DOI: 10.1002/ejic.200700845

The *N*-Acylated Derivatives of Parent Complex [{(μ-SCH_2)$_2$NH}$Fe_2(CO)_6$] as Active Site Models of Fe-Only Hydrogenases: Synthesis, Characterization, and Related Properties

Li-Cheng Song,*[a] Liang-Xing Wang,[a] Bang-Shao Yin,[a] Yu-Long Li,[a] Xiao-Guang Zhang,[a] Yuan-Wei Zhang,[a] Xiang Luo,[a] and Qing-Mei Hu[a]

Keywords: Bioinorgnic chemistry / Iron / Electrochemistry / Hydrogenase models

A series of *N*-acylated diiron azadithiolate complexes as H-cluster models was synthesized and structurally characterized. Treatment of parent complex [{(μ-SCH_2)$_2$NH}$Fe_2(CO)_6$] (**A**) with 2-chloroacetic acid in the presence of dicyclohexylcarbodiimide or with 2-chloroacetyl chloride in the presence of Et_3N gave *N*-chloroacetyl complex [{(μ-SCH_2)$_2$NC(O)CH_2Cl}$Fe_2(CO)_6$] (**1**). Further treatment of **1** with MeC(O)SK afforded *N*-acetylthioacetyl complex [{(μ-SCH_2)$_2$NC(O)CH_2SC(O)Me}$Fe_2(CO)_6$] (**2**). *N*-Ethoxylcarbonylacetyl complex [{(μ-SCH_2)$_2$NC(O)CH_2CO_2Et}$Fe_2(CO)_6$] (**3**) and N-heterocyclic complexes [{(μ-SCH_2)$_2$NC(O)C_4H_3Y-2}$Fe_2(CO)_6$] (**4**, Y = O; **5**, Y = S) were produced by reactions of **A** with $EtO_2CCH_2C(O)Cl$, 2-furancarbonyl chloride, and 2-thiophenecarbonyl chloride in the presence of pyridine or Et_3N. Similarly, *N*-malonyl complex [{$Fe_2(CO)_6$(μ-SCH_2)$_2$NC(O)}$_2CH_2$] (**6**) and *N*-carbonylbenzaldehyde complex [{(μ-SCH_2)$_2$NC(O)C_6H_4CHO-*p*}$Fe_2(CO)_6$] (**7**) could be obtained by reaction of **A** with malonyl dichloride in the presence of pyridine and with *p*-$CHOC_6H_4C(O)Cl$ in the presence of Et_3N. More interestingly, further reaction of **7** with PhCHO and pyrrole in a 1:3:4 molar ratio in the presence of BF_3·OEt_2 followed by *p*-chloranil yielded the first light-driven type of model complex containing an *N*-carbonylphenylporphyrin moiety [{(μ-SCH_2)$_2$NC(O)(TPP)}$Fe_2(CO)_6$] (**8**, TPP = tetraphenylporphyrin group). Whereas the molecular structures of **2**, **5**, and **7** were established by X-ray crystallography, the electrochemical properties of **2**–**5** as well as the proton reduction to hydrogen gas catalyzed by **2** and **3** were studied by CV techniques.

Introduction

Fe-only hydrogenases have received special attention in recent years, mainly due to their unique structure and particularly their unusual capacity to catalyze proton reduction to the "clean" and highly efficient fuel: hydrogen gas.[1] Protein crystallographic[2–4] and FTIR spectroscopic[5–7] studies revealed that the active site of Fe-only hydrogenases, the so-called H-cluster, consists of a cubane-like [Fe_4S_4] cluster linked to a butterfly [Fe_2S_2] cluster through the S atom of a cysteinyl bridge. In the [Fe_2S_2] cluster, the two iron atoms are bridged by three-light-atom (possibly carbon or any combination of C, N, and O)-containing dithiolate ligands, and they are also coordinated by CO and CN^- ligands (Figure 1). This well-elucidated structure has greatly inspired chemists to design and synthesize a variety of structural and functional models for the active site of Fe-only hydrogenases.[8–19] As H-cluster models, the N-functionalized diiron azadithiolate (ADT) complexes are of particular interest, as they are not only simple models, but they can also be used as starting materials to make complicated models, such as light-driven[20] and whole H-cluster models[21] by functional transformation reactions. Herein we report the synthesis and structural characterization of a series of N-functionalized ADT-type models. In addition, the related electrochemical and catalytic properties for some of the newly synthesized models are also described.

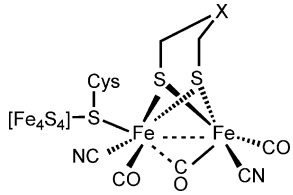


Figure 1. Basic structure of the H-cluster (X = CH_2, NH, or O).

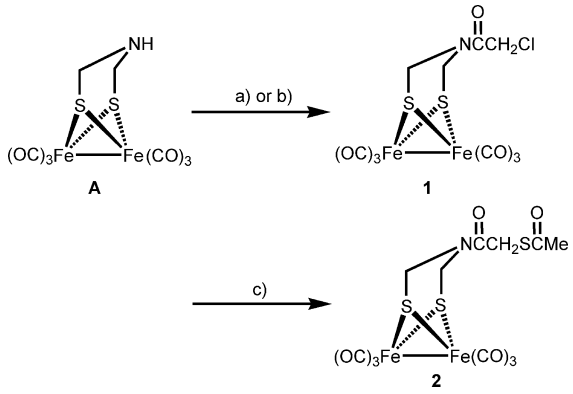
Results and Discussion

Synthesis and Characterization of Model Complexes [{(μ-SCH_2)$_2$NC(O)CH_2Cl}$Fe_2(CO)_6$] (1) and [{(μ-SCH_2)$_2$NC(O)CH_2SC(O)Me}$Fe_2(CO)_6$] (2)

N-Functionalized ADT-type model complexes **1** and **2** could be prepared conveniently starting from parent com-

[a] Department of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China
Fax: +86-22-23504853
E-mail: lcsong@nankai.edu.cn

plex [{(μ-SCH_2)$_2$NH}$Fe_2(CO)_6$] (**A**).[22] Treatment of **A** with 2-chloroacetic acid in the presence of the carboxylic group activating reagent dicyclohexylcarbodiimide (DCC) gave *N*-chloroacetyl complex **1** in 53% yield; **1** was also prepared in a much higher yield (86%) by treatment of **A** with 2-chloroacetyl chloride in the presence of Et_3N. Further treatment of **1** with MeC(O)SK afforded corresponding N-functionalized complex **2** in 56% yield (Scheme 1).



Scheme 1. (a) $ClCH_2CO_2H$, DCC, CH_2Cl_2, 0 °C to room temp.; (b) $ClCH_2C(O)Cl$, Et_3N, THF, 0 °C to room temp.; (c) MeC(O)-SK, THF, MeOH, 0 °C to room temp.

Compounds **1** and **2** are air-stable red solids, which were characterized by elemental analysis and spectroscopy. For instance, the IR spectra of **1** and **2** showed four absorption bands in the region 2083–1969 cm^{-1} for their terminal carbonyl groups, whereas they displayed one or two additional absorption bands in the range 1698–1676 cm^{-1} for their ester and amide carbonyl groups. The ^1H NMR spectra of **1** and **2** exhibited one singlet at δ = 4.12 and 4.13 ppm for the two equivalent protons in each of their two NCH_2S groups, respectively.

The molecular structure of **2** was unequivocally confirmed by X-ray diffraction analysis (Figure 2, Table 1). As shown in Figure 2, this molecule has an acetylthioacetyl functionality, which is axially attached to the N1 atom of the two fused six-membered rings: a chair-shaped Fe1–S1–C7–N1–C8–S2 and a boat-shaped Fe2–S1–C7–N1–C8–S2.

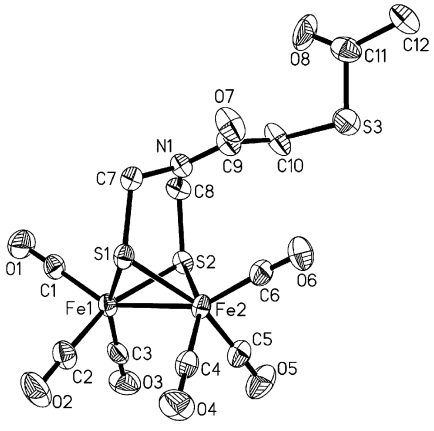


Figure 2. Molecular structure of **2** with 30% probability level ellipsoids.

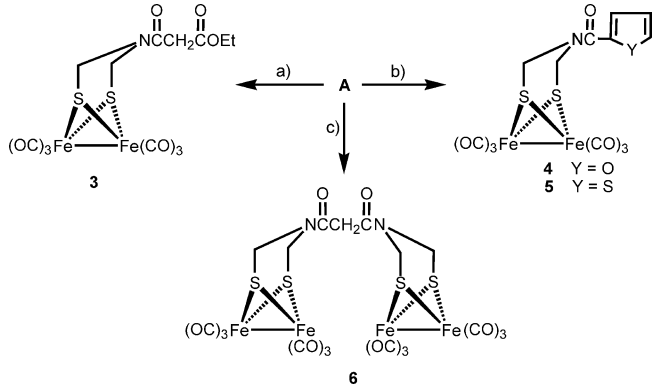
Both the Fe1 and Fe2 atoms adopt the expected square-pyramidal geometry and the Fe1–Fe2 bond length (2.5062 Å) is close to the corresponding lengths of similar diiron dithiolate complexes.[14–19,23]

Table 1. Selected bond lengths and angles for **2**.

Bond lengths [Å]			
Fe1–S1	2.2598(15)	Fe2–S2	2.2653(15)
Fe1–S2	2.2597(15)	S3–C10	1.831(5)
Fe1–Fe2	2.5062(10)	S3–C11	1.741(7)
Fe2–S1	2.2592(15)	C9–O7	1.204(5)
Bond angles [°]			
S2–Fe1–S1	85.06(5)	S1–Fe2–Fe1	56.33(4)
S2–Fe1–Fe2	56.47(4)	S2–Fe2–Fe1	56.26(4)
S1–Fe1–Fe2	56.31(4)	Fe2–S1–Fe1	67.37(4)
S1–Fe2–S2	84.94(5)	Fe1–S2–Fe2	67.26(4)

Synthesis and Characterization of Model Complexes [{(μ-SCH_2)$_2$NC(O)CH_2CO_2Et}$Fe_2(CO)_6$] (3), [{(μ-SCH_2)$_2$NC(O)C_4H_3Y-2}$Fe_2(CO)_6$] (4, Y = O; 5, Y = S) and [{$Fe_2(CO)_6$(μ-SCH_2)$_2$NC(O)}$_2CH_2$] (6)

Similarly, N-functionalized ADT-type model complexes **3**–**6** could also be prepared readily from parent complex **A**. Treatment of **A** with $EtO_2CCH_2C(O)Cl$, 2-furancarbonyl, or 2-thiophenecarbonyl chloride in the presence of pyridine or Et_3N produced diiron complexes **3**–**5** in 52–79% yields, whereas the reaction of **A** with malonyl dichloride in the presence of pyridine resulted in the formation of tetrairon complex **6** in 53% yield (Scheme 2).



Scheme 2. (a) $EtO_2CCH_2C(O)Cl$, pyridine, CH_2Cl_2, 0 °C to room temp.; (b) $C_4H_3YC(O)Cl$, Et_3N, CH_2Cl_2, room temp.; (c) $ClC(O)$-$CH_2C(O)Cl$, pyridine, CH_2Cl_2, 0 °C to room temp.

Compounds **3**–**6** are also air-stable red solids, which were fully characterized by elemental analysis and IR and ^1H NMR spectroscopy. The IR spectra of **3**–**6** exhibited four absorption bands in the region 2082–1972 cm^{-1} for their terminal carbonyl groups. In addition, **3** displayed two absorption bands at 1663 and 1753 cm^{-1} for its amide and ester carbonyl groups, whereas **4**–**6** showed one absorption band in the range 1621–1660 cm^{-1} for their amide carbonyl groups. The ^1H NMR spectra of **3**–**6** showed one or two

singlets at ca. 4.2 ppm for the two equivalent protons in each of their NCH_2S groups. These chemical values are shifted downfield by ca. 0.5 ppm relative to that of parent complex **A**,[22] obviously due to the stronger electron-withdrawing effects of their N-functionalities.

X-ray crystallographic analysis revealed that complex **5** (Figure 3, Table 2) contains a thiophenecarbonyl group attached to the N1 atom by the common axial bond of the two fused six-membered Fe2–S2–C8–N1–C7–S1 and Fe1–S2–C8–N1–C7–S1 rings. In addition, the Fe1–Fe2 bond length of **5** is 2.5068 Å, which is nearly the same as that of **2**, but it is slightly shorter than the corresponding lengths (2.55–2.62 Å) in the natural enzymes.[2–4] The dihedral angle between the thiophene ring and the C10–C9–O7 plane is 28.5°. This means that some p–π conjugation between these two parts is present, which may explain why the double bond between C9 and O7 (1.226 Å) in this complex is slightly longer than that between C9 and O7 (1.204 Å) in complex **2**.

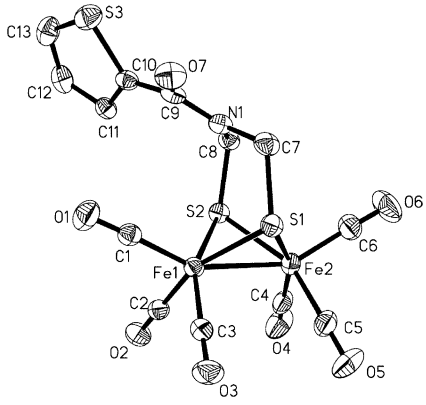


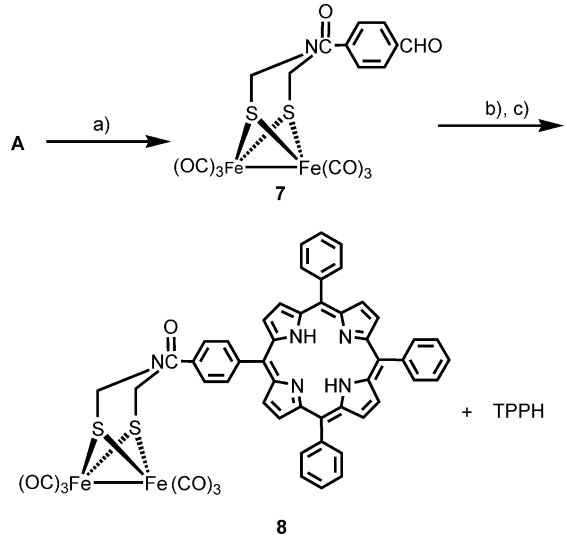
Figure 3. Molecular structure of **5** with 30% probability level ellipsoids.

Table 2. Selected bond lengths and angles for **5**.

Bond lengths [Å]			
Fe1–S1	2.2524(10)	Fe2–S2	2.2595(9)
Fe1–S2	2.2654(9)	N1–C9	1.369(4)
Fe1–Fe2	2.5068(8)	N1–C8	1.436(4)
Fe2–S1	2.2641(10)	C9–O7	1.226(4)
Bond angles [°]			
S1–Fe1–S2	84.88(3)	S2–Fe2–Fe1	56.47(2)
S1–Fe1–Fe2	56.51(3)	S1–Fe2–Fe1	56.06(3)
S2–Fe1–Fe2	56.25(3)	Fe1–S1–Fe2	67.42(3)
S2–Fe2–S1	84.75(3)	C9–N1–C7	118.9(3)

Synthesis and Characterization of Model Complexes [{(μ-SCH_2)$_2$NC(O)C_6H_4CHO-*p*}$Fe_2(CO)_6$] (7) and [{(μ-SCH_2)$_2$NC(O)(TPP)}$Fe_2(CO)_6$] (8)

Interestingly, on the basis of synthesizing *N*-benzaldehyde complex **7**, the first light-driven type of model complex containing an *N*-carbonylphenylporphyrin moiety, namely **8**, was successfully synthesized. Treatment of complex **A** with *p*-formylbenzoyl chloride in the presence of Et_3N gave rise to complex **7** in 52% yield; further treatment of **7** with benzaldehyde and pyrrole in a 1:3:4 molar ratio in the presence of catalytic BF_3·OEt_2 followed by the oxidant *p*-chloranil[20,24] resulted in the formation of complex **8** in 20% yield along with tetraphenylporphyrin (TPPH) in 18% yield (Scheme 3).



Scheme 3. (a) *p*-$CHOC_6H_4C(O)Cl$, Et_3N, CH_2Cl_2, 0 °C to room temp.; (b) PhCHO, pyrrole, BF_3·Et_2O, CH_2Cl_2, room temp.; (c) *p*-chloranil, CH_2Cl_2, reflux.

Whereas **7** is an air-stable red solid, **8** is an air-stable purple-red solid. They were all characterized by elemental analysis and IR and ^{1}H NMR spectroscopic techniques. For example, the IR spectrum of **7** displayed four absorption bands in the range 2077–1985 cm^{-1} for its terminal carbonyl groups and two absorption bands at 1695 and 1656 cm^{-1} for its formyl and amide carbonyl groups, whereas **8** showed three absorption bands in the range 2077–2000 cm^{-1} for its terminal carbonyl groups, one absorption band at 1653 cm^{-1} for its amide carbonyl group, and three absorption bands at 1558, 1473, and 1350 cm^{-1} for the skeleton vibrations of the pyrrole rings in the porphyrin macrocycle.[25] In addition, the ^{1}H NMR spectrum of **7** exhibited one singlet at δ = 4.32 ppm and one singlet at δ = 4.11 ppm for the two protons in each of its two NCH_2S groups, and another singlet at δ = 10.08 ppm for the proton in its formyl group, whereas **8** displayed one singlet at δ = 4.53 ppm for the two protons in each of its two NCH_2S groups and another singlet at δ = –2.79 ppm for the protons attached to N atoms in the porphyrin moiety.[26]

X-ray crystallographic analysis revealed that the structure of **7** (Figure 4, Table 3) resembles the above-described structures of **2** and **5**; compound **7** is a functionalized azadithiolate ligand that is bridged between the Fe1 and Fe2 atoms to form two fused six-membered rings: a chair-shaped Fe1–S1–C8–N1–C7–S2 and a boat-shaped Fe2–S1–C8–N1–C7–S2. In addition, the N-functionality of **7**, namely the carbonylbenzaldehyde group, is connected to the bridgehead N1 atom by an axial bond.

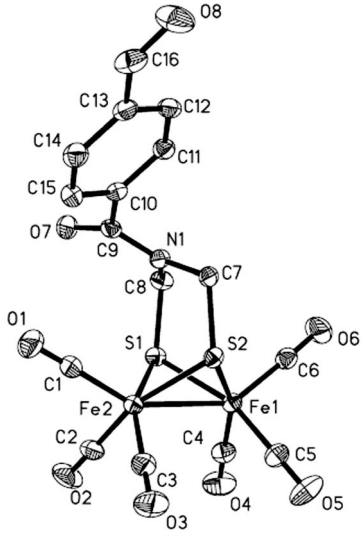


Figure 4. Molecular structure of **7** with 30% probability level ellipsoids.

Table 3. Selected bond lengths and angles for **7**.

Bond lengths [Å]			
Fe1–S1	2.2517(8)	Fe2–S2	2.2490(8)
Fe1–S2	2.2561(8)	N1–C9	1.374(3)
Fe1–Fe2	2.5265(6)	N1–C8	1.436(3)
Fe2–S1	2.2541(8)	C9–O7	1.223(3)
Bond angles [°]			
S1–Fe1–S2	84.89(3)	Fe1–S1–Fe2	68.21(3)
S1–Fe1–Fe2	55.94(2)	S1–Fe2–Fe1	55.85(2)
S2–Fe1–Fe2	55.76(2)	O7–C9–C10	121.4(3)
S2–Fe2–S1	85.00(3)	C9–N1–C7	124.1(2)
S2–Fe2–Fe1	56.02(2)	C8–N1–C7	115.4(2)

Electrochemistry of Model Complexes 2–5

The electrochemical behavior of **2**–**5** was investigated by cyclic voltammetry in MeCN under a N_2 or CO atmosphere. Whereas Table 4 lists the electrochemical data of **2**–**5**, Figure 5 shows the cyclic voltammogram of **2**. These complexes each display one quasi-reversible reduction, one irreversible reduction, and one irreversible oxidation. All the reductions and oxidations are one-electron processes (supported by bulk electrolysis), which can be assigned to reduction of $Fe^{I}Fe^{I}$ to $Fe^{I}Fe^{0}$, further reduction of $Fe^{I}Fe^{0}$ to $Fe^{0}Fe^{0}$, and oxidation of $Fe^{I}Fe^{I}$ to $Fe^{I}Fe^{II}$, respectively. It is noteworthy that the reduction and oxidation potentials of **2**–**5** are more positive than those corresponding to the methoxyphenyl-functionalized complex $[\{(\mu\text{-}SCH_2)_2NC_6H_4OMe\text{-}p\}Fe_2(CO)_6]$,[15] obviously due to the fact that the N-functionalities of **2**–**5** are stronger electron-withdrawing groups than the *N*-methoxyphenyl group. Such electrochemical behavior of **2**–**5** is similar to that of the previously reported diiron dithiolate model complexes.[27,28]

Table 4. Electrochemical data of **2**–**5**.[a]

Compound	E_{pc} [V]	E_{pc} [V]	E_{pa} [V]
2	–1.49	–1.96	+0.86
3	–1.51	–2.00	+0.87
4	–1.54	–1.99	+0.81
5	–1.52	–1.97	+0.82

[a] All potentials are versus Fc/Fc^+ in 0.1 M nBu_4NPF_6/MeCN.

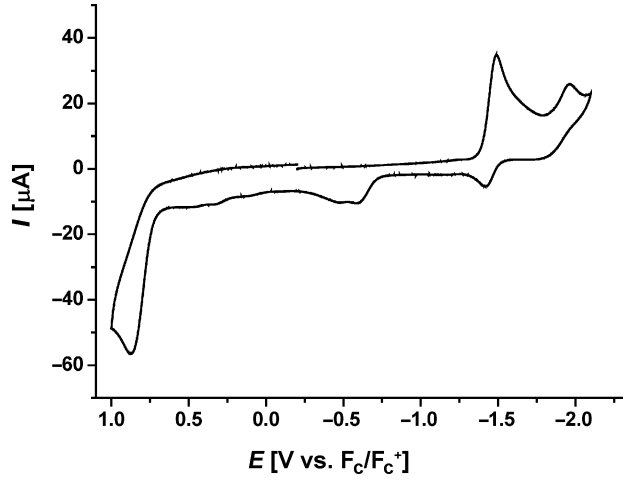


Figure 5. Cyclic voltammogram of **2** (1.0 mM) in 0.1 M nBu_4NPF_6/MeCN at a scan rate of 100 mV s^{-1}.

Further cyclic voltammetric studies revealed that **2** and **3** have the ability to undergo proton reduction to hydrogen gas in the presence of weak acid HOAc (pK_a = 22.6 in MeCN). The cyclic voltammogram of **2** with HOAc is presented in Figure 6. It shows that when the first 5 mM of HOAc is added, the original first reduction peak at –1.49 V slightly increases but does not continue to increase with sequential addition of the acid. However, in contrast to this, when the first 5 mM of HOAc is added, the original second reduction peak at –1.96 V markedly increases and continues to increase with sequential addition of the acid. Such observations are typical of an electrochemical catalytic process.[27–30] The bulk electrolysis of HOAc (25 mM) catalyzed

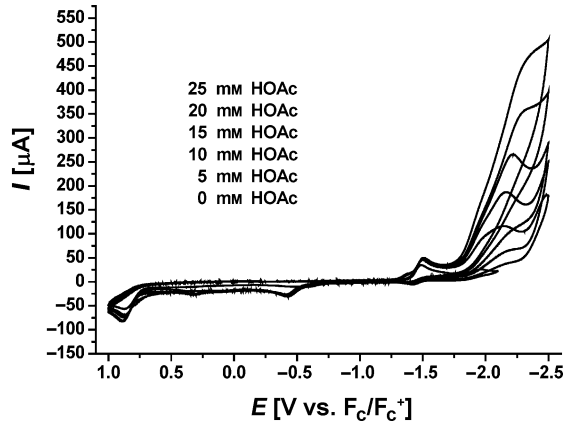
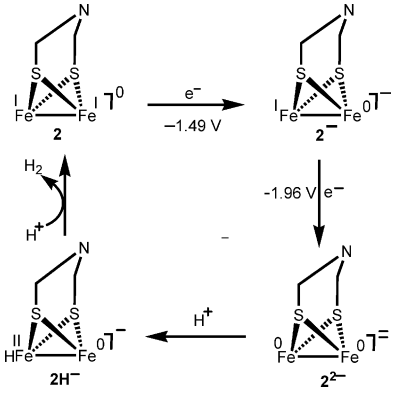


Figure 6. Cyclic voltammogram of **2** (1.0 mM) with HOAc (0–25 mM) in 0.1 M nBu_4NPF_6/MeCN at a scan rate of 100 mV s^{-1}.

by **2** (0.50 mM) in MeCN at –2.34 V indicated a total of 12.3 F per mol of **2** to be passed during half an hour. This corresponds to 6.1 turnovers. Gas chromatography showed that the yield of hydrogen gas was about 90%.

On the basis of the previously reported similar cases[27–30] and the electrochemical observations described above, a 2E2C (E = electrochemical, C = chemical) mechanism could be proposed to account for this electrocatalytic process. As shown in Scheme 4, complex **2** is first reduced at –1.49 V to give monoanion **2**$^-$. Then, **2**$^-$ is further reduced at –1.96 V to generate dianion **2**$^{2-}$. After electron-rich dianion **2**$^{2-}$ is protonated by HOAc to form the Fe–H species **2H**$^-$, it accepts an additional proton from HOAc to complete the catalytic cycle with H_2 evolution. Although this suggested mechanism is essentially the same as that suggested for the corresponding process catalyzed by complex [(μ-SCH_2)$_2$$NC_6H_4$OMe-*p*]$Fe_2(CO)_6$],[15] the first and second reduction potentials of **2** are shifted positively by 120 and 140 mV, respectively, relative to those corresponding to the above-mentioned complex. It follows that the presence of stronger electron-withdrawing groups at the bridgehead N atom could lower the reduction potentials of the two Fe atoms of the diiron subsite and thus make the proton reduction to hydrogen gas much easier.



Scheme 4. Proposed 2E2C mechanism for H_2 evolution catalyzed by **2**. All terminal carbonyl groups and the N-functionalities are omitted for clarity.

Experimental Section

General Comments: All reactions were carried out by using standard Schlenk and vacuum-line techniques under a N_2 atmosphere. Dichloromethane was distilled from CaH_2, THF from sodium/benzophenone ketyl, and methanol from Mg powders under a N_2 atmosphere. 2-Chloroacetic acid, 2-chloroacetyl chloride, MeC(O)SK, *N*,*N*′-dicyclohexylcarbodiimide (DCC), PhCHO, pyrrole, BF_3·OEt_2, and 2,3,5,6-tetrachlorobenzoquinone (*p*-chloranil) were available from commercial suppliers and used without further purification. [{(μ-SCH_2)$_2$NH}$Fe_2(CO)_6$] (**A**),[22] furancarbonyl chloride,[31] thiophenecarbonyl chloride,[32] malonyl dichloride,[33] $EtO_2CCH_2C(O)Cl$,[34] and *p*-$CHOC_6H_4C(O)Cl$[35a,35b] 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 with a Bruker Vector 22 infrared spectrophotometer. ^{1}H NMR spectra were obtained with a Bruker Avance 300 or a Varian Mercury Plus 400 spectrometer. Elemental analyses were performed with an Elementar Vario EL analyzer. Melting points were determined with a Yanaco MP-500 apparatus and are uncorrected.

[{(μ-SCH_2)$_2$$NC(O)CH_2Cl$}$Fe_2(CO)_6$] (1)

Method 1: A solution of DCC (0.093 g, 0.45 mmol) in CH_2Cl_2 (5 mL) was added to a stirred and cooled (0 °C) solution of complex **A** (0.176 g, 0.45 mmol) and $ClCH_2CO_2H$ (0.043 g, 0.45 mmol) in CH_2Cl_2 (20 mL). After the mixture was stirred at 0 °C for 1 h and at room temperature for 3 h, the solvent was removed in vacuo, and the residue was subjected to TLC separation (CH_2Cl_2/petroleum ether, 1:1). From the main red band, **1** was obtained as a red solid (0.110 g, 53%). M.p. 105–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.12 (s, 4 H, 2 NCH_2S), 4.08 (s, 2 H, CH_2Cl) ppm. IR (KBr disk): $\tilde{\nu}$ = 2083 (s), 2035 (vs), 1996 (vs), 1969 (vs) C≡O, 1677 (s) NC=O cm^{-1}. $C_{10}H_6ClFe_2NO_7S_2$ (463.44): calcd. C 25.92, H 1.30, N 3.02; found C 26.00, H 1.48, N 3.09.

Method 2: To a stirred red solution of complex **A** (0.387 g, 1.00 mmol) in THF (20 mL) at 0 °C was added $ClC(O)CH_2Cl$ (0.16 mL, 2.00 mmol) and Et_3N (0.28 mL, 2.00 mmol). After the mixture was stirred at 0 °C for 0.5 h and at room temperature for 2 h, the same work-up as Method (i) was applied to give **1** (0.398 g, 86%).

[{(μ-SCH_2)$_2$$NC(O)CH_2SC(O)Me$}$Fe_2(CO)_6$] (2): A stirred red solution of **1** (0.232 g, 0.50 mmol) in THF (20 mL) and MeOH (10 mL) was cooled to 0 °C and then MeC(O)SK (0.057 g, 0.50 mmol) was added. The mixture was warmed to room temperature and then stirred at this temperature for 3 h. The same work-up as that for the preparation of **1** was employed to afford **2** as a red solid (0.141 g, 56%). M.p. 127–129 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.13 (s, 4 H, 2 NCH_2S), 3.81 (s, 2 H, $COCH_2S$), 2.40 (s, 3 H, CH_3) ppm. IR (KBr disk): $\tilde{\nu}$ = 2074 (s), 2039 (vs), 2007 (vs), 1989 (vs) C≡O, 1698 (s) SC=O, 1676 (s) NC=O cm^{-1}. $C_{12}H_9Fe_2NO_8S_3$ (503.08): calcd. C 28.65, H 1.80, N 2.78; found C 28.72, H 1.91, N 2.89.

[{(μ-SCH_2)$_2$$NC(O)CH_2CO_2Et$}$Fe_2(CO)_6$] (3): A red solution of complex **A** (0.078 g, 0.20 mmol) and pyridine (0.02 mL, 0.25 mmol) in CH_2Cl_2 (15 mL) was cooled to 0 °C and then $ClC(O)CH_2CO_2Et$ (0.06 mL, 0.50 mmol) was added. After the mixture was stirred at 0 °C for 15 min, it was warmed to room temperature and then stirred at this temperature for 3 h. Volatiles were removed in vacuo and the residue was subjected to TLC separation (CH_2Cl_2/petroleum ether, 3:1). From the main band, **3** was obtained as a red solid (0.081 g, 80%). M.p. 154–156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.17 (s, 4 H, 2 NCH_2S), 4.07 (s, 2 H, OCH_2CH_3), 3.49 (s, 2 H, $COCH_2CO$), 1.26 (s, 3 H, CH_3) ppm. IR (KBr disk): $\tilde{\nu}$ = 2080 (s), 2037 (vs), 2004 (vs), 1984 (vs) C≡O, 1753 (s) OC=O, 1663 (s) NC=O cm^{-1}. $C_{13}H_{11}Fe_2NO_9S_2$ (501.10): calcd. C 31.16, H 2.21, N 2.80; found C 31.29, H 2.28, N 2.85.

[{(μ-SCH_2)$_2$$NC(O)C_4H_3O$-2}$Fe_2(CO)_6$] (4): A red solution of **A** (0.230 g, 0.60 mmol), 2-$C_4H_3OC(O)Cl$ (0.45 mL, 4.57 mmol), and Et_3N (1.0 mL, 7.15 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 5 h. After the mixture was evaporated to dryness under vacuum, the residue was subjected to TLC separation (acetone/petroleum ether, 1:2). From the main red band, **4** was obtained as a red solid (0.202 g, 70%). M.p. 109–111 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50, 7.13, 6.49 (3 s, 3 H, C_4H_3O), 4.44, 4.21 (2 s, 4 H, 2 NCH_2S) ppm. IR (KBr disk): $\tilde{\nu}$ = 2082 (s), 2034 (vs), 1994 (vs), 1976 (vs) C≡O, 1639 (s) NC=O cm^{-1}. $C_{13}H_7Fe_2NO_8S_2$ (481.02): calcd. C 32.46, H 1.47, N 2.95; found C 32.67, H 1.64, N 2.91.

[{(μ-SCH$_2$)$_2$NC(O)C$_4$H$_3$S-2}Fe$_2$(CO)$_6$] (5): The same procedure as that for the preparation of **4** was followed. From complex **A** (0.200 g, 0.52 mmol) and 2-C$_4$H$_3$SC(O)Cl (0.45 mL, 4.21 mmol), **5** was obtained as a red solid (0.135 g, 52%). M.p. 118–120 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56, 7.42, 7.12 (3 s, 3 H, C$_4$H$_3$S), 4.34 (s, 4 H, 2 NCH$_2$S) ppm. IR (KBr disk): $\tilde{\nu}$ = 2081 (s), 2051 (vs), 2000 (vs), 1972 (vs) C≡O, 1621 (s) NC=O cm^{-1}. $C_{13}H_7Fe_2NO_7S_3$ (497.08): calcd. C 31.41, H 1.42, N 2.82; found C 31.39, H 1.56, N 2.92.

[{(μ-SCH$_2$)$_2$NC(O)Fe$_2$(CO)$_6$}$_2$CH$_2$] (6): A red solution of complex **A** (0.116 g, 0.30 mmol) and pyridine (0.03 mL, 0.37 mmol) in CH_2Cl_2 (15 mL) was cooled to 0 °C and then malonyl dichloride (0.015 mL, 0.15 mmol) was added. The mixture was stirred at 0 °C for 15 min and then at room temperature for 4 h. The solvent was removed under reduced pressure, and the residue was subjected to TLC separation (CH_2Cl_2/petroleum ether, 2:1) to afford **6** as a red solid (0.067 g, 53%). M.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.22, 4.07 (2 s, 8 H, 4 NCH$_2$S), 3.55 (s, 2 H, COCH$_2$) ppm. IR (KBr disk): $\tilde{\nu}$ = 2078 (s), 2039 (vs), 2011 (vs), 1994 (vs) C≡O, 1660 (s) NC=O cm^{-1}. $C_{19}H_{10}Fe_4N_2O_{16}S_4$ (841.79): calcd. C 27.11, H 1.20, N 3.33; found C 27.09, H 1.18, N 3.32.

[{(μ-SCH$_2$)$_2$NC(O)C$_6$H$_4$CHO-*p*}Fe$_2$(CO)$_6$] (7): A solution of complex **A** (0.314 g, 0.80 mmol) and Et_3N (0.2 mL, 1.43 mmol) in CH_2Cl_2 (10 mL) was cooled to 0 °C and then *p*-CHOC$_6$H$_4$C(O)Cl (0.158 g, 0.94 mmol) was added. The mixture was stirred at 0 °C for 0.5 h and at room temperature for 2 h until TLC showed complete consumption of **A**. The solvent was removed in vacuo, and the residue was subjected to TLC separation (CH_2Cl_2/petroleum ether, 1:1). From the main red band, **7** was obtained as a red solid (0.218 g, 52%). M.p. 206–207 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.08 (s, 1 H, CHO), 7.99, 7.97, 7.63, 7.61 (AB quartet, 4 H, C$_6$H$_4$), 4.32, 4.11 (2 s, 4 H, 2 NCH$_2$S) ppm. IR (KBr disk): $\tilde{\nu}$ = 2077 (s), 2038 (vs), 2006 (vs), 1985 (vs) C≡O, 1695 (s) HC=O, 1656 (s) NC=O cm^{-1}. $C_{16}H_9Fe_2NO_8S_2$ (519.06): calcd. C 37.02, H 1.75, N 2.70; found C 36.99, H 1.70, N 2.67.

[{(μ-SCH$_2$)$_2$NC(O)(TPP)}Fe$_2$(CO)$_6$] (8): A solution of **7** (0.376 g, 0.72 mmol), pyrrole (0.20 mL, 2.88 mmol), PhCHO (0.246 mL, 2.16 mmol), and BF_3·OEt_2 (0.036 mL, 0.29 mmol) in CH_2Cl_2 (288 mL) was stirred in the dark at room temperature for 16 h to give a brown-red solution. To this solution was added *p*-chloranil (0.708 g, 2.88 mmol), and the new mixture was heated at reflux for 2 h to give a brown-black solution. Solvent was removed under reduced pressure, and the residue was subjected to flash column chromatography (Al_2O_3, CH_2Cl_2). The eluate was reduced to a suitable volume for TLC separation (CH_2Cl_2/petroleum ether, 6:1) as eluent. From the first band, tetraphenylporphyrin (TPPH; 0.081g, 18%) was obtained as a purple solid, which was identified by comparison of its IR and ^{1}H NMR spectra with those of an authentic sample.[25,26] From the second purple band, complex **8** was obtained as a purple-red solid (0.146 g, 20%). M.p. >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.88–8.81 (m, 8 H, pyrrole rings), 8.33, 8.31 (2 s, 2 H, 2 *m*-H of C$_6$H$_4$CO), 8.22, 8.21 (2 s, 6 H, 6 *o*-H of C$_6$H$_5$), 7.87,7.85 (2 s, 2 H, 2 *o*-H of C$_6$H$_4$CO), 7.77, 7.76 (2 s, 9 H, 6 *m*-H of C$_6$H$_5$, 3 *p*-H of C$_6$H$_5$), 4.53 (s, 4 H, 2 NCH$_2$S), –2.79 (s, 2 H, 2 NH) ppm. IR (KBr disk): $\tilde{\nu}$ = 2077 (s), 2037 (vs), 2000 (vs) C≡O, 1653 (s) NC=O cm^{-1}. $C_{53}H_{33}Fe_2N_5O_7S_2$ (1027.69): calcd. C 61.94, H 3.24, N 6.81; found C 62.04, H 3.29, N 6.60.

X-ray Structure Determinations of 2, 5, and 7: Single crystals of **2**, **5**, and **7** suitable for X-ray diffraction analyses were grown by slow evaporation of a CH_2Cl_2/hexane solution of **2** or **5** at –10 °C and a CH_2Cl_2 solution of **7** at room temperature. A single crystal of **2**, **5**, or **7** was 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.[36] The structures were solved by direct methods by using the SHELXS-97 program[37] and refined by full-matrix least-squares techniques (SHELXL-97)[38] 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 5.

Table 5. Crystal data and structure refinement details for **2**, **5** and **7**.

	2	**5**	**7**
Formula	$C_{12}H_9Fe_2NO_8S_3$	$C_{13}H_7Fe_2NO_7S_3$	$C_{16}H_9Fe_2NO_8S_2$
Mr [g mol^{-1}]	503.08	497.08	519.06
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a [Å]	14.348(3)	16.057 (3)	14.569(3)
b [Å]	10.341(2)	6.7670(13)	11.792(2)
c [Å]	12.883(2)	16.874(3)	11.697(2)
α [°]	90	90	90
β [°]	96.259(4)	100.225(3)	104.355(3)
γ [°]	90	90	90
V [Å^3]	1900.1(6)	1804.4(6)	1946.9(6)
Z	4	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.759	1.830	1.771
μ [mm^{-1}]	1.894	1.990	1.749
F(000)	1008	992	1040
Index ranges	$-17 \le h \le 17$	$-20 \le h \le 19$	$-16 \le h \le 18$
	$-8 \le k \le 12$	$-6 \le k \le 8$	$-14 \le k \le 13$
	$-16 \le l \le 15$	$-21 \le l \le 15$	$-14 \le l \le 13$
Reflections collected	10522	9779	10740
Independent reflections	3879	3697	3967
$2\theta_{max}$ [°]	52.88	52.84	52.76
R	0.0489	0.0350	0.0309
Rw	0.0874	0.0762	0.0638
Goodness-of-fit	1.029	1.000	1.024
Largest diff. peak/hole [e Å^{-3}]	0.585/–0.590	0.311/–0.346	0.301/–0.303

CCDC-656305, -656306, and -656307 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemistry: Acetonitrile (Fisher Chemicals, HPLC grade) was used for electrochemistry assays. A solution of 0.1 M *n*Bu$_4$NPF$_6$ in MeCN was used as the electrolyte in all cyclic voltammetric experiments. Electrochemical measurements were made with 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*Bu$_4$NPF$_6$ in MeCN) reference electrode under a N_2 or CO atmosphere. The working electrode was polished with 0.05-μm alumina paste and sonicated in water for 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 gas chromatograph GC-9A under isothermal conditions with nitrogen as a carrier gas and a thermal conductivity detector.

Acknowledgments

We are grateful to the National Natural Science Foundation of China and the Specialized Research Fund for the Doctoral Program of Higher Education of China for financial support of this work.

[1] a) M. Y. Darensbourg, E. J. Lyon, J. J. Smee, *Coord. Chem. Rev.* **2000**, *206–207*, 533–561; b) D. J. Evans, C. J. Pickett, *Chem. Soc. Rev.* **2003**, *32*, 268–275; c) L.-C. Song, *Acc. Chem. Res.* **2005**, *38*, 21–28; d) J.-F. Capon, F. Gloaguen, P. Schollhammer, J. Talarmin, *Coord. Chem. Rev.* **2005**, *249*, 1664–1676.
[2] J. W. Peters, W. N. Lanzilotta, B. J. Lemon, L. C. Seefeldt, *Science* **1998**, *282*, 1853–1858.
[3] Y. Nicolet, C. Piras, P. Legrand, E. C. Hatchikian, J. C. Fontecilla-Camps, *Structure* **1999**, *7*, 13–23.
[4] Y. Nicolet, A. L. De Lacey, X. Vernède, V. M. Fernandez, E. C. Hatchikian, J. C. Fontecilla-Camps, *J. Am. Chem. Soc.* **2001**, *123*, 1596–1601.
[5] A. J. Pierik, M. Hulstein, W. R. Hagen, S. P. J. Albracht, *Eur. J. Biochem.* **1998**, *258*, 572–578.
[6] A. L. De Lacey, C. Stadler, C. Cavazza, E. C. Hatchikian, V. M. Fernandez, *J. Am. Chem. Soc.* **2000**, *122*, 11232–11233.
[7] Z. Chen, B. J. Lemon, S. Huang, D. J. Swartz, J. W. Peters, K. A. Bagley, *Biochemistry* **2002**, *41*, 2036–2043.
[8] F. Gloaguen, J. D. Lawrence, M. Schmidt, S. R. Wilson, T. B. Rauchfuss, *J. Am. Chem. Soc.* **2001**, *123*, 12518–12527.
[9] E. J. Lyon, I. P. Georgakaki, J. H. Reibenspies, M. Y. Darensbourg, *J. Am. Chem. Soc.* **2001**, *123*, 3268–3278.
[10] M. Razavet, S. C. Davies, D. L. Hughes, J. E. Barclay, D. J. Evans, S. A. Fairhurst, X. Liu, C. J. Pickett, *Dalton Trans.* **2003**, 586–595.
[11] L.-C. Song, J. Cheng, J. Yan, H.-T. Wang, X.-F. Liu, Q.-M. Hu, *Organometallics* **2006**, *25*, 1544–1547.
[12] J.-F. Capon, S. E. Hassnaoui, F. Gloaguen, P. Schollhammer, J. Talarmin, *Organometallics* **2005**, *24*, 2020–2022.
[13] F. I. Adam, G. Hogarth, I. Richards, B. E. Sanchez, *Dalton Trans.* **2007**, 2495–2498.
[14] a) J. D. Lawrence, H. Li, T. B. Rauchfuss, *Chem. Commun.* **2001**, 1482–1483; b) J. L. Stanley, T. B. Rauchfuss, S. R. Wilson, *Organometallics* **2007**, *26*, 1907–1911.
[15] L.-C. Song, J.-H. Ge, X.-G. Zhang, Y. Liu, Q.-M. Hu, *Eur. J. Inorg. Chem.* **2006**, 3204–3210.
[16] W. Gao, J. Ekström, J. Liu, C. Chen, L. Eriksson, L. Weng, B. Åkermark, L. Sun, *Inorg. Chem.* **2007**, *46*, 1981–1991.
[17] L. Schwartz, G. Eilers, L. Eriksson, A. Gogoll, R. Lomoth, S. Ott, *Chem. Commun.* **2006**, 520–522.
[18] L.-C. Song, Z.-Y. Yang, H.-Z. Bian, Y. Liu, H.-T. Wang, X.-F. Liu, Q.-M. Hu, *Organometallics* **2005**, *24*, 6126–6135.
[19] L.-C. Song, Z.-Y. Yang, Y.-J. Hua, H.-T. Wang, Y. Liu, Q.-M. Hu, *Organometallics* **2007**, *26*, 2106–2110.
[20] a) L.-C. Song, M.-Y. Tang, F.-H. Su, Q.-M. Hu, *Angew. Chem. Int. Ed.* **2006**, *45*, 1130–1133; b) L.-C. Song, M.-Y. Tang, S.-Z. Mei, J.-H. Huang, Q.-M. Hu, *Organometallics* **2007**, *26*, 1575–1577.
[21] C. Tard, X. Liu, S. K. Ibrahim, M. Bruschi, L. De Gioia, S. C. Davies, X. Yang, L.-S. Wang, G. Sawers, C. J. Pickett, *Nature* **2005**, *433*, 610–613.
[22] H. Li, T. B. Rauchfuss, *J. Am. Chem. Soc.* **2002**, *124*, 726–727.
[23] a) J. D. Lawrence, H. Li, T. B. Rauchfuss, M. Bénard, M.-M. Rohmer, *Angew. Chem. Int. Ed.* **2001**, *40*, 1768–1771; b) E. J. Lyon, I. P. Georgakaki, J. H. Reibenspies, M. Y. Darensbourg, *Angew. Chem. Int. Ed.* **1999**, *38*, 3178–3180.
[24] J. S. Lindsey, I. C. Schreiman, H. C. Hsu, P. C. Kearney, A. M. Marguerettaz, *J. Org. Chem.* **1987**, *52*, 827–836.
[25] D. W. Thomas, A. E. Martell, *J. Am. Chem. Soc.* **1959**, *81*, 5111–5119.
[26] B. C. Bookser, T. C. Bruice, *J. Am. Chem. Soc.* **1991**, *113*, 4208–4218.
[27] F. Gloaguen, J. D. Lawrence, T. B. Rauchfuss, *J. Am. Chem. Soc.* **2001**, *123*, 9476–9477.
[28] D. Chong, I. P. Georgakaki, R. Mejia-Rodriguez, J. Sanabria-Chinchilla, M. P. Soriaga, M. Y. Darensbourg, *Dalton Trans.* **2003**, 4158–4163.
[29] I. Bhugun, D. Lexa, J.-M. Savéant, *J. Am. Chem. Soc.* **1996**, *118*, 3982–3983.
[30] R. Mejia-Rodriguez, D. Chong, J. H. Reibenspies, M. P. Soriaga, M. Y. Darensbourg, *J. Am. Chem. Soc.* **2004**, *126*, 12004–12014.
[31] D. J. Chadwick, M. V. McKnight, R. Ngochindo, *J. Chem. Soc. Perkin Trans. 1* **1982**, 1343–1347.
[32] A. J. Carpenter, D. J. Chadwick, *J. Chem. Soc. Perkin Trans. 1* **1985**, 173–181.
[33] N. Rabjohn, *Organic Syntheses*, John Wiley, New York, **1963**, vol. 4, p. 261.
[34] D. S. Breslow, E. Baumgarten, C. Hauser, *J. Am. Chem. Soc.* **1944**, *66*, 1286–1288.
[35] a) D. Delorme, C. Berthelette, R. Lavoie, E. Roberts, *Tetrahedron: Asymmetry* **1998**, *9*, 3963–3966; b) E. J. Kuhlmann, J. J. Alexander, *Inorg. Chim. Acta* **1979**, *34*, 197–209.
[36] G. M. Sheldrick, *SADABS: A Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany, **1996**.
[37] G. M. Sheldrick, *SHELXS97: A Program for Crystal Structure Solution*, University of Göttingen, Germany, **1997**.
[38] G. M. Sheldrick, *SHELXL97: A Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.

Received: August 14, 2007
Published Online: October 26, 2007

