

Synthesis and Characterization of Diiron Thiadithiolate Complexes Related to the Active Site of [FeFe]-Hydrogenases

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On the basis of preparation of the known complex $[\text{Fe}_2(\mu\text{-SCH}_2)_2\text{S}(\text{CO})_6]$ (**A**) by a new method involving condensation of $[(\mu\text{-LiS})_2\text{Fe}_2(\text{CO})_6]$ with excess $\text{S}(\text{CH}_2\text{Br})_2$, twelve new diiron thiadithiolates as mimics of the [FeFe]-hydrogenase active site have been synthesized by substitution of the CO ligand and coordination at the central S atom of complex **A** with appropriate reagents. Treatment of **A** with 1 equiv. of the monodentate ligands PPh_3 and $[(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-Ph}_2\text{PC}_5\text{H}_4)\text{-Fe}]$ in the presence of Me_3NO and with 1 equiv. *t*BuNC and cyclohexyl isocyanide gave the single $[\text{2Fe3S}]$ -cluster-containing monosubstituted complexes $[\text{Fe}_2(\mu\text{-SCH}_2)_2\text{S}(\text{CO})_5\text{-}(\text{L}_1)]$ (**1**, $\text{L}_1 = \text{PPh}_3$; **2**, $\text{L}_1 = (\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-Ph}_2\text{PC}_5\text{H}_4)\text{Fe}$; **3**, $\text{L}_1 = t\text{BuNC}$; **4**, $\text{L}_1 = \text{C}_6\text{H}_{11}\text{NC}$), whereas the double $[\text{2Fe3S}]$ -cluster-containing disubstituted complexes $[\{\text{Fe}_2(\mu\text{-SCH}_2)_2\text{S}(\text{CO})_5\}_2(\text{L}_2)]$ (**5**, $\text{L}_2 = 4,4'-(\text{Ph}_2\text{P})_2(\text{C}_6\text{H}_4)_2$; **6**, $\text{L}_2 = \text{trans-Ph}_2\text{P-CH=CHPPh}_2$; **7**, $\text{L}_2 = 1,4\text{-(CN)}_2\text{C}_6\text{H}_4$; **8**, $\text{L}_2 = (\eta^5\text{-Ph}_2\text{PC}_5\text{H}_4)_2\text{-Fe}$; **9**, $\text{L}_2 = (\eta^5\text{-Ph}_2\text{PC}_5\text{H}_4)_2\text{Ru}$) were produced by reaction of

A with 0.5 equiv. of the corresponding bidentate ligands in the presence of Me_3NO . In addition, the single $[\text{2Fe3S}]$ -cluster-containing complexes in which the central S atom is coordinated, $[\{\text{Fe}_2(\mu\text{-SCH}_2)_2\text{S}(\text{CO})_6\}\{(\eta^5\text{-MeC}_5\text{H}_4)(\text{CO})_2\text{Fe}\}(\text{BF}_4)]$ (**10**), $[\{\text{Fe}_2(\mu\text{-SCH}_2)_2\text{S}(\text{CO})_6\}\{\text{Cr}(\text{CO})_5\}]$ (**11**), and $[\{\text{Fe}_2(\mu\text{-SCH}_2)_2\text{S}(\text{CO})_6\}\{\text{W}(\text{CO})_5\}]$ (**12**), could be obtained by reaction of complex **A** with the in situ prepared $[(\eta^5\text{-MeC}_5\text{H}_4)(\text{CO})_2\text{-Fe}](\text{BF}_4)$, $[\text{Cr}(\text{CO})_5(\text{thf})]$, and $[\text{W}(\text{CO})_5(\text{thf})]$, respectively. While complex **3** was found to be able to reduce the proton of the weak acid Et_3NHCl to give H_2 , the X-ray crystallographic study confirmed that (i) each P atom of the phosphane ligands in **1** and **8** occupies an apical position at the Fe atoms, (ii) the isocyanide ligand in **3** lies in a basal position of the Fe atom, and (iii) the $(\eta^5\text{-MeC}_5\text{H}_4)(\text{CO})_2\text{Fe}$, $\text{Cr}(\text{CO})_5$, and $\text{W}(\text{CO})_5$ units in **10–12** are linked to the central S atom of complex **A** by an equatorial bond from the two fused six-membered rings of their $[\text{2Fe3S}]$ -cluster cores.

Introduction

[FeFe]-hydrogenases have attracted great attention in recent years, since they can catalyze proton reduction to hydrogen in numerous aerobic and anaerobic microorganisms at very high rates.^[1] Crystallographic^[2] and IR spectroscopic^[3] studies on the two types of [FeFe]-hydrogenases, Cpl (*Clostridium pasteurianum*) and DdH (*Desulfovibrio desulfuricans*) have revealed that their active site (the so-called H-cluster) consists of a butterfly $[\text{2Fe2S}]$ -cluster subsite bearing CO and CN^- ligands and a cubic $[\text{4Fe4S}]$ -cluster subsite bearing cysteinyl ligands (Figure 1). To date, a large number of biomimetic models for the active site of [FeFe]-hydrogenases have been prepared and structurally characterized, and some have demonstrated the ability to catalyze proton reduction to hydrogen.^[4–8] Among such models, we are particularly interested in the central heteroatom-containing models, such as diiron azadithiolate (ADT),^[5] oxadithiolate (ODT),^[6] and thiadithiolate (TDT) type models.^[7,8]

This is because the central N atom in the ADT cofactor was recently suggested to play an important role in the heterolytic cleavage of H_2 or H_2 evolution in natural enzymes.^[9] In addition, the central S atom in the TDT cofactor has a strong coordination ability with transition metals,^[7] which may provide an easy route to structural modification. On the basis of our previous study on central heteroatom-containing models, we now report the synthesis and structural characterization of a series of new single and double diiron TDT-type models prepared by CO substitution and by coordination at the central S atom of the parent complex $[\text{Fe}_2(\mu\text{-SCH}_2)_2\text{S}(\text{CO})_6]$ (**A**). In addition, a new synthetic method for the preparation of complex **A** is also reported.

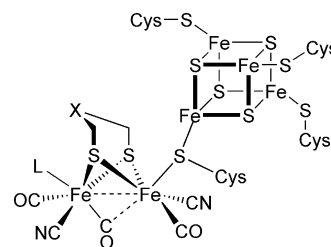
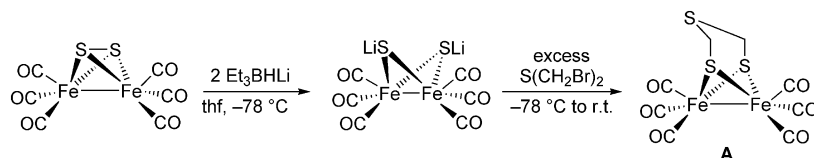


Figure 1. The simplified structure of the H-cluster in different functional states ($\text{L} = \text{vacant}, \text{H}_2\text{O}, \text{CO}, \text{H}, \text{or } \text{H}_2$; $\text{X} = \text{CH}_2, \text{NH}, \text{or } \text{O}$).

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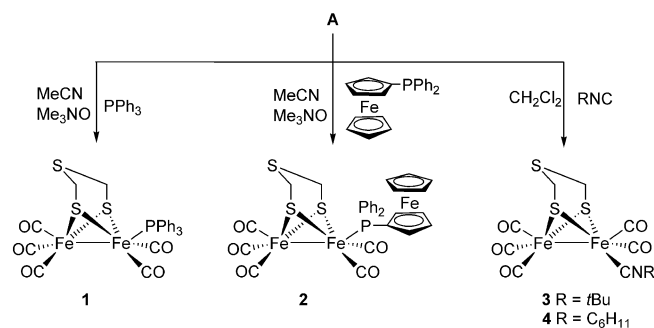
Scheme 1.

Results and Discussion

Synthesis and Characterization of the Single [2Fe3S]-Cluster-Containing TDT-Type Models A and 1–4

There have been two methods previously reported for the synthesis of complex A, which involve the oxidative addition reaction of 1,2,4-trithiolane with $\text{Fe}_3(\text{CO})_{12}$ ^[7] and $\text{Fe}_2(\text{CO})_9$ ^[8] in thf. Now, we report a new method for the synthesis of complex A, which involves two elementary steps in one pot (i) the initial reductive cleavage of the S–S bond of $[(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6]$ with Et_3BHLi and (ii) the subsequent condensation of the resulting intermediate $[(\mu\text{-LiS})_2\text{Fe}_2(\text{CO})_6]$ ^[10] with excess thioether $\text{S}(\text{CH}_2\text{Br})_2$ (Scheme 1).

On studying the synthetic method for parent complex A, we further found that complex A could react with 1 equiv. of monodentate phosphane PPh_3 or $[(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-Ph}_2\text{PC}_5\text{H}_4)\text{Fe}]$ in the presence of decarbonylating agent Me_3NO in MeCN to afford the single [2Fe3S]-cluster-containing monosubstituted model complexes $[\text{Fe}_2(\mu\text{-SCH}_2)_2\text{S}(\text{CO})_5(\text{PPh}_3)]$ (**1**) or $[\text{Fe}_2(\mu\text{-SCH}_2)_2\text{S}(\text{CO})_5\{(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-Ph}_2\text{PC}_5\text{H}_4)\text{Fe}\}]$ (**2**) in 89 and 81% yields, respectively. In addition, it was further found that complex A could also react with 1 equiv. of monodentate isocyanide $t\text{BuNC}$ or $\text{C}_6\text{H}_{11}\text{NC}$ in CH_2Cl_2 in the absence of Me_3NO to give the corresponding monosubstituted model complexes $[\text{Fe}_2(\mu\text{-SCH}_2)_2\text{S}(\text{CO})_5(t\text{BuNC})]$ (**3**) or $[\text{Fe}_2(\mu\text{-SCH}_2)_2\text{S}(\text{CO})_5(\text{C}_6\text{H}_{11}\text{NC})]$ (**4**) in 61 and 60% yields, respectively (Scheme 2).

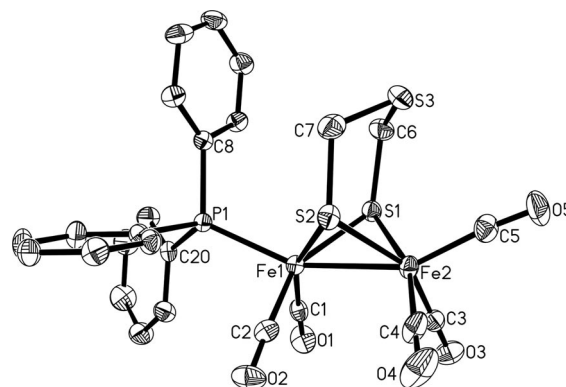
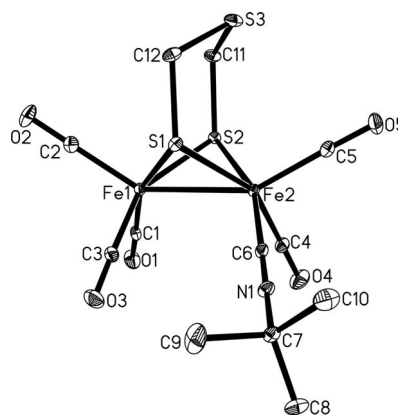


Scheme 2.

Complexes **1–4** are air-stable red solids, which were characterized by elemental analysis and NMR and IR spectroscopy. In their IR spectra there are three to four absorption bands in the range of $2047\text{--}1934\text{ cm}^{-1}$ assigned to the terminal carbonyls, which are shifted towards lower frequencies relative to those ($2075\text{--}1990\text{ cm}^{-1}$) of the parent complex A.^[7] This is obviously due to the increased strength of the π back bonding between the iron atoms and the at-

tached carbonyl groups by substitution of the CO group by the stronger electron-donating phosphane or isocyanide ligands.^[11] In addition, the IR spectra of **3** and **4** show one absorption band at ca. 2160 cm^{-1} , which is characteristic of the terminal isocyanide ligands. The ^1H NMR spectra of **1** and **2** display two doublets at ca. 2.30 and 2.80 ppm for the two magnetically different protons in the methylene groups, while those of **3** and **4** exhibit one singlet at $\delta = 3.14$ ppm for the two magnetically identical protons in the corresponding methylene groups. Apparently, the latter case is caused by fast folding of the two fused six-membered rings in the [2Fe3S]-cluster cores.^[12] The ^{31}P NMR signals for the coordinated P atoms in **1** and **2** appear as a singlet at $\delta = 64.44$ and 55.26 ppm, respectively.

The molecular structures of **1** and **3** were confirmed by X-ray crystal diffraction analysis. While molecular structures of **1** and **3** are presented in Figures 2 and 3, their se-

Figure 2. Molecular structure of **1** with 30% probability level ellipsoids.Figure 3. Molecular structure of **3** with 30% probability level ellipsoids.

lected bond lengths and angles are given in Table 1. As shown in Figure 2, complex **1** contains one [2Fe3S]-cluster core that carries five CO and one PPh₃ ligands. The PPh₃ ligand occupies an apical coordination site of the octahedral geometry of the Fe1 atom (the Fe1–Fe2 bond is regarded as a coordination site), which is in accordance with the previously reported phosphane-substituted diiron carbonyl complexes.^[13] Interestingly, although complex **3** has the same [2Fe3S]-cluster core with five CO ligands, the *t*BuNC ligand, in contrast to PPh₃ of **1**, lies in the basal position of one Fe atom. To the best of our knowledge, this is the first crystal structure of the isocyanide-monosubsti-

tuted [FeFe]-hydrogenase model complex reported so far, although the crystal structures of some isocyanide-disubstituted model complexes are known. It is interesting to note that the two isocyanide ligands in the crystal structure of the model complex [Fe₂(μ-SCH₂)₂CH₂(CO)₄(*t*BuNC)₂] all reside in apical positions,^[14] whereas in the crystal structure of the model complex [Fe₂(μ-SCH₂)₂S(CO)₄(*t*BuNC)₂], one isocyanide group resides in an apical position and the other in a basal position.^[7]

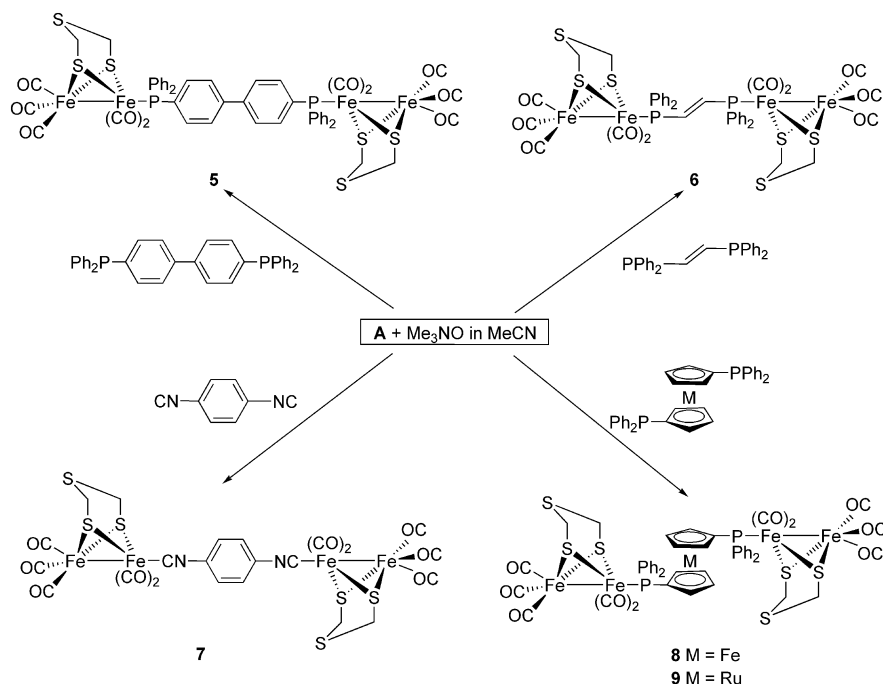
Synthesis and Characterization of the Double [2Fe3S]-Cluster-Containing TDT-Type Models 5–9

Interestingly, it was found that the double [2Fe3S]-cluster-containing disubstituted model compounds [{Fe₂(μ-SCH₂)₂S(CO)₅}₂(L₂)] [**5**, L₂ = 4,4'-(Ph₂P)₂(C₆H₄)₂; **6**, *trans*-Ph₂PCH=CHPPh₂; **7**, 1,4-(CN)₂C₆H₄; **8**, (η⁵-Ph₂PC₅H₄)₂-Fe (dppf); **9**, (η⁵-Ph₂PC₅H₄)₂Ru (dppr)] {1,1'-bis(diphenylphosphanyl)ferrocene (dppf) and 1,1'-bis(diphenylphosphanyl)ruthenocene (dppr)} could similarly be prepared in 42–73 % yields by CO substitution reactions of parent complex **A** with 0.5 equiv. of the corresponding bidentate ligands in the presence of Me₃NO in MeCN (Scheme 3).

Compounds **5–9** are air-stable dark-red solids, which were characterized by elemental analysis and NMR and IR spectroscopy, and for **8** by X-ray crystallography. For example, the IR spectra of **5–9** display three absorption bands in the range 2047–1932 cm^{−1}, which can be assigned to the terminal carbonyl groups, whereas complex **7** exhibits an additional absorption band at 2118 cm^{−1} for the bridged diisocyanide. In addition, the ¹H NMR spectra of **5–9** show the corresponding proton signals for the organic groups.

Table 1. Selected bond lengths [Å] and angles [°] for **1** and **3**.

1		3	
Fe1–P1	2.2527(14)	Fe1–S1	2.2594(6)
Fe1–S1	2.2934(12)	Fe1–S2	2.2681(6)
Fe2–S1	2.2691(12)	Fe1–Fe2	2.5313(5)
S1–C6	1.834(4)	Fe2–S2	2.2405(5)
S3–C7	1.770(4)	Fe2–S1	2.2636(5)
Fe1–S2	2.2620(12)	S1–C12	1.8303(17)
Fe1–Fe2	2.5108(11)	S2–C11	1.8316(17)
Fe2–S2	2.2747(13)	S3–C11	1.7846(17)
S2–C7	1.842(4)	S3–C12	1.7847(19)
S3–C6	1.783(4)	N1–C6	1.157(2)
P1–Fe1–Fe2	155.31(4)	S1–Fe1–S2	86.182(18)
S1–Fe1–Fe2	56.15(3)	S1–Fe1–Fe2	56.047(14)
S1–Fe2–Fe1	57.08(3)	S2–Fe1–Fe2	55.330(12)
C6–S1–Fe2	110.04(13)	S2–Fe2–S1	86.74(2)
Fe2–S1–Fe1	66.77(4)	S2–Fe2–Fe1	56.365(17)
S2–Fe1–Fe2	56.64(3)	S1–Fe2–Fe1	55.890(15)
S1–Fe2–S2	85.49(5)	Fe1–S1–Fe2	68.06(2)
S2–Fe2–Fe1	56.16(4)	Fe2–S2–Fe1	68.305(17)
C6–S1–Fe1	120.47(14)	C11–S3–C12	99.33(8)
Fe1–S2–Fe2	67.20(4)	C6–N1–C7	173.07(17)



Scheme 3.

The ^{31}P NMR spectra of **5**, **6**, **8** and **9** each exhibit one singlet in the range 54–65 ppm for the two identical P atoms in each of the diphosphane ligands. The molecular structure of **8** determined by X-ray crystallography is shown in Figure 4, while Table 2 lists its selected bond lengths and angles. As can be seen in Figure 4, complex **8** indeed comprises two $[\text{Fe}_2\text{S}]$ -cluster cores, which are joined together through the apically positioned P1 and P1A atoms of the bridging dppf ligand. This molecule is centrosymmetric. Both the S3 and S3A atoms lie opposite the diphosphane ligand, probably in order to avoid the strong steric repulsion between the two sulfur atoms and the bulky dppf ligand. Actually, this structure is isostructural with that of the ODT-type model $[\{\text{Fe}_2(\mu\text{-SCH}_2)_2\text{O}(\text{CO})_5\}_2(\text{dppf})]$.^[6]

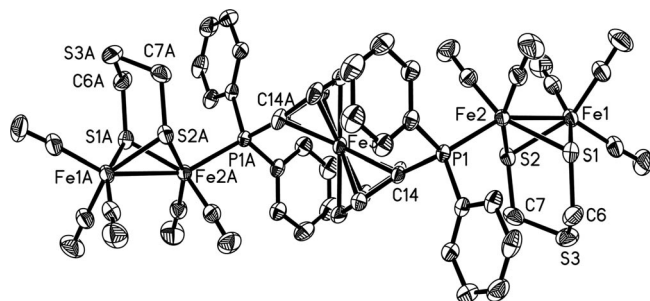


Figure 4. Molecular structure of **8** with 30% probability level ellipsoids.

Table 2. Selected bond lengths [Å] and angles [°] for **8**.

Fe1–S2	2.2581(8)	Fe2–S1	2.2732(9)
Fe1–S1	2.2726(9)	S1–C6	1.825(4)
Fe1–Fe2	2.5255(6)	S2–C7	1.824(4)
Fe2–P1	2.2505(8)	S3–C7	1.770(4)
Fe2–S2	2.2573(8)	S3–C6	1.791(4)
S2–Fe1–S1	85.52(3)	S2–Fe2–Fe1	56.01(2)
S2–Fe1–Fe2	55.98(2)	S1–Fe2–Fe1	56.24(2)
S1–Fe1–Fe2	56.26(2)	Fe1–S1–Fe2	67.50(3)
P1–Fe2–S1	108.98(3)	Fe2–S2–Fe1	68.02(3)
P1–Fe2–Fe1	152.91(3)	C7–S3–C6	99.71(17)

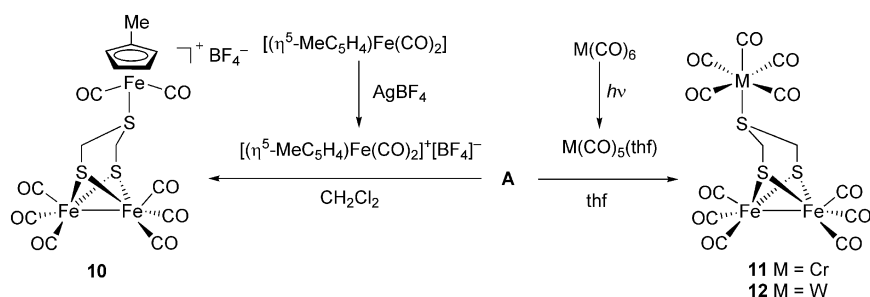
Synthesis and Characterization of the Central-S-Coordinated TDT-Type Models 10–12

To date, only two types of reactions are known that involve the central S atom of complex **A**. One is the coordination reaction with $\text{Cp}(\text{CO})_2\text{Fe}(\text{BF}_4)$ to give the first central-

S-coordinated TDT-type model $[\{\text{Fe}_2(\mu\text{-SCH}_2)_2\text{S}(\text{CO})_6\}\{\text{Cp}(\text{CO})_2\text{Fe}\}(\text{BF}_4)]$ ^[7] and the other is the oxidation reaction with dimethyldioxirane to afford, for example, the organometallic sulfoxide and sulfone products $[\text{Fe}_2(\mu\text{-SCH}_2)_2\text{S}(\text{O})(\text{CO})_6]$ and $[\text{Fe}_2(\mu\text{-SCH}_2)_2\text{S}(\text{O}_2)(\text{CO})_6]$.^[15] To demonstrate the coordination ability of the central S atom of complex **A** with different organometallic substrates, we carried out reactions of complex **A** with $[(\eta^5\text{-MeC}_5\text{H}_4)(\text{CO})_2\text{Fe}](\text{BF}_4)$ (prepared in situ from $[(\eta^5\text{-MeC}_5\text{H}_4)(\text{CO})_2\text{Fe}]$ and AgBF_4)^[16] in CH_2Cl_2 at room temperature and with $\text{M}(\text{CO})_5(\text{thf})$ ($\text{M} = \text{Cr}, \text{W}$) (prepared in situ by photolysis of $\text{M}(\text{CO})_6$ with thf)^[17] in thf at room temperature. As a result, the corresponding S-coordinated TDT-type model complexes $[\{\text{Fe}_2(\mu\text{-SCH}_2)_2\text{S}(\text{CO})_6\}\{(\eta^5\text{-MeC}_5\text{H}_4)(\text{CO})_2\text{Fe}\}(\text{BF}_4)]$ (**10**), $[\{\text{Fe}_2(\mu\text{-SCH}_2)_2\text{S}(\text{CO})_6\}\{\text{Cr}(\text{CO})_5\}]$ (**11**), and $[\{\text{Fe}_2(\mu\text{-SCH}_2)_2\text{S}(\text{CO})_6\}\{\text{W}(\text{CO})_5\}]$ (**12**) were obtained in 76, 83, and 82% yields, respectively (Scheme 4).

Complexes **10–12** are air-stable red solids, which were fully characterized by elemental analysis, NMR and IR spectroscopy, and X-ray crystallography. The IR spectra of **10–12** show four to eight strong absorption bands in the range 2086–1897 cm^{-1} assigned to the terminal carbonyl groups. The highest absorption bands assigned to the two $\text{Fe}(\text{CO})_3$ units lie at frequencies higher (2086–2083 cm^{-1}) than that (2075 cm^{-1}) of parent complex **A**.^[7] This is apparently due to the decreased π back bonding after the electron-withdrawing groups of $[(\eta^5\text{-MeC}_5\text{H}_4)(\text{CO})_2\text{Fe}]^+$ and $\text{M}(\text{CO})_5$ coordinate to the central S atom.^[11] Similarly to the spectra of **1–4**, the ^1H NMR spectrum of **10** shows two doublets at $\delta = 3.49$ and 4.03 ppm for the two magnetically different protons in the CH_2 groups, whereas those of **11** and **12** display one singlet at $\delta = 3.17$ and 3.34 ppm for the two magnetically identical protons in their CH_2 groups. In addition, the ^{19}F NMR spectrum of **10** shows one singlet at -151.67 ppm, which can be assigned to the BF_4^- anion.^[18]

The molecular structures of **10–12** are depicted in Figures 5, 6, and 7, whereas their selected bond lengths and angles are presented in Table 3. As can be seen intuitively from Figures 5, 6, and 7, the three complexes are indeed the expected derivatives generated by coordination of the central S atom of the parent complex **A** with transition-metal atoms Fe1, Cr1, and W1 through a common equatorial bond of the two fused six-membered rings ($\text{Fe2–S2–C9–S1–C10–S3}/\text{Fe3–S2–C9–S1–C10–S3}$ for **10**, and $\text{Fe1–S1–C12–S3–C13–S2}/\text{Fe2–S1–C12–S3–C13–S2}$ for **11** and **12**). Such an equatorial type of conformational arrangement in **10–12**



Scheme 4.

apparently occurs in order to avoid the strong steric repulsion between the apically located carbonyl ligand in moiety **A** and the bulky axially attached $[(\eta^5\text{-MeC}_5\text{H}_4)(\text{CO})_2\text{Fe}]$ or $\text{M}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{W}$) moiety. In addition, all the iron atoms in **10–12**, as well as both Cr1 and W1 atoms in **11** and **12**, have a distorted octahedral geometry. Finally, it should be

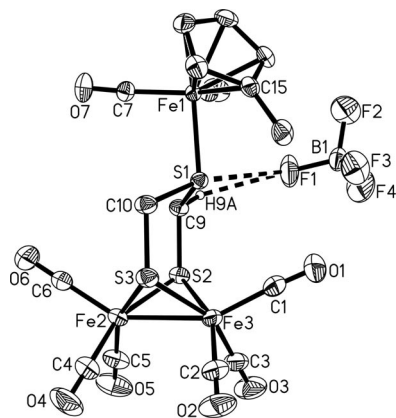


Figure 5. Molecular structure of **10** with 30% probability level ellipsoids.

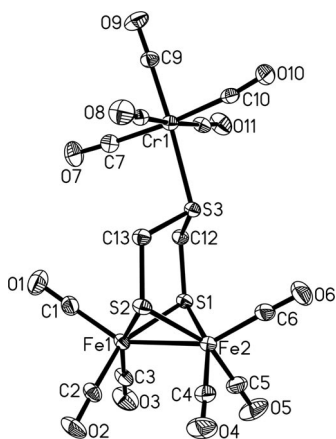


Figure 6. Molecular structure of **11** with 30% probability level ellipsoids.

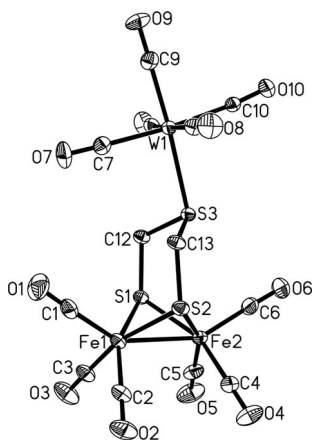


Figure 7. Molecular structure of **12** with 30% probability level ellipsoids.

noted that in the solid-state structure of **10** there are two types of weak interactions between its complex cation and the anion BF_4^- : (i) the F1 atom is involved in a weak hydrogen-bond interaction in $\text{C9-H9A}\cdots\text{F1}$,^[19] since the $\text{F1}\cdots\text{H9A}$ distance (2.526 Å) is smaller than the sum of the van der Waal's radii of the hydrogen atom (1.20 Å)^[20] and the fluorine atom (1.47 Å),^[21] and (ii) a weak interaction occurs between the negatively charged F1 atom and the positively charged S1 atom as a result of delocalization of the positive charge of the cationic Fe1 atom. This is consistent with the fact that the $\text{F1}\cdots\text{S1}$ distance (3.165 Å) is smaller than the sum of the van der Waal's radii of the fluorine atom (1.47 Å) and the sulfur atom (1.80 Å).^[21]

Table 3. Selected bond lengths [Å] and angles [°] for **10–12**.

10			
Fe1–S1	2.2448(13)	Fe3–S3	2.2568(13)
Fe2–S3	2.2382(14)	S1–C9	1.789(4)
Fe2–S2	2.2479(12)	S1–C10	1.797(4)
Fe2–Fe3	2.5094(11)	S2–C9	1.809(4)
Fe3–S2	2.2523(13)	S3–C10	1.806(4)
S3–Fe2–S2	86.60(4)	S3–Fe3–Fe2	55.71(4)
S3–Fe2–Fe3	56.42(3)	C9–S1–C10	98.87(18)
S2–Fe2–Fe3	56.19(4)	Fe2–S2–Fe3	67.78(4)
S2–Fe3–S3	86.05(5)	Fe2–S3–Fe3	67.87(4)
S2–Fe3–Fe2	56.03(3)	S1–C9–S2	115.71(19)
11			
Fe1–S2	2.2496(12)	Cr1–S3	2.4368(12)
Fe1–S1	2.2568(13)	S1–C12	1.816(4)
Fe1–Fe2	2.5116(10)	S2–C13	1.818(4)
Fe2–S2	2.2477(12)	S3–C12	1.794(4)
Fe2–S1	2.2558(12)	S3–C13	1.795(4)
S2–Fe1–S1	86.33(4)	S1–Fe2–Fe1	56.20(4)
S2–Fe1–Fe2	56.01(3)	Fe2–S1–Fe1	67.64(4)
S1–Fe1–Fe2	56.16(3)	Fe2–S2–Fe1	67.90(4)
S2–Fe2–S1	86.40(4)	C12–S3–C13	99.19(18)
S2–Fe2–Fe1	56.08(3)	C7–Cr1–S3	89.54(13)
12			
Fe1–S1	2.2569(18)	W1–S3	2.5656(15)
Fe1–S2	2.2585(19)	S1–C12	1.826(6)
Fe1–Fe2	2.5139(14)	S2–C13	1.818(5)
Fe2–S2	2.253(2)	S3–C12	1.795(6)
Fe2–S1	2.2569(18)	S3–C13	1.795(6)
S1–Fe1–S2	86.38(6)	S1–Fe2–Fe1	56.16(5)
S1–Fe1–Fe2	56.15(5)	Fe2–S1–Fe1	67.69(5)
S2–Fe1–Fe2	56.04(5)	Fe2–S2–Fe1	67.72(6)
S2–Fe2–S1	86.50(7)	C12–S3–C13	99.3(3)
S2–Fe2–Fe1	56.24(5)	C7–W1–S3	89.28(18)

Electrochemical H_2 Evolution Catalyzed by Model Complex **3**

On the basis of our previous study on the electrochemical and electrocatalytic properties of parent complex **A**,^[7] we continue to investigate these properties of model complex **3** under the same conditions as those reported for its parent complex **A**. As can be seen from the cyclic voltammogram (Figure 8) and differential pulse voltammogram (inset in Figure 8), complex **3** displays a quasi-reversible reduction at $E_{\text{pc}} = -1.76$ V, an irreversible reduction at $E_{\text{pc}} = -1.98$ V,

and an irreversible oxidation at $E_{\text{pa}} = +0.49$ V. Similarly to the redox processes of parent complex **A**, the first reduction process could be assigned to the one-electron reduction of $[\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}]$ to $[\text{Fe}^{\text{I}}\text{Fe}^0]$, the second reduction process to the reduction of $[\text{Fe}^{\text{I}}\text{Fe}^0]$ to $[\text{Fe}^0\text{Fe}^0]$, and the oxidation process to the oxidation of $[\text{Fe}^{\text{I}}\text{Fe}^{\text{I}}]$ to $[\text{Fe}^{\text{I}}\text{Fe}^{\text{II}}]$. Actually, the cyclic voltammetric behavior of model complex **3** is very similar to that of its parent complex **A**, with the exception that the reduction and oxidation potentials of **3** are more negative than those of the corresponding processes of its parent complex **A** (−1.51, −1.94 and +0.79 V), because of the greater electron-donating ability of the isocyanide ligand *t*BuNC than the carbonyl ligand.

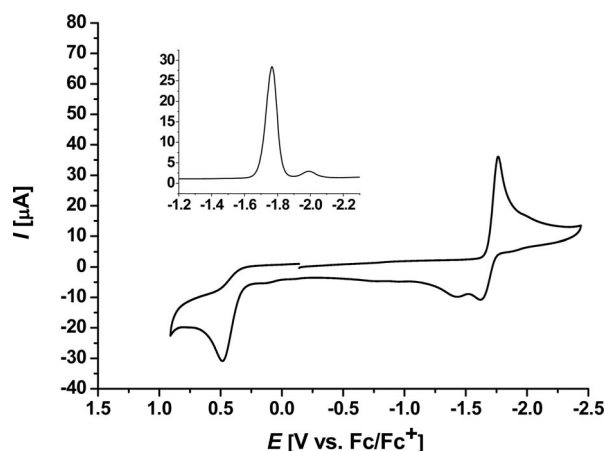


Figure 8. Cyclic voltammogram of **3** (1.0 mM) in 0.1 M *n*Bu₄NPF₆/MeCN at a scan rate of 100 mV s^{−1}; inset: differential pulse voltammogram of **3**.

A further cyclic voltammetric study indicates that model **3** has the ability to reduce a proton of a proton donor such as Et₃NHCl ($\text{p}K_{\text{a}} = 18.7$ in MeCN) to give hydrogen. As shown in Figure 9, upon addition of the first 2 mg of Et₃NHCl to the solution of **3**, the initial first reduction peak at −1.76 V slightly increases, but does not continue to grow with sequential addition of Et₃NHCl. However, in contrast to this, upon addition of the first 2 mg of Et₃NHCl, the initial second reduction peak at −1.98 V remarkably increases and continues to increase with increasing concentration of the acid. Such observations are typical of an electrocatalytic proton-reduction process.^[6,22–24]

The electrocatalytic activity of **3** was determined by bulk electrolysis of a MeCN solution of **3** (0.5 mM) with excess Et₃NHCl (25 mM) under the same conditions as those reported for parent complex **A**.^[7] The total charge passed through the cell is 16.5 F mol^{−1} of **3** during the course of 0.5 h, which corresponds to 8.2 turnovers. Gas chromatographic analysis shows that the hydrogen yield is about 95%. It follows that the electrocatalytic activity of parent complex **A**^[7] is not improved by substitution of the CO group with *t*BuNC (to give **3**). It is worth pointing out that our attempts to compare the electrochemical and electrocatalytic properties of the central-S-coordinated complexes **11**

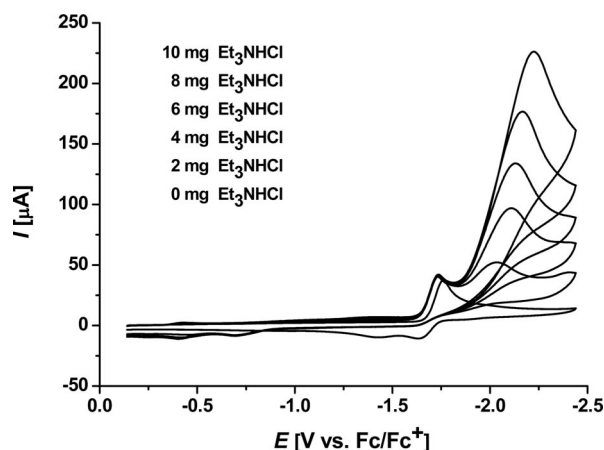


Figure 9. Cyclic voltammogram of **3** (1.0 mM) with Et₃NHCl (0–10 mg) in 0.1 M *n*Bu₄NPF₆/MeCN at a scan rate of 100 mV s^{−1}.

and **12** with complex **A** were unsuccessful because of their serious decomposition under the electrochemical conditions used.

Conclusions

Substitution of the CO group and coordination at the central S atom of parent complex **A** have been systematically studied, which allows us to obtain not only the single [2Fe3S]-cluster-containing monodentate-ligand-substituted TDT-type models **1–4**, but also the double [2Fe3S]-cluster-containing bidentate-ligand-bridged TDT-type models **5–9**, and the central-S-coordinated TDT-type models **10–12**. The spectroscopic and X-ray crystallographic studies on these new complexes have provided detailed structural and conformational information, while a comparative study on the electrochemical and electrocatalytic properties of model **3** and the parent complex **A** is preliminarily carried out. Further studies on the structural modification of parent complex **A**, as well as on the reduction of the proton to hydrogen catalyzed by such structurally modified TDT-type models are in progress in this laboratory.

Experimental Section

General Comments: All manipulations were performed by using standard Schlenk and vacuum-line techniques under N₂ atmosphere. Dichloromethane and acetonitrile were distilled from P₂O₅ under N₂. Hexane and thf were purified by distillation under N₂ from Na/benzophenone ketyl. Et₃BHLi (1 M in thf), *tert*-butyl isocyanide, cyclohexyl isocyanide, Cr(CO)₆, W(CO)₆, AgBF₄, PPh₃, and *trans*-Ph₂PCH=CHPPh₂ were available commercially and used without further purification. [(μ-S)₂Fe₂(CO)₆],^[10] S(CH₂Br)₂,^[25] 1,1'-bis(diphenylphosphanyl)ferrocene (dppf),^[26] 1,1'-bis(diphenylphosphanyl)ruthenocene (dppr),^[27] 1,4-(CN)₂C₆H₄,^[28] [(η⁵-C₅H₅)-(η⁵-Ph₂PC₅H₄)Fe],^[29] 4,4'-(Ph₂P)₂C₆H₄,^[30] and [(η⁵-MeC₅H₄)-Fe(CO)₂I]^[31] were prepared according to literature procedures. Preparative TLC was carried out on glass plates (26 × 20 × 0.25 cm) coated with silica gel H (10–40 μm). IR spectra were recorded on a Bio-Rad FTS 135 infrared spectrophotometer. ¹H, ³¹P, and ¹⁹F NMR spectra were recorded on a Bruker AC-P 200, a Bruker Av-

ance 300, and a Varian Mercury Plus 400 NMR spectrometer. Chemical shifts are given in ppm and referenced to tms (^1H), 85% H_3PO_4 (^{31}P), and CFCl_3 (^{19}F), respectively. Elemental analyses were performed on an Elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus.

[Fe₂(μ-SCH₂)₂S(CO)₆] (A): A solution of [(μ-S₂)Fe₂(CO)₆] (0.344 g, 1.0 mmol) in thf (15 mL) was cooled to -78 °C, and LiEt₃BH (2 mL, 2.0 mmol) was then slowly added. After stirring the resulting green solution for 10 min, S(CH₂Br)₂ (0.2 mL, 1.5 mmol) was added. The new mixture was warmed to room temperature and stirred at this temperature for 2 h to give a red solution. The solvent was removed in vacuo, and the residue was subjected to TLC separation by using CH₂Cl₂/petroleum ether (v/v = 1:10) as eluent. From the main red band, **A** was obtained as a red solid (0.098 g, 24%), which was identified by comparison of its melting point, and IR and ^1H NMR spectra with those of an authentic sample.^[7]

[Fe₂(μ-SCH₂)₂S(CO)₅(PPh₃)] (1): To a solution of **A** (0.081 g, 0.2 mmol) and Ph₃P (0.053 g, 0.2 mmol) in MeCN (10 mL) was added a solution of Me₃NO·2H₂O (0.022 g, 0.2 mmol) in MeCN (5 mL), and the mixture was then stirred at room temperature for 0.5 h. The solvent was removed in vacuo, and the residue was subjected to TLC separation by using CH₂Cl₂/petroleum ether (v/v = 1:5) as eluent. From the main red band, **1** was obtained as a dark red solid (0.113 g, 89%). M.p. 174–176 °C. ^1H NMR (200 MHz, CDCl₃): δ = 7.76, 7.42 (2s, 15 H, 3 C₆H₅), 2.84, 2.33 (2d, *J* = 13.6 Hz, 4 H, 2 CH₂) ppm. ^{31}P NMR (121 MHz, CDCl₃): δ = 64.44 (s) ppm. IR (KBr disk): $\tilde{\nu}$ = 2045 (vs), 1976 (vs), 1934 (C=O) (s) cm⁻¹. C₂₅H₁₉Fe₂O₅PS₃ (638.27): calcd. C 47.04, H 3.00; found C 46.94, H 3.02.

[Fe₂(μ-SCH₂)₂S(CO)₅{(η⁵-C₅H₅)(η⁵-Ph₂PC₅H₄)Fe}] (2): The same procedure as that of **1** was followed, except that PPh₃ was replaced by [(η⁵-C₅H₅)(η⁵-Ph₂PC₅H₄)Fe] (0.074 g, 0.2 mmol). From the main red band, **2** (0.121 g, 81%) was obtained as a dark red solid. M.p. 149–150 °C. ^1H NMR (300 MHz, CDCl₃): δ = 7.68, 7.42 (2s, 10 H, 2 C₆H₅), 4.52 (s, 4 H, C₅H₄), 3.92 (s, 5 H, C₅H₅), 2.78, 2.31 (2d, *J* = 12.5 Hz, 4 H, 2 CH₂) ppm. ^{31}P NMR (121 MHz, CDCl₃): δ = 55.26 (s) ppm. IR (KBr disk): $\tilde{\nu}$ = 2047 (vs), 1981 (vs), 1934 (C=O) (s) cm⁻¹. C₂₉H₂₃Fe₃O₅PS₃ (746.19): calcd. C 46.68, H 3.11; found C 46.45, H 3.26.

[Fe₂(μ-SCH₂)₂S(CO)₅(*t*BuNC)] (3): To a solution of **A** (0.202 g, 0.5 mmol) in CH₂Cl₂ (20 mL) was added *t*BuNC (0.056 mL, 0.5 mmol), and the mixture was then stirred at room temperature for 20 h. After removal of the solvent at reduced pressure, the residue was subjected to TLC separation by using CH₂Cl₂/petroleum ether (v/v = 1:3) as eluent. From the main red band, **3** (0.141 g, 61%) was obtained as a red solid. M.p. 121–122 °C. ^1H NMR (400 MHz, CDCl₃): δ = 3.14 (s, 4 H, 2 CH₂), 1.43 (s, 9 H, C-(CH₃)₃) ppm. IR (KBr disk): $\tilde{\nu}$ = 2163 (vs) N≡C, 2038 (vs), 2006 (vs), 1992 (vs), 1969 (C=O) (vs) cm⁻¹. C₁₂H₁₃Fe₂NO₅S₃ (459.12): calcd. C 31.39, H 2.85, N 3.05; found C 31.47, H 2.85, N 3.10.

[Fe₂(μ-SCH₂)₂S(CO)₅(C₆H₁₁NC)] (4): To a solution of **A** (0.081 g, 0.2 mmol) in CH₂Cl₂ (10 mL) was added C₆H₁₁NC (0.025 mL, 0.2 mmol), and the mixture was then stirred at room temperature for 20 h. The same workup as that of **3** gave compound **4** (0.058 g, 60%) as a red solid. M.p. 74–75 °C. ^1H NMR (400 MHz, CDCl₃): δ = 3.79 (s, 1 H, CH of cyclohexyl), 3.14 (s, 4 H, 2 CH₂S), 1.88, 1.70, 1.39 (3s, 10 H, 5 CH₂ of cyclohexyl) ppm. IR (KBr disk): $\tilde{\nu}$ = 2161 (N≡C) (s), 2044 (s), 2000 (vs), 1969 (C=O) (vs) cm⁻¹. C₁₄H₁₅Fe₂NO₅S₃ (485.16): calcd. C 34.66, H 3.12, N 2.89; found C 34.89, H 3.24, N 2.85.

[{Fe₂(μ-SCH₂)₂S(CO)₅}₂{4,4'-(Ph₂P)₂(C₆H₄)₂}] (5): To a solution of **A** (0.081 g, 0.2 mmol) and 4,4'-(Ph₂P)₂(C₆H₄)₂ (0.053 g,

0.1 mmol) in MeCN (10 mL) was added a solution of Me₃NO·2H₂O (0.022 g, 0.2 mmol) in MeCN (5 mL), and the mixture was then stirred at room temperature for 0.5 h. After the solvent was removed in vacuo, the residue was subjected to TLC separation by using CH₂Cl₂/petroleum ether (v/v = 1:4) as eluent. From the main red band, **5** (0.093 g, 73%) was obtained as a dark red solid. M.p. 203 °C (dec.). ^1H NMR (300 MHz, CDCl₃): δ = 7.76, 7.44 (2s, 28 H, 4 C₆H₅ and 2 C₆H₄), 2.86, 2.39 (2d, *J* = 10.6 Hz, 8 H, 4CH₂) ppm. ^{31}P NMR (121 MHz, CDCl₃): δ = 64.07 (s) ppm. IR (KBr disk): $\tilde{\nu}$ = 2047 (vs), 1984 (vs), 1935 (C=O) (s) cm⁻¹. C₅₀H₃₆Fe₄O₁₀P₂S₆ (1274.53): calcd. C 47.12, H 2.85; found C 46.99, H 3.01.

[{Fe₂(μ-SCH₂)₂S(CO)₅}₂(*trans*-Ph₂PCH=CHPPh₂)] (6): The same procedure as that of **5** was followed, with the exception that 4,4'-(Ph₂P)₂(C₆H₄)₂ was replaced by *trans*-Ph₂PCH=CHPPh₂ (0.040 g, 0.1 mmol). From the main red band, **6** (0.068 g, 59%) was obtained as a dark red solid. M.p. 195 °C (dec.). ^1H NMR (300 MHz, CDCl₃): δ = 7.73, 7.46 (2s, 20 H, 4 C₆H₅), 7.12, 7.06 (2d, *J* = 11.0 Hz, 2 H, *trans*-CH=CH), 2.80, 2.28 (2d, *J* = 11.8 Hz, 8 H, 4 CH₂) ppm. ^{31}P NMR (121 MHz, CDCl₃): δ = 59.27 (s) ppm. IR (KBr disk): $\tilde{\nu}$ = 2047 (vs), 1985 (vs), 1934 (C=O) (s), 1651 (C=C) (w) cm⁻¹. C₄₀H₃₀Fe₄O₁₀P₂S₆ (1148.38): calcd. C 41.84, H 2.63; found C 42.07, H 2.62.

[{Fe₂(μ-SCH₂)₂S(CO)₅}₂{1,4-(CN)₂C₆H₄}] (7): To a solution of **A** (0.081 g, 0.2 mmol) in MeCN (10 mL) was added Me₃NO·2H₂O (0.022 g, 0.2 mmol). After the mixture was stirred at room temperature for 20 min, 1,4-(CN)₂C₆H₄ (0.013 g, 0.1 mmol) was added. The new mixture was stirred for 4 h. The solvent was removed at reduced pressure, and the residue was subjected to TLC separation by using CH₂Cl₂/petroleum ether (v/v = 1:4) as eluent. From the main red band, **7** (0.040 g, 45%) was obtained as a dark red solid. M.p. 138 °C (dec.). ^1H NMR (200 MHz, CDCl₃): δ = 7.28 (s, 4 H, C₆H₄), 3.19 (s, 8 H, 4 CH₂) ppm. IR (KBr disk): $\tilde{\nu}$ = 2118 (N≡C) (vs), 2043 (vs), 2005 (vs), 1978 (C=O) (vs) cm⁻¹. C₂₂H₁₂Fe₄N₂O₁₀S₆ (880.11): calcd. C 30.02, H 1.37, N 3.18; found C 30.08, H 1.41, N 3.17.

[{Fe₂(μ-SCH₂)₂S(CO)₅}₂(dppf)] (8): The same procedure as that of **7** was followed, with the exception that 1,4-(CN)₂C₆H₄ was replaced by dppf (0.056 g, 0.1 mmol). From the main red band, **8** (0.055 g, 42%) was obtained as a dark red solid. M.p. 137 °C (dec.). ^1H NMR (300 MHz, CDCl₃): δ = 7.57, 7.40 (2s, 20 H, 4 C₆H₅), 4.26 (s, 8 H, 2 C₃H₄), 2.78, 2.31 (2d, *J* = 11.7 Hz, 8 H, 4 CH₂) ppm. ^{31}P NMR (121 MHz, CDCl₃): δ = 55.79 (s) ppm. IR (KBr disk): $\tilde{\nu}$ = 2047 (vs), 1982 (vs), 1932 (C=O) (s) cm⁻¹. C₄₈H₃₆Fe₄O₁₀P₂S₆ (1306.36): calcd. C 44.13, H 2.78; found C 44.23, H 2.78.

[{Fe₂(μ-SCH₂)₂S(CO)₅}₂(dppr)] (9): The same procedure as that of **7** was followed, with the exception that 1,4-(CN)₂C₆H₄ was replaced by dppr (0.060 g, 0.1 mmol). From the main red band, **9** (0.093 g, 69%) was obtained as a dark red solid. M.p. 174 °C (dec.). ^1H NMR (200 MHz, CDCl₃): δ = 7.63–7.38 (m, 20 H, 4 C₆H₅), 4.61, 4.49 (2s, 8 H, 2 C₃H₄), 2.82, 2.39 (2d, *J* = 13.4 Hz, 8 H, 4 CH₂) ppm. ^{31}P NMR (81 MHz, CDCl₃): δ = 54.61 (s) ppm. IR (KBr disk): $\tilde{\nu}$ = 2047 (vs), 1986 (vs), 1934 (C=O) (s) cm⁻¹. C₄₈H₃₆Fe₄O₁₀P₂RuS₆ (1351.58): calcd. C 42.66, H 2.68; found C 42.38, H 2.48.

[{Fe₂(μ-SCH₂)₂S(CO)₆}{(η⁵-MeC₅H₄)(CO)₂Fe}(BF₄)] (10): To a suspension of AgBF₄ (0.049 g, 0.25 mmol) in CH₂Cl₂ (15 mL) was added [(η⁵-MeC₅H₄)(CO)₂Fe] (0.079 g, 0.25 mmol). The mixture was stirred in the dark for 2 h. During this period, the amount of white AgBF₄ diminished, and a red solution containing [(η⁵-MeC₅H₄)(CO)₂Fe}(BF₄)] was formed. To this solution was added

A (0.121 g, 0.30 mmol), and the mixture was then stirred for an additional 2 h. The resulting mixture was filtered to remove insoluble materials, and the filtrate was evaporated to dryness in vacuo. The crude product was washed thoroughly with hexane and dried in vacuo to give **10** (0.130 g, 76%) as a red solid. M.p. 186 °C (dec.). ¹H NMR [400 MHz, (CD₃)₂CO]: δ = 5.55–5.53 (m, 4 H, C₅H₄), 4.03, 3.49 (2d, *J* = 11.2 Hz, 2 H, 2 CH₂), 2.07 (s, 3 H, CH₃) ppm. ¹⁹F NMR [376 MHz, (CD₃)₂CO]: δ = –151.67 (s, BF₄) ppm. IR (KBr disk): ν̄ = 2086 (s), 2052 (vs), 2039 (vs), 2012 (C≡O) (vs), 1123 (m), 1083 (s), 1035 (B–F) (m) cm^{–1}. C₁₆H₁₁BF₄Fe₃O₈S₃ (681.79): calcd. C 28.19, H 1.63; found C 28.07, H 1.60.

[{Fe₂(μ-SCH₂)₂S(CO)₆}{Cr(CO)₅}] (11): A stirred solution of [Cr(CO)₅] (0.066 g, 0.30 mmol) in thf (25 mL) was irradiated for 1.5 h at room temperature by using a water-cooled UV 450-W mercury vapor lamp to give an orange solution containing ca. 0.30 mmol [Cr(CO)₅(thf)]. To this solution was added **A** (0.061 g, 0.15 mmol), and the mixture was then stirred at room temperature for 2 h. The solvent was removed in vacuo, and the residue was subjected to TLC separation by using CH₂Cl₂/petroleum ether (*v/v* = 1:15) as eluent. From the main red band, **11** (0.074 g, 83%) was obtained as a red solid. M.p. 128 °C (dec.). ¹H NMR (200 MHz, CDCl₃): δ = 3.17 (s, 4 H, 2 CH₂) ppm. IR (KBr disk): ν̄ = 2083 (s), 2069 (vs), 2045 (vs), 2006 (vs), 1959 (vs), 1937 (vs), 1926 (vs), 1904 (C≡O) (vs) cm^{–1}. C₁₃H₄CrFe₂O₁₁S₃ (596.05): calcd. C 26.20, H 0.68; found C 26.28, H 0.78.

[{Fe₂(μ-SCH₂)₂S(CO)₆}{W(CO)₅}] (12): To an orange solution of [W(CO)₅(thf)] (ca. 0.4 mmol), which was prepared in situ by photolysis of [W(CO)₆] (0.141 g, 0.4 mmol) in thf (40 mL) under the same conditions as described above for **11**, was added **A** (0.081 g, 0.2 mmol). After the mixture was stirred at room temperature for 2 h, the same workup as that of **11** afforded compound **12** (0.120 g, 82%) as a red solid. M.p. 136 °C (dec.). ¹H NMR (200 MHz, CDCl₃): δ = 3.34 (s, 4 H, 2 CH₂) ppm. IR (KBr disk): ν̄ = 2084 (s), 2074 (vs), 2045 (vs), 2008 (vs), 1959 (vs), 1937 (vs), 1918 (vs), 1897 (C≡O) (vs) cm^{–1}. C₁₃H₄Fe₂O₁₁S₃W (727.89): calcd. C 21.45, H 0.55; found C 21.38, H 0.52.

Electrochemistry: A solution of 0.1 M *n*Bu₄NPF₆ in MeCN (Fisher Chemicals, HPLC grade) was used as the electrolyte in all cyclic voltammetric experiments. The electrolyte solution was degassed by bubbling dry N₂ through for 10 min before measurement. Electrochemical measurements were made by using a BAS Epsilon potentiostat. All voltammograms were obtained in a three-electrode cell with a 3-mm diameter glassy carbon working, a platinum counter, and an Ag/Ag⁺ (0.01 M AgNO₃/0.1 M *n*Bu₄NPF₆ in MeCN) reference electrode under N₂ atmosphere. The working electrode was polished with 1 μm alumina paste and sonicated in water for 10 min prior to use. All potentials are quoted against the ferrocene/ferrocenium (Fc/Fc⁺) potential. Bulk electrolyses for electrocatalytic reactions were carried out under N₂ or CO atmosphere by using a BAS Epsilon potentiostat. Electrocatalytic experiments were run on a glassy carbon rod (2.9 cm²) in a two-compartment, gastight, H-type electrolysis cell containing MeCN (25 mL). The electrolyses of solutions were carried out under hydrodynamic conditions, by vigorously stirring the solution to mitigate mass transport complications. Gas chromatography was performed with a Shimadzu gas chromatograph GC-9A under isothermal conditions with nitrogen as a carrier gas and a thermal conductivity detector.

X-ray Structure Determinations of 1, 3, 8, and 10–12: Single crystals of **1**, **3**, **8**, and **10–12** suitable for X-ray diffraction analyses were grown by slow evaporation of CH₂Cl₂/*n*-hexane solutions of **1**, **3**, and **8** and CH₂Cl₂/petroleum ether solutions of **11** and **12** at 4 °C, while a single crystal of **10** was obtained by slow diffusion of anhydrous diethyl ether into a saturated solution of **10** in acetone at –20 °C. The single crystals of **1**, **8**, and **10–12** were mounted on a Bruker SMART 1000 automated diffractometer. Data were collected at room temperature by using a graphite monochromator with Mo-*K*_α radiation (λ = 0.71073 Å) in the ω-φ scanning mode. Absorption correction was performed by the SADABS program.^[32] The single crystal of **3** was mounted on a Rigaku MM-007 (rotating anode) diffractometer equipped with Saturn 70CCD. Data collection, reduction, and absorption correction were performed by

Table 4. Crystal data and structure refinement details for **1**, **3** and **8**.

	1	3	8
Formula	C ₂₅ H ₁₉ Fe ₂ O ₅ PS ₃	C ₁₂ H ₁₃ Fe ₂ NO ₅ S ₃	C ₄₈ H ₃₆ Fe ₅ O ₁₀ P ₂ S ₆ ·2CH ₂ Cl ₂
<i>M</i> _r [g mol ^{–1}]	638.25	459.11	1476.17
<i>T</i> [K]	293(2)	113(2)	293(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	11.459(5)	21.830(4)	9.5418(10)
<i>b</i> [Å]	15.054(6)	9.5532(17)	12.7287(14)
<i>c</i> [Å]	16.358(6)	18.433(4)	13.6727(15)
<i>α</i> [°]	90	90	100.0210(10)
<i>β</i> [°]	108.615(7)	112.912(3)	102.4920(10)
<i>γ</i> [°]	90	90	109.9180(10)
<i>V</i> [Å ³]	2674.3(18)	3540.9(12)	1467.8(3)
<i>Z</i>	4	8	1
ρ _{calcd.} [g cm ^{–3}]	1.585	1.722	1.670
μ [mm ^{–1}]	1.413	2.012	1.710
Crystal size [mm]	0.20 × 0.16 × 0.10	0.18 × 0.16 × 0.14	0.28 × 0.20 × 0.10
<i>F</i> (000)	1296	1856	744
2θ _{max} [°]	50.02	55.72	50.06
Reflections collected	13627	16082	8042
Independent reflections	4720	4218	5132
Goodness-of-fit	0.986	1.028	1.071
<i>R</i>	0.0400	0.0243	0.0321
<i>R</i> _w	0.0746	0.0580	0.0922
Largest diff peak and hole [e Å ^{–3}]	0.340/–0.312	0.388/–0.505	0.493/–0.496

Table 5. Crystal data and structure refinement details for **10–12**.

	10	11	12
Formula	C ₁₆ H ₁₁ BF ₄ Fe ₃ O ₈ S ₃	C ₁₃ H ₄ CrFe ₂ O ₁₁ S ₃	C ₁₃ H ₄ Fe ₂ O ₁₁ S ₃ W
<i>M</i> _r [g mol ^{−1}]	681.79	596.04	727.89
<i>T</i> [K]	293(2)	293(2)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> [Å]	21.903(8)	29.648(9)	29.871(9)
<i>b</i> [Å]	7.456(3)	9.633(3)	9.697(3)
<i>c</i> [Å]	15.189(5)	14.589(4)	14.750(5)
<i>α</i> [°]	90	90	90
<i>β</i> [°]	99.374(6)	94.644(5)	95.114(6)
<i>γ</i> [°]	90	90	90
<i>V</i> [Å ³]	2447.6(15)	4153(2)	4256(2)
<i>Z</i>	4	8	8
<i>ρ</i> _{calcd.} [g cm ^{−3}]	1.850	1.907	2.272
<i>μ</i> [mm ^{−1}]	2.080	2.247	7.084
Crystal size [mm]	0.18 × 0.14 × 0.08	0.24 × 0.20 × 0.16	0.16 × 0.12 × 0.08
<i>F</i> (000)	1352	2352	2752
2 <i>θ</i> _{max} [°]	52.54	50.02	52.86
Reflections collected	13464	9905	12022
Independent reflections	4880	3650	4368
Goodness-of-fit	1.065	0.982	0.967
<i>R</i>	0.0349	0.0381	0.0363
<i>R</i> _w	0.0710	0.0567	0.0578
Largest diff peak and hole [e Å ^{−3}]	0.455/−0.453	0.347/−0.312	0.979/−0.955

the CRYSTALCLEAR program.^[33] The structures were solved by direct methods with the SHELXS-97 program^[34] and refined by full-matrix least-squares techniques (SHELXL-97)^[35] on *F*². Hydrogen atoms were located by using the geometric method. Details of the crystal data, data collections, and structure refinements are summarized in Tables 4 and 5. CCDC-745905 for **1**, −745906 for **3**, −745907 for **8**, −745908 for **10**, −745909 for **11**, and −745910 for **12** contain the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data-request/cif.

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