)₆(dppe)], where only one phosphorus atom of dppm coordinated in a monodentate fashion to one Fe₂S₂ 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]](image)

### 2.2.4 Carbenes-substituted derivatives

During the past decade, the synthesis of N-heterocyclic carbene (NHC) containing [FeFe]H₂ase 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 \([\text{Fe}_2(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})(\text{CO})_5(\text{L}_\text{Me})]\) (33) and \([\text{Fe}_2(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})(\text{CO})_4(\text{L}_\text{Me})_2]\) (34) (\(\text{L}_\text{Me} = 1,3\text{-dimethylimidazol-2-ylidene}\)).\(^{[154]}\) Darensbourg et al. subsequently prepared the N-heterocyclic carbene containing model compound, \([\text{Fe}_2(\text{SCH}_2\text{CH}_2\text{CH}_2\text{S})(\text{CO})_3(\text{IMes})]\) (35) (\(\text{IMes} = 1,3\text{-bis}(2,4,6\text{-trimethylphenyl})\text{-imidazol-2-ylidene}\)).\(^{[157]}\) Recently, disubstituted diiron complexes containing (NHC) have been reported.\(^{[158]}\)

2.3 \{2\text{Fe}_2\text{Se}\}- and \{2\text{Fe}_2\text{Te}\}-Model complexes

The replacement of thiolates by selenolates or tellurolates in the [FeFe]-hydrogenases model complexes, which lead to an increase of the electron density at the iron atoms, and this, could enhance 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 \([\{\mu\text{-SeCH}_2\}\text{NC}_6\text{H}_4\text{R}\}\text{Fe}_2(\text{CO})_6]\) (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, \(\text{Fe}_2(\mu\text{-SeC}_3\text{H}_6\text{Se})(\text{CO})_6\) (39), \(\text{Fe}_2(\mu\text{-SeC}_2\text{H}_4\text{CH}_3)(\text{CO})_6\) (40) and \(\text{Fe}_2(\mu\text{-SeCH}_2\_2\text{Se})(\text{CO})_6\) (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, \(\text{Fe}_2(\mu\text{-SC}_3\text{H}_2\text{Se})(\text{CO})_6\) (42) and \(\text{Fe}_2(\mu\text{-SC}_3\text{H}_6\text{Te})(\text{CO})_6\) (43).\(^{[168]}\) Furthermore, thiolates have been also replaced by phosphide,\(^{[169-171]}\) amide,\(^{[172, 173]}\) and peptide groups.\(^{[174, 175]}\)
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.\textsuperscript{[168]} Sun and coworkers reported three mono-substituted diiron complexes $[\text{Fe}_2(\mu\text{-SeC}_3\text{H}_4\text{Se})(\text{CO})_5\text{L}]$ \textsuperscript{37} \text{L} = \text{PPh}_3 \text{ (44), PPh}_2\text{H (45)} \text{ and IMes (46)} changing the steric demand of the phosphine ligands.\textsuperscript{[167]} In this field, we investigated the replacement of one or two carbonyl groups of $[\text{Fe}_2(\mu\text{-SeC}_3\text{H}_4\text{CH}_3)(\text{CO})_6]$ \textsuperscript{38} by $\text{PPh}_3 \text{ (47), P(OMe)}_3 \text{ (48; 49)} \text{ and dppm (50; 51)}$ as shown in Figure 11.\textsuperscript{[AD1]}

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

![Figure 11. Phosphine substituted model complexes of Fe$_2$(μ-SeC$_3$H$_4$CH$_3$)(CO)$_6$ (40).](image)

36; $R = H$
37; $R = \text{NO}_2$
38; $R = \text{CH}_3$
39; $X = \text{CH}_2, R = H$
40; $X = \text{CH}_2, R = \text{CH}_3$
41; $X = \text{Se}, R = H$
42; $E = \text{Se}$
43; $E = \text{Te}$
44; $R = \text{CH}_3, \text{L} = \text{PPh}_3$
45; $R = \text{CH}_3, \text{L} = \text{P(OMe)}_3$
46; $R = \text{CH}_3, \text{L} = \text{L'} = \text{P(OMe)}_3$
47; $R = \text{CH}_3, \text{L} = \text{PPh}_3, \text{L'} = \text{CO}$
48; $R = \text{CH}_3, \text{L} = \text{P(OMe)}_3, \text{L'} = \text{CO}$
49; $R = \text{CH}_3, \text{L} = \text{L'} = \text{P(OMe)}_3$
50; $R = \text{CH}_3, \text{L} = \text{P(OMe)}_3$
51; $R = \text{CH}_3, \text{L} = \text{PPh}_2\text{PPh}_2$
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\}.

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)]](image-url)

\[ R = \text{alkyl, aryl, alkylchloride} \]
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. 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$_2$[μ-S$_2$(C$_3$H$_6$)$_2$S-μ](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.](image)

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$_2$C(Me)(CH$_2$S)$_2$}] (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 [Fe₂(CO)₅(CN){RSCH₂C(Me)(CH₂S-μ)₂}]⁻ (61) has not been isolated (Scheme 4).[176-180]

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 Fe₂[μ-S₂(C₃H₆)₂S-μ](CO)₅ (59), toward neutral nucleophiles such as P(OMe)₃ and PMe₃.[AD2] In this work, we were able to isolate and characterize a complex containing free thioether (65) Fe₂(μ-S₂(C₃H₆)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 Fe₂(μ-S₂(C₃H₆)₂S-μ)(CO)₄P(OMe)₃ (66) and the dissubstituted Fe₂(μ-S₂(C₃H₆)₂S)(CO)₄[P(OMe)₃]₂ (67), and Fe₂(μ-S₂(C₃H₆)₂S)(CO)₄[PMe₃]₂ (68) complexes (Figure 13).
2.5 \{2\text{FeS}\}- and \{2\text{Fe2S}\}-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.\cite{184-189} Recently, we investigated the reactions of the di- or tetra-substituted 5-membered 1,2,4-trithiolans with Fe\(_2\)(CO)\(_9\), to give model complexes as shown in Scheme 5.\cite{142}

\[
\begin{align*}
3 \text{Fe}_2\text{(CO)}_9 & \quad + \quad \text{R}_1 = \text{R}_2 = \text{H, Me, Et; R}_1 = \text{H, R}_2 = \text{cyclohexyl} \\
\text{Scheme 5. The reaction of 1,2,4-trithiolanes with Fe}_2\text{(CO)}_9. \quad \text{[After ref 142]} 
\end{align*}
\]

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)\(_{12}\).\cite{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. The fragments (e.g., Ph$_2$C=S (70)) react with Fe$_3$(CO)$_{12}$ to yield the ortho-metallated complex Fe$_2$(CO)$_6$(κ,μ-S,η$_2$-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)$_6$(κ,μ-S,η$_2$-C$_{13}$H$_{10}$S) (71), Fe$_2$(CO)$_6$(κ,μ-S,η$_2$-C$_{17}$H$_{20}$N$_2$S) (77), Fe$_2$(CO)$_6$(κ,μ-S,η$_2$-C$_{15}$H$_{12}$S) (78) and Fe$_2$(CO)$_6$(κ,μ-S,η$_2$-C$_{13}$H$_8$OS) (79) were prepared and well characterized (Figure 14). The formation of similar thiobenzophenone-iron complex 71 and 77 was described by Alper et al. several decades ago. 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).

\[
\begin{align*}
R & = \text{aryl} \\
X & = \text{S, Se, Te, CN, CO, CR}_2, \text{etc}
\end{align*}
\]

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 (71) or 9H-xanthene-9-thione (80), under different conditions. In the case of 1:1 molar ratio of reactants, the ortho-metallated complexes \( \text{Fe}_2(\text{CO})_6(\kappa,\mu-\text{S},\eta^2-\text{C}_{13}\text{H}_{10}\text{S}) \) (71) and \( \text{Fe}_2(\text{CO})_6(\kappa,\mu-\text{S},\eta^2-(\text{C}_{13}\text{H}_8\text{S}_2)) \) (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; \( \text{Fe}_2(\text{CO})_6(\mu-\text{SCH(C}_6\text{H}_5)\text{C}_6\text{H}_4\text{S-}\mu) \) (82) and \( \text{Fe}_2(\text{CO})_6(\mu-\text{SCH(C}_6\text{H}_4)-\text{S-C}_6\text{H}_3\text{S-}\mu) \) (83), respectively. In addition to these complexes, the two reactions also afforded \( \text{Fe}_2(\text{CO})_6(\mu-\text{SC(C}_6\text{H}_5)_2)\text{S-}\mu) \) (84) and \( \text{Fe}_2(\text{CO})_6(\mu-\text{SC(C}_6\text{H}_4\text{S-C}_6\text{H}_4)\text{S-}\mu) \) (85), respectively. Furthermore, \( [\text{Fe}_2(\text{CO})_6(\mu-\text{SCH(C}_6\text{H}_5)_2)]_2(\mu^4-\text{S}) \) (86) was isolated from the reaction of \( \text{Fe}_3(\text{CO})_{12} \) 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)).\textsuperscript{[200, 201]}

Unfortunately, no reported model complex of the [FeFe]-hydrogenase active site has so far met these characteristics satisfactorily.\textsuperscript{[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.\textsuperscript{[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.\textsuperscript{[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.\textsuperscript{[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 \([\text{Fe}_2(\text{CO})_6(\mu-\text{pdt})]\) (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 \([\text{Fe}_2(\text{CO})_6(\mu-\text{bdt})]\) (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). 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, μ2 to μ1 rearrangement of a bridging thiolate is suggested.

Scheme 9. DFT calculated structures and mechanism of the catalytic reduction of protons to H2 by [Fe2(CO)6(μ-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. The protonation of nitrogen atom depends on the acid strength. Song and co-workers investigated the electrocatalytic generation of H2 by [{(μ-SCH2)2N(C6H4OMe-p)}Fe2(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. In contrast, Ott and co-workers, proposed ECEC mechanism for the H2
production from HClO₄ catalyzed by \([\{\mu\text{-SCH}_{2}\text{H}_{2}\text{N}\text{(C}_6\text{H}_4\text{Br-p})\}\text{Fe}_2\text{(CO)}_6]\) complex (94) (Scheme 10B).[211]

![Scheme 11. Proposed mechanisms for electrocatalytic production of H₂ by A) \([\{\mu\text{-SCH}_{2}\text{H}_{2}\text{N}\text{(C}_6\text{H}_4\text{OMe-p})\}\text{Fe}_2\text{(CO)}_6]\) (93) [After ref 134]; B) \([\{\mu\text{-SCH}_{2}\text{H}_{2}\text{N}\text{(C}_6\text{H}_4\text{Br-p})\}\text{Fe}_2\text{(CO)}_6]\) (94). [After ref 211]

In the present work, we examined complex Fe₂(CO)₆(µ-SCH(C₆H₃)C₆H₄S-µ) (82), as electocatalysis for the H₂ 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)$_6$(μ-SCH(C$_6$H$_5$)C$_6$H$_4$S-μ) (82) and Fe$_2$(CO)$_6$(pdt) (2), the Fe$_2$(CO)$_6$(bdt) complex, shows an initial two-electron reduction to a [Fe$^0$Fe$^0$] 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)$_6$(μ-S$_2$C$_{13}$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.


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


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 Fe₂(μ-Se₂C₃H₅CH₃)(CO)₆ (1) by triphenylphosphane, trimethyl phosphite, and bis(diphenylphosphanyl)ethane (dppe) ligands is investigated. Treatment of 1 with 1 equiv. of triphenylphosphane afforded Fe₂(μ-Se₂C₃H₅CH₃)(CO)₅(PPh₃) (2). The mono- and disubstituted phosphite complexes Fe₂(μ-Se₂C₃H₅CH₃)(CO)₅P(OMe)₃ (3) and Fe₂(μ-Se₂C₃H₅CH₃)(CO)₄[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 Me₃NO gave a mixture of Fe₂(μ-Se₂C₃H₅CH₃)(CO)₄(κ²-dppe) (5) and [Fe₂(μ-Se₂C₃H₅CH₃)(CO)₃]₂(μ-dppe) (6). The newly synthesized complexes 2–6 were fully characterized by IR, ¹H NMR, ¹³C NMR, ⁷⁷Se{¹H} NMR, and ³¹P{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 m³ 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 of Fe₂(μ-Se₂C₃H₅CH₃)(CO)₆ (1) by PPh₃ 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 = CH₂, NH, O, S). (b) Models of [FeFe]-hydrogenases containing diselenolato ligands (Y = CH₂, Se, NPh).
Results and Discussion

Stirring of \( \text{Fe}_2(\mu-\text{Se}_2\text{C}_2\text{H}_3\text{CH}_3)(\text{CO})_6 \) (1) at room temperature with 1 equiv. of triphenylphosphane in the presence of trimethylamine N-oxide dihydrate (Me_3NO-2H_2O) gives the complex \( \text{Fe}_2(\mu-\text{Se}_2\text{C}_2\text{H}_3\text{CH}_3)(\text{CO})_6(\text{PPPh}_3) \) (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 \( \text{Fe}_2(\mu-\text{Se}_2\text{C}_2\text{H}_3\text{CH}_3)(\text{CO})_6(\text{PPPh}_3)(\text{Me}_3\text{NO}) \) (3) and \( \text{Fe}_2(\mu-\text{Se}_2\text{C}_2\text{H}_3\text{CH}_3)(\text{CO})_6(\text{PPh}_3)_2(\text{P}(\text{OMe})_3)_2 \) (4) (Scheme 2), in which one (3) or two (4) carbonyl ligands are substituted by P(OMe)_3.

The reaction of compound 1 with 1 equiv. of dppe in the presence of Me_3NO-2H_2O gives a mixture of the chelated diiron complex \( \text{Fe}_2(\mu-\text{Se}_2\text{C}_2\text{H}_3\text{CH}_3)(\text{CO})_6(\text{P}(\text{OMe})_3)_2(\text{dppe}) \) (5) and the bridged tetracoiron complex \( \text{Fe}_2(\mu-\text{Se}_2\text{C}_2\text{H}_3\text{CH}_3)(\text{CO})_6(\text{P}(\text{OMe})_3)_2(\text{dppe})_2 \) (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 \(^1\text{H}\) NMR spectra for 2-6 exhibit a doublet at \( \delta = 1.09, 1.28, 1.24, 1.52, \) and 1.03 ppm, respectively, for the methyl group of the diselenolato ligand. \(^1\text{H},^1\text{H}\) COSY, \(^1\text{H},^1\text{C}\) HSQC, and \(^1\text{H},^1\text{C}\) 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 \(^{13}\text{C}\){\(^{1}\text{H}\)} 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 \(^{77}\text{Se}\){\(^{1}\text{H}\)} NMR spectra for complexes 2-6 because of the presence of two different Se atoms. The \(^1\text{H}\)-\(^{77}\text{Se}\) HMBC spectrum allows the assignment of the two different Se atoms. The \(^{31}\text{P}\){\(^{1}\text{H}\)} NMR spectra of 2 and 3 show one signal at \( \delta = 72.1 \) and 193.1 ppm, respectively, whereas for 4 two resonances are observed at \( \delta = 186.5 \) and 189.2 ppm from the nonequivalent iron atoms.

The \(^{31}\text{P}\){\(^{1}\text{H}\)} NMR spectrum of 5 displays signals at \( \delta = 98.7 \) and 96.3 ppm (\( ^2\text{J}_{PP} = 20.3 \) 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 \(^{31}\text{P}\){\(^{1}\text{H}\)} NMR spectrum at \( \delta = 66.1 \) 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 \(^{31}\text{P}\){\(^{1}\text{H}\)} 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 \(^{31}\text{P}\){\(^{1}\text{H}\)} 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 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-
alogues\textsuperscript{[26,31–34]} The displacement of one or two carbonyl groups by phosphines or phosphite has only a small effect on the Fe–Fe distances as compared to that of \textbf{1} [2.5471(15) Å].\textsuperscript{[38]} The Fe–Fe bonds in \textbf{2}–\textbf{6} are longer than those in the sulfur derivatives (\textbf{2}: 2.5573(16) Å [sulfur derivative: 2.5247(6) Å\textsuperscript{[26]}], \textbf{3}: 2.5881(12) Å [sulfur derivative: 2.5142(9) Å\textsuperscript{[30]}], \textbf{4}: 2.5506(6) Å, \textbf{5}: 2.6180(7) Å [sulfur derivative: 2.547(7) Å\textsuperscript{[26]}], \textbf{6}: 2.5506(13) Å [sulfur derivative: 2.5108(14) Å\textsuperscript{[31]}]) because of the larger size of the selenium atoms\textsuperscript{[26,31–34]} The Fe–Se bonds in \textbf{2}–\textbf{6} are slightly longer (ca. 0.017 Å) than that in the unsubstituted compound \textbf{1} due to the stronger $\sigma$-donor properties of phosphines or phosphite ligands compared to carbonyl groups.\textsuperscript{[38]} The Fe–P bond lengths (\textbf{2}: 2.246(2) Å, \textbf{3}: 2.1596(17) Å, \textbf{4}: 2.1651(8) Å and 2.1601(9) Å, \textbf{5}: 2.2323(11) Å and 2.1913(9) Å, \textbf{6}: 2.2236(18) Å) are comparable to those observed for sulfur and selenium analogues.\textsuperscript{[26,31–34,40]} In compounds \textbf{2}–\textbf{4} and \textbf{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 \textbf{5} (Figure 4). In principle, for the monosubstituted complexes \textbf{2} and \textbf{3} the phosphate ligand may occupy an apical or basal position. The X-ray crystal structure of \textbf{2} shows that the phosphate ligand occupies an apical position. In addition, the stereochemistry of \textbf{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$_2$CH$_2$CH(CH$_3$)$_2$ moiety resulting in an equatorial or axial CH$_3$ group and the flap pointing toward or away from the phosphate ligand. It can be seen from the X-ray structure of \textbf{2} that the CH$_3$ group is equatorial and trans to the phosphate ligand and the flap points away from the phosphate ligand. As pointed out above, the $^{31}$P NMR spectrum of \textbf{2} shows only one resonance signal suggesting that only one diastereomer is present. In \textbf{3} the P ligand is basal. There are two different basal positions owing to the dissymmetry induced by the CH$_2$CH$_2$CH(CH$_3$)$_2$ bridge. In \textbf{3} the phosphate ligand occupies the basal position syn to the equatorial CH$_3$ group, and the flap points toward the phosphate ligand. In \textbf{4} the phosphate ligands are on different Fe atoms, and both occupy apical positions with the equatorial CH$_3$ group. Owing to the dissymmetry of the CH$_2$CH$_2$CH(CH$_3$)$_2$ moiety the two phosphate ligands are nonequivalent as already noted above in the $^{31}$P NMR spectroscopic analysis. For \textbf{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 \textbf{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 phosphate ligand, and the flap points toward the phosphate ligand. The stereochemistry for the two 2Fe2Se centers is the same.
Diiron Diselenolato Complexes as Models for [Fe-Fe]-Hydrogenases

Figure 4. ORTEP drawing of Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_4$(κ$^2$-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 5. ORTEP drawing of [Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_5$]$_2$(μ-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. Addition of acetic acid results in catalytic reduction at the main peak rather than a separate, more negative peak as seen with 1 (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$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(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$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_4$(κ$^2$-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$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_5$]$_2$(μ-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,$^{15}$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$_2$O as the reference. The $^{77}$Se chemical shifts are reported relative to neat Me$_2$Se [δ(MeSe) = δ(SeO$_2$) + 1302.6 ppm]. External standard 85% H$_3$PO$_4$ was used as a reference for $^{13}$C($^1$H) NMR spectroscopy. The mass spectra were recorded with a Finnigan 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$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_5$(PMe$_3$)$_2$ (I) was prepared according to a literature procedure.[10]

**Preparation of Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_5$PPh$_3$ (2):** A solution of I (60 mg, 0.12 mmol) and Me$_3$NO·2H$_2$O (24 mg, 0.22 mmol) in MeCN was stirred at room temperature for 10 min. Then, triphenylphosphine (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$_2$Cl$_2$ and the solution column-chromatographed (SiO$_2$/hexane). From the major red fraction, which was also recrystallized from pentane at –25 °C. Yield 67 mg (77 %).

**Preparation of Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_5$PPh$_3$ (3):** A solution of Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_5$(PMe$_3$)$_2$ (I) was prepared according to a literature procedure.[38] A solution of Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_5$(PMe$_3$)$_2$ (4):[10] was prepared according to a literature procedure.[38]

**Synthesis of Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_5$(PMe$_3$)$_2$ (4):** A solution of I (98 mg, 0.20 mmol) and Me$_3$NO·2H$_2$O (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$_2$Cl$_2$ (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$_2$Cl$_2$ (1:2) as the eluent. Complex 5 was obtained from the first red fraction and recrystallized from hexane/CH$_2$Cl$_2$ at –25 °C. A second red brownish band provided complex 6, which was also recrystallized from hexane/CH$_2$Cl$_2$ at –25 °C.

**Preparation of Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_5$PMe$_3$ (3):** A solution of trimethyl phosphite [P(OMe)$_3$; 67 mg, 0.54 mmol] and I (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$_2$Cl$_2$ 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$_2$Cl$_2$ (1:2) and then pure CH$_2$Cl$_2$ as eluents. Complex 3 was recrystallized from hexane at –25 °C and 4 from ethyl ether at 0 °C.

Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_5$PMe$_3$ (3): Yield 38 mg (36 %). M.p. 25.75 °C. $^1$H NMR (50 MHz, CDCl$_3$): δ = 29.4 (SeCH$_3$), 32.8 (CH$_2$), 37.1 (SeCH), 38.6 (SeCH$_2$CH$_3$), 52.0, 52.4 (P(OMe)$_3$), 210.4, 210.9 (CO) ppm. $^{77}$Se($^1$H) NMR (76 MHz, CDCl$_3$): δ = 396 (SeCH$_3$), 403 (SeCH) ppm. $^{31}$P($^1$H) NMR (200 MHz, CDCl$_3$): δ = 193.9 (P(OMe)$_3$) ppm. FTIR (KBr): ν = 2040 (s), 1985 (vs), 1931 (m) 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].
Table 1. Crystal data and refinement details for the X-ray structure determinations.

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

(200 MHz, CDCl$_3$); $δ = 66.1, 66.2$ (2 PPh$_3$) ppm. FTIR (KBr): $\tilde{ν} = 3053$ (vs), $1972$ (vs), $1916$ (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 Kappa CCD diffractometer 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 $F^2$ (SHELXL-97).[47] All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. 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.

Acknowledgments

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References


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 phosphate and phosphine ligands at compound Fe₂(μ-S₂(C₃H₆)S)-μ(CO)₃ (1) have been investigated. The reaction of 1 with 1 equiv of trimethylphosphite gave the kinetically controlled product Fe₂(μ-S₂(C₃H₆)S)(CO)₅(P(OMe)₃) (2) or the thermodynamically controlled product Fe₂(μ-S₂(C₃H₆)S)-μ(CO)₅(P(OMe)₃) (3) depending on the reaction conditions. Moreover, Fe₂(μ-S₂(C₃H₆)S)-μ(CO)₅[P(OMe)₃] (4) and Fe₂(μ-S₂(C₃H₆)S)-μ(CO)₅(PMe₃) (5) were obtained from the reactions of 1 with excess P(OMe)₃ and excess PMe₃, respectively. These novel complexes have been characterized by IR, 1H, 13C{1H}, and 31P{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. 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 Fe₂(μ-S₂(C₃H₆)S)-μ(CO)₃ (1), which can be envisioned as a model complex 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.² Seven

Pickett described the effect of the thioether sulfur atom on the substitution of CO ligands at the complex [Fe₂(CO)₅(MeSCH₂C(Me)(CH₂S₂))-μ(CN)] and its benzyl thioether analogue by cyanide. The mechanism and the kinetics of these reactions have been extensively studied. However the proposed intermediate [Fe₂(CO)₅(MeSCH₂C(Me)(CH₂S₂))-μ(CN)] in the reaction mechanism has never been isolated. Because of this, 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 trimethylphosphine (PMe₃).

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 Fe₂(μ-S₂(C₃H₆)S)-μ(CO)₅(P(OMe)₃) (2), which upon standing at room temperature for 90 min converted to Fe₂(μ-S₂(C₃H₆)S)-μ(CO)₅(P(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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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 $^{13}C$ NMR spectra of 2 always contain resonance signals of 3. The $^{1}H$ and $^{13}C$ NMR spectra of 3 exhibit a singlet at 3.74 ppm and at 52.0 ppm, respectively, corresponding to the $\text{P(OMe)}_{3}$ 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 $\text{S(CH}_{2}\text{)}_{3}\text{S(CH}_{2}\text{)}_{3}\text{S}$ moiety. These resonances are in the same range as those observed for 1.$^{1}$ The $^{31}\text{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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CO ligands. The Fe–Fe bond length of 3 is significantly longer than that of 1 due to replacement of a CO group by P(OMe)$_3$, and it is slightly longer than that observed for [Et$_4$N][Fe$_2$(MeSCH$_2$C(Me)(CH$_2$S)$_2$)(CN)(CO)$_5$P(OMe)$_3$]$_2$. 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 and [Et$_4$N][Fe$_2$(MeSCH$_2$C(Me)(CH$_2$S)$_2$)(CN)(CO)$_5$P(OMe)$_3$]$_2$. The iron–thiolato bond lengths in 2 and 3 are in the same range reported for analogous complexes. The reaction of 1 with excess P(OMe)$_3$ under reflux gave the disubstituted complex Fe$_2$($\mu$-S$_2$C($H_2$)$_2$S)$\mu$-P(OMe)$_3$$_2$ (4) in 85% yield (Scheme 4). Moreover, stirring of 1 with excess PMe$_3$ at 120 °C for 24 h gave the PMe$_3$ substituted complex Fe$_2$($\mu$-S$_2$C($H_2$)$_2$S)$\mu$-P(OMe)$_3$$_2$(PMe$_3$)$_2$ (5).
afforded the analogous disubstituted complex $\text{Fe}_2(\mu-S_2\text{C}_6\text{H}_{12})_2\text{S}((\text{CO})_4\text{PMe}_3)_2$ (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 $^1\text{H}$ 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 $\text{SCH}_2\text{CH}_2$, $\text{SCH}_2\text{CH}_2$, and $\text{CH}_2\text{SCH}_2$ moieties, respectively. Their $^1\text{H},^1\text{H}$ COSY and $^1\text{H},^{13}\text{C}$ HSQC analysis verified the assignments of the $^{13}\text{C}$ resonances at 26.9, 31.9, 32.6 ppm (4) and 28.2, 32.1, 32.4 ppm (5). In addition, the $^{13}\text{C}$ resonances for the methyl groups of 4 (51.8 ppm), 5 (20.3 ppm) and the carbonyl groups were observed as expected. The $^{31}\text{P}[^1\text{H}]$ NMR spectrum of 4 displays one broad resonance at $\delta$ 180.6 ppm at 25 °C, indicative of the two phosphite ligands, which are fast exchange on the NMR time scale. Upon cooling the sample to $-40^\circ\text{C}$, this signal splits into an AB spin system (180.6 and 183.7 ppm) with coupling constant $J_{\text{P,H}} = 38.9$ Hz, due to the apical and basal positions of the two phosphite ligands. The $^{31}\text{P}[^1\text{H}]$ NMR spectrum of 5 consists of a broad singlet at $\delta$ 29.2 ppm, which upon cooling to $-40^\circ\text{C}$ 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 $\nu = 1906, 1522, 2040$ cm$^{-1}$ (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 $\pi$-acceptor property of $\text{P}((\text{OMe})_3$ compared to that of the thioether sulfur atom. The values of $\nu$(CO) in complexes 3–5 are as expected for the well-known electronic properties of the P-donor ligands.

**Conclusion**

Substitution reactions of CO by $\text{P}((\text{OMe})_3$ 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 $[2\text{FeS}]$ cluster.

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 Finngan 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$_2(\mu-S_2\text{C}_6\text{H}_{12})_2\text{S}((\text{CO})_4\text{PMe}_3)_2$ (1) was prepared according to a literature protocol.

Preparation of Fe$_2(\mu-S_2\text{C}_6\text{H}_{12})_2\text{S}((\text{CO})_4\text{PMe}_3)_2$ (2). Tri-methylphosphate (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

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Volatiles were removed under vacuum. The bright red solid 2 was recrystallized from a mixture of CH₂Cl₂/pentane at −25 °C. Yield 48 mg (93%). Anal. Calcld for C₁₄H₂₁Fe₂O₇S₃P: C, 31.07; H, 4.13; S, 17.56. ¹H NMR (400 MHz, CDCl₃): θ = 1.800−0.482 ppm. ppm. ³¹P(¹H) NMR (200 MHz, CDCl₃): δ = 180.6 (s, br, 2P(OMe)₃) ppm. ³¹P(¹H) NMR (200 MHz, CDCl₃): δ = 180.6 (d, J₃P = 38.9 Hz, P(OMe)₃), 183.7 (d, J₃P = 38.9 Hz, P(OMe)₃) ppm. IR (KBr disk): ν = 2008 (s), 1962 (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 Fe₂(μ-μ₂-S₂(C₃H₆P=S)₂)₃(P(OMe)₃) (4). Triethylphosphine (30.4 mg, 0.4 mmol) was added to a solution of 3 (55 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. Calcld for C₁₈H₂₁Fe₂O₃P₈S₄: C, 34.55; H, 5.44; S, 17.29. Found: C, 34.54; H, 5.46; S, 17.35. ¹H NMR (400 MHz, CDCl₃): δ = 1.51 (d, J₂P = 7.6 Hz, 18H, P(OMe)₃), 1.98 (m, 4H, SCH₂CH₂), 2.42 (m, 4H, FeSCH₂), 2.62 (m, 4H, SCH₂CH₂) ppm. ³¹C(¹H) NMR (50 MHz, CDCl₃): δ = 20.3 (P(OMe)₃), 28.2 (FeSCH₂), 32.1 (SCH₂CH₂), 32.4 (SCH₂CH₂), 215.8 (CO) ppm. ³¹P(¹H) NMR (200 MHz, CDCl₃): δ = 29.2, (s, br, 2PMe₃) ppm. ³¹P(¹H) NMR (200 MHz, CDCl₃): δ = 22.9, (s, br, PMe₃), 37.6 (s, br, PMe₃) ppm. IR (KBr disk): ν = 2003 (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. Crystallographic data as well as structure solution and refinement details are summarized in Table 1. The structures were solved by direct methods (SHELXS) and refined by full-matrix least-squares techniques against F² (SHELXL-97). All hydrogen atoms were included at calculated positions.


positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. 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.


Reactions of Selected Aromatic Thioketones with Dodecarbonyltriiron


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

Dodecarbonyltriiron reacts with 3,3,5,5-tetraphenyl-1,2,4-trithiolanes (1e) to give the ortho-metalated complex Fe2(CO)9[S2Fe2(CO)6] (9a), complexes of the type (Ph3C)2S2Fe2(CO)6 and the well known trinuclear complex Fe3S2(CO)9 as by-products. Complex 9a can also be obtained from the reaction of Fe3(CO)12 with thiobenzophenone (2a). In a similar way, 4,4′-bis(dimethylamino)thiobenzophenone (2b) reacts with Fe3(CO)12 to give three major products of hetero-metalation at the formation of similar thiobenzophenone–iron complexes 4a, b, c, and d 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]-cycloaddition at around 50 °C and forms an equilibrium mixture of thiobenzophenone S-sulfide (7), diphenylthiirane (8), and thiobenzophenone (2a) (Scheme 3).[31–37] Reactions of aromatic thioketones 2a, b with Fe3(CO)9 yielded the ortho-metalated complexes 4a, b as the major products, together with small amounts of complexes of the type (Ar2C)2S2Fe2(CO)9 (5 and 6) and the well-known trinuclear complex Fe3S2(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.

Introduction

In two recent papers we described the oxidative addition reactions of heterocyclic trisulfides, such as 1,2,4-trithiolenes, 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 Fe3(CO)9 to give three major products containing dithiolatoiron 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 Fe3(CO)9 are reported to give the complexes shown in Scheme 1.[22]

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 Fe3(CO)9. 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

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Results and Discussion

The reaction of 1e with Fe₃(CO)₁₂ in boiling THF furnished complex 9a as the major product, and complexes of the type (Ph₂C)S₂Fe₂(CO)₆ and Fe₃S₂(CO)₉ as by-products (Scheme 4). Complex Fe₃(CO)₁₂ is used for the reaction instead of Fe₂(CO)₉ because of its higher solubility and selectivity. Complex 9a can also be obtained from the reaction of Fe₃(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.

To date, reports of the reactions of aromatic thio ketones with carbonyliron complexes are scarce. Only very recently, a paper appeared in which the reactions of thiobenzophenone (2a) and 4,4'-bis(dimethylamino)thiobenzophenone (2b) with Fe₂(CO)₉ in anhydrous benzene at room temperature.

Scheme 2. Treatment of thiobenzophenone (2a) and 4,4'-bis (dimethylamino)thiobenzophenone (2b) with Fe₂(CO)₉ in anhydrous benzene at room temperature.

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

Scheme 4. Reaction of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (1e) with Fe₃(CO)₁₂.

Scheme 5. Reactions of thiobenzophenone (2a) and 4,4'-bis (dimethylamino)thiobenzophenone (2b) with Fe₃(CO)₁₂ to give the ortho-metalated complexes 9a and 9b, respectively.

The reaction of 4,4'-bis(dimethylamino)thiobenzophenone (2b) with Fe₃(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\textsuperscript{28–30} and based on the spectroscopic data complexes 9a and 9b seem to be identical to those reported by Alper et al.\textsuperscript{[29]}

Refluxing a THF solution of dibenzosuberenethione (2c) or xanthione (2d) with Fe\textsubscript{3}(CO)\textsubscript{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\textsubscript{3}(CO)\textsubscript{12}, trace amounts of a red-colored fraction (with an \(R\_t\) 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\textsuperscript{-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.\textsuperscript{[29]} The C–S bond stretching frequency for compounds 9a–d is found in the range 572–581 cm\textsuperscript{-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.

The \(^1\text{H}\) NMR spectra of 9a–d show singlet resonances at \(\delta = 5.55, 5.28, 6.12,\) and 4.60 ppm, respectively, corresponding to the methine protons. The \(^1\text{H}\) NMR resonances of the methylene protons in complex 9c appear as three sets of multiplets at \(\delta = 2.96, 3.40,\) and 3.66 ppm. The \(^1\text{H}\) NMR spectrum of 9b consists of singlets at \(\delta = 2.86\) and 3.02 ppm assigned to the 12 protons of the two NMe\textsubscript{2} groups. The hydrogen atoms on the coordinated aromatic rings in compounds 9a–d are generally deshielded, possibly by the tricarboylnir group, with the protons next to the Fe–C sigma bond being the most deshielded. Their resonances appear as doublets at \(\delta = 8.36\) (9a; \(\textit{J} = 8.2\) Hz), 7.49 ppm (9b; \(\textit{J} = 9.0\) Hz), and 7.95 ppm (9d; \(\textit{J} = 8.0\) Hz) and a multiplet at \(\delta = 7.97\) ppm (9e). The C–S sigma bonds in 9a–d are evidence by the characteristic chemical shifts in the \(^{13}\text{C}\{^1\text{H}\}\) NMR (\(\delta = 63.3, 63.3, 60.2,\) and 52.5 ppm for 9a–d, respectively). In addition, the \(^{13}\text{C}\) 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

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{ORTEP drawing of Fe\textsubscript{3}(CO)\textsubscript{12}[\(\kappa_{\mu-S}\eta^2-(\text{Ph}_2\text{CHS})\)] (9a) with thermal ellipsoids set at the 50\textsuperscript{\%} 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), F2–C13–Fe1 73.15(14), Fe1–Fe2–S1 56.77(3), Fe1–Fe2–S1 56.77(3), Fe1–S1–Fe2 67.46(4), Fe2–Fe1–S1 55.78(3).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{ORTEP drawing of Fe\textsubscript{3}(CO)\textsubscript{12}[\(\kappa_{\mu-S}\eta^2-(\text{C}_9\text{H}_{18}\text{N}_2\text{S})\)] (9b) with thermal ellipsoids set at the 50\textsuperscript{\%} 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).}
\end{figure}
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.[11–15] The Fe–S bond lengths are found to be within the same range observed for the hydrogenase model complexes.[10–18,24–29] 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) and is significantly longer than the corresponding bond of Fe(PMe3)_2(Me)(κ,S,C-Ph2C=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]

**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 Fe3(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., Ph2C=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 Fe3(CO)9[κ,μ-S,η2-(C13H12Si)] (9a), Fe3(CO)9[κ,μ-S,η2-(C15H20N2S)] (9b), Fe3(CO)9[κ,μ-S,η2-(C17H18OS)] (9c), and Fe3(CO)9[κ,μ-S,η2-(C15H8OS)] (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 heterodiienes with Fe3(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 2e and 2d with Fe3(CO)12. In contrast, the reactions of 2a and 2b with Fe3(CO)12 yielded the ortho-metalated complexes 9a and 9b as major products, together with complexes of the type (Ar5C)9SiFe3(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 13C{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 200 FT-IR spectrometer. Thiobenzenophene,[41] 4,4′-bis(dimethylamino)thiobenzenophene,[41] 3,3,5,5-tetraphenyl-1,2,4-trithiolanes,[42] dibenzosuberenethione,[43] and xanthione[44] were prepared according to literature procedures. Solvents and Fe3(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 aluminium sheets Silica gel 60 F254. Elemental analyses were performed with a Vario EL III CHNS (Elementaranalyse GmbH Hanau) as single determinations.

**Fe(CO)₃(S₆O₆)(PhCH₂CH) (9a):** Thiobenzophenone (2a) (50 mg, 0.25 mmol) or 1e (107 mg, 0.25 mmol) was added to a solution of Fe(CO)₃Cl (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%).

**Fe2(CO)6(2-(C13H8OS)) (9d):** 4,4'-Bis(dimethylamino)thiobenzophenone (2b) (50 mg, 0.18 mmol) was added to a solution of Fe(CO)₃Cl (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%).

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

<table>
<thead>
<tr>
<th></th>
<th>9a</th>
<th>9b</th>
<th>9c</th>
<th>9d</th>
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<tbody>
<tr>
<td>Formula</td>
<td>C₁₉H₁₀Fe₂O₆S</td>
<td>C₂₃H₂₀Fe₂O₆S</td>
<td>C₁₁H₁₂Fe₂O₆S</td>
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<tr>
<td>M (g mol⁻¹)</td>
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<td>564.17</td>
<td>504.07</td>
<td>492.01</td>
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<tr>
<td>T (°C)</td>
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<td>–90(2)</td>
<td>–90(2)</td>
<td>–140(2)</td>
</tr>
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<td>triclinic</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
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<td>P2₁/c</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>a [Å]</td>
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<td>9.5488(4)</td>
<td>8.0761(4)</td>
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<td>7.9376(5)</td>
<td>10.0657(4)</td>
<td>10.3929(6)</td>
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<td>c [Å]</td>
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<td>33.3515(16)</td>
<td>11.6416(4)</td>
<td>11.4083(6)</td>
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<td>90</td>
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<td>90</td>
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<td>2414.62(2)</td>
<td>994.32(7)</td>
<td>928.37(9)</td>
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<td>2</td>
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<td>1.760</td>
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<td>6851</td>
<td>6525</td>
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<td>3199</td>
<td>3452</td>
<td>3156</td>
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<td>53190/1058</td>
<td>44780/0.0281</td>
<td>42370/0.0333</td>
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<td>wR₂ [all data, on F²][b]</td>
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<td>0.1802</td>
<td>0.0843</td>
<td>0.0823</td>
</tr>
<tr>
<td>R₁ [I &gt; 2σ(I)][b]</td>
<td>0.0524</td>
<td>0.0714</td>
<td>0.0358</td>
<td>0.0414</td>
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<tr>
<td>R[F²]</td>
<td>0.959</td>
<td>1.042</td>
<td>1.008</td>
<td>0.999</td>
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<td>Residual electron density [eÅ⁻³]</td>
<td>0.512(5–0.523)</td>
<td>0.639(5–0.479)</td>
<td>0.339(5–0.377)</td>
<td>0.395(5–0.412)</td>
</tr>
</tbody>
</table>

[a] Definition of the R indices: R₁ = (Σ||F₁|| – |F₂||)/Σ|F₁|, wR₂ = (Σ[w(|F₁|² – |F₂|²)]²)/Σ[w(|F₁|²)]² w⁻¹ = σ(|F₁|²) + (αP)² + bP, P = [2F₁² + max(F₁²)³]/3. [b] s = (Σ(|F₁|² – |F₂|²)/(N₀ – N₀′))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_{3}H_{3}Fe_{2}O_{5} (491.8): calculated C 46.38, H 1.64, S 6.52; found C 46.01, H 1.84, S 6.06. 1H NMR (400 MHz, CDCl₃, 25 °C): δ = 4.63 (s, 1 H, 12-H), 6.81 (d, J = 7.6 Hz, 1 H, 7-H), 7.00 (dd, J = 7.8 Hz, 1 H, 9-H), 7.2 (d, J = 8.2 Hz, 1 H, 10-H), 7.27 (dd, J = 7.7 Hz, 1 H, 8-H), 7.38 (dd, J = 7.7 Hz, 1 H, 3-H), 7.53 (d, J = 7.6 Hz, 1 H, 4-H), 7.95 (d, J = 8.0 Hz, 1 H, 2-H) ppm. 13C[H] NMR (400 MHz, CDCl₃): 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_{6}H_{12}): ν = 2072 (vs), 2037 (vs), 2001 (v), 1985 (s, sh) ν = 583 cm⁻¹. DEI-MS: m/z = 492 [M⁺], 464 [M⁺ – CO], 236 [M⁺ – 2CO], 208 [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-Kα radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects.[4-6] Crystallographic data as well as structure solution and refinement details are summarized in Table 1. The structures were solved by direct methods (SHELXS)[6] and refined by full-matrix least-squares techniques against F² (SHELXL-97).[7] The hydrogen on 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.[7] 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.

Acknowledgments

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Reactions of Aromatic Thioketones with Dodecarbonyltriiron


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

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Ulrich S. Schubert,[b] Mohammad El-khateeb,[e][‡‡] Grzegorz Młoston,*[d] and
Wolfgang Weigand*[a]

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 9H-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 [Fe2(CO)6[μ-k,S,SCH(C6H4)C6H4-η2]] (3a) and [Fe2(CO)6[μ-k,S,SCH(C6H4)-S-C6H4-η2]] (4a) were obtained as the major products, respectively. In contrast, the treatment of triiron dodecacarbonyl with an excess of 2a or 2b afforded [Fe2(CO)6[μ-SCH(C6H4)C6H4S-μ]] (3b) and [Fe2(CO)6[μ-S,SCH(C6H4)-S-C6H4S-μ]] (4b), respectively, which are both bioinspired models for the active site of [FeFe]-hydrogenase. In addition to these complexes, the two reactions afforded [Fe2(CO)6[μ-SC(C6H4)2S-μ]] (3c) and [Fe2(CO)6[μ-SC(C6H4-STS-C6H4S-μ)] (4c). Furthermore, [Fe2-(CO)6[μ-SCH(C6H4)2]2(μ4-S)] (3d) was isolated from the reaction of Fe3(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 H2.[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 evolution ability compared to that of other hydrogenases.[6–8] Microorganisms have used H2 as a primary fuel source for billions of years and consume an enormous amount of H2 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 dio- 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 Fe3(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]-cycloversion reaction[12,13a] and the fragments [e.g., Ph2C=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-
matic thioketones, 4,4′-bis(dimethylamino)-thiobenzophenone, dibenzosuberene-thione, and xanthione, respectively, were treated with Fe₃(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 Fe₃(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 Fe₃(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, [Fe₃(CO)₁₂{μ-κ,S,SCH(C₆H₄)C₆H₄–η²}] (3a) and [Fe₃(CO)₁₂{μ-κ,S,SCH(C₆H₄) –C₆H₄–η²}] (4a), respectively, as the major products. In addition to 3a, complexes [Fe₃(CO)₁₂{μ-S,SCH(C₆H₄)C₆H₄–μ}] (3b) and [Fe₃(CO)₁₂{μ-SC(C₆H₄)S–μ}] (3c) produced from the reaction of Fe₃(CO)₁₂ with 2a. Similarly, complexes [Fe₃(CO)₁₂{μ-SC(C₆H₄) –C₆H₄–S–μ}] (4b) and [Fe₃(CO)₁₂{μ-SC(C₆H₄) –C₆H₄–S–μ}] (4c) were isolated along with 4a from the reaction of Fe₃(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 Fe₃(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, [{Fe₃(CO)₁₂{μ-SCH(C₆H₄)₂}μ–S}] (3d), and known tetrphenylethylene

Scheme 1. The reaction of Fe₃(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 Fe₃(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 Fe₃(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 Fe₃(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]

Complex 3c is believed to be produced by the oxidative addition of Fe₃(CO)₁₂ along the S-S bond of the in situ-generated diphenylthiirane (7). The latter could be formed from 2a by means of a stepwise mechanism (Scheme 4) under the catalytic influence of the carboxylon 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 S₈. 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”.

The ¹H and ¹³C{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 ¹³C{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 δ < 6.2 ppm to indicate the presence of

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[Images of the schemes are not transcribed, but they are described in the text.]

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

Scheme 4. The reaction pathway for the formation of 3c via the intermediate diphenylthiirane (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.
methine protons in these complexes. The $^1$H NMR spectra of 3b and 4b show a singlet at $\delta = 5.90$ and 5.28 ppm, respectively, which corresponds to the methine protons. These values are shifted downfield compared to those of the analogues 3a and 4a, respectively. The $^1$H NMR spectrum of 3d reveals the presence of two methine groups and the resonances for these protons are found at $\delta = 4.21$ and 4.66 ppm, respectively. The $^{13}$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 $\mu^2$-coordinated to Fe(1) and Fe(2) in the structures of 3c, 4b, and 4c. However, the two sulfur atoms of the bridging di-thiolato ligand of complex 4b are connected to different carbon atoms. One of the sulfur atoms is bonded to an aliphatic carbon while the other one is bonded to an aromatic carbon. In complexes 3c and 4c, on the other hand, the sulfur atoms are both bonded to the same aliphatic carbon. All of the iron atoms in tetranuclear complex 3d are bonded to the same sulfur atom (S3) and, in addition, the thiolato sulfur atoms S(1) and S(2) are $\mu^2$-coordinated to Fe(1), Fe(2) and Fe(3), Fe(4), respectively. The Fe–Fe bond length of 4b [2.5218(5) Å] is comparable to those reported for the [FeFe]-hydrogenase model complexes$^{[10,10l,14–20]}$ and to that of 3d [2.5246 Å (mean)], but it is longer than the corresponding bond lengths in the analogous complexes 3e [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 [2.486[6](6) Å]$^{[11b]}$. The angles of S(1)–Fe(1)–S(2) [85.22(2)°] and S(1)–Fe(1)–Fe(2) [68.46(2), Fe(1)–S(1)–Fe(2) 67.789(16), Fe(1)–S(1)–Fe(3) 68.505(15), Fe(3)–S(2)–Fe(4) 72.831(14), Fe(3)–S(3)–Fe(4) 68.849(15), Fe(1)–S(3)–Fe(3) 136(74), S(2)–Fe(4)–S(3) 76.342(17), and S(1)–Fe(2)–Fe(1) 55.974(13).

Figure 2. The ORTEP drawing of [Fe$_2$(CO)$_6$($\mu$-SCH(C$_6$H$_5$)$_2$)$_2$] (3e) with the thermal ellipsoids set at the 50% probability level. The selected distances [Å] and angles [°] are Fe(1)–Fe(2) 2.4867(4), Fe(1)–S(1) 2.2785(6), Fe(1)–S(2) 2.2625(6), Fe(2)–S(1) 2.2757(6), Fe(2)–S(2) 2.2608(6), Fe(1)–S(1)–Fe(2) 66.190(19), Fe(1)–S(2)–Fe(2) 66.699(19), S(1)–Fe(1)–S(2) 72.21(2), and S(1)–Fe(2)–Fe(1) 56.618(17).

Figure 3. The ORTEP drawing of [Fe$_2$(CO)$_6$($\mu$-SCH(C$_6$H$_5$)$_2$)$_2$] (3d) with the thermal ellipsoids set at the 50% probability level. 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) 67.505(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) 76.342(17), and S(1)–Fe(2)–Fe(1) 55.974(13).

Figure 4. The ORTEP drawing of [Fe$_2$(CO)$_6$($\mu$-SCH(C$_6$H$_5$)$_2$)$_2$] (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(5), Fe(2)–S(2) 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) 72.831(14), Fe(3)–S(3)–Fe(4) 68.849(15), Fe(1)–S(3)–Fe(3) 136(74), S(2)–Fe(4)–S(3) 76.342(17), and S(1)–Fe(2)–Fe(1) 55.974(13).
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) [72.26(2)°] and S(1)–Fe(2)–S(2) [72.29(2)°] in 3c, and of S(1)–Fe(1)–S(2) [72.26(2)°] and S(1)–Fe(2)–S(2) [72.17(2)°] in 3e, which is attributed to the bonding of the two sulfur atoms of the dithiolato ligand to the same carbon in 3e or 4c.

Figure 5. The ORTEP drawing of [Fe2(CO)6{μ-SC(C6H4–S–C6H4)-S-μ1}] (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) 2.2543(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 $E_{p, red} = –1.58 \text{ V}$. In comparison to the internal standard ferrocene, this signal is most likely a one-electron reduction and was therefore attributed to the [Fe$^2$Fe$^0$]→[Fe$^1$Fe$^0$] process. The signal remained completely irreversible at the different scan rates (1.5, 1.0, 0.8, 0.1, and 0.05 V/s). This behavior suggests an EC mechanism where the [Fe$^2$Fe$^0$] state is transferred into [Fe$^1$Fe$^0$] 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 $–2.15 \text{ V}$ a further reduction of the chemically changed [Fe$^1$Fe$^0$] species was observed, which was attributed to the [Fe$^0$Fe$^0$]→[Fe$^0$Fe$^0$]$^2$ process in accordance with Fe$_2$(CO)$_6$(pdt) (pdt = propanedithiolato).[31] Two sparsely separated reoxidation signals were observed at $–2.07$ and $–2.00 \text{ V}$. An additional oxidation peak appears at $–0.80 \text{ V}$. This signal was only observed upon the initial one-electron reduction of the initial [Fe$^2$Fe$^0$] species at $–1.58 \text{ V}$. According to the literature, this might be the reoxidation of a chemically transformed [Fe$^1$Fe$^0$] species.[29] At ca. +1.28 V the irreversible oxidation of the [Fe$^0$Fe$^0$] cluster can be observed. A corresponding reduction signal appeared at $–0.67 \text{ mV}$, which suggests that there was structural reorganization after the oxidation and that it was not solely a simple reduction of the obtained [Fe$^0$Fe$^0$] complex as has been already described for similar reduction processes.

The influence of compound 3b towards the electrochemical reduction of protons to dihydrogen was investigated between 0.0 and $–2.5 \text{ V}$ by the addition of acetic acid (pKa = 22.3 in CH$_3$CN) (Figure 7). In the presence of acid, the initial one-electron reduction signal remains unchanged. Neither a significant increase nor a shift of the signal was observed. An acid-dependent increase in the peak current...
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 [Fe2(CO)6(pdt)] (pdt = propanedithiolato) (Fe–S-alkyl bond) and [Fe2(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 [Fe2(CO)6(pdt)],[31] [Fe2(CO)6(bdt)][10b] shows an initial two-electron reduction to a [Fe6Fe9] complex at −1.25 V (Table 1). This reduction, however, appears at two different potentials. The one-electron reduction of [Fe2(CO)6(pdt)] and 3b is observed at −1.34 and −1.58 V, respectively. In contrast to [Fe2(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, [{Fe2(CO)6(pdt)}], and [{Fe2(CO)6(bdt)}].

<table>
<thead>
<tr>
<th></th>
<th>(E_{\text{red}}) 1 [V]</th>
<th>(E_{\text{red}}) 2 [V]</th>
<th>(E_{\text{ox}}) [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>3b[a]</td>
<td>−1.58</td>
<td>−2.15</td>
<td>+1.28</td>
</tr>
<tr>
<td>[{Fe2(CO)6(pdt)}][b]</td>
<td>−1.34</td>
<td>−1.95</td>
<td>+1.14</td>
</tr>
<tr>
<td>[{Fe2(CO)6(bdt)}][10b]</td>
<td>−1.27</td>
<td>−1.23</td>
<td>irreversible</td>
</tr>
</tbody>
</table>

[a] Glassy carbon electrode (potentials given in V, ±0.01 vs. Fe/Fe\(^+\)).
[b] CH3CN solution (0.1 M) as the supporting electrolyte.
[c] CH3CN solution (0.01 M) with a glassy carbon working electrode standard vs. Fe/Fe\(^+\).

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 Fe2(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 \(\sigma\)-bond of 3a. It was found that complex 3b behaves as a catalyst for the electrochemical production of hydrogen in the presence of a weak acid, for example acetic acid, at a moderate potential.

The most remarkable feature of this investigation, however, is the assembly of a [FeFe]-hydrogenase active-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.[32b] 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 [Fe2(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.[32b]

Experimental Section

General Comments: All of the reactions were carried out under an argon atmosphere by using the standard Schlenk techniques. The \(^1\)H and \(^13\)C{\(^1\)H} NMR and 2D NMR spectra were recorded with a Bruker AVANCE 200 or 400 MHz spectrometer at room temperature and the solvent was used as the standard. The Mass spectra were obtained with a FINNIGAN MAT SSQ 710 instrument. The infra-red spectra were measured with a Perkin–Elmer System 2000 FTIR spectrometer. Thiobenzonaphene (2a)[32d] and 9H-thioxanthene-9-thione (2b)[13b] were prepared according to the literature procedures. The solvents and FeCO\(_2\) 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 F254. The elemental analyses were performed with a Vario EL III CHNS (Elementaranalysen GmbH Hanau) as single determinations.

\[\text{Fe}_2(\text{CO})_6(\mu-\text{SCH(CH}_3\text{)H}_2\text{H}_2\text{S})\cdot \text{Bu}_4\text{N}[\text{PF}_6] (3b), \text{Fe}_2(\text{CO})_6(\mu-\text{SC(CH}_3\text{)H}_2\text{)-S})\cdot \text{Bu}_4\text{N}[\text{PF}_6] (3c), \text{and } \{\text{Fe}_2(\text{CO})_6(\mu-\text{SCH(CH}_3\text{)H}_2\text{)-S})\cdot \text{Bu}_4\text{N}[\text{PF}_6]\}} \text{(3d). Method A: } \text{Fe}_2(\text{CO})_12 (100 mg, 0.2 mmol) \text{ and thiobenzonaphene (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 3b (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\(_{16}\)Fe\(_2\)O\(_2\)S\(_2\) (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): \(\delta = 5.90 \text{ [s, } 1 \text{ H, H(1)}\], 7.03–7.23 \text{ (m, } 5 \text{ H, } \text{Ar-H}), 7.32 \text{ [dd, } J = 7.7 \text{ Hz, } 1 \text{ H, H(10)}\], 7.37 \text{ [dd, } J = 8.1 \text{ Hz, } 1 \text{ H, H(11)}\], 7.75 \text{ [d, } J = 8.0 \text{ Hz, } 1 \text{ H, H(9)}\], 8.51 \text{ [d, } J = 8.2 \text{ Hz, } 1 \text{ H, H(12)}\] ppm. \(^1\)C{\(^1\)H} NMR (400 MHz, CDCl\(_3\), 70.7°C): \(\delta = 70.7 \text{ (C1)}, 123.8, 125.9, 125.7, 121.7, 128.2, 130.8, 136.3, 141.8, 143.7, 144.6, 152.5, 157.8 \text{ (2 Ph), 207.3, 208.9, 210.5 \text{ (CO) ppm. FTIR (KBr): } \nu_{\text{CO}} = 2073 \text{ (vs), 2035 \text{ (vs), 2080 \text{ (s), 1994 \text{ (s), 1979 \text{ (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].
New Approach to [FeFe]-Hydrogenase Models

3c: Yield 25 mg (25%). C10H8Fe2O2S2 (509.9): calcld. C 44.74, H 1.98, S 12.57; found C 44.96, H 1.72, S 12.23. 1H NMR (400 MHz, CDCl3, 25 °C): δ = 7.57 (br. s, 10 H, 2 Ph) ppm. 13C1H NMR (400 MHz, CDCl3): δ = 59.0 (SCS), 132.6, 127.7, 128.5 (2 Ph), 207.0, 208.2 (CO) ppm. FTIR (KBr): ν = 2076 (vs), 2035 (vs), 1900 (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%). C19H8Fe2O6S2 (540.1): calcld. C 46.09, H 2.24, S 9.72; found C 46.52, H 2.47, S 9.39. 1H NMR (200 MHz, CDCl3, 25 °C, assignment analogous to 3c). Yield 92 mg (37%). C19H8Fe2O6S3 (540.1): calcld. C 42.25, H 1.49, S 17.80; found C 42.58, H 1.68, S 17.30. 1H NMR (400 MHz, CDCl3, 25 °C, assignment analogous to 3d): δ = 5.28 ppm. 13C{1H} NMR (200 MHz, CDCl3): 6.07 ppm. 13C{1H} NMR (200 MHz, CDCl3): 6.29 ppm. 13C{1H} NMR (200 MHz, CDCl3): 6.40 ppm. 13C{1H} NMR (200 MHz, CDCl3): 6.51 ppm. 13C{1H} NMR (200 MHz, CDCl3): 6.62 ppm.

3e: Yield 48 mg (37%). C10H8Fe2O2S (504.1): calcld. C 42.25, H 1.49, S 17.80; found C 42.58, H 1.68, S 17.30. 1H NMR (400 MHz, CDCl3, 25 °C, assignment analogous to 3e): δ = 5.28 ppm. 13C{1H} NMR (200 MHz, CDCl3): 6.07 ppm. 13C{1H} NMR (200 MHz, CDCl3): 6.29 ppm. 13C{1H} NMR (200 MHz, CDCl3): 6.40 ppm. 13C{1H} NMR (200 MHz, CDCl3): 6.51 ppm. 13C{1H} NMR (200 MHz, CDCl3): 6.62 ppm.

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

| Compound | Formula | fw [g mol⁻¹] | T °C | Crystal system | Space group | a [Å] | b [Å] | c [Å] | α [°] | β [°] | γ [°] | V [Å³] | Z | ρ [g cm⁻³] | μ [cm⁻¹] | Measured data | Data with I > 2σ(I) | Unique data | wR2 | R1 [I > 2σ(I)] | χ² | χ²/ν | Residual electron density [e Å⁻³] | Absorption correction |
|----------|---------|-------------|------|----------------|-------------|------|------|------|------|------|------|------|-----|--------|--------|--------------|--------------|----------------|------|------|----------------|----------------------|
| 3c       | C6H6Fe2O3S3 | 540.13 | 190(2) | monoclinic | P2₁/n | 10.3982(3) | 9.1211(2) | 13.7459(2) | 110.7 | 90.0 | 90.0 | 2000.65(6) | 4 | 1.832 | 16.39 | 12241 | 8546 | 0.0727 | 0.0306 | 1.027 | 0.475–0.409 | none |
| 3d       | C6H6Fe2O3S3 | 529.13 | 140(2) | monoclinic | P2₁/c | 9.9014 | 13.7459(2) | 110.7 | 90.0 | 90.0 | 2000.65(6) | 4 | 1.644 | 16.39 | 12241 | 8546 | 0.0727 | 0.0306 | 1.027 | 0.475–0.409 | none |
| 3e       | C6H6Fe2O3S3 | 539.13 | 140(2) | monoclinic | P2₁/c | 9.9014 | 13.7459(2) | 110.7 | 90.0 | 90.0 | 2000.65(6) | 4 | 1.644 | 16.39 | 12241 | 8546 | 0.0727 | 0.0306 | 1.027 | 0.475–0.409 | none |
| 3f       | C6H6Fe2O3S3 | 519.09 | 140(2) | monoclinic | P2₁/c | 9.9014 | 13.7459(2) | 110.7 | 90.0 | 90.0 | 2000.65(6) | 4 | 1.644 | 16.39 | 12241 | 8546 | 0.0727 | 0.0306 | 1.027 | 0.475–0.409 | none |

[1] R1 = (Σ|Fobs| − |Fcalc|) / Σ|Fobs|; wR2 = (Σ[w(Fo² – Fc²)]² / Σ[w(Fo²)]²)¹/₂; w = σ(Fc) + (αP² + βP³) / |Fc|; P = 2|Fc| + max(|Fc|)/3. [b] s = |Σ[w(Fo² – Fc²)]² / (Nf – Np)|¹/₂.
Ph) ppm. $^{13}$C[1H] NMR (400 MHz, CDCl$_3$): $\delta$ = 93.9 (SCS, 123.8, 132.9, 137.0), 107, 4331–4365; b) C. Tard, C. J. Pickett, Chem. Rev. 2009, 109, 2245–2274.


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New Approach to [FeFe]-Hydrogenase Models


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The generation of the [FeFe]-hydrogenase model complexes \([\text{Fe}_2(\text{CO})_6\{\mu-\text{SCH-}
\text{C}_6\text{H}_2\text{C}_6\text{H}_4\text{S-}\mu\}]\) (3b) and \([\text{Fe}_2(\text{CO})_6\{\mu-
\text{SCH(C}_6\text{H}_2)-\text{S-C}_6\text{H}_2\text{S-}\mu\}]\) (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 \([\text{Fe}_2(\text{CO})_6\{\mu,\kappa,\kappa,\text{SCH(C}_6\text{H}_2\text{C}_6\text{H}_4-
\eta^1}\}]\) (3a) is the reaction pathway intermediate.

**Keywords:** Bioinorganic chemistry / Enzyme mimics / Hydrogenase models / Electrochemistry / Sulfur heterocycles / Thioketones / Iron
5. Documentation of authorship


- M. K. Harb: Synthesis and characterization of all complexes
- 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
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- W. Weigand: Supervision, Preparation of the manuscript


- A. Q. Daraosheh: Synthesis and characterization of all complexes
- M. K. Harb: Assistance in complex preparation
- J. Windhager: Assistance in manuscript preparation
- H. Görls: X-Ray structures analyses
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A. Q. Daraosheh: Synthesis and characterization of all complexes
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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 Fe₂(µ-Se₂C₃H₅CH₃)(CO)₆ (1) by PPh₃, P(OMe)₃, and bis(diphenylphosphanyl)ethane (dppe) has been investigated. The reaction of 1 with 1 equiv. of PPh₃ in acetonitrile at room temperature gave Fe₂(µ-Se₂C₃H₅CH₃)(CO)₅PPh₃ (2). Whereas treatment of 1 with excess P(OMe)₃ in refluxing toluene offered, the mono- and disubstituted phosphite complexes Fe₂(µ-Se₂C₃H₅CH₃)(CO)₅P(OMe)₃ (3) and Fe₂(µ-Se₂C₃H₅CH₃)(CO)₄[P(OMe)₃]₂ (4). In addition, the reaction of 1 with 1 equiv. of dppe in the presence of Me₃NO·2H₂O yielded two complexes Fe₂(µ-Se₂C₃H₅CH₃)(CO)₄(κ₂-dppe) (5), wherein the dppe ligand is chelated to a single iron atom, and [Fe₂(µ-Se₂C₃H₅CH₃)(CO)₃]₂(κ₂-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 Fe₂(µ-S₂(C₃H₆)₂S-µ)(CO)₅ (1), By P(OMe)₃ and PMe₃. The reaction of 1 with 1 equiv. of P(OMe)₃ in THF at room temperature afforded the first-formed kinetically controlled product Fe₂(µ-S₂(C₃H₆)₂S)(CO)₃P(OMe)₃ (2), which upon standing at room temperature for 90 min converted to Fe₂(µ-S₂(C₃H₆)₂S-µ)(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 PMe₃ gave exclusively the disubstituted complexes Fe₂(μ-
S₂(C₃H₆)₂S)(CO)₄[P(OMe)₃]₂ (4) and Fe₂(μ-S₂-(C₃H₆)₂S)(CO)₄(PMe₃)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
categorized 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), dibenzosuberethione (2c) and
xanthione (2d) with Fe₃(CO)₁₂. The ortho-metalated complex Fe₂(CO)₆-[κ,μ-S,η²-
(C₁₃H₁₀S)] (9a) was obtained by refluxing Fe₃(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 Fe₃(CO)₁₂ to yield 9a complex as the major
product. In addition, treatment of Fe₃(CO)₁₂ with 2b, 2c and 2d gave Fe₂(CO)₆[κ,μ-
S,η²-(C₁₇H₂ON₂S)] 9b, Fe₂(CO)₆[κ,μ-S,η²-(C₁₅H₁₂S)] 9c and Fe₂(CO)₆[κ,μ-S,η²-
(C₁₃H₈OS)] 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 Fe₃(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-metalated
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 Fe₃(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-metalated complexes Fe₂(CO)₆(μ,κ-
S, SCH(C₆H₅)C₆H₄-η²) (3a) and Fe₂(CO)₆(μ,κ; S, SCH[(C₆H₄)-S-C₆H₄-η²]) (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; Fe₂(CO)₆(μ-SCH(C₆H₅)C₆H₄S-μ) (3b) and Fe₂(CO)₆(μ-SCH(C₆H₄)-S-C₆H₄S-μ) (4b), respectively. In addition to these complexes, the two reactions also afforded Fe₂(CO)₆(μ-SC(C₆H₅)₂S-μ) (3c) and Fe₂(CO)₆(μ-SC(C₆H₄-S-C₆H₄)S-μ) (4c), respectively. Furthermore, [Fe₂(CO)₆(μ-SCH(C₆H₅)₂]₂(μ⁴-S)] (3d) was isolated from the reaction of Fe₃(CO)₁₂ with 2a. Additionally, a plausible formation mechanism of complexes 3b and 3c is described. Moreover, the electrocatalytic production of H₂ 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.


[AD1]: In diesem Artikel wurde die Substitution von CO-Liganden in Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(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$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_5$PPh$_3$ (2), wohingegen die Behandlung von 1 mit einem Überschuss an P(OMe)$_3$ unter Rückfluss in Toluol die mono- und disubstituierten Phosphitkomplexe Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_5$P(OMe)$_3$ (3) und Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_4$[P(OMe)$_3$]$_2$ (4) ergab. Darüber hinaus lieferte die Reaktion von 1 mit 1 eq. dppe in Gegenwart von Me$_3$NO·2H$_2$O zwei Komplexe: Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_4$(κ$_2$-dppe) (5), worin der dppe-Ligand mit einem Eisenatom chelatisiert, und [Fe$_2$(μ-Se$_2$C$_3$H$_5$CH$_3$)(CO)$_5$]$_2$(μ-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$_2$(μ-S$_2$(C$_3$H$_6$)$_2$S-μ)(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$_2$(μ-S$_2$(C$_3$H$_6$)$_2$S)(CO)$_3$P(OMe)$_3$ (2), welches nach Lagern bei Raumtemperatur innerhalb von 90 Minuten in das thermodynamisch kontrollierte
Produkt \( \text{Fe}_2(\mu-S_2(C_3H_6)_2S)(\mu)(\text{CO})_4\text{P(OMe)}_3 \) (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 \( \text{Fe}_2(\mu-S_2(C_3H_6)_2S)(\mu)(\text{CO})_4\text{P(OMe)}_3 \) (4) beziehungsweise \( \text{Fe}_2(\mu-S_2-(C_3H_6)_2S)(\mu)(\text{PMe})_3 \) (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 \( \text{Fe}_2(\text{CO})_6[(\text{C}_{13}H_{10}S)] \) (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 \( \text{Fe}_2(\text{CO})_6[(\text{C}_{17}H_{20}ON_2S)] \) (9b), \( \text{Fe}_2(\text{CO})_6[(\text{C}_{15}H_{12}S)] \) (9c) und \( \text{Fe}_2(\text{CO})_6[(\text{C}_{13}H_8OS)] \) (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.

wurden Reaktionen von Fe₃(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 Fe₂(CO)₆(μ,κ, S, SCH(C₆H₅)C₆H₄-η²) (3a) beziehungsweise Fe₂(CO)₆(μ,κ, S, SCH[(C₆H₄)-S-C₆H₄-η³]) (4a) erhalten. Im Gegensatz dazu ergab die Umsetzung von Fe₃(CO)₁₂ mit einem Überschuss an 2a oder 2e zwei biomimetische Modellverbindungen für das aktive Zentrum der [FeFe]-Hydrogenase: Fe₂(CO)₆(μ-SCH(C₆H₅)C₆H₄S-μ) (3b) bzw. Fe₂(CO)₆(μ-SCH(C₆H₄)-S-C₆H₄S-μ) (4b). Zudem lieferten die Reaktionen Fe₂(CO)₆(μ-SC(C₆H₅)₂S-μ) (3c) sowie Fe₂(CO)₆(μ-SC(C₆H₄-S-C₆H₄)S-μ) (4c). Weiterhin entstand [Fe₂(CO)₆(μ-SCH(C₆H₅)₂,μ⁴-S)] (3d) bei der Reaktion von Fe₃(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.
7. References


53. P. M. Matias, C. M. Soares, L. M. Saraiva, R. Coelho, J. Morais, J. LeGall, M.


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