

Synthetic and Structural Studies of Butterfly Fe/S/P Cluster Complexes Related to the Active Site of [FeFe]-Hydrogenases. Proton Reduction to H₂ Catalyzed by (η^1 -Ph₂PS- η^1)₂Fe₂(CO)₆

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The butterfly Fe/S cluster anions (μ -RS)(μ -S[−])Fe₂(CO)₆ (**A**, R = Et, *p*-MeC₆H₄), (μ -S[−])₂Fe₂(CO)₆ (**C**), [(μ -S[−])Fe₂(CO)₆]₂(4- μ -SC₆H₄C₆H₄S- μ -4') (**D**), and [(μ -S[−])Fe₂(CO)₆]₂[4- μ -SC₆H₄OCH₂CH₂OC₆H₄S- μ -4'] (**E**) (generated in situ via reactions of (μ -S₂)Fe₂(CO)₆ with RMgBr, Et₃BHLi, 4-LiC₆H₄C₆H₄Li-4', and 4-LiC₆H₄OCH₂CH₂OC₆H₄Li-4') were found to react with Ph₂PCl to give a series of novel butterfly Fe/S/P cluster complexes. Treatment of monoanions **A** (R = Et, *p*-MeC₆H₄) with 1 equiv of Ph₂PCl in THF from −78 °C to room temperature gave the single-butterfly Fe₂S₂P complexes (μ -RS)(η^1 -Ph₂PS- η^1)Fe₂(CO)₆ (**7**, R = Et; **9**, R = *p*-MeC₆H₄) and (μ -RS)(η^1 -Ph₂PS- η^1)Fe₂(CO)₅(Ph₂PY) (**8**, R = Et, Y = Cl; **10**, R = *p*-MeC₆H₄, Y = *p*-MeC₆H₄), whereas dianions **C**, **D**, and **E** reacted with 2 equiv of Ph₂PCl to give single-butterfly Fe₂S₂P complex (η^1 -Ph₂PS- η^1)₂Fe₂(CO)₆ (**11**) and double-butterfly Fe₄S₄P₂ complexes [(η^1 -Ph₂PS- η^1)Fe₂(CO)₆]₂(4- μ -SC₆H₄C₆H₄S- μ -4') (**12**) and [(η^1 -Ph₂PS- η^1)Fe₂(CO)₆]₂[4- μ -SC₆H₄OCH₂CH₂OC₆H₄S- μ -4'] (**13**), respectively. More interestingly, the novel μ_4 -S-containing double-butterfly Fe₄S₂P complexes [(μ -RS)Fe₂(CO)₆](μ_4 -S)[(μ -Ph₂P)Fe₂(CO)₆] (**14**, R = Me; **15**, R = Ph; **16**, R = Et) could be prepared by reactions of single-butterfly complexes (μ -RS)(η^1 -Ph₂PS- η^1)Fe₂(CO)₆ (**1**, R = Me; **3**, R = Ph; **7**, R = Et) with excess Fe₂(CO)₉ in THF at room temperature, whereas the quadruple-butterfly Fe₈S₄P₂ complexes [(μ -Ph₂P)Fe₂(CO)₆](μ_4 -S)Fe₂(CO)₆[4- μ -SC₆H₄C₆H₄S- μ -4'] (**17**) and [(μ -Ph₂P)Fe₂(CO)₆](μ_4 -S)Fe₂(CO)₆[4- μ -SC₆H₄OCH₂CH₂OC₆H₄S- μ -4'] (**18**) were similarly prepared by reactions of the corresponding double-butterfly complexes **12** and **13** with excess Fe₂(CO)₉, respectively. All the new complexes **7–18** have been characterized by elemental analysis, by spectroscopy, and for **9**, **11**, and **14** by X-ray crystallography. In view of the structural similarity of these Fe/S/P complexes to the [FeFe]-hydrogenase active site, they might be regarded as H-cluster models. As a representative, model complex **11** was found to be able to catalyze proton reduction to hydrogen under CV conditions.

Introduction

Although Reihlen prepared the first dinuclear Fe/S cluster complex (μ -RS)₂Fe₂(CO)₆ (R = Et) as early as 1928,¹ the butterfly-shaped Fe₂S₂ structures of such complexes were confirmed only in 1963 by means of X-ray crystal diffraction techniques.² In view of their unique structures and the potentially novel reactivities, Seyferth and co-workers began in the 1970s to systematically study the chemistry of such butterfly Fe/S cluster complexes, which was then thought to be nearly mature at the end of the 1990s.^{3,4} However, just around this period of time research interest in butterfly Fe/S cluster complexes was extensively revived. This is due to the realization that the active site of [FeFe]-hydrogenases (so-called H-clusters) resembles the archetypal (μ -RS)₂Fe₂(CO)₆ derivatives, which consist of a

butterfly Fe₂S₂ cluster core and four unusual ligands: CO, CN[−], [Fe₄S₄(SCys)₄], and a dithiolate (Figure 1).⁵ So far, a great variety of butterfly Fe/S cluster complexes that act as structural and functional models of the H-cluster have been prepared and characterized, which has considerably promoted our understanding of the natural enzymes.^{6,7} Recently, we published a

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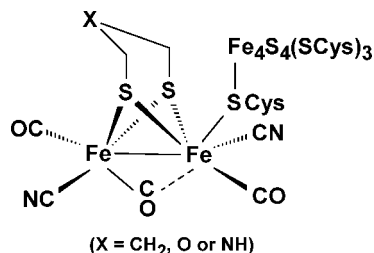


Figure 1. Basic structure of the H-cluster obtained from protein crystallography.

communication⁸ that describes the unexpected formation of the Fe/S/P cluster complexes **1–6** from reactions of the butterfly Fe/S cluster anions **A** ($R = \text{Me, Ph}$) and **B** ($R = n\text{-Bu, Ph}$) with Ph_2PCl (Scheme 1). Since these Fe/S/P complexes contain a butterfly Fe_2S_2 or $\text{Fe}_2\text{S}_2\text{P}$ cluster core that carries a given amount of CO ligands, they might be regarded as the structural analogues of the active site of $[\text{FeFe}]$ -hydrogenases.⁵ In order to show the generality of such new reactions that produce the interesting Fe/S/P complexes, we further carried out the reactions of Ph_2PCl with other butterfly Fe/S cluster anions, such as $(\mu\text{-RS})(\mu\text{-S}^-)\text{Fe}_2(\text{CO})_6$ (**A**, $R = \text{Et, } p\text{-MeC}_6\text{H}_4$), $(\mu\text{-S}^-)_2\text{Fe}_2(\text{CO})_6$ (**C**), $[(\mu\text{-S}^-)\text{Fe}_2(\text{CO})_6]_2[4\text{-}\mu\text{-SC}_6\text{H}_4\text{C}_6\text{H}_4\text{S-}\mu\text{-4'}]$ (**D**), and $[(\mu\text{-S}^-)\text{Fe}_2(\text{CO})_6]_2[4\text{-}\mu\text{-SC}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{OC}_6\text{H}_4\text{S-}\mu\text{-4'}]$ (**E**). As a result, the reactions afforded a series of expected single- and double-butterfly Fe/S/P cluster complexes. Particularly, when such single- and double-butterfly complexes were further treated with $\text{Fe}_2(\text{CO})_9$, another series of novel $\mu\text{-S}$ -containing double- and quadruple-butterfly Fe/S/P complexes were unexpectedly produced. In addition, the single-butterfly Fe/S/P complex $(\eta^1\text{-Ph}_2\text{PS-}\eta^1)_2\text{Fe}_2(\text{CO})_6$ has been found to be a catalyst for proton reduction to H_2 under electrochemical conditions. Herein we report these interesting results.

Results and Discussion

Synthesis and Characterization of Single-Butterfly $\text{Fe}_2\text{S}_2\text{P}$ / $\text{Fe}_2\text{S}_2\text{P}_2$ Complexes **7–11 and Double-Butterfly $\text{Fe}_4\text{S}_4\text{P}_2$ Complexes **12** and **13**.** As mentioned above, the single- and double-butterfly complexes **1–6** can be prepared by reactions of the BrMg salts of monoanions **A** ($R = \text{Me, Ph}$) and the lithium salts of monoanions **B** ($R = n\text{-Bu, Ph}$) with Ph_2PCl , respectively (Scheme 1).⁸ Similarly, we could further prepare the single-butterfly $\text{Fe}_2\text{S}_2\text{P}$ complexes **7–10** by treatment of the BrMg salts of monoanions **A** ($R = \text{Et, } p\text{-MeC}_6\text{H}_4$) (prepared in situ from 1 equiv of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ and 1 equiv of the Grignard reagents RMgBr)⁹ with 1 equiv of Ph_2PCl in THF from -78°C to room temperature (Scheme 2).

Although the mechanism for formation of **7–10** is not clear to date, the previously suggested mechanism for formation of

1–4⁸ should apply to the formation of **7–10** since both cases involve the same type of highly nucleophilic S-centered monoanions **A** and give the same type of products. As shown in Scheme 2, the nucleophilic substitution between monoanions **A** and Ph_2PCl will first give the butterfly Fe/S cluster phosphines **M**₁. Then, major products **7** and **9** can be produced from **M**₁ by nucleophilic attack of its P atom at the neighboring iron atom accompanied by displacement of mercaptide from it.¹⁰ The minor products **8** and **10** can be produced by further CO substitution of **7** or **9** with unreacted Ph_2PCl or $\text{Ph}_2\text{PC}_6\text{H}_4\text{Me-}p$ (formed in situ from Ph_2PCl and the Grignard reagent $p\text{-MeC}_6\text{H}_4\text{MgBr}$ present in the reaction system), respectively.

The single-butterfly $\text{Fe}_2\text{S}_2\text{P}_2$ complex **11** and double-butterfly $\text{Fe}_4\text{S}_4\text{P}_2$ complexes **12** and **13** could also be prepared from Ph_2PCl and the corresponding dianions **C**, **D**, and **E**, respectively. Treatment of 1 equiv of the dilithium salt of dianion **C** (generated in situ from $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ and 2 equiv of Et_3BHLi)¹¹ with 2 equiv of Ph_2PCl in THF from -78°C to room temperature afforded the single-butterfly complex **11** (Scheme 3), whereas treatment of 2 equiv of Ph_2PCl with ca. 1 equiv of the dilithium salt of dianion **D** (formed by reaction of 1 equiv of 4,4'-dibromodiphenyl with 2 equiv of $n\text{-BuLi}$ followed by treatment of the intermediate $4\text{-LiC}_6\text{H}_4\text{C}_6\text{H}_4\text{Li-4'}^{12}$ with $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$)¹³ or treatment of 2 equiv of Ph_2PCl with ca. 1 equiv of the dilithium salts of dianions **E** (generated similarly by reaction of 1 equiv of the ether chain-bridged 4,4'-dibromodiphenyls with 2 equiv of $n\text{-BuLi}$ followed by treatment of the intermediate $4\text{-LiC}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{OC}_6\text{H}_4\text{Li-4'}^{12}$ with $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$)¹³ gave rise to the double-butterfly complexes **12** (Scheme 4) and **13** (Scheme 5), respectively.

Complexes **7–13** are air-stable solids, which have been characterized by elemental analysis and IR, ^1H NMR, and ^{31}P NMR spectroscopies. For example, the IR spectra of **8** and **10** displayed four absorption bands in the range $2040\text{--}1934\text{ cm}^{-1}$ for their terminal carbonyls, whereas those of **7**, **9**, and **11–13** exhibited four to six absorption bands in the region $2070\text{--}1958\text{ cm}^{-1}$ for their terminal carbonyls. Compared to the highest $\nu_{\text{C=O}}$ frequencies of **7**, **9**, and **11–13**, those of **8** and **10** are shifted by ca. 30 cm^{-1} toward lower values due to the stronger electron-donating effects of $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{Me-}p)$ and Ph_2PCl than CO.¹⁴ In addition, the ^{31}P NMR spectra of **8** and **10** each showed two singlets at ca. 71 and 151 and ca. 58 and 70 ppm, respectively, for P atoms in their Ph_2PS , Ph_2PCl , and $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{Me-}p)$ ligands, whereas those of **7**, **9**, and **11–13** all displayed one singlet in the range $44\text{--}67\text{ ppm}$ for P atoms in their Ph_2PS ligands.

In order to unequivocally confirm the butterfly $\text{Fe}_2\text{S}_2\text{P}$ cluster cores present in complexes **7–10**, **12**, and **13**, as well as the butterfly $\text{Fe}_2\text{S}_2\text{P}_2$ cluster core present in complex **11**, we determined the crystal structures of complexes **9** and **11** by X-ray diffraction techniques. ORTEP plots of **9** and **11** are presented in Figures 2 and 3, whereas Table 1 shows selected bond lengths and angles. As can be seen in Figure 2, complex **9** is actually isostructural with the previously reported complex **1**,⁸ which contains a butterfly $\text{Fe}(1)\text{Fe}(2)\text{S}(1)\text{P}(1)\text{S}(2)$ cluster

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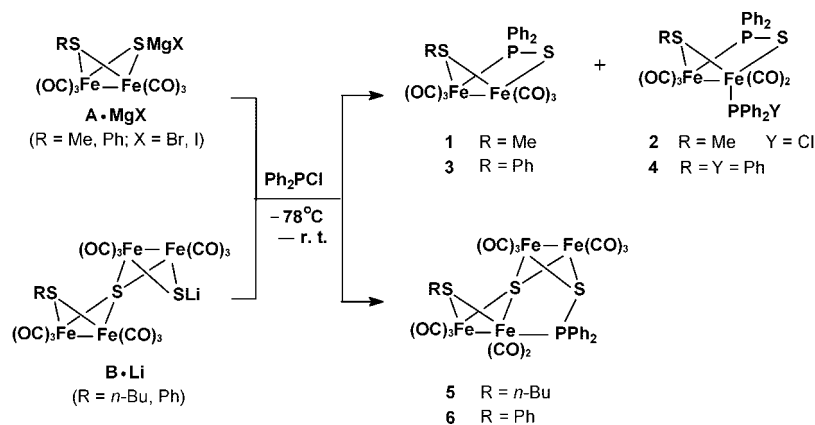
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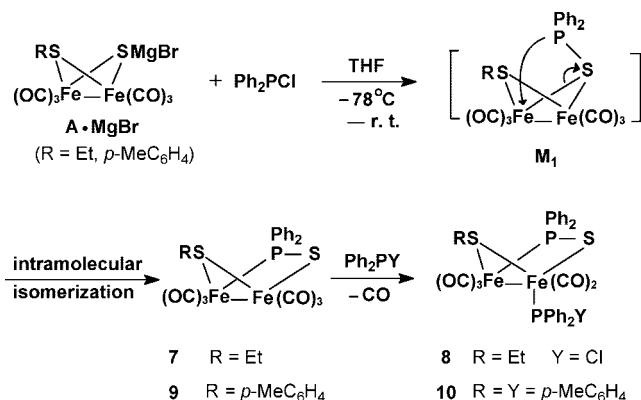
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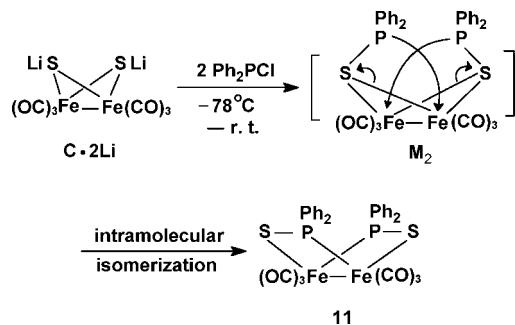
Scheme 1



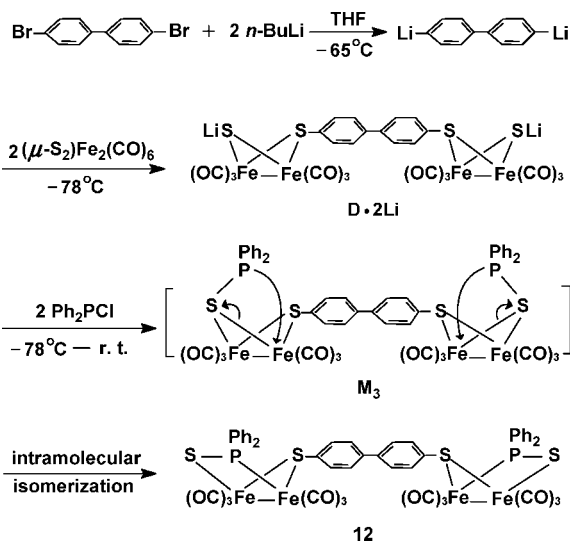
Scheme 2



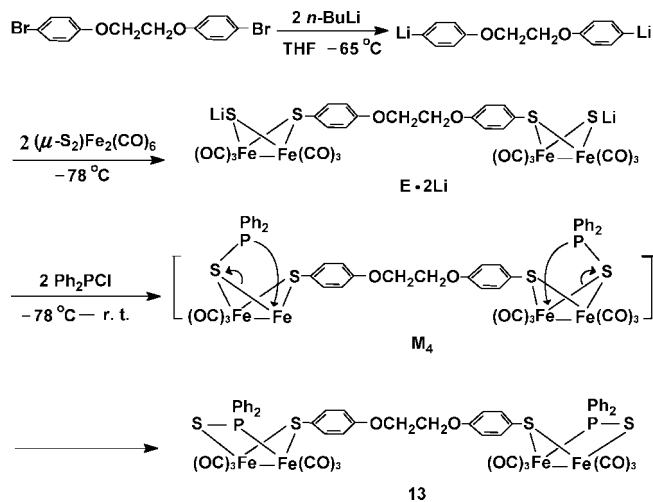
Scheme 3



Scheme 4



Scheme 5



core that carries two phenyl groups, one $p\text{-MeC}_6\text{H}_4$ group, and six terminal carbonyls. The X-ray crystallographic study revealed that the dihedral angle of **9** between its triangular wing $\text{Fe}(1)\text{Fe}(2)\text{S}(2)$ and tetragonal wing $\text{Fe}(1)\text{Fe}(2)\text{P}(1)\text{S}(1)$ is 90.3° , which is almost the same as the corresponding one of **1** (89.1°). In addition, the $\text{S}(2)$ atom of **9** is attached to the substituent $p\text{-MeC}_6\text{H}_4$ group by an equatorial bond in order to avoid the strong steric repulsion with one of the two phenyl groups attached to $\text{P}(1)$.¹⁵ The X-ray crystallographic study of complex **11** (Figure 3) indicated that it consists of a butterfly $\text{Fe}(1)\text{Fe}(2)\text{P}(1)\text{S}(1)\text{P}(2)\text{S}(2)$ cluster core in which the $\text{P}(1)/\text{P}(2)$ atoms each carry two phenyl groups and the $\text{Fe}(1)/\text{Fe}(2)$ atoms are each attached to three terminal carbonyls. The dihedral angle of **11** between its two tetragonal wings $\text{Fe}(1)\text{Fe}(2)\text{P}(1)\text{S}(1)$ and $\text{Fe}(1)\text{Fe}(2)\text{P}(2)\text{S}(2)$ is 87.4° . The $\text{Fe}\text{--}\text{Fe}$ bond length of **11** ($2.7790 \text{ \AA}$) is much longer than the corresponding bond lengths of **1** ($2.6431 \text{ \AA}$)⁸ and particularly $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$ ($2.537 \text{ \AA}$).²

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This is obviously because the $\text{Fe}\text{--}\text{Fe}$ bond of **11** is bridged by two diatom (P, S) units, that of **1** by one diatom (P, S) unit and one monoatom (S) unit and that of $(\mu\text{-EtS})_2\text{Fe}_2(\text{CO})_6$ by two monoatom (S, S) units. It is worth pointing out that **11** is the first butterfly $\text{Fe}/\text{S}/\text{P}$ complex with two tetragonal wings, although some butterfly $\text{Fe}/\text{S}/\text{P}$ complexes are known to have one triangular wing and one tetragonal wing, such as the previously reported **1**–**4**, or to have two triangular wings such

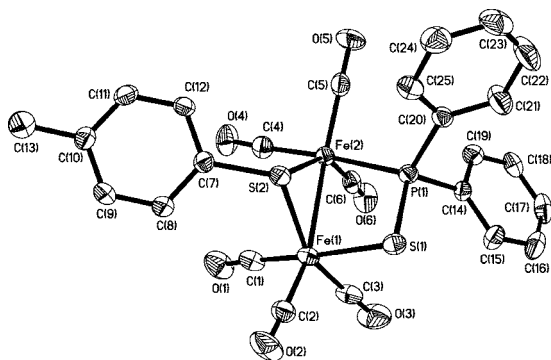


Figure 2. Molecular structure of **9** with 30% probability level ellipsoids.

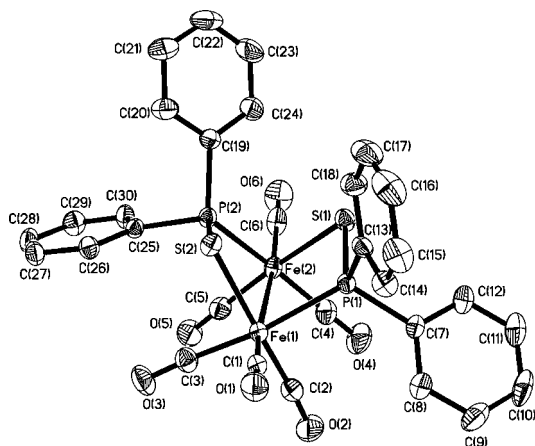


Figure 3. Molecular structure of **11** with 30% probability level ellipsoids.

as $(\mu\text{-Ph}_2\text{P})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$ ($\text{R} = \text{Ph}$,¹⁶ Et ,¹⁷ C_6H_{11} ¹⁸), $(\mu\text{-PhPCl})(\mu\text{-}t\text{-BuS})\text{Fe}_2(\text{CO})_6$,¹⁹ and $(\mu\text{-Me}_2\text{P})(\mu\text{-}t\text{-BuS})\text{Fe}_2(\text{CO})_6$.²⁰

Synthesis and Characterization of Double-Butterfly $\text{Fe}_4\text{S}_2\text{P}_2$ Complexes 14–16 and Quadruple-Butterfly $\text{Fe}_8\text{S}_4\text{P}_2$ Complexes 17 and 18. In order to examine the chemical reactivities of the above-prepared Fe/S/P cluster complexes, we chose some of the prepared complexes such as **1**, **3**, **7**, **12**, and **13** to react with $\text{Fe}_2(\text{CO})_9$ to see if the higher nuclearity Fe/S/P cluster complexes could be obtained. The higher nuclearity double-butterfly $\text{Fe}_4\text{S}_2\text{P}_2$ complexes **14–16** were prepared upon treatment of single-butterfly $\text{Fe}_2\text{S}_2\text{P}_2$ complexes **1**, **3**, and **7** with excess $\text{Fe}_2(\text{CO})_9$ in THF at room temperature (Scheme 6), whereas the higher nuclearity quadruple-butterfly $\text{Fe}_8\text{S}_4\text{P}_2$ complexes **17** and **18** could be obtained by reactions of double-butterfly $\text{Fe}_4\text{S}_2\text{P}_2$ complexes **12** and **13** with excess $\text{Fe}_2(\text{CO})_9$ under similar conditions (Scheme 7).

It is apparent that the formation of **14–18** is actually the consequence of the transformation of each Ph_2 -substituted tetragonal Fe_2SP wing in the starting butterfly Fe/S/P complexes to the $(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6$ -substituted Fe_2S triangular wing. Although the mechanism regarding this type of transformation

Scheme 6

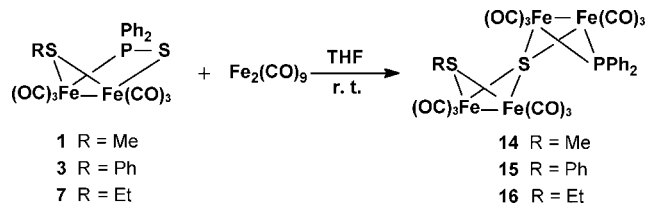


Table 1. Selected Bond Lengths (Å) and Angles (deg) for **9**, **11**, and **14**

9			
Fe(1)–S(2)	2.2424(14)	Fe(2)–S(2)	2.2767(13)
Fe(1)–S(1)	2.3655(14)	P(1)–S(1)	2.0336(15)
Fe(2)–P(1)	2.2772(13)	S(2)–C(7)	1.789(4)
P(1)–C(14)	1.824(4)	Fe(1)–Fe(2)	2.6327(9)
S(2)–Fe(1)–S(1)	83.22(4)	P(1)–Fe(2)–Fe(1)	77.35(4)
S(2)–Fe(1)–Fe(2)	54.98(3)	S(1)–P(1)–Fe(2)	104.77(6)
S(1)–Fe(1)–Fe(2)	86.12(4)	Fe(1)–S(2)–Fe(2)	71.26(4)
S(2)–Fe(2)–P(1)	87.47(5)	S(2)–Fe(2)–Fe(1)	53.77(4)
11			
Fe(1)–P(1)	2.2576(16)	P(1)–C(7)	1.830(5)
Fe(1)–S(2)	2.3487(17)	P(1)–S(1)	2.027(2)
Fe(2)–P(2)	2.2602(16)	S(2)–P(2)	2.032(2)
Fe(2)–S(1)	2.3469(17)	Fe(1)–Fe(2)	2.7790(13)
S(2)–Fe(1)–P(1)	86.12(6)	S(2)–Fe(1)–Fe(2)	83.78(5)
S(2)–P(2)–Fe(2)	106.36(8)	S(1)–Fe(2)–Fe(1)	83.50(5)
P(1)–S(1)–Fe(2)	90.55(7)	P(2)–Fe(2)–S(1)	87.20(6)
P(2)–S(2)–Fe(1)	89.76(7)	P(2)–Fe(2)–Fe(1)	75.13(5)
14			
Fe(1)–P(1)	2.223(2)	Fe(3)–Fe(4)	2.5118(17)
Fe(1)–S(1)	2.263(2)	Fe(1)–Fe(2)	2.5889(17)
Fe(2)–P(1)	2.223(2)	Fe(3)–S(1)	2.260(2)
Fe(2)–S(1)	2.229(2)	Fe(4)–S(1)	2.275(2)
P(1)–Fe(1)–S(1)	80.79(8)	Fe(1)–P(1)–Fe(2)	71.22(8)
S(1)–Fe(1)–Fe(2)	54.20(6)	Fe(2)–S(1)–Fe(3)	139.25(10)
P(1)–Fe(2)–Fe(1)	54.40(7)	Fe(3)–S(1)–Fe(4)	67.27(7)
S(1)–Fe(2)–Fe(1)	55.42(6)	Fe(4)–S(2)–Fe(3)	67.49(7)

is not completely understood, a possible transformation pathway (Scheme 8) might be proposed according to the following facts: (i) $\text{Fe}_2(\text{CO})_9$ in THF solution at room temperature is known to give the intermediate $\text{Fe}(\text{CO})_4(\text{THF})$, from which the heteroatom nitrogen donors can displace the THF,²¹ and (ii) the coordination unsaturated species, such as $\text{Cr}(\text{CO})_5$, can readily add to a metal-attached S atom to give the nuclearity increased metal cluster.²² The pathway includes the following steps: (i) the heteroatom S in the tetragonal Fe_2SP wing of the single-butterfly $\text{Fe}_2\text{S}_2\text{P}_2$ cluster **m**₁ attacks the Fe atom of one molecule of $\text{Fe}(\text{CO})_4(\text{THF})$ (generated in situ from $\text{Fe}_2(\text{CO})_9$ and THF) to give intermediate **m**₂; (ii) further intramolecular attack of the same S atom at its neighboring Fe atom with displacement of Ph_2P from it affords intermediate **m**₃ (the favored isomerization from tetragonal Fe_2SP wing to triangular Fe_2S wing is presumably due to coordination of the S atom with $\text{Fe}(\text{CO})_4$); (iii) the pendant Ph_2P group of **m**₃ displaces THF of another molecule of $\text{Fe}(\text{CO})_4(\text{THF})$ to produce intermediate **m**₄; and finally (iv) the double-butterfly $\text{Fe}_4\text{S}_2\text{P}_2$ cluster **m**₅ is formed by steps such as loss of two CO ligands from the two $\text{Fe}(\text{CO})_4$ units and formation of the new Fe–Fe, Fe–S, and Fe–P bonds followed by cleavage of the old P–S bond. It should be noted that this butterfly cluster transformation mechanism for formation of

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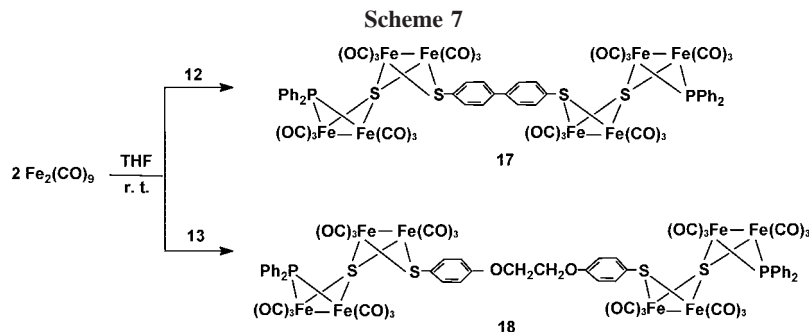
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14–18 seems to be reasonable, but it is mainly speculative. So, more work needs to be done in the future.

Complexes **14–18** are also air-stable solids, which were characterized by elemental analysis and various spectroscopies. For example, the IR spectra of **14–18** showed four to six absorption bands in the region 2079–1943 cm^{-1} for their terminal carbonyls. The ^1H NMR spectra of **14** and **16** each displayed a singlet at 2.07 and 1.33 ppm for CH_3 protons in their MeS and EtS groups, whereas the spectrum of **18** exhibited an AB quartet in the range 6.7–7.2 ppm for its two phenylene groups. In addition, the ^{31}P NMR spectra of **14–18** displayed a singlet at ca. 145 ppm for P atoms in their Ph_2P groups, very close to those displayed by P atoms in complexes $(\mu\text{-Ph}_2\text{P})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6$ ($\text{R} = \text{C}_6\text{H}_{11}$,¹⁸ $\text{R} = n\text{-Pr}$, $i\text{-Pr}$, $t\text{-Bu}$)²³ and $[(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6]_2[\mu\text{-SCH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2\text{S}-\mu]$.²⁴

To further confirm the $\mu_4\text{-S}$ -containing double-butterfly $\text{Fe}_4\text{S}_2\text{P}_2$ cluster cores present in complexes **14–18**, X-ray diffraction analysis for the representative complex **14** was undertaken. The molecular structure of **14** is depicted in Figure 4, whereas selected bond lengths and angles are listed in Table 1. Complex **14** is composed of two butterfly subclusters, $\text{Fe}(1)\text{Fe}(2)\text{S}(1)\text{P}(1)$ and $\text{Fe}(3)\text{Fe}(4)\text{S}(1)\text{S}(2)$, joined to a pyran type of $\mu_4\text{-S}(1)$ atom. While the $\text{S}(2)$ atom is attached to C(13) of the methyl group by an equatorial bond, the $\text{P}(1)$ atom is

attached to C(14) and C(20) of the two phenyl groups by an equatorial and an axial bond,¹³ respectively. In addition, each of the three carbonyls attached to $\text{Fe}(1)$, $\text{Fe}(2)$, $\text{Fe}(3)$, and $\text{Fe}(4)$ are terminal. In butterfly subcluster $\text{Fe}(1)\text{Fe}(2)\text{S}(1)\text{P}(1)$ the dihedral angle between its two triangular wings is 105.9° , which is obviously larger than the corresponding dihedral angle (96.81°) in subcluster $\text{Fe}(3)\text{Fe}(4)\text{S}(1)\text{S}(2)$. In addition, the $\text{Fe}(1)\text{--Fe}(2)$ bond length (2.5889 Å) is slightly longer than the $\text{Fe}(3)\text{--Fe}(4)$ bond length (2.5118 Å). It should be noted that complexes **14–18** are the first butterfly Fe/S/P complexes with two different subclusters, Fe_2S_2 and Fe_2SP , joined together through a common $\mu_4\text{-S}$ atom, although numerous $\mu_4\text{-E}$ ($\text{E} = \text{S}$, Se)-containing butterfly cluster complexes are known, such as $[(\mu\text{-RS})\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$ ($\text{R} = \text{Me}$,²⁵ Et)²⁶, $[(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6][(\mu\text{-PhC}\equiv\text{CS})\text{Fe}_2(\text{CO})_6](\mu_4\text{-S})$,²⁷ $[(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-Se})$,²⁸ and $[(\mu\text{-EtTe})\text{Fe}_2(\text{CO})_6]_2(\mu_4\text{-S})$.²⁹

Electrochemistry of Complex 11. The electrochemical properties of **11** were studied by cyclic voltammetry (CV) in MeCN solution under an atmosphere of N_2 . As shown in Figure 5, the cyclic voltammogram of **11** shows two irreversible one-electron reductions at $E_{\text{pc}} = -1.32$ and -2.09 V and one irreversible one-electron oxidation at $E_{\text{pa}} = +0.74$ V, which could be ascribed to the $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}/\text{Fe}^{\text{I}}\text{Fe}^0$, $\text{Fe}^{\text{I}}\text{Fe}^0/\text{Fe}^0\text{Fe}^0$, and $\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}/\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}$ couples, respectively. The one-electron assignments for these redox processes were supported by the calculated value of 0.95 faraday/equiv (obtained through study of bulk electrolysis of a MeCN solution of **11**) and the calculated value of $(i_p/v^{1/2})/(i_l^{1/2}) = 3.3$ (obtained through study of CV and chronoamperometry (CA) of **11**).³⁰ The cyclic voltammograms of **11** with HOAc and without HOAc (for comparative purposes) are presented in Figure 6. Interestingly, as shown in Figure 6, when the first 2 mM HOAc was added to the MeCN solution of **11**, the original first reduction peak at -1.32 V did not change, but the second reduction peak at -2.09 V considerably increased and continued to grow up with sequential addition of the acid. Apparently, these observations are characteristic of an electrocatalytic proton reduction process.^{31–33} More interest-

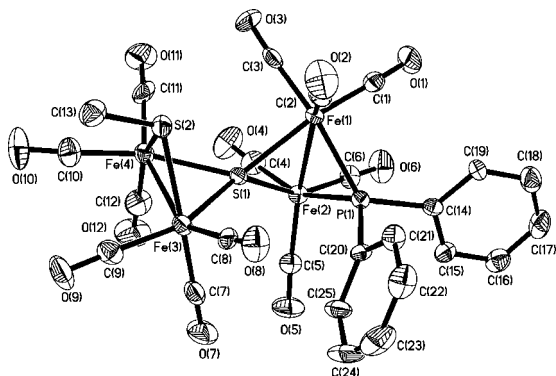


Figure 4. Molecular structure of **14** with 30% probability level ellipsoids.

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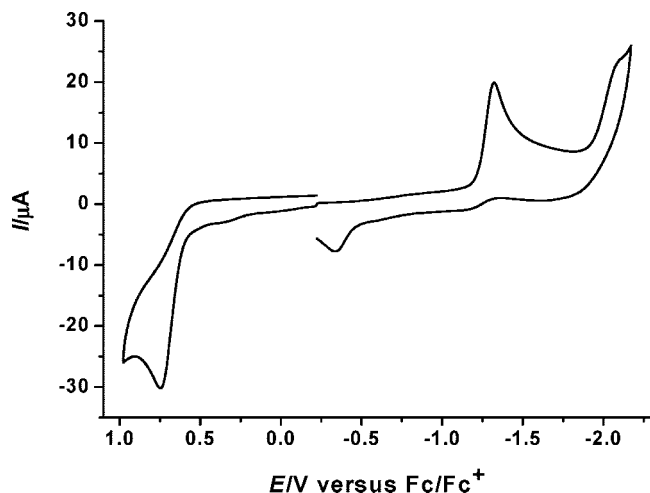


Figure 5. Cyclic voltammogram of **11** (1.0 mM) in 0.1 M *n*-Bu₄NPF₆/MeCN at a scan rate of 100 mV s⁻¹.

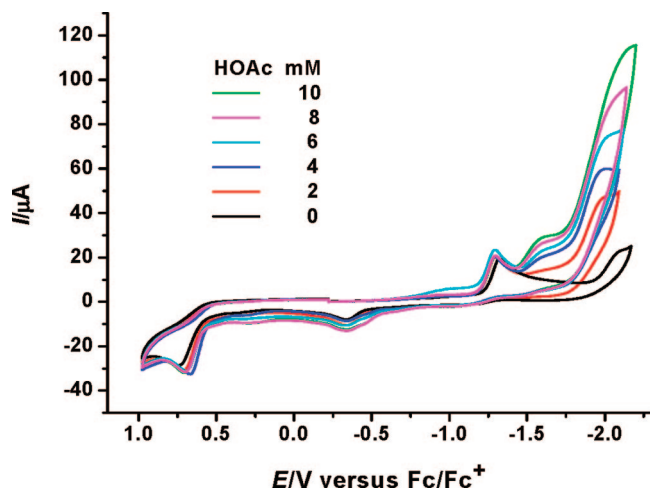


Figure 6. Cyclic voltammogram of **11** (1.0 mM) with HOAc (0–10 mM) in 0.1 M *n*-Bu₄NPF₆/MeCN at a scan rate of 100 mV s⁻¹.

ingly, this process was further proved by bulk electrolysis of a MeCN solution of **11** (0.5 mM) with HOAc (25 mM) at -2.20 V. During 0.5 h of the bulk electrolysis, 10.2 F per mol of **11** was passed, which corresponds to 5.1 turnovers. H₂ bubbles could be seen during the large-scale electrolytic experiment. GC analysis showed that the hydrogen yield was nearly 100%.

Conclusion

We have synthesized and characterized a series of new butterfly Fe/S/P cluster complexes, which include (i) complexes **7–10**, having one butterfly Fe₂S₂P cluster core, (ii) complex **11**, having one butterfly Fe₂S₂P₂ cluster core, (iii) complexes **12** and **13**, having two butterfly Fe₂S₂P cluster cores, (iv) complexes **14–16**, containing one double-butterfly Fe₄S₂P core with a common μ₄-S atom, and (v) complexes **17** and **18**, containing two double-butterfly Fe₄S₂P cluster cores each with a common μ₄-S atom. Interestingly, while **7–13** were synthesized via a novel type of reactions of the S-centered butterfly anions **A** (R = Et, *p*-MeC₆H₄), **C**, **D**, and **E** with Ph₂PCl,

complexes **14–18** could be prepared by another novel type of reactions of complexes **1**, **3**, **7**, **12**, and **13** with Fe₂(CO)₉, respectively. That is, the first type of reactions can accomplish the conversion from the S-centered triangular Fe₂S wings in anions **A**, **C**, **D**, and **E** to the tetragonal Fe₂SP wings in complexes **7–13**, whereas the second type of reactions can achieve the conversion from the Ph₂-substituted tetragonal Fe₂SP wings in complexes **1**, **3**, **7**, **12**, and **13** to the (μ-Ph₂P)Fe₂(CO)₆-substituted Fe₂S triangular wings in complexes **14–18**, respectively. Considering the structural similarity of complexes **7–18** to the active site of [FeFe]-hydrogenases, as well as the H₂ production catalyzed by complex **11**, these butterfly Fe/S/P complexes might be regarded as H-cluster models. Further studies regarding the formation mechanism for such butterfly Fe/S/P complexes and the electrocatalytic mechanism for proton reduction catalyzed by such complexes are underway.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen using standard Schlenk and vacuum-line techniques. Tetrahydrofuran (THF) was purified by distillation under nitrogen from Na/benzophenone ketyl. (μ-S₂)Fe₂(CO)₆,³⁴ Fe₂(CO)₉,³⁵ RMgBr (R = Et, *p*-MeC₆H₄),³⁶ Ph₂PCl,³⁷ 4-BrC₆H₄C₆H₄Br-4',³⁸ 4-BrC₆H₄OCH₂CH₂OC₆H₄Br-4',³⁹ and (μ-RS)(η¹-Ph₂PS-η¹)Fe₂(CO)₆ (R = Me, Ph)⁸ were prepared according to the published procedures. *n*-BuLi (1 M in hexane) and Et₃BHLi (1 M in THF) were available commercially. While products were separated by preparative TLC (25 × 15 × 0.25 cm) on glass plates coated with silica gel 60 H, samples for analysis were further purified by recrystallization from common organic solvents. IR spectra were recorded on a Nicolet Magna 500 FTIR or a Bruker Vector 22 infrared spectrophotometer. ¹H NMR and ³¹P NMR spectra were taken on a Bruker AC-P200 NMR spectrometer. C/H analyses were performed with an Elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus and are uncorrected.

Preparation of (μ-EtS)(η¹-Ph₂PS-η¹)Fe₂(CO)₆ (7**) and (μ-EtS)(η¹-Ph₂PS-η¹)Fe₂(CO)₅(Ph₂PCl) (**8**).** A red solution of (μ-S₂)Fe₂(CO)₆ (0.344 g, 1.0 mmol) in THF (20 mL) was cooled to -78 °C under stirring by a dry ice/acetone bath. To this solution was added a diethyl ether solution of EtMgBr (ca. 1 mmol) by syringe until the mixture turned emerald green. The green mixture was stirred at this temperature for 15 min, and then Ph₂PCl (0.2 mL, 1.0 mmol) was added to cause an immediate color change to red. The new mixture was allowed to warm to room temperature and stirred at this temperature for 1 h. Volatiles were removed under reduced pressure, and the residue was subjected to TLC separation using CH₂Cl₂/petroleum ether (1:4 v/v) as eluent. From the first, orange-red band **7** was obtained as a red solid (0.346 g, 62%). Mp: 120–121 °C. Anal. Calcd for C₂₀H₁₅Fe₂O₆PS₂: C, 43.04; H, 2.71. Found: C, 42.83; H, 2.69. IR (KBr disk): ν_{C=O} 2066 (vs), 2020 (vs), 2007 (vs), 1992 (vs), 1972 (s), 1958 (s) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): 1.66 (t, *J* = 7.2 Hz, 3H, CH₃), 2.82 (q, *J* = 7.2 Hz, 2H, CH₂), 7.24–7.78 (m, 10H, 2C₆H₅) ppm. ³¹P NMR (81.0 MHz, CDCl₃, 85% H₃PO₄): 66.99 (s) ppm. From the second, brown-red band **8** was obtained as a red solid (0.061 g, 8%). Mp: 151–152 °C. Anal. Calcd for C₃₁H₂₅ClFe₂O₅P₂S₂: C, 49.57; H, 3.33. Found:

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Table 2. Crystal Data and Structure Refinement Details for 9, 11, and 14

	9	11	14
mol formula	C ₂₅ H ₁₇ Fe ₂ O ₆ P ₂ S ₂	C ₃₀ H ₂₀ Fe ₂ O ₆ P ₂ S ₂	C ₂₅ H ₁₃ Fe ₄ O ₁₂ P ₂ S ₂
mol wt	620.18	714.22	823.84
cryst syst	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2(1)/ <i>c</i>	<i>P</i> $\bar{1}$	<i>Cc</i>
<i>a</i> /Å	15.333(5)	9.991(4)	10.268(4)
<i>b</i> /Å	10.876(3)	11.558(5)	15.146(7)
<i>c</i> /Å	17.090(5)	14.893(6)	20.165(9)
α /deg	90	71.732(7)	90
β /deg	112.554(5)	88.952(7)	98.215(7)
γ /deg	90	70.292(7)	90
<i>V</i> /Å ³	2632.2(13)	1530.1(11)	3104(2)
<i>Z</i>	4	2	4
<i>D</i> _c /g cm ⁻³	1.565	1.550	1.736
abs coeff/mm ⁻¹	1.360	1.231	2.077
<i>F</i> (000)	1256	724	1640
index ranges	−19 ≤ <i>h</i> ≤ 15 −13 ≤ <i>k</i> ≤ 11 −9 ≤ <i>l</i> ≤ 21	−12 ≤ <i>h</i> ≤ 12 −5 ≤ <i>k</i> ≤ 13 −17 ≤ <i>l</i> ≤ 17	−11 ≤ <i>h</i> ≤ 12 −9 ≤ <i>k</i> ≤ 18 −23 ≤ <i>l</i> ≤ 23
no. of rflns	12 136	6543	5417
no. of indep rflns	5374	5530	4895
2 θ _{max} /deg	52.82	50.70	50.04
<i>R</i>	0.0552	0.0494	0.0490
<i>R</i> _w	0.0734	0.0945	0.0710
goodness of fit	0.961	0.992	1.043
largest diff peak and hole/e Å ⁻³	0.411/−0.377	0.469/−0.464	0.376/−0.349

C, 49.70; H, 3.48. IR (KBr disk): $\nu_{\text{C=O}}$ 2039 (vs), 1985 (vs), 1953 (vs), 1941 (s) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): 1.42 (t, *J* = 7.2 Hz, 3H, CH₃), 2.35–2.50 (m, 2H, CH₂), 7.27–7.97 (m, 20H, 4C₆H₅) ppm. ³¹P NMR (81.0 MHz, CDCl₃, 85% H₃PO₄): 70.99 (s), 151.04 (s) ppm.

Preparation of (μ -*p*-MeC₆H₄S)(η ¹-Ph₂PS- η ¹)Fe₂(CO)₆ (9) and (μ -*p*-MeC₆H₄S)(η ¹-Ph₂PS- η ¹)Fe₂(CO)₅(Ph₂PC₆H₄Me-*p*) (10). The same procedure was followed as for 7 and 8, except that *p*-MeC₆H₄MgBr was used instead of EtMgBr. Elution with CH₂Cl₂/petroleum ether (1:6 v/v) afforded 9 as a red solid (0.397 g, 64%). Mp: 146–147 °C. Anal. Calcd for C₂₅H₁₇Fe₂O₆P₂S₂: C, 48.84; H, 2.76. Found: C, 48.69; H, 2.75. IR (KBr disk): $\nu_{\text{C=O}}$ 2066 (vs), 2028 (vs), 1992 (vs), 1968 (vs) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): 2.32 (s, 3H, CH₃), 7.07–7.80 (m, 14H, 2C₆H₅, C₆H₄) ppm. ³¹P NMR (81.0 MHz, CDCl₃, 85% H₃PO₄): 44.50 (s) ppm. From the second, brown-red band 10 was obtained as a red solid (0.208 g, 24%). Mp: 127–128 °C. Anal. Calcd for C₄₃H₃₄Fe₂O₅P₂S₂: C, 59.45; H, 3.92. Found: C, 59.48; H, 4.06. IR (KBr disk): $\nu_{\text{C=O}}$ 2040 (vs), 1974 (vs), 1947 (s), 1934 (s) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): 2.20 (s, 3H, CH₃C₆H₄P), 2.39 (s, 3H, CH₃C₆H₄S), 6.73–7.72 (m, 28H, 4C₆H₅, 2C₆H₄) ppm. ³¹P NMR (81.0 MHz, CDCl₃, 85% H₃PO₄): 57.99 (s), 70.41 (s) ppm.

Preparation of (η ¹-Ph₂PS- η ¹)₂Fe₂(CO)₆(11). To a stirred solution of (μ -S₂)Fe₂(CO)₆ (0.344 g, 1.0 mmol) in THF (20 mL) (cooled to −78 °C) was added a solution of Et₃BHLi (2 mL, 2 mmol) by syringe. At the midpoint of the addition, the solution turned from red to emerald green; for the rest of the addition it remained green. The green mixture was stirred at −78 °C for 15 min, and then Ph₂PCl (0.4 mL, 2.0 mmol) was added, causing an immediate color change back to red. The new mixture was allowed to warm to room temperature and stirred at this temperature for 1 h. The same workup as that for 7 and 8 gave 11 as a red solid (0.302 g, 42%). Mp: 132 °C (dec). Anal. Calcd for C₃₀H₂₀Fe₂O₆P₂S₂: C, 50.45; H, 2.82. Found: C, 50.72; H, 3.08. IR (KBr disk): $\nu_{\text{C=O}}$ 2066 (vs), 2029 (vs), 2001 (vs), 1967 (s) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): 7.25–8.07 (m, 20H, 4C₆H₅) ppm. ³¹P NMR (81.0 MHz, CDCl₃, 85% H₃PO₄): 49.71 (s) ppm.

Preparation of (η ¹-Ph₂PS- η ¹)Fe₂(CO)₆[(4- μ -SC₆H₄C₆H₄S- μ -4') (12). While stirring, a solution of 4-BrC₆H₄C₆H₄Br-4' (0.312 g, 1.0 mmol) in THF (20 mL) was cooled to ca. −65 °C, and then a hexane solution of *n*-BuLi (ca. 2 mmol) was dropwise added to give an off-white mixture. The mixture was stirred for an additional

0.5 h from −65 to 0 °C and then recooled to −78 °C. To this mixture was added (μ -S₂)Fe₂(CO)₆ (0.688 g, 2.0 mmol), and after stirring for 15 min, Ph₂PCl (0.4 mL, 2.0 mmol) was added. The new mixture was stirred at −78 °C for 15 min and then allowed to warm to room temperature. After the mixture continued stirring at room temperature for 2 h, volatiles were removed and the residue was subjected to TLC separation using CH₂Cl₂/petroleum ether (1:2 v/v) as eluent. From the first, orange-red band 12 was obtained as a red solid (0.278 g, 23%). Mp: 145 °C (dec). Anal. Calcd for C₄₈H₂₈Fe₄O₁₂P₂S₄: C, 47.65; H, 2.33. Found: C, 47.64; H, 2.78. IR (KBr disk): $\nu_{\text{C=O}}$ 2070 (vs), 2032 (vs), 2004 (vs), 1970 (s) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): 7.33–7.85 (m, 28H, 4C₆H₅, 2C₆H₄) ppm. ³¹P NMR (81.0 MHz, CDCl₃, 85% H₃PO₄): 44.69 (s) ppm.

Preparation of (η ¹-Ph₂PS- η ¹)Fe₂(CO)₆[(4- μ -SC₆H₄OCH₂CH₂-OC₆H₄S- μ -4') (13). The same procedure was followed as for 12, except that 4-BrC₆H₄OCH₂CH₂OC₆H₄Br-4' (0.372 g, 1.0 mmol) and excess *n*-BuLi (ca. 3 mmol) were used. From the first, orange-red band 13 was obtained as a red solid (0.523 g, 41%). Mp: 154 °C (dec). Anal. Calcd for C₅₀H₃₂Fe₄O₁₄P₂S₄: C, 47.24; H, 2.52. Found: C, 47.21; H, 2.55. IR (KBr disk): $\nu_{\text{C=O}}$ 2069 (vs), 2031 (vs), 2003 (vs), 1985 (s), 1970 (s) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): 4.28 (s, 4H, 2CH₂), 6.84–7.83 (m, 28H, 4C₆H₅, 2C₆H₄) ppm. ³¹P NMR (81.0 MHz, CDCl₃, 85% H₃PO₄): 67.02 (s) ppm.

Preparation of (μ -MeS)Fe₂(CO)₆[(μ -4-S)](μ -Ph₂P)Fe₂(CO)₆ (14). A mixture of (μ -MeS)(η ¹-Ph₂PS- η ¹)Fe₂(CO)₆ (1, 0.181 g, 0.33 mmol) and Fe₂(CO)₉ (0.728 g, 2.0 mmol) in THF (20 mL) was stirred for 6 h at room temperature. After the solvent was removed under reduced pressure, the residue was subjected to TLC separation using CH₂Cl₂/petroleum ether (1:4 v/v) as eluent. From the major, orange-red band 14 was obtained as a red solid (0.069 g, 25%). Mp: 182 °C (dec). Anal. Calcd for C₂₅H₁₃Fe₄O₁₂P₂S₂: C, 36.41; H, 1.58. Found: C, 36.04; H, 1.70. IR (KBr disk): $\nu_{\text{C=O}}$ 2078 (s), 2054 (vs), 2031 (vs), 1990 (vs), 1943 (s) cm⁻¹. ¹H NMR (200 MHz, CDCl₃): 2.07 (s, 3H, CH₃), 7.24–7.65 (m, 10H, 2C₆H₅) ppm. ³¹P NMR (81.0 MHz, CDCl₃, H₃PO₄): 145.63 (s) ppm.

Preparation of (μ -PhS)Fe₂(CO)₆[(μ -4-S)](μ -Ph₂P)Fe₂(CO)₆ (15). The same procedure was followed as for 14, except that (μ -PhS)(η ¹-Ph₂PS- η ¹)Fe₂(CO)₆ (3, 0.202 g, 0.33 mmol) was used instead of 1. From the major band 15 was obtained as a red solid (0.032 g, 11%). Mp: 190–191 °C. Anal. Calcd for C₃₀H₁₅Fe₄O₁₂P₂S₂: C, 40.63; H, 1.69. Found: C, 40.42; H, 1.85. IR (KBr disk): $\nu_{\text{C=O}}$ 2079 (s), 2052 (vs), 2030 (vs), 1994 (vs) cm⁻¹.

^1H NMR (200 MHz, CDCl_3): 7.19–7.74 (m, 15H, $3\text{C}_6\text{H}_5$) ppm. ^{31}P NMR (81.0 MHz, CDCl_3 , 85% H_3PO_4): 145.53 (s) ppm.

Preparation of $[(\mu\text{-EtS})\text{Fe}_2(\text{CO})_6](\mu_4\text{-S})[(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6]$ (16**).** The same procedure was followed as for **14**, except that $(\mu\text{-EtS})(\eta^1\text{-Ph}_2\text{PS-}\eta^1)\text{Fe}_2(\text{CO})_6$ (**7**, 0.186 g, 0.33 mmol) was employed in place of **1**. From the major band **16** was obtained as a red solid (0.053 g, 19%). Mp: 173–174 °C. Anal. Calcd for $\text{C}_{26}\text{H}_{15}\text{Fe}_4\text{O}_{12}\text{PS}_2$: C, 37.23; H, 1.79. Found: C, 37.05; H, 2.24. IR (KBr disk): $\nu_{\text{C=O}}$ 2078 (s), 2051 (vs), 2026 (vs), 1993 (vs), 1976 (vs), 1950 (m) cm^{-1} . ^1H NMR (200 MHz, CDCl_3): 1.33 (t, $J = 7.2$ Hz, 3H, CH_3), 2.41 (q, $J = 7.2$ Hz, 2H, CH_2), 7.31–7.70 (m, 10H, $2\text{C}_6\text{H}_5$) ppm. ^{31}P NMR (81.0 MHz, CDCl_3 , 85% H_3PO_4): 145.78 (s) ppm.

Preparation of $[(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6](\mu_4\text{-S})\text{Fe}_2(\text{CO})_6[2(4\text{-}\mu\text{-SC}_6\text{H}_4\text{-C}_6\text{H}_4\text{S-}\mu\text{-4'})]$ (17**).** A solution of $[(\eta^1\text{-Ph}_2\text{PS-}\eta^1)\text{Fe}_2(\text{CO})_6]_2[4\text{-}\mu\text{-SC}_6\text{H}_4\text{C}_6\text{H}_4\text{S-}\mu\text{-4'}]$ (**12**, 0.204 g, 0.20 mmol) and $\text{Fe}_2(\text{CO})_9$ (1.092 g, 3.0 mmol) in THF (20 mL) was stirred for 48 h at room temperature. After the solvent was removed under reduced pressure, the residue was subjected to TLC separation using THF/petroleum ether (1:5 v/v) as eluent. From the major, orange-red band **17** was obtained as a red solid (0.072 g, 20%). Mp: 90 °C (dec). Anal. Calcd for $\text{C}_{60}\text{H}_{28}\text{Fe}_8\text{O}_{24}\text{P}_2\text{S}_4$: C, 40.68; H, 1.58. Found: C, 40.81; H, 1.75. IR (KBr disk): $\nu_{\text{C=O}}$ 2079 (s), 2053 (vs), 2031 (vs), 1994 (vs) cm^{-1} . ^1H NMR (200 MHz, CDCl_3): 7.32–7.80 (m, 28H, $4\text{C}_6\text{H}_5$, $2\text{C}_6\text{H}_4$) ppm. ^{31}P NMR (81.0 MHz, CDCl_3 , 85% H_3PO_4): 145.51 (s) ppm.

Preparation of $[(\mu\text{-Ph}_2\text{P})\text{Fe}_2(\text{CO})_6](\mu_4\text{-S})\text{Fe}_2(\text{CO})_6[2(4\text{-}\mu\text{-SC}_6\text{H}_4\text{-OCH}_2\text{CH}_2\text{OC}_6\text{H}_4\text{S-}\mu\text{-4'})]$ (18**).** The same procedure was followed as for **17**, but $[(\eta^1\text{-Ph}_2\text{PS-}\eta^1)\text{Fe}_2(\text{CO})_6]_2[4\text{-}\mu\text{-SC}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{OC}_6\text{H}_4\text{S-}\mu\text{-4'}]$ (**13**, 0.254 g, 0.20 mmol) was used in place of **12**. Elution of the major, orange-red band with CH_2Cl_2 /petroleum ether (5:1 v/v) produced **18** as a red solid (0.092 g, 25%). Mp: 85–87 °C. Anal. Calcd for $\text{C}_{62}\text{H}_{32}\text{Fe}_8\text{O}_{26}\text{P}_2\text{S}_4$: C, 40.66; H, 1.75. Found: C, 40.48; H, 1.88. IR (KBr disk): $\nu_{\text{C=O}}$ 2079 (s), 2052 (vs), 2030 (vs), 1994 (vs) cm^{-1} . ^1H NMR (200 MHz, CDCl_3): 4.20 (s, 4H, 2CH_2), 6.70, 6.74, 7.13, 7.17 (AB quartet, 8H, $2\text{C}_6\text{H}_4$), 7.30–7.67 (m, 20H, $4\text{C}_6\text{H}_5$) ppm. ^{31}P NMR (81.0 MHz, CDCl_3 , 85% H_3PO_4): 145.60 (s) ppm.

X-ray Structure Determinations of **9, **11**, and **14**.** Single crystals of **9**, **11**, and **14** suitable for X-ray diffraction analyses were grown by slow evaporation of a hexane solution of **9** and a hexane/ CH_2Cl_2 solution of **14** at about 4 °C, and by slow diffusion of hexane into a diethyl ether solution of **11** at about 4 °C, respectively. A single crystal of **9**, **11**, or **14** was mounted on a

Bruker SMART 1000 automated diffractometer. Data were collected at room temperature, using a graphite monochromator with Mo K α radiation ($\lambda = 0.71073$ Å) in the ω - ϕ scanning mode. Absorption correction was performed by the SADABS program.⁴⁰ The structures were solved by direct methods using the SHELXS-97 program⁴¹ and refined by full-matrix least-squares techniques (SHELXL-97)⁴² on F^2 . Hydrogen atoms were located by using the geometric method. Details of crystal data, data collections, and structure refinements are summarized in Table 2.

Electrochemistry. Acetonitrile (Fisher Chemicals, HPLC grade) was used for electrochemistry assays. A solution of 0.1 M $n\text{-Bu}_4\text{NPF}_6$ in MeCN was used as electrolyte in all cyclic voltammetric experiments. Electrochemical measurements were made using a BAS Epsilon potentiostat. All voltammograms were obtained in a three-electrode cell with a 3 mm diameter glassy carbon working electrode, a platinum counter electrode, and an Ag/Ag $^+$ (0.01 M AgNO_3 /0.1 M $n\text{-Bu}_4\text{NPF}_6$ in MeCN) reference electrode under N_2 atmosphere. The working electrode was polished with 0.05 μm alumina paste and sonicated in water for at least 10 min prior to use. Bulk electrolysis was run on a vitreous carbon rod (ca. 3 cm^2) in a two-compartment, gastight, H-type electrolysis cell containing ca. 20 mL of MeCN. All potentials are quoted against the ferrocene/ferrocenium (Fc/Fc^+) potential. Gas chromatography was performed with a Shimadzu GC-9A gas chromatograph under isothermal conditions with nitrogen as a carrier gas and a thermal conductivity detector.

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Supporting Information Available: Full tables of crystal data, atomic coordinates and thermal parameters, and bond lengths and angles for **9**, **11**, and **14** as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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