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Article

Synthetic and Structural Studies on L-Cysteinyl Group-Containing Diiron/Triiron Azadithiolates as Active Site Models of [FeFe]-Hydrogenases

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Five new L-cysteinyl group-containing diiron/triiron azadithiolate complexes (**3**−**6**, **10**), which could be regarded as the active site models of [FeFe]-hydrogenases, have been successfully synthesized. Treatment of L-cysteinyl sodium mercaptide CytSNa (**1**, Cyt = $CH_2CH(CO_2Et)NH(CO_2Bu\text{-}t)$) with complex $[(\mu\text{-}SCH_2)_2NCH_2CH_2Br]Fe_2(CO)_6$ (**2**) in THF at room temperature resulted in formation of model complex $[(\mu\text{-}SCH_2)_2NCH_2CH_2SCyt]Fe_2(CO)_6$ (**3**). Further treatment of **3** with decarbonylating agent Me_3NO in MeCN at room temperature afforded model complex $[(\mu\text{-}SCH_2)_2NCH_2CH_2SCyt]Fe_2(CO)_5$ (**4**). Similarly, treatment of **3** with an equimolar mixture of Me_3NO and Ph_3P gave model complex $[(\mu\text{-}SCH_2)_2NCH_2CH_2SCyt]Fe_2(CO)_5(Ph_3P)$ (**5**) and further treatment of **5** with Me_3NO produced model complex $[(\mu\text{-}SCH_2)_2NCH_2CH_2SCyt]Fe_2(CO)_4(Ph_3P)$ (**6**). More interestingly, model complex $[(\mu\text{-}SCH_2)_2NCH(CO_2Et)CH_2SFe(CO)_2Cp]Fe_2(CO)_5$ (**10**) could be synthesized by a "one pot" reaction of the in situ prepared $(\mu\text{-}HS)_2Fe_2(CO)_6$ (**9**) with 37% aqueous formaldehyde followed by treatment with the N-deprotected L-cysteinyl iron mercaptide $Cp(CO)_2FeSCH_2CH(CO_2Et)NH_2$ (**8**). Complex **8** is new, which was prepared by treatment of complex $Cp(CO)_2FeSCyt$ (**7**) with CF_3CO_2H followed by 25% aqueous NH_3. All the new complexes **3**−**6**, **8**, and **10** were characterized by elemental analysis and various spectroscopic techniques, whereas complexes **5** and **10** were further characterized by X-ray crystallography.

Introduction

Hydrogenases are a class of natural enzymes that can catalyze hydrogen metabolism in a broad range of prokaryotic and eukaryotic microbes.[1−4] According to the metal composition in the active site, hydrogenases are generally classified into three major groups: [NiFe]-hydrogenases,[5−8] [FeFe]-hydrogenases,[9−12] and [Fe]-hydrogenases (Hmd).[13] Recently, [FeFe]-hydrogenases have received special attention, largely due to their unusual structures and particularly their highly catalytic ability for production of hydrogen, an alternative "clean" and renewable fuel.[14] Crystallographic[15−18] and FTIR spectroscopic[19] studies revealed that the active site of [FeFe]-hydrogenases, so-called H-cluster,[11] consists of a butterfly 2Fe2S cluster linked to a cubic 4Fe4S cluster via the sulfur atom of a L-cysteinyl group. In addition, the two Fe atoms of the butterfly 2Fe2S cluster are coordinated with the biologically unusual CO and CN^- ligands and are bridged by a less defined dithiolate ligand. Further crystallographic and theoretical studies[9,20] demonstrated

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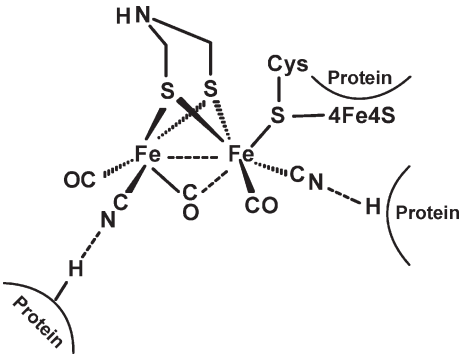
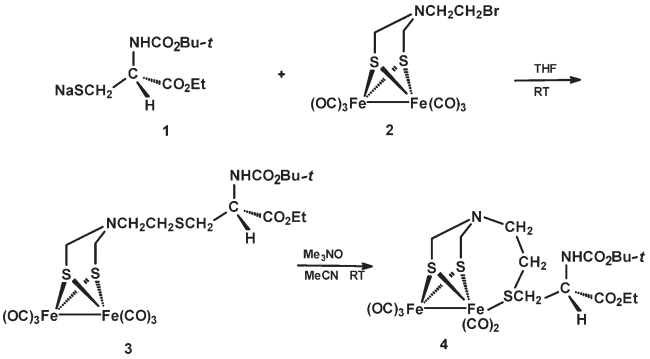
Scheme 1



Scheme 2



that this dithiolate could be most likely an azadithiolate (ADT, SCH_2NCH_2S), whose central N atom plays an important role for the formation and heterolytic cleavage of hydrogen in the natural enzymes (Scheme 1).

The aforementioned successful structural studies have prompted chemists to design and synthesize a great variety of the active site models.[21−28] Very recently, we reported our studied results regarding a new type of L-cysteinyl group-containing models, in which a L-cysteinyl group is coordinated via its S atom to one Fe atom of the diiron subsite.[29] On the basis of this study we continued to carry out a study on another new type of L-cysteinyl group-containing models, whose L-cysteinyl groups are either simply covalently bound to the bridgehead N atom of an ADT-bridged diiron subsite or not only covalently bound to the bridgehead N atom but also coordinatively bound to one Fe atom of the ADT-bridged diiron subsite. Why did we design and prepare such types of model complexes? This is because such complexes are expected to be much more difficult to dissociate and lose their L-cysteinyl groups than those simply coordinatively bound ones,[29] and thus they may serve as better models for mimicking study of the active site of [FeFe]-hydrogenases. In this article, we report the synthesis and structural characterization of five such new L-cysteinyl group-containing model complexes, as well as one new starting complex for preparing one of the five model complexes.

Results and Discussion

Synthesis and Characterization of Model Complexes $[(\mu\text{-}SCH_2)_2NCH_2CH_2SCyt]Fe_2(CO)_6$ (3), $[(\mu\text{-}SCH_2)_2NCH_2CH_2SCyt]Fe_2(CO)_5$ (4), $[(\mu\text{-}SCH_2)_2NCH_2CH_2SCyt]Fe_2(CO)_5(Ph_3P)$ (5), and $[(\mu\text{-}SCH_2)_2NCH_2CH_2SCyt]Fe_2(CO)_4(Ph_3P)$ (6). We found that treatment of the in situ prepared N-protected L-cysteinyl sodium mercaptide CytSNa (**1**, Cyt = $CH_2CH(CO_2Et)NH(CO_2Bu\text{-}t)$[29] with N-bromoethyl-substituted complex $[(\mu\text{-}SCH_2)_2NCH_2CH_2Br]Fe_2(CO)_6$ (**2**) in THF at room temperature gave the L-cysteinyl-containing model complex **3** in 41% yield; in addition, treatment of **3** with Me_3NO in MeCN at room temperature afforded the L-cysteinyl-substituted model complex **4** in 50% yield (Scheme 2). Similarly, we further found that treatment of **3** with an equimolar mixture of Me_3NO and Ph_3P in MeCN at room temperature produced the Ph_3P-substituted model complex **5** in 68% yield; in addition, treatment of **5** with Me_3NO in MeCN at room temperature resulted in formation of the Ph_3P and L-cysteinyl-substituted model **6** in 76% yield (Scheme 3). It follows that the intermolecular CO substitution of **3** with Ph_3P is much easier than the intramolecular CO substitution of **3** by its L-cysteinyl group in the presence of decarbonylating agent Me_3NO.[30]

Compounds **3**−**6** are new, which were characterized by elemental analysis and various spectroscopic techniques. For example, the IR spectra of **3**−**6** displayed three strong absorption bands in the region 2071−1930 cm^{-1} for their terminal carbonyls and two strong absorption bands in the range 1740−1706 cm^{-1} for their two different organic carbonyls. The ^1H NMR spectra of **3**−**6** showed a singlet at approximately 1.5 ppm for their *t*-Bu groups, a doublet at approximately 5.4 ppm for their NH groups, and the corresponding signals in the range 2.7−3.6 ppm for their $(SCH_2)_2N$ groups. In addition, the ^{13}C NMR spectra of **3**−**6** exhibited two signals at approximately 155 and 170 ppm for their two different organic carbonyls and the corresponding signals in the range 207−215 ppm for their terminal carbonyls, whereas the ^{31}P NMR spectra of

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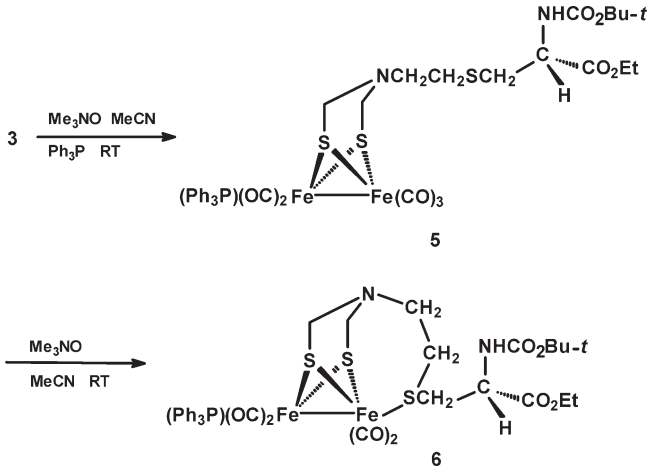
Scheme 3



5 and **6** showed one singlet at 64.78 and 25.87 ppm for their Ph_3P ligand, respectively. It is worthy to note that the highest $\nu_{C\equiv O}$ frequencies of the L-cysteinyl and Ph_3P-substituted derivatives **4**−**6** are shifted toward lower values by 24−45 cm^{-1} relative to that of parent complex **3** (Figure 1). This indicates that the L-cysteinyl-S and Ph_3P ligands are all stronger electron donors than CO.[29,31−33]

The molecular structure of **5** was unequivocally confirmed by X-ray single crystal diffraction analysis. Figure 2 displays its ORTEP view, whereas Table 1 lists its selected bond lengths and angles. As shown in Figure 2, complex **5** indeed contains a L-cysteinyl group covalently bound (via S3, C27, and C26 atoms) to the bridgehead nitrogen (N1) atom of an azadithiolate ligand, which in turn bridges the two iron atoms of $Fe(CO)_3$ and $Fe(CO)_2(Ph_3P)$ units to form two fused six-membered rings: a chairlike ring Fe1−S1−C24−N1−C25−S2 and a boat-like ring Fe2−S1−C24−N1−C25−S2. While the L-cysteinyl group is attached to the N1 atom in a common equatorial position of the two fused six-membered rings, ligand Ph_3P is coordinated to Fe1 in an apical position of the Fe1 square-pyramidal geometry. The Fe1−Fe2 bond length (2.5215 Å) is very close to the corresponding bond lengths in the simple diiron carbonyl complexes such as $[(\mu\text{-}SCH_2)_2CH_2]Fe_2(CO)_6$ (2.5103 Å),[34] $[(\mu\text{-}SCH_2)_2O]Fe_2(CO)_6$ (2.5113 Å),[31] and $[(\mu\text{-}SCH_2)_2S]Fe_2(CO)_6$ (2.5159 Å),[35] but it is slightly shorter than those reported for the reduced and oxidized state diiron subsites in the natural enzymes (2.55, 2.60, and 2.62 Å).[15−17]

Synthesis and Characterization of Starting Complex $Cp(CO)_2FeSCH_2CH(CO_2Et)NH_2$ (8) and Model Complex $[(\mu\text{-}SCH_2)_2NCH(CO_2Et)CH_2SFe(CO)_2Cp]Fe_2(CO)_5$ (10). According to our designed synthetic method for synthesis of model complex **10**, we should first prepare its starting complex **8**, the N-deprotected L-cysteinyl iron mercaptide. We found that new complex **8** could be easily prepared in 67% yield by reaction of complex $Cp(CO)_2FeSCyt$ (**7**) with CF_3CO_2H followed by treatment with 25% aqueous NH_3 in CH_2Cl_2 at room temperature (Scheme 4). Then, model complex **10** was conveniently synthesized in 23% yield by a "one pot" reaction of the in situ generated $(\mu\text{-}HS)_2Fe_2(CO)_6$[36] with 37% aqueous CH_2O followed by treatment of the intermediate $(\mu\text{-}HOCH_2S)_2Fe_2(CO)_6$[37] with complex **8** (Scheme 5).

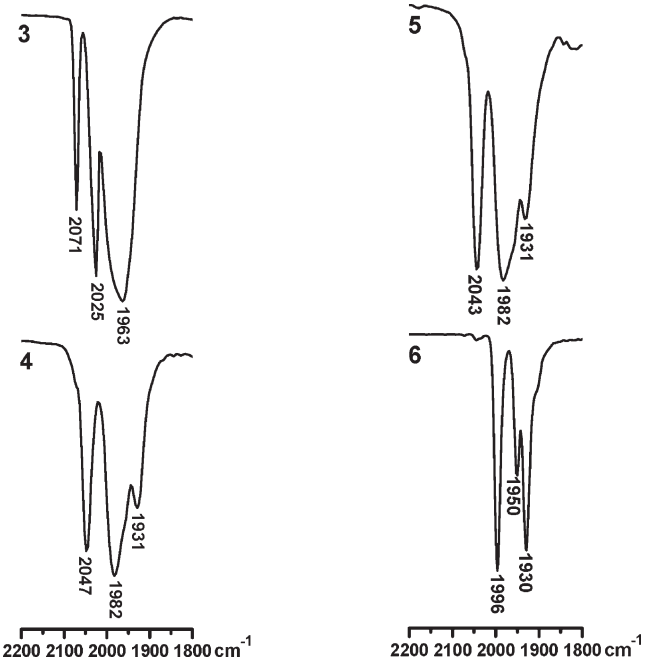


Figure 1. Comparison of the terminal carbonyl IR spectrum of parent complex **3** with those of its substituted derivatives **4**−**6**.

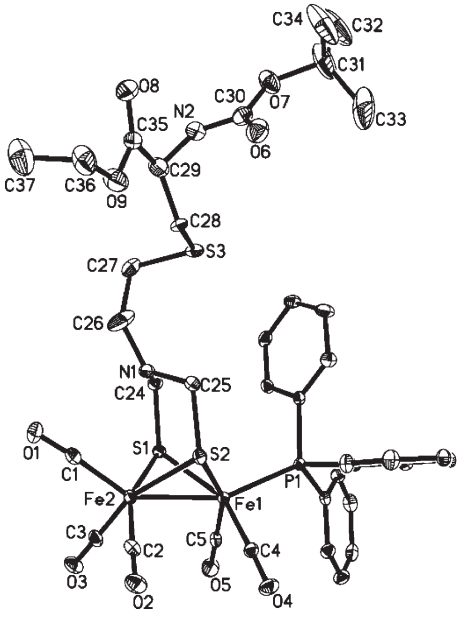


Figure 2. ORTEP view of **5** with 30% probability level ellipsoids.

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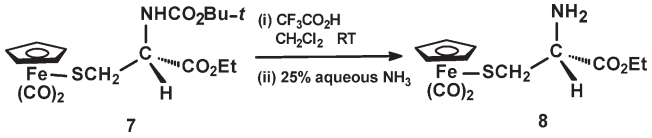
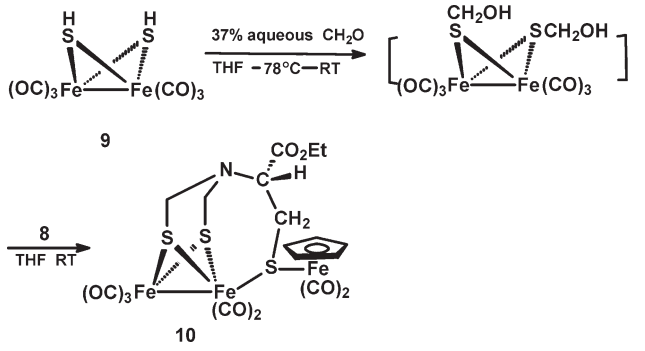
Table 1. Selected Bond Lengths (Å) and Angles (deg) for **5** and **10**

		5	
Fe(1)−P(1)	2.2466(12)	Fe(1)−Fe(2)	2.5215(10)
Fe(1)−S(2)	2.2561(12)	Fe(2)−S(1)	2.2701(13)
Fe(1)−S(1)	2.2748(12)	Fe(2)−S(2)	2.2731(12)
N(1)−C(26)	1.4546(6)	N(2)−C(29)	1.427(6)
S(1)−Fe(1)−Fe(2)	56.21(4)	S(1)−Fe(2)−Fe(1)	56.39(4)
S(1)−Fe(2)−S(2)	84.49(5)	S(2)−Fe(2)−Fe(1)	55.85(4)
S(2)−Fe(1)−S(1)	84.77(5)	Fe(2)−S(1)−Fe(1)	67.39(4)
S(2)−Fe(1)−Fe(2)	56.49(3)	Fe(1)−S(2)−Fe(2)	67.66(4)
		10	
Fe(1)−S(1)	2.2760(8)	Fe(2)−S(1)	2.2802(8)
Fe(1)−S(2)	2.2788(7)	Fe(2)−S(3)	2.2999(7)
Fe(1)−Fe(2)	2.5257(6)	Fe(3)−S(3)	2.3028(7)
Fe(2)−S(2)	2.2670(8)	Fe(1)−C(1)	1.790(3)
S(1)−Fe(1)−S(2)	85.34(3)	S(1)−Fe(2)−Fe(1)	56.25(2)
S(1)−Fe(1)−Fe(2)	56.41(2)	Fe(1)−S(1)−Fe(2)	67.33(2)
S(2)−Fe(1)−Fe(2)	56.02(2)	Fe(2)−S(2)−Fe(1)	67.51(2)
S(2)−Fe(2)−S(1)	85.52(3)	Fe(2)−S(3)−Fe(3)	118.16(3)
S(2)−Fe(2)−S(3)	97.05(3)	C(8)−N(1)−C(9)	115.51(19)
S(1)−Fe(2)−S(3)	103.53(2)	C(8)−N(1)−C(10)	118.1(2)

Scheme 4



Scheme 5



New complexes **8** and **10** were also characterized by elemental analysis and spectroscopy. For example, the IR spectrum of **8** showed two absorption bands at 2024 and 1973 cm^{-1} for its two terminal carbonyls and one absorption band at 1732 cm^{-1} for its ester carbonyl, whereas the IR spectrum of **10** displayed five absorption bands in the range 2040−1911 cm^{-1} for its seven terminal carbonyls and one absorption band at 1735 cm^{-1} for its ester carbonyl. In addition, the ^1H NMR spectra of **8** and **10** displayed a singlet at 5.04 and 5.43 ppm for their Cp groups, whereas the ^{13}C NMR spectra of **8** and **10** exhibited one signal at approximately 85 ppm for their Cp groups, one signal at approximately 170 ppm for their ester carbonyls, and two or five signals in the range 214−208 ppm for their terminal carbonyls, respectively.

The molecular structure of **10** was unambiguously confirmed by X-ray single crystal diffraction technique. The ORTEP view of **10** is shown in Figure 3, and its selected bond lengths and angles are given in Table 1.

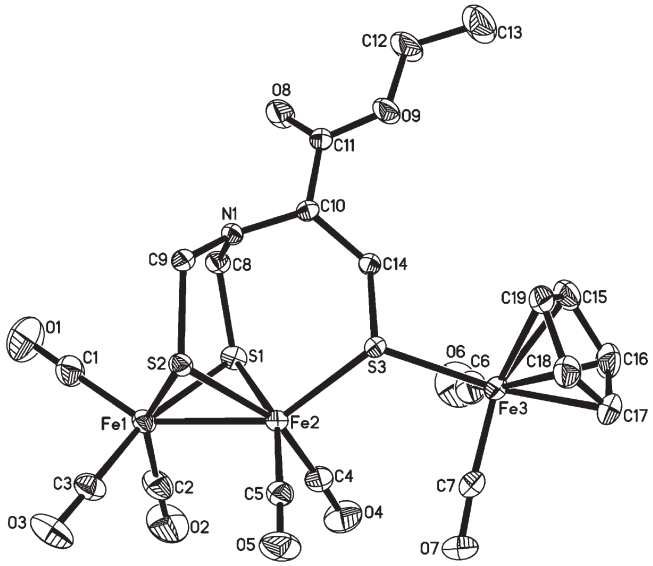


Figure 3. ORTEP view of **10** with 30% probability level ellipsoids.

As shown in Figure 3, model complex **10** can be formally regarded as a novel derivative of parent complex [(μ-$SCH_2)_2NH]Fe_2(CO)_6$ via displacement of its bridgehead NH and one apical CO by the corresponding N1 and S3 atoms of a special L-cysteinyl group $NCH(CO_2Et)$-$CH_2SFe(CO)_2Cp$. That is, the L-cysteinyl group of **10** has a common nitrogen (N1) atom with the parent complex and S3 atom of the L-cysteinyl group is apically coordinated to Fe2 atom to form a linkage [Fe3-(μ-cysteinyl-S)-Fe2]. Interestingly, this linkage much resembles the [Fe_{Cubane}-(μ-cysteinyl-S)-$Fe_{subsite}$] linkage found in the natural enzymes.[16,17] In addition, the bridgehead N1 atom of **10**, in contrast to complex **5**, is connected to C10 atom in a common axial position of the two fused six-membered rings Fe2−S1−C8−N1−C9−S2 and Fe1−S1−C8−N1−C9−S2, apparently due to the complex **10** having an additional seven-membered ring Fe2−S1−C8−N1−C10−C14−S3 fused with the aforementioned two six-membered rings. Finally, it is worth pointing out that the Fe1−Fe2 bond length (2.5257 Å) of our [3Fe3S] model complex **10** is very close to the corresponding Fe1−Fe2 bond lengths (2.4969−2.5378 Å) of the previously reported [2Fe3S] model complexes, and the Fe2−S3 bond length (2.2999 Å) of **10** is slightly longer than the corresponding those (2.2347−2.2567 Å) of the reported [2Fe3S] models.[27c]

Conclusion

We have synthesized five new L-cysteinyl-containing ADT-type models (**3**−**6**, **10**) by the condensation reaction of sodium mercaptide **1** with diiron complex **2** (to give **3**), the intramolecular CO substitution of **3** (to afford **4**), the intermolecular CO substitution of **3** with Ph_3P (to produce **5**), the intramolecular CO substitution of **5** (to give **6**), and the "one pot" reaction involving a final cyclization of (μ-$HOCH_2S)_2Fe_2(CO)_6$ with iron mercaptide **8** (leading to **10**). While new starting complex **8** was characterized and prepared by removal of the N-protected group from complex **7**, structural characterization of the new model complexes have demonstrated that (i) diiron models **3** and **5** each have an appendant L-cysteinyl group attached to their bridgehead N atoms, whereas the

Table 2. Crystal Data and Structure Refinement Details for **5** and **10**

	5	**10**
mol formula	$C_{37}H_{41}Fe_2N_2O_9PS_3$	$C_{19}H_{17}Fe_3NO_9S_3$
mol wt	896.57	667.07
temp, K	113(2)	294(2)
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/n$
a, Å	9.3216(19)	10.6154(18)
b, Å	12.769(3)	20.306(4)
c, Å	17.815(4)	12.405(2)
α, deg	102.22(3)	90
β, deg	97.95(3)	108.237(2)
γ, deg	91.78(3)	90
V, Å^3	2048.6(7)	2539.6(8)
Z	2	4
D_c, g cm^{-3}	1.453	1.745
abs coeff, mm^{-1}	0.954	1.986
F(000)	928	1344
index ranges	$-10 \le h \le 11$	$-13 \le h \le 11$
	$-15 \le k \le 13$	$-25 \le k \le 18$
	$-21 \le l \le 19$	$-12 \le l \le 15$
rflns	12878	14449
indep rflns	7201	5201
$2\theta_{max}$, deg	50.04	52.82
R	0.0654	0.0304
Rw	0.1560	0.0664
GOF	1.166	1.038
largest diff peak and hole, e Å^{-3}	1.003/−0.474	0.400/−0.329

bridgehead N-attached L-cysteinyl groups in diiron models **4** and **6** are simultaneously coordinated via their L-cysteinyl-S to one Fe atom of their diiron subsites; and (ii) triiron model complex **10** contains a $Cp(CO)_2Fe$-substituted L-cysteinyl group, whose N atom also acts as the bridgehead N atom of its ADT moiety.

Experimental Section

General Comments. All reactions were carried out using standard Schlenk and vacuum-line techniques under an atmosphere of nitrogen. Acetonitrile was purified by distillation once from P_2O_5 and then from CaH_2, while dichloromethane and THF were purified by distillation from CaH_2 and sodium/benzophenone ketyl, respectively. Et_3BHLi (1 M in THF), 25% aqueous ammonia, 37% aqueous formaldehyde, CF_3CO_2H, Ph_3P, and $Me_3NO\cdot 2H_2O$ were available commercially. CytSNa (**1**, Cyt = $CH_2CH(CO_2Et)NH(CO_2Bu\text{-}t)$)[29] was prepared from CytSH; CytSH was prepared from commercially available *L*-$HCl\cdot H_2NCH(CO_2Et)CH_2SH$;[38] and $(\mu\text{-S})_2Fe_2(CO)_6$,[39] $[(\mu\text{-}SCH_2)_2NCH_2CH_2Br]Fe_2(CO)_6$ (**2**),[40] and $Cp(CO)_2FeSCyt$ (**7**)[29] were prepared according to the published procedures. The reaction progresses were monitored by conventional thin-layer-chromatography (TLC). 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 Bruker Vector 22 or Bruker FT-IR Equinox 55 infrared spectrophotometer. ^{1}H (^{13}C, ^{31}P) NMR spectra were obtained on a Bruker Avance 300 NMR or a Varian Mercury Plus 400 NMR spectrometer. Elemental analyses were performed on an Elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus and were uncorrected.

Preparation of $[(\mu\text{-}SCH_2)_2NCH_2CH_2SCyt]Fe_2(CO)_6$ (3). A 100-mL three-necked flask fitted with a magnetic stirring bar, a rubber septum, and a nitrogen inlet tube was charged with CytSH (0.075 g, 0.30 mmol), THF (10 mL), and the freshly prepared EtONa (0.020 g, 0.30 mmol). The mixture was stirred for 10 min at room temperature to give a solution containing CytSNa (**1**). To this solution was added $[(\mu\text{-}SCH_2)_2NCH_2CH_2Br]Fe_2(CO)_6$ (**2**, 0.148 g, 0.30 mmol), and the new mixture was stirred at room temperature for 2 h. Solvent was removed at reduced pressure, and the residue was subjected to TLC separation using Et_2O/petroleum ether (v/v = 1: 4) as eluent. From the main orange-red band, **3** (0.083 g, 41%) was obtained as a red oil. Anal. Calcd for $C_{20}H_{26}Fe_2N_2O_{10}S_3$: C, 36.27; H, 3.96; N, 4.23. Found: C, 36.12; H, 4.19; N, 4.28. IR (KBr disk): $\nu_{C\equiv O}$ 2071 (s), 2025 (vs), 1963 (vs); $\nu_{CHC=O}$ 1738 (s); $\nu_{NHC=O}$ 1706 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 1.29 (t, 3H, J = 7.2 Hz, CH_2CH_3), 1.45 (s, 9H, $C(CH_3)_3$), 2.45 (t, 2H, J = 6.8 Hz, SCH_2CH_2N), 2.90−2.95 (m, 4H, $NCH_2CH_2SCH_2$), 3.63 (s, 4H, $2NCH_2S$), 4.21 (q, 2H, J = 7.2 Hz, OCH_2), 4.44−4.48 (m, 1H, CH), 5.34 (d, 1H, J = 7.2 Hz, NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): 14.25 (CH_2CH_3), 28.40 ($C(CH_3)_3$), 31.14 (SCH_2CH_2), 34.82 (SCH_2CH), 53.09 (NCH_2S), 53.58 (CH), 56.74 (NCH_2CH_2), 61.92 (OCH_2), 80.30 ($C(CH_3)_3$), 155.18 (NHC=O), 170.85 (CHC=O), 207.75 (C≡O) ppm.

Preparation of $[(\mu\text{-}SCH_2)_2NCH_2CH_2SCyt]Fe_2(CO)_5$ (4). The same equipped flask was charged with **3** (0.413 g, 0.62 mmol), MeCN (10 mL), and $Me_3NO\cdot 2H_2O$ (0.069 g, 0.62 mmol). The mixture was stirred at room temperature for 3 h to give a brown solution. After the solvent was removed at reduced pressure, the residue was subjected to TLC separation using Et_2O/petroleum ether (v/v = 2:1) as eluent. From the main purple-red band, **4** (0.195 g, 50%) was obtained as a dark-red solid. Mp 50−51 °C. Anal. Calcd for $C_{19}H_{26}Fe_2N_2O_9S_3$: C, 35.98; H, 4.13; N, 4.42. Found: C, 35.87; H, 4.28; N, 4.58. IR (KBr disk): $\nu_{C\equiv O}$ 2047 (vs), 1982 (vs), 1930 (s); $\nu_{CHC=O}$ 1737 (s); $\nu_{NHC=O}$ 1715 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 1.38 (t, 3H, J = 7.2 Hz, CH_2CH_3), 1.47 (s, 9H, $C(CH_3)_3$), 3.15 (br.s, 4H, NCH_2CH_2S), 3.27−3.32, 3.59−3.63 (2 m, 2H, SCH_2CH), 3.91−4.02 (m, 4H, $2NCH_2S$), 4.35 (q, 2H, J = 6.8 Hz, OCH_2), 4.58−4.65 (m, 1H, CH), 5.47 (d, 1H, J = 6.4 Hz, NH) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): 14.27 (CH_2CH_3), 28.42 ($C(CH_3)_3$), 42.50 (SCH_2CH_2), 45.03 (SCH_2CH), 53.17, 53.30 (NCH_2S), 53.50 (CH), 53.74 (NCH_2CH_2), 62.72 (OCH_2), 80.97 ($C(CH_3)_3$), 155.38 (NHC=O), 169.98 (CHC=O), 208.18, 210.95, 211.09 (C≡O) ppm.

Preparation of $[(\mu\text{-}SCH_2)_2NCH_2CH_2SCyt]Fe_2(CO)_5(Ph_3P)$ (5). The same equipped flask was charged with **3** (0.848 g, 1.28 mmol), MeCN (10 mL), $Me_3NO\cdot 2H_2O$ (0.142 g, 1.28 mmol), and Ph_3P (0.336 g, 1.28 mmol). The mixture was stirred at room temperature for 3 h to give a brown-red solution. Solvent was removed under vacuum, and the residue was subjected to TLC separation using Et_2O/petroleum ether (v/v = 2: 1) as eluent. From the main red band, **5** (0.780 g, 68%) was obtained as a dark-red solid. Mp 48−50 °C. Anal. Calcd for $C_{37}H_{41}Fe_2N_2O_9PS_3$: C, 49.57; H, 4.61; N, 3.12. Found: C, 49.67; H, 4.65; N, 3.09. IR (KBr disk): $\nu_{C\equiv O}$ 2043 (vs), 1982 (vs), 1931 (s); $\nu_{CHC=O}$ 1734 (s); $\nu_{NHC=O}$ 1715 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 1.27 (t, 3H, J = 7.2 Hz, CH_2CH_3), 1.44 (s, 9H, $3C(CH_3)_3$), 2.12−2.17, 2.26−2.31, 2.38−2.44 (3 m, 6H, $NCH_2CH_2SCH_2$), 2.76−2.80, 2.90−2.96 (2 m, 4H, $2NCH_2S$), 4.18 (q, 2H, J = 7.2 Hz, OCH_2), 4.39−4.41 (m, 1H, CH), 5.25 (d, 1H, J = 7.6 Hz, NH), 7.44−7.69 (m, 15H, $3C_6H_5$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): 14.28 (CH_2CH_3), 28.42 ($C(CH_3)_3$), 29.37 (SCH_2CH_2), 34.74 (SCH_2CH), 50.55 (NCH_2S), 53.50 (CH), 58.10 (NCH_2CH_2), 61.91 (OCH_2), 80.33 ($C(CH_3)_3$), 128.55, 128.64, 130.24, 133.54, 133.64, 135.66, 136.05 (C_6H_5), 155.16 (NHC=O), 170.87 (CHC=O), 209.85, 213.44, 213.54 (C≡O) ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 85% H_3PO_4): 64.78 (s) ppm.

Preparation of $[(\mu\text{-}SCH_2)_2NCH_2CH_2SCyt]Fe_2(CO)_4(Ph_3P)$ (6). The same equipped flask was charged with **5** (0.780 g, 0.87 mmol), MeCN (10 mL), and $Me_3NO\cdot 2H_2O$ (0.097 g,

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0.87 mmol). The mixture was stirred at room temperature for 4 h to give a brown solution. After removal of solvent, the residue was subjected to TLC separation using Et_2O/petroleum ether (v/v = 3: 1) as eluent. From the main brown band, **6** (0.574 g, 76%) was obtained as a brown-black solid. Mp 76−78 °C. Anal. Calcd for $C_{36}H_{41}Fe_2N_2O_8PS_3$: C, 49.78; H, 4.76; N, 3.23. Found: C, 49.92; H, 4.88; N, 3.25. IR (KBr disk): $\nu_{C\equiv O}$ 1996 (vs), 1950 (s), 1930(vs); $\nu_{CHC=O}$ 1740 (s); $\nu_{NHC=O}$ 1710 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 1.36 (t, 3H, J = 7.2 Hz, CH_2CH_3), 1.45 (s, 9H, $C(CH_3)_3$), 2.91−2.99 (m, 4H, NCH_2CH_2S), 3.07−3.13, 3.22−3.28, 3.37−3.45, 3.50−3.58 (4 m, 6H, $2NCH_2S$, SCH_2CH), 4.31 (q, 2H, J = 6.8 Hz, OCH_2), 4.55−4.60 (m, 1H, CH), 5.43 (d, 1H, J = 6.8 Hz, NH), 7.41−7.76 (m, 15H, $3C_6H_5$) ppm. ^{13}C NMR (75.5 MHz, C_6D_6): 15.58 (CH_2CH_3), 28.34 ($C(CH_3)_3$), 42.07 (SCH_2CH_2), 44.92 (SCH_2CH), 50.32, 52.42 (NCH_2S), 53.26 (CH), 53.90 (NCH_2CH_2), 65.90 (OCH_2), 80.18 ($C(CH_3)_3$), 128.62, 128.74, 130.00, 131.31, 132.60, 132.74, 134.02, 134.17, 136.82, 137.30 (C_6H_5), 155.51 (NHC=O), 170.55 (CHC=O), 213.93, 214.06, 214.76, 214.87 (C≡O) ppm. ^{31}P NMR (C_6D_6, 121 MHz, 85% H_3PO_4): 25.87 (s) ppm.

Preparation of $Cp(CO)_2FeSCH_2CH(CO_2Et)NH_2$ (8). The same equipped flask was charged with $CpFe(CO)_2FeSCyt$ (**7**, 0.800 g, 1.88 mmol), CH_2Cl_2 (3 mL), and CF_3CO_2H (3 mL). The resulting red solution was stirred at room temperature for 0.5 h until **7** completely disappeared. Volatiles were removed at reduced pressure, and the residue was dissolved in CH_2Cl_2 (5 mL). To this CH_2Cl_2 solution was added 25% aqueous ammonia (2 mL), and then the mixture was stirred at room temperature for 10 min. The aqueous layer was separated from the organic layer and then was extracted with CH_2Cl_2 (5 mL). The combined organic layer was subjected to TLC separation using MeOH/CH_2Cl_2/25% aqueous ammonia (v/v/v = 1:25:0.5) as eluent. From the main red band, **8** (0.412 g, 67%) was obtained as a red oil. Anal. Calcd for $C_{12}H_{15}FeNO_4S$: C, 44.33; H, 4.65; N, 4.31. Found: C, 44.13; H, 4.84; N, 4.45. IR (KBr disk): $\nu_{C\equiv O}$ 2024 (vs), 1973 (vs); $\nu_{C=O}$ 1732 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): 1.28 (s, 3H, CH_3), 2.72 (s, 2H, CH_2S), 4.07 (s, 1H, CH), 4.26 (s, 2H, OCH_2), 5.04 (s, 5H, C_5H_5) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): 14.23 (CH_2CH_3), 35.64 (SCH_2), 60.85 (CH), 67.72 (OCH_2), 85.54 (C_5H_5), 170.54 (CHC=O), 213.33, 213.41 (C≡O) ppm.

Preparation of $[(\mu\text{-}SCH_2)_2NCH(CO_2Et)CH_2SFe(CO)_2Cp]Fe_2(CO)_5$ (10). The same equipped flask was charged with $(\mu\text{-}S)_2Fe_2(CO)_6$ (0.344 g, 1.0 mmol) and THF (15 mL). The stirred red solution was cooled to −78 °C and then treated dropwise with Et_3BHLi (2 mL, 2.0 mmol) to give a green solution. After CF_3CO_2H (0.16 mL, 2.0 mmol) was added, the mixture was stirred for an additional 10 min to give a red solution containing $(\mu\text{-}HS)_2Fe_2(CO)_6$. To this solution was added 37% aqueous formaldehyde (0.17 mL, 2.0 mmol). The new mixture was allowed to warm to room temperature and was stirred at this temperature for 1 h. After complex **8** (0.400 g, 1.2 mmol) was added, the new mixture was stirred for an additional 2 h. Volatiles were removed under vacuum, and the residue was subjected to TLC separation using CH_2Cl_2/petroleum ether (v/v = 1:1) as eluent. From the main red band, **10** (0.150 g, 23%) was obtained as a dark-red solid, Mp 156−158 °C. Anal. Calcd for $C_{19}H_{17}Fe_3NO_9S_3$: C, 34.21; H, 2.57; N, 2.10. Found: C, 33.95; H, 2.69; N, 2.07. IR (KBr disk): $\nu_{C\equiv O}$ 2040 (vs), 2023 (s), 1987 (vs), 1962 (vs), 1911 (s); $\nu_{C=O}$ 1735 (s) cm^{-1}. ^1H NMR (400 MHz, CD_3CN): 1.29 (t, 3H, J = 7.2 Hz, CH_3), 2.82, 3.84 (2d, 2H, J = 12.4 and 14.0 Hz, SCH_2CH), 3.52−3.58 (m, 1H, CH), 4.11−4.16 (m, 2H, OCH_2), 4.24−4.33 (m, 4H, $2NCH_2S$), 5.43 (s, 5H, C_5H_5) ppm. ^{13}C NMR (100.6 MHz, C_6D_6): 12.63 (CH_2CH_3), 43.77 (SCH_2CH), 46.91, 55.76 (NCH_2S), 59.74 (CH), 69.16 (OCH_2), 84.88 (C_5H_5), 168.81 (CHC=O), 208.01, 211.05, 211.45, 212.70, 213.29 (C≡O) ppm.

X-ray Structure Determinations of 5 and 10. Single crystals of **5** suitable for X-ray diffraction analysis were grown by slow evaporation of its ether/hexane solution at 4 °C, whereas those of **10** were grown by slow evaporation of its CH_2Cl_2/hexane solution at −20 °C. A single crystal of **5** or **10** was mounted on a Bruker SMART 1000 automated diffractometer. Data were collected by using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å) in the $\omega-\phi$ scanning mode. Absorption correction was performed by SADABS program.[41] Both structures were solved by direct methods using the SHELXS-97 program[42] and refined by full-matrix least-squares techniques (SHELXL-97)[43] on F^2. Hydrogen atoms were located using the geometric method. Details of crystal data, data collections, and structure refinements are summarized in Table 2.

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Supporting Information Available: Full tables of crystal data, atomic coordinates, thermal parameters, and bond lengths and angles for **5** and **10** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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